Programme of the

57th Annual Meeting of the International Society of Electrochemistry

Edinburgh, UK
27 August to 1 September, 2006

in association with

Royal Society of Chemistry Electrochemistry Group
Royal Society of Chemistry Electroanalytical Group
Society for Chemical Industry Electrochemical Technology Group
Institute of Corrosion
IONMET

Organising Committee

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Patrick Unwin (University of Warwick, UK)
Lesley Yellowlees (University of Edinburgh, UK)

Other ISE Meetings in Edinburgh

Meeting	Room allocation	Date	Time
ISE Exec Comm.	Beech Room	26 August (Sat)	All day
ISE Exec Comm	Beech Room	27 August (Sun)	Morning
Scientific Meetings Committee	Wardlaw Room	1 September (Fri)	2-5 pm

Tutorials

Potential and Current Distributions in Electrochemical Systems	Lecture Theatre 3	27 August (Sun)	2-5 pm
Imaging of Electrochemical Systems	Lecture Theatre 1	27 August (Sun)	2-5 pm

Division Officers' Meeting	Wardlaw Room	28 August (Mon)	1-3 pm
Regional Representives' Meeting	Bruce Room	28 August (Mon)	1-3 pm
Council Meeting	Carnegie Room	29 August (Tues)	1-3 pm
General Assembly	Main Hall	31 August (Thurs)	12-1 pm

Electrochimica Acta Advisory Board	Wardlaw Room	29 August (Tues)	2-3 pm
ISE Division 6 Meeting	Bruce Room	29 August (Tues)	1-3 pm
RSC Electrochemistry Group & AGM	Lecture Theatre 1	29 August (Tues)	6-8 pm
RSC EAG	Bruce Room	29 August (Tues)	6-8 pm
SCI ETG	Wardlaw Room	29 August (Tues)	6-8 pm
Schultze reception, ISE Division 2 Meeting	Carnegie Room	29 August (Tues)	6.30-8 pm
ICorr CSD	Wardlaw Room	31 August (Thurs)	12-1 pm
ISE Division 2 Meeting	Bruce Room	31 August (Thurs)	1-3 pm
ICorr students	Carnegie Room	31 August (Thurs)	6.30-8 pm

Programme of Oral and Poster presentations

at the
57th Annual Meeting
of the International Society of Electrochemistry
in Edinburgh

ISE2006, Programme per day

Monday 28th August 2006

0900 Opening Ceremony: Main Hall

1000 Break

S1 Batteries: Battery systems
Carnegie Room
Chair: J. Owen

Time	Author, Title
1010	● Keynote **D. Pletcher** — Batteries for a Renewable Energy Economy
1040	**R. Tunold** — Kinetic Studies of the V4+/V5+ Red/Ox – system in Sulphuric Acid
1100	**G. Wills** — Soluble lead redox flow cell for electrochemical
1110	*Break*
1140	**P. Notten** — The hydrogen evolution and recombination kinetics in sealed rechargeable NiMH batteries
1200	**J. Tuebke** — Lithium Ion Batteries for Hybrid Applications
1220	**R. Aogaki** — A new type of battery using a magnetic field
1240	**L. Stoica** — Selective modification of nanopore electrodes as sensitive biosensing platform

S2 Electroanalysis: Miniaturised Systems
Lecture Theatre 3
Chair: D. Arrigan

Time	Author, Title
1010	**L. Nyholm** — On- and off-Chip Electrochemistry coupled to Electrospray Mass Spectrometry
1030	**F. Matysik** — Capillary batch injection – a novel concept for sample introduction into microfluidic systems
1050	**A. Oleinick** — In-situ and Online Monitoring of Hydrodynamic Flow Profiles in Microfluidic Channels
1110	**S. Baldock** — Disposable, Low-cost, Injection-moulded Electrochemical Flowcells with Integrated Carbon Fibre-Loaded Polymer Electrodes for Voltammetric Applications
1130	*Break*
1150	● Keynote **J. Cooper** — Lab-on-a-Chip and Lab-on-a-Pill Technologies Providing the Functional Framework for New Biological Measurements
1220	**K. Nagamine** — Microfluidic device for the manipulation and electrochemical analysis of single cellular activities
1240	**L. Stoica** — Selective modification of nanopore electrodes as sensitive biosensing platform

S4 Electrochemical Nanotechnology: Nanowires, Nanotubes, Nanorods & Q-Dots
Lecture Theatre 4
Chair: J. Macpherson

Time	Author, Title
1010	● Keynote **D. Vanmaekelbergh** — Electrochemical gating, a way to control the orbital occupation of quantum-dot solids
1040	**A. Munoz** — Intercalation of Cations into TiO_2 nanotubes, Photoelectrochemical processe
1100	**M. Linh Tran** — Non-spherical Gold Nanoparticles – Synthesis and Optical Properties
1120	**L. Berlouis** — Reflectance, Electroreflance and SERS from Au Nanowire Arrays
1140	*Break*
1200	**E. Leiva**, On the stability of modified Au nanowires
1220	**K. Ozoemena** — Unfolding Electrocatalytic Properties of Carbon Nanotube-Metallophthalocyanine (CNT-MPc) Sensing Platforms
1240	**N. Wilson** — Correlating the electrochemical properties of carbon nanotubes to their electrical characteristics

S5 Electrochemical Engineering: Metal extraction from non-aqueous electrolytes
Lecture Theatre 1
Chair: K. Ryder

Time	Author, Title
1010	● Keynote **D. Hodgson** — Development and Scale up of the FFC Cambridge Process
1040	**X. Jin** — Electro-Reduction of Solid SiO_2 in Molten $CaCl_2$
1100	**G. Haarberg** — Electrodeposition of iron from molten salts
1120	*Break*
1140	**S. Delpech** — Electrochemical investigation of the oxoacidic properties of zirconium (IV) in the LiF-NaF-KF molten salt at 500°C
1200	**S.X. Li** — High current density cathode for electrorefining of spent nuclear fuel in molten electrolyte
1220	**P. Fellner** — The electrode processes in sulphate-containing chloride and fluoride melts
1240	**O. Babushkina** — Electrochemistry of tantalum(V) in the mixtures 1-butyl-1-methyl-pyrrolidinium chloride - $TaCl_5$

S8 Surface Chemistry & Dynamics: 1
Cedar Suite
Chair: G. Attard

Time	Author, Title
1010	**C. Lucas** — Surface Structure and Electrochemistry of Model Electrocatalysts
1040	**M. Janik** — A First-Principles Analysis of the Electrooxidation of Methanol over Pt and Pt-based Alloys
1100	**E. Ahlberg** — Oxygen reduction on cobalt hydroxide and oxyhydroxide. Experiments and quantum chemical modelling
1120	*Break*
1140	**G. Jerkiewicz** — Nature and Strength of the Pt(111)-AgUPD Surface Bond and the AgUPD – AgUPD Lateral Interactions
1200	**A. Wieckowski** — Spectroscopic and Reactivity Measurements of Catalytic Nanoparticles for Methanol and Formic Acid Oxidation, EC-NMR, XPS and Theoretical Studies
1220	**H. Noguchi** — Dynamics of adsorbed CO on a Pt electrode surface under irradiation of ps laser pulses
1240	**J. Kunze** — Characterization of a Thiolipid SAM of DPTL - a Spacer in Model Membrane Systems

S10 Fuel Cells: Electrocatalysis
Main Hall
Chair: B. Hayden

Time	Author, Title
1010	**A. Kucernak** — Introduction to Fuel cell Symposium
1030	**J. Solla-Gullón** — CO monolayer oxidation on Pt nanoparticles
1050	**M. Tsampas** — Electrocatalysis and electrochemical promotion of CO oxidation in PEM fuel cells, The role of oxygen crossover
1110	**T. Vidakovi** — Can CO stripping voltammetry be used as a quantitative method for in situ fuel cell catalyst characterisation?
1130	*Break*
1150	● Keynote **E. Cairns** — Characterizing Novel Electrocatalytic Surfaces, Combined Electrochemical and Nuclear Magnetic Resonance Studies
1220	**Z. Zhou** — Studies of Electrochemical Kinetics by Time-Resolved FTIR Reflection Spectroscopy
1240	**M. Bron** — Model studies in electrocatalysis, oxygen reduction at Ruthenium and Gold nanoparticles

Institute of Corrosion: Aluminium alloys
Bruce Room
Chair: G. Scamans

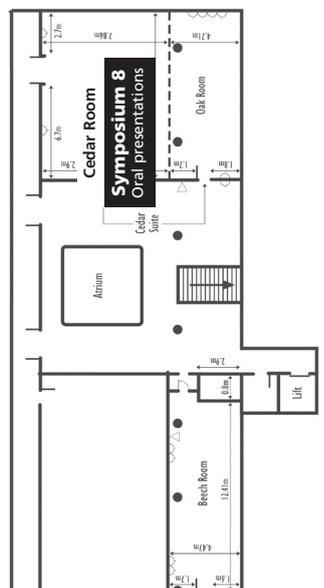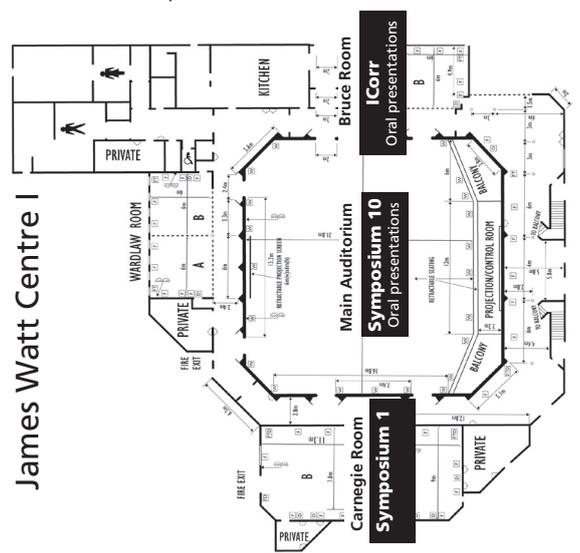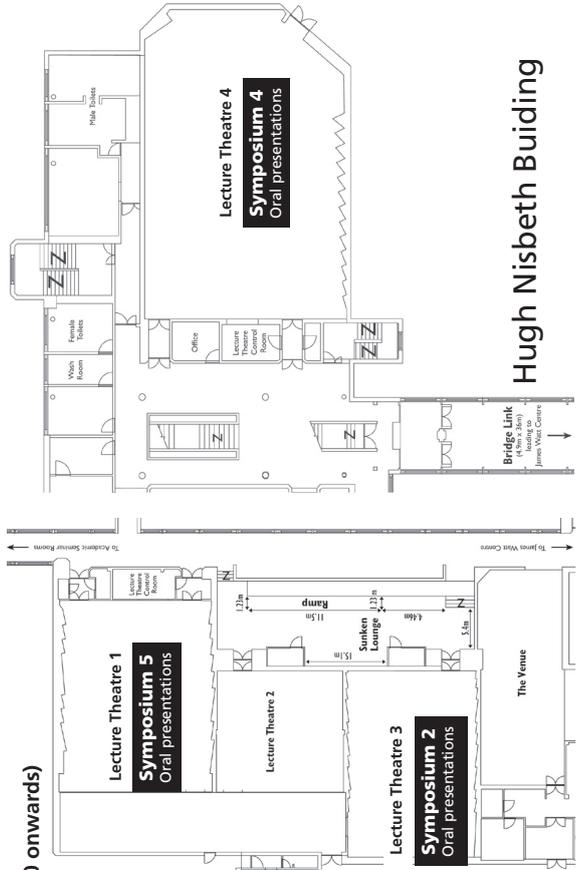| Time	Author, Title
1010	**E. Roberts** — Aluminium, Corrosion Protection Testing
1030	**Speckert** — The Effect of Alloying Elements on the Pitting Corrosion of Aluminium and its Alloys in Hydrochloric Acid
1050	**Tareelap** — Laser Surface Alloying of Aerospace Aluminium Alloys
1110	**Winsley** — Effect of Heat Treatment and Friction Stir Welding on Corrosion of AA5083
1130	*Break*
1150	**Larsen** — Intergranular corrosion of AlMgSi(Cu) model alloys
1220	**S. Ghosh** — Effect of Stress on Localised Corrosion Initiation and Propagation in Aluminium Alloys
1240	**C. Padovani** — Use of Laser Surface Melting to Improve Corrosion Resistance of High Strength Aluminium Alloy Friction Stir Welds

1300 Lunch

Posters *(see below)*

1500 Plenary Lecture, Main Hall: B.B. Damaskin: Adsorption of Organic Molecules on Electrodes
Frumkin Memorial Medal lecture

1600 Break

Time	S1 Batteries: Supercapacitors — *Carnegie Room* — Chair: R. Koetz	S2, Electroanalysis: Ion Sensors — *Lecture Theatre 3* — Chair: P. Unwin	S4, Electrochemical Nanotechnology: Nanoparticle modified electrodes — *Lecture Theatre 4* — Chair: D. Vanmaelbergh	S5, Electrochemical Engineering: IONMET - metal electrodeposition using ionic liquids — *Lecture Theatre 1* — Chair: D. Hodgson	S8. Surface Chemistry & Dynamics: 2 — *Cedar Suite* — Chair: A. Wieckowski	S10, Fuel Cells: New catalysts, supports & electrodes — *Main Hall* — Chair: E. Cairns	Institute of Corrosion: Surface analysis and corrosion mechanisms — *Bruce Room* — Chair: B. Wilson
1610	● Keynote **A. Burke** Research and Development Considerations for the Performance and Application of Supercapacitors	● Keynote **E. Bakker** New Frontiers of Ion-Selective Electrodes	● Tajima Prize Lecture **Shaowei Chen** Quantized Charge Transfer in Nanoparticle Organized Arrays	● Keynote **F. Endres** Electrodeposition of nanomaterials in air and water stable ionic liquids	● Keynote **A. Tadjeddine** Investigation of Pt(hkl)/Ethanol interface	● Keynote **S. Pronkin** Electrochemical and electrocatalytic properties of supported mono- and bimetallic Pd nanoparticles	**Graham** Surface-analytical Techniques in Corrosion and Oxidation
1640	**N. Yoshimoto** Hydrous Ruthenium Oxide Electrode for Non-aqueous Proton-Conducting Gel Electrolyte	**J. Bobacka** All-solid-state chloride sensors based on electronically conducting, semiconducting and insulating polymer membranes	**D. Fermin** Nanoparticle Mediated Electron Transfer Across Ultrathin Self-Assembled Films	**P. Benaben** Hard Chromium deposition using ionic liquids as a potential substitute to hexavalent chromium plating	**H. Hoster** Electrocatalytic properties	**T. Okada** Anode and Fuel Cell Performances of CO Tolerant Pt Composite Catalysts with Organic Metal Complexes	**Zheng** Assessing Mechanisms of Corrosion in Hydraulic Fluid and Hydraulic Fluid/Seawater for Subsea Applications
1700	**M. Mastragostino** Electrode materials for supercapacitors with ionic liquid electrolytes	**Z. Samec** Amperometric sensor for heparin, Sensing mechanism and application in human blood plasma analysis	**A. Silva** Electrochemical Study of Composite Nanostructures, Contrasting behaviour of two redox pairs on Polyelectrolyte/Gold Nanoparticle Multilayers	**K. Ryder** Electrodeposition of Zinc-Tin Alloys, Bright Metal Coatings and Composites From Deep Eutectic Solvents Based on Choline Chloride	**J. Fernandes-Gomes** Influence of catalyst particle size on the CO2 yield of ethanol oxidation on Pt/C electrodes, a DEMS study	**Xinqxing Chen** Platinized Carbon Nanotube-Modified Carbon Material for Fuel Cell Applications	**Kapatou** Study of the Post-Excavation Corrosion of Archaeological Iron in Terms of the Chloride Presence and the Levels Of Relative Humidity, Application of the Electrical Resistance Monitor
1720	**R. Koetz** Relation between electronic resistance and capacitance for highly aqueous RuO$_2$	**F. Kivlehan** Electrochemical Sensing of Phosphate via Calix[4]arene Anion Receptors	**R. Lahtinen** Thin Film Photovoltaic Cell with Porphyrin-Fullerene Dyads and Gold Nanoparticles	**J. Collins** Electrodeposition of Zn, Ni, Sn and Fe Alloys From Deep Eutectic Solvents Based on Choline Chloride	**E. Herrero** Single probe characterization of the surface of platinum nanoparticles	**K. Sawai** Highly-Active Non-Platinum Electrocatalysts for Oxygen Reduction Reaction	**S. O'Toole** Atomic Scale Modelling of Oxygen Mobility in Defected Chromite systems
1740	**A. Pandolfo** Performance of Asymmetric Ni(OH)$_2$-Carbon Supercapacitors	**A. Michalska** Optimizing all-solid-state polyacrylate based ion-selective electrodes	**V. Ruiz** Characterisation of MPC's films by UV-VIS spectroelectrochemical and QCM	**A. Silva** Electrochemical studies of the interfaces	**G. Burstein** Cyclic Thermammetry-Electrochemical Reactions as a Function of Temperature	**A. Reiner** Co-Sputtering, a novel approach for low Pt loading fuel cell electrodes	**B. Egger** Micro cell array for in-situ monitoring of crevice corrosion

POSTER SESSION 1: Mon 28th Aug (13.00 – 15.00 & 18.00 onwards)

Symposium 1: S1-P-1 to S1-P-49
Symposium 2: S2-P-1 to S2-P-68
Symposium 5: S5-P-1 to S5-P-80
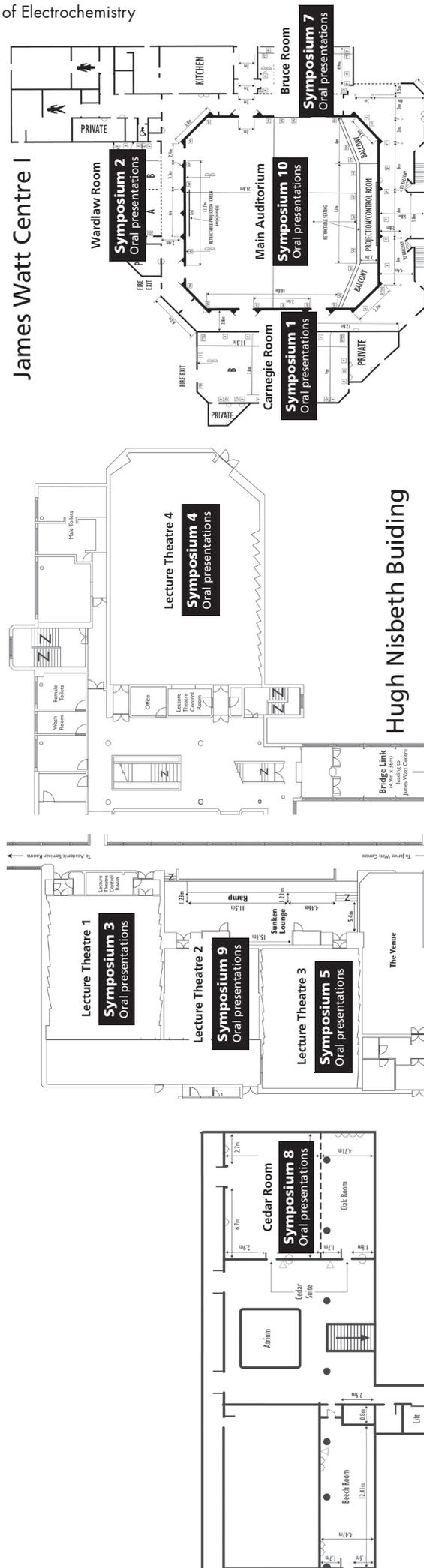**Symposium 7:** S7-P-1 to S7-P-44
Symposium 8: S8-P-1 to S8-P-64

James Watt Centre I

Bruce Room — ICorr Oral presentations
Main Auditorium — Symposium 10 Oral presentations
Carnegie Room — Symposium 1

Hugh Nisbeth Buiding

Lecture Theatre 4 — Symposium 4 Oral presentations
Lecture Theatre 1 — Symposium 5 Oral presentations
Lecture Theatre 3 — Symposium 2 Oral presentations
Cedar Room — Symposium 8 Oral presentations

ISE2006, Programme per day

Tuesday 29th August 2006

0900   Plenary Lecture, Main Hall: P.G. Bruce: Electrochemical Energy Storage - Beyond The Horizon

1000   Break

S1, Batteries: Electrolytes
Carnegie Room
Chair: E. Cairns

Time	Author, Title
1010	● Keynote **H. Saka ebe** — Application of Ionic Liquids to Li batteries and Supercapacitors
1040	**Y. Andreev** — The conductivity of crystalline polymer electrolytes
1100	**B. Kerr** — Synthesis And Characterization Of Comb Shape Single Ion Conductors Based On Polyepoxide Ethers And Perfluorinataed Lithium Salts
1120	*Break*
1140	**F. Alloin** — New lithium salts for liquid or solid polymer electrolyte

S2, Electroanalysis: Sensor Materials
Wardlaw Room
Chair: D. Mandler

Time	Author, Title
1010	**M. Brett** — New protective polymer membrane coating strategies for sol-gel enzyme biosensors
1030	**C. Gabrielli** — Effect of the conditioning time on the ISE electrochemical behaviour
1050	**G. Inzelt** — Electrochemical nanogravimetric studies of solid RuCl3 and RuCl3-polyaniline nanocomposite
1110	**L. Chen** — Repair of defects in thin thermally grown silicon by anodic oxidation
1130	*Break*

S3, Enterprise and Innovation
Lecture Theatre 1
Chair: P. Bartlett

Time	Author, Title
1010	**Sibbett** — Opening Address
1030	**A. Heller** — Electroanalysis in diabetes management
1100	**J. Rossier** — ImmuSpeed, microfludic electrochemical platform applied to Enzyme Linked Immunosorbent Assay
1130	*Break*

S4, Electrochemical Nanotechnology: Single Molecule Conductivity
Lecture Theatre 4
Chair: D. Fermin

Time	Author, Title
1010	● Keynote **J. Ulstrup** — Electrochemical Tunnelling Spectroscopy Studies on Redox-Active Molecules
1040	**A. Kornyshev** — A new type of in situ single molecule rectifier
1100	**A. Kuznetsov** — Bridge-mediated Electron Tunneling in situ Electrochemical Junctions, Physical Mechanisms, Rectification, Relaxation, Hysterises, and all that
1120	**R. Nichols** — Single molecule conductance in ambient conductions and electrolytes
1140	*Break*

S5, Electrochemical Engineering: Environmental electrochemistry and energy
Lecture Theatre 3
Chair: T. Roberts

Time	Author, Title
1010	● De Nora Prize, Technology Lecture **M. Panizza** — Electrochemical oxidation of synthetic dyes
1040	**A. Attour** — Electrochemistry of the anodic oxidation of 4-methoxytoluene, mechanism and selectivity
1100	**R. Rocha-Filho** — Anodic oxidation of the blue reactive 19 dye on pure or Fe,F-doped lead dioxide electrodes
1120	**R. Amadelli** — Visibile – Light Photoelectrochemical Degradation of Pollutants
1140	*Break*

S7, Soft Materials: Self-assembly and Surface Modification
Bruce Room
Chairs: S. Roscoe / A. Glidle

Time	Author, Title
1010	● Keynote **R. Guidelli** — Ion Transport Across Biomimetic Membranes (Niki Prize)
1040	**P. Krysinski** — Immobilisation of laccase on gold, silver and indium tin oxide by zirconium-phosphonate-carboxylate coordination chemistry
1100	**J. Kwak** — Control of Electron Transfer in Self-Assembled Monolayers
1120	*Break*
1140	**D. Johannsmann** — Formation of Surface-Attached Responsive Gel Layers via Electrochemically Induced Free-Radical Polymerization

S8, Surface Chemistry & Dynamics: 3
Cedar Suite
Chair: A. Russell

Time	Author, Title
1010	● Keynote **M. Watanabe** — Adsorption/ oxidation of CO on a highly dispersed Pt/C electrocatalyst studied by combined electrochemical and ATR-FTIRAS
1040	**G.A. Attard** — New method for the preparation of PtPd single crystal alloys
1100	**V. Climent** — Effect of adatoms on the potential of maximum entropy of Pt(111) from pulsed laser experiments
1120	*Break*
1140	**A. Cuesta** — Electrochemical and ftirs characterisation of no adlayers on cyanide-modified-pt(111) electrodes, the mechanism of nitric oxide electroreduction on Pt

S9, Corrosion: Localised Corrosion
Lecture Theatre 2
Chair: S. Lyon

Time	Author, Title
1010	**G. Scamans** — The Role of Near-surface Microstructure on Corrosion Behaviour of Wrought Aluminium Alloys
1030	**A. Pailleret** — Electrochemical and AFM investigations of dendritic growth and corrosion processes occurring in the course of the "post-CMP cleaning" in microelectronics
1050	**Malik** — Scanning electrochemical microscopic imaging of surfaces of Nd-Fe-B-type magnets during pitting corrosion
1110	**M. De Cristofaro** — MIC monitoring in environments containing manganese oxidising bacteria
1130	*Break*

S10, Fuel Cells: Electrocatalysis
Main Hall
Chair: E. Spohr

Time	Author, Title
1010	**B. Podlovchenko** — Interaction of methanol and formic acid with preliminarily adsorbed oxygen on polycrystalline platinum electrode at open-circuit conditions
1030	**J. Jaksic** — Spillover of primary oxides as a dynamic catalytic effect of interactive supports
1050	**D. dos Anjosa** — Electrocatalytic behaviour of molybdenum modified platinum electrodes for electrooxidation of ethanol in acid medium
1110	**P. Kulesza** — Enhancement of the oxidation of methyl formate at multifunctional electrocatalyst composed Pt/Pd and Pt/Ru nanoparticles
1130	*Break*

1200 W. S. Li — Additives for performance improvement of Li ion battery	**1150** ● *Keynote* G. Denuault — A microelectrode dissolved oxygen sensor for oceanography	**1200** G. Sanghera — Nanopores of GATTACCA	**1200** Th. Wandlowski — Two-dimensional assembly and local redox-activity of molecular and ionic hybrid structures in an electrochemical environment	**1200** G. Kelsall — Circulating Particulate Bed Cathode for Metal Recovery	**1200** D. Bélanger — Electrochemical and chemical modification of carbon and metal surfaces	**1200** ● *Keynote* M. Heinen — CO Adsorption/Oxidation Kinetics studied by combined ATR-FTIR Spectroscopy and Differential Electrochemical Mass Spectrometry under Continuous Flow Conditions	**1150** ● *Keynote* R. Newman — Nanoporous dealloyed metals: From atomistic modeling to applications	**1150** ● *Keynote* B. Hayden — A Combinatorial Approach to the Study of Particle Size and Substrate Effects in Electrocatalysis
1220 A. Janes — Ethylene carbonate - organic ester based mixed electrolytes for electrical double layer capacitors	**1220** R. Szamocki — Highly ordered macroporous surfaces as electrochemical systems with optimized biocatalytic efficiency		**1220** S. Sek — Molecular Junctions Incorporating alpha-Helical Peptides	**1220** F. Martinez — Coagulation and electrocoagulation with aluminium hydrolyzing salts	**1220** B. Speiser — Redox-Active Covalent Modifications on Spherical Non-porous Silica Nanometric Particles	**1220** L. Kibler — Electrocatalytic properties of metallic monolayers on foreign single crystal electrodes	**1220** A. Davenport — In Situ Synchrotron Microtomography Studies of Localised Corrosion of an Mg-Y Alloy	**1220** F. Nart — Particle size and particle size distribution effect on the methanol and ethanol oxidation
1240 R. Torresi — Effect of lithium salt addition on a C-2 substituted imidazolium ionic liquid	**1240** Hong-Yuan Chen — Enhanced Performance of Mesoporous SnO₂ Multilayered Film in Direct Electron Transfer of Hemoglobin	**1230** S. Brooke — Taking science to market	**1240** Shengli Chen — Electrochemistry at nano-sized electrodes	**1240** M. Bergmann, What is the ominous chlorine consumption in the disinfectant production by drinking water electrolysis	**1240** S. Palacin — Interfacial signature of the polymer-to-metal bonding	**1240** V. Rosca — Mechanistic aspects of electrocatalytic oxidation of ammonia on Pt(111) and Pt(100) surfaces	**1240** N. Wilson — Investigation of Aluminium pitting corrosion in modified acid solution as a method for controlling surface roughness	**1240** F. Jäger — Structure-Reactivity Relationship of Metallic Nanoparticles

1300 *Lunch*

POSTER SESSION 2: Tues 29th Aug (13.00 – 15.00 & 18.00 onwards)

Symposium 1:	S1-P-50 to S1-P-92
Symposium 2:	S2-P-69 to S2-P-135
Symposium 5:	S5-P-81 to S5-P-142
Symposium 6:	S6-P-1 to S6-P-32
Symposium 7:	S7-P-45 to S7-P-88
Symposium 8:	S8-P-65 to S8-P-96

James Watt Centre I

Wardlaw Room — **Symposium 2** Oral presentations
Main Auditorium — **Symposium 10** Oral presentations
Bruce Room — **Symposium 7** Oral presentations
Carnegie Room — **Symposium 1** Oral presentations

Hugh Nisbeth Buiding

Lecture Theatre 4 — **Symposium 4** Oral presentations
Lecture Theatre 1 — **Symposium 3** Oral presentations
Lecture Theatre 2 — **Symposium 9** Oral presentations
Lecture Theatre 3 — **Symposium 5** Oral presentations
Cedar Room — **Symposium 8** Oral presentations

S1, Batteries: Electrode Materials
Carnegie Room
Chair: P. Novak

- **1500** ● *Keynote* — **C. Grey**, NMR Studies of Lithium-Ion Battery Materials: Applications to the Li2MnO3-Li(NiMn)0.5O2 System, Layered Oxysulfides and Other Paramagnetic Materials
- **1530** **T. Takamura**, Nano Size Holes at the Basal Plane of Graphite Active Material Play an Important Role in Li-Ion Battery Anode
- **1550** **Y. Jung**, In-M (M = Ni, Cu) Film Electrodes for the Anode in Lithium Secondary Batteries
- **1610** *Break*
- **1630** **N. Oyama**, Electrochemistry of naphthalene derivatives with disulfide bonds and their application to cathode materials for Lithium secondary batteries
- **1650** **Y. Wu**, Effect of Cu_2O Coating on graphite as Anode Material of Lithium Ion Battery in PC-based electrolyte

S2, Electroanalysis: Trace Analysis
Wardlaw Room
Chair: J. Hart

- **1500** ● *Keynote* — **K. Honeychurch**, Determination of trace nitrophenol concentration in human urine by liquid chromatography dual electrochemical detection
- **1520** **W. Shin**, Electrochemical sensing in nM range by chemical amplification
- **1540** **T. Kondo**, Covalent Modification of Boron-Doped Diamond Electrode Surfaces for Electroanalysis
- **1600** **K. Pinkwart**, Room Temperature Ionic Liquids for Electrochemical Detection of Nitro Based Explosives
- **1620** **K. Takamura**, Liquid Chromatography with Electrochemical Detection as an Effective Method for Determining Femtomole Level Polyphenols in Human Blood
- **1640** *Break*

S3, Enterprise and Innovation
Lecture Theatre 1
Chair: A. Abbott

- **1500** **B. Scrosatti**, The role of lithium batteries in fighting global warming and in reducing energy consumption
- **1530** **S. Cai**, The electric vehicles projects and related batteries in China
- **1610** *Break*
- **1630** **I. Edwards**, The ITI Energy model for the generation of new technologie

S4, Electrochemical Nanotechnology: NanoElectrocatalysis
Lecture Theatre 4
Chairs: R. Nichols/ E. Pastor

- **1500** ● *Keynote* — **W. Schuhmann**, Oxygen-competition mode of SECM. Application for localized visualization of fuel cell catalyst activity
- **1530** **S. Sun**, Study of electrocatalytic and IR properties of nanomaterials constructed by electrochemical methods
- **1550** **E. Pastor**, Nanostructured Electrodes for Methanol Electro Oxidation
- **1610** *Break*
- **1630** **S. Holmes**, Synthesis of Novel Nanostructured C

S5, Electrochemical Engineering: Environmental electrochemistry and energy
Lecture Theatre 3
Chair: F. Lapicque

- **1500** ● *Keynote* — **A. Vertova**, Electroreduction of polychloroethanes at silver electrodes
- **1530** **B. Boye**, *Electrochemical Treatment of Chlorinated Petrochemical Effluents and Wastewater in lab cell and pilot plant*
- **1550** **Y. Dzyazko**, Ni^{2+} removal from diluted solutions with an electro-deionization method using ion-exchangers of different nature
- **1610** *Break*
- **1630** **I. Petrushina**, NO Reduction in the NO,CH4,Ar/Pt/Cl/Polybenzimidazole-H3PO4//Pt/CH2,Ar at 135°C
- **1650** **C. Ponce de León**, Development in Direct Borohydride Fuel Cells

S7, Soft Materials: Surface Attachment and Advanced Materials
Bruce Room
Chairs: A. Glidle / S. Higgins

- **1500** ● *Keynote* — **M. de Groot**, Electron transfer and CO binding to immobilized cytochrome c' on thiol modified gold surfaces
- **1530** **G. Shustak**, Electrochemically Induced Formation of Fatty Acid Monolayers as Molecular Glue for Electrodeposited Polypyrrole Films
- **1550** **E. Calvo**, LbL Self-assembled redox multilayer films: Effect of acid-base equilibria on the ion exchange during redox switching
- **1610** *Break*
- **1630** **A. Bhattacharyya**, Heterogeneous Doping Effects in Solid and Liquid Ionic Conducting Systems
- **1650** **M. Vorotyntsev**, pectroelectrochemistry of reduction of titanocene dichloride complex in solution and inside a conducting-polymer film

S8, Surface Chemistry & Dynamics: 4
Cedar Suite
Chair: M. Koper

- **1500** ● *Tacussel Prize Lecture* — **M. Osawa**, Picosecond Time-Resolved Surface-Enhanced Infrared Spectroscopy at the Electrochemical Interface: Monitoring of the Potential Jump Induced by Visible Laser Pulses
- **1530** **C. Korzeniewski**, Water-Nafion interfacial interactions probed by infrared spectroscopy
- **1550** **M. Hara**, CO electro-oxidation with Pt-deposits on Au(hkl) and quasi-single crystalline gold film electrodes
- **1610** *Break*
- **1630** **L. Burke**, Active Sites, Non-equilibrium Surface States and Electrocatalysis
- **1650** **V. Tsionsky**, The liquid-like layer between metal and frozen aqueous electrolytes

S9, Corrosion: Protective Coatings
Lecture Theatre 2
Chair: A. Worsley

- **1500** **G. Grundmeier**, Applications of a Height-Regulated Scanning Kelvin Probe Blister Test in Corrosion and Adhesion Science
- **1520** **N. Fink**, Combination of Surface Gradient Chemistry and Kelvin Probe Studies of Thin Amorphous Conversion Films on Metals
- **1540** **M. Rohwerder**, Mechanism of corrosion protection by conducting polymers
- **1600** **S. Lyon**, Hydrophilic and Hydrophobic Interfaces: the Performance of Functional and Non-Functional Silane-Treated Epoxy-Coated Steel
- **1620** **A. Simoes**, Assessment of water transport in organic coatings using a.c. impedance in ionic liquids
- **1640** *Break*

S10, Fuel Cells: Membranes
Main Hall
Chair: L. Zhuang

- **1500** **A. Herring**, Understanding the Implications of Doping PFSA Ionomers with Heteropoly Acids
- **1520** **T. Okada**, New proton conducting semi-IPNs from PVA/PAMPS composites with plasticizer variants
- **1540** **J. Lobato**, PBI-based Membrane as Proton Conductor in HT-PEMFC. Synthesis, Physico-Chemical Characterisation, and Performance
- **1600** **M. Wark**, Composites of functionalized polysiloxanes and nanostructured porous silicas as novel fuel cell membranes
- **1620** **S. Nakazawa**, Development and evaluation of the pore-filling electrolyte membrane using aromatic hydrocarbon polymer
- **1640** *Break*

Time									
1700		● Keynote **S. van den Berg** Chemical speciation using microelectrodes	**G. Cooley** Exploitation of the FFC Cambridge Proces					● Keynote **A. Hassel** Nanoscale Dissolution and Passivation Processes for an Electrochemical Tailoring of Directionally Solidified Eutectics	● Keynote **E. Spohr** Proton Generation and Transport in the Fuel Cell Environment
1710	**S. Gopukumar** Propionic acid assisted sol-gel synthesis of $LiCu_xMn_{2-x}O_4$ (0.025 ³ x £ 0.10) as 5V cathode materials for lithium rechargeable batteries			**Y. Soppa** Preparation and electrocemical characterisation of nanostructured Pt/GC electrodes produced by metal loaded micelle technique	**C. Sáez** Optimization of the electrosynthesis industrial process of peroxodiphosphate with conductive diamond electrodes	**A. Doherty** Redox-active ionic liquids	**P. Vassilev** Electrochemical reduction of oxygen to hydrogen peroxide – an electron density functional theory study		
1730	**Q. Dong** Study on the $LiFePO_4$/CaB Composites used as cathode for a Li-ion Battery	**S. Daniele** Thin-shielded sphere-cap microelectrodes. Preparation, characterization and analytical applications		**A. Johansson** Oxygen Reduction on Nanostructured Nickel in Alkaline Solution. The Effect of Alkali Metal Intercalation	**K. Kokoh** Electrosynthesis of lactic acid and 2,3-dimethyltartaric acid from pyruvic acid on lead cathode in aqueous medium	**P. Zuman** Role of protonation in the reduction of hydrazone and oximes	**R. Nazmutdinov** Viscosity effects in the interfacial ET reactions: interplay between the solvent dynamics and electronic structure of reactants	**N. Boshkov** Corrosion studies of nanostructured composite coatings based on Zinc and Zinc-Cobalt alloys	**C. Vayenas** First principles computation of the conductivity of hydrated Nafion membranes
1750	**M. Ghanem** Focused Microwaves in Electrochemistry			**M. Wang** Research of physical and electrochemical property of single enzyme molecules	**R. Bertazzoli** Electrochemical synthesis of hydrogen peroxide on O2 fed graphite/PTFE electrodes modified by 2-ethylanthraquinone	**B. Yazdani** Electrochemical Synthesis of Polyaniline/Graphite Oxide Nanocomposite	**L. Falciola** Specific adsorption of halide anions from nonaqueous solutions on controlled-surface polycrystalline silver electrodes		**J. Kerr** New polymeric proton conductors for water-free and high temperature fuel cells

POSTER SESSION 2: Tues 29th Aug (13.00 – 15.00 & 18.00 onwards)

Symposium 1:	S1-P-50 to S1-P-92
Symposium 2:	S2-P-69 to S2-P-135
Symposium 5:	S5-P-81 to S5-P-142
Symposium 6:	S6-P-1 to S6-P-32
Symposium 7:	S7-P-45 to S7-P-88
Symposium 8:	S8-P-65 to S8-P-96

James Watt Centre I

Hugh Nisbeth Buiding

ISE2006 Programme per day

Wednesday 30th August 2006

0900   **Plenary Lecture**, Main Hall: **H. Girault**: Functionalised liquid/liquid interfaces

1000   *Break*

S1 Batteries: Nanomaterials,
Carnegie Room
Chair: J. Owen

Time	Author, Title
1010	**W. Sugimoto** Charge Storage Mechanism of Nanostructured RuO_2 and Fabrication of Highly Functional RuO_2 Nanosheet Electrodes (De Nora Prize, Energy)
1040	**Y. Guo** Nanostructured titania with improved properties as anode materials for lithium batteries
1100	**H. Habazaki** High Rate Capability of Platelet Structure Carbon Nanofibers as Anode Materials for Lithium Ion Batteries
1120	*Break*
1140	**H. Bryngelsson** Electrodeposited nano-sized thin films of Sb and Sb- Sb_2O_3 as anode materials in Li-ion batteries

S2, Electroanalysis: Bio-1,
Lecture Theatre 3
Chair: W. Schuhmann

Time	Author, Title
1010	**W. Alves** Molecular Wires Design Based on Supramolecular Structures for Glucose Biosensors
1030	**I. Becerik**, A Neural Network Application on the calibration of a Glucose Sensor
1050	**J. Xu** Electrochemically Activated Nanocrystalline Diamond Modified Gold Electrode for Glucose Biosensing
1110	**Chia-Chern Chen** Measurement of Human Whole Blood Coagulation Time with Small Sample Volume by Impedance Method
1130	Break

S4, Electrochemical Nanotechnology: Self-Assembly
Lecture Theatre 4
Chairs:
D. Mandler / E. Calvo

Time	Author, Title
1010	● *Keynote* **E. Calvo** Electron transfer at gold surfaces modified by tethered osmium complexes
1040	**H. Lewerenz** Self-Organized Nanostructure on Silicon by Photo-electrochemical Oscillation
1100	**J. Sinha** Controlling supramolecular assembly by SECM: redox active dendrimers at molecular printboards on glass
1120	*Break*
1140	**Th. Doneux** Mixed self-assembled monolayers of 2-mercaptobenzimidazole and 2-mercapto-benzimidazole-5-sulfonate: determination and control of the surface composition

S5, Electrochemical Engineering: Reaction environment and electro-synthesis
Lecture Theatre 1
Chair: G. Kelsall

Time	Author, Title
1010	● *Keynote* **A. Wragg** Electrochemical mass transfer modelling of a complex twp phase heat transfer problem: Case of a prototype slagging gasifier
1040	**P. Millet** Advanced PEM water electrolysers for the production of pressurized hydrogen and oxygen
1100	**P. Mandin** Biphasic electyrolysis modelling: coupling between phenomena and scales
1120	*Break*
1140	**E. Roberts** Modelling of a large scale redox flow battery system

S6, Liquid-liquid Electrochemistry: Interfacial Analysis & Structure
Wardlaw Room
Chair: T. Kakiuchi

Time	Author, Title
1010	**H. Tatsumi**, Voltammetric study of the interfacial electron transfer between ferrocene in organic solvent and hexacyanoferrate in water
1030	**M. Opallo,** Electrochemical processes of redox liquid deposited on nanoparticles- or nanofibers-silicate composite film electrodes
1050	**A. Berduque,** Electrochemistry of DAB-AM-n and PAMAM Dendrimers at the ITIES
1110	*Break*
1130	**A. Chiorca-Paquim** Atomic force microscopy characterization of nucleic acids

S7, Soft Materials: Bioelectrochemistry,
Lecture Theatre 2
Chair: S. Horswell

Time	Author, Title
1010	● *Keynote* **S. Roscoe** The Effect of Potential Field and pH on Protein Immobilization on Gold
1040	**R. Bilewicz** Bioelectrodes for catalytic reduction of oxygen
1100	**A. Nelson** Electrochemical analysis of a phospholipid phase transition
1120	*Break*
1140	**A. Chiorca-Paquim** Atomic force microscopy characterization of nucleic acids

S8, Surface Chemistry & Dynamics: 5
Bruce Room
Chair: C. Korzeniewski

Time	Author, Title
1010	● *Keynote* **Z. Tian** SERS Characterization of Surface Water and Hydrogen Using Core-shell Nanoparticles Modified Electrodes
1040	**M. Pasquale** Solutions of the Stefan problem applied to a solid phase growth on substrates of different geometries including then test of the theoretical equations
1100	**J. Orts** Thermodynamic analysis of the temperature dependence of OH adsorption on Pt(111) and Pt(100) electrodes in acidic media in the absence of specific anion adsorption
1120	*Break*
1140	**H. Baltruschat** From reactions at steps to reactions at monoatomic rows: adsorption, hydrogenation and hydrogen evolution

S9, Corrosion: Passive Oxide Films
Cedar Suite
Chair: A. Davenport

Time	Author, Title
1010	**Di Quarto** Characterization of Initial Films and Passivating Layers Grown on Magnesium Metal in Alkaline Solution
1030	**C. Deslouis** Mechanism of pure magnesium corrosion in sodium sulphate solutions
1050	**M. Santamaria** Effect of composition on the photoelectrochemical behaviour of anodic oxides grown on aluminium alloys
1110	**S. Ono** Fabrication of ultra thick porous oxide films on niobium by anodization
1130	*Break*

S10, Fuel Cells: New catalysts, supports & electrodes
Main Hall
Chair: A. Herring

Time	Author, Title
1010	**L. Zhuang** Humidity dependent surface diffusion on Pt and its implication to PEMFC electrodes
1030	**S. Deki** Preparation of Pt/ polypyrrole Loaded Carbon Composite for Improvement of Electrode Durability for PEFCs
1050	**J. Drillet** PEDOT as catalyst support and methanol barrier for DMFC applications
1110	**V. Baglio** Investigation of bimetallic Pt-M/C as DMFC cathode catalysts
1130	*Break*

Time									
1150		● *Vetter Prize Lecture* **G. Wittstock** Coupled enzymatic and electrochemical reactions on microstructured template surfaces investigated by scanning electrochemical microscopy			● *Keynote* **M. Urbakh** Unravelling ITIES: Theory update			● *Evans Award Lecture, ICorr* **G. Burstein** Developing the characteristics and properties of passive metal surfaces	**F. Soavi** Cryogel carbon supports for DMFC-PtRu catalysts
1200	**Z. Chen** Electrochemical synthesis and capacitance of porous composite of carbon nanotubes and polyaniline		**W. Kautek** Protein layers on surfaces	**T. Bystron** Study of the electrochemical 4-methylanisole methoxylation on the glassy carbon electrode		**S. Higgins** Derivatives of Poly(3,4-ethylene-dioxythiophene) for biosensing at microelectrodes	**M. Seo** Measurement of Changes in Surface Stress of Au Electrode during Underpotential Deposition of Cu		
1220	**V. Gupta** Electrochemically deposited nanostructured Ni-Co oxide for supercapacitor application	**E. Magner** Haem Proteins in Nonaqueous Solvents: Electrochemistry, Conformation and Catalysis	**Q. Chi** Sensitive Resolution of Electronic Structure and Interfacial Property of Alkanethiol Self-assembled Monolayers at Liquid/Solid Interfaces	**J. Iniesta** Synthesis and electrochemical behaviour of benzo[b]- and dibenzothiophenes, their S- oxides and metacyclo[2](2,5)-thiophenophanes with extended pi-systems	**C. Monroe** Understanding the Capacitance of ITIES	**D. Soares** Dynamics of SDS structures formation at gold electrodes	**J. Jin** New Insight into The Electro-catalysis of Small Organic Molecules on Ru(0001) Electrode	**P. Marcus** XPS and Flow-Cell EQCM Study of Protein Adsorption on Passivated Chromium Surfaces	**W. F. Lin** Novel Electrode Structures for Direct Methanol Fuel Cells
1240	**K. Kim** Mesoporous Nickel/CNT Nanocomposite Electrodes For Electrochemical Capacitors	**L. Gorton** The Effect of Light on the Electrocatalytic Oxidation of NADH Using Electrodes Modified Electropolymerized Mediators	*Break*	**B. Munder** Distributed impedance modelling and analysis of reactions and charge transport in Au-YSZ composite electrodes	**P. Brevet** Probing the organization of the ITIES	**C. Visy** Polypyrrole/vitamin B12 composite, a new redox mediator system	**A. Bondarenko** Investigation of Surface Reaction Dynamics by Potentiodynamic Impedance Spectroscopy	**B. Tribollet** Characterisation of an oxide film by EIS and LEIS	**M. Danilov** Controlled synthesis of catalyst – nanocarbon compositions for fuel cells
1300	*Lunch*								

POSTER SESSION 3: Weds 30th Aug (13.00 onwards),

Symposium 4:   S4-P-1 to S4-P-121
Symposium 9:   S9-P-1 to S9-P-73
Symposium 10:   S10-P-1 to S10-P-91
ICORR

1400   Excursions and/or free time

ISE2006 Programme per day

James Watt Centre I

Wardlaw Room

PRIVATE

KITCHEN

Bruce Room
Symposium 8 Oral presentations

Symposium 6 Oral presentations

Main Auditorium
Symposium 10 Oral presentations

Carnegie Room
Symposium 1 Oral presentations

PRIVATE

PROJECTION/CONTROL ROOM

BALCONY

FIRE EXIT

Hugh Nisbeth Buiding

Lecture Theatre 4
Symposium 4 Oral presentations

Male Toilets

Female Toilets

Office

Lecture Theatre Control Room

Bridge Link (4.9m x 3m) leading to James Watt Centre

Lecture Theatre 1
Symposium 5 Oral presentations

Lecture Theatre 2
Symposium 7 Oral presentations

Lecture Theatre 3
Symposium 2 Oral presentations

Sunken Lounge

The Venue

Cedar Room
Symposium 9 Oral presentations

Cedar Suite

Oak Room

Atrium

Bech Room

Lift

Thursday 31st August 2006

0900 Plenary Lecture, Main Hall: **V. Birss**: Solid Oxide Fuel Cells: Enhancing Their Performance and Lifetime

1000 Break

S1 Batteries: Novel concepts — Carnegie Room — Chair: P. Novak

Time	Author, Title
1010	● Keynote J. Dahn — Combinatorial and High Throughput Studies of Alloy Negative Electrodes for Li-ion Batteries
1040	A. Debart — Rechargeable lithium/air battery
1100	M. Roberts — High Throughput Positive Electrode Material Studies Using Post Synthesis Array Transfer Techniques
1120	X. He — Graphite/ sulfur lithium ion cell using lithium compensation of a lithium foil
1140	Break

S2, Electroanalysis: Bio-2 — Lecture Theatre 3 — Chair: L. Gorton

Time	Author, Title
1010	Wollonberger — Investigations on bio-electrocatalysis of neuronal nitric oxide synthase
1030	L. Falciola — Electrochemical activity of new PNA conjugates with ferrocene and Fischer-type carbine complexes to be applied to DNA and RNA detection
1050	A. Mount — The Stability, Ion Switching and DNA Sensing Characteristics of Holliday Junctions
1110	● Keynote J. Rishpon — A Novel Electrochemical Viral Sensor for the Detection of Pathogenic and Polluting Bacteria
1140	Break

S4, Electrochemical Nanotechnology: Nano-structure & Nanodeposition — Lecture Theatre 4 — Chair: W. Schuhmann

Time	Author, Title
1010	● Keynote D. Mandler — Local Electroless Deposition of Nanoparticles by Scanning Electrochemical Microscopy
1040	A. Daltin — Electrodeposition of cuprous oxide films and nanowires; growth mechanism and nucleation behaviour
1100	P. Lisboa — Polypyrrole Based Nano-Electrode Arrays
1120	M. Oyama — Effects of the seeding conditions on the crystal growth of gold nanoparticles on indium tin oxide surfaces in the seed-mediated growth method
1140	Break

S5, Electrochemical Engineering: Materials — Lecture Theatre 1 — Chair: T. Wragg

Time	Author, Title
1010	● Keynote S. Rondinini — Nanostructured SnO_2-IrO_2 sol-gel composite electrocatalysts: from powders to electrodes
1040	C. Levy-Clement — Quenching of H_2 evolution at Boron-doped diamond electrode in nitrate solutions
1100	A. Cieciwa — Investigations of Electrochemical Oxygen Transfer Reaction on BDD using Microelectrodes-array
1120	S. Campbell — Electrochemistry in Conservation
1140	Break

S6, Liquid-liquid Electrochemistry: New Directions — Wardlaw Room — Chair: R. Bilewicz

Time	Author, Title
1010	
1030	M. L'Her — Lutetium bisphthalocyanines, Lu(III)[Pc']2, as redox probes for charge and electron transfer studies across liquid-liquid interfaces between water and solvents or ionic liquids: thin-film and three-phase electrodes
1050	K. Maeda — Chemiluminescence Accompanied by Ion Transfer at the Aqueous-Organic Solution Interface
1110	● Keynote T. Kakiuchi — Voltammetry of ion transfer across the micro liquid-liquid interface formed at the orifice of a micropipette in the room-temperature ionic liquid
1140	Break

S7, Soft Materials: In situ Characterisation Techniques — Lecture Theatre 2 — Chair: S. Higgins

Time	Author, Title
1010	● Keynote A. Glidle — Dynamic neutron reflectivity studies providing temporally and spatially resolved composition of electroactive films
1040	A.R. Hillman — Viscoelastic investigations of polyaniline: correlation between film dynamics and composition
1100	O. Semenikhin — Correlation Between Morphology, Local Conductivity And Doping Charge Distribution In Conducting Polymer Films
1120	C. Freire — X-Ray characterisation of structural and functional metal ions in polymeric salen based thin films
1140	Break

S9, Corrosion: Modelling — Cedar Suite — Chair: P. Marcus

Time	Author, Title
1010	Azumi — Application of segmentized electrode system to corrosion monitoring
1030	L. Koene — Simulation of localised corrosion: a combined probabilistic/finite element approach
1050	Baroux — Progress in modelling the active-passive transition in localized corrosion processes. Consequences for materials selection
1110	● Keynote J. Scully — Modeling of the Barrier, Electro-chemical Protection and Active Corrosion Inhibition Properties of an Al-Co-Ce Amorphous Alloy Coating Protecting AA 2024-T3
1140	Break

S10, Fuel Cells: Systems and Diagnostics — Main Hall — Chair: G. Scherer

Time	Author, Title
1010	S. Freunberger — Investigation of Coupling Phenomena in PEFC Stacks
1030	M. Reum — Measuring the Current Density in PEFCs with Sub-Millimetre Resolution – Fundamental Insights
1050	N. Kamiya — Dissolution of Pt under stationary and accelerated conditions
1110	● Keynote A. Kulikovsky — Lessons learned from quasi–2D modeling of PEFC and DMFC
1140	Break

Institute of Corrosion: Infrastructure corrosion — Bruce Room — Chair: S. Lyon

Time	Author, title
1010	Smith — Studying Passive Materials under Erosion-Corrosion Conditions using Single Particle Impingement Experiments
1030	Tsausoglou — Electrochemical Impedance Spectroscopy of the Cement/Magnox Interface
1050	Woodhouse — Investigative contamination experiments related to steel storage vessels in the nuclear power industry
1110	Penney — The Use of the Scanning Vibrating Electrode Technique (SVET) to Study the Effects Processing Parameters have on the Corrosion Properties of Galvalloy
1140	Break

1200 General Assembly

1300 Lunch

POSTER SESSION 3: Thurs 31st Aug (13.00 – 14.30)

Symposium 4:	S4-P-1 to S4-P-121
Symposium 9:	S9-P-1 to S9-P-73
Symposium 10:	S10-P-1 to S10-P-91
ICORR	

S1 Batteries: Characterisation Methods
Carnegie Room
Chair: E. Cairns

Time	Talk
1500	● Keynote **R. Kostecki** — Microprobe Studies of Local Interfacial Phenomena at Lithium-Ion Battery Composite Cathodes
1530	**P. Novák** — In situ analysis of interfaces in nonaqueous electrochemical systems
1550	**C. Gabrielli** — Insertion of hydrogen in palladium films examined by combining EQCM and electroacoustic measurements
1610	*Break*
1630	**P. Ruch** — In situ Raman and XRD studies of carbons for supercapacitors
1650	**L. Dupont** — Electron Microscopy contribution to the characterization of cycled Li-ion electrode materials

S2, Electroanalysis Bio-3
Lecture Theatre 3
Chair: R. Kataky

Time	Talk
1500	**D. Mandler** — Monitoring Enzyme Activity (Lactoperoxidase) in Raw Milk by Electrochemical Methods
1520	**D. Jardel** — Self-signalling Antibodies In Homogeneous Diagnostics
1540	**Y. Kim** — Electroanalytical Studies of Protein Interactions
1600	**F. Lisdat** — Multi-protein, multi-layer assemblies on gold electrodes
1620	**A. Rhodes** — Raman Spectroelectrochemical investigations of Thiol Redox Proteins in the Endoplasmic Reticulum
1640	*Break*

S4, Electrochemical Nanotechnology: Nano-structure & Nanodeposition
Lecture Theatre 4
Chairs: T. Moffat / J. Riley

Time	Talk
1510	**A. Pailleret** — CS-AFM investigations of iron oxide nanoparticles/polypyrrole type electrochemically generated hybrid materials
1530	**B. Bello-Rodriguez** — Nanopore arrays from directionally solidified eutectics as templates for the electrodeposition of gold
1550	**F. Loglio**, Combined Electrochemical Atomic Layer Epitaxy and Microcontact Printing Techniques
1610	*Break*
1630	**X. Li** — Electrodeposition of Mesoporous PbTe Films from Lyotropic Liquid Crystalline Phases
1650	**T. Moffat** — Superconformal Film Growth: Mechanism and Quantification

S5, Electrochemical Engineering: Surface finishing and electrodeposition
Lecture Theatre 1
Chair: S. Campbell

Time	Talk
1500	● Keynote **A. Deconinck** — Advanced modelling of 3D electrochemical machining with time dependent imposed current or potential
1530	**A. Mount** — The Electrochemical Characterisation of Electrochemical Machining
1550	**B. Jovic** — Electrodeposition and morphology of Ni and Co powders
1610	*Break*
1630	**Z. Lodhi** — Cathodic inhibition and anomalous electrodeposition of Zn-Co alloys
1650	**A. Dietz** — A new process for electroplating of magnesium

S6, Liquid-liquid Electrochemistry: Deposition at Liquid-liquid Interfaces
Wardlaw Room
Chair: M Mirkin

Time	Talk
1500	
1520	
1540	**C. Pereira** — Adsorption of phosphatidylcolines at oil/water interfaces
1600	**P. Unwin** — SECM as a Probe of Metal Particle Nucleation at Liquid/Liquid Interfaces
1620	**R. Dryfe** — Metal Deposition at the Liquid/Liquid Interface
1640	*Break*

S7, Soft Materials: Electroactive Polymer Materials & Applications
Lecture Theatre 2
Chair: C. Visy

Time	Talk
1500	● Keynote **J. Mortimer** — Electrochromic properties of disubstituted poly(propylenedioxythiophene)s
1530	**A. Melato** — Preparation of PEDOT/Fe(CN)63- films and their electrocatalytic activity towards the Vitamin C oxidation
1550	**K. Mangold** — Ion exchange properties and selectivity of PPy/PSS composites
1610	*Break*
1630	**D. Fermin** — Molecularly Flat Films of Os Containing Redox Polymer on HOPG Electrodes
1650	**P. Kulesza** — Electrochemical charging and reactivity of conducting polymer-linked polyoxometalate-modified carbon nanostructures

S9, Corrosion: Environmetally-assisted cracking and crevice corrosion
Cedar Suite
Chair: G. Hinds

Time	Talk
1500	**Jae-Bong Lee** — Crevice Corrosion Behavior of Nickel-based Alloys Alloy 600 and Alloy 690 in Acidic Solution Containing Chloride Ions
1520	**J. Wharton** — Effect of nickel-aluminium bronze microstructure and crevice solution chemistry on the initiation of crevice corrosion
1540	**M. Orazem** — Models of Close-Interval Potential Surveys for Buried Pipelines
1600	**K. Bilkova** — Kinetic Study of Model CO2 Corrosion Inhibitors
1620	**Y. Kim** — Lifetime Extension Methods for Components in Nuclear Nuclear Reactor
1640	*Break*

S10, Fuel Cells Systems and Diagnostics
Main Hall
Chair: A. Kulikovsky

Time	Talk
1500	**Jaeyoung Lee** — The development of a direct formic acid fuel cell power system for lap-top computer operation
1520	**A. Arico** — Performance of Direct Ethanol Fuel Cells
1540	**M. Mamlouk** — Performance of a Direct Alcohol Fuel Cell Stack
1600	**T. Oekermann** — A "proton pump" concept for the evaluation of proton transport and electrode kinetics in PEM fuel cells
1620	**M. Chang** — Analysis of membraneless micro fuel cell using decomposition of hydrogen peroxide in a Y-shaped microchannel
1640	*Break*

Institute of Corrosion: Protection by coatings
Bruce Room
Chair: D. Worsley

Time	Talk
1500	**Abdollah** — Improving Corrosion Resistance of Thermal Sprayed (HVOF) Coatings
1520	**Bennett** — Spatially and temporally resolved optical and potentiometric studies of corrosion-driven redox processes in polyaniline coatings
1540	**Lewis** — Composite Organic Coatings for Coil Coating Applications
1600	**Martin** — The Effect of Phthalate and Sulphonic Acid Ester Plasticisers on the TiO2 Catalysed Photodegradation of PVC
1620	**Elvins** — The effect of magnesium additions on the microstructure and cut edge corrosion resistance of zinc aluminium alloy galvanised steel
1640	*Break*

Time	Track 1	Track 2	Track 3	Track 4	Track 5	Track 6	Track 7	Track 8
1700		● Keynote **S. Lakard** Adhesion and proliferation of neuronal cells on electrosynthesized polymers. Development of a biosensor for odour detection			● Keynote **Z. Samec:** Electrocatalysis of oxygen reduction at a polarised liquid-liquid interface by electrodeposited metal particles		● Keynote **S. Fujimoto** Stress Corrosion Cracking of Severely Deformed Type316L Stainless Steels in High Temperature and High Pressure Aqueous Solution	● Keynote **G. Scherer** Aspects of Materials Research for Polymer Electrolyte Fuel Cells	**Al Khaldi** Self assembled Monolayers for Enhancing the Corrosion Performance of Organic Coatings
1710	**R. Koetz** A dilatometric study of ion intercalation from aprotic solutions into carbonaceous materials	**Y. Lanyon** Fabrication of nanobands and nanoband arrays by focused ion beam (FIB) milling and characterisation by voltammetry	**E. Chassaing** First stages of CIS electrodeposition from Cu(II)-In(III)-Se(IV) acidic solutions on polycrystalline Mo films			**I. Cordoba de Torresi** Electrochemical behavior of poly(aniline) and poly(phenylene sulfide) copolymer in ionic liquids		
1730	**K. Nishikawa** Ionic Mass Transfer of Li+ Ion near the Li Ion Battery Electrode / **V. Lvovich** Electrochemical Detection and Characterization of Commercial Globular Proteins	**Y. Guo** Synthesis of nanoporous crystalline metals or compounds with superior catalytic and capacitive activity via electrochemical lithiation	**E. Matykina** Real time imaging of the growth of anodic oxide coatings on titanium under sparking conditions		**A. Ballantyne** Novel Room Temperature Ionic Liquids for the development of Highly Poliarisable Ionic Liquid/Water Interfaces	**P. Bertoncello** Fabrication and High Resolution Characterisation of Charge Transport in Ultra-Thin Langmuir-Schaefer Nafion Films	**A. Turnbull** Predicting the evolution of stress corrosion cracks from corrosion pits	**A. Heller** Miniature, Potentially Implantable, Batteries and Glucose-O2 Fuel Cells / **Minzari** Surface activation by corona for adhesive multi-layer coatings on aluminium
1750		**R. Pemberton** A Screen Printed Carbon Electrochemical Immunosensor Array for the Determination of Mycotoxins in Grain	**M. Abdelsalam** SERS at structured Pt and Pd surfaces			**N. Vlachopoulos** Electrochromic systems based on self-assembled monolayers of phosphonated viologens anchored on high surface area titanium dioxide	**C. Rangel** Susceptibility to Stress Corrosion Cracking of Stainless Steels: The Role of Molybdenum	**D. Schiffrin** Co-generation of hydrogen peroxide and energy in fuel cells / **Bohm** Evaluation of the effect of Chromate and Chromate-free pretreatments on the durability of organic coating on galvanised steel

POSTER SESSION 3: Thurs 31st Aug (13.00 – 15.00 & 18.00 onwards)

Symposium 4:   S4-P-1 to S4-P-121
Symposium 9:   S9-P-1 to S9-P-73
Symposium 10:   S10-P-1 to S10-P-91
ICORR

James Watt Centre I

- Wardlaw Room — **Symposium 6** Oral presentations
- Bruce Room — **ICorr** Oral presentations
- Main Auditorium — **Symposium 10** Oral presentations
- Carnegie Room — **Symposium 1** Oral presentations
- KITCHEN
- PRIVATE

Hugh Nisbeth Buiding

- Lecture Theatre 4 — **Symposium 4** Oral presentations
- Lecture Theatre 1 — **Symposium 5** Oral presentation
- Lecture Theatre 2 — **Symposium 7** Oral presentations
- Lecture Theatre 3 — **Symposium 2** Oral presentations
- Cedar Room — **Symposium 9** Oral presentations
- Bridge Link (4.9m x 24.8m) leading to James Watt Centre
- The Venue

ISE2006: Programme per day

Friday 1st September 2006

0900 Plenary Lecture: Main Hall: **O. Inganas:** Electroactive polymers in redox devices- from printed electrochemical hybrid systems to soft matter actuators and electrical biointerfaces

1000 *Break*

S5 Electrochemical Engineering: Electrodeposition
Lecture Theatre 1
Chair: A. Mount

Time	Author, Title
1010	**S. Nakanishi** Formation of micro- and nano-sized ordered structures by self-organisation in electrochemical systems (Engell Prize)
1040	**T. Kim** Through-Hole Filling by Copper Electroplating Using Two Step Method
1100	**R. Sharna** Investigation of the Electrochemical Impedance of Copper in Acid Plating Solutions
1120	*Break*
1140	**S. Odakura** Influence of accelerator consumption to the filling of copper by electroplating
1200	**B. Kim** Copper Deposition within High Aspect Ratio Vias for 3D Through-Silicon-Via Interconnects
1220	**M. Hasegawa** Effect of polyethylene glycol as an inhibiting additive on electroless copper deposition in submicrometer trenches
1240	*Break*

S6, Liquid-liquid Electrochemistry: Interfacial Dynamics
Wardlaw Room
Chair: R. Dryfe

Time	Author, Title
1010	
1030	**D. Schiffrin** Electroassisted two-dimensional phase formation at a liquid/liquid interface
1050	**Y. Shao** Double-barrel micropipet and its applications
1110	*Break*
1130	● *Keynote* **M. Mirkin** Membrane-Mimetic Shuttling Mechanism of Ion Transfer at the Liquid-Liquid Interface
1200	**Z. Stojek** Electrochemistry with cylindrical microelectrode in contact with two immiscible liquids
1220	**H. Nagatani** Direct spectroelectrochemical measurement of rhodamine dyes at the polarized liquid/liquid interface
1240	*Break*

S7, Soft Materials: Electroactive Polymer Composites
Lecture Theatre 2
Chair: R. Mortimer

Time	Author, Title
1010	● *Keynote* **L. Edman** Light-Emitting Electrochemical Cells: Direct Probing of Doping Progression and Emission
1040	**J. Zhou** Nafion [Ru(bpy)32+] as the Solid Organic Charge Transport Material for the Solid-State Photovoltaic Cell
1100	**T. Otero** Soft, wet, swelling and shrinking three-dimensional electrodes at molecular level: theoretical treatment
1120	*Break*
1140	**P. Pieta** In situ ESR spectroscopic detection of an electrochemically generated superoxide radical, O2*-, by spin trapping
1200	**G. Denuault** Fabrication and characterization of nanostructured electrochromic films
1220	**F. Terzi** Synthesis and characterisation of composite materials based on polythiophenes including metal nanoparticles
1240	*Break*

S9, Corrosion: Inhibiting coatings
Cedar Suite
Chair: J. Wharton

Time	Author, Title
1010	**E. Kálmán** Surface modification of passive iron by alkyl-phosphonic acid layers
1030	**J. Telegdi** Copper corrosion inhibition by amphiphiles in nanolayers
1050	**R. Ramanauskas** Structure and Corrosion Resistance of Pulse Plated Nanocrystalline Zinc and Zinc Alloy Coatings
1110	*Break*
1130	● *Engell Prize Lecture* **D. Chidambaram** Application of Surface Analytical Methods to the Development of Environmentally Friendly Coatings
1200	**V. Barranco** Corrosion protection behaviour of new hybrid sol-gel thin films
1220	**I. Fonseca** Corrosion resistance of Cr-free anodised Al 2024-T3 after long term atmospheric exposures
1240	*Break*

S10, Fuel Cells: SOFC and MCFC
Main Hall
Chair: A. Kornyshev

Time	Author, Title
1010	**M. Koyama** Development of a Three-Dimensional Porous Structure Simulator and Its Application to Fuel Cells
1030	**A. Barbucci** Distribution of the active sites for oxygen reduction in composite electrodes for IT-SOFC
1050	**A. Braun** Investigations on the electronic, ionic, and thermal conductivity of nickel and cobalt substituted lathanum strontium ferrous oxides
1110	*Break*
1130	● *Keynote* **D. Bastidas** Novel LSCM based SOFC for direct electrochemical oxidation of LPG
1200	**D. La Rosa** Direct Electrochemical Oxidation of Propane in Solid Oxide Fuel Cells
1220	**H. Fukunaga** Relationship between the overpotential and the structure of Ni-SDC anode for solid oxide fuel cell
1240	*Break*

1250 Closing Ceremony

Symposium 1

Batteries and Supercapacitors

S1·KN-1

Batteries for a Renewable Energy Economy

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The need to find energy sources to replace oil, gas and coal is increasingly urgent both because of diminishing supplies and global warming. Solar, wind and tidal generation of electricity probably all have a role to play but share a common problem – nature controls when the power is generated and the pattern of generation does not match the demands of consumers, whether industrial or domestic. Hence, energy storage is essential as a buffer between generation and use of such electricity. Moreover, the challenge is to store energy on the MW scale in each unit and such units are inevitably comparable to a chemical plant. Fuel cells and batteries seem a natural way to store electricity. Cycles based on water electrolysis and a fuel cell, however, presently suffer from a very poor energy efficiency, probably ~ 40 %, largely due to the overpotentials still associated with oxygen evolution and reduction. In comparison, batteries can deliver energy efficiencies > 80 % for a charge/discharge cycle.

Redox flow cells have a particular advantage for large scale energy storage - namely, the amount of energy stored is determined by the volume of the electrolyte(s) and the concentration of reactants and the electrolyte(s) are stored external to the cells. Moreover, their engineering and factors determining performance are quite different to other batteries and an energy storage system would be more akin to an electrolytic plant for the manufacture of a chemical than a conventional battery.

The considerations that determine the selection of cell chemistry will be discussed and illustrated using data from systems presently under investigation. Typical performance data will be presented and the factors that limit performance will be discussed. Potential problems with both the electrode reactions and separator will be highlighted.

In Southampton, we have a programme to develop 'the soluble lead acid battery'. This is a lead acid battery with a methanesulfonic acid electrolyte in which lead(II) is highly soluble (> 3 M). Its key advantage over other redox flow batteries is that it operates without a membrane/separator. Detailed performance data for the system will be presented in a later lecture during the conference.

Application of Ionic Liquids to Li batteries and Supercapacitors

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Ionic liquids (ILs) have recently attracted many researchers as novel electrolyte materials for the electrochemical devices. The thermally-stable and non-flammable nature of ILs can improve the safety of Li batteries and supercapacitors in abuse. In addition, condensed ionic state in ILs is favorable for the increase of energy density of supercapacitors. Authors have applied several ILs to these devices [1-3] and tried to sort out what happens in the electrochemical devices using ILs.

Among a lot of the series of ILs, quaternary ammonium (QA) cation – imide combination is fairly interesting for the higher electrochemical stability especially in the reduction [3,4]. This is advantageous for the application to the Li battery system and Li/$LiCoO_2$ cell with the ILs as an electrolyte base could work reversibly (one example is shown in Figure 1), indicating that QA-imide ILs were quite stable even at the Li reduction potential [2].

In the presentation, for the Li battery system, the way we reached the cyclic QA-imide I L "PP13-TFSI (N-methyl-N-propylpiperidinium bis (trifluoro methanesulfonyl)imide)" will be introduced. Surface analysis results of the electrode after the cell operation, which is closely related to the electrochemical stability against the electrode, will be focused. A brief introduction of the current status of the supercapacitors using ILs will also be made.
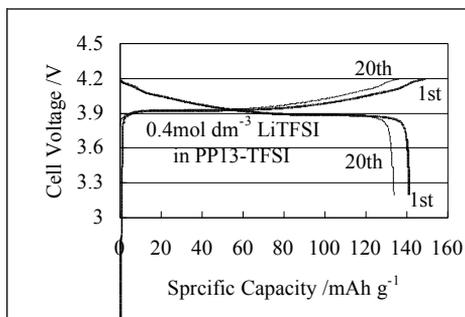
Figure 1:

First and 20th charge-discharge curves for Li/$LiCoO_2$ cell containing 0.4 mol dm^{-3} LiTFSI in PP13-TFSI,. Charge cut off:4.2 V CC mode, discharge cut off: 3.2 V CC mode, charge and discharge current rate: C/10. Modified from ref. [2].

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Research and Development Considerations for the Performance and Application of Supercapacitors

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Electrochemical capacitors (ultracapacitors) are being developed as an alternative to pulse power batteries. In this paper, the differences between pulse batteries and ultracapacitors are discussed and how these differences are reflected in the design and testing of the two types of devices. Research and development on high power ultracapacitors has been underway for over 15 years. Properly configured, ultracapacitors are inherently high power devices so that much of the research has been directed toward increasing their energy density (Wh/kg) without unduly sacrificing their high power and long cycle life. The characteristics of the ultracapacitors depend primarily on the specific capacitance (F/gm and F/cm3) of the electrode materials and the ionic resistivity and voltage window of the electrolyte. In addition to the energy density, the key performance characteristics of the cells are their resistance, RC time constant, and pulse power (W/kg) for high efficiency (95%). Most of the research on ultracapacitors has utilized activated carbons for at least one of the electrodes. In these carbons, charge is stored in the micropores by double-layer processes. Recently carbons are being used that store charge using intercalation and absorption processes that result in much higher specific capacitance than is achievable using double-layer processes. In this paper, the recent work using the advanced carbons is reviewed and future use in ultracapacitors projected. Another approach to increasing the energy density of ultracapacitor- like devices is to combine a carbon electrode with an electrode using pseudo-capacitance or Faradaic chemical processes for charge storage. Considerable progress has been made in the development of such devices in recent years and that research is reviewed in this paper.

Symposium 1 - Keynote

Batteries and Supercapacitors

NMR Studies of Lithium-Ion Battery Materials: Applications to the Li_2MnO_3-$Li(NiMn)_{0.5}O_2$ System, Layered Oxysulfides and Other Paramagnetic Materials

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Y. Shirley Meng,[b] Kisuk Kang,[b] Gerbrand Ceder,[b] Oliver J. Rutt[c] and
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[6]Li MAS NMR spectroscopy has been used to study local electronic structures and Li local environments in a variety of potential cathode materials for lithium ion batteries including spinels and layered cathode materials such as $Li[M'_xM_{1-x}]O_2$ (M,M' = Mn, Ni, Co etc.). We first developed a fundamental understanding of the causes of the large (hyperfine) NMR shifts typically observed in these paramagnetic samples. This knowledge was then applied, in conjunction with X-ray and neutron diffraction studies, to follow structural changes after charging and discharging of a battery, to help establish why some materials function well as electrode materials and others fail.

We will discuss results for two systems. In the first example, the effect of synthesis method and electrochemical cycling on the local and long range structure of members of the Li_2MnO_3-$Li(NiMn)_{0.5}O_2$ pseudobinary will be described. Second, an investigation of new materials including layered oxysulfides will be presented. Insertion reactions and lithium-mobility in these compounds will be described.

Microprobe Studies of Local Interfacial Phenomena at Lithium-Ion Battery Composite Cathodes

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A continuous degradation of lithium-ion batteries upon aging and/or cycling often limits the performance of portable electronic devices and presents a significant barrier for vehicular applications. The impedance growth that is observed at both electrodes is associated with an ion-blocking surface film as well as an electronically insulating barrier formed within the electrode. The resistances to both ion and electron transfer constitute the overall charge transfer impedance and contribute to the overall electrode impedance. In contrast to the anode, the cathode SEI layer is so thin that its presence has not been confirmed until recently. Surface sensitive techniques were used to detect, monitor and analyze surface layers on composite cathodes [1,2,3].

Interfacial phenomena occur and manifest themselves at nano- or micro-scales and can be detected and characterized only by techniques of suitable sensitivity and resolution. *In-situ* and *ex-situ* application of non-invasive and non-destructive microscopies to characterize local physico-chemical properties of the electrode/electrolyte interface provide unique insight into the mechanism of chemical and electrochemical processes, which are responsible for the electrode degradation. *Ex situ* Raman mapping of cathodes from tested high-power Li-ion cells, showed that the state of charge (SOC) of oxide particles on the cathode surface was highly non-uniform despite deep discharge of the Li-ion cells at the end of the test. *In situ* Raman microprobe monitoring of the SOC of individual oxide particles in the composite cathode revealed that the charge/discharge rate varied with time and location [4]. CSAFM and SEM images of aged composite electrodes showed surface deposits and morphology changes. Surface analysis revealed that surface decomposition products originate from $LiPF_6$ decomposition and oxygen, water, and C-O-H, -C=O surface functional groups adsorbed at carbon additives catalyze and/or react with the electrolyte. These surface reaction products create electronic barriers within the composite electrode, which lead to inconsistent kinetic behavior of individual oxide particles and contribute to the overall impedance of the composite cathodes.

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Symposium 1 - Keynote

Batteries and Supercapacitors

Combinatorial and High Throughput Studies of Alloy Negative Electrodes for Li-ion Batteries

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Although carbon or graphite was shown to be a possible practical negative electrode for lithium-ion batteries in the 1980's it took almost a decade for all manufacturers to agree that graphitized materials were the most suitable of carbonaceous materials. Now, almost all Li-ion batteries use highly graphitic carbons as negative electrode materials.

The recent launch of a 14430-sized lithium-ion battery using a tin-based negative electrode (Sony, Japan) makes it clear that silicon and tin-based alloys will begin displacing graphite as the dominant negative electrode material in Li-ion batteries. Sony has announced that the electrode material in their cell is an "amorphous tin-cobalt-carbon" material.

Given that it took the Li-ion battery community about 10 years to settle on graphitic carbons as the best choice for Li-ion battery negative electrode materials based on the **single** element, carbon, how long will it take to find the "best" alloy negative electrode material given the myriad of possible choices available? For example in a patent by Kawakami et al. [1], the inventors claim Sn-A-X materials as excellent negative electrode materials where A indicates at least one transition metal element and X indicates at least one element selected from the group consisting of O, F, N, Mg, Ba, Sr, Ca, La, Ce, Si, Ge, C, P, B, Pb, Bi, Sb, Al, Ga, In, Tl, Zn, Be, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, As, Se, Te, Li and S, where the element X is not always necessary. Which combination of these elements is "best" from the viewpoints of capacity, capacity retention, potential, safety, toxicity, manufacturability and cost?

It is clear that combinatorial methods for synthesizing and screening the myriad of choices are needed. In this lecture, I will describe the combinatorial infrastructure in place at Dalhousie University [e.g. 2] and how it is being used to help **understand** those factors that lead to the "best" negative electrode material.

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New lithium salts for liquid or solid polymer electrolyte

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Symposium 1 Batteries and supercapacitors.

In electrolyte, the salt selection obeys to several criteria, the first of all being its electrochemical stability. The other salt criteria are their conductivity, cationic transference number, cost and molar weight. Due to the low dielectric constant of polymeric solvents, the use of organic lithium salts, in particular of superacid, became widespread. Indeed they have both low lattice energy and poorly nucleophilic anions. As ether is a hard base and lithium cation a hard acid, the interaction between POE matrix and Li^+ is very strong, resulting in a low cationic transference number, t^+, generally markedly lower than 0.5. While $POE/(CF_3SO_2)_2NLi$ and $POE/(CF_3SO_2)_3CLi$ complexes are the highest conducting polymer electrolytes, both have a poor cationic transference number in poly(oxyethylene) as compared, in particular, to lithium triflate. Now, an improvement in the battery performance can be obtained by an increase of the cationic transference number [1,2].

We therefore prepared new organic salts based on fluorinated and non-fluorinated anion.

To find an alternative to the fluorinated salts, Reibel et al. [3] developed aromatic sulfonimides. Anionic charge delocalization is essential in aprotic electrolytes to increase the dissociation of this non-fluorinated salt, therefore its ionic conductivity. We selected therefore aromatic amidure salts. The evaluation of the charge delocalization effect of aromatic nitro substituents was performed.

As for non-fluorinated, aromatic anions were selected according to the possibility (i) to introduce electron-withdrawing groups and (ii) to graft the salt in polymer backbone (t_+=1). Moreover, aromatic anions generally presented low mobility [4], which might be due to their rigid skeleton. We selected, for example pentafluoro benzene sulfonate lithium salt. The syntheses and electrochemical characterizations: conductivity, transference number, electrochemical stability, of these salts were evaluated.

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Symposium 1 - Oral

Batteries and Supercapacitors

The conductivity of crystalline polymer electrolytes

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For some thirty years it was believed that ion transport in polymers occurred only in the amorphous state above the glass transition temperature T_g, with the polymer segmental motion playing a pivotal role in enabling ion transport. Such thinking has raised the level of conductivity to values in excess of 10^{-5} Scm^{-1}. However, the level of conductivity that may be achieved in these amorphous polymer electrolytes has proved insufficient for many applications, including the important application of rechargeable lithium batteries.

Crystalline counterparts of amorphous polymer electrolytes were considered to be insulators. This view has been recently overturned by the discovery of ionic conductivity in the crystalline polymer-salt complexes $PEO_6:LiXF_6$ where x= P, As, Sb.[1] These three complexes have been shown not only to conduct but to do so better than the amorphous phases of the same composition, Fig. 1. The key to the ionic conduction in the crystalline polymer electrolytes is their structure, Fig. 2.[2] The structure is composed of cylindrical tunnels, formed by PEO chains, within which the Li$^+$ ions reside. The anions do not coordinate the cations and located outside the tunnels. The tunnels provide convenient pathways along which the lithium ions may migrate. The levels of conductivity of these electrolytes are not high, however, they can be significantly improved by modifying the stoichiometric materials by isovalent and aliovalent doping.[3,4] There are other factors that influence the conductivty of these materials which include molecular weight of the polymer, its dispersity, end-capping of polymer chains. We shall discuss various strategies for modifying these materials that permit elevation of the conductivities beyond those obtained with traditional components.
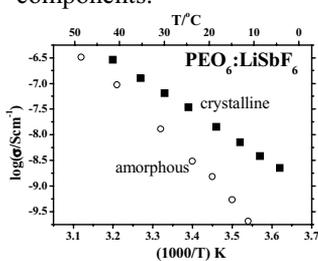
Fig.1
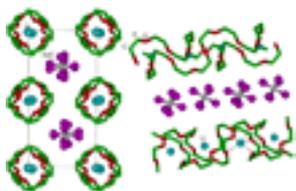
Fig.2
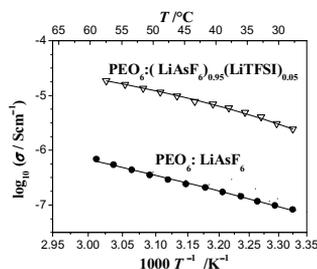
Fig.3

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S1·O-3

A New Type of Battery Using a Magnetic Field

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A new type of battery is proposed that utilizes the occurrence of an inviscid flow in a magnetic channel to maintain the oxidant stream separated from the reductant solution in diffusional contact by a magnetic wall. The main part of the system is, as shown in Fig. 1a, composed of an invisible magnetic channel formed by a magnetic field and a ferromagnetic track, which confines, e.g., a liquid stream of oxidant solution on the cathode. As shown in Figs. 1b and 1c, under a magnetic field, in the neighbourhood of ferromagnetic materials or diamagnetic materials, magnetic flux densities take a heterogeneous distribution, so that the magnetic channel shown in Fig. 1a is formed.

The concept of the magnetic-channel-flow battery is shown in Fig. 2; for a paramagnetic solution containing cathodic active species, though invisible, magnetic channels formed on platinum plated iron tracks imbedded in a plastic plate are established, which are surrounded by a diamagnetic solution with anodic active species. The tracks are also used as the cathode, whereas the anode is placed over the cathode. As the magnetic wall sustains the magnetic channel flow from all sides, the channel also acts as an elastic tube, which allows us to make an inviscid flow of the oxidant. These facts are quite useful for high battery performance since a large amount of active material can be supplied, and much larger area of liquid-liquid interface than that of conventional systems can be available.

As for the possibility and performance of this type of battery, a Daniel-cell-type battery was first examined; copper ion from copper sulphate is employed as an oxidant and zinc sulphate as a reductant. Copper ion is paramagnetic, so that an oxidant solution containing 1 mol dm^{-3} copper sulphate is injected to a magnetic channel formed by an iron track placed in a magnetic field. As an ambient reductant solution, 1 mol dm^{-3} diamagnetic zinc sulphate solution surrounds the magnetic channel, slowly circulated. The performance attained up to 22 mA cm^{-2}.
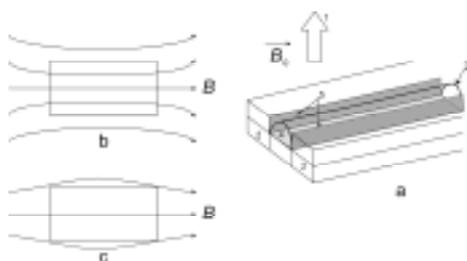
Fig. 1 Formation of magnetic channel.
a, a magnetic channel; b and c, magnetic flux densities for ferromagnetic and diamagnetic materials, respectively.
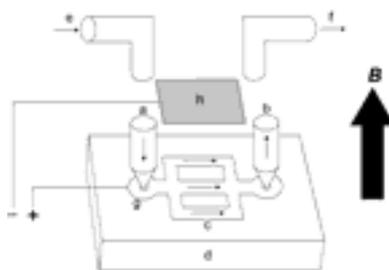
Fig. 2 A magnetic-channel-flow battery

Electrodeposited nano-sized thin films of Sb and Sb-Sb2O3 as anode materials in Li- ion batteries.

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In today's commercial batteries graphite is used as anode material, but research is made on metal-based anode materials to enhance capacity and improve rate capability. Sb can react with Li to form Li_3Sb, which leads to a theoretical capacity of 660 mAhg^{-1} compared to 372 mAhg^{-1} for graphite. However, the problem is (as is the case for a number of different lithium-alloying metals) that large volume changes during cycling leads to particle pulverization and loss of electronic contact. The use of nano alloys or intermetallics (with metals active and inactive to lithium alloying) can minimize the volume stress avoiding cracking and pulverisation of the anode. We have chosen to study electrochemically deposited nanothin films of Sb and Sb-Sb_2O_3. As no binder or electron conducting material is needed in making the films, the electrodes are also suitable model systems for SEI (Solid Electrolyte Interface) studies.
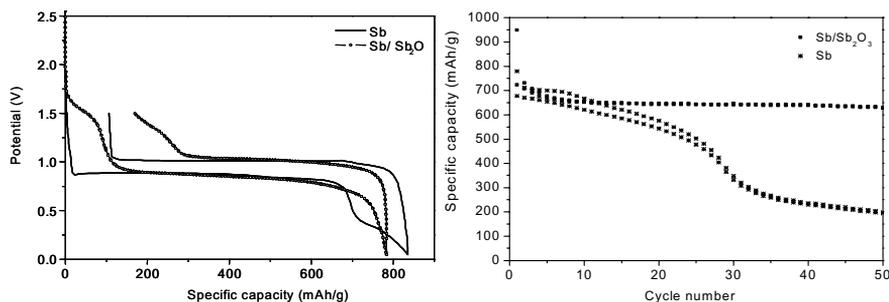
Figure 1. Electrochemical results of a pure Sb electrode and an electrode with co-deposited Sb/Sb_2O_3; the first cycle (a) and the cycling capacity (b).

By adjusting the pH in the electro deposition electrolyte, pure Sb films and Sb films with codeposition of Sb_2O_3 are achieved. In Figure 1a the first cycle of the two films are shown. The presence of the oxide is seen in the reduction potential around 1.6 V where the plateau is most likely due to formation of Li_2O. For pure Sb a plateau, not observed for the Sb_2O_3, is seen below 0.4 V. A possible explanation to this plateau is an additionally formed SEI layer. The cycling stability of the electrodes is improved dramatically, when Sb_2O_3 is codeposited in the films (Figure 1b). In this presentation it will be discussed how the presence of oxide and the SEI layer influences cycling performance. The results will be used to shed some light on the complex reactions occurring in composite electrodes containing antimony, such as Cu_2Sb and AlSb.

Electrochemical synthesis and capacitance of porous composite of carbon nanotubes and polyaniline

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Previously, the authors reported codeposition of polypyrrole (PPy) and multiwalled carbon nanotubes (MWNTs) composite films, via electrochemical oxidation from a solution/suspension of pyrrole monomer and acid-treated MWNTs[1-3]. The acid treatment introduces carboxyl and hydroxyl functional groups that are increasingly negatively charged when deprotonated by raising the pH of the aqueous suspension. The charge on the nanotubes both stabilises the dispersion and allows them to act as the counter ion or dopant for the electropolymerisation of the monomer. Subsequently, the nanotubes are, to some degree, ionically bound to the polymer. This interaction has been shown to produce a large negative potential shift in the composite redox peaks, and to result in the intercalation of both cations and anions during the redox processes; both effects contribute positively to the high electrochemical capacitance of the composite material [1-4]. The current study was motivated by the hope that incorporating negatively charged nanotubes into polyaniline (PAn) might produce similar effects; electrodes based on PAn are desired in order to extend the voltage range of supercapacitors based on polymer nanocomposites[4]. Nanoporous composite films of MWNTs and PAn were grown electrochemically from acidic aqueous solutions, such that the constituents were deposited simultaneously onto graphite electrodes. Scanning electron microscopy revealed that the composite films consisted of nanoporous networks of MWNTs coated with PAn. Cyclic voltammetry and electrochemical impedance spectroscopy demonstrated that these composite films had similar electrochemical response rates to pure PAn films, but a lower resistance and much improved mechanical integrity. The specific capacitance of the composite films, per unit area of the original electrode, reached as high as 3.5 F/cm^2, a significantly greater value than that of 2.3 F/cm^2 for pure PAn films prepared similarly.

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Symposium 1 - Oral

Batteries and Supercapacitors

Rechargeable lithium/air battery

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Rechargeable lithium batteries are now a major technology, driven by their superior energy density compared with alternative rechargeable batteries. There is much interest in increasing further the energy density. This is limited by the positive electrode, $LiCoO_2$, which can cycle only around 0.5 Li per formula unit. Intensive research world-wide on new intercalation cathodes will increase the amount of Li that may be stored, but only by a factor of 2. To achieve the desired leap forward in the performance of rechargeable lithium-ion batteries, we must investigate electrode reactions that are radically different from the conventional intercalation process. One approach is the use of an air cathode.

Abandoning the intercalation cathode in a lithium battery and allowing Li to react directly with O_2 from the air at a porous electrode increases the theoretical charge storage to 1800 mAhg^{-1}! The reactants no longer have to be carried on-board the cell and the supply of O_2 is, in principle, infinite. The result is a form of battery/fuel cell hybrid. Whereas the air electrode in aqueous batteries is well known, studies addressing the O_2 electrode in non-aqueous Li batteries have been very limited in number.[1-2] The electrode reactions are fundamentally different in non aqueous cell. Here we demonstrate two essential prerequisites for the successful operation of a rechargeable Li/O_2 battery; that the Li_2O_2 formed on discharging such an O_2 electrode is decomposed to Li and O_2 on charging (shown here by *in situ* mass spec, Fig1), with or without a catalyst, and that charge/discharge cycling is sustainable for many cycles.

More details on the characterisation of the O_2 cathode will be presented, including the influence of catalysts on the electrode reaction. Results of studies by X-ray diffraction and gravimetric analysis will also be presented.

Figure 1. **Variation of ion current corresponding to O_2 evolution as a function of time during the charge of an Li_2O_2 electrode. The voltage was increased by 100 mV every 120 min.**
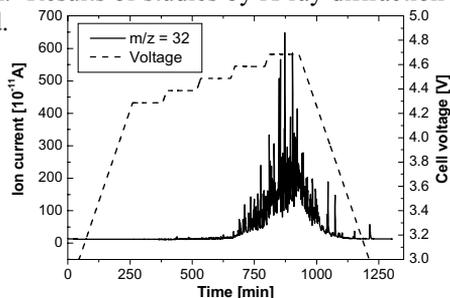
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Study on the $LiFePO_4/CaB_6$ Composites used as cathode for a Li-ion Battery

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As an alternative cathode material $LiFePO_4$ has two fatal disadvantages: low electric conductivity and low tap density, which makes it difficult that $LiFePO_4$ is used as the cathode for the commercial lithium ion battery.

A novel composite used CaB_6 as an additive was firstly found to use to improve the electrochemical performance of $LiFePO_4$. Pure $LiFePO_4$ was synthesized by solid sate reaction and $LiFePO_4/CaB_6$ composite with different contents of CaB_6 was prepared by two different methods. The samples were characterized by the granularity, morphology, electric conductivity, tap density, X-ray diffraction and electrochemical performance. The results showed that the tap density and electronic conductivity of $LiFePO_4$ doped with CaB_6 were significantly improved. The electronic conductivity of $LiFePO_4/CaB_6$ composite prepared was increased by five orders of magnitude and its tap density was enhanced by 65%.
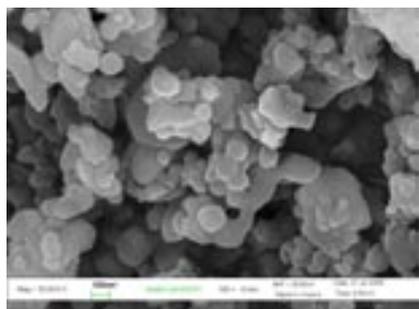
Fig.1 SEM of prepared $LiFePO_4/CaB_6$ composite
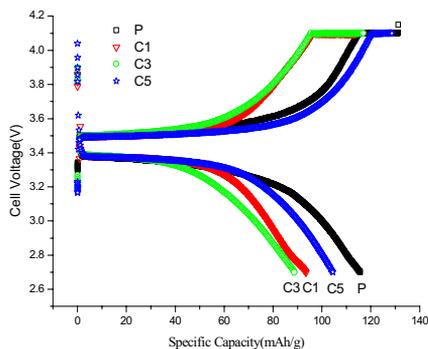
Fig.2 Charge-discharge curves of the batteries at 40mA/g employing the different $LiFePO_4/CaB_6$ composites as cathodes respectively

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Electron Microscopy contribution to the characterization of cycled Li-ion electrode materials (Conversion and CDI mechanisms)

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Batteries performances depend on many factors amongst which the most critical are the selection/synthesis of the appropriate electrode material and the control of the electrode/electrolyte interface upon cycling. In order to address these issues, electrochemists have to design new electrode materials, to finely tune the electrode texture for maximum electrochemical efficiency, to spot interfacial modifications/growing layers or, in short, to 'enter the private life' of a battery.

Electron Microscopy is a powerful tool to help scientists throughout these different steps. This point will be exemplified with descriptive examples selected from our recent works on electrode materials reacting without alloying or insertion of lithium.

Two different types of mechanism will be studied:

- Conversion Reaction for most of transition metal compounds (oxides, nitrides, borates, fluorides, sulphides), with the decomposition of a transition metal oxide into metallic nanograins embedded in a lithiated matrix during discharge, and the re-oxidation of the so-formed nanoparticles during the following charge.
TEM studies realized on phosphides will be shown[1-2].

- Combination displacement/intercalation (CDI) mechanism giving reversible capacities as high as 270 mAh·g^{-1} (more than twice that of electrode materials presently used in commercial Li ion batteries) Studies realized on CuM_2X_4/Electrolyte/Li cells (where M=Ti, Cr and X=S or Se) will be presented[3].

These promising results could enable a breakthrough in the performance improvement of future batteries.

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Effect of Cu_2O Coating on graphite as Anode Material of Lithium Ion Battery in PC-based electrolyte

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Graphite has been regarded as the most dominant anode material in lithium ion battery for its good cycle performance, high energy density, low cost, and low toxicity. However, its application in propylene carbonate (PC) based electrolyte has been greatly hindered due to its severe exfoliation caused by PC solvated lithium ions. A lot of efforts have been made to solve this problem since propylene carbonate system obtains better low-temperature performance compared with ethylene carbonate system. Here we introduced a method to suppress the degradation of graphite in PC electrolyte by coating Cu_2O as a protective layer.
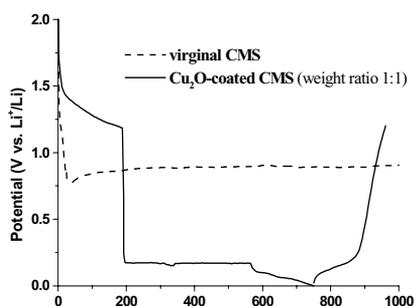
Fig. 1.The discharge and charge profiles of CMS and Cu_2O-coated CMS in PC-DMC (1:1 v/v) electrolyte.

Fig.1 shows the discharge and charge curves of CMS (an artificial graphite) and Cu_2O coating CMS in PC-DMC (1:1 v/v) electrolyte during the first charge and discharge cycle. For virginal CMS, the voltage plateau of the discharge curve indicates that there is no intercalation of lithium ion into graphite, because the graphite structure was destroyed by PC solvated lithium ion and a good SEI film could not be formed. However, after coating with Cu_2O on the surface, there is no potential plateau around 0.8V, revealing that the exfoliation has been greatly suppressed by the coating Cu_2O layer. The potential plateau around 1.3V is due to the lithium ion intercalation into Cu_2O. The reversible capacity of modified CMS is as high as 240mAh/g. By the way, CV and EIS were measured to investigate the effects of the coating.

In summary, with simple coating of Cu_2O on an artificial graphite, the exfoliation of the graphite in PC-based electrolyte has been suppressed.

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Nanostructured titania with improved properties as anode materials for lithium batteries

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Nanostructured TiO_2 has been one of the widely investigated transition metal oxides for Li insertion because it is not only a low-voltage insertion host for Li, but also a fast Li insertion/extraction host, which renders it a potential anode material for high-power lithium batteries [1, 2].

The electrochemical behaviors (lithium insertion/extraction) of anatase and rutile with different particle sizes and shapes have been studied in this paper. In the case of anatase [3], mesoporous TiO_2 sub-micron spheres consisting of interconnected nanoparticles with size of *ca.* 7 nm show much higher capacity, better capacity retention and improved rate performance than those of the commercial samples having the same particle size (~ 300 nm). About 0.95 mol Li can be inserted into the mesoporous TiO_2 while only 0.44 mol Li can be inserted into commercial TiO_2 in the first discharge process. Mesoporous TiO_2 spheres are able to reversibly accommodate Li up to $Li_{0.63}TiO_2$ (210 mA h g^{-1}) at 1-3 V *vs.* Li^+/Li with a good capacity retention on cycling. Another excellent property of this mesoporous TiO_2 spheres is the high rate capability. A specific charge capacity of around 210 mA h g^{-1} was obtained at a rate of C/5 after 40 cycles; this value is lowered to 190 mA h g^{-1} at C/2, 175 mA h g^{-1} at 1C, 155 mA h g^{-1} at 2C, 116 mA h g^{-1} at 5C, and finally, 88 mA h g^{-1} at 10C.

In the case of rutile [4], up to 0.8 mol Li can be inserted into nano-sized rutile at room temperature while only 0.1 - 0.25 mol Li can be inserted into micro-sized rutile (500 nm - 20 µm). Nano-sized rutile is able to reversibly accommodate Li up to $Li_{0.5}TiO_2$ at 1 - 3 V *vs.* Li^+/Li with excellent capacity retention and high rate capability on cycling. A specific charge capacity of around 160 mA h g^{-1} was obtained at a rate of C/20 after 50 cycles; this value is lowered to 150 mA h g^{-1} at C/5, 132 mA h g^{-1} at 1C, 110 mA h g^{-1} at 5C, 100 mA h g^{-1} at 10C, 81 mA h g^{-1} at 20C, and finally, 70 mA h g^{-1} at 30C. As far as titania is concerned, it is the best rate performance ever measured especially at higher rate.

Present results provide evidence for the usefulness of nanostructured titania as novel anode materials for lithium batteries.

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Electrochemically deposited nanostructured ni-co oxide for supercapacitor application

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Electrochemical capacitors are the charge-storage devices having the capability to store higher power density than batteries and higher energy density than dielectric capacitors. They are of significant importance in the portable devices as well as electric vehicles. Several metal oxides were synthesized for supercapacitor electrode in the past few years. In the present study, electrochemical synthesis and capacitive characterization of nanostructured Ni-Co oxide are presented

The Co-Ni oxide was potentiodynamically deposited on a stainless-steel electrode of 1 cm x 1 cm area in the electrolyte solution of 0.1 M $NiCl_2 \cdot 6H_2O$ + 0.05 M $CoCl_2 \cdot 6H_2O$. The deposited electrodes were further heat-treated at 300°C and characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV) and charge-discharge (CD) cycling. The electrochemical characterization was performed in a three-electrode cell with different concentration of KOH solution as electrolyte.

The SEM images of the deposited Ni-Co oxide indicate that the deposite is highly porous and the Ni-Co oxide is in the form of nano-rods. The EDX elemental mapping study showed that the Ni, Co and O elements are present uniformaly in the deposite. The CV measurements showed that the nature of the CV curve was close to rectangular shape. From the CD measurements, a specific capacitance (SC) of 331 F/g was obtained at 1 mA/cm^2. Fig. 1 shows the CD cycling data for 1st and 1000th cycles. A SC decrease of only ~2% was

Fig. 1 CD cycling stability curves of the Co-Ni oxide electrode at various current densities.

observed after the CD cycling of 10000 cycles. This indicates that the Ni-Co oxide electrode is a potential candidate for supercapacitor applications.

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High Rate Capability of Platelet Structure Carbon Nanofibers as Anode Materials for Lithium Ion Batteries

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Porous anodic alumina is a useful template for the preparation of various nanofibers with controlled fiber diameter. The authors have prepared carbon nanofibers by liquid phase carbonization of poly(vinyl)chloride (PVC) in pores of the template. The carbon nanofibers thus obtained have a platelet structure with the graphitization degree increasing with heat treatment temperature. The platelet structure carbon nanofibers are of interest as anode materials for lithium ion batteries since diffusion length of the intercalated lithium ions is short, possibly improving the rate capability. Thus, in the present study we have examined the influence of fiber diameter and heat treatment temperature on anode characteristics of the carbon nanofibers for lithium ion batteries, with particular attention paid to their rate capability.

A mixture of PVC powders and porous anodic alumina template with pore diameters of 30 or 200 nm were heated in a stream of high purity argon gas to 600°C. Then, the template was dissolved and fibrous carbon precursors were obtained. The precursors were further heated to 1000, 1500 and 2800°C. The anodes were prepared by coating a mixture of carbon nanofilaments and polyvinylidene fluoride on porous nickel sheets. The anodes with acetylene black as a conducting material were also prepared. A liquid electrolyte of 1.0 mol dm^{-3} $LiClO_4$ dissolved in EC+DEC (1:1 by volume) was used.

The carbon nanofibers heat-treated at 2800°C was highly graphitized, and their charge-discharge curves revealed a plateau region close to 0.1 V vs Li/Li$^+$, being similar to typical graphite. However, the reversible capacity was less than 200 mA h g^{-1} at a current density of 50 mA g^{-1}, which was far lower than the theoretical capacity of graphite (372 mA h g^{-1}). The lower capacity of this material might be related to the development of loops connecting each ~5 layers at the edge of graphene layers.

Higher capacity and higher rate capability was obtained for the carbon nanofibers heat-treated at 1000°C. Further, it was confirmed that the reversible capacity became higher with reducing fiber diameter, particularly at high current density, for the carbon nanofibers heat-treated at this temperature. The addition of conducting material in electrode further improves the rate capability due to low electrical conductivity of the active materials formed at 1000°C.

Graphite/sulfur lithium ion cell using lithium compensation of a lithium foil

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Non-lithiated cathode materials were widely investigated for use with lithium metal anodes, in cells based on polyethylene oxide electrolytes. Sulfur-based materials have capacities of more than trible that of lithium cobalt oxide, though at a lower average discharge voltage. These materials are inherently safer than lithiated cathode materials because they cannot be overcharged. To be used in a lithium ion cell, an alternative source of lithium must be provided. The lower voltage is not necessarily a problem, given reduction in the operating voltage of electronic circuits.

In this study, graphite/sulfur composite lithium ion cells have been constructed with a lithium metal foil incorporated in the anode. The foil can be used to compensate for the irreversible capacity of the anode, allowing anode materials with large reversible and irreversible capacities to be used. The foil also enables high capacity, non-**lithiated** cathode materials (nano sulfur composite, which is prepared as described in [1]) to be used in lithium ion cells.

The cathode was nano sulfur composite. The anode used was graphite. In a dry glove box, the Celgard 2400 porous membrane was used as the separator, and put between the cathode and the anode to form a model cell, and a lithium metal foil was put between the anode and the separator, which was sealed in a coin type battery after addition of 1 M $LiPF_6$-EC/DEC electrolyte solution. The test was carried out at a constant current density of 0.25 mA cm^{-2} and within the voltage range of 1.0-3.0 V.

Fig. 1 shows the cycling performance of the test cell. It indicates that the test cell can be cycled. This paves the way to fabricate cell with the sulfur based cathode materials.
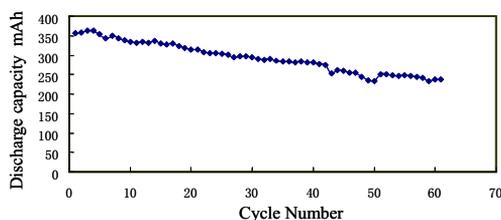
Fig 1 Cycling performance of Nano sulfur composite/graphite test cell

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Ethylene carbonate — organic ester based mixed electrolytes for electrical double layer capacitors

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The electrochemical characteristics of electrical double layer capacitor (EDLC) single cells, based on the nanoporous carbon cloth electrode (thickness ~300 µm) in 1M $(C_2H_5)_3CH_3NBF_4$ solution in various non-aqueous organic carbonate and organic ester binary, ternary and quaternary solvent systems (ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), methyl formate (MF), methyl acetate (MA) and ethyl acetate (EA)) mixed in the x:y, x:y:z and x:y:z:f volume ratios, respectively) have been studied using the cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) methods [1]. The specific capacitance C_s, phase angle δ, series (R_s) and parallel resistance (R_p) values dependent on the conductivity of solvent system used have been calculated. The region of ideal polarisability of nanoporous carbon electrodes $\Delta E \geq 3.0V$ for 1M TEMABF$_4$ in various non-aqueous solvent systems has been achieved. Specific conductivity values have been obtained from $-40°C<$ to $< 50°C$ and compared with electrochemical characteristics. All experiments discussed were made inside the glove box Labmaster 130 at very clean and dry conditions. The two-electrode system was set in a hermetic aluminium test cell to ensure the gas tightness of the cell. Between working electrodes the 25 µm thick Celgard separator sheet was used. Impedance spectra were recorded using Solartron FRA 1255 and potentiostat 1286 over a frequency range $5\times10^3…1\times10^{-3}$ Hz, and 5 mV modulation was used. The ac response of the EDLC filled with the electrolyte having a good specific conductivity (EC:EA, EC:MA, EC:MF (1:1), EC:DMC:EA, EC:DMC:MA or EC:DMC:MF (1:1:1) solvent + 1M $(C_2H_5)_3CH_3NBF_4$) shows only very weak dependence of R_{pore} on the potential difference applied if $\Delta E \leq$ 2.7 V, and R_{pore} increases noticeably with ΔE only at $\Delta E > 2.7$ V. For other systems, having lower specific conductivity the values of R_E and R_{pore} depend noticeably on ΔE in a good agreement with the dependence of the phase angle δ on ΔE, obtained at low frequencies. Thus according to the experimental data, the deviation of mixed solvent + 1M $(C_2H_5)_3CH_3NBF_4$ | NPCE interface from the purely adsorption limited system increases with ΔE. According to the experimental results, comparatively low values of phase angle δ at $f < 5\times10^{-2}$ Hz ($\delta \leq -82°$ at $f \leq 1$mHz) have been obtained for EC:EA, EC:DMC:EA and EC:DMC:MA (1:1 and 1:1:1 volume ratio) containing single cells. Thus, the nearly ideal capacitive behaviour, like for NPCE | AN has been observed only for systems having high specific conductivities.

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Synthesis And Characterization Of Comb Shape Single Ion Conductors Based On Polyepoxide Ethers And Perfluorinataed Lithium Salts

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Most single ion conductors for lithium batteries are synthesized by fixing either alkyl sulfonate or carboxylate to the polymer backbones. However, due to their limited solubility and dissociation in polyether media, their ambient conductivities are usually in the range of 10^{-7}-10^{-8} S.cm^{-1} [1,2]. There are several approaches to improve the ambient conductivities of single ion conductors. One is to modify the structure of the host polymer to lower its glass transition temperature and thus improve ionic conductivity through increased ion mobility. Another is to modify the structure of the anion by placing strong electron-withdrawing atoms, such as fluorine, adjacent to it to decrease the electron density on the anions and thus increase the ionic conductivity through increased number of free conducting lithium cations. The best approach, of course, is to combine the above two favorable changes in one structure. It was shown in our group[3] that the comb-shaped polyepoxides with trimethylene oxide (TMO) as side chains have lower glass transition temperatures with increasing lithium salt concentration than those with EO as side chains, which is more effective in providing higher chain mobility especially at lower temperatures. In this paper we synthesized two polyepoxide ether prepolymers, one with TMO units in the side chain and the other with EO units in the side chain, and different allyl groups containing lithium salts, either perfluorinated or non fluorinated. The focus of this paper is to compare the effect of the structure of polymer and lithium salts on the ionic conductivities of the resulting single ion conductors. The TMO polymers showed a much lower conductivity than the EO polymers for the alkyl and fluoroalkylsulfonate anions due to poor dissociation of the lithium cations, apparently due to the lower dielectric constant of the TMO polymers. The larger and more electron withdrawing imide anions appear to overcome this problem.

Although the polyelectrolytes reported here appear to meet the bulk conductivity requirements of practical lithium batteries, there appears to be a major problem asociated with yje interfacial impedance. Measurements of this property have shown unaccetably high impedance values for practical operation.

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Relation between electronic resistance and capacitance for highly aqueous RuO_2

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Due to promising high capacity per gram supercapacitors based on the pseudo capacitance of hydrous ruthenium oxide (RuO_2 xH_2O) have been the focus of numerous recent studies. In order to optimize the performance of this transition-metal-oxide compound a good understanding of the influence of the preparation parameters on its electrochemical behaviour is required and especially the influence of annealing treatments on the gravimetric capacitance C_g (F/g) of the material. Many authors have pointed out that two parameters are very important for an optimal behaviour of the material: first a good electronic conductivity in the bulk material and second a high ionic conductivity of protons in the hydrated pores and boundary regions in between the material's particles [1].

Samples annealed at high temperature (17 hours at 300°C in air) exhibit a small capacitance as the bound water in the pores is removed during the heat treatment. On the other hand samples annealed at low temperatures (17 hours at 25°C or 75°C in air) also exhibit low capacitance albeit they contain more water.

In order to understand why the voltammogram of these last samples show a characteristic reduction of capacitance at low potential we compared the potential dependent capacitance, during the anodic sweep of the CV between +0.8V and -0.2V toward a carbon quasi reference, with the evolution of the potential dependent bulk electronic resistance Z_e of the material measured in situ for the same potential range. The set-up for in situ measurements of the potential dependent electronic resistance has been described before [2].

The observed close similarity of the curves suggests that the electronic resistance of the bulk is the main parameter controlling the capacitance of highly hydrous RuO_2 at low potential. This result is supported by Electrochemical Impedance Spectrometry (EIS) measurements showing that the real part, Z_r at 10 mHz, of the overall impedance (ionic and electronic) exhibits the same evolution with the potential than Z_e.

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A dilatometric study of ion intercalation from aprotic solutions into carbonaceous materials

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Lithium-ion batteries (LiB) and electrochemical double layer capacitors (EDLC) both take advantage of electrochemical ion insertion into carbonaceous electrode materials. For the graphite based LiB anode, the intercalation of Li ions is the actual mechanism of charge storage. For the activated (hard) carbon based EDLC electrodes, the insertion of the electrolyte ions, usually R_4N^+ and BF_4^-, may well contribute to charge storage, besides double layer charging. The role of insertion processes for EDLC voltage limitation has only recently been suggested [1].

Electrochemical dilatometry was applied to highlight the influence of different material parameters – the type of carbon, solute and solvent – on the charge specific expansion of LiB and EDLC systems.

The updated setup allows measurements of single oriented crystals (HOPG), bound powder based electrodes, as well as binder-free carbon powders. The separate determination of both height and volume changes of one and the same material provides valuable information on the preferential particle orientation in powder-type electrodes.

In general, the charge specific expansion is much more pronounced for Et_4N^+ and BF_4^- than for Li^+ insertion, obviously accounting for the different size of the ions. On the other hand, the qualitative behaviour is in most cases similar: An irreversible swelling during the first cycle is followed by a rather reversible expansion / contraction during subsequent cycling. Furthermore, the progressive exfoliation of graphite in some propylene carbonate LiB electrolytes is demonstrated.
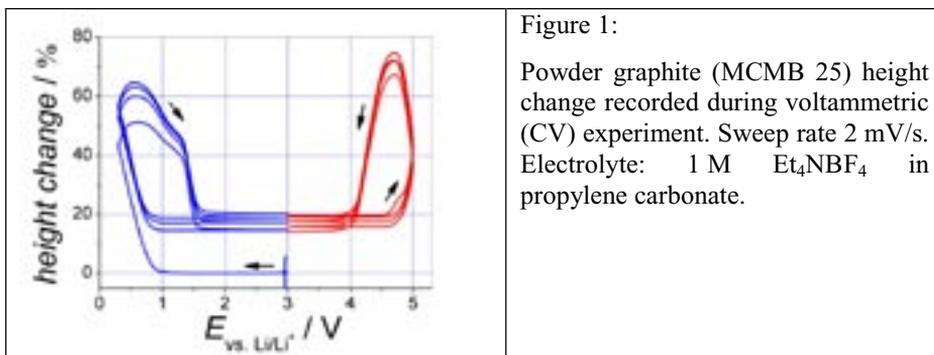
Figure 1:

Powder graphite (MCMB 25) height change recorded during voltammetric (CV) experiment. Sweep rate 2 mV/s. Electrolyte: 1 M Et_4NBF_4 in propylene carbonate.

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Mesoporous Nickel/CNT Nanocomposite Electrodes For Electrochemical Capacitors

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Electrochemical capacitors are becoming attractive energy storage systems particularly for applications involving high power requirements. The capacitance in an electrochemical capacitor can arise from the charging or discharging of the electrical double layers (electrical double layer capacitance) or from faradaic redox reactions (pseudocapacitance). Carbon materials with very high-surface area are widely used for electrical double layer capacitors (EDLC). Subsequently, conducting polymers and transition metal oxides with relatively high-surface-area have been identified as possible electrode materials for supercapacitors (pseudocapacitors). Among the various materials investigated over the years, amorphous $RuO_2 \cdot xH_2O$ prepared by the sol-gel process has become the leading electrode material for supercapacitors as it exhibits a high specific capacitance (720 F/g). However, the high cost of ruthenium and environmental problem of electrolyte such as strong acidic media have limited its commercial use. Accordingly, there is a strong incentive to find alternative electrode materials, which are inexpensive and exhibit pseudocapacitive behavior similar to that of hydrous RuO_2. Much attention is now focused on the oxides of manganese, nickel, cobalt, and vanadium as candidates for development of supercapacitors.

It was known that the charge storage reaction of transition metal oxides confined mainly to their surface layer. Therefore, in order to obtain high performance with both high power and high energy densities, it is important to design and fabricate nanostructured electrode materials that provide interconnected nanopaths for electrolyte-ion transport and electronic conduction. Since conventional nanoparticulate systems have a disordered porosity with voids of varying cross section interconnected by narrower intervoid spaces, materials moving within the pore structure encounter a considerably tortuous path, impeding reaction rates. By contrast, materials with high surface areas and a uniform, ordered pore network would be expected to exhibit superior performance in electrochemical systems which rely on liquid diffusion within the electrode material.

In this study, ordered mesoporous nickel electrodes including CNTs as conducting agents were fabricated by the liquid-crystal template assited electrodeposition in the presence of surfactants. More details about the synthesis and electrochemical properties of mesoporous nickel/CNT nanocomposite electrodes will be presented at the meeting.

Additives for performance improvement of Li ion battery

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Three kinds of additives, electrolyte stabilizer, solid electrolyte interphase (SEI) forming additive, and over-charging inhibitor, were considered for the performance improvement of lithium ion battery.

Ethanolamine was used as an electrolyte stabilizer. The cyclic voltammograms of graphite and $LiCoO_2$ electrodes in $LiPF_6$/EC+DMC+EMC with and without ethanolamine, and the cyclic stability of $C/LiCoO_2$ battery were measured. It was found that the voltammetric performance of the electrodes was hardly influenced by the addition of ethanolamine into the electrolyte, however, the stability of the electrolyte containing water could be improved by ethanolamine. The contents of H_2O and HF changed from 101.3ppm and 9.5ppm to 3.2ppm and 205.1ppm in electrolyte without ethanolamine, but to 65.6ppm and 92.7ppm in the electrolyte containing 0.1% ethanolamine, respectively, after storing the electrolytes at 45℃ for 24hr. The cyclic stability of $C/LiCoO_2$ battery using water containing electrolyte was improved to a great extent.

Two kinds of sultones were used as SEI forming additives. The electrochemical reduction of sultones, the composition of the formed SEI films and the performance of the batteries with the application of the additives were investigated. The reduction of the additives took place at the potential more positive than those of solvents. Sulphur was detected in the SEI films formed on graphite in electrolyte containing sultones. The discharge performance of batteries was improved with the application of sultones under either low or higher temperature.

Cyclohexylbenzene (CHB) was used as an over-charging inhibitor. The cyclic voltammogram of platinum electrode, the charging-discharge curve of $LiMn_2O_4$ electrode in electrolyte containing CHB, and the voltage and the inner resistance of the battery using CHB containing electrolyte were measured. It was found that the decomposition of solvents at high potential could be inhibited by CHB. The charging and discharge performance of $LiMn_2O_4$ electrode was hardly influenced by CHB. The voltage of the battery was hardly changed but the inner resistance of the battery increased sharply with charging time when CHB was used.

Key words: Additives, Electrolyte stabilizer, SEI film forming additive, Over-charging inhibitor.

Symposium 1 - Oral

Batteries and Supercapacitors

Electrode materials for supercapacitors with ionic liquid electrolytes

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Supercapacitors of high specific power play a crucial role in the development of electric vehicles where they can be coupled with lithium batteries or fuel cells to provide power peaks during acceleration as well as for energy recovery during braking. The typical operating temperature for these applications are higher than RT. Thus, in order to develop high voltage supercapacitors operating above RT we are pursuing the strategy of using ionic liquids (ILs) as "solvent-free" electrolytes of high thermal stability, wide electrochemical stability window and good conductivity. We already demonstrated the viability of this strategy in activated carbon (AC) // poly(3-methylthiophene) (pMeT) hybrid supercapacitors: when a high purity and hydrophobic IL such as N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide was used these supercapacitors provided maximum cell voltages higher than 3.4V as well as long cycling stability over 15,000 cycles at 60 °C [1]. Furthermore, this very interesting result was achieved with commercial electrode materials and we demonstrated that improvements of such IL-based hybrid supercapacitors are feasible via optimization of the affinity of electrode materials for the ILs [2].

Here we present and discuss results on the development of materials with morphologies and surface chemistry tailored for operation at 60°C in hydrophobic ILs. Particularly, data on mesoporous cryogel carbons and pMeT synthesized in the frame of the ILHYPOS "Ionic Liquid-based Hybrid Power Supercapacitors" UE Project are reported and discussed.

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Ionic Mass Transfer of Li+ Ion near the Li Ion Battery Electrode

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Li ion battery is now widely used as power sources of mobile electronic devices. It is also expected for the power supply of the electronic vehicles. However, a new negative electrode material must be developed, because the capacity of graphite material as the negative electrode has almost reached the theoretical limit.

Li metal is an attractive candidate for the negative electrode, because it has highest energy density. The dendrite growth of Li metal during the charging operation however, introduces a fatal problem. Generally speaking, the dendritic growth of metal is influenced by the ionic mass transfer phenomena. Therefore, it is indispensable to understand the coupling phenomena between ionic mass transfer phenomena and the dendritic growth of Li metal. On the other hand, Sn based alloys provide promising materials for the negative electrode. Many researchers have focused on the cycle efficiency and the mass transfer inside the electrode materials. The ionic mass transfer in the electrolyte has not been examined.

In this study, the mutual diffusion coefficients of $LiClO_4$ and $LiPF_6$ in PC electrolyte are measured by the Moiré Pattern method. However, the ionic mass transfer rate during the electrodeposition or electrochemical dissolution of Li metal (or charging to Sn based alloy) was in-situ measured by the holographic interferometry technique. The horizontal installed working electrode is facing downward in order to restrict the natural convection induced by the electrodeposition.

Figure 1 shows the transient behaviour of the electrode surface concentration accompanied with the electrodeposition of Li metal (circle) and insertion of Li+ into Ni-Sn alloy (triangle)in the $LiClO_4$-PC electrolyte solution.

In case of the electrodeposition of Li Metal, "incubation period" explicitly appears before the interference fringes starts to shift. This phenomena may be caused by the formation of SEI layer on the electrodeposited Li metal surface.
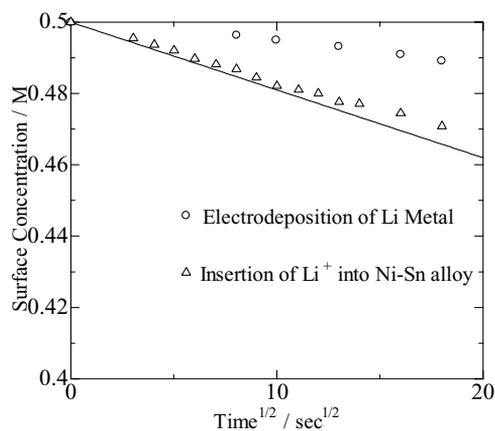
Figure 1: Transient Behavior of Surface Concentration of Li+ Ion (at 0.5mA/cm2)

Symposium 1 - Oral

Batteries and Supercapacitors

The hydrogen evolution and recombination kinetics in sealed rechargeable NiMH batteries

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The hydrogen evolution and recombination kinetics in NiMH batteries have been investigated under temperature-controlled, steady-state, overdischarging conditions within a temperature range of 10 and 50 °C and at discharging currents of 1 to 350 mA (0.0009 to 0.3 C-rate). *In situ* Raman spectroscopic analyses of the gas phase showed that hydrogen is the only gas evolving inside the battery during overdischarge at the above-mentioned conditions. The pressure increase could be very critical at low temperatures, leading to opening of the safety vent at relatively low discharging currents, for example, only 220 mA at 10 ^{0}C. The polarisation parameters for the hydrogen evolution reaction, such as Tafel slopes and exchange currents were determined at the different temperatures (see Eq. (1) and Fig. 1) as well as the parameters for the recombination process (see Eq. (2) and Fig. 2). The reaction mechanism and the rate-determining steps will be discussed. For modelling NiMH batteries this is highly valuable information as they are directly obtained from the system of interest. Furthermore, the obtained results make battery simulations more realistic by minimising the number of parameters involved and making the correct assumptions.

$$ln(I_{her,Ni}) = ln(I_{her,Ni}^{0,ref}) - (1-\alpha_{her})\frac{nF}{RT}\left(E_{Ni} - E_{H_2}^0(T)\right) \tag{1}$$

$$I_{hrr,MH} = I_{hrr,MH}^{0,ref}\left(\frac{p_{H_2}}{p_{H_2}^{ref}}\right)^{x_{hrr}} exp\left(\alpha_{hrr}\frac{nF}{RT}\left(E_{MH} - E_{H_2}^0(T)\right)\right) \tag{2}$$

Fig. 1. Tafel slopes for the hydrogen evolution kinetics.
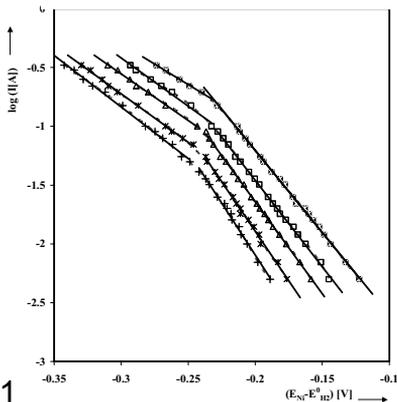
Fig. 2. The hydrogen recombination kinetics.
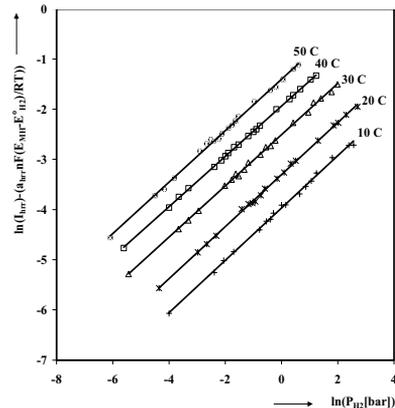
In situ analysis of interfaces in nonaqueous electrochemical systems

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The high energy density available from lithium-ion batteries is the reason for their key importance in both the current high-end consumer electronics and the development of hybrid vehicles. In such batteries both the negative and positive electrodes are made from electronically conductive matrix materials which are able to reversibly accommodate (insert) variable quantities of lithium ions. So far, electroactive insertion materials used in commercial lithium-ion cells are based on lithiated carbon (LiC_6) and lithium transition metal oxide $LiMO_2$, typically on the basis of cobalt, nickel, and manganese. Several new, alternative electroactive materials like nano-silicon are also promising for application in rechargeable lithium-ion batteries.

In the contribution basic scientific questions will be discussed, principally related to the surfaces' electrocatalytic activities. The challenge here is the understanding of how the structure and composition of these materials are correlated with their electrochemical properties, in particular with their specific charge, cycling stability, and rate and mechanism of side reactions.

The electrode potential of most of the electroactive materials is far beyond the thermodynamic stability window of the most commonly used organic electrolytes. Hence reductive and oxidative electrolyte decomposition occurs. Typically propylene, ethylene, hydrogen, and (in a few electrolytes) CO_2 are generated during electrochemical electrolyte reduction. On oxide positive electrodes, carbon dioxide and occasionally oxygen are characteristic gaseous reaction products. Gas evolution increases the cell internal pressure, which may result in raised safety risks and reduced cycle stability. Fortunately a protective layer called the Solid Electrolyte Interphase (SEI) forms normally at the surface of negative electrode materials, preventing further reductive electrolyte decomposition. A similar protective film is also reported for positive electrode materials such as $LiMn_2O_4$ and $LiCoO_2$.

In the contribution results of several advanced *in situ* methods, like FTIR- and Raman spectroscopy, as well as *post mortem* Scanning Electron Microscopy (SEM) will be discussed. Emphasis will be given to the Differential Electrochemical Mass Spectrometry (DEMS).

Symposium 1 - Oral

Batteries and Supercapacitors

Symposium 1 - Oral

Batteries and Supercapacitors

Electrochemistry of naphthalene derivatives with disulfide bonds and their application to cathode materials for lithium secondary batteries

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Electrochemical behaviors of dithionaphthalene(DTN) and tetrathiolenes(TTL) such as tetrathionaphthalene(TTN), tetrachlorotetrathionaphthalene(TCTTN), tetrathiotracene(TTN) and bis(phenylenedithio)tetrathionaphthalene(PDTTN) have been investigated. It is expected that these molecules would undergo reversible multi electron transfer reactions at S-S bond, which is active center in energy storage [1][2] . All molecules are planar with highly delocalized π systems but the HOMO in these molecules changes dramatically upon replacement of the hydrogens at some positions of naphthyle ring with sulfur and halogen [3]. Therefore, the redox potentials of compounds would change dramatically. Below 2.5 V vs. Li/Li$^+$, an S-S bond ring in these molecules was accepted to reduce with one or two electrons. Above 2.8 V vs. Li/Li$^+$, the ring was oxidized to stable cationic radical. The cyclic voltammetric responses demonstrated good possibility as cathodic materials with high energy density, as shown in Fig.2. The cell performance will be reported.

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DTN   TTN   TCTTN

TTT   PDTTN
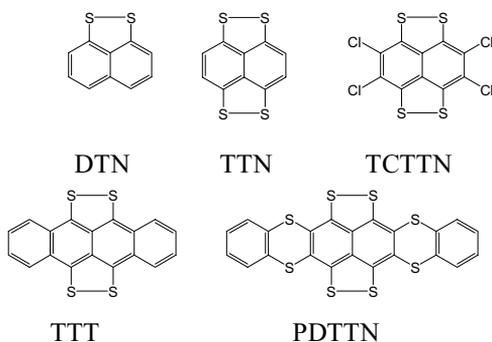
Fig.1 Structures of the compounds

I[uA]

E[V](vs. Ag/Ag$^+$)
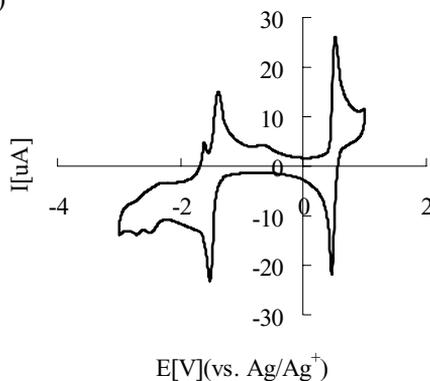
Fig.2 Cyclic voltammogram of 0.5mM DTN in 0.1M Et$_4$NBF$_4$/AN at GCE. Scan rate : 100mV/s.

Insertion of hydrogen in palladium films examined by combining EQCM and electroacoustic measurements.

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Palladium can offer interesting potentialities for hydrogen storage and can be used as a model for understanding the metal hydride systems [1,2]. Hydrogen dissolves and occupies interstitial sites in the host metal. The mechanism of insertion is not very well understood and this insertion is accompagnied by an expansion of the crystal lattice where strain and stress fields results.

The aim of this investigation is to characterize the hydrogen absorption by combining classical electrochemical measurements with acoustic transducer measurements used in different modes: active mode (EQCM), time resolved mode (*ac*-electrogravimetry) and passive mode (electroacoustic impedance).

Palladium films were electrodeposited onto one of the gold electrodes of a quartz resonator working at 9 MHz. Classical EQCM measurements were realised with a home made oscillator set-up and *ac*-electrogravimetry measurements with high stable frequency/voltage electronic converters. They allow fast measurement with a high frequency resolution and the mass-potentiel transfer function were estimated. In parallel, electroacoustic impedances were carried out on the same samples. All the measurements were performed in sulfuric acid 0.1M.

Thus, one interesting parameter i.e. the mass/charge ratio can be estimated according to different approaches. On the one hand, during voltage cycles, the mass was estimated through EQCM measurements during a complete cycle. On the other hand, the mass/charge ratio was directly calculated at certain potentials by using the mass-potential transfer function. If for small overvoltages this ratio is around one for higher overvoltages, the ratio becomes higher and differs from the hydrogen molar weight. This problem is certainly due to stress effects which occured during hydrogen insertion. To corroborate this effect motional resistance of the equivalent circuit of the resonator were measured by using electroacoustic impedance analysis. A change of this resistance is correlated to the stress increase shown by means of a laser beam deflection technique [3].

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Symposium 1 - Oral

Batteries and Supercapacitors

High Throughput Positive Electrode Material Studies Using Post Synthesis Array Transfer Techniques

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In recent years high throughput methods for the discovery of new materials for lithium batteries has grown in popularity. Several groups have demonstrated parallel synthesis and screening for the study of lithium battery negative and positive electrode materials, e.g. Si-Al-Mn alloys [1, 2] and $LiCoO_2$ [3].

This paper reports a study investigating the performance of $LiFePO_4$ [4] when coated with different amounts of carbon. This will showcase a new high throughput approach referred to as post synthesis array transfer (PoSAT). Details of the technique will be outlined and comparisons will be drawn to alternative methods.

The PoSAT approach uses an array of 64 quartz tubes in which precursor solutions are mixed before high temperature synthesis to produce the active materials. During the preparation materials can be homogenised using a rotating glass-bar attached to a drill. After sintering the materials are then ground to a powder and composite inks are prepared in the quartz tubes by the addition of acetylene black and PVDF binder. Electrode films are then deposited on an array of 64 aluminium current collectors for parallel electrochemical testing and high throughput XRD measurement. The advantages of this technique are accelerated material screening, its similarity to bulk synthesis and the use of composite electrodes is similar to the industrial standard. Further advantages are the freedom in preparation conditions, e.g. atmosphere, synthesis temperature, and the addition of mixing steps.

The scatter in the current density and specific capacity have been reduced by accurately measuring the active material mass for each of the electrodes in a time efficient way. This has been achieved by weighing the composite electrodes prepared using the PoSAT technique with a computer connected balance followed by TGA of the 64 composite inks. This has allowed the determination of the effect of precursor [4] composition on the electrode performance. It was found that percolation of the electronic conduction path required a sucrose to $LiFePO_4$ molar ratio of 0.24 ± 0.012.

Results showing the application of the PoSAT method to investigate solid solutions such as $Li_{1-2x}Mg_xFePO_4$, $LiFe_{1-x}Mg_xPO_4$ and $LiFe_{1-x}Co_xPO_4$ will also be reported at the meeting.

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Symposium 1 - Oral

Batteries and Supercapacitors

In situ Raman and XRD studies of carbons for supercapacitors

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Energy storage in electrochemical double-layer capacitors (EDLCs), also referred to as supercapacitors, is based on charge separation at the interface between an electronic conductor and an electrolyte solution with ionic conductivity. Energy is stored in the electric field established in the double-layer comprising electronic charges in the electrode and the according counter-ions in the electrolyte. The use of high surface area carbon electrodes leads to a significant charge storage capability and therefore to high specific capacitances and power densities. When the energy storage occurs solely via double-layer charging and discharging, the lifetime of an EDLC device is expected to be considerable.

However, it can be shown that processes other than those related to double-layer effects may readily occur under working conditions. In particular, ion intercalation may lead to degradation of the carbon electrodes, which can be anticipated to reduce the lifetime of EDLCs. We demonstrate how *in situ* Raman microscopy, X-ray diffraction (XRD), and atomic force microscopy (AFM) provide information on the intercalation of electrolyte species into carbon electrodes in EDLCs.

Using *in situ* Raman microscopy, we could show the insertion of $(C_2H_5)_4N^+$ into graphite for the negative electrode at an onset potential of +1.1V *vs.* Li/Li^+, while BF_4^- was shown to intercalate into the positive graphite electrode positive to +4.5V *vs.* Li/Li^+. These results were confirmed by *in situ* XRD measurements performed at the Swiss Light Source (SLS) and also by *in situ* AFM investigations on highly oriented pyrolytic graphite (HOPG) model electrodes.

These new findings complement earlier results from electrochemical dilatometry measurements [1], and the role of ion intercalation into carbon electrodes in EDLC systems is discussed on the basis of these methods with an emphasis on lifetime limitations and increased capacitor voltage for the optimization of today's EDLCs.

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Symposium 1 - Oral

Batteries and Supercapacitors

Charge Storage Mechanism of Nanostructured RuO$_2$ and Fabrication of Highly Functional RuO$_2$ Nanosheet Electrodes

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Electrochemical capacitors based on ruthenium oxides have attracted increased interest owing to their capability of providing higher energy density than conventional electric double-layer capacitors that employ carbon-based electrodes.[1,2] Specific capacitance of 600-800 F g^{-1} can be achieved by using nanostrucutred RuO$_2$ such as hydrous RuO$_2$, layered H$_{0.2}$RuO$_{2.1}$ (HRO), and H$_{0.2}$RuO$_{2.1}$ nanosheets (HROns) as electrode material.[3,4] The hydrous regions within the nanoparticles allow facile electrolyte permeation for efficient charge storage while the interconnected ruthenium oxide regions accounts for the electronic conduction. The key is to design electrode materials with high mixed electronic-ionic conductivity, large electrochemically active surface area, and practical electrochemical stability, at a reasonable price. Here, we discuss the charge storage mechanism of various ruthenium oxides. Results on the use of ruthenium oxide nanosheets for advanced functional applications will also be presented.

The charge storage mechanism of nanostructured ruthenium-based oxides (anhydrous RuO$_2$, hydrous RuO$_2$, layered HRO, HROns) was evaluated by various electrochemical techniques (CV, RDE, CA, impedance). The overall capacitance could be deconvoluted into three major contributions; namely, the electric double layer capacitance (C_{dl}), adsorption related charge (C_{ad}), and charging of the grain boundaries (C_{irr}). C_{ad} is strongly dependent on the structure of material. Layered HRO and HROns exhibit large C_{ad}, whereas it is not as obvious in hydrous RuO$_2$. C_{irr} was not observed in hydrous materials such as hydrous RuO$_2$, HRO and HROns, which is attributed to the lack of charging of the grain boundary. The hydrous state is a key factor in terms of both energy and power density. Ionic conduction via hydrous micro and mesopores, or interlayer seems to dominate the capacitive behavior.

HROns electrodes were fabricated on various substrates by electrophoretic deposition. Transparent or flexible electrodes could be fabricated by using ITO electrodes as the substrate. The deposited amount of material could easily be controlled by the extent of deposition, which was confirmed from the linear increase in specific capacitance as a function of the deposition time. Capacitance in the order of mF to F cm^{-2}(geometric) could be achieved using such HROns electrodes.

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Propionic acid assisted sol-gel synthesis of $LiCu_xMn_{2-x}O_4$ (0.025 ≥ x ≤ 0.10) as 5V cathode materials for lithium rechargeable batteries

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Spinel $LiCu_xMn_{2-x}O_4$ (0.025 – 0.1) has been synthesized using propionic acid as chelating agent by a sol-gel method to obtain sub-micron sized particles, good surface morphology, better homogeneity, good agglomeration and better crystallinity involving short heating time. X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR), thermo gravimetric and differential thermal analysis (TG/DTA) were carried out for the physical characterization of the synthesized powder. The XRD patterns of $LiCu_xMn_{2-x}O_4$ show the single-phase spinel product, which is in good agreement with JCPDS Card (35-782). SEM pictures show a decrease in particle size with increase in copper stoichiometry in the spinel product. Electrochemical cycling studies of the compound was carried out between 3−5V to understand the redox behaviour of Cu^{2+} ions. Further, the charge discharge characteristics reveal that 10% substitution of manganese by copper enhances the electrochemical reactivity of the spinel.
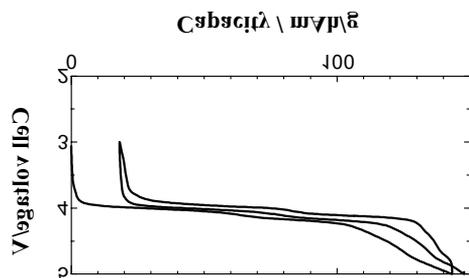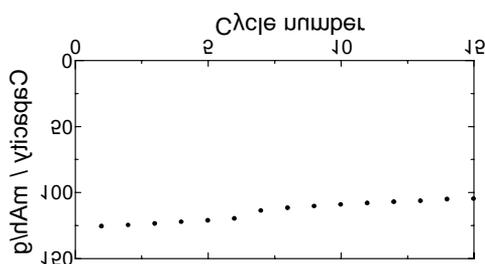
Nano Size Holes at the Basal Plane of Graphite Active Material Play an Important Role in Li-Ion Battery Anode

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The most common active material for the anode of Li-ion batteries is spherical shape graphitized material **(Fig. 1)**. Since Li has been understood to be able to permeate into the interior of graphite only from the edge plane of the graphite structure and not from the basal plane, it seems unlikely for Li to be inserted easily from the outside of the rounded shape active material whose outer sphere is comprised of basal plane. But actually, the rounded material accepts Li very easily. For the purpose of elucidating this perplexing problem we propose the presence of nano-size holes at the surface of the basal plane of the active material, and Li can permeate easily into the interior of the active material through the holes. In this paper we would like to show the presence of the holes by TEM images for several graphitized samples (**Fig**.**2**).
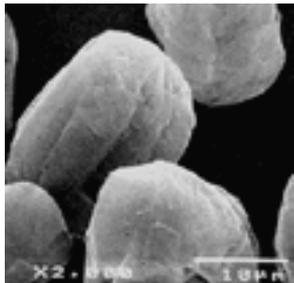
Fig. 1 (left) Round shaped graphite active material.
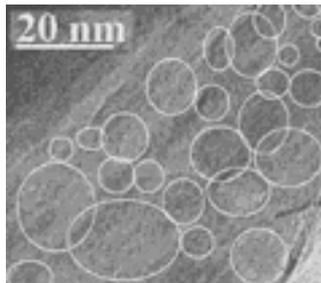
Fig. 2 (right) TEM image showing the presence of nano-holes at the graphite surface (in the white circle)

The graphite samples examined were natural graphite powder, and commercially available three different types of round shape active materials (An example is shown in **Fig.1**). The evaluation was performed for electrochemical performance (cyclic voltammetry and constant current insertion/deinsertion cycle test), XRD, SEM, Raman spectra and TEM images.

A sample giving an excellent electrochemical performance revealed the presence of a number of holes on the TEM image as shown in Fig. 2, while a sample having an inferior performance exhibited a limited number of small size holes.

Pristine natural graphite revealed the holes as well, implying the crystallite is not perfect but has many defects although the XRD pattern shows no evidence of imperfection. A rather stable cycle performance was obtained with natural graphite for Li insertion and extraction reaction, which can be attributed to the presence of a number of nano holes at the surface.

Effect of lithium salt addition on a C-2 substituted imidazolium ionic liquid

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Various organic solvent-based solutions have been used as solvent in lithium batteries. However, the organic solvents are flammable and volatile, which makes the batteries that employ them a safety risk. One promising solution is to use a non-flammable, non-volatile electrolyte, such as room-temperature molten salts. Ionic liquids consist of solely of ions and these ions are typically not electroactive in lithium batteries thus requiring the addition of a suitable LiX salt[1,2]. Herein, we have studied the effect of a lithium salt (LiTFSI) on a new ionic liquid, called 1,2-dimethyl-3-n-butylimidazolium bis(trifluoromethanesulfonyl)imide (BMMITFSI).

BMMITFSI was synthesized by the ion exchange reaction of the corresponding imidazolium bromide with LiTFSI in water. This colorless liquid was characterized by FTIR, NMR and elemental analysis. We also have determinate the density, viscosity and ionic conductivity in different temperatures. The electrochemical window was estimated by cyclic voltammetry as 5 V.

The LiTFSI/BMMITFSI solutions were prepared by the addition of the lithium salt on the ionic liquid, followed by heating. The graphs of viscosity and ionic conductivity measurements plotted against the content of solute salts have shown an inverse behavior. While the addition of LiTFSI increases the viscosity of the solution, the ionic conductivity decreases (Figure 1). The only considerable reason for the decrease of conductivity by the addition of salt is the formation of ion pairs, which do not contribute for charge conduction in solution and the consequent increase of viscosity. Raman spectra of these solutions have shown the decrease of the peak intensity at 742 cm^{-1} and the increase of another one at 760 cm^{-1} when the LiTFSI concentration increases. This result confirms the formation and the increase of ion pair concentration with the LiTFSI addition, since the peak fragment at 760 cm^{-1} is attributed to the existence of strong interaction between cations and anions.

Figure 1
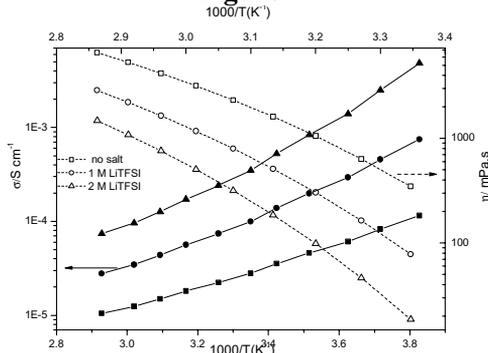
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Symposium 1 - Oral

Batteries and Supercapacitors

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Batteries and Supercapacitors

Lithium Ion Batteries for Hybrid Applications

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The development of high-performance rechargeable batteries for power tools or hybrid vehicles has proved to be an extremely challenging task because of the need to simultaneously meet multiple battery performance requirements, like high energy (watt-hours per unit battery mass or volume), high power (watts per unit battery mass or volume), long life (5-10 years and some hundreds of deep charge-discharge cycles), low cost (measured per unit battery capacity), resistance to abuse and operating temperature extremes, perfect safety and minimal environmental impact. Despite years of intensive worldwide R&D, no battery can meet all of these goals. The use of lithium ion batteries in power tools, vehicles or other applications were high amounts of energy have to be stored in the battery are limited because of safety risks and the lack of safety mechanisms.

A wider use of lithium ion batteries for power tools or hybrid vehicles requires safer battery materials and intelligent battery packaging concepts. The required physical and electrical properties and safety of the lithium ion batteries are supposed to be achieved by the introduction of new materials, e.g. alternative electrode materials and electrolytes. The focussed applications require new designs for the electrode contact deposition, for the heat management and the combination of the single cells into battery modules.

In this paper we will focus on two points. At first, the possibilities to improve safety and high temperature performance of lithium ion batteries will be discussed. The focus will be on electrode materials and alternative electrolytes, especially ionic liquids. Ionic liquids are the ideal material for use as an electrolyte because they are non-volatile and flame resistive. Second, we will discuss possible designs of battery packages in terms of thermal management and safety.

Kinetic Studies of the V^{4+}/V^{5+} Red/Ox – system in Sulphuric Acid

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A Vanadium red/ox flow battery is a hybrid between a regenerative fuel cell and a rechargeable battery. The coulombic efficiency is excellent, 90 to 100 % and the energy efficiency is high, 70 to 90 % (1). Main problems have been low stability and solubility of the 4 and 5 valent species defined as VO^{2+} and VO_2^+(2). Raman spectroscopy shows very complex ions in the V(V) system in sulphuric acid solution (3). We have studied the kinetics of the positive red/ox electrode with V(IV) and V(V) ions in concentrated sulphuric acid.

Experiments were performed with a rotating disk electrode in sulphuric acid solutions with V(V) and V(IV) ions in equal concentrations ranging from $10^{-2.5}$ to $10^{-1.25}$ M. The concentration of H_2SO_4 varied between 0.4 and 4 M. Electrode materials tried were Pt, Au and Glassy carbon (GC). Both metallic electrodes showed a time dependency which could be related to changes in the complexes in solution interfering with oxides on the electrodes. GC gave stable current/potential curves.

Anodic and cathodic polarisation curves were obtained at different concentrations for a GC electrode. The polarisation curves were corrected for diffusion control, using the relation $i_k = i_m (i_d/ i_d – i)^p$. Here i_k is the kinetic cd, i_m the measured cd and i_d is the diffusion limited cd. p is the reaction order of the reduced and oxidized species, respectively. The polarisation curves show Tafel behaviour at low cds. At increased cds an almost symmetrical increase in potential for both directions, relative to the Tafel line, is observed.

The kinetic parameters are rather symmetrical for the GC electrode showing a one electron rate determining step in both directions with a chemical step taking over at higher rates. In the case of Au the process is different with a lower cathodic Tafel gradient and a semi-passive behaviour in the anodic direction. The following kinetic parameters were found; *GC electrode*: b_a = 133mV/dec.; b_k= - 108mV/dec.; α_a = 0.45; α_k= 0.55; k^o = 5.61E10^{-8} cm s^{-1}; *Au electrode*: b_k = - 65 mV/dec.

The diffusion coefficient for the V(V) species is $(2.7 \pm 0.2) \times 10^{-6}$ cm^{2}s^{-1} determined with both electrodes. For the V(IV) species more or less the same value is found on GC. This indicates that the same type of species is diffusing in both processes.

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Symposium 1 - Oral

Batteries and Supercapacitors

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Soluble lead redox flow cell for electrochemical energy conversion

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Large scale and efficient energy storage is important for applications such as load levelling, standby power supplies, strategic power distribution and vehicle propulsion. Redox flow batteries have several advantages over traditional energy storage systems and commercial technologies are currently being developed.

Typically, redox flow batteries, such as the all vanadium or bromine/polysulfide technologies, rely on an ion exchange membrane to separate the anolyte and catholyte. However, considerable engineering and chemical challenges need to be overcome when using two electrolytes separated by a membrane.

Performance data and technical aspects for the design and testing of a membrane-less redox flow cell are presented. The system is based on an electrolyte containing soluble lead:

Positive electrode $Pb^{2+} + 2H_2O - 2e^- \leftrightarrow PbO_2 + 4H^+$
Negative electrode $\quad\quad Pb^{2+} + 2e^- \leftrightarrow Pb$

Charge/discharge characteristics and deposit formation/dissolution (Pb and PbO_2) at the electrode surface will be discussed along with electrode selection and selected aspects of the design for a laboratory test rig.

In-M (M = Ni, Cu) Film Electrodes for the Anode in Lithium Secondary Batteries

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The lithium alloy materials (Si, Sn, Al, In) have attracted much attention as an alternative to the commercialized graphite anode for lithium secondary batteries. In spite of their high theoretical capacity, however, their practical application is still hindered due to a severe volume change upon cycling. As one of the approaches to solve this problem, the alloy materials have been prepared as the active/inactive intermetallics.[1] Some of the active/inactive intermetallics are reported to be inactive for alloying reaction at room temperature even though the reaction is thermodynamically allowed.[1,2] The kinetic problems encountered with these materials have not been fully understood until now.

In this study, the anodic performance of In-M (M = Ni, Cu) film electrodes was examined. The reaction mechanism was studied using *in-situ* and *ex-situ* XRD analysis. Both In-Cu and In-Ni electrodes were active for the alloying reaction at elevated temperature, but with different onset temperature. It is found that the In-M bond is broken during the alloying reaction, thereby the reaction kinetics is controlled by the bond strength of In-M. The onset temperature of In-Ni was higher than that of In-Cu, which must be the direct result of bond strength difference. The bond strength of In-Ni (271 kJ mol^{-1}) is known to be higher than that of In-Cu (147 kJ mol^{-1}).[3]
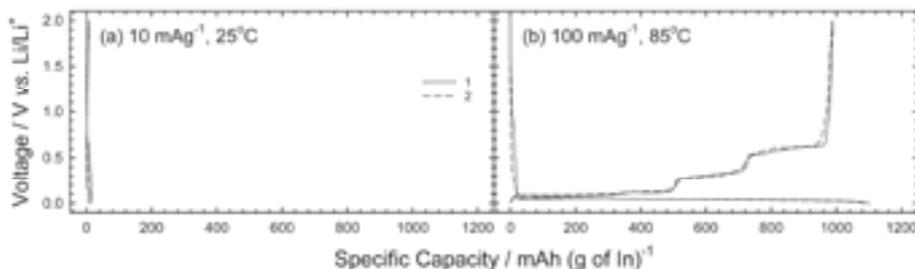
Fig. 1. Voltage profiles of Li/In-Cu cell: (a) 10 mAg^{-1} at 25°C and (b) 100 mAg^{-1} at 85°C.

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Symposium 1 - Oral

Batteries and Supercapacitors

Hydrous Ruthenium Oxide Electrode for Non-aqueous Proton-Conducting Gel Electrolyte

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Electrochemical capacitors (ECCs) based on hydrous metal oxides, such as $RuO_2 \cdot xH_2O$, $MnO_2 \cdot xH_2O$, are expected to provide higher energy density than conventional electric double layer capacitors. ECCs reqire a proper proton (H^+) conductor as an electrolyte, and an aqueous solution of sulfuric acid is usually applied as the electrolyte of ECCs. We previously reported the poly(ethylene oxide)-modified polymethacrylate (PEO-PMA)-based, poly(vinyliden fluoride) (PVdF)-based and poly(vinyliden fluoride-co-hexafluoropropylene)-based gel electrolytes as the proton conductor for electrochemical capacitors[1, 2]. We found that the gel consisting of PVdF-HFP dissolving trifluoromethanesulfonic acid (CF_3SO_3H) act as the proton conductor for $RuO_2 \cdot xH_2O$ electrode at ambient temperature. In this paper, we have optimized the $RuO_2 \cdot xH_2O$ composite electrode suitable for non-aqueous proton-conducting gel electrolyte based on PVdF-HFP for improving the characteristics of the ECCs with gel electrolytes.

The proton-conducting gel electrolyte was prepared by thermal casting method as described previously[2]. The electrochemical properties of $RuO_2 \cdot xH_2O$ prepared by a sol-gel method[3] was investigated in the proton-conducting polymeric gels.

Fig. 1 shows the discharge capacitance of $RuO_2 \cdot xH_2O$ symmetric cells at room temperature. The discharge capacitance of the electrode containing a gel component was higher than that of the electrode consisting of $RuO_2 \cdot xH_2O$ and a binder (PVdF). About 300 F g^{-1} of the discharge capacitance (per mass of single electrode) was obtained at 5 mA cm^{-2}, although some pre-cycles were required to obtain the constant capacitance.
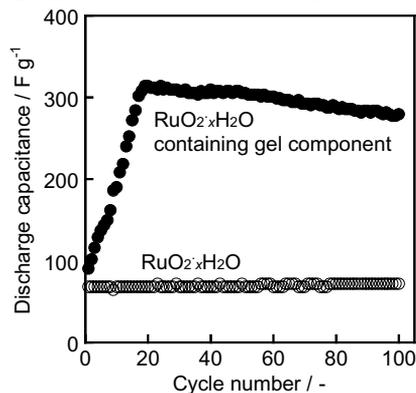
Fig. 1 Discharge capacitance of $RuO_2 \cdot xH_2O$ symmetric cell at room temperature. Electrolyte:PVdF-HFP/0.5 M CF_3SO_3H (DMF) Current density : 5 mA cm^{-2}

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Performance of Asymmetric $Ni(OH)_2$ – Carbon Supercapacitors

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An asymmetric supercapacitor typically consists a battery type electrode (usually a *faradaic* or intercalating metal oxide) and an electrochemical capacitor type electrode (high surface area carbon). In such an arrangement, the battery electrode has a greater capacity than the carbon electrode, resulting in twice the energy storage capability of a comparable symmetric carbon based supercapacitor. The battery electrode is selected such that the potential is near either the low or high end of the potential window, which can maximize the operational voltage as well as the energy density of the cell. As the voltage swing of the cell during charge/discharge occurs mainly across the carbon, the battery electrode experiences a relatively low depth of discharge and provides the conditions required for high cycle life. Results on the electrochemical characteristics and the performance of a 14 Wh/kg (and 2000 W/kg) packaged nickel hydroxide - carbon asymmetric device are presented. This device has the potential to offer both high power and high energy in a single long cycle life device.

Symposium 1 - Oral

Batteries and Supercapacitors

High Throughput Evaluation of Polymer Electrolytes

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This work aims to use the combinatorial array techniques reported earlier for the evaluation for the composition dependence of ionic conductivity, and other properties of polymer electrolytes. These materials are particularly suited to the combinatorial approach because they generally consist of three or more components, e.g.

• matrix polymer, responsible for structural stability
• salt
• co-solvent or plasticizer
• other additives, e.g. fillers

The ionic conductivity of lithium based solid polymer films prepared from polyvinylidene fluoride hexa-fluoropropylene (PVDF-HFP) and lithium bis(trifluoromethane)sulfonimide (LiTFSI) with varying compositions of plasticizer propylene carbonate (PC) and ethylene carbonate (EC) were measured sequentially by AC Impedance Spectroscopy and then adapted to a 64 electrode combinatorial array. Conductivity values of 10^{-3} S cm^{-1} were observed in films with high plasticizer compositions which could be attributed to an enhancement in conduction pathways formed by the coordination of the lithium ions with the ester linkages in the plasticizer.

Results to be reported at the meeting, will include conductivity plots for the above lithium systems as well as studies on Nafion-based polymers and other compositions used as membranes in fuel cells and other applications.

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Nanostructured Vanadium Oxide Prepared Hydrothermally as a Cathode Material for Lithium Batteries

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By decreasing the crystal dimensions, the solid-state Li^+ diffusion in lithium batteries is progressively replaced by surface-confined Li-storage [1]. Thus, synthesis of nanostructured materials is of particular interest, and hydrothermal route would be the most common method for this purpose. Nanostructured vanadium oxides provide high surface area which is considerably favorable for practical applications as a cathode material in lithium-ion batteries. Here, we report a simple hydrothermal method for the synthesis of these nanostructered materials. The physical and chemical as well as morphological aspects of these oxides are particularly investigated from both fundamental and applied points of view. This method results in the formation of bunches of nanofibers as illustrated in the SEM. Although the nanostructured vanadium oxides prepared by this method generally show a good electrochemical performance for lithium battery application, it was found that experimental conditions also play an important role in the electrochemical properties of the product. For instance, as can be seen in the illustrated CV, the electrochemical behaviors of two vanadium oxide samples prepared under similar conditions but using different vanadium sources namely V_2O_5 and NH_4VO_3 are significantly different. Thus, a particular attention should be paid to this issue to choose the most appropriate experimental conditions.
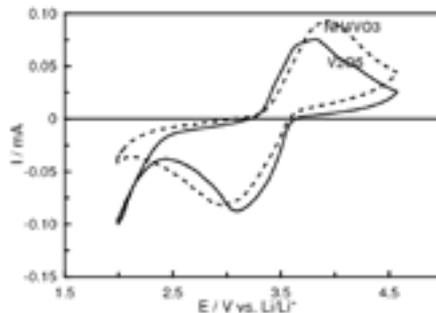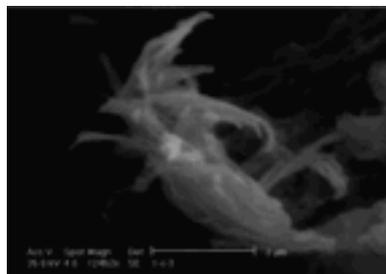
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Development of poly(acrylonitrile) / Poly(vinyl acetate) - pan/pva - based gel Electrolytes for lithium ion batteries

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Polymeric gel electrolytes have been extensively studied for application in lithium ion batteries, since the electrolyte can be fabricated as a thin film that leads to major performance improvements. This is mainly due to the higher ionic mobility and the higher concentration of charge carriers, yielding ionic conductivities of about 10^{-3} $S.cm^{-1}$ at room temperature and sufficient mechanical strength. PAN-based gels have been studied together with a wide range of plasticizers and tested in lithium batteries systems with excellent results. Based on these results, we developed PAN-based gels with EC/PC and EC/DMC mixtures as plasticizers, $LiClO_4$ or $LiBF_4$ as the ionic salt and the copolymer PAN-PVA as the polymer matrix to be used as separator and electrolyte in lithium ion batteries. The choice of the copolymer was made due to its hydrophobic properties, low cost and easy access, since it is well used in textile industries as precursor for acrylic fibers manufacture. These new electrolytes were characterized by electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to determine their stability window and conductivity. The charge/discharge performance of the PAN-PVA based gel electrolytes was investigated, by the galvanostatic battery test, for two different systems: a $Li/gel/LiMnO_2$ and an all polymeric system made of Ppy/gel/Pani (Ppy = polypirrol and Pani = polyaniline). FT-IR analyses showed that PAN-PVA is not a passive polymer host but an active component in the gel, were Li^+ ions are located close to C=O groups from plasticizers and CN groups of PAN. In addition to ionic conductivities between 10^{-3} and 10^{-4} $S.cm^{-1}$, these gels presented excellent electrochemical and chemical stabilities, which means a slight increased performance compared to only PAN-based gels, and suitable charge/discharge profiles.

Symposium 1 - Poster

Batteries and Supercapacitors

Effect of surface functional groups in the electrochemical behaviour of porous carbon materials: their relevance in supercapacitors

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The main object of this work is to study the electrochemical behaviour of activated carbons with different surface chemistry properties.

For this purpose, microporous activated carbons were obtained from an anthracite by chemical activation using both KOH and NaOH as activating agents. As a result, activated carbons with high BET surface area (2300-2900 m^2/g) have been obtained. In order to obtain porous carbon materials with different amounts of surface oxygen complexes, the former samples were oxidized with HNO_3 and thermally treated in N_2 flow at different temperatures.

On the other hand, the activated carbons were doped with nitrogen using a novel method based on the reaction of aniline with surface oxygen groups. Thus, this procedure consists on condensation reactions as a result of which oxygen functionalities are replaced by nitrogen ones. With this method, an amount of nitrogen close to 4 wt% can be introduced in the sample

The surface chemistry of the materials was systematically characterized by TPD experiments and XPS measurements. Galvanostatic and voltammetric techniques were used to deepen into the electrochemical behaviour of the modified porous carbon materials. The combination of both, chemical and electrochemical methods provides unique information.

The contribution of oxygen and nitrogen functionalities to the electrochemical behaviour of porous carbon materials is of relevance to optimise their use as electrochemical capacitors. Oxygen functionalities present a twofold contribution to capacitance. On one hand, these groups increase the accessible surface area improving carbon wettability and on the other, they promote pseudocapacitance, since some oxygen complexes undergo redox processes. Dealing with nitrogen functionalities, the role of the nitrogen-doping to increase the potential stability window will be discussed.

Symposium 1 - Poster

Batteries and Supercapacitors

Structural and electrochemical properties of the doped spinels $Li_{1.05}M_{0.02}Mn_{2-y}O_{4-0.02}N_{0.02}$ (M = Ga^{3+}, Al^{3+}, Co^{3+}; N = F^-, S^{2-}) for use in lithium batteries

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In previous εγ studies[1] we showed that the spinel $Li_{1.05}Mn_2O_4$ can be easily obtained by a solid-state reaction from ε-MnO_2 (with more structural defects than the γ-form), using only one heating step in the thermal treatment. Aiming at improving the capacity performance, in the present work doped spinels were obtained by a solid state reaction at 750 ºC for 72 h between the precursors ε-MnO_2, LiOH and the respective oxide/salt of ±the doping ions. In order to control the particle size, all the spinels were milled in a ball milling for 30 min. Mechanical milling, associated or not to further calcination, was also used to obtain the pure spinel. The obtained spinels were characterized by the average manganese valence (n), X-ray diffractometry, scanning electron microscopy, particle size distribution and specific superficial area. From the X-ray diffractograms, spinels of single cubic phase belonging to the *Fd3m* space group were identified. The values of the unity cell parameter (a) calculated for all the doped spinels (8.221 Å – 8.229 Å) were always lower than that for the pure one (8.234 Å), decreasing in the following order: $a(Li_{1.05}Ga_{0.02}Mn_{1.98}O_4) > a(Li_{1.05}Co_{0.02}Mn_{1.98}O_4) > a(Li_{1.05}Al_{0.02}Mn_{1.98}O_4) > a(Li_{1.05}M_{0.02}Mn_{1.98}O_{3.98}S_{0.02}) > a(Li_{1.05}M_{0.02}Mn_{1.98}O_{3.98}F_{0.02})$. The values of n, determined by Vetter´s method, for the doped spinels (3.56 – 3.50) were higher than that for the pure spinel (3.53 ± 0.01), decreasing in the following order: $n(Li_{1.05}Ga_{0.02}Mn_{1.98}O_4) > n(Li_{1.05}Co_{0.02}Mn_{1.98}O_4) > n(Li_{1.05}Al_{0.02}Mn_{1.98}O_4) > n(Li_{1.05}M_{0.02}Mn_{1.98}O_{3.98}F_{0.02}) > n(Li_{1.05}M_{0.02}Mn_{1.98}O_{3.98}S_{0.02})$. Mechanical milling with further calcination changed the spinel particles, since formation of nanometric particles, generation of lattice strain and partial oxidation of the Mn ions occurred. The pure spinel obtained using only mechanical milling presented nanometric particles, a highly disordered lattice structure and a high number of structural defects. In the charge and discharge tests, the cathodes of the doped spinels presented values of the specific discharge capacity decreasing in the following order:

$C(Li_{1.05}Al_{0.02}Mn_{1.98}S_{3.02}O_{3.98}) > C(Li_{1.05}Al_{0.02}Mn_{1.98}F_{3.02}O_{3.98}) >$
$C(Li_{1.05}Ga_{0.02}Mn_{1.98}S_{3.02}O_{3.98}) > C(Li_{1.05}Ga_{0.02}Mn_{1.98}F_{3.02}O_{3.98}) >$
$C(Li_{1.05}Co_{0.02}Mn_{1.98}S_{3.02}O_{3.98}) > C(Li_{1.05}Co_{0.02}Mn_{1.98}F_{3.02}O_{3.98})$.

Although the $Li_{1.05}Al_{0.02}Mn_{1.98}S_{3.02}O_{3.98}$ cathode presented the highest initial capacity (126 mA h g^{-1}), the $Li_{1.05}Ga_{0.02}Mn_{1.98}S_{3.02}O_{3.98}$ cathode presented the lowest capacity fading (from 120 mA h g^{-1} to 115 mA h g^{-1}) after 300 charge-discharge cycles.

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Symposium 1 - Poster

Batteries and Supercapacitors

Solvent-Solvent and Ionic Liquid-Solvent Mixtures for Lithium Batteries

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In order to enhance lithium ion batteries performances, and particularly at low temperatures, the formulation of the electrolyte is critical. A new trend in the batteries research is the search of binary or ternary mixtures of solvents thermodynamically stable at low temperature (below -20°C). For this purpose, few of studies deal with phase diagrams of mixtures of organic dipolar aprotic solvents. For example, the phase diagrams of mixtures of cyclic ethylene carbonate (EC) and linear carbonates as dimethylcarbonate (DMC) or ethylmethylcarbonate (EMC) have been studied by Ding [1]. The obtained phase diagrams are simple and characterised by an eutectic point which is close to the compound having the lowest melting point. Moreover, there is no miscibility gap in the liquid state whereas in solid state there is no mutual solubility.

In this work, Differential Scanning Calorimetry (DSC) and X-Ray diffraction (XRD) have been performed to investigate the thermal behaviour at low temperature (between -120°C to 20°C) of solvent-solvent and ionic liquid-solvent binary mixtures. These mixtures are made up of gamma-butyrolactone (BL), DMC, EC as organic solvents and 1-butyl-3-methyl-imidazolium hexafluoroborate ($BMIPF_6$) and tetrafluoroborate ($BMIBF_4$) as ionic liquids.

Phase diagrams of BL-DMC and BL-EC are as simple as alkylcarbonates binary mixtures. They are characterised by an eutectic point at $x_{EC}=0.12$ and T=-57.5°C for BL-DMC mixtures and $x_{EC}=0.10$ and T=-56.3°C for BL-EC mixtures.

Phase diagrams of ionic liquid-solvent binary mixtures evidenced the apparition of a vitreous phase when the mole fraction in ionic liquid is higher than a critical mole fraction (x_{critic}). This means that all solvent molecules, embedded in the amorphous phase, belong to the solvation shell of the imidazolium salts. From the value of the critical mole fraction, it is possible to calculate the number of solvent molecules in the solvation shell of BMI^+. In $BMIBF_4$-BL and $BMIPF_6$-BL systems the number of solvent molecules is respectively 4 and 5. The difference in the number of solvent molecules in the solvation shell of BMI^+ may be explained by the presence of one BF_4^- in the solvation shell of the imidazolium ion in $BMIBF_4$-BL and no PF_6^- anion in the solvation shell of BMI^+ in $BMIPF_6$-BL.

Charge-discharge capacities at a graphite electrode of these binary mixtures in presence of lithium salts such as lithium tetrafluoroborate and lithium hexafluorophosphate are also presented in this work.

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The iron electrode revisited

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The alkaline metal hydride/Ni oxide secondary cells have superseded in most applications the old Fe/Ni battery.

However the negative Fe electrode when coupled with a positive air electrode is still attractive since combining good energy density (75 W h kg^{-1}) with robustness, low cost and high environmental safety.

The development for this battery of the air electrode can now take advantage from the alkaline fuel cell technological progress, but for Fe, in spite of the active investigation from the beginning of last century till the late '70s, several points are still questioned.

For instance, the importance of Li$^+$ in the electrolyte for the reduction of Fe oxides has only recently been clarified, whereas unanswered questions concerns:

•the discharge pathway, generally assumed to involve the successive Fe $\square$ Fe^{II} and Fe^{II} $\square$ Fe^{III} oxidations;

•the fact that at room temperature or below, only a minor fraction of the large theoretical capacity (960 A h kg^{-1}) can be exploited;

•whether and how the depth of discharge affects the electrode performances, etc.

The present paper shows that poor Fe utilization and two stage oxidation both correlate with resistance phenomena: in fact by using Fe/TiO$_2$ or Fe/ZnO composite electrodes the full theoretical capacity is exploited within a single Fe $\square$ Fe^{II} oxidation pathway. Deep discharges seem furthermore important to inhibit Fe activation towards the hydrogen evolution reaction. With respect to this latter point the compatibility of mixing active Fe with intermetallic compounds (IMCs) as hydrogen buffers is eventually discussed.

Correlation of ac-impedance and in situ X-ray spectra of LiCoO$_2$

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We report in this presentation *in-situ* X-ray and AC-impedance spectra obtained simultaneously during the deintercalation of lithium from LiCoO$_2$ using a specially designed electrochemical cell. The AC-dispersions have been correlated with the cell parameters obtained from the X-ray spectra. The correlation confirms previous hypothesis on the interpretation of the AC-dispersions in terms of an equivalent circuit comprising an element that relates the change of the intrinsic electronic conductivity, occurring at the early stages of deintercalation, to the semiconductor to metal transition caused by the change of the cell parameters.

Study on Conductive Bipolar Plates for Vanadium Redox Flow Battery

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Vanadium redox flow battery used for energy storage system provides several favorable characteristics in energy distribution. Good conductivity, stress intensity, imperviousness, and antioxidant capability are required to the bipolar plate. Two kinds of bipolar plates, composite imperforate graphite plate and conductive carbon-plastic plate, were prepared and studied in this article.

The composite imperforate graphite plates were prepared by infusing the fine-structured graphite plates (ϱ= 1.84g/cm^3) into the resin, and then were sintered in high-pressure inert gas at high temperature to carbonify the resin. The conductivity of composite graphite plates of thickness 3mm is $1*10^{-3}\Omega \cdot$cm. And the feather test showed that they have good impermeability. Cyclic voltammetry was used to test the graphite plates being infused and carbonified and to compare with the one without dealing. The working electrode was the tested graphite plate. The reference electrode was a Hg/Hg_2SO_4(in saturated K_2SO_4) electrode. A platinum plate was used as a counter electrode. The electrolyte was a $1.5MVOSO_4+1.5MH_2SO_4$ solution. The sweep rate was 100mv/s. The cyclic voltammograms showed that the graphite plate after modification got a lower current peak both of oxidation and reduction. The vanadium redox battery of 8 cells with the composite graphite bipolar plates was discharged at 120 mA/cm^2 and output a satisfying power density of 125mw/ cm^2. The battery output a stable power and the columbic efficiency achieved 84% with the modified graphite plate. After enlarging the area of composite graphite plate from 256 to 961 cm^2 and increasing the number of cells from 8 to 15, the battery kept the same efficiency. The power of vanadium redox battery with composite graphite plates achieved 1000w.

More cheaper carbon-plastic plates were prepared too. The composition of this material are 50~60% polymer and conductive additives such as carbon black and graphite particles about 40~50%. The conductive additives and the resin were mixed to be the composite, and the admixture was extruded to be composite particles, then these particles were injection-molded to form the carbon-plastic plates (thickness was 2.5mm, surface area was 961 cm^2). The conductivity of the carbon-plastic plates is $0.20\Omega \cdot$cm. The test of carbon-plastic plates in the vanadium battery of 10 cells showed that the battery run well at the 40A of charging and discharging current (the current density was 50mA/ cm^2).

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Batteries and Supercapacitors

Electrochemical behavior of lead foam negative electrode in spiral VRLA batteries

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Besides having the merits of conventional flat VRLA batteries, spirally VRLA batteries possess special advantages, such as, good charge acceptances and high instantaneous output powers, which can ensure their reliability and validity [1]. The use of thin lead foil and lead fiber as the current collectors of spirally VRLA batteries has been reported [2]. However, there have been few reports about lead foam being used as the negative grid material and the behaviors of lead foam negative electrodes in spirally VRLA batteries. The present paper deals with the effects of lead foam on the electrochemical behaviors by comparison with those of lead foil.

Spirally VRLA batteries were prepared by using lead foam as the negative current collector material. The electrochemical behaviors of a lead foam negative electrode in sulfuric acid were studied by means of chronoamperometry, cyclic voltammetry (CV), electrochemical impedance spectrometry (EIS) and charge-discharge tests.

The real surface area of a lead foam negative electrode is larger than that of a lead foil negative electrode, while the overpotential of the lead foam negative electrode is lower. Compared with those of a lead foil negative electrode, the mass specific capacities of a lead foam negative electrode are 25.9%, 30.0 % and 48.2% higher at 10h, 5h and 2h discharge rates, respectively. So the test results of the discharge performances of the spirally VRLA batteries show that for a lead foam negative electrode, both the utilization efficiency of the negative active material and the mass specific capacity of the negative electrode are higher. Besides, the observation of SEM shows that the active material on the lead foam negative electrode has smaller crystals and higher porosity. Compared with that of a lead foil negative electrode, the electrochemical reaction resistance R_{ct} and Warburg resistance (Z_w) of lead-foam negative electrode are obviously lower at the same state of charge, while the exchange current density i^0 [3] is higher, which means that the charge-discharge reactions of a lead foam negative electrode can proceed relatively more easily. This is probably due to the fact that the electric conductivity of lead foam grids is better than that of lead foil grids and lead foam grids have a three-dimensional net structure. Therefore, lead foam grids have larger contact areas of an negative active material, and the reaction of the negative active material is more uniform on lead foam grids. The $PbSO_4$ film is thinner and the ions transfer is more easily on a lead foam negative grid; accordingly, the electrochemical reaction resistance of at a lead foam electrode is obviously lower than that at a lead foil electrode. In a word, when used as grids of spiral VRLA batteries, lead foam has advantages over lead foil.

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Synthesis and electrochemical polymerization of 3, 6-bis (2-thienyl)-n-carbazole

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The most important topics of the rapidly developing field of conducting polymers especially on carbazole containing ones are reported recent literatures [1]. The carbazole family have been extensively studied for the different applications due to their good hole transport, luminescent and electroactive properties [2].

Since the first reports on the electrochemistry of polythiophene films several reviews appeared on the electrical conductivity and other physical properties [3].

Obtaining electrically conductive and redox active polymers by electropolymerization of a heterocyclic monomer depends on the oxidation potential of the monomer. In the case of a monomer such as thiophene, having a high oxidation potential compared to the polymer, the high applied potential causes some degradation of the polymer. This problem can be overcome by extending the conjugation of the monomer by introducing different monomers, resulting in a significant reduction in the oxidation potential. Organometallic polycondensations mediated by organotransition metal complexes have been used to obtain such materials [4]. Recently, we have been reported the preparation of 3, 6-bis (2-thenyl)-N-ethylcarbazole having low oxidation potential due to extended conjugation that underwent facile electrochemical polymerization to form stable electroactive polymers [5]. This type of polymers gives rise to an array of different colors, which is dependent upon an electrochemical potential, making these polymers effective in such applications as electrochromic devices/windows.

Therefore, in this study, we report synthesis and electropolymerization of Th-Cz-Th, co-monomer and the properties of polymeric films compared with poly (Th-ECZ-Th). The properties of electrochemically obtained polymer films from this monomer were characterized by simultaneous voltammetric and spectrophotometric measurements. EIS measurements on Pt/P (Th-Cz-Th) film electrodes were carried out in monomer free solution in dependence of , thickness, supporting electrolyte concentration, polarization potential. Capacitance properties, the ionization potentials I_p, electron affinity E_a, optical band gap E_g, peak potentials, E_p, and doping degree y, of polymer films were calculated from these measurements.

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Symposium 1 - Poster

Batteries and Supercapacitors

Research of improvement the circulation performance of zinc electrode

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The zinc alloy powder as the active material of zinc electrode was prepared by the electrolysis way. Through the Linear Sweep Voltammetry(LSV), Chronoamperometry(CA) and charge and discharge test, ect. The results indicate that the corrosion intensity of zinc electrode in the lye is reduced about 60% by using the electrolytic alloy zinc powder, and it has higher electrochemical activity, the initial capacity reaches 277 mAh/g. The electrolytic ternary alloy Zn-Bi-In is best in synthesis performances. According to the working environment that the zinc electrode is used in, organic additives were added into the electrolyte, in order to improve electrodeposition shapes of the zinc in the course of charge and discharge. Through LSV, CA and charge and discharge test, ect. The results indicate that, the electrodeposition shapes of the zinc is improved effectively by adding the organic additive ZFD in the electrolyte, the growth of zinc dendriteic is restrained, and the circulation performance of zinc electrode is improved. The circulation performance of zinc electrode can also be improved remarkably by micro capsule processing on the zinc powder surface. The crystalloid nuclear positions of zinc electrodeposition might be provided by the membrane structure, at the same time reduced the discharge product to dissolve and diffuse in the electrolyte , restrained corrosion of zinc electrode in electrolyte. Through the Cyclic Voltammetry, AC Impednace and charge and discharge test, The results show that the best way to improve the circulation performance of secondary zinc electrode is adoption dark passivation of copper salt for 5 minutes in zinc powder surface. The electrolytic alloy zinc powder, the additive of electrolyte and surface modifiability of zinc powder were combined together, and the zinc electrode performances were investigated. After 40 times charge and discharge circulations, electrode capacity loss is 18.4%; But the zinc electrode of no optimized capacity loss is 49.6%.

S1·P-13

Suppressive Effect of Ag-coating on Decomposition of PC on the Surface of Graphite

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Lithium ion batteries are widely used in many fields. Researchers have focused on improvement of low temperature performance. Propylene carbonate (PC)-based electrolytes are more desirable than ethylene carbonate (EC)-based electrolytes because of their low-temperature characteristics. Unfortunately, PC is not used in commercial lithium-ion batteries due to its cointercalation and graphite exfoliation. Here we found that coating carbonaceous mesophase spherules (CMS: an artificial graphite) with Ag could prevent the decomposition of PC, which shows promising of PC-based electrolytes in practical applications.
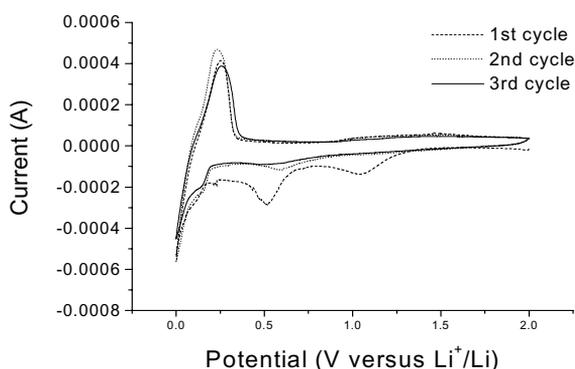
Fig. 1. Cyclic voltammogram of Ag-coated CMS electrode in 1M $LiClO_4$ /PC:DMC(1:1.86 by volume) at a scan rate of 0.1 mV/s.

Fig. 1 shows the cyclic voltammogram of an Ag-coated CMS electrode in 1M $LiClO_4$ /PC:DMC (1:1.86 by volume). At the first scan, there are two irreversible peaks at 0.5 and 1.1 V versus Li^+/Li, respectively, which can be attributed to the decomposition of the electrolyte to build up the SEI film. These irreversible peaks disappear gradually with repeated scanning. The peak near 0.8V corresponding to the decomposition of PC is not observed. The anodic peak corresponding to lithium deintercalation is very strong at every scan. These results indicate that a stable SEI film can be formed on the surface of CMS coated with Ag in PC-based electrolyte. Consequently, continuous decomposition of PC is effectively suppressed by Ag coating.

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The effect of Co on the electrochemical characteristics of nickel-rich layered LiCo$_X$Mn$_Y$Ni$_{1-X-Y}$O$_2$

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Nowadays, LiCoO$_2$ is the prevalent cathode material and many reports address the problem in synthesizing a lower cost, higher-capacity, and safer cathode material than LiCoO$_2$[1]. LiCo$_X$Mn$_Y$Ni$_{1-X-Y}$O$_2$ is the most studied material. LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ could be one of the promising cathode materials, but its unstable cycling performance results in gradual capacity fade, especially when charged to higher voltage.

Venkatraman et al. [2] have showed that oxygen loss from layered metal oxide cathodes becomes significant above 4.25V.This may contribute to observed cycling losses and limits the achievable practical capacities that can be obtained, unless steps are taken to reduce oxygen activity. The decline in cycle ability of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ could be related to the chemical instability of the Co$^{3+/4+}$ redox couple due to its significant overlap with the top of the O^{2-}:2p band. Experiments shows that oxygen loss from nickel-rich layered LiCo$_X$Mn$_Y$Ni$_{1-X-Y}$O$_2$ becomes more serious with the amount of Co increasing ,especially at higher voltage. While, Dahn et al found that transition metal atoms especially Ni^{2+} have a tendency to enter the Li layers when the Co content is low in the material. Experiments indicates that Co can stabilize the structural of nickel-rich layered LiCo$_X$Mn$_Y$Ni$_{1-X-Y}$O$_2$ as the influence of Co on the structural stability of LiNiO$_2$.Its rate performance is improved with the rising Co content, which is probably caused by reducing the propensity of transition metal atoms to enter Li layers. So the amount of Co in the nickel-rich layered LiCo$_X$Mn$_Y$Ni$_{1-X-Y}$O$_2$ is detrimental to its performance and safety .

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S1·P-15

Electrochemical behavior of nickel-rich layered $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ cathode material

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Recently, layered $LiCo_XMn_YNi_{1-X-Y}O_2$ was adopted and studied to overcome the drawback of $LiNiO_2, LiMnO_2$ and $LiCoO_2$. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is amongst the most studied material for higher capacity and lower cost. But the unstable cycling performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ results in gradual capacity fade, especially when charged to higher voltage [1]. Concluded from previous chemical experiments shows that the chemical instability of material arising from an overlap of metal:3d band with the top of oxygen:2p band and the consequent tendency to lose oxygen from the lattice decreases in the order $Co^{3+/4+}>Ni^{3+/4+}>Mn^{3+/4+}$. So nickel-and manganese-rich compositions have higher reversible capacities than cobalt-rich compositions. But experiments show that manganese-rich compositions with a large irreversible anodic peak at 4.5V, while nickel-rich compositions with a good stability when charged to higher voltage.

$LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ cathode material was synthesized by sol-gel method in air, successfully. The cyclic voltammogram curve of $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ showed two couples of peaks at 4.06V/3.63V and 4.29V/4.26V, respectively. There isn't any irreversible peak at higher voltage until the value of voltage is higher than 4.75V, which may indicate that $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ is stabile when charged to 4.75V.The cycling performance test operated in the voltage range of 2.95~4.75V of $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ testified this point : $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ showed stable cycleability after some capacity loss during the initial cycle; it maintained the discharge capacities larger than 220 mAh g^{-1} even after the 100th cycle; the capacity of its first cycle was 246.3 mAh g^{-1}. Venkatraman et al. [2] have shown that oxygen loss from layered metal oxide cathodes becomes significant above 4.25V .This may contribute to observed cycling losses and limits the achievable practical capacities that can be obtained, unless steps are taken to reduce oxygen activity. Obviously, the oxygen loss of $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ at higher voltage is restrained effectively.

Fig.1.cyclic voltammogram curve of $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$

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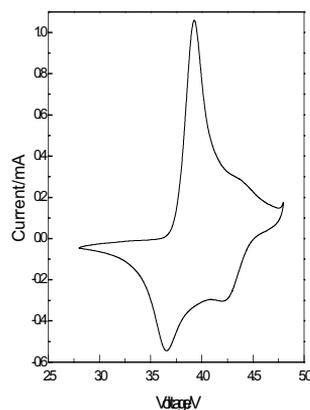
Stannum Doping of Spherical Spinel $LiMn_2O_4$

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Rechargeable Li-ion battery, with high energy density and long life, has been applied successfully in portable electronic appliances such as mobile telephones and laptop computers, and is also considered to be a promising alternative for application in electric vehicles (EV) and hybrid electric vehicles (HEV). But conventional $LiCoO_2$ has the shortage of cost and thermal safety problems, significant efforts have been made by many groups in recent years to develop a cheaper, higher capacity, and safer cathode material to replace $LiCoO_2$. $LiMn_2O_4$ and its derivatives, have been studied extensively as possible substitution due to the safety issue.

In this study, stannum is used to dope spherical spinel $LiMn_2O_4$ at first time. The doping can improve the performance of the spinel. The preparation is as follows[1]. The spherical $MnCO_3$ was firstly synthesized by controlled crystallization of $MnSO_4 \cdot H_2O$, $NH4HCO_3$ and $NH_3 \cdot H_2O$. The spherical Mn_2O_3 precursor was then obtained by heat treatment of $MnCO_3$. A mixture of Mn_2O_3 and Li_2CO_3 was calcined to produce $LiMn_2O_4$. A mixture of SnO_2, Mn_2O_3 and Li_2CO_3 was calcined to produce Sn doped spinel $LiMn_2O_4$.

Fig. 1 shows the cycling performance of the test cell. It indicates the doping of stannum can improve the performance of the spinel.
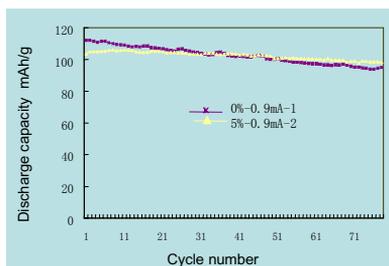
Fig 1 Cycling performance of Sn doped spinel $LiMn_2O_4$

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Li$_{2.6}$Co$_{0.4}$N Composite of Hard carbon for Its Initial irreversible Capacity Improvement

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The outstanding merit of hard carbon is large discharge capacity, but the first irreversible capacity is too large, leading to very low initial efficiency. We believe that the micro pores (2nm-5nm) in the hard carbon inhibit lithium-ion to de-intercalate. On the other hand, Li$_{2.6}$Co$_{0.4}$N cannot be directly treated as being in the delithiated state and lithium must be extracted from the structure in an initial anodic oxidation by either chemical or electrochemical ways. So we put forward the idea to constitute composite anodes based on hard carbon and Li$_{2.6}$Co$_{0.4}$N for lithium ion batteries.

The electrochemical performance of hard carbon as an anode for lithium ion batteries was investigated. SEM, XRD and the constant-current charge-discharge properties of hard carbon and the composite were studied. Results showed that the composite demonstrated a high first cycle efficiency at 104.8％. A large initial discharge capacity of ca. 435.9 m Ah g^{-1} (Fig1) is achieved after the composite.

The discharge capacity of the composite remained higher than hard carbon even after 20 cycles. So the cycling performance of hard carbon can be greatly improved.

The composite appears to be a promising anode material for lithium ion batteries. This work may contribute to an effective way to compensate the high irreversibility capacities of the SnSb$_X$, SnO and SiOx based electrodes in the first cycle for lithium ion batteries.
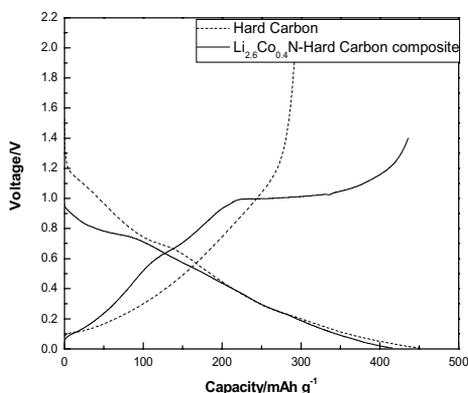
Fig. 1. Charge and discharge curves of the Li$_{2.6}$Co$_{0.4}$N-Hard Carbon composite and the Hard Carbon electrodes at the first cycle.

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Batteries and Supercapacitors

Electrochemical Studies of Electrode Material for Sealed Ni-MH Battery

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Nickel metal hydride (Ni-MH) battery is attracting much attention for the application in electric devices and emission-free electric vehicles because of their several advantages such as high energy density and environmentally acceptable components. Ni-MH battery is consisted of a hydrogen absorbing alloy for a negative electrode and a nickel hydroxide for a positive electrode. However, when charge and discharge cycles are repeated, a gas absorbing performance and charge efficiency at the negative electrode is reduced due to oxidation of hydrogen absorbing alloy. Therefore, there have been such problems as a rise in battery inside pressure, which is increase a loss of electrolyte and a lowering of battery performance. It is intended to improve the service life of negative electrode by adding additive elements to the nickel hydroxide. A potential difference (η value) between an oxidation potential and an oxygen evolution potential of the nickel hydroxide correlates with the charge efficiency, and it is expected that charge efficiency has a tendency to become large with an increase in the η value. When the additive elements such as Ca, Sn, Cd, Zn etc. are added to the nickel hydroxide, oxygen evolution potential of nickel hydroxide shifted to the noble side. we reported on the electrochemical properties of a single particle of spherical nickel hydroxide treated with some additive elements. The electrochemical measurements were done by a microelectrode technique.
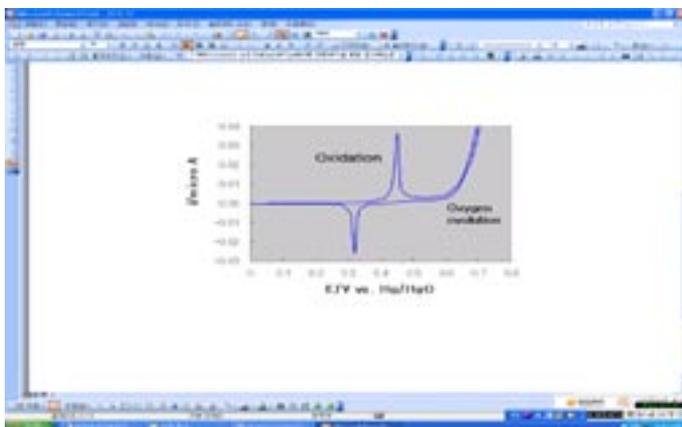
Fig. 1 Cyclic voltammogram for a single particle and a composite film electrode of nickel hydroxide in 5M KOH solution. Scan rate was 1mV/s.

Li Reaction Behavior of GaP Nanoparticles Prepared by Sodium Naphthalenide Reduction Method

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Recently, transition metal phosphides, such as CoP_3, MnP_4, FeP_2, Sn_3P_4, VP_4, and Cu_2P have been investigated as possible candidates for anode materials in Li-ion batteries and can be categorized into two groups depending on transition metal and phosphors bonding stability upon lithium reaction. MnP_4, Cu_2P, and VP_4 showed the topotactic lithium insertion without breaking bonds between transition metal and phosphor, and overall reaction can be written as follows:

$$M_xP_y \rightarrow Li_tM_xP_y \rightarrow Li_tP + M_xP_y \leftrightarrow Li_zM_xP_y \ (1).$$
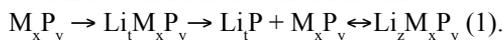
For instance, Kim et al. reported that VP_4 reacted with lithium through topotactic reaction, phase transformation from monoclinic Li_3VP_4 into cubic Li_6VP_4 phase, and decomposition to form Li_3P and VP followed by lithium insertion into VP phase.
On the other hand, Sn_3P_4, FeP_2, CoP_3 showed the direct decomposition of metal phosphide into metal and lithum phosphide, and lithium phosphide and transition metal can participate in the lithium reaction. For instance, Li reaction in CoP_3 can be written as:

$$CoP_3 \rightarrow Li_3P + Co \leftrightarrow 3LiP + Co \ (2)$$
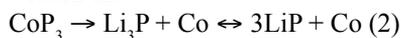
In case of CoP_3, initial uptake of Li forms highly dispersed cobalt clusters embedded in matrix of Li_3P; extraction of Li from this ion-conductive matrix on charge yields nano-particles of LiP, with no oxidation of Co. However, when an active transition metal was formed from the decomposition reaction, lithium can reversibly react with the active metal. Sn_3P_4 was formed in a final reaction:

$$Sn + LiP \text{ and } Sn \rightarrow Li_4Sn \ , \ LiP \rightarrow Li_3P \ (3).$$
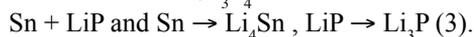
In reactions (1,2 and 3), since LiP is an insulator, and once Li_3P changed into LiP, it is detrimental effect on reversibility of the phosphorous electrode. As long as electrochemical window is limited below 0.72 V, the Li_3P matrix is believed to be relatively stable. However, above 0.75 V, capacity fading was severe and showed ~ 0mAh/g after 30 cycles. However, preparation method for metal phosphides described above used ball-milling or high temperature solid-state reactions mostly.
In this study, we report lithium reaction behavior of the GaP nanoparticles with different particle sizes produced by sodium naphthalenide reduction of $GaCl_3$ in ethylene glycol dimethyl ether (glyme), and concurrent reaction with P at 390ºC without pressured condition.

Symposium 1 - Poster

Batteries and Supercapacitors

A novel composite solid-state polymer electrolyte of methyl group-functionalized SBA-15 for rechargeable lithium batteries

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Since the idea that some polyether-based polymer with alkali metal salts was presented by Wright [1,2] and Armand [3], the development of polymer electrolytes with high ionic conductivity has become one of the objectives in polymer research due to their potential application in electronic devices such as all-solid-state rechargeable batteries. The polyethylene oxide (PEO)-based system is the most comprehensively investigated because of the unique properties of PEO to form 'polymer solutions' of good ionic conductivity. The system, however, still suffers from inadequate room temperature ionic conductivity ($< 10^{-7}$ S cm^{-1} at 25°C). Extensive research efforts have been made to optimize the properties of polymer electrolytes to satisfy the need of all-solid-state lithium-polymer electrolyte battery [4,5].

In this study, molecular sieve SBA-15 was functionalized via trimethylchlorosilane, which was used as inorganic filler in a poly (ethyleneoxide) (PEO) polymer matrix to synthesize composite solid-state polymer electrolytes (CSPEs) for rechargeable lithium batteries using LiClO$_4$ as the doping salts. The methyl group-functionalized SBA-15 powder possesses hydrophobic pore surfaces that facilitate the combination between SBA-15 filler and PEO matrix, which improves its compatibility with the polymer matrix. The methods of linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were employed to study the electrochemical properties and interfacial stability of the CSPEs. The experimental results illustrated that the incorporation of ~5% functionalized SBA-15 yields a stable and homogeneous CSPE with the maximum ionic conductivity (1.87×10^{-6} S cm^{-1}) at room temperature. Addition of functionalized SBA-15 with high concentration (~15%) leads to nevertheless a decrease in the ionic conductivity of the CSPE. Emission FTIR spectroscopy at different temperature was first used to explore the temperature dependent of structure of polymer, and experimental results show that the existence of amorphous phase induces a great contribution to the ionic conductivity. Combining with other experiments we have set up a mechanism of ion conducting. Furthermore, the addition of functionalized SBA-15 has improved also the electrochemical stability window of CSPEs.

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Nano-Scale LiFePO$_4$/C Composites Doped by Ti as Cathode Materials of Lithium Ion Battery

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Ordered olivine structure material LiFePO$_4$ is a very attractive cathode material with the advantages of low cost, environmental benignity, high cycle stability, and high theoretical capacity. But in practice LiFePO$_4$ has not been used extensively due to its low electric conductivity and low electrochemical diffusion kinetics. In this paper, LiFePO$_4$ was synthesized using LiOH·H$_2$O, FeC$_2$O$_4$·2H$_2$O, and NH$_4$H$_2$PO$_4$. Three kind samples were prepared under high rotary ball-milling: mixed with carbon (as LiFePO$_4$/C) ; doped with low amount Ti (as Li$_{0.99}$Ti$_{0.01}$FePO$_4$), and treated with both ways (as Li$_{0.99}$Ti$_{0.01}$FePO$_4$/C composite).

The SEM image in Fig.1 presents the morphology of Li$_{0.99}$Ti$_{0.01}$FePO$_4$/C. The nano-particles were coated by carbon. The composition of samples influences the charge/discharge cycle performance obviously , as shown in Fig.2. Li$_{0.99}$Ti$_{0.01}$FePO$_4$/C composite presents the best behavior (curve a) with the initial capacity of 154.5mAh/g. And after 120 cycles it maintains 92% of initial capacity. It can be attributed to the improving diffusion character by Ti doping and conductivity between particles by carbon mixing. The sample treated only by carbon mixing presents also good cycle stability (curve b), but the discharge capacity is much lower than that of Li$_{0.99}$Ti$_{0.01}$FePO$_4$/C. A sharp capacity decrease was observed for the sample only doped with Ti (curve c).

Acknowledgments
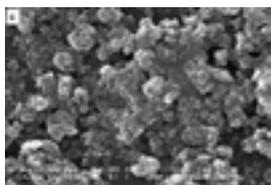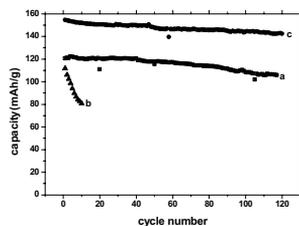
Fig.1   **Fig.2**

Reference: A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.* 144, 1188(1997).

Symposium 1 - Poster

Batteries and Supercapacitors

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Batteries and Supercapacitors

Determination of Li$^+$ solid diffusion coefficient of LiCoO$_2$ by capacity intermittent titration technique (CITT)

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Investigation on the solid diffusion process of Li$^+$ within Li insertion-host materials plays an important role in improving properties of electrode materials and optimizing designs of lithium-ion batteries because the diffusion process is the key step for the energy storage and output. By the capacity intermittent titration technique (CITT), the Li$^+$ solid diffusion coefficients within LiCoO$_2$ have been determined at different voltages and different charge-discharge cycles. Results show that the Li$^+$ solid diffusion coefficient(D) values vary non-linearly from 10^{-12} cm$^2\cdot$s^{-1} to 10^{-13} cm$^2\cdot$s^{-1} in the voltage range from 3.9V to 4.3V, with a minimum at E=3.95V. During charge-discharge cycles, the variation of Li$^+$ solid diffusion coefficient come through three steps because of the crystal structure changes. The XRD and FTIR were used to describe the structure changes during charge-discharge cycles.

Preparation of porous carbon using surfactant and its rate capability in electric double-layer capacitor

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The electric double-layer capacitor (EDLC) has been considered as a promising high power energy source for digital communication devices and electric vehicles. EDLC electrode materials should have a large surface area for charge storage, and an appropriate pore structure for electrolyte wetting and rapid ionic motion.

In this work, porous carbons were prepared *via* resorcinol-formaldehyde polymerization [1-3] and carbonization, where a surfactant was added after a certain period of pre-curing. The prepared carbons possess two different types of pores; one inside carbon spheres (intra-particle pores) and the other at the interstitial sites made by carbon spheres (inter-particle pores). The surface area developed at the intra-particle pores is much larger than that at the inter-particle pores, such that the EDLC performance is predominantly determined by the pore structure of the intra-particle pores. The size of carbon spheres decreases with an increase in the pre-curing time, thereby the length of intra-particle pores is shortened. The carbons comprising smaller spheres show a better rate capability due to a smaller pore resistance and higher ion penetrability.
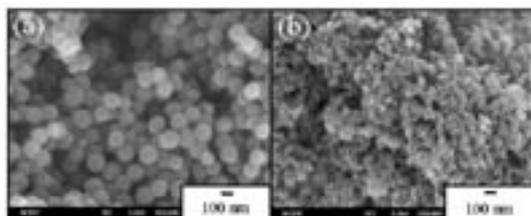
Fig. 1. FE-SEM images of carbons as a function of pre-curing time: (a); 0 min and (b); 90 min.
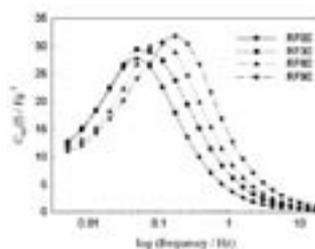
Fig. 2. Imaginary capacitance plots derived from impedance data.

Reference

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Batteries and Supercapacitors

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Batteries and Supercapacitors

Synthesis, phase composition and structure of spinel type catode materials based on manganese compounds for Li-ion batteries

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Lithium manganese spinel represents promising cathode materials for rechargeable lithium and lithium ion batteries. However lithium manganese spinels obtained by conventional solid state method are characterized by relatively low specific capacity and capacity fading during cycling. The method of obtaining pure phase, high dispersal, homogenous samples of cathode materials from solutions is considered at present as the most promising.

Series of modified $Li_xMn_{2-y}Me_yO_4$ spinels, where Me = Ni, Co was obtained by a simplified method as compared with the sol-gel method. Appropriate initial mixtures of Li, Mn, Ni, Co - containing reagents were obtained directly from homogenous solutions by heating and evaporation without using special complex formation agent. Lithium hydroxide was used as Li- containing reagent, and as Mn, Ni, Co – containing reagents nitrates and acetates were used. It was established that it is possible to use nitrates as initial Mn, Ni, Co- containing reagents formation of $Li_xMn_{2-y}Me_yO_4$ type samples with Me=Co, Ni, $1 \leq x \leq 1.2$ and y = 0.1 unit formula. Formation of pure phase, superlithiate, doped cubic spinels with parameter $a = 8.180 \pm 0.004$Å and dispersion $\sim 2 \cdot 10^{-7 cm}$ takes place as a result of corresponding initial batch heating at 600°C during 6 hours. Using manganese and nickel nitrates as initial reagents leads to formation of pure phase samples with cubic singony, lattice parameters $a = 8.186 \div 8.208 \pm 0.03$Å and dispersion $\sim 10^{-7 cm}$. Simplified method allows for obtaining of high dispersal samples of $Li_xMn_{2-y}Me_yO_4$, $1 \leq x \leq 1.2$ and y = 0.1, at 450°C (τ = 6h). High dispersion and homogeneity, relatively low temperature and minimum time of cathode material synthesis as well as samples doping with Co or Ni and creating lithium excess in spinel structure provides for increased electrochemical performance and cycleability of cathode materials, and subsequently of lithium-ion battery.

Evaluation of Anodic 0xidation Durability of PAN Based Carbon Fibers

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In the early time, carbon materials were used for many types of batteries including a Ni-H secondary battery as conductive materials. However, because of the weakness against the anodic oxidation, carbon materials were not used as electrodes, especially for Ni-H secondary battery. So, a new conductive carbon material, which has high durability against both over discharge and charge is strongly required.

It seems to be that there are a few exact investigations about the durability of anodic oxidation of carbon materials with wide range of heat-treatment temperature in high-concentration (6N) alkaline solution. On this background, we tried to improve the durability of carbon fiber in the anodic oxidation conditions. Three kinds of PAN based carbon fibers produced by different makers, namely, CFA: 3 micron meter diameter, epoxy sized 12K filaments. CFB and CFC:7 micron meter diameter, epoxy sized 12K filaments were examined. Thebundles of these CF were heat-treated at 2000℃ and 2400℃ in the vacuum furnace under N_2 gas atmosphere. Heating ratio was 100℃/hr. Holding time at the maximum temperature was 5 hrs. Heat treatment of 2800℃ was performed in the small Acheson furnace under self-atmosphere. Heating ratio was 280℃/hr. Holding time at the maximum temperature was 4 hrs. All fiber bundles were heat-treated in the graphite crucible (under no stress). As the results were shown in Fig.1, the durability of CF (electricity was passed until the cut off of CF) in the anodic oxidation was remarkably increased by heat treatment.

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Batteries and Supercapacitors
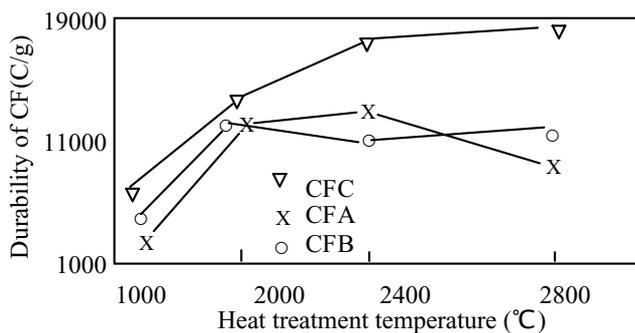
Electrochemical capacitors based on highly porous carbon prepared by chemical treatment

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Activated carbon was activated with chemical treatment to attain high surface area with porous structure. We have been considered activated carbon is the ideal material for high voltage electric double layer capacitor due to their high specific surface area, good conductivity and chemical stability. In this study we found that increase in electrochemical capacitance due to activated carbon. Also chemically activated carbon and water treatment have resulted larger capacitance and also exhibits better electrochemical behavior, and is about 15% more than in untreated state. The structural change in activated carbon through chemical treatment activation was investigated by using SEM and XRD. In this study, the dependence of the activation behavior with KOH in the micro structure of host materials will be discussed. Furthermore, the relation to the electric double layer capacitance, especially the specific capacitance per unit area, is also discussed.

The treated activated carbon was obtained by KOH solution and activated carbon (YP-17) mixed warm up in a double boiler at 60°C for 12h. The resultant materials were washed repeatedly with 0.1M solution of HCl and distilled water to remove chloride ions and next were dried at 110 □C for 6 h. The BET surface area of carbons was measured from N_2 adsorption isotherms at 77K with asorptiometer. Two-electrode capacitors were built from the KOH activated carbon samples and 1 mol l–1 H_2SO_4 and 10M KOH solution was an electrolytic solution. The electrodes consist of 80% of carbon, 5% of polyvinylidene fluoride(PVDF) and 15% of super-P.

The electrochemical behavior of treated activated carbon was characterized by cyclic voltammogram as shown in Fig. 1. A voltammogram close to the ideal rectangular shape was observed treated activated carbon.

The isotherms of N_2 adsorption at 77K for the KOH activated carbons are presented in Fig. 2. The highly developed surface area of KOH activated carbons with a suitable particle size seems to be a primary reason of the exceptionally high capability charge accumulation in electric double layer of such carbon.

Synthesis and electrochemical characterization of activated carbon/metal oxide thin film electrodes for micro electric capacitor applications

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Activated Carbon is most popular materials for EDLCs (Electrical double layer capacitors) owing to its characteristics of large surface area, good conductivity and chemical stability. Nowadays, there has been considerable interest in carbon–metal oxide composites to improve specific capacitance of carbon based electrode materials. There are two typical approaches ; development of new class of carbon based materials and modification of existing carbon based materials with transition metal oxides and conducting polymers.

For micro electrochemical capacitors, a very thin layer of electroactive materials need to be prepared and conventional slurry coating technology may face technical difficulties in its preparation. We have reported metal oxide thin films, CNT thin films and metal oxide/CNT nanocomposite thin films for electrochemical capacitor applications using electrostatic spray deposition (ESD) technique.

In this study, we report on the synthesis of Activated Carbon thin film electrodes and Activated Carbon/Metal oxide thin film electrodes without any additives using electrostatic spray deposition (ESD) technique. Morphological, structural and electrochemical studies were performed with SEM, TEM, XRD and Cyclic voltammetry, and charge-discharge tests. Detailed results and discussion will be presented in the meeting.
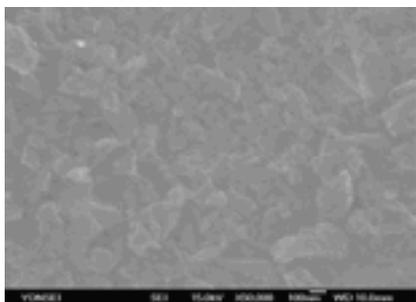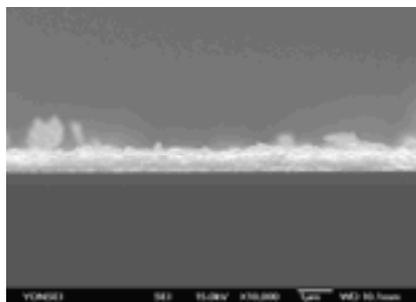
(a)   (b)

Fig.1. SEM images of activated carbon thin film (a) planer view and (b) cross sectional view

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Batteries and Supercapacitors

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Batteries and Supercapacitors

SnO$_2$ Filled Mesoporous Tin Phosphate: High Capacity Negative Electrode for Lithium Secondary Battery

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SnO$_2$ filled mesoporous tin phosphate was prepared by impregnating an Sn melt into the mesopores of hexagonal mesoporous tin phosphate with a pore size of 3 nm at 300ºC under vacuum. Although Sn was oxidized to SnO$_2$ via a reaction with the oxygen ions consisting of one of tin phosphate porewall frameworks at 300ºC, the porewall material remained amorphous without showing any other phases. The electrochemical results revealed significant improvement of the reversible capacity to 805 mAh/g from 400 mAh/g after the mesopores were filled with SnO$_2$. This was because the SnO$_2$ not only added capacity but also decreased high BET surface area of the mesoporous tin phosphate that caused the large irreversible capacity.

Lithium Insertion/Extraction Characteristics of Carbon Nanofibers Formed from PAA using Porous Template

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Nanocarbon materials, including carbon nanotubes, have attracted much attention due to their wide spread applications. The some of the authors have prepared carbon nanofibers by liquid phase carbonization of polyvinyl chloride (PVC) and polyvinyl alcohol (PVA) in pores of the porous anodic alumina template. By using this template technique, the carbon nanofibers of controlled diameter can be produced. The carbon nanofibers thus prepared have a platelet structure, in which graphene layers are normal to the fiber axis. The nanocarbon materials of this type are of great interest as an anode material with high rate capability for lithium ion batteries, since the diffusion path of intercalated lithium ions is short. In fact, the authors have found the good rate capability of the carbon nanofibers prepared at 1000°C. PVC and PVA are classified as soft carbon materials. However, hard carbon materials are known to have higher capacity than soft carbon materials at heat treatment temperatures around 1000°C. Thus, in the present study, carbon nanofibers have been prepared from polyacrylamide (PAA), which is one of hard carbon precursors and porous template.

 The templates used were porous anodic alumina with pore diameters of about 30 and 200 nm. A mixture of PAA powders and the template were heated in a stream of high purity argon gas to 600°C. Then, the template was dissolved and fibrous carbon precursors were obtained. The precursors were further heated to 1000 and 1500°C. The anodes were prepared by coating a mixture of carbon nanofilaments, acetylene black and polyvinylidene fluoride on porous nickel sheets. A liquid electrolyte of 1.0 mol dm^{-3} LiClO$_4$ dissolved in EC+DEC (1:1 by volume) was used.

The carbon nanofibers with the diameter corresponding to the pore diameter of the template were obtained successfully. TEM observations revealed that the carbon nanofibers had a platelet structure. Apparent gas bubbles are present in the carbon nanofibers, possibly associated with the high viscosity of the liquid formed during the carbonization process.

The charge-discharge curves of the carbon nanofibers were similar to those of typical hard carbon materials. As expected, the reversible capacity was larger than those prepared from PVC, being ~400 mA h g^{-1} at a current density of 50 mA g^{-1} for the carbon nanofibers heat-treated at 1000°C. The beneficial effect of smaller diameter of the carbon nanofibers on the reversible capacity at high current densities up to 2 A g^{-1} was also found. The rate capability of the carbon nanofibers prepared from PAA was as high as that prepared from PVC.

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Batteries and Supercapacitors

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Electrochemical Impedance Spectroscopy of Poly(3,4-ethylenedioxythiophene) films: effects of electrolyte composition and film thickness

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The EIS responses of p-doped poly(3,4-ethylenedioxythiophene) (PEDOT) modified electrodes were investigated in acetonitrile and propylenecarbonate solutions, containing different counter-ions (ClO_4^-, PF_6^-, BF_4^-). The polymer films of various thickness were obtained on platinum electrodes by galvanostatic polymerization of 0.05 – 0.1M monomer in acetonitrile in the presence of 0.5 M $LiClO_4$.

For all experimental conditions two characteristic parts of spectra are observed in Nyquist plots: at high frequencies a semicircle due to a parallel RC-element and at low frequencies a nearly vertical capacitive response. The EIS data were analyzed on the basis of a homogeneous film model. It was found that the low-frequency capacitance was independent on the $LiClO_4$ concentration (0.05-1.0 M) and slightly dependent on the nature of counter-ions. The C_{LF} values were linearly dependent on the charge consumed during the electrosynthesis, i.e. were proportional to the film thickness. The parameters of RC-element were derived from semi-circle and analyzed as functions of experimental variables.

The electrochemical behaviour of PEDOT films was compared to that of poly-3-alkylthiophenes (PAT). PEDOT films show more stable electrochemical response (CV, EIS) in comparison with PATs which show noticeable degradation of electrochemical properties at positive potentials (1 – 1.2 V vs. Ag/AgCl). The possible reasons of difference in electrochemical behaviour of PEDOT and PAT films will be discussed.

Lithium diffusion in thin-film amorphous silicon electrodes

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Batteries and Supercapacitors

The electrochemical lithium intercalation into amorphous hydrogenated silicon (a-Si:H) thin-film electrodes is studied by chronopotentiometry, cyclic voltammetry, and electrochemical impedance spectroscopy. The electrodes with thickness from 0.25 to 1.35 μm were obtained from SiH_4 by a method of high-frequency glow discharge on stainless-steel substrates at 250 °C. 1 M $LiClO_4$ in a mixture of propylene carbonate with dimethoxyethane was used as an electrolyte.

The cyclic voltamograms contain cathodic peaks of lithium insertion and corresponding anodic peaks of lithium extraction. The peak current density i_p is proportional to square root of potential scan rate v. The lithium diffusion coefficient D was calculated by the following formula:

$$D^{1/2} = i_p / (2.69 \cdot 10^5 \, n^{3/2} \, c_{Li} \, v^{1/2}),$$

where n is the number of electrons transferred per one diffusing particle, c_{Li} is the lithium concentration in the intercalate calculated by the integration of the cathodic curve taken at the smallest potential scan rate. For the a-Si:H electrodes D came to 10^{-13} cm^2/s.

Frequency dependencies of impedance were obtained at different potentials at different charge-discharge cycles in a range $2.5*10^{-2}$ to 10^5 Hz. An equivalent circuit of the electrodes is suggested, which comprises the electrolyte resistance and three chains in series, each chain being a parallel connection of a resistance and a constant-phase element (CPE). The phase shift of the first CPE is close to $\pi/2$, and this CPE relates to charge transfer at the silicon/electrolyte interface. The second CPE relates to charge transport in the passive film on silicon. The phase shift of the third CPE is some more than $\pi/4$, and this CPE relates to lithium diffusion in the silicon film with finite thickness. With the potential cycling in progress, the most significant changes are observed in the chain relating to the passive film. The Li diffusion coefficient in a-Si:H was calculated from impedance data at not very low frequencies according equation

$$D = \frac{(dE/dQ)^2}{2\rho^2 W^2}$$

where W is Warburg constant, dE/dQ is a slope of quasi-equilibrium galvanostatic charging curve, and ρ is a-Si:H density (2.2 g/cm^3). D values calculated from impedance is very good coincides with that estimated from cyclic voltammetry.

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Batteries and Supercapacitors

Synthesis of mesoporous manganese oxide/carbon nanocomposites for pseudocapacitor applications

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There have been an increasing number of reports about high rate electrochemical energy devices for possible applications as auxiliary power sources for hybrid electric vehicles and fuel cell vehicles. Current technology of secondary batteries, which have high energy density, does not appear to meet the high power requirements for hybrid electric vehicles and fuel cell vehicles. Electrochemical capacitors are attractive energy storage systems, particularly for applications involving high power requirement, however, their energy density is far less than one tenth of secondary batteries.

Since the discovery of M41S silica molecular sieves in 1992, mesoporous materials, possessing remarkably large internal surface area and narrow pore size distribution, have attracted considerable attention because of their potential applications ranging from catalysts, absorbents, gas sensors to batteries and electrochemical capacitors. Mesoporous metal oxides are expected to be an ideal solid-pore architectured material which could improve power density of secondary battery materials or energy density of pseudocapacitor materials because of their large surface area, their thin wall thickness which is equivalent to a short diffusion length and their interconnected nanopores for easy ion transport.

In this study, we report on the surfactant-assisted synthesis and electrochemical properties of mesoporous manganese oxides electrodes for supercapacitor applications. In order to increase the energy density and high rate capability of the materials, the mesoporous manganese oxide electrodes including carbon materials as conducting agent were fabricated by electrodeposition in the presence of surfactants. Rate capability and specific capacitance were estimated with cyclic voltammetry and charge/discharge tests in aqueous solutions.

More details will be presented at the meeting

Structural Characterization of the Surface Modified $Li_xNi_{0.9}Co_{0.1}O_2$ Cathode Materials by MPO_4 Coating (M = Al, Ce, SrH, and Fe) for Li-ion Cells

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Structural characterization of surface modified $Li_xNi_{0.9}Co_{0.1}O_2$ cathodes (x = 0.3 and 0.15) using a MPO_4 coating (M = Al, Ce, SrH, and Fe) were investigated for their potential applications to Li-ion cells. MPO_4 nanoparticles that were precipitated from metal nitrate and $(NH_4)_2HPO_4$ in water at pH = 10 were coated on the cathodes via mixing and heat-treatment at 700°C. The $CePO_4$ and $SrHPO_4$-coated $Li_{0.3}Ni_{0.9}Co_{0.1}O_2$ cathodes heat-treated at 300°C were mainly made up of the rock-salt phase (Fm3m) while $AlPO_4$ and $FePO_4$-coated cathodes showed disordered $[Li_{1-x}(Ni,Co)_x]_{3b}[(Ni,Co)_y]_{3a}O_2$-type hexagonal structure (R-3m) with a cation-mixing. However, when x value decreased from 0.3 to 0.15, bare and coated cathodes which had a spinel (F3dm) or hexagonal structure (R-3m) at x = 0.3 were transformed into a NiO-type rock salt structure. Structural changes of the coated cathodes at 300°C was influenced by the coating materials, depending on x value in $Li_xNi_{0.9}Co_{0.1}O_2$. Among the bare and coated samples, $AlPO_4$-coated sample exhibited lowest degree of oxygen generation after 300°C annealing at x = 0.15, indicating the highest thermal stability among the bare and coated cathodes.

Symposium 1 - Poster

Batteries and Supercapacitors

Capacitance of the Solid Electrode -Ionic Liquid Double - Layer

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Ionic liquids (IL) - salts characterized by low melting points, have been studied extensively during the last decade. These liquid salts may be used as solvents as well as electrolytes in electrochemical devices. At the same time double-layer electrochemical capacitors, based on carbon materials having very high-surface area, have also been studied with very promising results. Both aqueous and various non-aqueous liquid electrolytes as well as polymer electrolytes have been applied there in, including ionic liquids. There are only a few publications about double layer capacity measured at well defined electrode/electrolyte surface. Except the report on ionic liquids based on the chloroaluminate ion [1], a paper about specific capacitance for glassy carbon (GC), mercury and a commercial carbon as electrode materials and four ionic liquids based on 1-ethyl-3-methyl imidazolium cation can be found in the literature [2]. The general aim of this work was to examine the differential capacity at the solid electrode/IL interface for a number of ionic liquids.

Differential capacity at the electrode/IL interface (electrode material was: glassy carbon (GC), Pt or Au) was measured applying (i) chronoamperometry (ii) cyclic voltamperometry and (iii) ac impedance measurements. The chronoamperometric measurements were done in a two electrode system. The working (GC, Pt or Au) electrode was charged by superimposing a ± 10, 20, 30, 50 up to 90 mV potential dc signal, U, and the current flowing during electrode charging or discharging was recorded as a function of the time. The charge Q accumulated at the electrode was obtained by integrating the I = f(t) curves and the capacity was obtained directly from the slope of the dQ = C dU. The impedance spectra were measured in a three compartment cell over a frequency range from 0.01 Hz to 99 kHz with an ac potential amplitude of 10 mV. The double layer capacity at the GC/IL interface, obtained from chronoamperometry, is at the level of ca. 10-25 microF/cm^2 at potentials close to the open circuit potential, while the corresponding values for the Pt/IL and Au/IL systems were significantly lower, typically at the level of 1-8 microF/cm^2. This difference is probably due to possible faradaic reactions that can take place at the GC electrode.The capacity value was approximately constant within a broad potential range (of ca 3V).

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Impacts of surface conversion on determination of hydrogen diffusion coefficient in hydrogen storage alloys

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As an important parameter characterizing hydrogen storage alloys, the hydrogen diffusion coefficient (D) has attracted much research interest. However, the data reported in literature are largely scattered ($10^{-7}\sim10^{-13}$ cm^2/s). Moreover, while most researchers claimed D increasing with decreasing SOC (state of charge), some others reported D being independent of SOC. This paper will show that these controversies are due by large to the difference in dealing with the surface conversion process.

The surface conversion is a chemical step converting the hydrogen stored in the surface layer of the alloy to the hydrogen adsorbed on the alloy surface, and only the adsorbed hydrogen is able to be oxidized during discharge. According to this model, the diffusion coefficient deduced from transient measurements without correction for the surface conversion effect will be an apparent diffusion coefficient D_{app} in stead of D:

$$D_{app} = D\{1- (D/\delta)/[(1 - \theta) k + (D/\delta)]\} \qquad (1)$$

where δ is the effective diffusion layer thickness (a function of time), k the surface conversion rate constant, θ the surface coverage of adsorbed hydrogen (decreasing with increasing potential and approaching zero at sufficiently positive potentials). Most of the reported D values are actually D_{app} values. Most of the works claiming "SOC dependent D" used different potentials (influencing θ) and time scales (influencing δ) according to SOC values, resulting in an apparent (NOT intrinsic!) correlation between D_{app} and SOC and this correlation was unfortunately mistaken as the causality between D and SOC changes. In this presentation, individual cases in the literature will be critically reviewed in the light of Eq. 1 to support the above statement.

Reasonable approaches must take into account the surface conversion step properly, as exemplified by Fig. 1. The chronoamperometry for a single spherical particle LaNi$_5$ (ϕ30 μm) can be well simulated only if the surface conversion is considered. The results obtained from Fig. 1 are $D = 6\times10^{-10}$ cm^2/s, $kf = 8\times10^{-6}$ cm/s (f is the roughness factor of the particle surface). The long range linearity (corresponding to SOC=0.3 to 0) in the insert of Fig. 1 also serves additional evidence of SOC independence for D.

Symposium 1 - Poster

Batteries and Supercapacitors

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Batteries and Supercapacitors
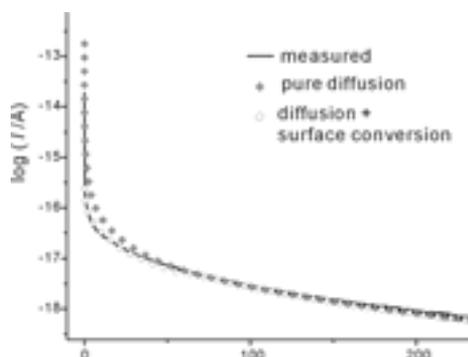
Studies on Structure and Electrochemical Properties of Pillared M-MnO$_2$ (M = Ba^{2+}, Sr^{2+}, ZrO^{2+})

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Supramolecular pillared oxides M-MnO$_2$ (M = Ba^{2+}, Sr^{2+}, ZrO^{2+}) were prepared through the intercalation of M^{2+} cations into MnO$_2$ host matrix by the method of ion exchange between the precursor δ-K$_x$MnO$_2$ and the corresponding guest. The materials M-MnO$_2$ crystallize in the hexagonal system, the same structure as the precursor, with a larger interlamellar spacing. In the case of ZrO-MnO$_2$, extended X-ray absorption fine structure (EXAFS) determination indicates that Zr atom locates between the MnO$_2$ layers forming a stable octahedral interlayer complex. Compared with the precursor, the cycling property of M-MnO$_2$ was improved distinctly, while the capacity decreased to some degree due to the strong interaction between pillars and the host matrix. Among these pillared materials, ZrO-MnO$_2$ has a reversible capacity of 161.5 mAh·g^{-1} and rather stable cycling behavior compared with the precursor.

Keywords: Layered M-MnO$_2$; Cathode materials; Lithium secondary batteries; Intercalation; Electrochemical properties
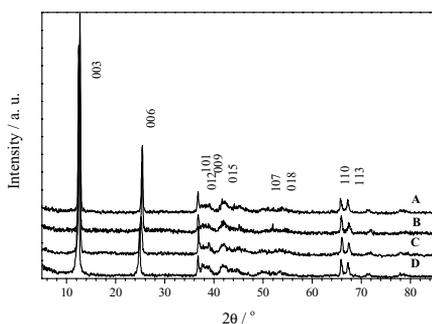
Fig. 1 XRD patterns for the precursor and the products M-MnO$_2$ (M = Ba^{2+}, Sr^{2+}, ZrO^{2+})
A. the precursor K$_x$MnO$_2$; B. Ba-MnO$_2$; C. Sr-MnO$_2$; D. ZrO-MnO$_2$
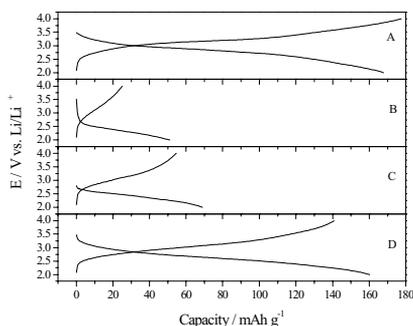
Fig. 2 Charge-discharge curves of the precursor and M-MnO$_2$ used as cathode materials
A. the precursor K$_x$MnO$_2$; B. Ba-MnO$_2$; C. Sr-MnO$_2$; D. ZrO-MnO$_2$

Synthesis of Nanostructured carbon and Sulfonate polysulfone Ionomer for Solid-State Supercapacitors

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An ordered mesoporous carbon material has been synthesized and used together with solid polymer electrolyte (SPE) to realize a solid-state supercapacitor (SC). The synthesis of carbon consisted in the preliminary preparation of highly ordered mesoporous silica (SBA-15), used as a template material, that in a second step was impregnated with sucrose that after thermal treatment at 850 °C was transformed in carbon. The so prepared carbon is know as CMK-3 type carbon. The solid polymer electrolyte was synthesized using trimethyl silyl chlorosulfonate as sulfonating agent in homogeneous polymer solution of chloroform. The silyl sulfonate polysulfone is modified in the sulfonate form by reaction with sodium methoxide. The membranes were prepared by casting method. The prepared membranes were washed with water, dried and converted in protonic form for immersion in HCl solution before their characterization. Two samples of sulfonated polysulfone membrane (SPSf) were employed as electrolyte in the fabrication of solid-state supercapacitors. The former sample contained only the SPSf, whereas the second was in composite form being SPSf filled with 5% of SBA-15 silica. The electrodes for the supercapacitors was prepared with CMK-3 mesoporous carbon and Nafion ionomer. The latter had both the functions of binder and ion conductor. The structures of nanostructured silica template and carbon material was evaluated by transmission electron microscopy (TEM) small angle X-Ray diffraction (XRD) and BET analyses. The solid-state supercapacitors based on carbon electrodes and solid polymer electrolytes were characterized by cyclic voltammetry (CV), galvanostatic charge/discharge measurements and, electrochemical impedance spectroscopy (EIS) analyses. As a result, it was found that the supercapacitor with the composite SPSf membrane exhibited higher specific capacitance (105 F/g) compared to that with the membrane containing only SPSf (86 F/g). Further results on the structural features of synthesised nanostructured carbon, on the proton conductivity of the polymeric membranes and, on the effect of filler on supercapacitor performance will be shown during the presentation.

Symposium 1 - Poster

Batteries and Supercapacitors

Symposium 1 - Poster

Batteries and Supercapacitors

Preparation, Structure and Electrochemical Properties of $Li_2Na_4V_{10}O_{28}$ as a New Cathode Material in Li-ion Battery

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It is well known that $LiCoO_2$ is commercially used as cathode material for lithium-ion batteries. Nonetheless, cobalt has economic and environmental problems. Among the alternative candidates, Lithium vanadium oxide is considered as a promising material based on its lower price and higher specific capacity compared to $LiCoO_2$[1]. In this work, new material, $Li_2Na_4V_{10}O_{28}$ was prepared by using hydrothermal synthesis and annealing method.

$\{[LiNa_2(H_2O)_9]2_{10}O_{28}\}_2\}_n$ single crystal has been firstly synthesized as reported in Ref.[2] . The as-prepared sample was placed into a furnace to anneal at 513K for 5h in N_2 gas, and then was pulverized to fine powder with ball milling after cooling to room temperature. $Li_2Na_4V_{10}O_{28}$ sample was obtained   The structures of this sample, $Li_2Na_4V_{10}O_{28}$, were determined by XDR with $CuK\alpha$ radiation resources and SEM. A half-cell composed of lithium foil as anode and cathode made of $Li_2Na_4V_{10}O_{28}$ powder was used to check the electrochemical properties. The electrolyte was 1M $LiPF_6$ in EC/DMC (1:1) solution. The cathode was prepared by pasting a mixture of the prepared lithium vanadium oxides, acetylene black and PVdF binder (weight ratio: 85:5:10) onto Al substrate. The size of the testing cathode was around 1.0 cm^2, and the weight of active material in the electrode was around 1.45 mg. Galvanostatic charge / discharge cycling studies were carried out at 0.03mA/cm^2 rate in a voltage range 1.5 to 4.5 V.

Experimental result shows that there is a long path in a, b, c orientations in structure of the sample respectively, and its size of cross section is around 5.9456Å×5.3165Å; 5.9456Å×4.2693Å; 4.2693Å×5.3165Å. The three paths communicate each other. It would be helpful to the movement of lithium ion during charge/discharge process.

It has been noticed that the material exhibits high OCV, around 3.43V (vs. Li/Li^+) and high discharge capacity, around 350 mAh/g. The electrode made of $Li_2Na_4V_{10}O_{28}$ sample shows good electrical conductivity and electrochemical reversibility during charge/discharge process, which maybe be attributed to the novel structure of the three paths. All the results show that this new cathode material would be a promising alternative material for lithium secondary batteries.

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Synthesis and characterization of birnessite nanorods on carbon nano tube (CNT) for electrochemical capacitor applications
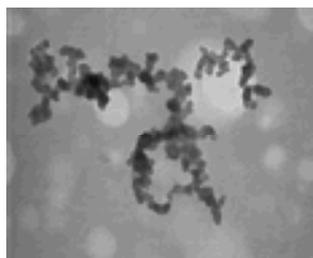
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Manganese oxide is a promising electrode material for pseudocapacitors on account of its pseudocapacitive behavior, low cost and environmental compatibility. CNTs have been continuously studied as electrode materials for electrochemical capacitors, as additives to improve the electrode performance of conducting polymers and metal oxides or as deposition substrates for metal oxide particles and conducting polymers for pesudocapacitors because of their chemical stability, good conductivity and large surface area. In addition, CNTs are strongly entangled, providing a network of open mesopores.

Lately, several studies on the synthesis of manganese oxide / CNT composites have been carried out with the aim of improving the electrochemical utilization of manganese oxide and the high rate capability. Previous approaches to the synthesis of manganese oxide / carbon composite include various methods such as physical mixing, thermal decomposition, ball milling, electrodeposition, sonochemical synthesis, and redox reaction.

Because the pseudocapacitive reaction of manganese oxide is known to be a surface reaction, only the surface or a very thin surface layer can participate in the pseudocapacitive reaction. Therefore, in the synthesis of manganese oxide / CNT composites, it is ideal to deposit a very thin layer (~ nm) of manganese oxides onto CNT with a large surface area in order to improve the electrochemical utilization of manganese oxide. An increase in the effective interfacial area between the manganese oxide and an electrolyte can lead to a higher electrochemical utilization of manganese oxide in the manganese oxide / CNT composites. Greater chemical contact and increased contact area between the manganese oxide and CNT can improve the electric conductivity of the electrode on account of the high electric conductivity of CNT.

In this study, we report on the synthesis of birnessite nanorods of manganese oxide spontaneously deposited onto CNT at the nanometer scale by the simple immersion of CNT into aqueous potassium permanganate solution for electrochemical capacitor application and on the synthesis mechanism of the heterogeneous nucleation of manganese oxide on CNT using in situ monitoring of the solution chemistry.

More details on the synthesis and characterization of birnessite nanorods on CNT will be presented at the meeting.

Symposium 1 - Poster

Batteries and Supercapacitors

Symposium 1 - Poster

Batteries and Supercapacitors

Electrochemical characterization of spontaneously deposited manganese oxide on carbon nano tube (CNT) for electrochemical capacitor applications

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Electrochemical capacitors (ECs) are energy storage devices that possess higher energy and power density than conventional dielectric capacitors and batteries, respectively. According to the mechanism of energy storage, ECs can be categorized into two classes: electrochemical double layer capacitor (EDLC) and pseudocapacitor. EDLC is based on double layer capacitance due to charge separation at the electrode/ solution interface, and pseudocapacitor is based on the pseudocapacitance of faradaic redox reactions at active electrode materials. The electroactive materials of supercapacitors are conducting polymers and transition-metal oxides.

Among the various transition metal oxide materials for pseudocapacitor, amorphous and hydrated ruthenium oxide exhibits remarkably high specific capacitance (~720 F/ g) compared with other oxides. However, its commercial use is limited by its high cost. Therefore, a great effort has been devoted to identifying alternative and inexpensive metal oxide electrode materials with acceptable electrochemical properties. In this sense, manganese oxide is a promising electrode material for pseudocapacitors on account of its pseudocapacitive behavior, low cost and environmental compatibility.

Various carbonaceous materials, with their large specific surface areas and good conductivity, can serve as promising candidates for high surface area substrates. Among them, the carbon nanotubes (CNTs) are attractive substrate materials for the metal oxide due to their chemical stability, good conductivity, and large surface area. CNTs have uniform diameters of several tens of nanometers, and they have unique properties such as entanglement and mesoporous character.

In this paper, we report the preparation and electrochemical characterization of spontaneously deposited manganese oxide with various morphologies on carbon nano tube (CNT) for electrochemical capacitors.Permanganate ions were reduced to manganese dioxide by CNT as reducing agent. Its morphology was controlled by a change in pH of a potassium permanganate solution.

More details on the electrochemical properties of manganese oxide on CNT will be presented at the meeting

Pseudocapacitive behaviors of hydorothermally synthesized nano Ni(OH)$_2$/CNT composites

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Research on nanoparticles synthesis, characterization and applications continues unabated as the nanomaterials make a revolution in macrosystems. The major advantage of nanoparticle assembly over conventional materials is the high surface area to volume ratio. For instance, a nanocrystalline metal oxide may have an internal surface area approximately 1000 times greater than the geometric area which answers for the better capacitances and electronic conductance on exposure to a conducting electrolyte solution. The existence of such size effects offers a new pathway to regulate reactivity, either chemically or electrochemically or both by controlling the particle size. Electrochemistry plays a key role in nanoparticle science as it paves a way for coupling particle activity to external circuitry.

To increase the performance of electrochemical capacitors in terms of energy density and high rate capability, nano metal oxy/hydroxides of nickel in combination with carbon nano tubes were investigated in our present work. The metal oxide/CNT composite electrodes utilize both advantages of double layer capacitance and pseudo-capacitance. Phase pure alpha nickel hydroxide is synthesized by a hydrothermal method using urea and nickel nitrate in an autoclave. Composites are made by wet impregnation and controlled precipitation of metal oxide on CNT. Metal oxide to CNT ratio is optimized based on the electrochemical studies. Characterization techniques like XRD, SEM/TEM, BET surface area, XPS etc. were used to study the physical and chemical properties of the materials. Individual as well as the composites of nickel oxide and CNT were subjected to electrochemical characterization both in aqueous and non-aqueous electrolytes. Composites of metal oxide/CNT showed better energy density and high rate capability when compared to individual metal oxides and CNTs. In an aqueous electrolyte, specific electrochemical capacitance of Ni(OH)2/CNT composite was ~ 1000 Fg-1, compared to 289.8 Fg-1of pure α-Ni(OH)2.

Spherical nano Ni(OH)$_2$

Symposium 1 - Poster

Batteries and Supercapacitors

Mesoporous NiO/CNT composites : potential electrode material for pseudocapacitor applications

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Recently, efforts are being made to improve the energy density of the EDLC by increasing the effective surface area of carbon-based materials, although the resulting densities are still too low. The major bottlenecks to be addressed are a) optimization of particle size of active materials; b) high cycle life during the rapid charge–discharge process; and c) increase the electronic conductivity of the electrode materials. For an ideal double layer capacitor, the charge is transferred into the double layer and there are no Faradaic reactions between the solid material and the electrolyte. In this case, the capacitance is constant and independent of voltage. On the other hand, for capacitors that use metal oxides, pseudo-capacitance due to Faradaic reactions between the solid material and the electrolyte arises and it is voltage dependent. The double layer capacitance has a typical value of 10–40 μF cm^{-2} for a real surface, while pseudo-capacitance may be 10–100 times greater. The metal oxide/CNT composite electrodes utilize both advantages of double layer capacitance and pseudo-capacitance. Prototypes made of ruthenium and tantalum oxides have been highly successful and are commercialized. As these oxides are highly expensive, alternative metal oxides are explored.

In order to increase the performance of electrochemical capacitors in terms of energy, power and voltage, ordered mesoporous NiO in combination with carbon nano tubes were investigated in our present work. Due to high surface area of both electroactive and conducting materials, we expect better specific capacitance compared to nonporous oxide active materials. Many approaches have been presented in literature to synthesize ordered mesoporous transition metal oxides which have yielded in mixed results. Our aim is to prepare mesoporous NiO by a) using cationic and neutral surfactants as templates; b) using SBA-15 as hard template; and c) in situ generation of mesoporous silica followed by mesoporous NiO. We have followed very simple aqueous hydrothermal route to prepare mesoporous NiO and also its composites with CNT. The materials were characterized by XRD, SEM, TEM, BET surface area and XPS. These nanomaterial were immobilized on paraffin impregnated graphite electrode by abrasive transfer technique and the electrochemical behavior was studied in aqueous electrolytes employing techniques like cyclic voltammetry, charge–discharge and impedance spectroscopy

Effect of Substrate on Synthesis and Electrochemical Behavior of Manganese Oxide for Lithium Battery Application

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Manganese oxide is very interesting as a positive electrode material for lithium-ion batteries due to its superior electrochemical performance, environmentally friendly nature and low cost [1]. Since electrodeposition is an efficient approach for the preparation of stable films of electroactive materials on substrate surfaces [2], we have chosen this method and investigated the effect of three different substrates (platinum, gold and glassy carbon) on the synthesis and electrochemical performance of manganese oxide. We found that the addition of a small amount of carbon nanotubes to electrodeposition bath (at low current densities) causes the improvement of electrochemical performance of manganese oxide for lithium battery application, because nanostructures minimize the Li^+ diffusion path in solid state diffusion. According to the value of the potential in galvanostatic deposition, various types of manganese oxide can be formed on the substrate surfaces. For Pt, two plateaus are observed at potentials of ca. 0.8 and 1.0 V corresponding to the formation of manganese oxides based on Mn^{3+} or Mn^{4+}. In other two cases, higher valances of Mn can be generated as a result of higher electrodeposition potentials. In their corresponding CVs, no peaks are observed for the film electrodeposited on GC electrode; while in the case of Au, two distinct redox couples are observable. In CV of the manganese oxide electrodeposited on Pt, one redox couple related to Mn^{3+}/Mn^{4+} transformation is observed, which makes it a suitable cathode for 4V lithium batteries.
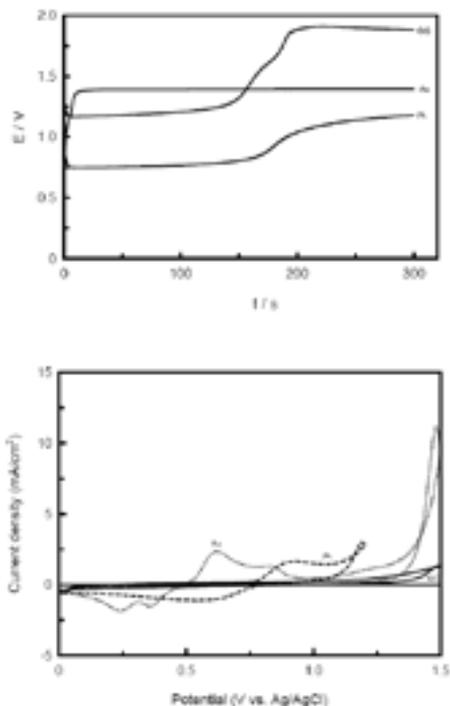
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Polyaniline nanofibers as electrodes for electrochemical supercapacitors

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Electronically conducting polymers such as pyrrole, aniline, thiophene, etc, are attractive materials for lightweight rechargeable batteries and electrochemical supercapacitors, due to their good high conductivity, good redox reversibility, ease of synthesis and relatively low prize.

During the last decade, many attempts have been devoted to the synthesis of high porosity, high surface area, micro and nanostructured conducting polymers, resulting from their potential application in areas such as catalysis, optics, drug-deliver, microelectronics, etc. In the present work we report on the synthesis of acid-doped polyaniline nanofibers without the use of templates, via an interfacial polymerization process at an aqueous/organic interface, and their application as active electrode material in electrochemical supercapacitors.. Symmetric supercapacitors were assembled from two 12 mm diameter, 50 mg weight polyaniline composite electrodes (70 wt% PANI, 20 wt% Super P carbon and 10 wt% KF2801 binder) that were kept apart by a glass paper soaked in a 1M solution of the same acid used in the PANI synthesis as electrolyte. The specific capacitance of the supercapacitors was evaluated by means of cyclic voltamnetry, impedance measurements and galvanostatic charge-discharge tests (Figure 1).
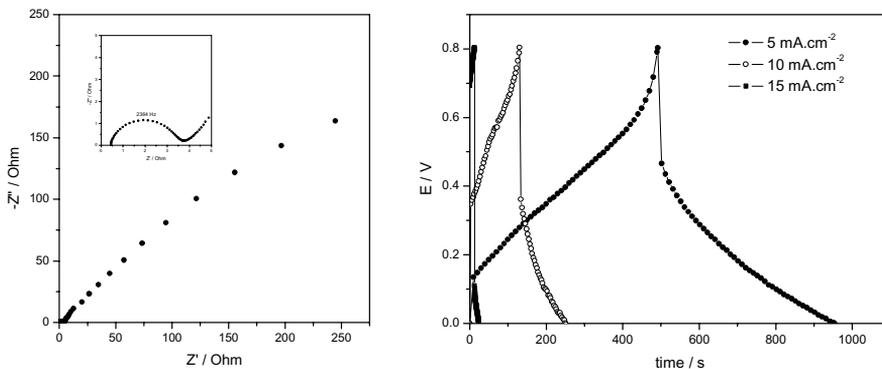
Electrochemical impedance spectra (0.8 cell voltage after 300 s 0.8V) and galvanostatic charge/discharge curves for a SO_4H_2-doped PANI-based symmetric supercapacitor

The results obtained indicate that both polyaniline morphology and electrical conductivity depends on the chemical nature of the acid dopant. Regarding to specific capacitance and efficiency, the calculated values obtained are strongly dependent on the nature of the acid dopant and the electrolyte used.

Symposium 1 - Poster

Batteries and Supercapacitors

Sonochemical assisted oxidation of pbo to nanostructured lead dioxide and its use as cathodic material of lead – acid battery

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In recent years, an increasing interest has been focused on the preparation and application of nano-structured materials (e.g. metal oxides) [1]. Various techniques have been used for the preparation of nano-structured materials [2]. Recently, a sonochemical method has been used to generate materials of nanometer dimension [3, 4] which show improved properties such as better energy storage [5].

In our previous work, we used electrochemically prepared nano-structured PbO_2 as the active material of lead acid batteries [6]. In this work, we report on the ultrasonically assisted synthesis of lead dioxide. Here, PbO_2 nano-powder was synthesized from an aqueous dispersed PbO solution. In the presence of the ultrasonic irridation, the oxidation of lead oxide was initiated with addition of $(NH_4)_2S_2O_8$ (ammonium persulfate) as an oxidant. The effect of various parameters such as the amount of lead oxide and ammonium persulfate, temperature and pulse amplitude was investigated on the particle size and phase structure of the prepared lead dioxide. The oxidation of lead oxide was completed with increasing the amount of ammonium persulfate and temperature after 2 h of solution ultrasonication. A dark brown powder was obtained after centrifuge of the solution. The resulting PbO_2 nano-powders were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The PbO_2 particles were composed of aggregated nano-structured lead dioxide, the size of which was found to be in the range of 50-100 nm. The XRD pattern shows that, when the reaction is completed, only the crystalline β -PbO_2 was obtained, while in the case of incomplete reaction, both $PbSO_4$ and β-PbO_2 were observed in the texture. The prepared lead dioxide was used as a cathodic material of lead- acid battery. Energy storage abilities of the battery including discharge capacity, specific energy and power were investigated.

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Batteries and Supercapacitors

Change in morphology of polyaniline/graphite composite: a fractal dimension approach

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Investigation of surface roughness is an important issue in surface science. Electrode surface characteristics are exceptionally important for all electrochemical process because they can determine the adsorption and ion exchange behavior of the electrode [1]. Fractal geometry is a mathematical concept that describes objects of irregular shape. Some natural geometrical shapes, that can be irregular, tortuous, and rough or fragmented, can be described using concepts of fractal geometry as long as the requirement of self-similarity is satisfied [2]. Moreover, fractal geometry provides a powerful opportunity to investigate surface roughness via geometrical models [3,4]. Fractals have been characterized by several methods that can be classified as physical, chemical and electrochemical. Electrochemical methods have been supported by mathematical simulations and experimental evidences and are one of the most useful and reliable methods for the determination of fractal dimension of surfaces [5].

In the present work, graphite (G) particles with different sizes were incorporated in polyaniline (PANi) matrix to form polyaniline/graphite composites by repeated potential cycling at the Pt electrode from – 0.20 to 0.85 V for 100 cycles at a sweep rate of 50 mVs^{-1} in a stirring solution containing 1.0 M hydrochloric acid, 0.1 M aniline, 5.0×10^{-3} M SDS and 4% of graphite in suspension. SDS was used as an additive in order to suspend of graphite particles and to improve the stability and electroactivity of the resulting films [6]. The surface morphology of PANi/G composites with different graphite particle sizes were studied by using the fractal dimension concept. The fractal dimensions evaluated from the cyclic voltammetry and electrochemical impedance spectroscopy measurements do indeed coincide. The results obtained from both these methods are in good agreement indicating the reliability of the estimated fractal dimension (D_f).

As shown by using SEM and fractal dimension, the PANi/G composites possess more porous structure with an increase in graphite particle size. The results indicated that the electrochemical methods described in this work could be used as a simple tool for analyzing the fractal structure of conducting polymers and their composites.

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Electrodeposition and Characterization of Chromium-Containing Manganese Oxide Films for Electrochemical Capacitors

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Amorphous hydrous manganese oxide has received attention as a new supercapacitor electrode candidate. Advantages of manganese oxide are the lower cost for raw materials and the fact that manganese-based capacitors are environmentally benign in the point of view that they can operate in neutral electrolyte. Incorporation of other transition metals into MnO_2 compounds is a common strategy to improve their charge-storage capability. Hence, the development of a simple procedure for the synthesis of Mn-based mixed oxides in a thin film form will provide a breakthrough to fabricate electrode materials for supercapacitors. Herein, we describe a new electrochemical route to construct manganese and chromium mixed oxide films. The process includes anodic oxidation of aqueous Mn^{2+} ions in the presence of chromate anions. This method is similar to what we previously reported for the formation of V- and Mo-containing Mn oxide films.[1,2]

A Mn/Cr mixed oxide film was prepared on a Pt plate electrode by applying a constant potential of +0.7 V versus Ag/AgCl in a 2 mM $MnSO_4$ aqueous solution with 20 mM $(NH_4)_2CrO_4$. The resulting Pt-supported film was characterized by FE-SEM, XRD, and CV in a 0.5 M Na_2SO_4 solution at a scan rate of 20 mVs^{-1}.

A FE-SEM image of the deposited film is depicted in Fig. 1, presenting spherical particles with high porosity that were not observed for the film prepared without CrO_4^{2-}. XPS revealed that the deposit is composed mainly of Mn oxide with minor amount of Cr^{3+}. The reduced state of Cr indicates the involvement of chemical reduction of Cr^{6+} in the electrodeposition process. Fig. 2 shows voltamograms of the Mn/Cr oxide film when cycled repeatedly in 0.5 M Na_2SO_4 electrolyte, yielding a roughly rectangular shape characteristic of capacitor behaviour. The voltammetric charge was much larger than that of pure Mn oxide and kept constant during repetitive cycles.

Fig. 1 FE-SEM images of the electrodeposited film.
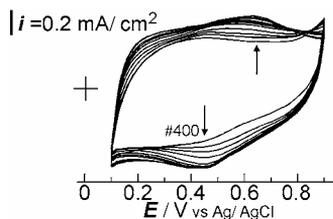
Fig. 2 CV of the film-coated electrode in 0.5 M Na_2SO_4.

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Batteries and Supercapacitors

Activation Energy of the Lithium Diffusion in Graphite

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Various modifications of graphite and other carbonaceous materials have been used as the negative electrode materials for lithium-ion batteries. Due to a slow solid-phase diffusion rate such batteries can operate only at relatively low discharge rates. Values of diffusion coefficient D of lithium in graphite are documented in numerous references but quantitative data on the effect the temperature exerts on D are scarce and refer to narrow temperature ranges. The present work is devoted to studying the effect of temperature on the rate of lithium diffusion in graphite FG-A [1].

The values of D were obtained by switch-on-curves method in the temperature range from –40 to +40 $^{\circ}$C. Experiments were run in three-electrode cells with Li counter and reference electrodes and with 1M $LiClO_4$ in a 7:3 mixture of propylene carbonate and dimethoxyethane.

Before embarking on pulse chronopotentiometric measurements, a quasi-equilibrium curve for Li intercalation and deintercalation were registered to obtain the quantitative correlation between electrode potential E and charge Q corresponding to amount of intercalated Li.

Galvanostatic switch-on curves were registered at potentials of 0.09–0.10 V. The initial portions of the curves were linear in the E, $\sqrt{t}$ coordinates, and the slope $dE/d\sqrt{t}$ (here t is time from switching current) was proportional to current density i. These facts confirm that conditions of semi-infinite diffusion were fulfilled. Values of D were calculated according to equation

$$D = \frac{4}{\rho^2 \pi}\left(\frac{dE}{dQ}\right)^2 \Big/ \left(\frac{d^2E}{di\,d\sqrt{t}}\right)^2$$

Here ρ is the graphite density.

The slope $d^2E/di\,d\sqrt{t}$ happened to equal 3.27 ohm·cm^2·s$^{-1/2}$. The slope of quasi-equilibrium curve dE/dQ is equal to $1.78\cdot10^{-4}$ V·g·C^{-1} at the potential 0.1 V. The D values amounted to $2.5\cdot10^{-12}$, $1.9\cdot10^{-11}$, $4.5\cdot10^{-11}$, $1.2\cdot10^{-10}$, and $2.7\cdot10^{-10}$ cm^2 s^{-1} at –40, –15, 0, +23, and +40 $^{\circ}$C, relatively. Such temperature dependence of D is well obeys to Arrhenius equation, activation energy being equal to 35 kJ·mole^{-1}.

Reference:
1. Russian Patent No. RU 2198137, 26.04.02.

Electric double layer capacitor
with acidic polymer hydrogel electrolyte

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Many studies on polymer gel electrolytes have been made for use in electric double layer capacitors (EDLCs). Previously, we prepared a new acidic polymer hydrogel electrolyte with high ionic conductivity, ca. 0.2 S cm^{-1} at 25°C, from 1 M H_2SO_4 aqueous solution, poly(vinyl alcohol) (PVA) and glutaraldehyde (GA) aqueous solution. However, from the practical viewpoint, it is essential that the polymer hydrogel electrolyte is prepared from H_2SO_4 aqueous solution of much higher concentration. Therefore, in this study, we tried to prepare the polymer hydrogel electrolyte from 4 M H_2SO_4 aqueous solution, PVA and GA aqueous solution. As a result, the polymer hydrogel electrolyte containing 4 M H_2SO_4 aqueous solution could be successfully obtained as homogeneous and transparent self-standing membrane under an adequate condition. The electrolyte exhibited higher ionic conductivity, ca. 0.6 S cm^{-1} at 25°C, than the previous one containing 1 M H_2SO_4 aqueous solution. An EDLC was assembled using the electrolyte membrane and two activated carbon electrodes. As can be seen from charge-discharge curves in Fig. 1, the cell with the electrolyte prepared in this study worked successfully as an EDLC, and its capacitance was higher than that for the previous one.
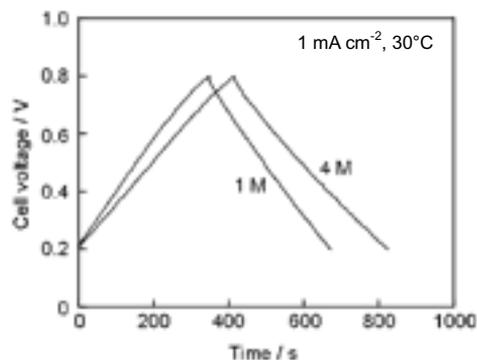
Fig. 1   Charge-discharge curves of EDLC cells with the polymer hydrogel electrolytes containing 4 M and 1 M H_2SO_4 aqueous

Capacitance and Pore Resistance Distribution Within Carbon Supported Ruthenium-Oxide Thin Porous Layers

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Carbon supported ruthenium-oxide composite pretends to be an excellent supercapacitive material, since its high capacitance is represented as the sum of double-layer capacitance of high surface area carbon blacks and oxide pseudocapacitance [1-3]. Composite capacitive performance and charging/discharging behavior strongly depends on morphology and physicochemical properties of composite itself, but also of carbon black and oxide as its constituents. In this work, the capacitive characteristics of carbon/RuO_2 composites, prepared by the impregnation of Black Pearls 2000® (BP) and Vulcan® XC-72R (XC) carbon blacks with oxide colloidal dispersion obtained by forced hydrolysis of Ru chloride, were investigated by electrochemical impedance spectroscopy (EIS). The ageing of oxide sol and oxide solid phase concentration strongly influence the composite capacitive response.
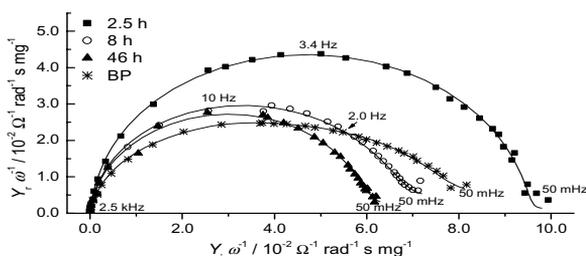
Fig. 1. Admitance complex plane plots of BP/RuO₂ composites (!,–,7), prepared from the sols of indicated ageings, and of BP ( ). EEC simulations are given by lines.

Fig. 1 shows the admitance complex plane plots registered for BP/RuO_2 composites, which are prepared from differently aged sols, and for BP support itself. The capacitive loops are seen as overlapped semicircles, which indicates capacitance distribution within the porous composite layer according to de Levie transmission line model [2]. The data of equivalent electrical circuits are represented by lines in Fig. 1. The distribution of capacitance and pore resistance within composite layer, obtained by simulation of EIS data, showed the absence of the impregnation of inner BP surface (within porous BP grains) if the sols of longer ageings are used.

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Performance improvement of LiCoO$_2$ paste electrodes for all solid state lithium ion microbattery

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A thick film cathode has been fabricated by the screen-printing technique using the LiCoO$_2$ paste to improve the discharge capacity in all solid state lithium ion micro-batteries. The LiCoO$_2$ thick film (about 6 μm) was obtained by screen printing using the ethyl cellulose based LiCoO$_2$ paste. Since the adhesion force between printed cathode and substrate was very weak, however, the delaminating was observed during sputtering of LIPON electrolyte on the cathode. In order to enhance the adhesion force, the small amount of epoxy was added in the ethyl cellulose based LiCoO$_2$ paste. The electrical conductance of the printed cathode much increased by coating LiCoO$_2$ powders with pyrolized carbon of resorcinol and the ion conductance was improved via adding lithium ion conducting glass. The printed cathode developed in this work showed the typical discharge curve of LiCoO$_2$ cathode with the high discharge capacity. The average and maximum values of surface roughness of printed LiCoO$_2$ films reduced effectively from 0.8 to 0.49 and from 14.3 to 5.46 μm, respectively, via controlling the composition of LiCoO$_2$ paste.

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A better way to improve the electrochemical performance of the Li-secondary battery with $LiMn_2O_4$ cathode

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A simpler method to improve the electrochemical properties of Li-secondary batteries with $LiMn_2O_4$ cathode is suggested. By investigating the electrochemical properties of the batteries produced by different routes of adding ZrO_2, we found that the presence of the ZrO_2 in the electrolyte also improved the performance of the Li-batteries, suggesting the possibility of simple mixing of ZrO_2 in the electrolyte to achieve enhanced electrochemical properties rather than coating the cathode with ZrO_2. In this study, $LiMn_2O_4$ was produced using a sol-gel method followed by heat treatments in oxygen atmosphere. As a conventional method to produce cathodes, 2 wt % ZrO_2 was mixed in the slurry before cast to examine the effect of ZrO_2. We also fabricated the cells containing various amounts of ZrO_2 suspended in the electrolyte (EC:DMC = 1:1 with 1M $LiPF_6$) to compare with celles with the $LiMn_2O_4$ cathode coated with ZrO_2. Charge-discharge experiments showed that the ZrO_2 added cathode decreased its initial capacity while it tended to be good capacity retention. On the other hand, certain amounts of ZrO_2 mixing in the electrolyte enhanced capacity retention without decreasing initial capacity. Based on these findings, detailed mechanism of the role of ZrO_2 on the electrochemical properteis of the Li-batteries with $LiMn_2O_4$ cathode is discussed in this paper.

Preparation of P (AN-MMA) Microporous Gel Electrolyte for Li-ion Batteries

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Gel polymer electrolyte (GPE) has been attractive for developing plastic Li-ion batteries. Owing to its unique hybrid network structure, its possess simultaneously both the diffusive transport properties of liquid electrolyte and cohesive properties of solid electrolyte. The lithium batteries based on a lithium metal anode and GPE have high ionic conductivity and free of leakage. The energy density, reliability and safety of the batteries have been much more improved than that the performance of the conventional Li-ion batteries based on carbonaceous anodes and liquid electrolytes

In this study, both in-situ nano SiO_2 composition and phase inversion process were used to prepare poly (acrylonitrile-methyl methacrylate) based microporous gel electrolyte for Li-ion batteries. The poly (acrylonitrile-methyl methacrylate (P (AMMA)) was synthesized by suspension polymerization and was dissolved into N, N-dimethylformamide (DMF) to form a uniformity solution, then tetraethyl orthosilicate (TEOS) was added into the solution according to weight ratio of copolymer/SiO2 = 85/15 and stirred for 6 h. TEOS was hydrolyzed by catalysis of alkali ammonia solution to form SiO2. The solution was cast onto a glass plate using a doctor blade, and exposed to humidified atmosphere produced by ultrasonic humidifier, followed by washing, rinsing and drying, successively. The gel electrolyte was obtained by putting the P (AMMA) microporous membrane in a liquid electrolyte for 30 min. The gelled microporous membrane sucked with 755 wt% of liquid electrolyte vs. the dried membrane. It had a prosirity of 70 %, about 1~5um of pores and presented an ionic conductivity of 2.52×10^{-3} S/cm at room temperature. Electrochemical stability window of the porous polymer electrolyte was determined by running a linear sweep Voltammetry. The decomposition voltage of the polymer electrolyte exceeds 4.5V versus Li, indicating that the addition of nano silica improves electrochemical stability of gel polymer electrolytes. The coin test battery with the microporous gel electrolyte showed a good cycling performance. The discharge capacity retention was above 87% at 0.1C rate at the 45th cycle.
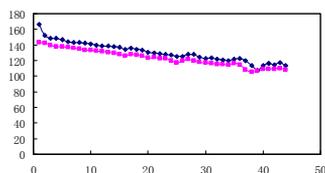
Fig 1 Cycling performance of LiCoO2/C test cell with P(AN-MMA)-based gel electrolyte

Ionic Conductivity in Acrylate Based Polymer Gel Electrolytes

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New polymer electrolytes with poly(ethyl methacrylate) PEMA and poly(2-ethoxyethyl methacrylate) PEOEMA with immobilised solution of $LiClO_4$ in propylene carbonate (PC) were prepared by direct UV initiated radical polymerisation. Prepared samples exhibit long-term stable mechanical and chemical properties. Our work in based on previously reported PMMA-based polymer electrolytes [1-3].

Influence of monomer composition, salt concentration, level of the polymer cross-linkage and the salt-solvent ratio on the electrolyte conductivity were investigated [4]. Temperature dependent conductivity measurements showed, that both PEMA and PEOEMA electrolytes exhibit suitable conductivity above -20 °C. The composition of the material was fluently optimised and the best samples exhibited high ionic conductivity up to ca. 0.23 mS/cm at 20 °C. Significant possitive effect of the polymer cross-linkage on conductivity was observed in PEMA-PC electrolytes [4]. Voltammetrical measurements showed the accessible potential window over 4 V. Recently we attempt to immobilise other solvents like dimethyl carbonate.
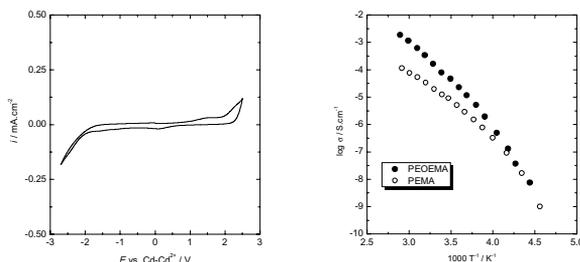
Fig. 1 (left) - Cyclic voltammogram of PEOEMA-PC-$LiClO_4$ on the glassy carbon.
Fig. 2 (right) - Arrhenius plot of the specific conductivity of PEOEMA-PC-$LiClO_4$ (41.2/37.5/21.3 mol. %) and PEMA-PC-$LiClO_4$ (58.1/38.6/3.3 mol. %) electrolyte.

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Preparation and Electrochemical Properties of Chemically Synthesized Polyindole

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Polyindole(PI) is an electroactive polymer, which can be usually obtained by electrochemical oxidation of indole in various electrolytes and chemical polymerization by oxidants like $FeCl_3$ and $CuCl_2$. The doping and dedoping of PI are possible by proton, similar to the case of polyaniline(PANI). This material can be used as electrochromic material, proton conductor, and sensor material. Especially, it has been used as electrode materials in proton battery due to the advantage that the redox window of PI is wider than that of PANI. In this work, we synthesized the PI by chemical oxidation polymerization of indole monomer in solutions of $FeCl_3$ dissolved $CHCl_3+H_2O$ mixture. The polymerization of PI was confirmed by FT-IR range from 4000 to 400 cm^{-1}. The dc conductivity was measured using a four-probe method. Brucker ESP300 spectrometer (X-band) was used to obtain the ESR spectra. We have measured the electrochemical properties of the unit cell, which was composed of PI based cathode, lithium metal anode, the glass filter separator, and EC:DMC:$LiPF_6$ (1:1v/v, 1M) as electrolyte solution. The cathode was prepared from the PI, poly(tetr afluoroethylene) binder, and carbon black conductor powder (Super P, MMM Carbon Co.) (6:1:3 in weight). These were sequentially accumulated like a sandwich by using a test cell holder in a dry box. The cells were tested using a galvanostatic charge/discharge cycler in the cut-off voltage range from 2.0 to 4.0V with constant current density of 0.1mA/cm^2. The specific discharge capacity value of these compositions was saturated after 10th cycle as ~58mAh/g.

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An investigation of structural changes of silicon during lithiation and de-lithiation by using raman spectroscopy

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The structural changes during lithiation and de-lithiation of Si thin film electrode have been investigated by using Raman spectroscopy. Two different Si samples were prepared by rf-sputtering and ion beam assisted deposition (IBAD) methods. The Raman spectrum obtained from as-deposited IBAD silicon thin film shows broad peak ranging from $450\sim500 cm^{-1}$, indicating a typical amorphous structure. On the other hand, rf-sputtered Si thin film is speculated to consist of nano-sized Si crystallites dispersed in amorphous phase from sharp Raman peak around $490 cm^{-1}$. The spectral studies in complement with morphological analysis during lithiation and de-lithiation imply that amorphous silicon thin film undergoes abrupt structural transition, resulting in excessive volume expansion and contraction. The distinct potential plateaus during lithiation and de-lithiation clearly confirms the structural phase transformation in amorphous Si thin film. On the contrary, thin film consisting of nano-sized Si crystallite shows mild structural change. From the experiment results, it is concluded that initial structure of Si plays a key role in determining the cycle life of the Si thin film electrode.

Sol-gel Synthesis and Electrochemical Behaviour of 5V $LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_4$ for use as cathode material for lithium rechargeable batteries

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$LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_4$ has been synthesized using sol-gel technique involving different chelating agents viz., acetic acid, oxalic acid and maleic acid. Physical characterization of the synthesized powder were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), thermo gravimetric and differential thermal analysis (TG/DTA). The XRD patterns reveal crystalline single-phase spinel product, which is in good agreement with JCPDS Card (35-782). SEM photographs indicate good agglomeration. Electrochemical studies have been carried out using the synthesized powder as cathode material in a 2032 type coin cell configuration. The anode used was lithium foil and the cells were cycled in the voltage range 3 to 5V in a non-aqueous electrolyte solution. Results indicate that a capacity of 110 mAh/g has been obtained in the case of oxalic acid as a chelating agent and remains constant even after 15 cycles.

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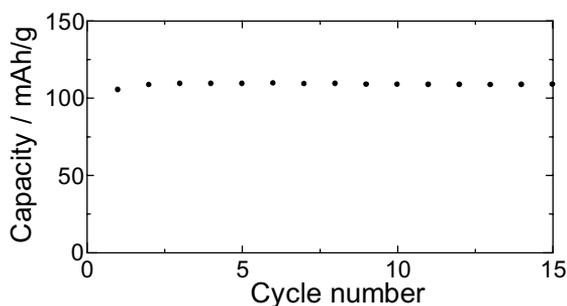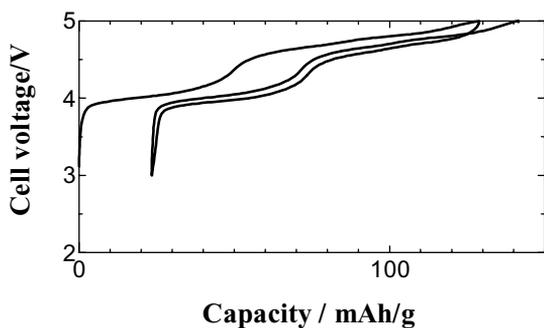
Alkaline cation intercalation into graphite used as a conducting material in nickel electrode of aqueous secondary batteries

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The discharge voltage profile of aqueous secondary batteries, such as nickel-cadmium and nickel-hydrogen with a metal hydride negative electrode consists of a voltage plateau at approximately 1.2 V mainly involving the β-$Ni(OH)_2$ /β-NiOOH redox couple corresponding to the useful operating voltage of these batteries. Moreover, these batteries are known to frequently show a discharge plateau at about 0.8 V. This phenomenon has already been reported as the second low voltage plateau [1] and is likely to be related to the positive electrode behavior.

In order to clarify the origin of the second low voltage plateau, we first reviewed the papers on this phenomenon and noticed that the effect of the conducting materials added to the Ni electrodes such as graphite. We found that the secondary low voltage plateau appeared only in the Ni electrode containing graphite as the conducting material. The discharge capacity of second low voltage plateau depends on the quantity of graphite added in Ni electrode and its maximum capacity is about 200 mAh/g-graphite. From the ^7Li-NMR spectra of charged or discharged Ni electrode containing graphite, it was found that Li^+ ions, i.e., also K^+ ions remaining in the Ni electrode intercalate into graphite in contact with NiOOH during the discharging process. Although the K^+ direct intercalation from an aqueous solution into graphite is hard to occur, the K^+ intercalation from NiOOH into graphite coexisting with NiOOH may be possible, where K^+ seems to be dissolved in solid electrolyte like NiOOH. This situation is similar to the case of Li^+ insertion into graphite during the charging process of Li^+ batteries, where Li^+ is dissolved in organic electrolytic solutions. K^+ and Li^+ intercalation into graphite may be the cause of the second low voltage plateau[2].

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A Novel Surface Modification Method on Hydrogen Storage Alloy of Ni/MH Batteries

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It is very important to develop electric vehicles for protecting environment, saving energy and improving energy structure. With enhancement of consciousness of environment protection and increasing exhaustion of oil resources, countries and groups all over the world have draw up development projects of electric vehicles (EV) and hybrid electric vehicles (HEV). However, the final acceptance of electric vehicles will depend strongly on the electrochemical performances of the battery and on its acquisition price and maintenance costs. Ni/MH is presently the most promising battery system for electric vehicles in the short and mid-term, which has many advantages such as high specific energy, high specific power, safety and no poisonous elements.

The performance of Ni/MH battery closely depends on the characteristic of negative MH electrode, and the active material of MH electrode is commonly the hydrogen storage alloy. Therefore, the electrochemical performance of alloy greatly affects battery properties. In present study, in order to improve the performances of the hydrogen storage alloy and to optimize the treating process, a new method of surface modification on the hydrogen storage alloy is studied. The hydrogen storage alloy is treated in $CuCl_2$ solution with HF acid as a catalyst. The optimal condition for the reaction is investigated, and the mechanism of this surface modification is probed. The modified alloys show improved electrochemical performance such as superior high rate discharge-ability, better charge acceptance ability, and longer cycle life, compared with unmodified one. EIS results reveal decreased contact resistances and charge transfer resistances of modified alloys, which indicates the high electronic conductivity and electrochemical activity of alloy after modification. The surface modification method employed in our study has many advantages such as low cost and simple process, and points to an effective way of improving electrochemical performances for hydrogen storage alloys.

A microcalorimetric investigation of pulse charging Ni/MH batteries under high rates

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Microcalorimetric technique was adopted to investigate the effects of pulse charge on the heat evolved from the cylindrical 1.3-Ah Ni/MH Ni/MH batteries by comparison with the conventional galvanostatic charge. The battery charged by pulse current exhibits a slower rise in heat generation rate at the same charge rate.
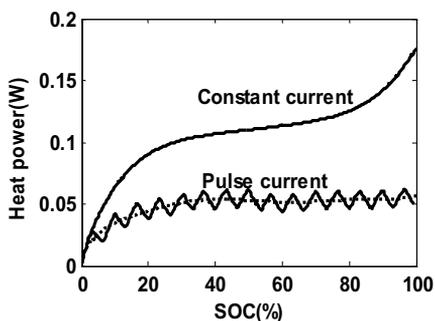
Fig. 1 Heat generation rate at 2C charge   Fig. 2 Heat generation rate at 3C charge
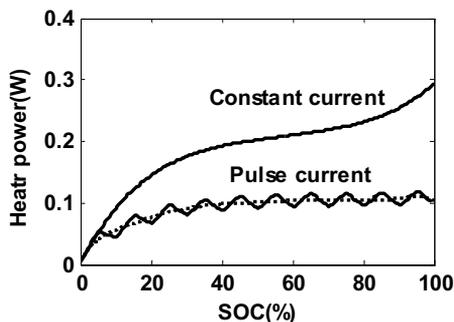
All the experimental was carried out on the Tian-Calvet microcalorimeter. Fig.1 and Fig.2 compared the differences of heat generation rate between the pulse charge and galvanostatic charge. At the end of charge, the generated heat at the galvanostatic charge attains 0.3W at 3C rate charge and 0.17W at 2C rate charge ,respectively ,while the values at pulse charge are only 0.05W at 2C rate charge and 0.1W at 3C rate charge respectively, namely, the generated heat drops about 66% .Furthermore, the generation rate of heat rises more quickly at the galvanostatic charge, while the rise in heat generation rate holds to be rather even at the pulse charge, which is indicated from the plateaus of heat generation rate in the figures. The plateaus extending from 10% SOC to 100% SOC indicate that heat evolution is rather uniform under all cases in the pulse charge regime.

Modeling of current and temperature distribution in a lithium-polymer battery

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The lithium-polymer battery is a preferred candidate as a power source for hybrid electric vehicle (HEV) and electric vehicle (EV) due to its outstanding characteristics such as high energy density, high voltage, low self-discharge rate, and good stability among others. However, much larger lithium-polymer batteries than those available in the market for consumer electronics are required for HEV and EV applications. Because the primary challenge in designing larger lithium-polymer batteries is safety, thermal stability problems must be overcome. The main concern with the thermal behavior of lithium-polymer battery is the possible significant temperature increase during high power extraction, which may cause battery degradation and thermal runaway. Thermal modeling can play a vital role to maintain the operating temperature and temperature uniformity of lithium-polymer battery within a suitable range.

In this work, a two-dimensional modeling is performed to calculate the potential and current density distribution on the electrodes of a lithium-polymer battery comprising a $Li[NiCoMn]O_2$ cathode, a graphite anode, and a plasticized electrolyte. The modeling of the potential and current density distribution on the electrodes is validated by the comparison between experimental and modeling discharge curves obtained at room temperature with various discharge rates from 1C to 10C. Then, the thermal modeling of the lithium-polymer battery is carried out, which accounts for the ohmic heating and the heat generated due to charge transfer at the electrode/electrolyte interface. The heat generation rate is computed by using the calculated results of the modeling of potential and current density distribution.

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Batteries and Supercapacitors

Symposium 1 - Poster

Batteries and Supercapacitors

Electrochemical properties of the carbon-coated and doped LiFePO$_4$

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In recent years, the demand for developing new cathode materials for high performance lithium ion batteries has increased much. Among them lithium iron phosphate is known as a promising candidate for low-cost lithium batteries due to its moderate capacity (170 mAh/g) and excellent safety. However, its low diffusivity and poor electrical conductivity lead to poor electrochemical performance. Much effort has been made to improve these inferior properties since the first report from Goodenough et al. [1-3]. In order to circumvent the low electronic conductivity of the lithium iron phosphate, conductive carbon was incorporated into the LiFePO$_4$ and also doped the LiFePO$_4$ with equi- or supervalent elements. The samples LiFe$_{1-x}$M$_x$PO$_4$/C (M=Mg, Cr, and Zr, x=0~0.05) were prepared from Li$_2$CO$_3$, FeC$_2$O$_4 \cdot$H$_2$O, (NH$_4$)$_2$HPO$_4$, doping agent, and carbon by ball milling [4], followed by calcination at 600~800°C. X-ray diffraction analysis and scanning electron microscopy observations revealed fine crystalline LiFe$_{1-x}$M$_x$PO$_4$/C particles. The electrochemical performance of the LiFe$_{1-x}$M$_x$PO$_4$/C was tested under various conditions. Results showed that the LiFe$_{1-x}$M$_x$PO$_4$/C showed higher specific capacity and better capacity retention compared to the bare LiFePO$_4$. The improved capacity retention during cycle tests was attributed to the reduced LiFePO$_4$ particle size and enhanced electrical conductivity by carbon-coating and doping.

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Novel polymer electrolytes based on poly(epichlorohydrin-co-ethylene-oxide)

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Since Wright *et al*. first reported the ionic conduction of poly(ethylene oxide) (PEO), solid polymer electrolytes (SPEs) have been intensely studied because of their potential application in solid-state primary and secondary batteries and other electrochemical devices [1- 3].

In this presentation the results of the preliminary studies of a novel electrolyte based on poly(epichlorohydrin-co-ethylene-oxide) $(-(CH_2-CH(CH_2Cl)-O-CH_2-CH_2-O)-$ and lithium salts, are described. Electrolytes compositions were represented as $p(EEO)_n LiX$ and produced with lithium salt compositions of n between ∞ and 0.5 (where *n* indicates the number of epichlorohydrin-co-ethylene-oxide repeat units per mole of Li^+ ions). Compositions were prepared by co-dissolution of the guest salt and host polymer in tetrahydrofuran. The solvent casting technique was used to prepare thin, free-standing films. Electrolytes were characterized by conductivity measurements, cyclic voltammetry at a gold microelectrode and thermal analysis.

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Symposium 1 - Poster

Batteries and Supercapacitors

Electrochemical Properties of Carbon Black Electrodes

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This work is dedicated to the memory of Professor Aleksandar Despić

Application of carbon black, for battery and fuel cell electrodes as well as in electrochemical supercapacitors, boosted scientific interest in their electrochemical properties [1,2]. In this work, the morphology and capacitive properties of the electrodes, made of commercial carbon blacks, Black Pearls 2000® (BP) and Vulcan® XC-72 R, (XC) were investigated by scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrodes were examined in the form of a thin layer applied from water suspensions of BP and XC onto Au disk.
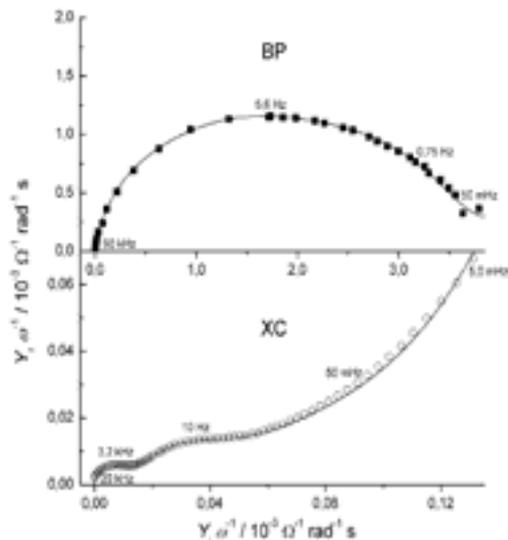
Fig. 1. Complex plane admittance plots for BP and XC carbon black electrodes, obtained at $0.55\ V_{SCE}$ in $0.50\ mol\ dm^{-3}\ H_2SO_4$. Simulations by equivalent circuits are represented by lines.

As expected, voltammetric charges were found to depend on the sweep rate, *v*. Dependence of total charge as well as overall capacitance on the sweep rate is commonly explained by the existence of less accessible surface in the porous electrodes [3]. Complex plane admittance plots for prepared carbon black electrodes are shown in Fig. 1. Overlapped capacitive loops are seen for both BP and XC electrodes. The plot for XC electrode indicates the appearance of a charge transfer resistance at low frequencies. EIS data were fitted by de Levie model of transmission line equivalent electrical circuit [2]. Structure of applied equivalent circuits, as well as capacitance and resistance values obtained by simulations of EIS data enabled estimation of capacitance and resistance profile throughout carbon black porous electrodes. The results of EIS investigation are correlated with the results obtained by SEM and CV measurements.

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Glycine-nitrate Method of Synthesis of $Li_{1+x}Cr_yMn_{2-x-y}O_4$ Spinels

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The largest improvement in preventing capacity fade of lithium manganate spinels, as potential cathode materials in lithium batteries, was achieved by substitution of some manganese by other metal cations. Chromium for manganese substitution gives one of the highest performance increases [1]. Doubly substituted spinels in which lithium ion as the second substitutional cation occupy not only tetrahedral but also octahedral crystallographic positions show even better charge-discharge characteristics [2]. These complex spinels are usually prepared by time and energy consuming solid state reaction.

In this work we applied rapid and simple glycine-nitrate method to synthesize complex $Li_{1+x}Cr_yMn_{2-x-y}O_4$ spinel compounds. This method we already used for preparation of lithium manganates [3,4]. Firstly metal nitrates and glycine were dissolved in water. The solution is gradually heated in a covered glass beaker up to 200oC. The evaporation of water was followed by spontaneous ignition. Resulting powder was collected and additionally heated in the furnace at 800oC for 4 h. XRPD measurements and Rietveld refinement confirmed the presence of pure spinel phase. For spinel with composition $Li_{1.05}Cr_{0.10}Mn_{1.85}O_4$ no capacity fade was observed after 20 charge-discharge cycles, but initial discharge capacity was reduced to 82 mAh g-1.

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Batteries and Supercapacitors

Syntheses of LiCoO$_2$ for cathode materials of secondary batteries at low temperature by the high-frequency microwave

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The use of microwaves for solid-state synthesis is a fairly new development but promises advantages in speed and energy efficiency. Synthesized LiCoO$_2$ by the high-frequency microwave is investigated in this paper. Used the superfine Co$_3$O$_4$ powders as start material, acquired LiCoO$_2$ at 400-500℃ in 1 hours. Experimented the factor affect the process. LiCoO$_2$ has well-crystallized with the layered structure. The consequences in terms of the phase purity, crystallization, and particle sizes are described. The charging capacity is up to 185mAh/g, and both the platform charging curve and time for charging/discharging demonstrate the electrochemical activity of the microwave synthesized LiCoO$_2$.

Key words: tricobalt tetraoxygen,   fine particles,   super-high-frequency microwave

1. Introduction

LiCoO$_2$ have been studied as cathode materials in lithium secondary batteries because of their high operating voltage and energy density, large capacity, and long cycle life. Despite the highest cost among the candidate materials, LiCoO$_2$ is used most widely for its better thermal and structural stability during electrochemical operations. But LiCoO$_2$ powders are usually synthesized by solid state reactions at high temperature (HT) 800℃.

The low temperature synthesis reactions can acquire more uniform LiCoO$_2$ fine particle, it is benefit to the battery electrode materials. The high-frequency microwave (10^{9-11}GHz) can acquire the apex temperature do not surpass 500℃. Present investigation focuses on synthesizing LiCoO$_2$ at 400-500℃.

In order to realize syntheses of LiCoO$_2$ by the super-high-frequency microwave method at 400-500℃, we use superfine the superfine Co$_3$O$_4$ powders as start material.

2. Experimental

2.1 Raw material Co$_3$O$_4$ characterization.

The structure of LiCoO$_2$ is the Li+ implanting in the Co$_3$O$_4$ crystal.   However, the structure of Co$_3$O$_4$ crystal is key factor for the LiCoO$_2$ crystal. The raw material were identified by X-ray powder diffracto-metry (D/Max-Ra,Cu K_α, 40kv,40ma)Fig1. The particles size distribution was identified by the SEISHIN LMS-30. Fig2 is the SEM photography of Co$_3$O$_4$ fine particles Fig3 the SEM photography of traditional Co$_3$O$_4$ particles. The fine particles are globular; the traditional Co$_3$O$_4$ particles are rodlike. The difference is obvious. The traditional Co$_3$O$_4$ particles size distribution, D50 is about 27 μm. The Co$_3$O$_4$ fine particles size distribution D50 is 2.4 μm.   In the experiment, using the

Charge-discharge characteristics of rechargeable alkaline manganese dioxide-zinc batteries with nickel hydroxide additive

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The rechargeable alkaline manganese dioxide (RAM™) battery is an environmentally benign, low cost battery system that can be used for all applications where primary cells (e.g. alkaline-manganese dioxide and zinc-carbon) are being used. In addition, the worldwide licensed RAM™ technology has the capability to replace Ni-Cd or Ni-MH batteries, especially in applications where charge retention at higher temperature and intermittent usage are important issues. The cathode and anode formula of the RAM™ battery was significantly improved during the last few years (XL Rechargeable Alkaline Battery) [1] and a few prototypes of flat plate design were successfully developed [2].

In this work we studied the charge-discharge characteristics of cylindrical RAM™ batteries (AA type) with nickel hydroxide as cathode additive. Due to its high power density, good cycling behaviour and relatively low price, nickel hydroxide is widely used as active material of alkaline rechargeable batteries, e.g. Ni-Cd, Ni-MH and Ni-Zn batteries [3]. RAM™ batteries that were prepared with an admixture of nickel hydroxide (approx. 20 %) to manganese dioxide show two sloping steps during discharge: (i) $NiOOH$ to $Ni(OH)_2$ and (ii) MnO_2 to $MnOOH$, resulting in a benefit of higher cell voltage and discharge current compared to batteries without additive. But the gelled zinc anode needs to be properly adjusted to cathode composition, as nickel hydroxide requires an equivalent amount of zinc oxide at the negative electrode, in order to yield excellent battery performance.

Charging of these batteries has to be carried out at higher voltage (up to 1.9 V) and is done with constant voltage (CV), constant current (CC) or with a combined mode (CC-CV charging). Battery cycling can either be started with the discharge procedure (reduction of MnO_2) or a capacity-limited charging procedure (NiOOH formation). This work mainly focuses on proper balancing of cathode/anode composition as well as on developing a suitable charging procedure to improve the charge-discharge characteristics and cycling performance of RAM™ batteries containing nickel hydroxide.

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Synthesis and electrochemical polymerization of nonconductive poly(n-vinly carbazole methly ethyl ketone formaldehyde -resin)

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Recently, carbazole, based polymer systems have received considerable attention, which is amply justified in view of the unusual electrical, photoelectric, thermal and other relevant properties of these materials [1]. The electrochemical copolymerization of N-vinly carbazole(NVCz) with MEKF-R have been reported [2].

In this study synthesis of conductive NVCz and methly ethyl ketone formaldehyde-resin (MEKF-R) copolymer has been reported. Non- conductive poly (N-vinly carbazole methly ethyl ketone formaldehyde-resin) [p(NVCz/MEKF)] was synthesized via the vinyl groups by electroinduced copolymerization system in the presence of a catalytic amount of the cerium ion in a separated anode compartment [3].

Conductive p[(NVCz/MEKF-R)] was synthesized by electrochemical polymerization.The solubility of polymers was compared with homopolymer. The characterization of homopolymer and copolymer films was performed by polarization curves and cyclovoltammetric measurements, solid state conductivity measurements and spectrophotometric methods comparatively. From these measurements, ionization potentials I_p, electron affinity E_a, optical band gap E_g, peak potentials, E_p, and doping degree y, of polymer calculated. Impedance spectroscopy of monomers and polymers for electrochemical capacitors are described.A possible sheme for the conductive copolymer has been suggested.
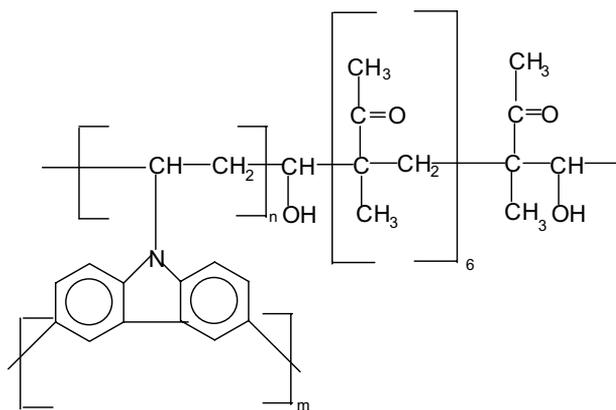
Scheme 1: Conductive p(NVCz/MEKF)

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Stability of an Ionic Liquid as Electrolyte for Lithium Ion Cells

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Poor electrochemical stability of 1-ethyl-3-methyl imidazolium cation (EMI^+) salts at cathodic potentials currently impedes lithium insertion/de-insertion in graphite. Therefore several studies have been made in an effort to identify additives that extend the cathodic limit.[1] This work investigates a microelectrode technique for the study of the effects of addition of water and bromide ions on both cathodic and anodic stability of EMI^+TFSI^- (EMITFSI).

EMITFSI was synthesised according to the procedure described in earlier publications[2], The product was dried for 12 hours at 0.2 mbar, 120 °C. For electrochemical measurements, platinum, copper and tin microelectrodes were used as the working electrode of a two-electrode cell containing the test electrolyte. A $Li_{1.5}Mn_2O_4$/carbon composite was used as the reference and counter electrode. Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV) were performed. Li salts or water were added to EMITFSI up to various concentrations and cathodic and anodic behaviour were investigated.
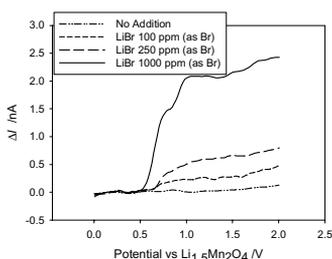
Fig. 1 Anodic LSV of EMITFSI with LiBr
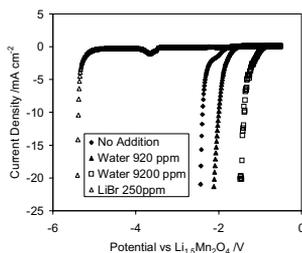
Fig. 2 Cathodic LSV of EMITFSI with LiBr or water
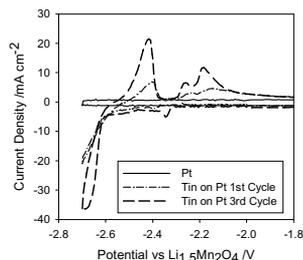
Fig. 3 CV of EMITFSI with LiTFSI on tin

With LiBr addition, anodic currents were observed above 0.5 V vs $Li_{1.5}Mn_2O_4$ (3.5 V vs Li), as shown in Fig. 1. The anodic limiting currents varied linearly with the concentration of Br^- according to a diffusion coefficient Br^- in EMITFSI of 2.4 x 10^{-7} cm²/s. Although no cathodic current can be generated from LiBr until lithium is plated, the potential corresponding to the rise in cathodic current at the stability limit of EMITFSI was shifted negative as shown in Fig. 2. The effect of added water on the cathodic stability limit is also shown in Fig. 2. It is suggested that the potential shift is due to an increase in the rate of reduction of EMI according to a water-catalysed EC' mechanism. Fig. 3 shows a preliminary result for lithium insertion into a tin electrode from this electrolyte.

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Batteries and Supercapacitors

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Effect of Ce(III) additive on crystal orientation and morphology of electrodeposited cobalt

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The structure and morphology of thick cobalt coatings on copper substrate by electrodeposits from mixture of sulfate and chloride electrolytes, either without or with addition of cerium sulfate, are investigated. From the SEM observation, the surface morphology of the electrodeposited cobalt obtained from the electrolytes with Ce(III) additive is the dependence of the amount of additive. The XRD analysis also indicates that the texture of electrodeposited cobalt was changed with the variety of the content of Ce(III) in the electrodeposited solution.
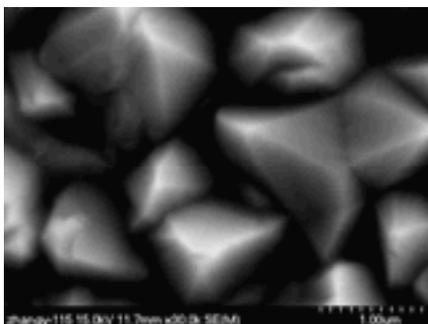
Fig.1 SEM of electrodeposited Co from 0.6M $CoSO_4$ + 0.2M $CoCl_2$ at 50°C with 5A·dm^{-2} pH=5
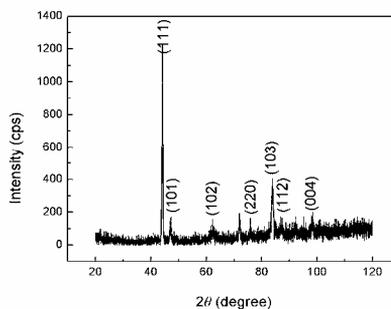
Fig.2 XRD of electrodeposited Co from 0.6M $CoSO_4$ + 0.2M $CoCl_2$ at 50°C with 5A·dm^{-2}pH=5
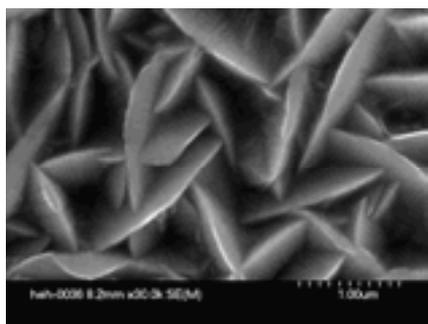
Fig.3 SEM of electrodeposited Co-Ce from 0.6M $CoSO_4$ + 0.2M $CoCl_2$ + 3.0gL^{-1} $Ce_2(SO_4)_3$ at 50°C with 5A·dm^{-2} pH=5
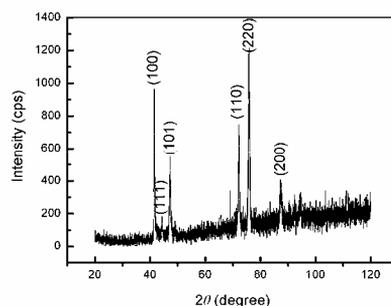
Fig.4 XRD of electrodeposited Co-Ce from 0.6M $CoSO_4$ + 0.2M $CoCl_2$ + 3.0gL^{-1} $Ce_2(SO_4)_3$ at 50°C with 5A·dm^{-2} pH=5

The research on surface behavior of pasted nickel electrodes with electrodeposited Co-Ce on the substrate

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MH/Ni battery of electro motion vehicle has become a hot point of studies. In this paper, electrodepositing Co-Ce alloys on the nickel substrate in order to enhance the MH/Ni battery's discharging performance at high rate modifies the pasted nickel electrode substrate. The results of CV, SEM, XPS, XRD indicated that (1) after nickel electrode formation, the film containing the CoOOH and $Co(OH)_2$ was formed on the substrate surface with electrodeposited Co-Ce; (2)the CoOOH on the electrodeposited Co-Ce alloys substrate increased combine intensity between substrate and active materials, electron conductivity, electricity transmission ability and performance of charging and discharging at high rate.
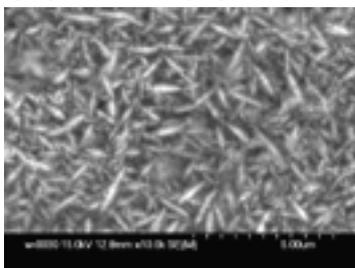
Fig.1 SEM of SOC on the Co-Ce substrate
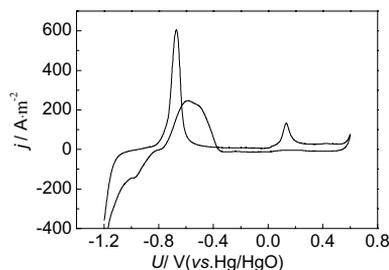
Fig.2 The CV curve of nickel substrate with electrodeposited Co-Ce
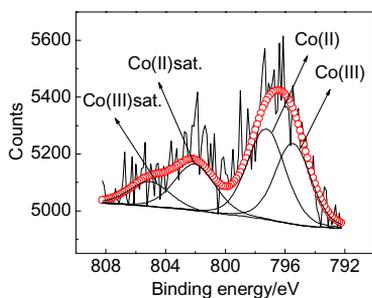
Fig.3 XP detailed spectra of $Co2p_{1/2}$ region for the SOC on the electrodeposited Co-Ce substrate
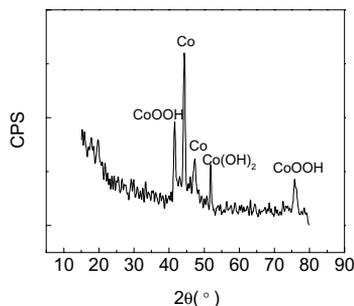
Fig.4 The XRD spectra of electrodeposited Co-Ce substrate at SOC

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Batteries and Supercapacitors

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Study of Degrade Mechanism of Alloy Negative Materials for Li-ion Batteries

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Lithium-ion batteries have been commercially used in popular portable devices, such as mobile telephone, notebook computer and digital camera. The development of modern electric devices and electric vehicle requires more compact batteries with higher energy density. New energy materials have been extensively and deeply studied [1]. Sn-based Li storage alloy materials have been focused on because of high specific gravimetric (994mAh/g) and volumetric capacity (7200mAh/cc) than that of carbon (372mAh/g, 800mAh/cc) in Li-ion batteries. However, large volume and structure changes occur associated with the reversible reaction of Li-insertion and extraction, which results in poor cycle life. It is believed that particle cracking of electrode resulting from volume expansion and phase transition is responsible for the poor cycle performance of Sn-based alloy electrode [2].

In our work, Sn thin film was deposited by magnetron sputtering technique in Cu foil. The electrochemical properties of Sn film have been investigated using a coin cell with a Li metal counter electrode in 1M $LiPF_6$/EC:DMC(1:2 volume ratio) solution.

Experimental result showed that the volume expansion of Sn film electrode during charging was around 200%, not so large compared with the theoretical calculation value, 370%. But most of the volume expansion, around 150% was resulted from the decomposition of electrolyte catalyzed by the alloy materials; only 50% could be attributed to Li insertion and phase transition. These results suggested that a novel electrolyte was necessary for the purpose of application of Sn-based alloy materials in Li-ion batteries.

[1] Besenhard J O, Yang J, Winter M. Will, J. Power Sources, 1997, 68:87-90
[2] C. Wang, A.J. Appleby, F.E. Little, *J. Power Sources* 93, (2001)174

S1·P-73

Passivation Phenomena on the Graphite Electrode/ Electrolyte Interphase in Li-ion Cells Containing Silicon Di- and Tripodands

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Passivation phenomena occurring on the graphite electrode surface during first reduction in aprotic solvents are a matter of great importance for proper functioning of lithium-ion (Li-ion) batteries, including rate capability and cyclic life. Present common solutions, based on the application of ethylene carbonate as film-forming component, are not fully satisfactory. This is primarily due to its high melting point, being an obstacle in operating the batteries in very low temperatures. Because of this, there is a tendency among battery researchers and engineers to return to propylene carbonate (PC) as electrolyte solvent. However, because of the phenomenon of solvent co-intercalation followed by its decomposition associated with destructive particle exfoliation, propylene carbonate is known to be inherently incompatible with most of the graphitic anodes. Therefore applying this solvent requires adding certain chemical species to the electrolyte, or pre-treatment of the graphite surface, both approaches aiming at preventing solvent intercalation, thus enabling creation of stable and good-quality passive layer on the graphite surface. Very recently we have found that certain peculiar silanes, belonging to the class referred to as silicon tri-podands, can serve as effective additives for propylene carbonate-based electrolytes for Li-ion cells. We proved that addition of vinyl tris-2-methoxyethoxy silane to PC prevented the graphite flake exfoliation and we attributed this phenomenon to a protective barrier formed by silane molecules self-assembled on the electrode surfaces. In the present contribution we continue this research by examining various di- and tripodands differing in the nature of functional groups, as well as the length and number of polyoxaethylene chains capable of complexing lithium cations. We consider two different strategies for studying the influence of examined Si-podands on the passivation phenomena. In the first approach the compound is added to PC-based electrolyte solution. In the second approach we pre-treat the graphite electrodes in the examined compound and then test such electrodes in electrochemical cells containing PC as electrolyte sole solvent. The passive layer formation was studied using galvanostatic charging/discharging in half-cells with metallic lithium counter electrode and cyclic voltammetry experiments. Structure of the passive layer was investigated by means of FTIR, SEM and other techniques.

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Batteries and Supercapacitors

Active Material for Li-ion Batteries and Supercapacitors Fabricated from Waste Car Tyres

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Utilization of waste car tyres is a matter of great practical importance in terms of economy and environmental impact. Recent legal regulations force more intensive works on fuller recycling of tyres, so that less amount of dangerous substances pollute the environment. In the course of processing of waste tyres large amounts of substances are produced, consisting mainly of low-crystalline carbonaceous materials with an important mineral impurities content. This low-temperature carbonizate has found application as a precursor for adsorbents and fillers. Taking into account the scale of the problem there is a need for searching for other possible industrial applications of carbon-based materials from recycling of waste tyres. Electrochemical industry has been utilizing a large variety of carbon materials for a long time, mainly as active electrode materials for various types of batteries, including lithium-ion batteries, but also as inactive additives for electrode mixtures. Very recently there has arisen a new prospective area of applications as electrode materials for the so-called supercapacitors.

The aim of the presented work is to demonstrate the possibility of applying the low-temperature carbonizate from processing of waste car tyres as active alectrode material for Li-ion batteries and supercapacitors. The starting material was obtained by pyrolysis of pre-treated tyres in rotary kiln at 500°C. After milling in a ball-mill the material was subjected to chemical purification to increase the carbon content. Finally carbonization at 1000°C in the flow of argon was applied aiming at elevating the crystallinity degree. At each step of processing the sample crystal structures were controlled by means of XRD technique and the lithium insertion/deinsertion behaviour was followed by constant current charging/discharging in the electrochemical cells, as well as other electrochemical techniques.

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Changes of Anode Material during Extended Cycling of Lithium Ion Battery

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Efficient use of energy and natural sources is becoming more and more important with the continuous growth of population. In the case of lithium ion battery, its cycling behavior is excellent and more advantageous than the other rechargeable batteries. However, its cycling is still urged to be extended to meet the requirements of electric vehicles so that its cost can be decreased much. As to the capacity fading of lithium ion batteries, there are some reports. However, most of the authors did not produce the lithium ion batteries by themselves. As a result, the real reason as to capacity fading cannot be well understood. Here we reported a lithium ion battery manufactured in our laboratory and the changes of anode material during extending cycling.
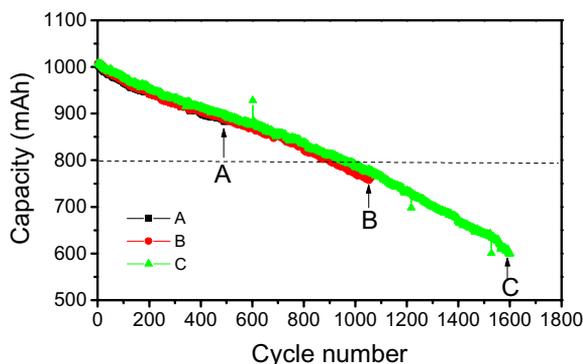
Fig. 1 Cycling behavior of three 063450 cells

Fig. 1 shows the cycling of three 063450 cells: A, B and C, which were manufactured by home made $LiCoO_2$ and graphite as cathode and anode. They were terminated at 500, 1060 and 1600 cycles, respectively. X-ray diffraction does not show much change of the graphitic structure. However, at the surface of the graphite more and more spots were produced, which were from the decomposition of electrolytes, consistent with the results from X-ray photoelectron spectroscopy. The impedance measurement also shows that the resistance increases with cycling. The reversible capacity also fades with cycling.

The above results show that the surface structure of anode materials is very important to extending cycling. A good anode material should not react with the electrolytes again after formation, which provides a next direction to achieve excellent cycling of lithium ion batteries.

Acknowledgment

Electrochemical Performance of Aqueous Rechargeable LiV_3O_8/$LiCoO_2$ cell

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Rechargeable lithium ion battery using aqueous electrolytes can overcome some disadvantages of the commercial lithium ion batteries such as high cost and safety problem, and it was regarded as the promising power for electric vehicles. $LiCoO_2$ and LiV_3O_8 have been well investigated as electrode materials in lithium ion batteries. Here we reported the electrochemical performance of an aqueous rechargeable lithium battery using LiV_3O_8 as anode, $LiCoO_2$ as cathode material and 1M $LiNO_3$ as aqueous electrolyte.

Both LiV_3O_8 and $LiCoO_2$ were synthesized in our laboratory by using solid state reaction. The charge and discharge curves of the LiV_3O_8/$LiCoO_2$ cell in aqueous electrolyte are shown in Fig.1. It can be seen that the first discharge capacity of LiV_3O_8/$LiCoO_2$ cell is 59.8 mAh/g based on the weight of the cathode, and the charge capacity 65.4 mAh/g. The coulomb efficiency in the first cycle is 91.3%. The discharge capacity in the second cycle is 54.9 mAh/g. After the second cycle the cycle performance of the cell becomes stable. The structural changes of the electrode materials were investigated, and the results show that there is much space for the improvement of the structural stability. However, it presents the promise of the aqueous rechargeable lithium batteries as practical application.

Fig.1. Charge and discharge profiles of aqueous rechargeable LiV_3O_8/$LiCoO_2$ cell.

Preparation and characterization of multiwalled carbon nanotube-supported platinum and ruthenium for methanol electrooxidation

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Multi-walled carbon nanotube-supported PtRu (PtRu/MWCNTs) catalysts were prepared by colloid method. The PtRu/XC-72 were prepared by the same method too. We compared the structures and the properties between PtRu/XC-72 and PtRu/MWCNTs catalysts. By measurements of transmission electron microscope(TEM) and X-ray photoelectron spectroscopy (XPS) on MWCNTs oxided in mixed acid, we find that most MWCNTs are isolated, nearly there is not carbon nanoparticle agglomeration and the ultrasonic makes MWCNTs orter and the port of tube are opened abundantly. At same time a high density of oxygen containing species are produced on the surface of carbon nanotubes, for example carboxyl, hydroxy and carbonyl. TEM images of catalysts show that the spherical PtRu metal particles on the PtRu/MWCNTs catalysts have a high and homogeneous dispersion and the particles are distributed in a narrow range of 3-6nm which is consistent with the value of 4.2nm obtained from the X-ray diffraction(XRD) calculation. XPS tests were used to characterize electronic properties and chemical state of catalysts. The results indicate that most of Pt and Ru exhibits oxidized phase of PtO and $RuO(OH)_2$, respectively. We find that there is interaction between PtRu and MWCNTs in PtRu/MWCNTs catalysts, and because of this interaction, the outer-shell electrons of Pt transfer to MWCNTs. XRD of catalysts show that every diffraction peaks in the power XRD patterns of PtRu/XC-72 and PtRu/MWCNTs catalysts is boardening to some extent. The phenomenon shows the presence of a significant mass-fraction of much larger crystallites, i.e.PtRu has high dispersion on those both carriers. Meanwhile we find each diffraction peaks of PtRu/MWCNTs catalysts are moved to higher value of 2θ and the parameters of crystal lattice get smaller. This phenomenon shows that Ru and Pt form alloy by a part of Ru entering the crystal structuren of Pt The electron effect of Pt produced by Ru can weaken the absorption of the middle intermedia products produced by methonal oxidation on Pt. During the oxidation of methonal, the remainder Ru existed in oxid provides enough oxygen to neighbour Pt which is available to the desorption and oxidation of the intermedia products. By a series of electrochemistry tests, the PtRu/MWCNTs catalysts display significantly higher performance than the PtRu/XC-72 catalysts for mathnol electrooxidation. The better catalytic performance of the MWCNT-supported catalysts is attributed to the high dispersion of PtRu on the MWCNTs as well as the existence of the PtRu alloy and Ru oxidation in PtRu/MWCNTs, i.e. on the effect of PtRu/MWCNTs catalysts, during the oxidation process of methonal two mechanisms foregoing stated exist at same time. According to the foregoing results of experience, we give the figures of the oxidation process of MWCNTs and the synthesis of PtRu/MWCNTs.

Structural and electrooxidation performance of Pd/CeO$_2$-γ-Al$_2$O$_3$ catalysts

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CeO$_2$ possesses the fluorite structure, which consists of a cubic close packed array of Ce cations with all tetrahedral holes occupied by oxygen. Three-way catalysts (TWC) compositions usually include up to CeO$_2$ in the component, it is also associated with thermal stabilization of the alumina support, and dispersion of the active noble metal phase. The Pd/CeO$_2$-Al$_2$O$_3$ nanocomposites were prepared by double impregnation method. Studied the influence of the amount of Ce for the structure and performance of catalysts by the test of XRD analysis, BET and XPS.XRD of catalysts show that along with the content of CeO$_2$ increasing, the diffraction peak of CeO$_2$ increase obviously. The diffraction peak of γ-Al$_2$O$_3$ become weaken, especially the (111) crystal face of γ-Al$_2$O$_3$. CeO$_2$ was added largely changed the structure of crystal face of γ-Al$_2$O$_3$. The diffraction lines are broad and the crystallite sizes calculated by using the Debye–Scherrer method are in the range of 9–25 nm. Diffraction lines due to Pd metal or any palladium oxides have not been seen. And when the percentage of Ce is 24%, catalysts has the smallest average crystal diameter it shows ceria dispersing on the carrier of γ-Al$_2$O$_3$ is good, making for Pd disperse on the suface equality. Having tested the ratio surface area and average aperture cubage for the carrier with different of the amount of Ce by BET. And when the percentage of Ce is 24%, the ratio surface area and average aperture cubage of catalysts is the most of all. The result accord with the result of XRD. And XPS of Pd$_{3d2/5}$ shows most of Pd is metal state. Concerning Ce 3d, the strong peaks at 886.4eV(v') and 904.1eV u' are typical for Ce^{3+}, while the main features of Ce^{4+} are at 883.5eV(v), 889.2eV(v''), 899.2eV(v'''), 901.6eV(u), 908.4eV(u'') and 917.4eV(u'''). And the Ce^{3+} showed a part of Ce^{4+} were deoxidized, in other word,Ce was existed on multivalence state in catalysts. And the XPS curve of O$_{1s}$ describe that the 529.2 eV peak may belong to CeO$_2$ and the 531.5 eV peak refers to Ce$_2$O$_3$. It shows that the most part of Ce are existed on oxide state. Through the electrochemistry testing in H$_2$SO$_4$ electrolyte , It shows that when the percentage of Ce is 24%, the electrocatalyse action of Pd/CeO$_2$-γ-Al$_2$O$_3$ is best of all. And the preferable electrocatalyse action owe to the CeO$_2$ have the upper decentralization on γ-Al$_2$O$_3$,and the abundant oxygen in Ceria help to oxidation the adsorption hydrogen Pd.

The synthezise and polymerization of carbazole and methyl ethyl ketone formaldehyde resin comonomer

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Among the various conducting polymers polycarbazole exhibits interesting electroactive characteristics [1]. Researches have continued for important properties of carbazole polymers by means of chemical modification or copolymerization [2]. Chemical copolymerization of pyrrole and electrochemical polymerization of carbazole in the presence of methyl ethyl ketone formaldehyde resin (MEKF-R) were reported [3,4]. In this study, carbazole (Cz)/ (MEKF-R) comonomer will be synthesized and oxidative polymerization with ceric ammonium nitrate (CAN) will be investigated. The characterization of products will be compared with homopolymer of carbazole and copolymer of Cz/MEKF-R. The concentration of Cerium (IV), MEKF-R and comonomer on polymerization will be investigated. Characterization of products will be realized with UV-visible, NMR, FT-IR and floresans spectrofotometric measurements, DSC, elementel and SEM analyses and 4.probe solid conductivity, cyclic voltammogram, impedance, photoconductivity and viscosity measurements.
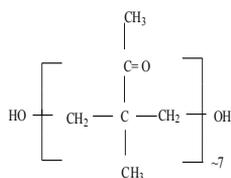
MEKF-R (Metil-Etil-Keton-Formaldehit Reçinesi)   Cz-9-Carbonyl Chloride
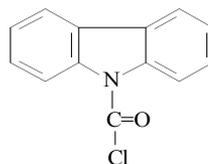
Cz-9-Carbonyl Chloride + MEKF-R _ Cz / MEKF-R (comonomer) _ Poly Cz/ MEKF-R

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Batteries and Supercapacitors
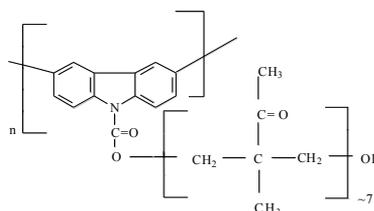
Preparation and performance of 5 V $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials by ultrasonic-assisted solution method

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In recent years, $LiNi_{0.5}Mn_{1.5}O_4$ material has received much attention for its high redox potential at around 4.7 V and shows good performance. In this paper, we synthesized single phase $LiNi_{0.5}Mn_{1.5}O_4$ material by ultrasonic-assisted solution method which has superior capacity retention upon cycling.

$LiNi_{0.5}Mn_{1.5}O_4$ powders were synthesized by reacting a stoichiometric mixture of $LiNO_3$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2$ (50% solution). The above chemicals were mixed at a predetermined molar ratio, and then in distilled water. The pH of the mixed solution was maintained 8.0. After constantly shocked at 80 ºC for 5 h in a homemade mini ultrasonic cleaner (50W, 28 kHz) to remove excess ammonia and water. The metal precipitate so formed was dried in vacuum drying oven for 12 h at 110 ºC. Then the precursors were heat treated at 850 ºC for 24 h at ambient condition, and then air-cooled to the room temperature, yielding dark powders. The complete coin cell compromises a cathode, a celgard 2300 as the separator and lithium foil anode. 1M $LiPF_6$ dissolved in a mixture of EC and DMC (1:1 by volume) was used as the electrolyte.

Discharge profiles of the firste cycle were obtained from different coin cells with $LiNi_{0.5}Mn_{1.5}O_4$ cathode as shown in Fig. 1. Both curves were obtained at about C/3 discharge and charge rate.
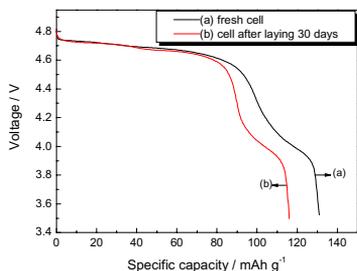
Fig.1 Discharge curve of different $LiNi_{0.5}Mn_{1.5}O_4$ cells
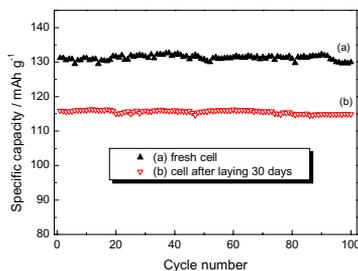
Fig.2 Cycle ability curve of different $LiNi_{0.5}Mn_{1.5}O_4$ cells

All discharge curves have two potential plateaus at 4.0 V and 4.7 V. A bonding energy of electron in e_g level of Mn and Ni ions are estimated to be 1.5-1.6 eV and 2.1 eV, respectively, with respect to that in t_{2g} level of Mn^{3+} ion. This leads to a higher discharge potential. The initial discharge capacity of fresh $LiNi_{0.5}Mn_{1.5}O_4$ cell is 131.2 mAh g^{-1}, and the cell laying 30 days also reaches 116.0 mAh g^{-1}. Fig. 2 exhibits capacity retention of the two kinds of cell. The capacity retention of the fresh and layed $LiNi_{0.5}Mn_{1.5}O_4$ cells exceed 99% after 100 cycles. Both cells have superior capacity retention upon cycling. All of above-mention indicates that ultrasonic-assisted solution method is a good method to prepare high performance $LiNi_{0.5}Mn_{1.5}O_4$ material.

The effect of different sintered temperatures on elecrochemical behavior of spinel $LiMn_2O_4$

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Lithium manganese oxide spinel $LiMn_2O_4$ is an interesting and promising cathode material for rechargeable lithium batteries. In this study, $LiMn_2O_4$ was synthesized by adipic acid-assisted sol-gel method. The main interest of this paper is to investigate the effects of different sintered temperatures on elecrochemical behavior of spinel $LiMn_2O_4$.

Manganese acetate and lithium acetate were dissolved in distilled water to give a saturated solution. A saturated aqueous solution of adipic acid was then added at 1:1 molar ratios with the total metal ions. The pH of the mixed solution was maintained 6.0, and then heated at 80°C to remove excess water. The metal adipate precipitate so formed was dried in vacuum drying oven for 12 h at 110°C. After drying, the precursors were calcined at 350°C ~900°C for 15 h in air.

The cycle ability curves for $LiMn_2O_4$ sintered at different temperatures for 15 h are presented in Fig.1.
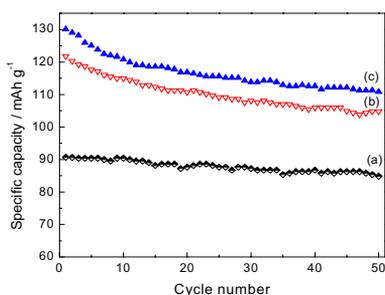
Fig.1 Cycle ability curves for $LiMn_2O_4$ calcined at different temperature in 50 cycles (a) 350°C, (b) 700°C and (c) 800°C
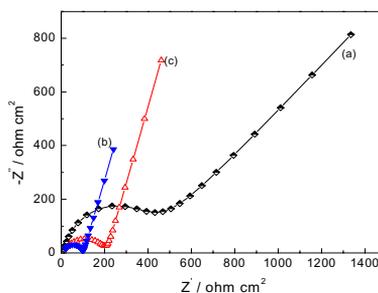
Fig. 2 Niquist plots for the $LiMn_2O_4$ samples calcined at (a) 350℃, (b) 800℃, (c) 900℃ at 100% discharge state after 20 cycles

The result show that $LiMn_2O_4$ powders calcined at higher temperatures has high discharge capacity and capacity loss, and $LiMn_2O_4$ powders calcined at lower temperatures has low discharge capacity and high capacity retention. EIS result of $LiMn_2O_4$ samples after 20 cycles with diffrient calcined temperatures at 100% discharge state (discharged to 3.3 V) is given in Fig.2. $LiMn_2O_4$ powders calcined 800 °C has the smallest R_t (electrochemical reaction impedance), which indicates that this samples have better discharge capacity; however, $LiMn_2O_4$ powders calcined 350 °C and 900 °C has the bigger R_t, which leads that these samples have small discharge capacity. It may be that $LiMn_2O_4$ powders calcined too high or low temperatures exit much lattice defect, which leads to the lattice distortion during the cycles.

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Batteries and Supercapacitors

Electrochemical Characteristics of $Ti_{0.32}Cr_{0.43}V_{0.25}$ Alloy Ball-milled with LM $Ni_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ Alloy as a New Anode Material for Ni-MH Secondary Battery

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[a] Chan-Jin Park*, [b] Jeon Choi

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In recent days, oil price maintains at a high level. The high price of oil makes the cost-effective hybrid electric vehicle (HEV), which contains an electrically charged battery pack coupled with an internal combustion engine, more attractive. Consequently, Ni-MH battery for HEV is now in great demand.

The Ti-Cr-V alloy with bcc crystal structure has been considered as a promising new anode material for Ni-MH battery on account of its excellent hydrogen storage capacity over 2 wt% and proper plateau pressure for hydrogen. The alloy, however, is hardly activated during charging due to the formation of stable oxide layer on the alloy. Therefore, the measured discharge capacity of the alloy is much smaller than the theoretical value.

To improve the surface activation of bcc-type Ti-Cr-V alloy, the alloy powder was mixed with AB_5 type alloy powder, which can be activated more easily and thus can possibly provide paths for hydrogen diffusion on the electrode surface. The mixture of the bcc-type $Ti_{0.32}Cr_{0.43}V_{0.25}$ alloy powder and the AB_5 type $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy powder was ball-milled by varying the ball-milling time and the proportion of $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy.

The discharge capacity of the electrode of $Ti_{0.32}Cr_{0.43}V_{0.25}$ alloy ball-milled with the $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy was significantly improved compared with the electrode of $Ti_{0.32}Cr_{0.43}V_{0.25}$ alloy without $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy. The greatest discharge capacity of 310 mAh g^{-1} was obtained when 20 wt% $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy had been added to the $V_{0.25}Ti_{0.32}Cr_{0.43}$ alloy and ball-milled for 20 min.
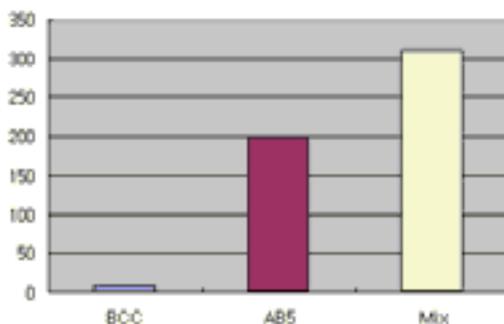

Fig. 1. Discharge capacity of the Ti-Cr-V and the AB5 alloy after ball milling

The Reasonable Fe(III) Compounds for Selective Electro-generation of Ferrate

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Ferrate, excellent super-oxidant[1,2], has been focused[3,4] recently for the appearance of super-iron battery [5]. However, complicacy of Fe(VI)/Fe(III) system[1] and OER play obstructive and harmful roles in research and the realization of secondary super-iron battery. The ferrite was made from the main component of the open-hearth dust of Inner Mongolia [6], Fe_2O_3. The electrochemical behavior of different Fe(III) compounds was investigated by the technique of powder microelectrode[7] .
The XRD profile of the roasted mixture of NaOH and Fe_2O_3, was presented in **Fig.1**. It proves that the molecular formula of the product is $NaFeO_2$. The electro-chemical results indicated that $NaFeO_2$ is the most reasonable Fe(III) compound for selective electro-generation of ferrate and Fe_2O_3 is an inert compound for the same electrochemical reaction from 293K to 333K in 12~14 mol/L NaOH solutions.
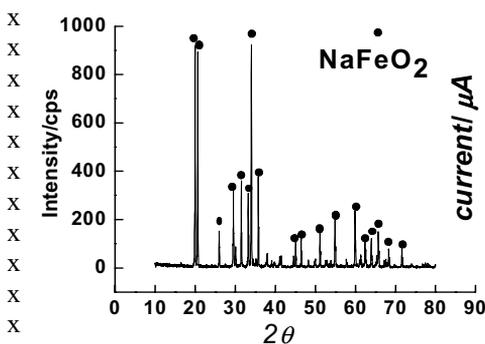
Fig. 1 The XRD results of sodium ferrite
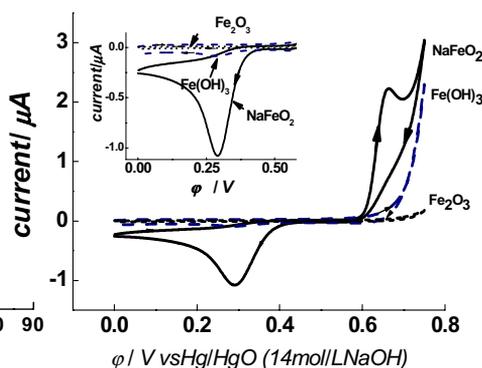
Fig. 2 The cyclic voltammetric curves of three Fe(III) compounds

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Symposium 1 - Poster

Batteries and Supercapacitors

Modified Natural Graphite Anode Materials for Lithium-ion Batteries

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Modified natural graphite is made by surface-coating and graphitizing process. The modified natural graphite is examined with a view to improve discharge capacity and coulombic efficiency on the first charge-discharge cycle. It processes superior cycleability. Modified process results in a marked improvement in electrochemical performance. These are investigated by means of X-ray power diffraction, scan electron microscopy, and measurement of electrochemical capacity. The proportion of rhombohedral crystal structure was reduced by the heat treatment process. The modified natural graphite exhibits 40 mAh/g reduction in the first irreversible capacity while the reversible capacity increased by 16 mAh/g in comparison with pristine graphite electrode. Also, it has an excellent capacity retention of about 94% after 100 cycles and about 87% after 300 cycles .

The natural graphite used in this experiment was SG18 (from BTR Energy Materials Co.). Surface modified graphite(MSG) was prepared as follows: SG18 was first dispersed in a solvent that contains the precursor of nongraphitic carbon and then the solvent was evaporated. Finally, the residue was treated at 3000℃ for 4 hours to 15 days. SEM images indicate that the surface of the modified graphite particles appears smoother than that of the SG18 particles. Some of the micrpores are filled with nongraphitic carbon.

The specific capacities of SG18 and MSG were listed in Tab.1. The modified graphite provides a very high discharge capacity of 358.7mAh/g (i.e. close to the theoretical value of 372 mAh/g based on LiC_6) and a perfect coulombic efficiency of 95.6%, the irreversible capacity is decreased to 16.7mAh/g, the irreversible capacity loss of the modified graphite electrode on the first charge-discharge process is only 4.4%, whereas the pristine graphite electrode suffers a capacity loss of 14.8%. From the first charge/discharge profiles, it is almost invisible for the plateau at about 0.75V, which is ascribed to the irreversible charge. On the other hand, the rhombohedral crystal structure has been eliminated to the maximum extent. All of them result in the improvement of the electrochemical performance of the anode.

Tab. 1 First charge/discharge test results

Sample	Discharge Capacity (mAh/g)	Charge capacity (mAh/g)	Irreversible capacity (mAh/g)	Efficiency (%)
SG18	402.4	342.7	59.7	85.2%
MSG	375.4	358.7	16.7	95.6%

The Effect of Mg Content on the Phase Structure and Electrochemical Properties of the Ml-Mg-Ni-based Hydrogen Storage Alloys

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Due to the demand for novel electrode materials with much higher hydrogen storage capacity is very urgent, the new kind R-Mg-Ni-based AB_3-type alloys with higher hydrogen storage capacity are regarded as one of promising candidates for electrochemical hydrogen storage materials. However, their cycle stability are unsatisfied. The main reason is the oxidation of La and Mg element in alkaline solution, which causes the electrode to lose activity. For improving the cycle stability of R-Mg-Ni-based hydrogen storage alloys, we used Ml instead of pure La element in A-sites and multi-component alloying in B-sites simultaneity to prepare the $Ml_{1-x}Mg_x(Ni\text{-}Co\text{-}Mn\text{-}Al)_{3.5}$ (x = 0.05, 0.10, 0.20, 0.30) alloys, and the effects of variable Mg content on the phase structure and electrochemical properties of Ml-Mg-Ni-based hydrogen storage alloys were studied in this paper. The results of XRD reveal that all the alloys consist mainly of $LaNi_3$ phase with the rhombohedral $PuNi_3$-type structure and $LaNi_5$ phase with the hexagonal $CaCu_5$-type structure. With the increasing of x, the intensity of $LaNi_3$ diffraction peaks increases gradually, the maximum capacity and low temperature dischargeability of the alloy electrodes increase first and then decrease. Moreover, when x is 0.20, the discharge capacity of the alloy electrode reaches 363 mA h/g at 293 K and 216 mA h/g at 233 K, respectively. The HRD of the alloy electrodes increases with the increasing of x. At the discharge current density I_d = 1200 mA/g, the HRD of the alloy electrodes increases from 16.2% to 43.3% with x from 0.05 to 0.30. The cycle stability of the alloy electrodes decreases gradually with the increase of Mg content.

Symposium 1 - Poster

Batteries and Supercapacitors

Investigation on the Performance of Nano-scale β-Ni(OH)$_2$ Prepared at Different Transformation pH

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Nano-scale Ni(OH)$_2$ is a new kind of batteries material. It exhibits many superior electrochemical performance, such as bigger proton diffusion coefficient and higher electrochemical reaction activity, and so on, so much interest has focused on investigation of nano-scale Ni(OH)$_2$. But a majority of researchers have laid their emphasis on the discoveries of new preparation methods, few investigation is against the systematical research on the effects of preparation conditions on the performance of nano-scale Ni(OH)$_2$, especially the electrochemical behaviour.

In this study, we have prepared a series of nano-scale Ni(OH)$_2$ under different transformation pH. The influence of transformation pH on the morphology and performance of nano-scale Ni(OH)$_2$ were investigated.

The measurement results indicate that the prepared nano-scale Ni(OH)$_2$ isβ(II)-phase, and the crystal lattice parameters of nano-scale Ni(OH)$_2$ prepared at different transformation pH is different; Transformation pH exerts a great influence on the agglomeration degree of nano-scale Ni(OH)$_2$. With the increase of transformation pH, the agglomeration of nano-scale Ni(OH)$_2$ becomes obvious. CV and EIS measurement results show that transformation pH affects the proton diffusion coefficient (D) and charge-transfer resistance (Rct) of the material, and the discharge performance of electrodes depends on both D and Rct, so the kinetics characteristics that electrodes reaction is controlled by both mass-transfer step and charge-transfer step was put forward.

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Room temperature lithium metal batteries based on elctrospun PVDF-based nanofibrous separator

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The Li-ion batteries generally employ polyolefin separators. These commercialized polyolefin separators have good mechanical properties. On the other hand, they exhibit poor compatibility with liquid electrolytes due to their hydrophobic property. It usually gives rise to resistance increases, which is responsible for the shortening of the battery lifetime and severely affect the battery performance, e.g., cycle life [1]. In order to overcome this disadvantage, it is possible to use more wettable polymer with liquid electrolytes. Electrospun PVDF-based membranes (EPMs) have been previously reported as a polymer matrix in lithium ion battery [2, 3].

In this study, we prepared EPMs for battery separators applications and mainly investigate the characteristics of interface between lithium metal and EPM separator. The Crystal structure and chain conformation of the EPMs also were investigated by differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD). Due to soften PVDF fibers in high temperature, the thermal treated EPMs can form an interconnected web structure, which greatly improve physical properties. Compared that with Celgard™ 2400 (PP separator), the cell with EPM shows good cycling performance with little capacity loss after 50 cycles.

From Fig.1, the cell with EPM showed the better cycling behaviour than that with PP separator. Structure properties of the EPMs, such as a fully interconnected open pore structure, a great deal of nano-scale fibers, enhanced the degree of PVDF swelling in polymer electrolyte. The gel phase can greatly improve interface affinity to lithium metal. Additionally, uniform pore distribution and low pore tortuosity of EPMs can be factors that suppress mechanically Li dendrites on lithium metal surface. The results of CV imply that EPMs could provide an effective approach to smoothing lithium deposition and improving battery cycle-ability.
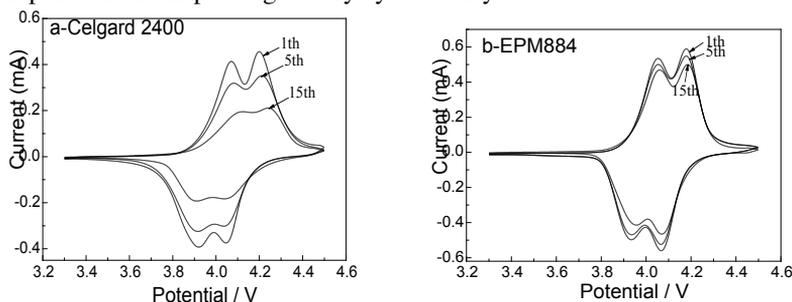

Fig.1 Cyclic voltammorgrams for the cells with (a) Celgard™ 2400 and (b) EPM884 at sweep rate 0.1 mV·s^{-1}.

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Effects of methanol contaminant in electrolyte on the performance of graphite electrodes for Li-ion batteries

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Commercial lithium-ion batteries with high energy density and good cycleability usually consist of a carbon-based negative electrode, a positive lithium metal oxide electrode, and a separator soaked with an organic electrolyte. Despite of the high level of development of the batteries, there are still unsolved problems remaining. One of them is the irreversible charge loss occurring during first charging of the carbon electrodes. It is generally accepted that this charge loss is mainly due to reductive decomposition of electrolyte on negative electrode. The resulting protective film, called solid electrolyte interphase (SEI), allows lithium-ion transfer but prevents electron transfer. The SEI formation mechanism is rather complex and not yet completely understood.

Methanol was a common impurity in the organic electrolyte. In this study, the electrochemical performance of graphite electrode cycled vs. Li in 1MLiPF$_6$–EC:DEC:DMC(1:1:1,v/v/v) electrolyte solution, containing different concentrations of methanol, was investigated by cyclic voltammetry and electrochemical impedance spectroscopy in the process of first lithiation. It has been demonstrated that methanol contaminant caused the deterioration of the electrochemical performance of graphite electrodes, and this effect is depends markedly on the concentration of methanol. Based on experimental results and analysis, a mechanism of methanol contaminant causing the deterioration of the electrochemical performance of graphite electrodes was proposed, in which methanol was reduced to lithium methoxide, deposited on the graphite electrode surface to form initial SEI at the potential near 2.0V(as shown in Fig.1). Such process resulted in ethylene carbonate excess decomposition and poor passive ability of SEI ultimately formed on the graphite electrode surface.

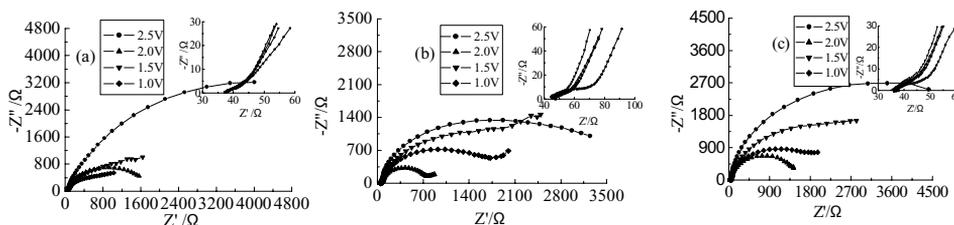Fig.1 Nyquist plots of graphite electrodes at 2.5, 2.0, 1.5 and 1.0 V in 1MLiPF$_6$-EC:DEC:DMC (1:1:1,v/v/v) electrolyte solutions. Frequency range10^5~10^{-2}Hz, concentrations of methanol: (a)0%, (b) 0.5% ,(c) 0.1%(v/v). The insets show the spectra enlarged over a 10^5Hz–10^2Hz frequency range.

Electrochemical studies of the Si-C composites as anode materials for rechargeable lithium ion batteries

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Silicon/carbon composites have so far been investigated extensively as anode materials for rechargeable lithium ion batteries because of their high specific capacity[1,2]. We succeeded to attain a Si/C composite with a high capacity and good cycle performance by pyrolysis of phenol-formaldehyde resin embedded with graphite and silicon powders.

In this study, the preparation of the Si/C composite was as follows: The phenol-formaldehyde resin (PFR) was dissolved into ethyl acetate. Silicon particles and graphite were added into the PFR solution and homogeneously mixed and the weight ratio of silicon: PFR: graphite was 5:12:5. The ethyl acetate solvent was evaporated under stirring to get a solid blend. The mixture was heated at 900 $^\circ$C in an Ar atmosphere for 2 h at a heating rate of 10 $^\circ$C min^{-1} and allowed cool down to room temperature normally. The products before sieved were further treated by high-energy mechanical milling in a sealed bowl in Ar at a rotational speed of 200 rpm for 2–10 h.

A coated electrode was prepared by mixing the composite material with PVdF binder, coated on a Cu sheet, and dried at 120 $^\circ$C for 14 h under Ar. Fig.1 shows the good cycle performance and reversible capacity of this material. The initial discharge capacity of the composite was 702 mAh·g^{-1}, the reversible capacity after 45 cycles being 525 mAh·g^{-1}.
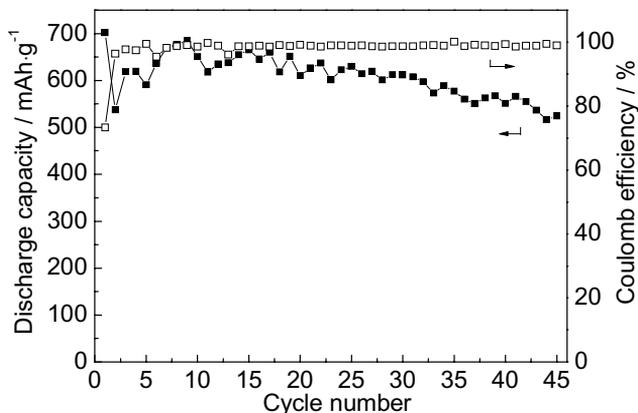
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Capacitance of the double-layer formed at the solid electrode – ionic liquid interface

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Ionic liquids (IL) have been investigated intensively due to their specific properties which makes them a good material as a electrolyte especially in Electric Double Layer Capacitors (EDLC) applications where wide electrochemical stability window is needed. Energy in EDLC's is stored in the double layer formed at electrode/electrolyte interfaces. Energy, *E* stored in EDLC strongly depends on applied potential, *V* therefore, it depends on electrochemical stability of electrolytes $E = QV^2/2$

Both aqueous and various non-aqueous liquid electrolytes as well as solid polymer electrolytes have been applied in EDLC, including ionic liquid [1]. There are only a few publications about double layer capacity measured at well defined electrode/electrolyte surface [2, 3].

The main aim of this work was to examine the differential capacity at the solid electrode|ionic liquid interface for a number of ionic liquids.

Differential double layer capacity at the electrode/ionic liquid interface (electrode: glassy carbon (GC), Pt, Au), was measured using chronoamperometry and *ac* impedance technique. Measurements were done in a two electrode system and made for 18 ionic liquid.

Dependencies of double layer on the potential were determined using *ac* impedance in a three electrode system with Ag/Ag+ electrode in dimethyl sulfoxide solution as a reference electrode.

The double layer capacity (by chronoamperometric method) at the GC/IL interface, was at the level of ca. 10-25 $\mu F/cm^2$ at potentials close to the open circuit potential, while the corresponding values for the Pt/IL and Au/IL systems were significantly lower, typically at the level of 1-8 $\mu F/cm^2$.

Evaluating double layer capacitance C_{dl} from impedance plots two equivalent circuits were taken into account. Constant phase element (CPE) exponent were usually in range 0,77 - 0,82 and shows that it is not pure capacitor-like behavior. Values determined by *ac* impedance technique are of 4-5 times higher than obtained by chronoamperometric method.

The capacity value was approximately constant within a broad potential range (of ca 3V).

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Discharge Characteristics of Polypyrrole/Silver Vanadium Oxide Composite Used for Lithium Primary Batteries

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Silver vanadium oxide (SVO), $Ag_2V_4O_{11}$, shows high gravimetric/volumetric energy densities. It also provides an electrode potential curve with multiple plateaus, which allows accurately to predict the lifetime of the battery. Therefore, SVO has generated commercial interest in the arena of medical devices, and has become the cathode of choice in lithium primary batteries used to power implantable cardioverter defibrillators (ICDs).

In an ICD, a Li/SVO cell performs most of the time at low power and occasionally delivers one or more high power pulses. It should be capable of delivering about 50 J within 5 to 10 s and in case of a continuous current drain on the order of microamperes for at least 5 years [1]. However, low utilization of SVO is typically attained, especially during pulse discharges with high rates. The internal cell resistance drastically increases with progressing discharge, resulting in a poor power capability of a Li/SVO cell.

In this work, a hybrid composite of polypyrrole (PPy)/SVO was synthesized by an oxidative polymerization of pyrrole monomer on the SVO surface in an acidic medium. Galvanostatic discharge experiments indicated that the composite electrode exhibits higher discharge capacity and better rate capability as compared with the pristine SVO electrode. The utilization study suggested that the improvement in electrochemical performance of the composite electrode is due to PPy which accommodates lithium ions and also enhances the SVO utilization.

In order to demonstrate the feasibility of the PPy/SVO composite system in an ICD, the pulse discharge characteristics were investigated at 38 ^{o}C under conditions that simulate battery operation inside an ICD [2]. The kinetic parameters which govern pulse discharge performance of the composite electrode (e.g. interfacial charge transfer resistance and chemical diffusion coefficient of lithium) were estimated as a function of depth of discharge, and compared with those parameters obtained for the pristine SVO electrode.

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Symposium 2

Electroanalysis and Sensors

Lab-on-a-Chip and Lab-on-a-Pill Technologies Providing the Functional Framework for New Biological Measurements.

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The growing need for accurate and fast methods of DNA and protein in the post-genome era has generated considerable interest in the development of new microfluidic analytical platforms, fabricated using methods adapted from the semi-conductor industry. These Lab-on-a-Chip methods often involve having a miniaturised biochip (as an analytical device), with rather larger instrumentation associated with the control of the associated sensors and of fluidics.

This talk will explore the development of new Lab-on-a-Chip platforms for DNA and cell screening, using microfluidics as a packaging technology in order to enable advances in nanoscale science to be implemented. Particular emphasis will be placed on a series of new sensor formats, including recent development in the use of optical nanoparticles as DNA sensors for rapid assessment of bacterial microbial infection, and soft-lithographic approaches to make novel electrophysiological measurements in cell chip formats.

The talk will also show how system-on-a-chip methods can also be integrated with Lab-on-a-Chip devices to create remote and distributed intelligent sensors, which can be used in a variety of diagnostic applications, including for example remote biosensing within the GI tract.

Symposium 2 - Keynote

Electroanalysis and Sensors

Symposium 2 - Keynote

Electroanalysis and Sensors

New Frontiers of Ion-Selective Electrodes

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Many new impulses into the field of ion-selective electrodes have occurred in recent years. They include a better understanding of the underlying response mechanism, which enabled one to assess complex formation constants of ionophores in polymeric sensing membranes and to determine the true selectivity of these sensors. Incidentally, these selectivities are often found to be orders of magnitude better than previously reported in the literatre. This in turn has initiated the search for the reason of the historically mediocre detection limits of these devices, and much progress has been achieved recently in the realization of ion sensors that can be used at true trace levels.

These advances have spurred further research activity. Ion-selective electrodes are now explored for the determination of trace leve concentrations in confined samples volumes. This has important implications in bioanalysis, where nanoparticle labels can be used that release ions that are detectable by potentiometry. Potentimetry is also being coupled to chemical or electrochemical accumulation processes, in analogy to stripping voltammetry, in order to achieve detection limits that surpass any known electroanalytical technique.

This talk will also touch on the development of instrumental methods to control ion-selective electrodes, which can be understood as a bridge between potentiometry and ion transfer voltammetry. Optimized electrochemical protocols can lead to sensor responses that have the same look and feel as traditional ion-selective electrodes, but the ion extraction process is controlled instrumentally. This lead to possibilities that have so far been outside the reach of potentiometric sensors, include the achievement of reversible sensors on the basis of irreversible reactions, and the controlled perturbation of the sample near the sensor membrane to gain additional information such as buffer capacity or to achieve an order of magnitude higher sensitivity compared to that dictated by the Nernstian equation.

S2·KN-3

Chemical speciation using microelectrodes

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Copper and other metals can be determined by anodic stripping voltammetry using mercury electrodes. In this process the metals are plated in metallic form and are subsequently reoxidised during the voltammetric scan. On a bare gold electrode this process is quite different, which is apparent in a large peak shift for copper and some other metals. Instead of deposition by plating, the process is based on adsorption of metal-halide species and is usually called underpotential deposition. We have investigated the process for the determination of copper and mercury in seawater and dilute hydrochloric acid using gold microwire electrodes (5 μm diameter). The experiments indicate that species with bromide and chloride control the deposition of these metals.

Using optimised conditions copper and mercury can be determined at picomolar levels in seawater. Further experiments will be reported in which effects of chemical speciation is investigated.

Symposium 2 - Keynote

Electroanalysis and Sensors

Symposium 2 - Keynote

Electroanalysis and Sensors

A microelectrode dissolved oxygen for oceanography

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A robust, low maintenance dissolved oxygen microelectrode sensor will be presented with a reliable calibration method suitable for any oxygen sensor. Primarily developed for oceanographic applications, the sensor measures the diffusion controlled current for oxygen reduction at a Pt microdisc. A potential waveform is used to recondition the electrode surface. Although the electrode roughness increases, the amperometric response is found to be very stable, Fig. 1. A calibration based on concentration and dilution was used to test the sensor. Excellent linearity, Fig. 2, was obtained for all electrodes tested and in each case, the number of apparent electrons for the reduction of oxygen was estimated. It will be shown that the dissolved oxygen concentration can also be obtained from the analytical expression for the limiting current taking into account the diffusion coefficient dependence on temperature and salinity. Errors were estimated: with fewer parameters needed, calibration leads to the lowest errors and yields a detection limit as low as 0.9 µM with a 50 µm diameter Pt disc; although dependent on several parameters the analytical approach was estimated to yield a concentration with a relative error circa 11% for the 50 µm diameter Pt disc. Overall the results obtained show that the microdisc electrodes yield remarkably stable amperometric response. Recordings of oxygen depth profiles in the ocean have been carried out.
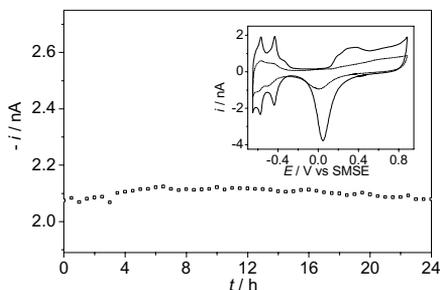
Fig. 1 Sensor response in air-saturated 0.5 M NaCl at 25 °C. Inset: voltammograms in 1 M H_2SO_4 before (…) and after (—) 24 h; v=200 mV s^{-1}. Pt microdisc 10 µm ⌀.
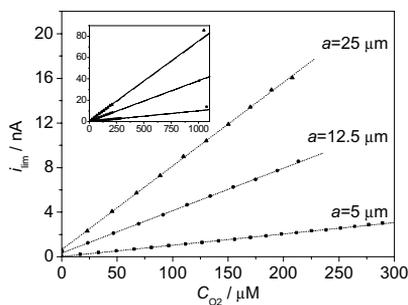
Fig. 2 Calibration curves in 0.5 M NaCl at 25 °C for different Pt microdiscs. Inset: same but including responses in oxygen saturated solutions.

Coupled enzymatic and electrochemical reactions on microstructured template surfaces investigated by scanning electrochemical microscopy (SECM)

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Templated surfaces provide an convenient way of creating spatial patterns of biocatalysts, that allow complex reaction sequences to be carried out by the close proximity of the various active regions. SECM can be used to provide spatial images of the reactivity by also to provide a more detailed analysis of the local kinetics. Our group has used templated self-assembled monolayers (SAM). They have been either produced by microcontact printing of by localized electrochemical desorption using SECM as a tool to surface modification. The templated monolayers have been further processed by covalent attachment of enzymes, by layer-by-layer deposition of polyelectrolytes into which one enzyme was integrated as a polyelectrolete. In this way the templates do not only provide the basis of lateral patterning but also allow a designed combination of crystalline inorganic supports with flexible molecular structures. Alternatively polymer microstructures with immobilized enzymes can be assembled on surfaces.

SECM has been used to monitor the passivating properties of different monolayer systems. While this may be interesting for itself, it allows to navigate an SECM probe on patterns that were created by other techniques such as microcontact printing. A subsequent application of a SECM-based surface modification technique allows to further modify such layers and thus provides a convenient flexible way of their further modification.

Recently we succeeded in quantitatively modelling the SECM response over such structures using the boundary element method (BEM). Steady-state systems of arbitrary 3D geometries can be treated if the boundary conditions can be described as linear functions of the local concentration - a condition that is full-filled for most SECM experiments.

Application of the above concepts can be seen in a number of chemically completely different systems: (i) Similar to artificial structures containing enzymes, also site directed cell adhesion can be directed using microelectrochemical methods to lift the cytophobic character of oligo (ethylene glycol)-terminated SAM and allows for the site directed sequential introduction of different cell populations. (ii) Oxide layers on titanium-based alloys show different passivating properties depending on the composition, crystallographic orientation, and the redox species by which they are probed. (iii) Imaging local enzymes acivity can be used to devise readout procedures for enzyme labels in biochips. It may also serve a signal generation process to read out high-density electrophoresis gels, in particular because this may be compared to sensitive but not selective reading after silver staining.

Symposium 2 - Keynote

Electroanalysis and Sensors

A Novel Electrochemical Viral Sensor for the Detection of Pathogenic and Polluting Bacteria

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We describe a new electrochemical sensor for the rapid identification and quantification of bacteria, based on detection by bacteriophage (phage), a virus that recognizes, infects, and lyses only one bacterial species among mixed populations. The phage acts both as a specific biological recognition element and a lytic agent, releasing intracellular bacterial enzymes. Enzymatic activity is measured amperometrically by on-line monitoring of a culture medium mixture containing substrate, placed in a disposable, screen-printed, electrochemical cell connected to an eight-channel-based potentiostat. For the specific detection of *E. coli*, we used the highly specific λ-phage/β-galactosidase system. The product of enzymatic activity, *p*-aminophenol, is oxidized at the working electrode with an applied potential of 220 mV vs the reference electrode Ag/AgCl, at a sensitivity of at least 10^5 cells/ml. Pre-concentration and preincubation enabled the detection of a single bacterial cell in 100 mL within 6 hours [1]. We used the same approach to detect other bacteria, using *Bacillus cereus*/ phage 7064-B1 as a model system for *B. anthracis* (causative agent of anthrax) and *Mycobacterium smegmatis/*phage D29 as a model system for *M. tuberculosis* (causative agent of tuberculosis). Phage specificity enabled the detection of all target bacteria even in the presence of other microorganisms at high concentrations. We also used a genetically engineered bacteriophage system for which we constructed a phagemid-a bacteriophage containing a bacterial plasmid bearing a gene encoding for the enzyme alkaline phosphatase. This modification increased the sensitivity of the *E. coli* sensor by ten folds and shortened the measuring time [2].

To conclude, the combination of amperometric detection of intrinsic enzymes as cell markers and phage-specific identification of bacteria provides a powerful tool for the rapid and highly specific sensitive detection of bacterial strains at low cost.

Adhesion and proliferation of neuronal cells on electrosynthesized polymers. Development of a biosensor for odour detection.

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Symposium 2: Electroanalysis and Sensors

In recent years, there has been a growing interest in polymers as a tool for biological and biomedical applications. Indeed, many polymer films, which can grow on an electrode surface by electrochemical polymerization, are interesting due to their biocompatibility. For example, we show in this study that olfactory cells can grow on polymer films previously coated on silicon or Fluorin doped Tin Oxide surfaces.

The first aim of this work was to determine which polymers could be useful for cell culture. Indeed, to be useful a polymer has to be biocompatible and to allow cells to adhere and proliferate. Thus, we have synthesized different biocompatible polymers (polyethyleneimine, polypropyleneimine, poly(p-phenylenediamine) and polypyrrole) on silicon or FTO surfaces using electrochemistry.

Then, we cultivated neuronal cells of rat and tested their adhesion and proliferation by putting olfactory cells in contact with conducting surfaces, previously coated with a polymer, in a culture medium. Then we let the olfactory cells adhere. During their growth we observed the evolution of their morphology using a confocal microscope. This qualitative observation allowed us to conclude that their development was normal. More the adhesion and the proliferation rates were calculated for each polymer to quantify and compare the ability of the cells to adhere and proliferate on the different polymers. These rates indicated that polyethyleneimine and polypropyleneimine are the most appropriate polymers to cultivate olfactory cells [1]. So we proved that a surface coated with PEI or PPI is a good substrate for the culture of olfactory cells.

Since we have already developed biosensors using polymer films coated on conducting surfaces and since we showed that the culture of olfactory cells is possible on electrosynthesized polymers, we have then elaborated a microsystem using these polymers as cell culture supports [2]. Since each olfactory cell is able to recognize a specific odour, this microsystem can be used as a sensor of odour, called a bio-nose, which could be very useful for water pollution control or drug's detection.

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On- and off-Chip Electrochemistry coupled to Electrospray Mass Spectrometry

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The coupling of an electrochemical cell to electrospray mass spectrometry (ESI-MS)[1] provides a very powerful tool for studies of electrochemical reactions as well as for the analysis of electroactive compounds. With ESI-MS it is possible to identify and quantitate electrochemically produced oxidation and reduction products. It is also possible to utilise electrochemical reactions for the preconcentration and/or ionisation of selected analytes as well as for tagging purposes[2]. The coupling of electrochemical cells to ESI-MS is however complicated by the need to decouple the electrochemical cell from the ESI-MS high voltage and the fact that the electrospray process itself involves electrochemical reactions[1]. Care also needs to be taken to ensure that the electrochemically generated products do not undergo unwanted redox reactions between the electrochemical cell and the mass spectrometer[3] and to reduce the transfer time between the electrochemical cell and the mass spectrometer. In the present communication, on- and off-chip couplings of electrochemistry to ESI-MS will be discussed with a particular emphasis on the design of the electrochemical cell. It will be demonstrated that the design of the electrochemical cell and the flow system in general can affect the appearence of the mass spectra and the possibilities to detect an electrochemically generated species. A PDMS based device[4] allowing an on-chip coupling of an electrochemical cell to ESI-MS with a subsecond transfer time will likewise be described.

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Symposium 2 - Oral

Electroanalysis and Sensors

Symposium 2 - Oral

Electroanalysis and Sensors

Capillary batch injection – a novel concept for sample introduction into microfluidic systems

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In recent years microfluidic systems with integrated electrochemical detection (ED) have attracted considerable research interest. Most of these studies were focused on chip-based electrophoresis which offers attractive features such as high-throughput and point-of-care analysis. In addition, electrophoresis chips may have the character of disposable devices.

Limitations of chip systems are related to problems of the interfacing of the chip-based fluidic device to the external environment, particularly regarding the requirements to fill the sample reservoirs. Another weak point of chip electrophoresis is the more or less complicated voltage control to switch between sample loading and separation. As a result of this voltage switching an end-column sensing electrode may experience short-time potential changes which lead to negative effects on the stabilization of the baseline response.

The present contribution introduces an alternative concept which is based on the use of a short piece of a fused silica capillary to perform electrophoretic separations as fast as in the chip format. Previous work on capillary batch injection (CBI) analysis[1] is adapted to manage sample introduction. Small sample volumes are handled with the help of a capillary connected to a microprocessor-controlled microlitre syringe. This arrangement allows precise injections of nanolitre volumes onto the inlet of a short-length separation capillary. The separation voltage of up to 2 kV is continuously applied to the separation system during sample injection and separation which results in favourable baseline characteristics of ED.

The analytical performance of the CBI-CE-ED system was studied using noradrenaline, L-dopa and ascorbic acid as model analytes in borate buffer solution. It was found that experimental parameters such as dimensions of the separation and injection capillaries, convection, alignment of separation and injection capillary and injection conditions have significant influence on the performance characteristics. For a suitable set of experimental parameters CBI-CE-ED offers fast and efficient separations complemented by reliable ED response characteristics.

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S2·O-3

In-situ and Online Monitoring of Hydrodynamic Flow Profiles in Microfluidic Channels

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Perhaps the most popular trend in modern science and technology is miniaturisation of various devices. Particularly, this is of importance in developing chemical or electrochemical sensors where the amount of sample required for the analysis must be minimized. In this work we will focus on a microfluidic channel system, i.e. a cell with one or more dimensions being of the order of a few microns. Such microfluidic channels have kinetic and analytical properties which can be finely tuned as a function of the hydrodynamic flow. However, although it is known from classical hydrodynamics [1] that a fully developed pressure-driven flow profile in a perfect rectangular channel ought to be parabolic, we have reasons to believe that it might not be the case under all experimental conditions. This consideration is based on the fact that experimental channels are often constructed of different materials, i.e. the floor and the ceiling of the channel may have different properties which may lead to different surface effects and henceforth to distorted flow profiles. Also the roughness of the surfaces in the case when channel height is of the order of a few microns cannot be ignored. Furthermore, when the roughness values are different at different channel walls this would again condition a distorted flow profile *vis-à-vis* expected classical one. Similarly, various combinations of local electro-osmotic drive occurring in parallel with the pressure-driven flow as well as other experimental situations would lead to extremely distorted flow profiles. However, presently, there is no simple and direct method to monitor the corresponding flows in situ.

We propose a method [2] for reconstructing any hydrodynamic flow profile occurring locally within a rectangular microfluidic channel based on experimental currents measured at single or double microband electrodes embedded in one channel wall. A perfectly adequate quasi-conformal mapping of spatial coordinates introduced in our previous work [3] and an exponentially expanding time grid, initially proposed in [4] are used for the numerical simulation of the direct problem (i.e. simulation of current responses corresponding to arbitrary flow profiles). Then the solution of the inverse problem (the problem of flow profile determination) is approached using the corresponding variational formulation whose solution is performed by the Ritz method.

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Symposium 2 - Oral

Electroanalysis and Sensors

Disposable, Low-cost, Injection-moulded Electrochemical Flowcells with Integrated Carbon Fibre-Loaded Polymer Electrodes for Voltammetric Applications.

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By applying polymer microfabrication technologies such as injection moulding to electrochemical sensor fabrication the mass production of reproducible, low-cost devices, which can essentially be considered disposable, is possible. A novel, fully polymeric, three electrode micro-flow cell has been created by using an overmoulding procedure to produce an integrated electrochemical flowcell (see figure 1). The working (WE), auxiliary (AUX) and reference electrodes (RE) were fabricated from a conducting grade of carbon fibre-loaded (40%) polystyrene and used either bare or modified (e.g. by e-beam deposition of metal Au or Ag layers, or by application of metal pastes such as Au and Ag/AgCl) to form working and reference electrodes.

The devices have been successfully evaluated for a range of electrochemical techniques such as cyclic voltammetry (CV), anodic stripping voltammetry (ASV), electrochemiluminescence and catalytic adsorptive stripping voltammetry. Device-to-device reproducibility was investigated with a study of ASV behaviour of a 500 ppb Cd solution and CV experiments of model redox compounds, such as dopamine and 4-methyl catechol (shown in figure 2), were performed to examine the electrochemical properties of the electrode materials.
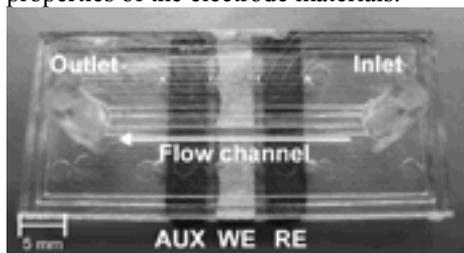
Figure 1. An injection moulded electrochemical flowcell, where RE, WE and AUX are the reference (Ag/AgCl paste), working (e-beam deposited Au, 80 nm) and auxiliary electrodes respectively.
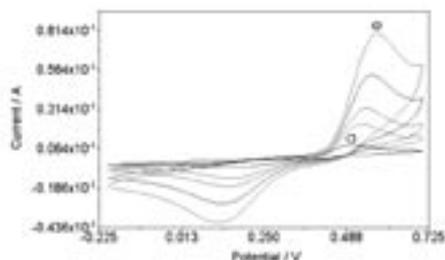

Figure 2. CV of 2mM 4-methyl catechol in a flowcell with an e-beam deposited Au WE carried out at different scan rates: (a) 0.01 to (e) 0.5 Vs^{-1}

A screen-printed carbon electrochemical immunosensor array for the determination of mycotoxins in grain

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The aflatoxins and ochratoxins are fungal metabolites with potent toxicity. Aflatoxins are highly toxic and potent carcinogens, while ochratoxin A (OTA) has nephrotoxic, teratogenic, carcinogenic and immunosuppresive properties and is implicated in human nephropathies and cancers. Legislation set by the EC and increasing numbers of countries worldwide[1] places limits on the permitted levels of mycotoxins in food and feed. In order to determine and control these levels, sensitive analytical techniques are therefore required. Current detection methods for aflatoxins and OTA include TLC, HPLC, and ELISA. There remains a niche for a user-friendly, robust and reliable method/instrument which can screen samples simultaneously for a range of toxins. In this respect, electrochemical analysis using screen-printed carbon electrodes (SPCEs)[2] offers the possibility of achieving low-level detection and rapid analysis times using low-cost consumable sensors.

Electrochemical immunosensors, fabricated by drop-coating antibody against aflatoxin or OTA onto SPCE arrays, were used in a competitive immunoassay for aflatoxin or OTA. All of the assay steps were conducted by immersing the SPCEs into 96-well plate microwells. Immunosensors were exposed to mycotoxin standards mixed with biotinylated toxin conjugate. After washing, they were exposed to a streptavidin-alkaline phosphatase conjugate and were finally immersed in a 1-naphthyl phosphate substrate solution. Enzymatically-produced 1-naphthol, measured voltammetrically, gave a peak current response at +170 mV versus the Ag/AgCl reference electrode.

The current EC limit for aflatoxin B_1 (AFB_1) is 2 ng/g (2 ppb) for groundnuts, dried fruits and cereals, and for OTA is 3 ppb for processed cereals and 5 ppb for raw cereals and spices. Experimental results will be presented from studies conducted to develop electrochemical immunoassays for AFB_1 and OTA using SPCEs bearing surface-adsorbed antibody. Reagent optimisation, calibration data and the results of determinations on spiked grain extracts will be presented. The intention is to construct an array of immunosensors for the simultaneous measurement of multiple mycotoxins in grain extracts.

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Selective modification of nanopore electrodes as sensitive biosensing platform

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The present work exemplifies the applications of a novel sensor platform, called *NanoBioPore*, for sensitive amperometric and impidimetric biosensors. *NanoBioPore* consists of an ensemble of nano-sized electrodes (presently 800 nm diameter) at the bottom of nanopores of a high-density (about 1.5×10^6 pores/mm^2) that are separated from the top electrode by only 100 - 200 nm insulator (see Fig. 1) [1]. The bottom and top electrodes are independently addressable allowing for the development of different immobilisation strategies aiming on the selective modification of either one of the electrodes with a biocomponent (such as ss-DNA, redox proteins, antibodies). Electrochemical sensing of a physical interaction or of a chemical reaction between an analyte and a biological recognition element taking place in such restricted and tiny nanoreactors enables a highly sensitive detection of the biorecognition event.

200 nm
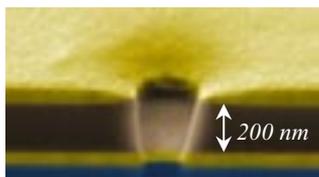
Figure 1. SEM picture of a nanopore structure.

Electrodeposition paints [2] can be exclusively precipitated within the nanopores by applying a potential at the bottom electrode which invokes a local modulation of the pH-value in the pore volume. By this, the polymer is changing its solubility and hence is precipitation in the pores under simultaneous entrapment of suitable biorecognition elements. Applying a suitable potential at the top electrode significantly diminishes any polymer deposition outside the nanopores.

A second strategy for selective immobilisation of biocomponents on the bottom electrode was seen in the sequential modification of top and bottom electrode with self-assembled monolayers of different thiol derivatives. This was achieved by means of potential assisted monolayer formation restricting the chemisorption at the second electrode. Using functionalized thiols the biocomponents can be immobilized selectively at the functionalized surface in a second step.

Results concerning the selective immobilization of a variety of different biological recognition elements in the nanopores will be shown allowing for the development of highly sensitive bioassays.

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All-solid-state chloride sensors based on electronically conducting, semiconducting and insulating polymer membranes

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Conducting polymers have been utilized as sensing membranes and transducers in different types of potentiometric chloride sensors since 1988 [1-5]. Combinations of polymeric membrane materials with different electronic and ionic conductivities should provide some information about the correlations between charge transfer processes and the potentiometric response. In this work, all-solid-state potentiometric chloride sensors were constructed from different combinations of the following three types of membranes deposited on a glassy carbon disk electrode (GC): (i) Electropolymerized poly(3,4-ethylenedioxythiophene) doped with chloride (here called "PEDOT") representing an electroactive membrane with high redox capacitance, high ionic and electronic conductivity, (ii) Solution-cast poly(3-octylthiophene) containing tridodecyl-methylammonium chloride (here called "POT") representing a semiconducting membrane with relatively low electronic conductivity, and (iii) Solution-cast plasticized poly(vinyl chloride) containing tridodecylmethylammonium chloride (here called "PVC") representing a membrane with purely ionic conductivity. Based on these membrane materials, the following electrodes were constructed and compared: (a) GC/PEDOT, (b) GC/POT, (c) GC/PEDOT/PVC, and (d) GC/PEDOT/POT. In these electrodes, PEDOT and POT worked as ion-to-electron transducers and/or sensing membranes, while PVC obviously could work only as sensing membrane. All electrodes gave a potentiometric response to chloride. The selectivity pattern followed the Hofmeister series only in the case of the GC/PEDOT/PVC electrode, which also showed least hysteresis in the calibration plot. Results from impedance measurements showed that PEDOT is superior as ion-to-electron transducer compared to POT, while POT showed slightly better sensitivity to chloride anions. Therefore GC/PEDOT/POT showed better overall potentiometric performance than GC/PEDOT or GC/POT alone.

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Symposium 2 - Oral

Electroanalysis and Sensors

Amperometric sensor for heparin: sensing mechanism and application in human blood plasma analysis

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Heparin is a mixture of highly sulphated linear polysaccharides, which has been used in surgical procedures (1-10 UmL^{-1}) and therapeutically (0.1-1 UmL^{-1}) to prevent blood coagulation. In this contribution, voltammetric measurements of heparin at a rotating glassy carbon (GC) electrode coated with a PVC membrane are reported. A spin-coating technique is used to prepare thin membranes (20-40 μm) with a composition of 25%(w/w) PVC, 1,1'-dimethylferrocene as a reference electron donor for the GC|membrane interface, o-nitrophenyl octyl ether (o-NPOE) or bis(2-ethylhexyl) sebacate (DOS) as a plasticizer, and hexadecyltrimethylammonium tetrakis(4-chlorophenyl) borate (HTMATPBCl) or tri-dodecylmethylammonium tetrakis(4-chlorophenyl) borate (TDMATPBCl) as a background electrolyte. The electrodes coated with either the $HTMA^+$/o-NPOE (DOS) or $TDMA^+$/o-NPOE (DOS) membrane provide a comparable amperometric response towards heparin (1-10 U mL^{-1}) in the aqueous solution of 0.1 M LiCl. However, only the membranes formulated with TDMATPBCl can be used for an amperometric assay of heparin in human blood plasma with a detection limit of 0.2 UmL^{-1}. Effects of membrane composition, heparin concentration, rotation speed and sweep rate on the voltammetric behaviour of heparin provide an insight into the sensing mechanism comprising the transport of heparin in the aqueous phase, the formation and accumulation of the complex between heparin and $HTMA^+$ or $TDMA^+$ at the membrane-solution interface, and the desorption and transport of the complex in the membrane phase. Amperometric response of the electrode coated with the $HTMA^+$/o-NPOE (DOS) membrane is controlled by the heparin transport in the aqueous phase and the adsorption of the heparin complex with $HTMA^+$ at the membrane-solution interface. A numeric simulation of the voltammetric behaviour supports this explanation. On the other hand, the amperometric response of the electrode coated with the $TDMA^+$/o-NPOE (DOS) membrane is governed by the transport of the heparin complex and the $TDMA^+$ cation inside the membrane phase. The potential-dependent extraction of $HTMA^+$ and its competitive interaction with a plasma component (e.g. albumin) impedes the amperometric assay of heparin in the human blood plasma using the electrode coated with the $HTMA^+$/o-NPOE membrane.

Electrochemical sensing of phosphate via calix[4]arene anion receptors

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Calixarenes are macrocyclic compounds, formed by the condensation of formaldehyde and phenol. They can be used as a scaffolding onto which a range of functional groups can be appended. The ability to modify a calixarene with different functional groups allows the construction and tailoring of a molecule having a specific binding environment. We are utilizing this flexibility to prepare calixarene-based anion receptors. These receptors will be used as the basis for anion-selective sensors.

For the anion receptors, we have chosen to use a calix[4]arene with two coordinating functionalities on the lower-rim (of the general structure [**1**]). The electronic and steric nature of the binding sites is selective for anions that coordinate to hydrogen bonding centres. Both amide and thioamide derivatives were prepared.

[1]
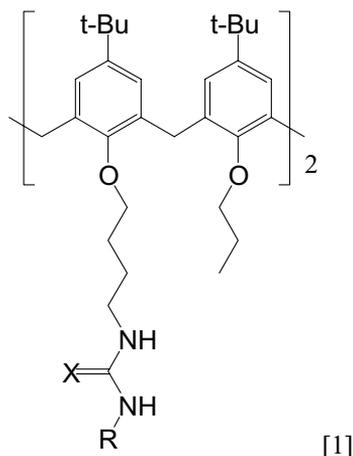
Characterisation of the properties of these calixarene derivatives using potentiometry at polymer membrane ion-selective electrodes (ISEs), in which the calixarene is a component of the membrane matrix, is presented. Selectivity coefficients for these ISEs were measured using the fixed interference method (FIM) and the matched potential method (MPM).

Results indicate a good selectivity towards phosphates, particularly monohydrogen phosphates (HPO_4^{2-}) under neutral conditions for both calixarene derivatives in the presence of sulfate, nitrate and chloride interferents. Results also show these ISEs

Symposium 2 - Oral

Electroanalysis and Sensors

Potentiometric determination of ion pairing constant by sandwich membrane technique

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The area of Ion Selective Electrodes (ISEs) has gained significant research momentum in the last decade due to the understanding of the mechanisms that dictate potential response. Spectacular experimental improvements of selectivity coefficients of up to twelve orders of magnitude, and detection limit of up to six orders of magnitude has resulted in a dramatic upsurge of research activity, driven by the potential for important new applications (e.g. trace analysis in environmental and clinical monitoring).

The phase boundary potential model has emerged as a convenient expression that allows theoretical treatment of zero-current membrane fluxes based on only experimentally available parameters. It has also been successfully used as a basis for theoretical description of a family of experimental methods called sandwich membrane techniques. These techniques have been implemented in the determination of electrode parameters such as stability constants, quantification of ionic impurities, evaluation of equilibrium processes that dictate upper detection limit etc. In the essence of this technique, two phase boundary potentials are uncoupled by inducing a well-defined initial ion concentration profile within the membrane. This is accomplished by combining two membrane segments each having a different composition forming a non-uniform sandwich membrane.

In this work, we utilize the sandwich membrane technique for the determination of ion-pairing constants. We demonstrate experimental methodology as well as give the theoretical description of the method.

Determination of trace *p*-nitrophenol concentrations in human urine by liquid chromatography dual electrochemical chemical detection

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The determination of trace p-nitrophenol (PNP) has been achieved by high performance liquid chromatography dual electrochemical detection (LC-DED), using a novel dual reductive mode electrochemical-chemical-electrochemical detection system. PNP eluting from the analytical LC column is first reduced to p-hydroxylaminophenol, at the first "generator" electrochemical cell at an applied potential of -2.0 V. This species undergoes chemical oxidation to generate principally p-aminophenol and p-aminoresorcinol which are then detected at the downstream "detector" electrode using an applied potential of -0.1 V. The optimal chromatographic conditions were found to comprise of a mobile phase containing 40 % acetonitrile, 60 % water, containing 25 mM o-phosphoric acid, at a flow rate of 0.5 ml/min, in conjunction with a Hypersil C_{18} 250 mm x 4.6 mm, 5 μm column. The assay was found to be linear over the range 7.0 ng to 500 ng on column, with an associated R^2 value of 0.9981, and a limit of detection of 1.0 ng PNP on column. No interferences were seen for a number of common drugs or for the principle electrochemical active components of human urine or serum. The developed assay was found to successfully be able to determine trace concentrations of PNP in human urine samples with very little sample preparation. A coefficient of variation of 7.1 % (n = 7) with a mean recovery of 94.7 % for human urine fortified at 522 ngml[-1] was found.

Symposium 2 - Oral

Electroanalysis and Sensors

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Electroanalysis and Sensors

Electrochemical sensing in nM range by chemical amplification

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Here we report a chemical amplification, in which detection limit of ferrocenemethanol (redox active analyte) is drastically increased by a redox amplifier, ferrocyanide or ferricyanide. For this purpose, the surface modification was necessary to inhibit the direct electron transfer between the amplifier and the electrode surface. The glassy carbon electrode surface was grafted with 4-nitrophenyl group by electrochemical reduction of 4-nitrobenzene diazonium compound in acetonitrile. The amount of the modifier was optimized by controlling the charged passed during the grafting. The detection signal could be amplified both anodic reaction by ferrocyanide and cathodic reaction by ferricyanide. The analyte, ferrocenemehanol could be detected down to nM range by cyclic voltammetry.
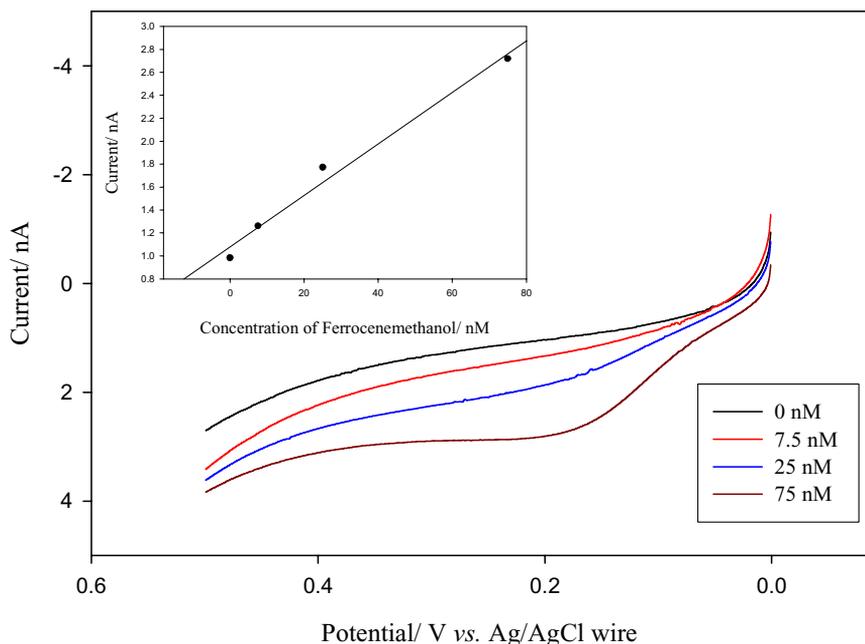
Figure 1.Detection of Ferrocenemethanol by 10 µM Ferrocyanide as amplifier.
4-nitrobenzendiazonium modified glassy carbon electrode (WE), Ag/AgCl wire (RE, CE);
scan rate 5mV/s, 60°C; In set; calibration curve at E=0.180 V vs. Ag/AgCl wire

Covalent Modification of Boron-Doped Diamond Electrode Surfaces for Electroanalysis

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Boron-doped diamond (BDD) has drawn attention as a functional electrode material for electroanalysis especially due to its wide potential window and low background current as well as extreme physical and chemical stability. In this study, in order to further functionalize BDD electrodes, photochemical covalent surface modification of hydrogen-terminated BDD with organic monolayers were investigated.

Cyclic voltammograms (CVs) in 0.1 M phosphate buffer solution (PBS, pH 7) at a BDD electrode modified with vinylferrocene (Fc-BDD) was found to show a reversible redox peak at ca. +0.3 V vs. Ag/AgCl with a small peak separation (11 mV at a potential sweep rate of 50 mV s^{-1}) (Fig. 1). In addition, the anodic peak current density was directly proportional to the potential sweep rate. These results indicate that the ferrocene derivative was immobilized onto a hydrogen-terminated BDD surface with the photochemical modification method.

BDD electrode modified with ATAB (ATAB-BDD) was also fabricated with the same technique. Elemental analysis with X-ray photoelectron spectroscopy revealed the presence of quaternary ammonium group on the ATAB-BDD, which may originate cationic surface properties. As an application of such a cationic BDD surface, electrochemical detection of oxalic acid (OA) was examined. Estimation with CV and electrochemical flow-injection analysis (FIA) showed superiority in sensitivity and stability at the ATAB-BDD electrode comparing to an unmodified (as-deposited) BDD electrode (Fig. 2).
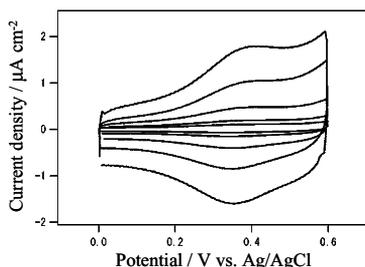

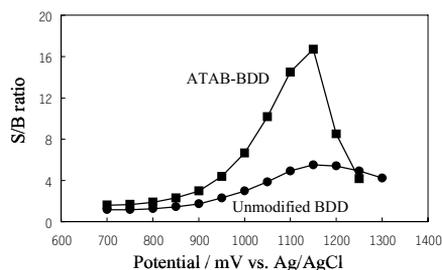Fig. 1 CVs for 0.1 M PBS (pH 7) at Fc-BDD. Potential sweep rate: 10, 20, 50 ,100 and 200 mV s^{-1}.

Fig. 2 Signal-to-background ratio of FIA amperometric current for detection of 10 μM OA at unmodified and ATAB-BDDs.

Symposium 2 - Oral

Electroanalysis and Sensors

Room Temperature Ionic Liquids for Electrochemical Detection of Nitro Based Explosives

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A huge number of chemical sensors is based on electrochemical measurement methods. Particularly amperometric (potentiostatic) sensor systems are applied for the fast detection of pollutants in industry and environment as well as for analytical systems in medical diagnosis. The reason for the wide applicability of electrochemical sensors is their high sensitivity. Additionally electrochemical sensor systems are mostly easy to operate, transportable and cheap. Up to now the electrochemical method of cyclic voltammetry (potentiodynamic) has been rarely used for sensors. In comparison to potentiostatic sensors potentiodynamic sensors show additional advantages. For instance qualitative and quantitative information are received during one measurement. The determination of very low trace concentrations is important in the explosives detection in the gaseous phase. The low vapour pressure of many explosives and the decreasing concentration with increasing distance to the source make high demands on detection methods. The vapour pressure of trinitrotoluene (TNT) is given with 7 ppb (parts per billion) at room temperature. Trinitrotoluene shows a characteristic reduction peak in aqueous electrolyte at approximately minus 0,15 V vs. SCE. This peak is attributed to electrochemical reduction of the nitro groups at the TNT. The used aqueous electrolyte does not satisfy the criteria of a successful application at the field. The long term stability of the electrolyte is too small as a result of the volatility of the aqueous solution. Room temperature ionic liquids (RTIL) can be used for many applications as they have a low melting point, a wide electrochemical window and high solubility for a wide range of materials. Furthermore RTIL are non volatile and they can be designed to dissolve a broad variety of chemical substances. The electrochemical detection of trinitrotoluene is investigated in different room temperature ionic liquids. Seven RTIL are selected on the basis of existing electrochemical data and applicability for sensors of trace concentrations in the gaseous phase. The solubility, the electrochemical current and the quality of the electrochemical signal are used for electro analytical evaluation of these RTIL. Three RTIL are selected for the electrochemical characterization of trinitrotoluene in the gaseous phase on the basis of this evaluation. The electrochemical reduction signal in RTIL shows more than one reduction peak for TNT in contrast to the aqueous electrolyte. Electrochemical characterization of mono- and dinitrotoluene are discussed. On basis of the investigations of mono- and dinitrotoluene a reaction scheme is discussed for the electrochemical reduction of nitro based explosives. Exemplarily we present our R&D-works on the detection of nitro based explosives in room temperature ionic liquids. The results are discussed in contrast to electro analytical experiments in aqueous electrolyte.

Symposium 2 - Oral

Electroanalysis and Sensors

Thin-shielded sphere-cap microelectrodes. Preparation, characterization and analytical applications

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Microelectrodes with geometry different from the commonest disk shape have becoming more popular recently. Conical, and spherical microelectrodes in particular have found increasing interest because they can be used as tips in scanning electrochemical microscopy (SECM). Theory for spherical microelectrodes has been developed. In particular, theoretical treatments, relying on digital simulation procedures, exist within the SECM domain for spherical microtips approaching either a conducting or an insulating surface. The theoretical treatments also include the effects of the insulating sheaths surrounding the active electrode surface, so called RG factor, that is the ratio of the insulating sheath thickness (b) to the basal radius (a) of the electrode, as well as the aspect ratio of the electrode, h/a, where h is the sphere-cap height. In these cases, however, only normalised current (i.e., current at a given tip-surface distance to the current far from the surface) are required. For sphere cap micreoelctrodes steady-state equations have been reported, but they were limited to the case where RG $\rightarrow \infty$ (i.e., sphere caps lying on an infinite insulating sheath).

The aim of this paper is to investigate from either a theoretical and experimental point of view on the steady state limiting currents as a function of both RG and h/a parameters for sphere caps microelectrodes. A digital simulation procedure is employed to obtain theoretical parameters. For measurements, sphere cap microelectrodes are prepared by electrodeposition of mercury onto thin-shielded platinum microdisks. These were prepared from platinum wires and insulated by deposition of a cathodic electrophoretic paint. The properties of such microelectrodes for analytical purposes are also investigated.

Symposium 2 - Oral

Electroanalysis and Sensors

New protective polymer membrane coating strategies for sol-gel enzyme biosensors

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Significant efforts have been devoted to developing long lifetime and sensitive biosensors by stabilising and immobilising enzymes on different electrode substrates. Different polymer materials are usually used for immobilisation or as a protective membrane against interference or enzyme leaching. An attractive enzyme entrapment method is the sol-gel technique and these films have been characterised by atomic force microscopy (AFM). Enzymes and the other active biomaterials encapsulated within sol-gels appeared to retain their activity and selectivity, particularly when silica alkoxides were used as sol-gel precursors. However, sol-gel electrodes in some cases gave unsatisfactory lifetimes [1], inappropriate for disposable biosensors.

Characterisation and optimisation of silica based sol-gel encapsulation of glucose oxidase, aldehyde dehydrogenase, and NADH oxidase based biosensors at poly(neutral red) (PNR) modified carbon film electrodes will be presented, some involving direct electron exchange between the redox polymer and the enzyme. Sol-gels were prepared using an optimised mixture of oxysilane precursors, particularly 3-glycidoxypropyl-trimethoxysilane (GOPMOS), and methyltrimethyloxysilane (MTMOS). The sol-gel protocol was improved by thermal removal of the alcohol, formed during oxysilane hydrolysis in acidic medium.

Enzyme was entrapped by mixing a solution of it with a neutralised sol-gel mixture and placing on a carbon film electrode, electrochemically modified with PNR. An outer protective polymer membrane was applied over the encapsulated enzyme layer in order to prevent enzyme leaching and loss of sensitivity from macromolecule adsorption [2]. Polyurethane and carboxylated polyvinyl chloride were used for membrane preparation and optimisation.

The results of glucose and acetaldehyde assays in relation to sensitivity, stability and response time in standard solutions and in natural samples will be discussed.

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Effect of the conditioning time on the ISE electrochemical behaviour.

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Electroacoustic measurements have shown interesting potentialities for examining the microrheology of different films deposited onto the top of piezoelectric resonators or to validate the gravimetric response of a classical microbalance sensor [1]. A recent approach based on transfert function measurements using a fast QCM have also shown attractive results. In the case of electroactive films, the ionic species involved in the electrochemical processes can be identified and also quantified [2].

Sophisticated films can be used to realize all solid state ion sensitive electrode. They were made with organic multilayers: one, based on an electronic conducting material (polypyrrole or Prussian Blue) deposited through an electrochemical procedure onto the metallic electrode and a second one, in contact with the solution, made of a plasticized PVC membrane deposited by a spin-coating technique. A sensitive ionophore is incorporated in this latter in order to detect ions through potentiometric measurements. The performances of these chemical sensors depend on the quality of these two layers and also on the preconditioning treatment applied. This step appears as crucial but seems not very well understood.

For that reason and in this work, we propose to examine the behaviour of these films when a preconditioning treatment is used by coupling two techniques: electroacoustic and electrogravimetric measurements. Ac-electrogravimetry revealed details on the influence of the solvent on ion insertion/expulsion mechanism. The solvent uptake seems to be necessary for the good functionning of the membrane. Electroacoustic measurements revealed the viscoelastic character of the membranes and the values of G', G" are modified according to the soaking time. Correlations were made between the two approachs in order to explain good responses obtained only after at least 24 hours of preconditioning.

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Symposium 2 - Oral

Electroanalysis and Sensors

Electrochemical nanogravimetric studies of solid RuCl$_3$ and RuCl$_3$-polyaniline nanocomposite

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Ruthenium and its compounds have been widely used especially in the field of homogeneous and heterogeneous catalysis including electrocatalysis and photocatalysis. Their catalytic activity regarding different oxidation and reduction as well as other reactions, e.g., polymerization, strongly depends on their oxidation state and on the media used because of the formation of different simple and polynuclear complexes. RuCl$_3$ – which is far the most common starting material in ruthenium chemistry – is insoluble in water and organic solvents which is connected with its polymeric structure in solid state. The method of voltammetry of immobilized microparticles in combination of electrochemical nanogravimetry by using quartz crystal microbalance is especially useful for the characterization of microcrystals attached to an electrode surface. It has been found that RuCl$_3$ microcrystals can be reduced and reoxidized in several steps in the presence of acidic and neutral aqueous solutions of different MCl and MCl$_2$ electrolytes. The results can be elucidated by the formation of complexes and intercalation compounds which contain mixed valence Ru^{III} / Ru^{II}-centers, Cl$^-$ ions, metals ions (M$^+$, M^{2+}) or H$^+$ ions, and water molecules, the ratio of which depends on the potential and the solution composition. The composition of microcrystalline layers formed at different potentials has been determined by total reflection X-ray fluorescence spectrometry. The redox transformations also involve solid-state phase transitions.

The insertion of aniline into α-RuCl$_3$ has been executed either from a solution of aniline in acetonitrile or pure aniline was added to the microcrystals. The RuCl$_3$ is a strongly oxidizing host which can take up electrons from the aniline leading to the formation of polyaniline (PANI). Simultaneously, a fraction of Ru^{3+} is reduced to Ru^{2+}, resulting in a mixed valence compound. The host material will have a negative charge, and RuCl$_3^-$ sites can act as counterions in the nanocomposite, (PANI)$_x^{z+}$(RuCl$_3$)$_y^{z-}$. It has been proven by infrared spectroscopy as well as by electrochemical investigations that PANI was formed between the RuCl$_3$ layers, which are composed of hexagonal sheets of Ru atoms sandwiched between two hexagonal sheets of Cl atoms with ABC stacking.

The redox transformations of the nanocomposites have also been investigated by electrochemical nanogravimetry. The transport of the charge compensating ions reflects the variation of the oxidation states of both PANI and RuCl$_3$.

The oxidation state of both the RuCl$_3$ microcrystals and the RuCl$_3$-PANI nanocomposites can be varied electrochemically, therefore the catalytic activity can be tuned.

The peak potentials of the voltammetric waves are characteristic of the counterions used and are shifted as a function of the activity of the electrolytes, consequently these systems are promising for the application in the area of electroanalysis.

Repair of defects in thin thermally grown silicon by anodic oxidation

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Scanning Photo-induced Impedance Microscopy (SPIM) and Light-Addressable Potentiometric Sensors (LAPS) are imaging techniques based on photocurrent measurements at field-effect structures. The sensitivity of SPIM is, to a large extent, determined by the capacitance of the insulator. The thinner the insulator and the greater its dielectric constant the stronger the photocurrent signal is dominated by the system to be investigated. An increase in the insulator capacitance would also lead to steeper slopes of the photocurrent-voltage curves resulting in an improved sensitivity of LAPS. In previous experiments, a thermally grown silicon dioxide layer with a thickness ranging from 10 to 70 nm was employed as the insulator. Compared to standard MOS applications, the conditions imposed by SPIM and LAPS measurements are quite demanding in that they require a defect free oxide layer over quite a large area (~ 7 mm^2). Using a 10 nm thick silicon dioxide, only moderate yields of working devices were obtained. A further reduction in the thickness is therefore difficult.

Anodic oxidation in 0.1 M HCl has been used for "repairing" defects in thin thermally grown layers of silicon dioxide on p-type silicon. Field effect capacitors with a gate oxide thickness of 3 nm and 6 nm and gate areas of 3.1 mm^2 showed leakage currents smaller than 1 nA after anodic repair (Figure 1). The results showed that the defects in the thermally grown oxide were repaired efficiently and also the oxide thickness did not increase during anodic oxidation for structures with 6 nm thick thermally grown oxide. A small increase in thickness was observed during anodic oxidation using silicon with 3 nm thick thermally grown oxide. AC impedance spectroscopy and XPS were employed to characterise the oxide layers.
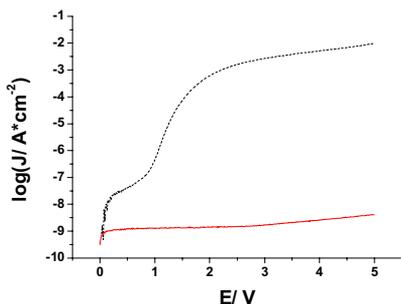

Figure 1 Current-voltage curve before (dashed line) and after (solid line) anodic repair of a 3 nm thick thermally grown oxide

Symposium 2 - Oral

Electroanalysis and Sensors

Highly ordered macroporous surfaces as electrochemical systems with optimized biocatalytic efficiency

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For several decades there is a great interest in the modification of electrodes with biomolecules for the application in biosensors and more recently also in biofuel cells. A particular aspect is the miniaturization of those systems for the use as implantable biomedical devices. The intrinsic problem is that the delivered currents are quite low and therefore the sensitivity or power output in the case of a sensor or a biofuel cell respectively is very small. An answer to this problem might be the use of highly ordered macroporous electrodes. We present a procedure, using monodisperse colloids and the Langmuir-Blodgett-method to build up colloidal crystals on a flat electrode, followed by electrodeposition of gold and dissolution of the colloidal endo-template, which produces a highly structured porous material [1]. The pore diameter d is controlled by the size of the used colloids and the final thickness of the porous layer by following the current oscillations during the electrodeposition through the template.
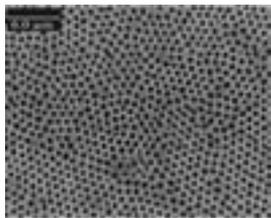
Fig.1: macroporous gold, d=1100nm
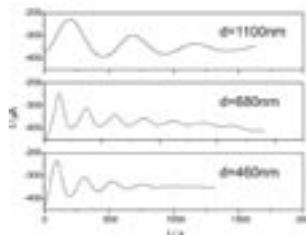
Fig.2: current oscillations obtained during plating through the template

All the pores being interconnected, the active surface area is increased by more than one order of magnitude. The inner surface of the pores can be modified with a biocatalytic chain containing a mediator, a coenzyme and an enzyme [2,3], leading finally to a bioelectrocatalytic device with a much higher current output compared to a flat modified electrode.

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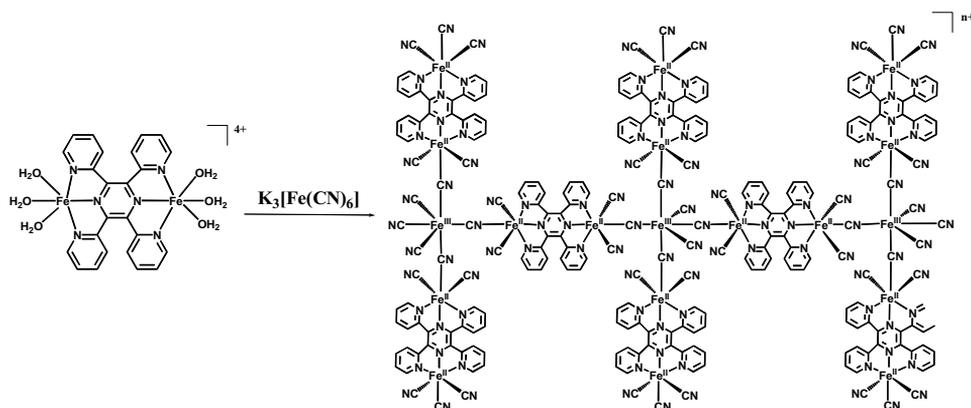[1] R.Szamocki, S.Reculusa, S.Ravaine, P.N. Bartlett, A.Kuhn, R.Hempelmann, Angew.Chem. Int.Ed. **45** (2006) 1317
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Molecular Wires Design Based on Supramolecular Structures for Glucose Biosensors

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In the present work, the synthesis and the spectroelectrochemical characterization of a novel iron compound derived of tetra-2-pyridyl-1,4-pyrazine (TPPZ) with hexacyanoferrate species forming a very stable supramolecular complex in the presence of polypyrrole (PPY) matrix, is described. The hybrid material has shown excellent catalytic activity towards H_2O_2 detection that makes it suitable for being used as redox mediator in glucose biosensor. The hybrid FeTPPZFeCN/PPY film presents satisfactory detection limits and high sensitivity for H_2O_2 in the presence of K^+ or Na^+ ions. For the glucose biosensor, a linear range up to 1.1 mmol l^{-1} of glucose was observed with no interferences. In this case, the sensitivities obtained were 7.88 and 5.90 $\mu A \cdot mmol^{-1}$ l cm^{-2} in phosphate buffer or NaCl solutions, respectively. The good sensitivity is related to the presence of a high-dimensional structure based on polypyridine type ligands providing an "electron antennae effect" facilitating electron tunneling between the protein and the electrode. The results suggest that this composite film is a promising material for potential applications in biosensors and in biofuel cells.

Symposium 2 - Oral

Electroanalysis and Sensors

Symposium 2 - Oral

Electroanalysis and Sensors

A neural network application on the calibration of a glucose sensor

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The immobilization of enzymes on an electrode surface is of great importance in bioelectrochemistry for the production of biosensors and in fabrication of microsensors in the preparation of multiplayer devices. On the other hand, artificial neural networks (ANNs), proposed by information and neural science as a result of the mechanisms and structures of the brain, are computer programs and they do not attempt to copy the fine detail of how the brain works, but try to reproduce its logical operation using a collection of neuron-like entities to perform processing. ANN can learn the system performance characteristics by monitoring the system test or running data. This technique has grown rapidly in chemistry and related fields of research since 1980's. Until now, ANN is considered as one of the best approaches to the nonlinear calibration and fitting problem.

In current study, glucose oxidase enzyme (GOD) that is specific for the glucose determination was entrapped into polypyrrole matrix containing p-benzoquinone in PIPES buffer and glucose sensitivity of the biosensor is investigated. A calibration curve is plotted for the enzyme electrode as a function of glucose concentration. Because the only useful part of the curve is the linear zone, which is only a small part of the calibration plot, only glucose concentrations in the narrow range can be determined. Whereas, accurate calibration may be reached on this real system by applying ANNs methodology. This implementation can be used for the sensor failure detection, as well. The estimation power of the neural network used in the direct and inverse modeling is examined by statistical methods. It presents the good performance for the estimation power.

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Electrochemically Activated Nanocrystalline Diamond Modified Gold Electrode for Glucose Biosensing

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Recently, novel carbon materials, such as carbon fullerenes, carbon nanotubes (CNT) and diamond lead new directions in the design of biosensors. They offer lots of possibilities for the biosensor construction, for example, electron mediation, nano-biosensor fabrication and enzyme entrapment. Diamond-based materials, because of their unique properties such as biocompatibility, chemical inertness, chemical stability, wide potential window and optical transparency properties, which are superior to the traditional carbon materials. Since for electrochemical applications, the diamond thin film must possess a good conductivity, most work in this field has been carried out using diamond layers doped with boron, which display almost metal-like properties. There are few reports on non-doped diamond because of its weak conductivity. Here, we reported a glucose biosensor based on electrochemical pretreatment of non-doped nanocrystalline diamond (N-NCD) modified gold electrode for the selective detection of glucose. N-NCD was coated on gold electrode and glucose oxidase (GOx) was immobilized onto the surfaces of N-NCD by forming amide linkages between their amine residues and carboxylic acid groups on N-NCD. While the anodic pretreatment of N-NCD modified electrode not only promoted the electron transfer rate of the N-NCD thin film, but also resulted in a dramatic improvement in the catalysis of the dissolved oxygen. This performance could be used to detect glucose at negative potential through monitoring the reduction of oxygen. The biosensor effectively performs a selective electrochemical analysis of glucose in the presence of common interferents, such as ascorbic acids (AA), acetaminophen (AP) and uric acid (UA). A wide linear calibration range from 10 μM to 15 mM and a low detection limit of 5 μM were achieved for the detection of glucose.

Symposium 2 - Oral

Electroanalysis and Sensors

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Measurement of Human Whole Blood Coagulation Time with Small Sample Volume by Impedance Method

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Measuring of human whole blood coagulation by impedance method on paired interdigital electrodes with sample volume equal or less than 10 μl has been studied. □The study of whole blood coagulation by impedance method began early in 1905 by Frank RT with results that were difficult to reproduce. Rosenthal RL and Tobias CW (1948) had first repeatable results with great efforts. Ur A (1970) made the first standard curve of human whole blood coagulation and tried to inquire into the meaning of it. Von Kaulla KN (1975) developed a commercial device for measuring human blood coagulation time, but quitted soon from the markets due to the complexity and uneasy to apply to the clinical conditions. The study of human blood coagulation by impedance method was almost stopped for a long period of time. Spence N (2002) made a series of studies and concluded that impedance method can be used as end points of regular blood coagulation tests. All these studies were done with whole blood or plasma of sample volume more than 40 μl tested on block electrodes. Mixing with reagents (either aqueous or powdered) to activate and initiate the coagulation process was necessary.□In my study, direct coating of reagents (calcium chloride) and activator (glass nanoparticles) on the surfaces of testing electrodes with sample volume equal or less than10 μl was achieved. There is strong correlation between impedance coagulation time and both normalized (R^2=0.72) and non-normalized (R^2=0.61) activated partial thromboplastin time (aPTT). The best frequency for impedance coagulation time measurements was also determined. Testing run at 250 kHz will yield best results under such system configuration. Significant differences between activated and non-activated impedance clotting time (paired t test, p<0.01) and strong linear correlation (R^2=0.758) were obtained. The 95.3 nm particles have better results for triggering human contact activation system than 6.4 μm particles during whole blood coagulation. Nevertheless, glass is not a good material even in its nanoparticle size for activating human contact activation system. It shortened the blood coagulation time only by 30% in this study. Impedance method is an ideal tool for whole blood coagulation time measurements on very small sample volume and really promising for developing point-of-care coagulation devices.

Haem Proteins in Nonaqueous Solvents; Electrochemistry, Conformation and Catalysis

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Enzymes have found numerous applications as practical catalysts in chemical synthesis and as recognition elements in biosensors. The realisation that enzymes can be catalytically active in organic solvents containing little or no water has expanded their repertoire of use [1]. Some of the advantages in utilising enzymes in non-aqueous solvents include the high solubility of many hydrophobic substrates in such solvents, the suppression of various side reactions promoted by water, high regio- and enantioselectivity, and the comparative simplicity of immobilization procedures due to the insolubility of enzymes in organic solvents. Numerous studies have been conducted in order to gain an understanding of the properties of organic solvents that are key to enzymatic activity. Factors such as water activity, solvent hydrophobicity, solvent polarity and substrate hydrophobicity can affect the rate of reaction. Due to their commercial potential, much of the work on nonaqueous enzymology has concentrated on the use of enzymes such as esterases with there being relatively few reports on the use of redox proteins and enzymes.

We are currently examining the electrochemical properties of a range of redox proteins and enzymes in nonaqueous solvents [2-6]. The enthalpic and entropic changes associated with the reduction of redox proteins frequently compensate each other. Such a balance exists with cytochrome c, for example. However in nonaqueous solvents these changes are opposite to those observed in aqueous buffer. Using microperoxidase as a model, properties of the solvent such as the dielectric constant and hydrophobicity do not influence Eº. Due to its highly exposed haem group, microperoxidase displays little selectivity. We have synthesised and characterised a cyclodextrin modified microperoxidase which is an effective catalyst for sulfoxidation reactions. Using AFM and circular dichroism (synchroton source at Daresbury), we have examined the conformational changes that attend reduction of a protein in nonaqueous solvents. In ethanol, changes in heat capacity (ca. 600 $JK^{-1}mol^{-1}$) occur on reduction of cyano-haemoglobin, indicating that the cyano form of the protein undergoes reversible, conformational changes, while haemoglobin retains its conformation. The development of sensors and biocatalysts will be described.

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Symposium 2 - Oral

Electroanalysis and Sensors

Symposium 2 - Oral

Electroanalysis and Sensors

The Effect of Light on the Electroctalytic Oxidation of NADH Using Electrodes Modified Electropolymerized Mediators

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Many studies on the electrocatalytic oxidation of reduced ß-nicotinamide adenine dinucleotide (NADH) have been reported (1,2). Especially some modified electrodes based on phenothiazine and phenoxazine dyes have been intensively used for electrocatalytic determination of NADH. However, photoelectrocatalytic oxidation of NADH has not yet been presented with these modified electrodes. There are only a restricted number of studies on photoelectrochemical oxidation and detection of ascorbic acid (3,4). In this study, photoelectrocatalytic oxidation of NADH is here described by irradiation of a glassy carbon electrode (GCE) surface modified with an electropolymerised dye (some phenothiazines phenoxazines and flavin adenin dinucleotide (FAD). Electropolymerisation of phenothiazine and phenoxazine dyes was achieved by sweeping (50 mV/s) a GCE in borate buffer solution, pH 9.1, containing 0.1 M $NaNO_3$. Electropolymerisation of FAD was obtained by sweeping a GCE in 0.1 M HCl and 0.1 M KCl. These modified GCEs show electrocatalytic activity for NADH oxidation in phosphate buffer solution, pH 6.9, with an overpotential of 350-400 mV lower than that at the bare electrode. The effect of light on the electrocatalytic oxidation of NADH at these electrodes was investigated using both amperometry and cyclic voltammetry in the presence and absence of NADH. When the modified electrode surface was irradiated by a 250 W halogen lamp, a photoelectrocatalytic effect was observed for NADH oxidation and the current was increased about 2.0 to 2.5 times.

It can be concluded that some polyphenothiazine, polyphenoxazine, and polyFAD modified GCEs exhibit excellent electrocatalytic and especially photoelectrocatalytic oxidation of NADH in neutral aqueous solution. The results from this study may found the basis for a further development for future studies in this direction.

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Investigations on bio-electrocatalysis of neuronal nitric oxide synthase

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In higher animals nitric oxide (NO) is synthesized by nitric oxide synthases (NOS, EC 1.14.13.39), which converts L-arginine to citrulline and NO in a NADPH dependent oxygenation reaction. The known NOS enzymes are flavocytochromes that exhibit a bi-domain structure, in which an oxygenase domain is linked by a calmodulin recognition site to a reductase domain. The oxygenase has a cysteine-ligated iron protoporphyrin IX (b-type heme), while the reductase contains FAD and FMN. Interestingly, the separate domains are catalytically active [Alderton et al. 2001]. Electrochemistry provides thermodynamic and kinetic informations and protein electrochemistry has potentials for biosynthesis and biosensing.

We report direct electrochemistry of the oxygenase domain of neuronal NOS (nNOS) on chemically modified electrodes. For this study two oxygenases were used, the N-terminal heme containing domain (oxyNOS) including the PDZ binding domain and the truncated mutant D290nNOS oxygenase (D290oxyNOS). Voltammograms display redox waves around -350 mV vs Ag/AgCl (1M KCl) for both the oxyNOS and D290oxyNOS(at pH 7), with slightly more negative value for the oxygenase with the reduced size. This signal is related to the Fe^{II}/Fe^{III} –couple of nNOS. A typical catalytic oxygen reduction is also observed for both oxygenases. However, the electrochemical reduction in the presence of L-arginine or N-hydroxy-L- arginine does not lead to a production of NO. Unique to the NOS is that it requires for its activity tetrahydrobiopterin (H_4B). We present investigations on the electron mediating effect of H_4B and the results for bioelectrocatalytic formation of NO with the electrode is the source of electrons.

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Symposium 2 - Oral

Electroanalysis and Sensors

Electrochemical activity of new pna conjugates with ferrocene and fischer-type carbene complexes to be applied to DNA and RNA detection

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Peptide Nucleic Acids (PNA) oligomers, on account of their very high DNA and RNA binding power resulting in high sequence specificity, are promising candidates [1] for the detection of nucleic acids, one of the foremost current topics in biochemical research [2]. To this aim they require an appropriate electrochemically or spectroscopically active marker, which has to be duly characterised. In this context, the Authors would like to present a systematic investigation of the electrochemical activity of newly synthesized PNA conjugates, to be tested as competitive probes for nucleic acid detection.

First of all, in our current development of PNA oligomers for DNA binding, labelled with one or three ferrocene groups per monomeric unit, we are currently focusing: (a) on the effect of the lengthening of the nucleotidic chain; (b) on the effect of PNA backbone modifications in order to improve the hydrophilicity of the metal conjugate. In particular, we are testing polyvinylpirrolidone-PNA (PVP-PNA) monomers and oligomers, investigating the effect of the length of the PVP polymer on the solubility in water and in other organic solvents, on the polymer conformational structure induced by the solvents, and therefore on the electrochemical activity of the molecule.

Moreover, searching for new electrochemically active groups as competitive alternative markers to ferrocene, we are studying PNA conjugates with pentacarbonyl Fischer-type carbene complexes of chromium and tungsten, evaluating the modulating effects of the metal nature and of the molecular structure. Both chromium and tungsten carbene complexes exhibit CV peaks of intensity comparable to the ferrocene ones, being chemically and electrochemically reversible in the chromium case, and irreversible in the tungsten one. Moreover, the redox peak potentials are widely modulable by changing the substituents and/or the metal of the carbene active group.

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Symposium 2 - Oral

Electroanalysis and Sensors

The Stability, Ion Switching and DNA Sensing Characteristics of Holliday Junctions

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The characteristics of DNA Holliday Junctions (HJ) as ion-controlled nanoscale biomolecular switches have been explored. The DNA Holliday structure is a junction of four double helices, with a unique topological element; a branch point discontinuity formed from hydrogen bonds (H-bonds) at the intersection of the component strands, giving four double helical arms. The junction structure is determined by strong electrostatic repulsion between backbone phosphate groups. In low ionic strength solutions, this repulsive Coulombic interaction favours maximum charge separation at the branch point, resulting in widely separated arms (an open conformation). The addition of cations above a critical concentration causes screening of this repulsion, inducing conformational change to a folded (closed) junction conformation.

Despite being structurally well characterized, there have been no systematic explorations of HJ structures with a view to assessing their performance as stable, electrochemically controllable nanoscale switches. The issues relevant in this context include critical ion concentration, sharpness of the ion-induced switching transition, reversibility and stability to HJ dissociation. This paper presents a systematic and quantitative survey of these characteristics for an HJ designed to switch predominantly between one open and one closed conformation. Ion-induced switching in solution has been detected optically using fluorescence resonance energy transfer (FRET) between donor and acceptor dye labels on different HJ arms. Ions of varying size and valence have been quantitatively assessed according to switching concentration and sharpness of the transition using this approach. HJ dissociation has also been assessed by using a combination of FRET and gel electrophoresis. This work shows that a short HJ construct (of typical arm length 8 base pairs) is prone to dissociation in the open conformation. This is consistent with previous observations for other HJs, and implies that electrostatic repulsion dominates interstrand H-bonding in this case. However, a longer HJ (of typical arm length 12 base pairs) does not dissociate and retains favourable ion switching characteristics. This stable HJ is shown to undergo both ion-induced switching between two distinct conformations and tailored DNA-biomolecule interactions; its potential for use as the biosensing component in novel electrochemically-controllable biosensor platforms for DNA detection through electrochemical ion generation will be discussed.

Symposium 2 - Oral

Electroanalysis and Sensors

Monitoring Enzyme Activity (Lactoperoxidase) in Raw Milk by Electrochemical Methods

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Peroxidases are enzymes that catalyze the reduction of peroxide, such as hydrogen peroxide by an electron donor (eq. 1). Determining the activity of enzymes can be a useful method for monitoring biological fluids. We have focused on lactoperoxidase (LPO), which is found in bovine milk and shows antimicrobial activity.

(eq. 1)
$$H_2O_2 + donor \xrightarrow{\quad Peroxidase \quad} H_2O + acceptor$$
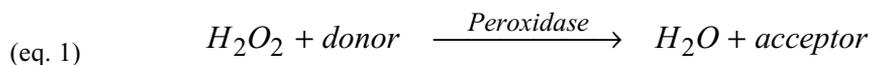
Determining the activity of an oxido-reductase enzyme, such as LPO, can be accomplished by following the changes of the concentration of the donor or acceptor as a function of time. Yet, milk is a complex medium, made of oil-in-water emulsion and contains tens of different substances. Therefore, many analytical methods, e.g., spectrophotometry, are not adequate for monitoring a concentration change of either the substrates or products. In spite of the drawbacks, spectrophotometry is still the method being used for determining LPO activity.

In our research we have used chronoamperometry and potentiometry as the principal techniques for measuring signals, which are proportional to the donor/acceptor concentration. Many donors such as pyrogallol, iodide, catechol, dihydroxyphenylacetic acid (dopac), dopamine, L-dopa and ferrocenemonocarboxylic acid, were tested. Eventually, the donor that showed the best properties for electrochemically monitoring LPO, has been the couple 1,4-benzoquinone/hydroquinone. We studied the system first in artificial solutions and then used also raw milk. Specifically, a rotating gold electrode was biased at a fixed potential to reduce the benzoquinone that was formed upon oxidation of hydroquinone by H_2O_2 catalyzed by LPO. The sensitivity of our method is so high that the raw milk had to be diluted by a factor of ca. 50. On the other hand, we have used also potentiometry for measuring the changes in the donor/acceptor concentrations. The advantages and disadvantages of our approach vs. the other approaches will be discussed.

Self-signalling Antibodies In Homogeneous Diagnostics

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Monoclonal antibodies are effective molecular probes that are reproducible, specific and cost effective, but their use outside of the laboratory is restricted by technical limitations. To address these constraints, the first self-signalling antibodies were described by Randle *et al.*, where specific antigen binding caused release of bound reporter from bispecific antibodies to generate a detectable signal [1]. The close proximity of two different antibody binding sites is thought to promote interaction between molecules recognized by these sites, generating a signal by molecular crowding, as illustrated in figure 1. The primary objective is to research an immuno-sensor capable of producing an immediate, real-time multi-parametric analysis of biological species.
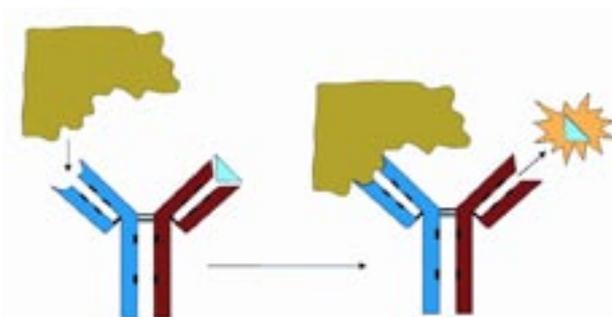
Figure 1 - Schematic of a bifunctional self-signalling antibody

Using the model of a self-signalling bifunctional antibody, several detection methods were investigated with the use of different labels. The chemiluminescent chemical luminol was investigated as a marker using both electrochemical methods and spectrometry. The use of CdSe nanoparticles as markers was investigated by taking advantage of tunable fluorescence and the fluorescence quenching effect of antibody-nanoparticle interaction. Nanoparticles were also used as a form of mass amplification to detect metal ions at very low concentrations using electrochemical preconcentration techniques.

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Symposium 2 - Oral

Electroanalysis and Sensors

Electroanalytical Studies of Protein Interactions

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Adsorption of proteins on the solid surface is the required initial and important step for many diverse applications such as biosensors, biochips, bioreactors, and other diagnostic procedures. Thus, several immobilization methods have been used for the construction of protein microarrays that can be used for such applications. The advantages of noncovalent physical adsorption are simple for the immobilization process and no conformation change after adsorption. However, this method suffers from little control of orientation and no quantitative information as well as it's instability. Therefore these disadvantages result in lower reproducibility, lower interaction and higher error rates. Self-assembled monolayer (SAM) based protein linking technologies, however, use electrostatic interactions or chemical covalent bonding between functional groups of SAM and proteins. They provide very stable and quantifiable amount of self-assembled molecules, but these strategies suffer from weak interactions or non-specificities.

In this study, we employed a specially designed calix[4]arene macromolecules containing crown-6 ring structure (ProLinker B from Proteogen Inc., Korea) which captures amine groups on protein surface. This linking method shows enhanced abilities in simple maner and orientation compared to conventional protein linking technologies based on self-assembled monolayer. Therefore the calix[4]crown-6 derivative was able to be used as a linker for the protein immobilization. It was directly self-assembled on gold electrodes of any type (flags or microarrays). Monolayer formation process as well as immobilization of various antibodies and antigens on the calix[4]crown-6 linker surface were monitored by electrochemical quartz crystal microbalance (EQCM).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were also employed to investigate the protein immobilizing process on the surface. With these electrodes, changes in electrochemical impedance before and after specific immunological bindings were compared, and these changes were interpreted to quantitative information on the specific interaction and the consequent changes in the electrode structure. Details of experimental procedures and electrochemical data will be discusses.

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Multi-protein, multi-layer assemblies on gold electrodes

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Biological redox processes in membrane architectures can serve as a model for the construction of sensors transfering an analytical signal into a measurable physical value or other (bio)artificial devices. Integration of redox proteins or enzymes into functionalities with definded structure and controlled preparation provides access to new functional biological nano-arrangements thus representing one appraoch to the development of analytical signal chains.

Here we report on artificial signal chains which are based on multilayer architectures formed by a self assembly process. The structures are based on a cytochrome c multilayer arrangement on gold electrodes ensuring full electroactivity of the immobilised redox protein. SERS measurements indicate a rather natural state of the heme environment. On top of this multilayer electrodes a second protein – xanthine oxidase (XOD) was immobilised using the same adsorption technique as for cytochrome c. However, in order to build multilayers of XOD another polyelectrolyte had to be used: polyethylenimine (PEI) instead of sulfonated polyanilline (PASA). The multilayer formation was followed by surface plasmon resonance. The resulting electrode was found to be sensitive for μmolar hypoxanthine concentrations i.e. an anlytical signal chain could be established with this two- protein, multi-layered arrangement. The influence of the layer architecture on the response behaviour was investigated in more detail. From the mechanistic point of view a mediation of the analyte conversion at the XOD by superoxide radicals towards the cytochrome c could be shown.

An alternative sytem was build up starting from cyt.c multilayers and immobilising laccase on top of this structure. Here PASA was used as polyelectrolyte building block throughout. Also here a signal chain from oxygen in solution via laccase and cytochrome c to the electrode could be established resulting in a reduction current in the presence of dissolved oxygen in solution. Within this structure a direct protein-protein communication is indicated.

Raman Spectroelectrochemical investigations of Thiol Redox Proteins in the Endoplasmic Reticulum.

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The endoplasmic reticulum (ER) is a specialised cellular organelle that manufactures secretory pathway proteins. Proteins made in the ER have a wide range of functions, and include hundreds of proteins important to health and disease such as the MHC transplantation antigens and the prion protein, PrP. All these proteins must fold and oxidise correctly in the ER if they are to function properly. Thus, the chemistry of protein oxidation (disulfide bond formation) in this compartment is of central importance to biology. Disulfide bond formation in the ER is mediated by at least two types of protein: the Protein Disulphide Isomerases (PDI's), which directly catalyse the formation of disulfides in a substrate protein, and the ERO proteins, which re-oxidise PDI after PDI has been reduced.

In this prestation we will discuss the redox processes in the ER present our investigatations on the effect of different hydrogen bonding environments on the ionisation of thiol proteins using a combination of electrochemistry and Raman spectroscopy.

Focused Microwaves in Electrochemistry

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In situ microwave activation of electrochemical processes can be achieved at electrodes placed into a microwave cavity [1]. In this presentation, effects and applications of microwave radiation for electron transfer in a wide range of solvent systems from aqueous solutions to organic solvents (DMSO, acetonitrile, DMF, formamide) and in an ionic liquid ($BMIM^+PF_6^-$) are reported. Three order of magnitude current increases and considerable temperature enhancements are observed and explained based on the interaction of microwaves with the liquid (electrolyte) and the physical properties of the liquids or solutions. Electrochemical processes in emulsions are shown to be facile in the presence of microwaves with novel applications in electroanalysis.
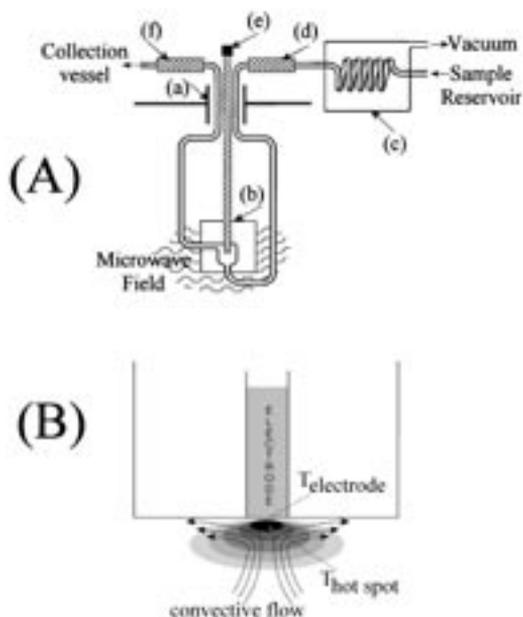
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Symposium 2 - Oral

Electroanalysis and Sensors

Symposium 2 - Oral

Electroanalysis and Sensors

Electrochemical Detection and Characterization of Commercial Globular Proteins

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On-line detection of serum proteins is of clinical relevance, in detecting leaks and biofouling in hemofiltration equipment, biofilm growth on prosthetic devices, or hemolysis within a prosthetic or therapeutic device. Presently detection of these processes involves inherently expensive or morbid laboratory processing of patient samples, radiographic techniques or surgical removal of the device.

We employed electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to detect and analyze micromolar concentrations of four commercially available globular proteins - Sweet Potato β-Amylase, Bovine Serum Albumin, Liver Alcohol Dehydrogenase, and Bovine Carbonic Anhydrase with molecular weights in the same range as serum proteins of clinical interest. These proteins were characterized in order to understand their electrochemical properties, study their interactions with each other and with the electrode material, simulate the proteins adsorption on solid state implanted devices, and develop cost effective and reliable methods to detect and quantify them. CV testing showed that identification and quantification of each of these proteins was possible through analysis of current changes at specific potentials on a voltammogram. Preliminary CV studies into the contamination of Bovine Serum Albumin with a microgram amount of one of the other three proteins illustrated that direct detection of the contaminant protein was possible. The impedance data was used to develop an equivalent circuit model for the protein solutions. The analysis of the impedance data demonstrated that with increase in relative concentration of proteins, the amount of electroactive proteins adsorption at the interface increases, leading to increase in surface charge density and capacitance, especially for lower molecular weight proteins. The values of Gibbs adsorption energy and adsorption coefficients for the four proteins were also determined from the EIS measurements. This information is important for demonstration of feasibility of constructing implantable electronic biosensors based on solid state electrodes. The strategy is scalable to the development of microfluidic systems and "smart" medical devices that will ultimately enable portable, cost-effective and rapid analysis of protein markers for point-of-care medical diagnostics leading to significant reductions in diagnostic ambiguity, unnecessary procedures, and patient distress.

Symposium 2 - Oral

Electroanalysis and Sensors

Microfluidic device for the manipulation and electrochemical analysis of single cellular activities

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An electrochemical microfluidic device was fabricated to characterize the activity of single cells. To avoid the contamination of silver ion, the reference electrode was positioned in the channel separated from the main channel with a working electrode. The microelectrode embedded in the detection area was used to manipulate single cells based on electrophoresis and detect oxygen generated from a single cyanobacterium *Microcystis viridis* by the photosynthesis.

Figure 1(A) shows the micrograph of the electrochemical microfluidic device. The device was composed of two parallel poly(dimethylsiloxane) (PDMS) microchannels. Pt working electrode (10 x 120 µm) and Pt counter electrode (20 x 120 µm) were positioned in one channel, and Ag/AgCl reference electrode (200 x 300 µm) was in the other. Two microchannels were electrochemically connected via small gaps constructed between the surface of Pt line (50 x 1000 µm) and PDMS. The detection channel was filled with 4.0 mM $K_4Fe(CN)_6$ and 0.1 M KCl as an electrolyte, and the channel for the reference electrode was saturated with KCl and AgCl. Electrochemical performance of the device was characterized by cyclic voltammetry (CV). Figure 1(B) shows a CV of 4.0 mM $Fe(CN)_6^{4-}$ using the device. The Pt line (showed in Fig. 1(A)) ensured the ionic movement between the channels for the working and reference electrodes and, as a result, giving reversible electrochemical response for $Fe(CN)_6^{4-/3-}$.

Figure 2 shows electrophoretic manipulation of a single *M. viridis* cell in the channel. The voltage of +2.0 V was applied to the working electrodes embedded in the detection area. *M. viridis* cell flowing in the main channel was easily captured and introduced into the detection area. In addition, when the opposite voltage was applied, the trapped cell was released to the main channel. We are currently carrying out the measurement of the photosynthetic activities of single *M. viridis* cells using this device.
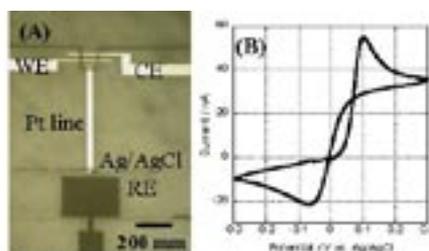

Figure 1(A) Micrograph of the electrochemical microfluidic device. (B) CV of 4.0 mM $Fe(CN)_6^{4-}$ using the device.
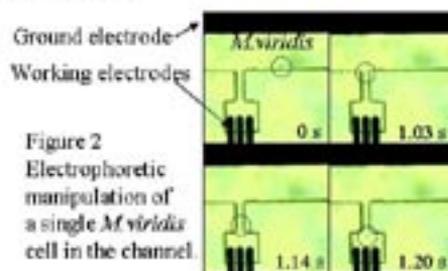

Figure 2 Electrophoretic manipulation of a single *M. viridis* cell in the channel.

Optimizing all-solid-state polyacrylate based ion-selective electrodes

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Ion-selective electrodes are established electroanalytical tools allowing rapid, relatively inexpensive and accurate determination of many analytes, including those important from a clinical or environmental point of view, in concentrations reaching trace levels[1]. An interesting modification leading to sensors that are easier to manufacture and handle is replacement of the internal solution with a conducting polymer transducer, leading to all-solid state sensors[2,3]. Other approaches look for membrane materials that can replace commonly used poly(vinyl chloride) (PVC). In this respect polyacrylates, characterized with lower diffusion coefficients compared to PVC are an interesting option [4], especially but not exclusively, selfplasticing ones and those that are obtained by photopolymerization.

The comparison of PVC and polyacrylate based sensors, in terms of achievable analytical parameters, especially detection limits and stability will be presented using the example of potassium and silver selective electrodes. Both coated wire and all-solid state conducting polymer based sensors were studied.

Despite the favourable parameters of polyacrylate based membranes sensors[5,6], further constructional improvements are of special interest. Thus, the composite ion-selective membranes containing poly(3,4ethylenedioxythiophene) polymer end capped with acrylate units (Oligotron ™) have been obtained. The membranes of this type can be conveniently photopolymerized directly on the substrate, yielding ion-selective electrodes characterized by Nernstian responses over wide activity ranges, stable (for a few months) low detection limits and favorable selectivity coefficients. The experimental results presented were obtained for calcium, lead and potassium sensors of composite membrane type.

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Enhanced Performance of Mesoporous SnO$_2$ Multilayered Film in Direct Electron Transfer of Hemoglobin

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Up to date, many efforts have been made to prepare desirable matrices to immobilize biomolecules, which is one of the most important factors and directly affecting the performance of a biosensor. Recently, nanoparticles as matrices to immobilize biomolecules, has become a hot subject in biosensing field for their unique properties such as size-dependent optical, electronic, and chemical properties. Among numerous nano-materials, mesoporous materials are more prospective, which have many attractive properties such as larger active surface area, higher mechanical, thermal and chemical stability, better adsorption capability and penetrability due to their regular structures, in comparison with those of non-mesoporous nanoparticles. These fascinating properties make them promising for assemblies as protective hosts to increase protein loading and facilitate the interfacial electron transfer. In our group, several mesoporous nanoparticles, such as mesoporous SnO$_2$, mesoporous tin phosphate, mesoporous carbon nanoparticles were used to fabricate uniform and stable multilayered films by layer-by-layer assembly method. Scanning electronic microscopy, UV-vis spectroscopy, electrochemical impedance spectroscopy and cyclic voltammetry measurements were employed to characterize these films growth. These films were further used to immobilize hemoglobin (Hb), and its direct electron transfer behaviours were observed on these mesoporous films modified electrodes. Serving mesoporous SnO$_2$ as a model, the multilayered films were grown on 4-aminobenzoic acid modified glassy carbon electrode by alternative adsorption of dextran sulfate (Dex) and mesoporous SnO$_2$ (meso-SnO$_2$). For comparison, the same-sized non-mesoporous SnO$_2$ nanoparticles (nonmeso-SnO$_2$) based films were also constructed. The electrochemical impedance spectra confirmed the electron transfer resistance increased linearly with the increase number of meso-SnO$_2$/Dex bilayers, which was smaller than that of corresponding nonmeso-SnO$_2$/Dex bilayers. Positions and intensity of Soret absorption spectra band showed that Hb retains its bioactivity in both films, and meso-SnO$_2$/Dex film exhibited improved immobilization ability of Hb in comparison with that of nonmeso-SnO$_2$/Dex film. Cyclic voltammograms of adsorbed Hb at meso-SnO$_2$/Dex film showed a good electrochemical behavior and excellent electrocatalysis to the reduction of O$_2$ and H$_2$O$_2$ at pH 7.0 PBS. The mesoporous film, made by the superposition of six layers, showed enhanced electron transfer efficiency by ca. 300% and electrocatalytic ability by ca. 350% to H$_2$O$_2$ and 440% to O$_2$ in comparison with that of nonmeso-SnO$_2$ film. Enhanced electron transfer efficiency and electrocatalytic ability were also obtained on the other mesoporous nanoparticles multilayered films and were concisely discussed.

Symposium 2 - Oral

Electroanalysis and Sensors

Liquid Chromatography with Electrochemical Detection as an Effective Method for Determining Femtomole Level Polyphenols in Human Blood

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Polyphenolic components such as catechins and quercetin in foods have become of interest in recent years for their preventive activities against cancer and coronary heart disease. Since their contents in human blood after tea ingestion are in extremely low levels, development of highly sensitive analytical method capable of detecting fmol (or below fmol) level analytes should be required to clarify the kinetic metabolism of polyphenols in human body.

. In this study, a high-performance liquid chromatography with electrochemical detection using a microbore ODS column (150 x 1.0 mm i.d.) was examined for determining catechins and quercetin in human blood following the ingestion of green tea. Water-methanol mixtures containing 0.5% phosphoric acid served as a mobile phase and made to flow at 25 μL/min. A 5 μL volume of a test solution prepared from human plasma was injected into the microbore column maintained at 40°C. Catechins or quercetin were detected at +0.6 or +0.5 V vs. Ag/AgCl, respectively, on a glassy carbon working electrode.

A chromatogram obtained for a mixture of 8 kinds of catechins gave well-separated peaks corresponding to the respective catechin. Each peak height was found to be linearly related to each catechin concentration ranging from 5 fmol~10 pmol/5 μL (r = 0.999, RSD = <0.86%). The time courses of the catechin concentrations in plasma after tea ingestion (340 mL of commercial canned green tea) could be followed by this method. Maximum levels were attained at 1~2 h later, and almost disappeared at 6 h following the tea ingestion.

Quercetin also gave a well-defined peak on a chromatogram and the time courses of the quercetin levels in plasma subsequent to the green tea ingestion showed similar features to those for catechins.

To obtain much higher sensitivity for the polyphenol determination, capillary liquid chromatography (150 x 0.2 mm i.d.) was further examined in this study. Detection limit as low as some tens of attomole levels could be attained by this method.

The present methods are characterized by far higher sensitivity compared to HPLC with a conventional column (several mm i.d.), as a result of the suppression of the diffusing dilution of the injected analytes in the separation column. Therefore, extremely low levels (fmol~amol levels) of catechins and quercetin in human plasma after the green tea ingestion were determined by the present methods. The time course measurements in such low levels cannot be followed by HPLC with a conventional column, and accordingly, the methods are expected as effective means for the metabolic studies of polyphenols in human body.

S2·P-1

Effect of electron transfer coefficients on the determination of standard potential

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In this study we investigated the effect of cathodic and anodic electron transfer coefficients on the determination of standard potentials from voltammograms. Current-potential curves were calculated for the quasi-reversible electron transfer reactions involving soluble-soluble and insoluble-soluble couples. The calculation was made based on the general Butler-Volmer kinetics. We have shown that standard potentials of redox couples can be determined by combination of voltammetry, semi-integration technique and Tafel plots.

We have verified that electron transfer coefficients have an important contribution in the calculation of standard potentials when the system involved insoluble-soluble couples. However, there is no significant influence in the case of soluble-soluble systems. Results were applied to determine the standard potentials of rhenium and hexacyanoferrate couples.

Symposium 2 - Poster

Electroanalysis and Sensors

Symposium 2 - Poster

Electroanalysis and Sensors

Characterization And Comparison Of Recessed Microdiscs Electrode Arrays (Rmeas) Assembled In Different Materials And Combinations

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The applications of microelectrodes arrays have been significantly increasing in recent years.

The reason is due to the development of microlithographic techniques for the fabrication of electrochemical devices. This technique was used to fabricate a range of recessed microdiscs electrode arrays (RMEAs) using Gold, Platinum and Carbon as materials composing the electrodes on Silicon wafers, analysing their behaviour.

In this work, as well, it was compared the RMEAs behaviour in the same materials with different centre-to-centre separation between active sites.

For the purpose of characterization of the electrochemical devices different techniques were used: cyclic voltammetry and chronoamperometry.

To analyse the RMEAs surface the scanning electrochemical microscopy (SECM) was applied.

Immobilization of Au nanoparticles on various terminated boron doped diamond electrode

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Boron-doped diamond (BDD) electrode has attractive electrochemical properties for electroanalysis such as wide potential window, low background current and high stability. Metal nanoparticles including Au nanoparticles or clusters have been widely investigated in the field of electrocatalysis. In this work, dependence of the adsorption properties of Au nanoparticle to BDD surfaces on the type of surface termination was investigated.

BDDs were obtained by microwave plasma-enhanced chemical vapor deposition (MPCVD) method. Oxidized BDD (O-BDD) surface was prepared by exposing the sample surface with UV light from a low-pressure mercury lamp in oxygen gas atmosphere. NH_2 and SH terminated BDD (NH_2- and SH-BDD, respectively) were made by simply immersing O-BDD in the solution containing the corresponding silane coupling agents. Au nanoparticles with an average diameter of 12 nm were prepared by a conventional citrate reduction method using $HAuCl_4$ aqueous solution. The BDDs were then immersed in Au nanoparticle solution to fabricate Au nanoparticle-modified BDDs.

SEM image shows that Au nanoparticles were not immobilized on O- BDDs after the immersion of the samples in the Au nanoparticle solution (Fig. 1a). On the other hand, homogeneous adsorption of dispersed Au nanoparticle was observed on NH_2- and SH-BDDs (Fig. 1b, 1c). Since the Au nanoparticle surface was adsorbed by negative citrate ions in this case, electrostatic interaction between the nanoparticle and NH_2-BDD surface should be attractive. In the case of SH-BDD, covalent Au-S bond formation is considered to be responsible for the adsorption. Therefore, site selective metal nanoparticle adsorption onto BDD surfaces should be realized by fabricating proper surface termination patterns.
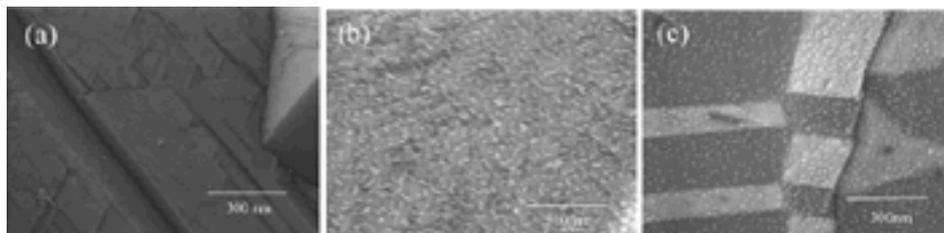

Fig.1 SEM images of Au nanoparticles on (a) O-BDD, (c) NH_2-BDD and (d) SH-BDD

Studies on electrochemical oxidation of azithromycin and Hemomycin ® at gold electrode in neutral electrolyte

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The aim of the present study was to examine the oxidative properties and an assay of azithromycin and Hemomycin® at a gold electrode in neutral electrolyte using cyclic linear sweep voltammetry. The maximum value of the current of the oxidation peak of pure azithromycin and azithromycin from Hemomycin® at 0.6 V vs. SCE in 0.05 M $NaHCO_3$ and in a mixture methanol - 0.05 M $NaHCO_3$ (1:1) at a scan rate of 50 mVs^{-1} is a linear function of the concentration in the range of 0.235 – 0.588 mg/cm^3. HPLC analysis of the bulk of electrolyte confirmed the data obtained by analysis of the values of the current peak concerning the concentration of antibiotic in the investigated concentration range.

The role of methanol, when present, is investigated. In the case of azithromycin, the presence of methanol leads to higher current peak values. However, in the case of Hemomycin®, methanol should be avoided because of its inhibiting influence on the qualitative and quantitative determination of azithromycin and on the azithromycin/lactose separation.

It can be concluded that a gold electrode can be successfully employed for the qualitative and quantitative electrochemical determination of azithromycin dihydrate and azithromycin from capsule (Hemomycin®) via its oxidation in the tested dosages.

This paper is dedicated to professor Aleksandar Despic+.

Symposium 2 - Poster

Electroanalysis and Sensors

Glass Electrode with Metallic Coating on the Inside

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First applicable glass electrodes with metallic coating on the inside, e.g. for determining the pH-value, exist since the 1920's [1]. The goal was, to connect the glass surface of pH glass by means of metals or alloys and to measure the electrochemical potential without an inner reference system of second kind in a liquid buffered salt solution. However, the measured potentials of the investigated metal layers, e.g. of silver, are non-reproducible, i.e. the absolute potential is different for a number of electrodes made by the same procedure.

The new approach is based on former investigations of our research groups [2]. In these studies planar electrochemical sensors were produced by electroless NiP-plating on dielectric substrates (glass, ceramic) by using ZnO as interface layer. The following electroless deposition of NiP was possible, when the ZnO-layer was activated in $PdCl_2$ solution. Because of the n-type semiconductor properties (E_g=3,4 eV) of zinc oxide for the coating of the glass electrode we used ZnO (3 in fig. 1) as interface layer for electroless NiP (4) deposition and as intermediary between the ionic conductor glass (1) and electron conductor NiP [3]. It may be represented by the following scheme:

NiP | ZnO | Glass ‖ Test solution   (1)

The design of the new glass electrode is given in Fig. 1. It consists of the pH glass membrane (1), the cylindrical shaft glass (2), the electric contact (5), the electrode head (6) and the internal space (7).

Spray pyrolysis were applied to deposit the thin zinc oxide layer on the inner glass surface using zinc acetate dehydrate in 2-Propanol, Ethanol or Methanol as precursor solution.
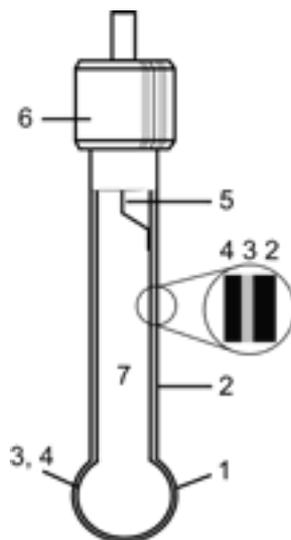
Fig. 1: Design of the new glass electrode

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Electrochemical evaluation of polymeric nanopatterned microelectrode arrays for biosensors application

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The application of lithographic techniques for the fabrication of microelectrode arrays results in an increasing interest in the realisation and application of micro-electrochemical sensors for environmental and clinical analysis. In the case of electrochemical biosensors, the main issues are the reduction of the non specific interactions of undesired molecules on the sensor surface that create background signal and the orientation of the biorecognition molecule (antibody, enzyme) to increase the biological reaction. A possible route to address theses issue is the coating of the electrode surface with polymeric layers with controlled chemical functionality. Moreover, such nano-structuring of the polymeric layer can improve the orientation capability of the biorecognition elements.

A possible strategy for depositing a uniform and stable polymeric layer onto a surface is the use of plasma enhanced chemical vapour deposition (PE-CVD). Furthermore, the combination of PE-CVD with colloidal lithography allows nano-patterning of the polymer to create nano-craters specifically designed to increase the orientation capability of the surface.

In this work an exhaustive investigation of the electrochemical behaviour of gold microelectrode arrays coated with Poly Ethylene Glycol (PEG), with Poly Acrylic Acid (PAA) and with PAA/PEG nano-craters was performed. The electrochemical response as a function of the probe ion charge has been investigated. Moreover the antifouling properties and selective binding properties of the polymer were tested by the use of Bovine Serum Albumin (BSA) as model protein which fouls sensor surfaces.

Symposium 2 - Poster

Electroanalysis and Sensors

Characterization of surface modifications using voltammetry combined with imaging SPR

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Self-assembled monolayers of alkanethiols, hydrogels and other surface modifications on metals play an important role as backbones in biosensors. The quality, blocking characteristics, and capacitance of such layers can be assessed by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy. Heterogeneous layers like patterned surfaces are, on the other hand, difficult to evaluate using traditional electrochemical methods, since there is no straightforward way of distinguishing the responses from different areas of the electrode. In this contribution we have combined CV with imaging Surface Plasmon Resonance (iSPR) to enable optical evaluation of electrochemical reactions taking place on, for example, thiol gradients and patterned electrodes.

Different surface modifications show different blocking properties towards electrochemical processes. For instance, shorter and less organized thiol monolayers are less able to block faradaic reactions, whereas thicker and more organized layers are more prone to prohibit such reactions. SPR is sensitive to species adsorbing on gold substrates, as well as changes in the refractive index in the vicinity of the surface. It is therefore possible to optically follow electrochemical processes during a voltammetric or amperometric experiment. The extent of the reactions is in this case not evaluated via the current, it is rather the change in refractive index induced by the electrochemical processes that is used to monitor the faradaic reactions. Since the iSPR instrument is equipped with a CCD-camera as detector, it is possible to indirectly use voltammetry to analyze for example patterned surfaces.

With our electrochemistry- and iSPR instrumentation, we are hence able to simultaneously perform surface imaging while controlling the potential of the electrode. To demonstrate the advantages with such instrumental setup, we patterned a gold electrode with alkanethiols (i.e. 100 micrometer wide lines of $HSC_{15}H_{30}COOH$), and filled the electrochemistry-iSPR cell with a redox couple dissolved in a supporting electrolyte. From the different intensities in the resulting SPR-image, it was possible to locate areas on the electrode where faradaic reactions took place, compared to parts of the surface covered with thiols. It was also found, compared to conventional SPR imaging, that the difference in refractive index induced by the electrochemical processes actually increased the contrast in the SPR image.

We plan to use this instrumental combination for investigations on the formation of for example gradients of thiols on surfaces, and for analysis of hydrogels formed by electrografting.

Symposium 2 - Poster

Electroanalysis and Sensors

In field preconcentration and voltammetric determination of heavy metals from different beverages using edta-modified magnetic silica microparticles

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Magnetised silica-based microparticles (average nominal diameter: 5 μm) with a high density of nanopores (30 nm) were modified with ethylenediaminetetraacetate as a complexing agent for heavy metals preconcentration and determination. Stripping voltammetry at a magnetized carbon paste electrode is described for the on-site analysis of cadmium, lead and copper from different beverages (wines, juices, spirit drinks) at low ppb levels (1 – 200 ppb). A detailed description of the construction of the set-up and systematic laboratory experiments to optimise its performance are reported. The electroanalytical procedure comprises two steps: the accumulation of the analyte under open-circuit conditions followed by a medium exchange, and the electrochemical detection of the preconcentrated species using square wave voltammetry.

Coupling the electrochemical sensor with a portable, commercially available, potentiostat can be performed for the decentralized analysis of trace metals in food, environmental and pharmaceutical samples.

Keywords: heavy metals, magnetic silica microparticles, square wave voltammetry

Scanning Electrochemical Microscopy (SECM) study of DNA biosensors based on chitosan carbon nanotubes

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The studies with DNA molecules are mainly devoted to study specific sequences or detection of DNA damage. In both cases the challenge for the analytical biosensor chemistry is to detect quantifiable differences between double strand DNA (dsDNA) and single strand DNA (ssDNA) or small variations in the signals that can correlates with a disruption of the DNA integrity. In this way the electrochemical DNA biosensors represent a rapid and sensitive alternative for these studies[1].

On the other hand, SECM is a versatile technique for extracting electron-transfer kinetics information and/or studying biological systems. The technique demonstrates to be very useful for controlling the preparation and the characterization of biosensors and sensor structures, as well as the optimization of their performance.

The aim of this work was to apply SECM imaging to study of DNA biosensors based on chitosan carbon nanotubes. A glassy carbon electrode was modified with chitosan or chitosan doped with carbon nanotubes previous to the adsorption of DNA.

The SECM feedback mode was selected to image each modified surfaces using ferrocene methanol in phosphate buffer pH 7.4 as redox mediator. It was found that chitosan modified GCE (red line voltammogram) has a reduced electroactive surface compare with a bare GCE (black line voltammogram), producing a decrease from 1.25 to 0.15 in the SECM normalized current. When chitosan is doped with CNT (blue line voltammogram) the conductivity enhances respect to GCE-CHIT electrode, but never reach the bare GCE conductivity and the surface is more irregular. Nevertheless, for DNA adsorption, CHIT/CNT film was the most suitable to obtain reproducible and sensitive signal of the guanine oxidation.
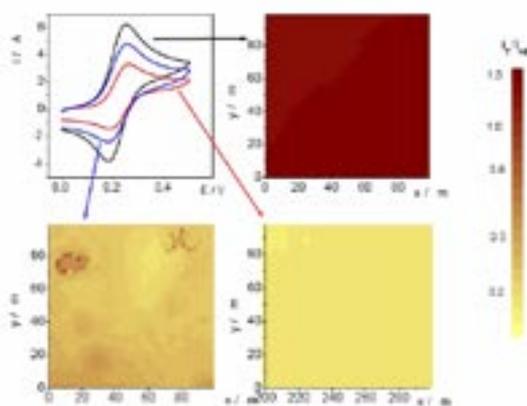
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Symposium 2 - Poster

Electroanalysis and Sensors

Symposium 2 - Poster

Electroanalysis and Sensors

Absorption, Diffusion, and Reactivity of Metal Complexes in Cellulose Membranes Immobilised at Electrode Surfaces and Immersed in Aqueous Buffer

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Cellulose is an excellent natural absorbent mainly due to amorphous cellulose regions in the nanocrystalline natural or regenerated fibrilar structure. It is shown here for the case of a cellulose membrane with variable thickness, cation and anion absorption and diffusion processes occur within cellulose. An electrochemical approach based on voltammetry is developed to investigate and quantify absorption and leaching processes as well as the chemical reactivity within cellulose.

The metal complexes $Fe(CN)_6^{3-}$, $Ru(NH_3)_6^{3+}$, and [Fe(III)(protoporphyrinato-IX)(H_2O)(OH)]$^{2-}$ or hemin are readily absorbed into cellulose in electrochemically active form. The ability of $Fe(CN)_6^{3-}$ and $Ru(NH_3)_6^{3+}$ to absorb appears to be due to "entrapment" without specific interaction with the amorphous cellulose. The relative rate of diffusion for these ions in cellulose is estimated to be a factor 4 slower when compared to the rate of diffusion in solution. In contrast, hemin diffuses much slower (by a factor 70) within the cellulose matrix. The slower diffusion is correlated with "specific" binding of the metal complex to sites within the amorphous cellulose. The immobilised hemin redox system may be employed in electroanalytical applications [1].
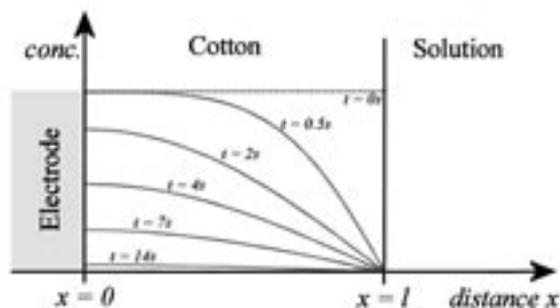
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Redox switching in polypyrrole films immersed in divalent anion solutions

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The electrochemical behavior and mass transport of polypyrrole films were investigated in divalent anion aqueous solutions of CO_3^{2-}, $C_2O_4^{2-}$, HPO_4^{2-} and SO_4^{2-} and compared to ClO_4^-. EQCM results are given for the first and the steady-state redox cycles. In divalent anion aqueous solutions, cation transport dominates during the charge compensation process. The hysteresis between anodic and cathodic waves of charge-potential responses is larger in divalent anion systems (SO_4^{2-}, $C_2O_4^{2-}$…) than in monovalent anion solutions (ClO_4^-). In both monovalent and divalent anion aqueous solutions the total film mass increase at the end of the first redox cycle is much larger than in subsequent cycles. The apparent molar masses of the mobile species reflects two factors. One is the larger amount of water that enters the film during oxidation in the first potential cycle than enters in steady state one. The other is the greater amount of cations that enter the film during oxidation than leave it during film reduction (for SO_4^{2-} and $C_2O_4^{2-}$ systems). With the exception of redox cycling in 0.1M Na_2SO_4 aqueous solution, no mass increase was observed in the steady-state redox cycle of divalent anion ($C_2O_4^{2-}$, HPO_4^{2-} and CO_3^{2-}) aqueous solutions. These are results are discussed in terms charge compensation by opposing fluxes of counter and co-ions, and non permselective behavior on the experiential time scale.

Symposium 2 - Poster

Electroanalysis and Sensors

Symposium 2 - Poster

Electroanalysis and Sensors

Amperometric detecion of H_2O_2 with covalent modified electrodes, using different generation of starburst pamam dendrimers and prussian blue

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Hydrogen peroxide (H_2O_2) is a useful compound for modern medicine, environmental control, and various branches of industry. This compound is the most valuable clinical marker for oxidative stress, recognized as one of the major risk factors in the progression of disease-related pathophysiological complications [1]. Prussian Blue (PB, $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$) on the other hand is an inorganic complex with a roomy crystal structure through which oxygen and hydrogen peroxide molecules can be transported. PB has been successfully adsorbed onto the surfaces of various electrode materials, such as gold, and has been found to be a good electrocatalyst for the electro-reduction of H_2O_2 under acidic (pH < 5) conditions [2]. Electrodes covalently modified with poly(amidoamine) (PAMAM) dendrimers (generation 4.0 and 3.5) have been found to support films of PB with improved surface coverage compared to PB-modified gold electrodes, which are prepared under acidic conditions. While, good stability at neutral pH values was obtained with PB tethered by PAMAM dendrimer, generation 4.0, no PB film forms on a bare gold electrode under these conditions. Since dendrimers resemble covalent micelles that provide well defined cavities, enhancing the hydrophobic nature of the electrode-solution interface can stabilize and concentrate a mediator such as PB, thus improving the sensitivity and selectivity of specific electrochemical reactions [3].

In this work, we make a comparison between the performance of covalent modified gold electrodes and naked gold electrodes with different generations of PAMAM dendrimers (2.0, 3.0 and 4.0) and PB films. The characterization of these electrodes is made with electrochemical (amperometry, voltammetry) and spectroscopical (SEM, EDX, FT-IR) techniques. Also, we present preliminary results on the electrocatalytic activity of the resulting films in neutral aqueous medium.

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Preconcentration and detection of cesium on metal-hexacyanoferrate modified electrodes

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Electrodeposits of Al_2O_3, $Ni\text{-}Al_2O_3$, $Cu\text{-}Al_2O_3$[1,2] and hexacyanoferrate[3], or electrodeposits of metal-hexacyanoferrate alone, on glassy carbon, Cu or Pt electrodes were employed to preconcentrate cesium[4] from low concentration solutions (0.1mM or lower). The electrochemical behavior of the various forms of the electroactive molecule was studied by cyclic voltammetry. The electrochemical behavior depended on the pH and the electrolytic media used. X-ray diffraction (DRX) and scanning electron microscopy (SEM) analyses revealed the composition and morphology of the composites. Energy dispersive X-ray spectrometry (EDS) showed the presence of Cs^+ attach to the composite films, when it was placed in solutions containing the metal ion, indicating an efficient preconcentration.

The electrochemical detection was developed following the generation of a mercury film on the previously preconcentrated metal ion, and then applying stripping voltammetry. The stripping analysis, thanks to the preconcentration procedure, could be followed in another media to protect the highly reactive cesium, once it was reduced at the electrode.

On the other hand, the Cs^+ attached to the film was transferred to another convenient solution, via electrolysis, to do the analysis by flame emission spectrometry. The results obtained on both techniques, stripping voltammetry and flame emission were compared. Detection limits, sensitivity and reproducibility were studied.

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Symposium 2 - Poster

Electroanalysis and Sensors

Dechlorination of organohalides by superreduced cyanocobalamin in bicontinuous microemulsion containing titanium(III) citrate

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This report is a study of the effectiveness of titanium(III) as reducing agent to transform the vitamin B_{12} (cyanocobalamin) to its superreduced form[1,2], B_{12s}, in a non-conventional electrolytic media, the bicontinuous microemulsion[3,4]. The micro-emulsion, a mixture of surfactant/oil/water, stabilized by a cosurfactant, usually an alcohol, is made bicontinuous by using the appropriate amount of each component. When the water (and the oil) in the mixture form a continuous phase, the conductivity of the solution is increased to a level that allows the development of electrochemical reactions, even without the supporting electrolyte. The superreduced vitamin, prepared by the action of titanium(III) in such media, was used to detoxify (dechlorinate) some organohalides.

The titanium(III) citrate in the microemulsion was obtained by electrochemical reduction of Ti(IV) citrate on glassy carbon or platinum electrodes. The starting material, titanium(IV) chloride, was stabilized with HCl and then treated to produce the titanium(IV) citrate. The microemulsion was a mixture (wt. %) of cetyltrimethyl-ammonium bromide (CTAB)/pentanol/tetradecane/water (17,5:35:12,5:35). The electrochemical behavior of both, the titanium citrate and the vitamin, was studied by cyclic voltammetry. When the microemulsion containing the protein and the reducing agent was electrolyzed in a N_2 purged and blanketed cell, the characteristic red color of the protein disappeared, indicating the transformation of the cyanocobalamin to its superreduced form, B_{12s}. The addition of organohalides such as benzyl chloride, dichloroethane, etc. regenerated the red color. Packed silica columns conveniently prepared to obtain an organic phase free from water an surfactant were used to permit, later on, the chromatographic studies. GC/MS analyses allowed to determine the products of the dechlorination process, while GC with electron capture detection allowed to detect and quantify the remaining organohalide when it was still present.

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Simultaneous Voltammetric Detection of Dopamine and Ascorbic Acid Using Film-Modified Electrodes

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A voltammetric method using a surfactant didodecyldimethylammonium bromide (DDAB) film-modified electrode was developed for simultaneous measurement of various combinations of neurotransmitters and ascorbic acid. The DDAB-modified film has the positive charge and neurotransmitters (dopamine, norepinephrine, and epinephrine) existed as the positively-charged species in the neutral solution whereas AA (ascorbic acid) as a negatively-charged one. Both the cyclic voltammetry (CV) and square wave voltammetry were used for the measurement of neurotransmitters by means of the DDAB/GC-modified electrode in phosphate buffer solution of pH=6.5. Well-separated voltammetric peaks were observed for dopamine and ascorbic acid at the DDAB/GC modified electrodes. The RRDE (rotating ring disk electrode) method was applied to study the redox reaction mechanism of dopamine and ascorbic acid. The DDAB/GC electrode resolved the voltammetric signals of the above analytes successfully. The electrochemical synthesis of polymer EDOT(3,4-Ethylenedioxy thiophene) modified electrodes from the aqueous acidic solution through cyclic voltammetry method. The EQCM method was used to study the polymer growth mechanism on the Au and Au/PEDOT-modified electrodes. The EQCM results confirmed that enhancement in the polymer peak currents of polymelatonin on the PEDOT-modified electrode was due to the hytrophobically entrapment of the monomer molecules within the PEDOT polymer film. The UV-vis spectroelectrochemical results confirmed the oxidation of indole ring of monomer. The electrochemical oxidations of ascorbic acid (AA) was performed on the GC and GC/PDEOT/polymelatonin film-modified electrodes. Based on the UV-vis and CV results, a mechanism for electropolymerization has been proposed. The poly(3,4-ethylenedioxythiophene)/ferricyanide (PEDOT/FCN) film was synthesized by a potentiostatic and also using potentiodynamic methods namely cyclic voltammetric and chronoamperometric techniques. The EQCM technique was used to study the mechanism of the incorporation of ferricyanide ions on the PEDOT film. The UV-vis absorption results too confirmed the presence of ferricyanide with the PEDOT film. The electrocatalytic oxidation of ascorbic acid was carried out and the diffusion coefficient of ascorbic acid was also estimated through the chronoamperometric and rotating disk electrode methods. This modified electrode was also used for the simultaneous determination of ascorbic acid and dopamine.

Symposium 2 - Poster

Electroanalysis and Sensors

A Disposable Amperometric Sensor for the Measurement of Secretory Immunoglobulin A in Sweat

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Secretory immunoglobulin A (sIgA) is widely used as a diagnostic tool for medical, physiological and for psychological purposes. Increased knowledge of the response of sIgA to physiological and psychological stimulation has resulted in increased interest in developing suitable in situ monitoring procedures.

Measurement of sIgA has predominately used saliva, serum and whole blood. The monitoring of sIgA in sweat is advantageous because it is non-invasive and the sampling and analysis can occur over a wide range of timescales without interfering with normal activities. The principle technique for sIgA analysis has been the enzyme-linked immunosorbant assay (ELISA). The purpose of the present study is to adapt and develop an ELISA system for use with polyvinylidene fluoride sweat patches with electrochemical detection. The proposed method uses an indirect approach of incubating sweat patch samples with anti-human sIgA conjugated to horse-radish peroxidase. The unbound conjugate can then be detected with the addition of 3,3',5,5'-tetramethylbenzidine dihydrochloride (TMB) followed by an acidic stop solution. TMB is a chromogenic substrate, but may also be detected by chronoamperometric measurements with a screen-printed carbon electrode (SPCE) at a potential of +0.05V before or after adding the stop solution. This paper describes the results of these studies and their experimental application to human sweat.

S2·P-17

Symposium 2 - Poster

Electroanalysis and Sensors

Studies of oxidation behaviors of electrodeposited cdte films on glasscarbon electrode in ammonia-chloride electrolytes

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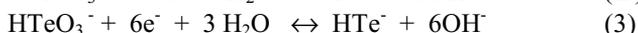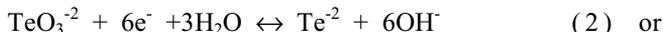*M_dergacheva@nursat.kz*

Electrochemical reactions with participation of anions, for example, such as TeO_3^{2-} proceed only at presence of protons donors in electrolyte. Thus previous chemical reaction of connection of a proton to anion is executed and only then electrochemical reduction of anion with transfer of electron is carried out. The quantity of proton donors at the electrode layer is defined by the nature of an electrode, the composition of electrolyte, the participation of surface-active substances in this processes.

In this work the mechanism of formation of CdTe compound is proposed on the basis of the voltammogram curves analysis of oxidation electrodeposited CdTe films in ammonia-chloride buffer electrolytes.

The two Faraday maximum of the current at potentials close to -0,95 V and -1,1 V are observed in the processes of electroreduction of TeO_3^{-2}($HTeO_3^-$) and $Cd(NH_3)_4^{-2}$ anions from ammonia-chloride buffer electrolytes with pH=8,4 ÷ 10,0, buffer capacity π= 0,4 and ionic force μ= 2,0 on glasscarbon electrode. The first maximum corresponds to electroreduction of cadmium ions on reaction:

$$Cd(NH_3)_4^{+2} + 2e^- \leftrightarrow Cd(0) + 4NH_3 \qquad (1)$$
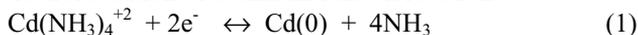
The second - to electroreduction of tellurium anions on reaction:

$$TeO_3^{-2} + 6e^- + 3H_2O \leftrightarrow Te^{-2} + 6OH^- \qquad (2) \quad \text{or}$$
$$HTeO_3^- + 6e^- + 3H_2O \leftrightarrow HTe^- + 6OH^- \qquad (3)$$

Interaction of cadmium complex cathions with tellurides-ions results to formation of CdTe compound according to reaction (4).

$$Cd(NH_3)_4^{+2} + Te^{-2} = \leftrightarrow CdTe + 4NH_3 \qquad (4)$$
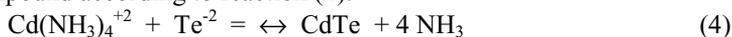
It is observed two anodic maximums of current at - 0,1 V and + 0,13 V on the potential sweep reversal. It is established that anodic maximum at E = - 0,1 V is answered with reaction (5):

$$CdTe - 2e^- + 4NH_3 \leftrightarrow Cd(NH_3)_4^{+2} + Te(0) \qquad (5)$$
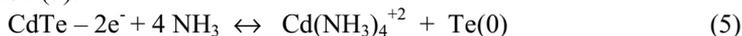
The anodic maximum at E_{ox}= +0,13 V is answered with reaction (6):

$$Te(0) + 6OH^- - 4e^- \leftrightarrow TeO_3^{-2} + 3H_2O \qquad (6)$$

The analysis of ratio change of anodic maximums currents, which is determined by contribution of CdTe and Te(0), formed on a surface of an electrode and realization of reaction (7), is carry out at different concentration of cadmium ions in electrolyte.

$$Te(IV) + 2Te^{2-} \rightarrow 3Te(0) \qquad (7)$$

Electrochemical behaviour of se (iv) on glass carbon electrode modified by nano- γ al$_2$o$_3$

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The pre-treatment of glass-carbon electrode by ϒ-Al$_2$O$_3$ powder polish leads to prepare the electrode surface with rise sensitive to Se (IV)-ions. The preservation of nanoparticle of ϒ-Al$_2$O$_3$ is observed on the surface of glass-carbon electrode. This nanoparticle did not delete from electrode surface after repeated washing by double distilled water.

The investigation of electrode surface morphology for material "glass-carbon-2000" and "carbon-sitall" was made by X-ray diffraction, scanning electron microscopy and microprobe analyses. The nanoparticle of ϒ-Al$_2$O$_3$ with size (5-20) nm was found on the electrodes surface. The glass-carbon electrode modified by nano-ϒ-Al$_2$O$_3$ was used for investigation of electrochemical behavior of Se(IV) ions in supporting electrolyte 0,45M Na$_2$SO$_4$ + 0,05M H$_2$SO$_4$ (pH=1,6) after removal of molecular O$_2$. This electrode had a high activity to adsorption of Se(IV) ions. This is allowed to receive two current maximum on the cathode voltamogramms. The first wave beginning from E$_1$= +0,075V (Ag/AgCl) relates to reaction (1)

$$HSeO_3^- + 4e^- + 5H^+ \quad \rightarrow \quad Se(0) + 3\,H_2O \qquad (1)$$
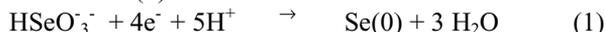
The second peak current (E$_2$ = -0,55V) corresponded to reduction of selenium to selenide ions on reaction (2).

$$Se(0) + 2e^- \leftrightarrow Se^{-2} \qquad (2)$$
$$Se(0) + e^- + H^+ \leftrightarrow HSe^{-1} \qquad (3)$$
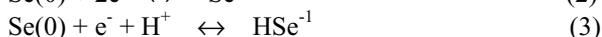
This peak was sharper than single peak on usual carbon electrode which corresponded to reaction (4) on data /1/.

$$HSeO_3^- + 7\,H^+ + 6\,e^- \leftrightarrow H_2Se + 3\,H_2O \qquad (4)$$
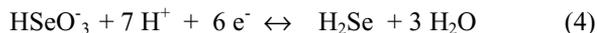
It was showed also that peak current of oxidation Se(0) (E= +1,2V) was more sharp and had more high current then on usual carbon electrode and corresponded reaction(5)

$$Se(0) + 3\,H_2O - 4e^- \rightarrow HSeO_3^- + 5\,H^+ \qquad (5)$$

It was confirmed that reactions (1) and (2) have been carried out on modified of nano ϒ-Al$_2$O$_3$ glass-carbon electrode with using analysis of oxidation current of Se(0) from electrode surface.

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Simultaneous Determination of Trace Amounts of Vanadium and Molybdenum in Foodstuff AND METALS Using Adsorptive Cathodic Stripping Voltammetry

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Vanadium and molybdenum have dual physiological properties. They are essential trace elements at low concentrations and are toxic at high concentrations. In biological systems, molybdenum is an essential constituent of enzymes which catalyze redox reactions, e.g. oxidation of aldehydes, xanthine and other purines [1], and reduction of nitrates and molecular nitrogen [2]. Vanadium is used in industrial process including the production of special steels, temperature resistant alloys, glass industry, manufacture of pigments, paints and catalyst. Vanadium compounds released in large quantities, mainly by burning fossil fuels and also from various industrial processes, and are precipitated on the soil drained by rain and groundwater and may be directly adsorbed by plants. The concentration of vanadium is used to assess the extent of pollution originating from fossil fuel combustion. The background vanadium and molybdenum concentration in natural water is in the order of $\Box$g l^{-1} and this can be even lower in fresh water. A new procedure is presented for the simultaneous determination of ultra trace amounts of vanadium and molybdenum based on adsorptive cathodic stripping voltammetry (AdCSV). Adsorptive accumulation of the V(V) and/or Mo(VI) with chromoxane cyanine R (CCR) onto a hanging mercury drop electrode, followed by reduction of the adsorbed species using differential pulse voltammetry method. Optimized conditions include a 60 s adsorption period at -0.10 V, 8.0 $\Box$M of CCR in 0.1 M acetate buffer, pH 3.6, and a voltammetric scan using differential pulse mode with 25 mVs^{-1} scan rate. Detection limits of 0.1 and 0.08 ng ml^{-1} were achieved for V(V) and Mo(VI), respectively which can be lowered down to 0.06 and 0.04 ng ml^{-1} by extending the adsorption time to 180 s. The reduction currents are linear in the range of 0.3-24.0 and 0.1-30.0 ng ml^{-1} for V(V) and Mo(VI), respectively. The relative standard deviation for 10 replicates determination of 4.0 ng ml^{-1} V(V) and Mo(VI) were 1.8 and 1.1%, respectively. The proposed method applied for the determination of vanadium and molybdenum in river water, tap water, well water, plant foodstuff such as cucumber, tomato, carrot, metals and tea.

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Symposium 2 - Poster

Electroanalysis and Sensors

Characterization of electrodeposited organo-silica thin films by scanning electrochemical microscopy

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Hybrid organic-inorganic silica-based materials have attracted considerable attention from the electrochemistry community during these last years [1]. Indeed, they combine the attractive properties of silica materials (high porosity, high specific surface area, possible organization at the mesoscopic level) and the specific reactivity of organic groups that can be chemically attached to the silica backbone.

The implication of insulating silica-based materials in electrochemistry requires however an intimate contact with an electrode material. Such a chemically modified electrode can be achieved, for example, by the deposition of silica-based thin films on solid electrode surfaces. In this respect, our group has developed an original approach for electro-assisted generation of thiol-functionalized silica films on gold [2]. The synthetic procedure combines the self-assembled monolayers (SAM) technology, the sol-gel process and the electrochemically-induced deposition method.

In practice, film formation occurs as followed: (1) the formation of a SAM of merc aptopropyltrimethoxysilane on gold; (2) the transfer of the pretreated electrode in a silica sol containing the hydrolyzed precursors: tetraethoxysilane and, e.g., mercapto propyltrimethoxysilane (but the method has been extended to other organosilane); (3) the application of a cathodic potential to increase pH locally at the electrode/solution interface and to induce the co-condensation of the precursors [3]. This led to well-adherent thiol-functionalized silica thin films on the gold surface.

In the present study, several physico-chemical techniques have been involved to characterize the films growth, morphology and permeability. Electrochemical Quartz Microbalance (EQCM) allowed the monitoring of mass changes at the electrode surface during electrodeposition. This information has been correlated to film thicknesses as measured with Atomic Force Microscopy (AFM). A particular attention has been given to the influence of electrolysis time on the film characteristics.

Finally electrochemical methods, Cyclic Voltammetry (CV) and Scanning ElectroChemical Microscopy (SECM), have been involved to characterize the different films. SECM has been used in the feedback mode using molecular probes displaying various charges and sizes. The high sensitivity of the SECM allows then to observe important variation in the feedback signal that can be related to modification of the apparent electron transfer rate constant [4].

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Quartz crystal microbalance determination of trace metal ions

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We describe the development of a combined acoustic wave and electrochemical sensor for detection of trace metal ions from aqueous solution, based on the formation of self-assembled monolayer (SAM) films functionalised with chelating groups. Gold electrodes on 10 MHz AT-cut piezoelectric quartz crystal resonators were modified with meso-2,3-dimercaptosuccinic acid (DMSA). Measurements of resonant frequency for bare and modified electrodes, both immersed and emersed, were used to determine the extent of ligand immobilisation; since the films are extremely thin, the frequency response can be interpreted in purely gravimetric terms using the Sauerbrey equation. The quality and integrity of the SAM films were assessed via cyclic voltammetric measurements of $[Fe(CN)_6]^{3-/4-}$ redox chemistry.

SAM-functionalised electrodes were exposed to solutions of metal ions in order to assess the ability of the surface-bound ligand to complex the metal ions. The target metal species, Pb(II), Cd(II) and Cu(II), were selected on the basis of their environmental relevance. Initially, single metal ion solutions were used and the extent of metal complexation was determined (via the QCM frequency change) as a function of concentration. Factors associated with solvent and solvation were explored via parallel sets of measurements under immersed and emersed conditions. The variation of surface concentration with solution concentration was evaluated using a range of isotherms - Langmuir, Temkin, Freundlich, Frumkin, El-Awady and Flory-Huggins – based on different physical models. The failure of the Langmuir isotherm indicates the presence of site-site interactions; the Frumkin isotherm best fitted the experimental data. Selectivity for different metal ions was assessed by comparing the binding constants derived from the isotherms for single metal ion solutions and by competitive binding experiments using mixed metal ion solutions.

The extent of metal ion uptake was also evaluated coulometrically by integration of voltammetric responses of electrodes exposed to metal ion solution and transferred to metal-free background electrolyte. Interestingly, the extent to which the metal species are retained on the surface during redox cycling varies for different metals. The combination of SAM selectivity and QCM sensitivity provides a potentially useful metal ion sensor in the nanomolar to micromolar range. Supporting XPS measurements provide unequivocal evidence of the presence of surface-bound metal(s), together with metal speciation (following various electrochemical manipulations), metal: ligand stoichiometry, and selectivity between metal ions in competitive binding experiments.

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Electroanalysis and Sensors

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Electroanalysis and Sensors

Spectroelectrochemical study on the deposition of bismuth films onto glassy carbon electrodes

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Bismuth film electrodes (BiFEs) intruduced recently [1] offer an attractive stripping voltammetric performance, thus representing a promising alternative to traditional electrodes based on controversial mercury. The bismuth film electrode can be prepared by *in-situ* or *ex-situ* electroplating of a thin layer of bismuth onto a solid electrode, depending on the analytical measurement required. The control of the bismuth deposits plays a major role in the resultant stripping performance and glassy carbon electrodes (GCEs) in the disc configuration have been the most widely used support for the bismuth films.

In this work, the processes of both the electrodeposition and the electrodissolution of bismuth onto GCEs are studied with the aid of spectroelectrochemistry. Changes in reflectance occur concomitantly with the reduction of the metal on the electrode surface. Figures below show the current and the reflectance changes with potential of a bismuth film deposited during 60 seconds on the GCE. The results have shown that different information on the coating process is obtained from the electrochemical and spectroscopic signal.
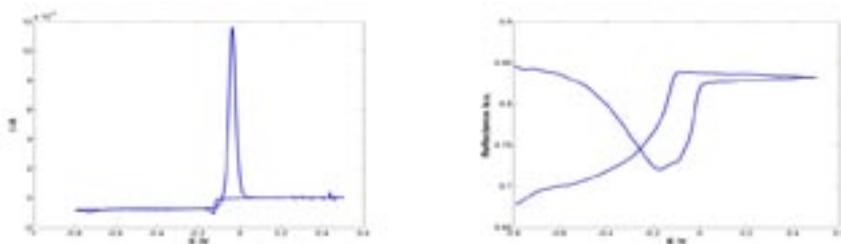
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Electrochemical behaviour of glutamate at a gold electrode

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Glutamic acid, the 2-aminopentanedioic acid, is one of the twenty amino acids present in human proteins. Glutamate is one of the most abundant excitatory neurotransmitters in the brain, and it has been implicated in the pathology of neurological and psychological diseases. There are evidences linking abnormalities in endogenous glutamate metabolism with certain diseases, such as Alzheimer's, Huntington's Chorea, and Amyotrophic lateral sclerosis.

Glutamic acid, as well as their sodium, potassium, calcium, magnesium and ammonium salts, has been added to foods on behalf of its flavour enhancer properties. In fact, this is an ancient procedure since the monosodium salt of glutamate has been used for thousands of years in Asia as a flavour enhancer of foodstuffs. Glutamate is however a non essential nutrient in terms of human diet because the body can manufacture it.

Thus, and for food safety purposes, it is important to monitor glutamate levels in food and biological fluids. Thus, the development of a simple and sensitive assay for measuring l-glutamate is of importance to clinical diagnosis and food industries.

Several methods have been reported for the determination of glutamate. These include spectrophotometric and fluorometric methods, enzyme biosensors, and high performance liquid chromatography methods. In general, these methods have drawbacks with either an undesirable sensitivity, or with procedures difficult to perform in a high-throughput format. As an alternative to previously reported methods, electrochemical ones present major advantages in terms of rapidity and simplicity. They provide accurate and precise results with consumption of reagents and emissions of low levels of effluents.

This work reports a detailed study of the electrochemical behaviour of glutamate at a gold electrode. Different voltammetric techniques have been regarded, namely, cyclic, square wave and differential pulse. The effect of the supporting electrolyte, the pH and the potential has been investigated at various scan rates to elucidate the reaction mechanism. Results obtained point out the possibility of application of the electrochemical method to the analysis of glutamate among complex sample matrices.

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Electroanalysis and Sensors

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Modelling amperometric enzyme electrodes in layer-by-layer self-assembled enzyme and redox polyelectrolytes

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It would be of great advantage that the response of an amperometric biosensor could be predicted without the need for device calibration. In this sense modelling the response of amperometric enzyme electrodes would be useful in the design and optimisation of their performance [1]. For integrated reagentless amperometric enzyme electrodes with the enzyme and the redox mediator both entrapped within the film, the interplay between diffusion and kinetics results in highly non linear equations for which there are no closed form analytical solutions. However, approximate solutions for selected limiting cases have been obtained [2] and methods for digital simulation are available.

Supramolecular organized enzyme multilayers composed of glucose oxidase (GOx) and $Os(byp)_2pyClCH_2NH$-tethered to the backbone of poly(allyl-amine) (PAH-Os) have been built by alternate electrostatic adsorption of the enzyme (anion) and the redox polyelectrolyte (cation) layer-by-layer [3]. The method allows fine control of the layer thickness and film structure by adjusting the adsorption solution pH and ionic strength [4]. Both cyclic voltammetry and chronopotentiometry have been employed to determine the catalytic current dependence on the experimental variables.

In work reported here, the amperometric response of Au electrodes modified by enzyme multilayers and immersed in solutions of β-D-glucose under potential control has been studied as a function of glucose concentration, ellipsometric thickness of the multilayer, enzyme surface concentration, osmium redox charge in the films and the nature of the topmost layer (GOx or PAH-Os). The experimental data have been compared with results from digital simulation as reported by Pratt [2] for selected values of the kinetic parameters, diffusion coeficients and surface concentration. The transition between different cases in the case diagram [2], for which analytical equations have been derived, is analysed by careful design of the experiment. For instance by change of the enzyme catalytic layer thickness. The approximations in the limiting cases have been also validated by analysis of the simulated concentration profiles. Initial values of the kinetic parameters were obtained from experiments with the $Os(bpy)_2pyClCOOH$ and glucose in solution by comparison with digital simulation and selected cases in the respective kinetic case diagram [5].

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Electrochemical determination of srb enzymatic activity

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In the latest few years there is an increased interest in the research on electrodes modified by biological layers. We have tried to construct such electrodes. We used glassy carbon, pyrolitic and pencil graphite electrodes.These electrodes were covered with biological compound – living bacterial cells. Used bacteria was mixture of SRB – sulfate reducing bacteria – *desulfovibrio* and *desulfotomaculum* in ratio 1:1. We tried to estimate their enzymatic activity – desulfurication.
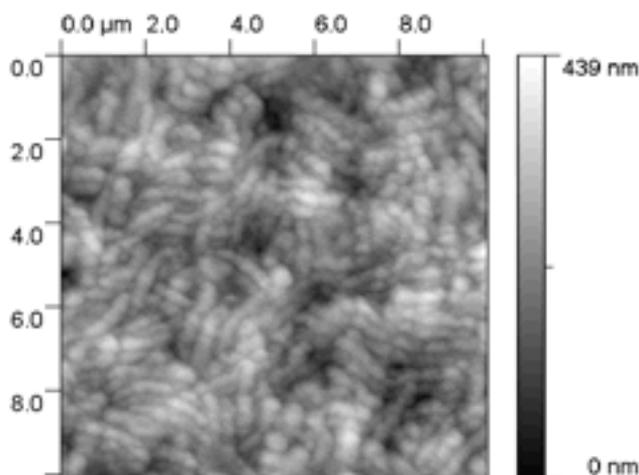
An AFM picture of used SRB layer deposed on glassy carbon electrode

This process is strictly anaerobous and serve for these bacteria as source of nutrition. For measurements was used PBS (phosphate buffer solution at pH=7) as electrolyte. The nitrogen atmosphere was maintenant to keep anaerobicity. We applied the cyclic voltametry to determine the response of bacteia modified electrodes.

Symposium 2 - Poster

Electroanalysis and Sensors

A Quartz Crystal Microbalance Operating under Laminar Flow for Adsorption Studies

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A QCM is a converse piezeoeletric mass sensor. It has been discovered that when immersed in liquids the quartz oscillations are similar to those in gases although strongly damped due to the additional mass of the vibrating liquid. In an electrochemical system the Sauerbrey derived QCM mass results can be verified by comparison with the Faraday mass. At present electrochemical QCM has been successfully combined with defined hydrodynamics *via* the rotating disk electrode and the wall jet electrode [1]. However EQCM has not yet been employed with defined laminar flow in a channel electrode.

This poster deals with the commissioning and characterisation of a QCM electrode mounted in a cell through which the fluid flow was laminar and controlled. The deposition of copper onto gold electrodes was used to verify cell performance. The Sauerbrey derived mass was compared with the Faraday derived mass to determine the experimental sensitivity factor. It has been found that the limiting current and the rate of mass deposition are proportional to the flow rate to the third indicating that an EQCM flow cell has been fabricated for which the Levich equation is valid.
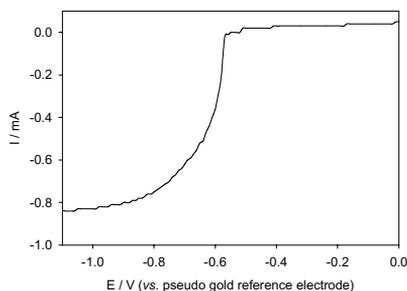
Figure 1: The current *vs.* voltage plot for the deposition of copper onto a gold electrode from a 10 mM $CuSO_4$, 0.1 M H_2SO_4 aqueous solution at a flow rate of 0.034 ml/s.
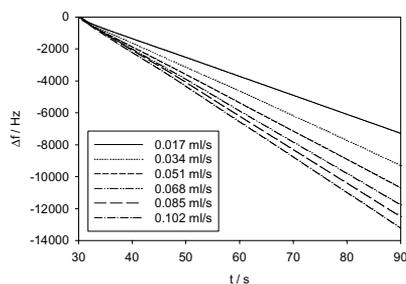

Figure 2: The change in resonant frequency for the deposition of copper onto gold from a 10 mM $CuSO_4$, 0.1 M H_2SO_4 aqueous solution at the indicated flow rates at an applied potential of -0.9 V *vs.* the gold pseudo reference electrode.

The device was employed to study the deposition and dissolution of copper as a function of the electrolyte composition and the oxygen content.

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The Effects of Temperature on pH Measurement

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Some of the effects of temperature on pH measurement have been described or alluded to in both instrument manufacturers instructions and independent scientific literature. Some of these have been presented in a very theoretical manner and thus have been of limited practical value, others have been described adequately from a practical perspective. However a comprehensive classification of the principal effects of temperature on pH with practical remedial actions to correct, reduce or eliminate these errors, has never previously been reported. This paper presents for the first time a clear classification of the practical effects of temperature on pH. It provides a definite set of guidelines on how the different errors can be reduced or eliminated thus giving the user greater confidence in the result of their pH measurements.

Symposium 2 - Poster

Electroanalysis and Sensors

Care, Maintenance and Fault Diagnosis for pH Electrodes

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Analysts frequently encounter pH measurement problems caused by poor electrode performance. Diagnosis and rectification of these problems can be time consuming, leading to poor analytical results and inefficient use of analysts time. The diagnosis of many individual pH electrode faults have previously been published but a complete, straightforward regime that diagnoses all common electrode faults has never been reported in the scientific literature. This paper presents a unique, comprehensive, easy to follow regime which can be used to identify and rectify electrode faults. As many common faults can be prevented through adequate care and maintenance the paper also describes the correct care and maintenance steps required to prevent the occurrence of these problems. Adopting the guidance given in this paper will allow analysts to achieve high quality pH measurements and reduced incidence of poor performance of their pH measurement system.

NADH electro-oxidation on carbon paste electrodes modified with adenine derivatives adsorbed on zirconium phosphate

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Immobilization of different mediators on zirconium phosphate (ZP) showed that, at neutral pH, their $E^{0'}$ values shifted anodically in comparison with the $E^{0'}$ values observed for free mediators or when they are adsorbed on graphite. Additionally, when the pH of the electrolyte solution was varied in a relatively wide pH range (from 1 to 9), the $E^{0'}$ values of the adsorbed mediator on ZP remained constant [1-3].

Continuing our previous work in this direction [2, 3], the electrochemical and electrocatalytic activities toward NADH oxidation of two adenine derivatives [4], adenosine and adenosine-5'-monophosphate (AMP), adsorbed on ZP and entrapped in carbon paste were investigated and compared. Using cyclic voltammetric measurements, the electrochemical behaviour of these modified electrodes was studied at different experimental conditions (pH and potential scan rates). A clear pH independence of the $E^{0'}$ value was observed (see figure). Using the Koutecky-Levich approach, the kinetic parameters corresponding to NADH oxidation process were evaluated from rotating disk electrode measurements, performed at different NADH concentrations and pH values.

pH dependence of the E°' values for ZP-modified CPEs: □ adenosine; △ AMP. Experimental conditions: starting potential, -200 mV *vs.* Ag|AgCl/KCl$_{sat}$; potential scan rate, 50 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer.

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Electroanalysis and Sensors

Electroanalysis of Dopamine using hydrophobically modified poly(N-vinyl carbazole) coated electrodes

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Organic semiconductor materials, having film forming properties are known to be used in different applications such as displays [1], organic transistors [2], photovoltaic cells[3], electrophotographic photoreceptors [4]. Modified Polymer Electrodes(MPEs), such as carbazole, aniline, thiophene have received extensive interest in the detection of analytes because of their selectivities, sensitivities, homogeneities in the electrochemical deposition, strong attachment to electrode surface and high chemical stability in air [5].Unfortunately, poly(N-vinyl carbazole) (PNVCz) films have poor mechanical properties, so its copolymers have been synthesized to solve this problem and improve its reversibility and sensitivity as a sensor electrode.

The synthesis, solution properties and electrochemical behaviors of poly (N-vinylcarbazole) (PNVCz), poly (itaconic acid) (PIA), poly (N-isopropyl acrylamide) (PNIPAAm) and their copolymers have been studied by various research groups [6-7].

Catecholamines including dopamine are an important class of neurotransmitters that are involved in a variety of central nervous system functions. Although chemical methods have been developed, there is not an appropriate chemosensor electrode for dopamine detection [8]

In this study, electroanalysis of dopamine at pH=7 was examined. MPEs used were prepared by electrooxidation of P(NVCz-co-NIPAAm), P(NVCz-co-IA) and P(NVCZ-co-monoester of IA). Polymer films having electroactive, ionic and hydrophobic properties were deposited by electrooxidation in CH_2Cl_2 containing 0.1 M tetra butylammonium teraflouroborate on Pt electrode.

The cyclic voltammetric curves of dopamine in phosphate buffer (pH=7.0) at these modified electrodes showed an anodic peak and a corresponding cathodic peak (Figure 1.a,b,c). From the comparison of the differences between the peak potentials of anodic and cathodic peaks of hydrophobically modified PNVCz electrodes, it can be seen that in the case of P(NVCz-co-NIPAAm 10.0 %), P(NVCz-co-monoctyl itaconate, 5.0 %) and P(NVCz-co-monocetyl itaconate, 5.0 %) electrodes, reversibility of polymer coated electrodes increased with increasing length of alkyl group.

It is known that Ascorbic acid (AA), which found in brain fluid, interferes with dopamine during the voltammetric analysis [9]. The effect of electrode composition on detection limits of dopamine in the presence of ascorbic acid will be examined.

(a)   (b)   (c)
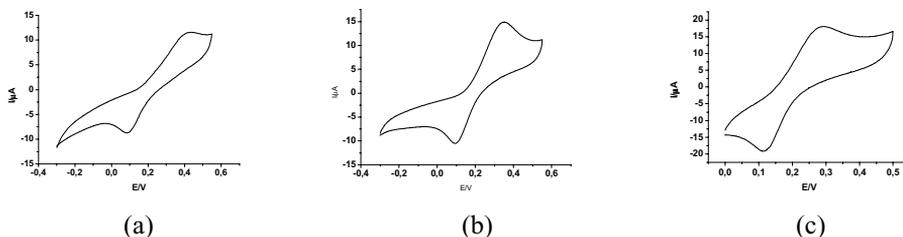
Figure 1. CV of 9 mM dopamine (DA) on **a)** P(NVCz) and **b)** P(NVCz-co-NIPAAm 10.0 %), **c)** P(NVCz-co-monooctyl itaconate, 5.0 %) modified electrodes at pH=7

Microbial Biosensor Based on Carbon Nanotube (CNT) Modified Electrode

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Carbon nanotube (CNT) received considerable attention as a new nanomaterial due to its unique mechanical, chemical and electronic properties. CNT has a high surface area, an ability to accumulate analyte and more importantly because of its electrocatalytic activity CNT has become very attractive for electrochemical and bioelectrochemical sensing [1]. Microbial cells are very promising for amperometric biosensor construction because of several advantages: the enzyme does not need to be isolated, enzymes are usually more stable and active in their natural environment in the cell, coenzymes and activators are already present in the system.

In this study, *Pseudomonas putida* DSM 50026 cells were used as biological component and the measurement was based on the respiratory activity of the cells. The cells were immobilised on CNT modified carbon paste electrodes (CPEs) by means of a redox osmium polymer; poly(1-vinylimidazole)$_{12}$-[Os-(4,4'-dimethyl-2,2'-di'pyridyl)$_2$Cl$_2$]$^{2+/+}$. The osmium polymer is polymeric mediator that attracts attention due to the efficient electron shuttling properties combined with the polymeric structure, which promote a stable adsorption as well as a possibility for multiple layers of immobilised protein molecules (cells) on the electrode surface [2, 3].

A proper amount of graphite, CNT and mineral oil were mixed manually to obtain the CNT modified CP electrode. After immobilisation of the osmium polymer together with the bacterial cells, the electrode surface was covered with a dialysis membrane. The effect of varying amounts of CNT and osmium polymer on the response to glucose was investigated to find the optimum composition of the sensor. Substrate specificity, reproducibility and operational stability as well as the effects of pH and temperature were examined.

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Electroanalysis and Sensors

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Electroanalysis and Sensors

Environmentally-Friendly Carbon and Bismuth Film Electrochemical Sensors

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New electrode materials have recently been studied for environmental and health applications, particularly to avoid the traditionally-used mercury. For application as electrochemical sensors, such materials must have a large potential window, low background current as well as simple surface regeneration and inertness [1]. Different forms of carbon, such as glassy carbon, carbon paste, boron-doped diamond and nitrogen-doped amorphous carbon represent good alternatives. Carbon film electrodes, made from carbon electrical resistors [2], show good promise for short-term-use and disposable sensors. Bismuth film electrodes can also serve as substitutes for mercury electrodes [3]: the ease of the nucleation process, due to bismuth's ability to form alloys with heavy metals, make these electrodes very useful in anodic stripping voltammetry (ASV) with sensitivity similar to mercury film electrodes.

The purpose of this work was to evaluate the properties of carbon film electrodes as electrochemical sensors and as substrates for bismuth film electrodes. Electrochemical impedance spectroscopy and voltammetric techniques were used for characterisation.

The irreversible adsorption of chemical species in environmental samples can be diminished or prevented by applying protective polymer films to the electrode surfaces. Protective Nafion coatings were applied and the ASV response was analysed for zinc, cadmium and lead in the presence of surfactants [4]. The influence of metal deposition and of the surfactant on the properties of the Nafion coatings was analysed in detail. Comparison was made with square wave stripping voltammetry data at Nafion-coated mercury thin film electrodes.

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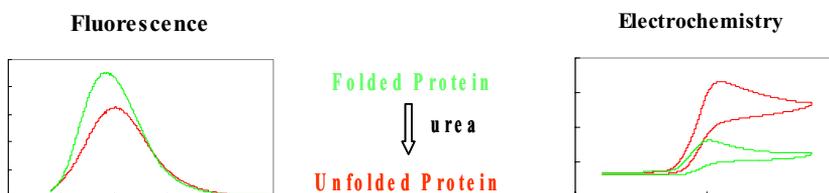4. C. Gouveia-Caridade, R. Pauliukaite, C.M.A. Brett, Electroanalysis, in press.

S2·P-33

Chemical Induced Unfolding of Cofactor-free Protein Monitored by Catalytic Voltammetry

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Protein folding has been studied extensively with an aim to better understanding the relationship between protein sequence, structure and function. A large variety of techniques have been developed and utilized to probe protein conformation and folding/unfolding transition. In this report, electrochemical monitoring of urea-induced unfolding of a large cofactor-free protein, bovine serum albumin (BSA), is described. Enhanced electrochemical oxidation of tyrosine and tryptophan in free amino acids and in BSA was achieved on indium tin oxide electrode by using an electron mediator, $Os(bpy)_2dppz$ (bpy = 2,2'-bipyridine, dppz = dipyrido [3,2-a:2',3'-c] phenazine). The oxidation current was used as a signal reporter in the monitoring of urea-induced BSA denaturation. At high urea concentrations, the electrochemical signal increased by 3 folds relative to the native protein. The increase is attributed to the closer contact between the oxidizable residues in the unfolded BSA and $Os(bpy)_2dppz$. The degree of unfolding assessed by electrochemistry correlates very well with the established fluorescence technique. The method can be used to investigate the unfolding process of other cofactor-free proteins.

Fluorescence   **Electrochemistry**

Folded Protein
urea
Unfolded Protein

Symposium 2 - Poster

Electroanalysis and Sensors

Effect of structural and electrochemical properties of different Cr-doped contents of Li[Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$]O$_2$

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Layered Li[Ni$_{(1-x)/3}$Mn$_{(1-x)/3}$Co$_{(1-x)/3}$Cr$_x$]O$_2$ materials with x=0, 0.01, 0.02, 0.03, 0.05 are prepared by a solid-state pyrolysis method. The oxide compounds were calcined with various Cr-doped contents, which results in greater difference in morphological (shape, particle size and specific surface area) and the electrochemical (first charge profile, reversible capacity and rate capability) differences. The Li[Ni$_{(1-x)/3}$Mn$_{(1-x)/3}$Co$_{(1-x)/3}$Cr$_x$]O$_2$ powders were characterized by means of X-ray diffraction (XRD), charge/discharge cycling, cyclic voltammetry, and SEM. XRD experiment revealed that the Li[Ni$_{(1-x)/3}$Mn$_{(1-x)/3}$Co$_{(1-x)/3}$Cr$_x$]O$_2$ (x=0, 0.01, 0.02, 0.03, 0.05) were crystallized to well layered α-NaFeO$_2$ structure. The first specific discharge capacity and coulombic efficiency of the electrode of Cr-doped materials were higher than that of pristine material. When x=0.02, the sample showed the highest first discharge capacity of 241.9mAh g^{-1} at a current density of 30mA g^{-1} in the voltage range 2.3–4.6V, and the Cr-doped samples exhibited higher discharge capacity and better cycleability under medium and high current densities at room temperature.
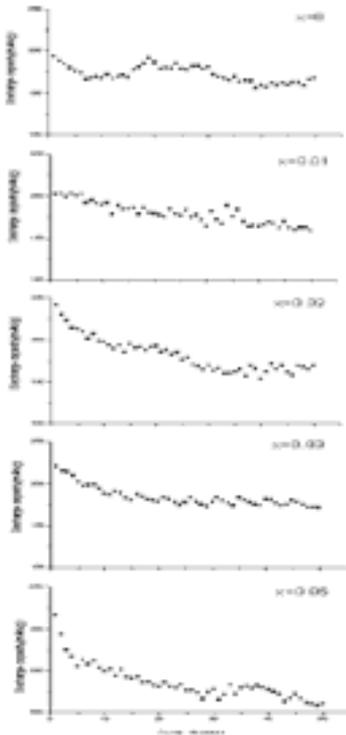

Fig.2 X-ray diffraction patterns of the doped composition

Fig.1 Discharge capacity vs. cycle number at 30mAg^{-1} between 2.3 and 4.6V
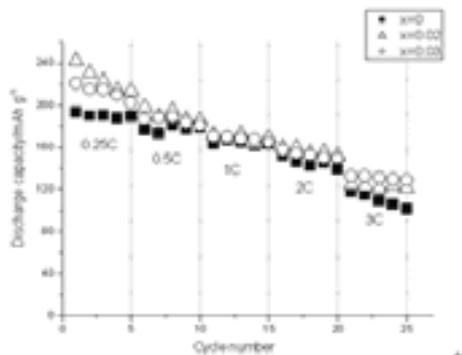
Fig.3 The capacity retention at various rates in the voltage at the range of 2.3–4.6V at room temperature

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Electroanalysis and Sensors

Development of an ESI-MS System for Quantification of Fuel Cell Related Partial Oxidation Products

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Electrochemical oxidation of alcohols has been a major topic in electrochemical energy technology. The oxidation is often only partial and several (toxic) by-products are formed. Differential electrochemical mass spectrometry (DEMS) has successfully been used to assess the product distribution of methanol and ethanol oxidation [1, 2]. The main limitations of conventional DEMS are 1) fragmentation of the analytes by electron impacts (EI) ionisation, 2) low volatility of larger molecules prevents their detection, and 3) operation at elevated pressure and temperature or with high alcohol concentrations results in excessive amounts of water and/or alcohols entering the MS vacuum chamber.

One alternative approach is to perform bulk electrolysis experiments and then use off-line methods like HPLC or IC for analysis of product distribution [3, 4]. The time resolution is lost with these approaches, and the electrolyte composition is not constant during the electrolysis period.

Recent development in ionization techniques for MS has focused on reducing or eliminating fragmentation to allow analysis of large (bio)molecules. These techniques include electro spray ionisation (ESI) and chemical ionization (APCI). ESI is particularly well suited for analytes present as ions, e.g. carboxylic acids in our case. Analysis of polar components like carbonyls and alcohols is more difficult. APCI may be used although derivatisation may be required. CO_2, alkanes etc. are not ionisable by these soft techniques and must be analysed separately. An EI source that is also capable of chemical ionisation (CI), a soft ionisation characterisation for gas phase samples, can be used instead of the ESI or APCI sources.

We present the first results related to optimisation of the commercial system for detection of relatively small organic molecules present in sulphuric acid with this approach and show how these results, combined with the conventional DEMS technique, provide kinetic and mechanistic information about fuel cell related electrocatalytic reactions.

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Symposium 2 - Poster

Electroanalysis and Sensors

Selective Detection of Dopamine in the Presence of Ascorbic Acid

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Dopamine is an important neurotransmitter in the mammalian central nervous system and abnormalities in its concentration can be linked to several disorders, such as Parkinson's disease. Accordingly, there is much interest in the development of new rapid, selective and simple methods for the detection of dopamine. In particular, there has been much interest in the development of electrochemical methods as dopamine is electrochemically active and the electrodes used in the sensing can be conveniently placed in the living organism. However, electrochemical detection methods suffer from selectivity; ascorbic acid, which is present at concentrations that are some hundred times higher than dopamine, is oxidised in the same potential region as dopamine. Various modified electrodes have been used in an attempt to resolve the oxidation peaks of dopamine and ascorbic acid[1,2]. However, these approaches are limited in terms of the applicability of the method.

In this paper we present results on the formation of a polymeric material with an incorporated cyclodextrin that has the potential to selectively detect dopamine in the presence of high concentrations of ascorbic acid. The dopamine was detected using cyclic voltammetry and differential pulse voltammetry giving peak currents at approximately 480 mV(SCE) in the cyclic voltammograms and at approximately 450 mV(SCE) in the differential pulse voltammograms. However, the material was unable to detect ascorbic acid even at relatively high concentrations of 0.01 mol dm^{-3}. Furthermore, the dopamine was detected at the same peak potential and peak currents in the absence and presence of varying amounts of ascorbic acid, to give a highly selective sensor for the detection of dopamine

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Voltammetric Behaviour of Zn^{2+} at a Plain Screen-Printed Carbon Electrode and its Trace Determination in Human Sweat Using DPASV.

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Cyclic voltammetry was used to investigate the electrochemical behaviour of Zn^{2+} in a wide range of supporting electrolytes using a plain screen-printed carbon electrode (SPCE). The most suitable supporting electrolyte was selected on the basis of the most sensitive anodic signal produced on the reverse scan. The optimum instrumental conditions for the DPASV measurement of zinc were deduced. Calibration studies were performed using these conditions and it was found that this analyte could be determined down to 5×10^{-7}M (33 ppb). A method was developed for the collection and determination of Zn^{2+} in human sweat samples. This paper will describe the results of these studies.

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Electroanalysis and Sensors

Detection of oligonucleotides by alternating current voltammetry and diffractive optical based sensor at solid amalgam-alloys

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We examined a tensammetric (adsorption/desorption) responses of different synthetic oligonucleotides (ODN) at metal electrodes modified by a nanometer layers of solid amalgam-alloys. From the analysis of height of AC voltammetric peak 3 (desorption and/or reorientation of the ODN segments adsorbed through hydrophobic base residues) and potential difference between the AC voltammetric peaks 1 (desorption of ODN segments adsorbed via ODN sugar-phosphate backbone) and 3 it is possible to identify: (a) different homopurine ODN lengths, and (b) a proportion of purine (adenine and/or adenine + guanine) units to the whole length of different ODNs containing both the purine and pyrimidine units (Figure 1).

In addition, we examined an adsorption of homo-oligonucleotides at solid platinum amalgam nanometer layers, including competitive adsorption between all possible pairs of such unmodified oligomers. Homo-oligonucleotides served as a model system that allows us to systematically study the base- and length-dependence of ssDNA-platinum amalgam-alloy interaction.

We also examined an adsorption of different oligonucleotides at solid platinum amalgam nanometer layers by a diffractive optical element (DOE) based sensor. From reflected wavefront, which is directed on the aperture of the anlysing DOE element it is possible to detect the change of refractive index and optical roughness of adsorbed oligonucleotide layers at the platinum amalgam-alloy surface. We observed that adsorption of pyrimidine oligonucleotides process is fast in comparison with lower adsorption process of purine ones. The optical roughness (R_a) of hybridisation duplex of DNA is about two times lower ($\Delta R_a \approx 5$ nm) than R_a of the nonhybridisation one.

Figure 1
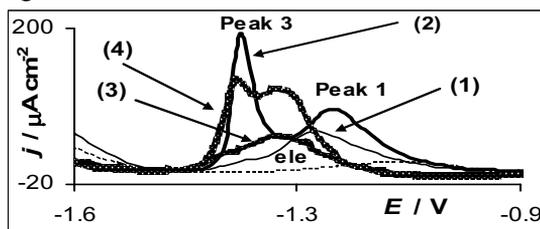
5´(AAA)$_3$A3´ (1)
5´(AAA)$_{26}$AA3´ (2)
5´(GAA)$_7$3´(3)
5´(GAA)$_{32}$(A)$_{25}$3´ (4)

S2·P-39

Polypyrrole for the Controlled Delivery of Anionic and Cationic Drugs

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In recent times, there has been considerable interest in various polymeric materials for the controlled release of drugs [1,2]. The advantage of such a system is that the drug is only administered when needed, as opposed to being released continuously. The advantages of such a controlled-delivery system are obvious: maximum effect of the drug, no wastage of the drug and minimal side effects. However, in order to devise a suitable technology, the polymeric material must be responsive i.e. it must be capable of altering so that the drug is released in a controlled fashion when needed.

In this paper we show that polypyrrole, a widely used conducting polymer with good biocompatibility properties, can be used for the controlled delivery of both anionic and cationic drugs. This is based on the redox chemistry of polypyrrole; a change in the net charge on the polypyrrole film during its reduction or oxidation requires ions to flow into or out of the film. This, in turn, allows the polypyrrole film to bind and expel ions in response to electrical signals. This concept was used for the controlled delivery of ATP and salicylate (model anionic drugs), and dopamine and derivatives of dopamine, as model cationic drugs. The polypyrrole films were synthesized by the electropolymerization of pyrrole in a solution of ATP or salicylic acid to give polypyrrole films loaded with the anionic ATP or salicylate dopants. The cationic dopamine and its derivatives were incorporated within the polypyrrole films following formation by reducing the polypyrrole films in appropriate solutions of the cationic dopants. The incorporation of the cationic species was followed using quartz crystal microbalance studies (EQCM). The release of the cationic and anionic drugs from the polypyrrole films was monitored using UV-visible spectrophotometry.

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Electroanalysis and Sensors

Affinity Sensor Development for Ochratoxin A

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Mycotoxins are toxic fungal metabolites that occur in food products, such as ochratoxin A which contaminates grapes as a result of mould growth. Ochratoxin A may be transferred to grape containing drinks such as wine due to its high chemical stability. There is an increasing concern for human health since ochratoxin A is known to be possibly carcinogenic and can be immunosuppressive for the mammalian system. Ochratoxin A free beverages are also of economic importance for the wine industry. Therefore, a need exists for a sensitive, selective, rapid and low-cost measurement of ochratoxin A contents that can be implemented on-site in wine yards.

Enzyme binding assays using ochratoxin A antibodies have been developed during this study and results were within the detection limit of 1 μg per kg. The affinity of a polyclonal antibody to the analyte ochratoxin A was evaluated using a surface plasmon resonance biosensor (Biacore). Kinetics of the binding interaction resulted in rate constants $k_a = 7 \times 10^3$ Ms^{-1}; $k_d = 6 \times 10^{-5}$ s^{-1} and affinity values $K_A = 3.15 \times 10^6$ M^{-1}; $K_D = 3.37 \times 10^{-7}$ M. These results indicate that the antibody is suitable for an affinity sensor development.

The successful preparation of an ochratoxin A conjugate with an enzyme label (Horseradish peroxidase) was integrated into investigations towards an electrochemical affinity sensor for ochratoxin A detection. Preliminary results using the optimised reagents and disposable screen printed electrode format indicate good sensitivity towards the toxin. Further optimisation of the system is required to achieve the desired detection limit in wine samples by coupling the electrochemical sensor with a solid phase extraction sample preparation method.

Determination of trace clenbuterol with MWCNTs/ Nafion modified electrode by Differential-Pulse Voltammetry

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Clenbuterol ($C_{12}H_{18}C_{12}N_2O$) is a β-agnonist drug which is important to be detected in the food industry. The multi-walled carbon nanotubes (MWCNTs) -Nafion modified glassy carbon electrode (GCE) was used to study the mechanism of the electrochemical behavior of clenbuterol and to detect the trace clenbuterol which show high sensitive and selective. After the detection condition optimized, the determination of clenbuterol is linear response on the modified electrode by DPV in the range of $1 \times 10^{-9} \sim 1 \times 10^{-6}$ mol/L with a detection limit of 5×10^{-10} mol/L in pH=1.2 Britton-Robinson buffer solution, at the pre-concentrating potential of -0.2 V. [see the Fig.1].
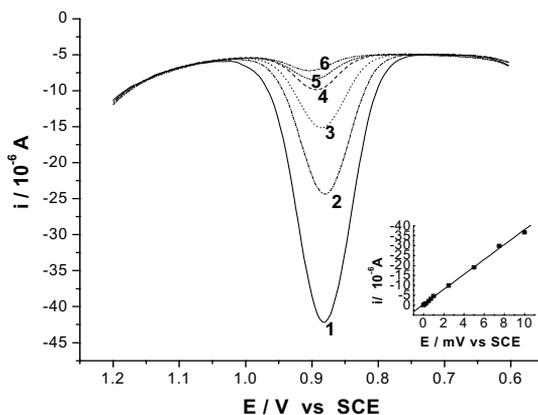
Fig. 1. DPV of clenbuterol on MWCNTs/Nafion modified GCE at different concentrations and plot of peak current vs. clenbuterol concentration (the insert figure). The clenbuterol concentration from 1 to 6 were: 1.0×10^{-6}, 5.0×10^{-7}, 2.5×10^{-7}, 1.0×10^{-7}, 7.5×10^{-8} and 5×10^{-8} M respectively.

Symposium 2 - Poster

Electroanalysis and Sensors

Detection of halogenated aromatic compounds by Membrane Introduction Mass Spectrometry with Nafion membrane

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Mass spectrometry is a type of experimental technique that is used to identify and quantify compounds according to quantification of relative abundances of ions in dependence on m/z. The direct connection of mass spectrometer and electrochemical cell called Differential electrochemical mass spectrometry (DEMS) combines mass spectrometer with electrochemical cell via direct input with membrane inlet (Membrane Introducing Mass Spectrometry – MIMS)[1,2]. MIMS uses semipermeable membrane acting as a separator that should hold a substantial part of solvent and supporting electrolyte but must allow the penetration of analyt to the mass spectrometer.

Used mass spectrometer was TRIO 1000 (Finnigan, USA) and home made direct membrane input. Sooner used Teflon membrane was in this work replaced by Nafion membrane (Nafion N112, Ion Power, USA) with 51μm thickness and 0.2 μm pore diameter. The properties of Nafion membrane has been tested with respect to penetration of several types of compounds: methanol, ethanol, n-propanol; benzene, toluene, p-xylene[3,4]; and in this work with: fluoro-, chloro- and bromobenzenes, and o-, m- and p-chlorophenols from water solution. Acquired, concentration-dependent mass spectra are compared with standard spectra taken from NIST library[5]. In all cases we observed the shift of molecular peak including the isotopic signal for one unit and significantly lower fragmentation. This suggests the formation of protonated species.

Use of Nafion membrane in MIMS can allow the more simple evaluation of data obtained with DEMS method.

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Stability of the radical nitro anion in heterogeneous systems: influence of the substituent

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Nitroimidazoles widely has been studied due to the antibacterial and antiprotozoarias properties that present. This biologica activity is directly related to formacion of the radical anion nitro (RNO2.) product of reducci?del group nitro. The substitution in the imidazolic ring is created directly affected reduccion of the group nitro, is for this reason that synthesized three compound ones that obeys to the following one formulates general:

Those that studied of the electrochemistry point of view of way to explain the influence of the sustituents in the 4-nitroimidazolico ring and as these affect formation and stability of the radical nitro anion. As increase the electroaceptor effect of the sustituent that is in position 2 observe a displacement of the potential of reduccion towards less cathodics values.

A very appropriate tecnica to study the behavior of a pair redox is voltametria ciclica, nevertheless in the middle 100% watery one for these compounds I am observed a unica? of type irreversible, corresponding to reduccion of the group nitro via 4 electrons 4 protons, due to the instability of the radical anion nitro in this means, with the purpose of being able to study and to characterize this pair redox, is that work in heterogeneous systems being used different surfactants, because solubilizacion of composed in aggregates micellar causes changes in the stability of the intermediary, obtaining itself that the optimal conditions of generation de the radical species is in the presence of micelles cationics to pH superior to 7,4. Ademas by means of a study of speeds of sweeping was possible to determine parameters quantitative, as they are the kinetics constants of decay of the radical and their half-life time.

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Electroanalysis and Sensors

Factors Effecting the Electrochemical Response of Ascorbic Acid at Polymer Modified Electrodes

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Conducting electro-active polymers still remain the subject of investigation by many research groups worldwide. Electro-activity, and thus the possibility of electro-sensing is one of the reasons why these polymers are investigated for their practical use. Factors that can affect redox processes that occur at the surface of an electro-active polymer include, among others, film and solution composition, the pH, the applied voltage scan rate and the potential region. Varying any of these can affect the oxidation of other species on these polymers, e.g. ascorbic acid (AA.) The aim of this work was to investigate the oxidation of AA on three polymer modified electrodes and to optimize the electrochemical response for its oxidation.

Polyvinylferrocene (PVF) perchlorate films were obtained by electrochemical precipitation in CH_2Cl_2. Reduced PVF (0.4 mM) in 0.1M tetrabuthylammonium perchlorate solution was potential-cycled at $v_s = 0.05$ V s^{-1} on a 0.3cm^2 Pt wire in the potential region 0 V to 0.7 V vs. SCE for 5 min or for 10 cycles ending the process at 0.7V. Polypyrrole (PPY) films were obtained by potential cycling in 0.1 M Na ClO$_4$ + 0.1M pyrrole solution in the potential region from -0.7 to 0.7 V. Ten cycles were made at $v_s = 0.1$V s^{-1}. A Pt wire was used as an auxiliary electrode. Polyaniline (PANI) films were obtained by potential cycling (10 cycles) Pt in 0.1M aniline + 0.5 M H$_2$SO$_4$ solutions in the potential region from -0.15V to 0.95V.

The oxidation of ascorbic acid was studied while cycling the polymer modified electrodes in slightly acid and neutral saline, phosphate buffer, 0.1M sodium perchlorate, sodium toluenesulphonate, and sodium naphthalenesulphonate solutions. The pH of these solutions varied from 4.5 to 7.4. EQCM data was obtained at quartz crystal, gold electrode. Full details are given in [1, 2]. The results of the oxidation of AA obtained on polymer modified electrodes are presented.

Key words: polymer films, electro-oxidation, ascorbic acid, pH, anion effect

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S2·P-45

A trial of voltammetric measurements on carbon slides with mirror surfaces for microscopic measurements

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[Introduction] Recently, a optical carbon slide has been made of an extremely flat carbon plate with mirror finish so that microscopic measurements can be made on the slide[1]. The carbon slides possess the following properties compared with conventional glass slides used for microscopic observation. (1) The slides are opaque and require mirror finishing. (2) the slides exhibits less scattering and no auto-fluorescence, which help to record sharp images of the samples with micrograph. (3) they can be used as carbon electrodes. Thus, we can record images of the cells or the microorganisms under the electrical stimulation on the carbon slides 'electrode' [2].

[Experimental] Graphite powder with a micrometer size was mixed in a thermosetting resin and the mixture was molded into a sheet, calcined at 1400 in inert atmosphere to produce a ground flat carbon plate(PFC) and finished like mirror as a slide. Glass like carbon plate(GC) was also formed from the same resin with the same method and finishing. Voltammetric measurements on the slides were performed with a potentiostat [Cypress Systems CS-1090] and microscopic observations were done with epi-illumination system.

[Results and discussion] Since surfaces of mirror finished carbon slides are delicate against over potential, we observed the surfaces with a microscope by increasing potentials for finding suitable potential ranges for living samples and differential capacity at each potential was also measured. On the slide as a voltammetric electrode, we have tried cyclic voltammetric measurements in ferro/ferricyanide solution. Alive cells in physiological medium under suitable potential have been observed on a carbon slide.

Refernce
 (1) Japanese patent, 2005-127965A, USA patent, 2005/0214164, (2) Japanese Patent, 2005-043605

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Electroanalysis and Sensors

Development of new mediators for the enzyme-based bioelectrocatalytic reduction of oxygen

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In the last few years there has been an increasing interest in the development of biochemical fuel cells (biofuel cells) aiming on biomedical applications and due to environmental demands for clean energy production. Biofuel cells are the analogues of conventional fuel cells except that they typically utilize biocatalysts (enzymes), biofules, and neutral or slightly acidic electrolytes. Unlike conventional fuel cells they operate at ambient temperatures and they don't require a membrane layer for separating the anode and cathode compartment due to the fact that immobilised enzymes on the electrodes provide selective catalytic pathways.

Typical redox processes considered for biofuel cells involve the oxidation of fuels such as glucose, ethyl alcohol or lactic acid combined with the reduction of oxygen at the cathode side. Optimisation of the latter process in terms of finding longterm stable and efficient enzymes seems to be crucial for the further development of improved biofuel cells.

Our present research focuses on the development of methods of immobilization of enzymes within different Osmium-complex containing redox polymers at electrode surfaces. Important issues are seen not only in the long-term stability and immobilized activity of suitable enzymes but the durability and ability of polymeric redox mediators to propagate charge between the enzyme integrated prosthetic groups via the polymer-bound redox centers to the electrode surface. In order to investigate and develop improved highly effective bio-electrocatalytic system for electroreduction of oxygen in neutral media, we have employed Osmium-complex modified redox polymers containing suitable terminal groups which enable their electrochemically induced deposition on the electrode surface under simultaneously entrapment of either laccase or bilirubin oxidase as selective oxygen reducing enzymes. Possibilities of using carbon nanostructures will be discussed. In particular, new methods of immobilisation the Osmium complex modified polymers together with suitable enzymes will be discussed. Special attention has been paid to the development and application of $Os^{2+/3+}$ functionalized polymers of different structures and redox potentials for efficient mediated electron transfers and utilization of the immobilized biocatalysts.

Electrode reaction of N-hydroxy imide derivatives in acetonitrile containing lutidine as a base

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Recently, we showed the kinetics of the catalytic oxidation of benzyl alcohols by the phthalimido-*N*-oxyl (PINO) radical electrogenerated in acetonitrile by the oxidation of highly conjugated *N*-hydroxy-phthalimide (NHPI) under a steady-state condition.[1] It was found that PINO⁻ works as a highly-effective mediator for veratryl alcohol oxidation compared to the other reported mediators. During a derivative of NHPI was sought for the immobilization on the electrode surface, our attention focused on the less conjugated *N*-hydroxy imides (NHIs), e.g., *N*-hydroxymaleimide (NHMI) and *N*-hydroxysuccinimide (NHSI). The maleimide group of NHMI have been widely employed to introduce the functional groups to the sulfhydryl group (-SH) with which the olefinic linkage of the maleimide moiety forms a stable thioether bond. In this study, we described the electrochemical properties of NHIs in acetonitrile and compared them to that of NHPI, and the reactivity of the NHIs to benzyl alcohols as acatalytic mediator was briefly mentioned.

NHMI, NHSI, anise alcohol, benzyl alcohol and veratryl alcohol (Aldrich) were used as received. Acetonitrile (∞pure grade, Wako Pure Chemical, Japan, H_2O 0.004%) containing tetraethyl ammonium perchlorate and 2,6-ludine as a Lewis base was used as an electrolyte. The electrochemical measurements were performed using the conventional three-electrode cell configuration. A glassy carbon disk electrode (1 mm diameter), a Pt wire and an $Ag^+|Ag$ (0.01 mol dm⁻³ (M) $AgNO^3$ in acetonitrile) electrode were the working, auxiliary and reference electrodes.

Fig.1 NHPI. NHMI. NHSI

Fig. 2 Reaction between –SH and maleimides

The cyclic voltammograms (CV) of NHPI in the presence of lutidine shows a chemically reversible response in the lower potential region, however, those of NHMI indicates a marked current enhancement of oxidation, which suggests the reaction between the oxidation product of NHMI and olefinic linkage. The reactivity of NHIs to benzyl alcohols was confirmed by the CV and kinetic analyses were performed using rotating disk electrode voltammetry. [2]
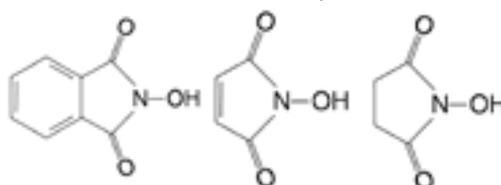
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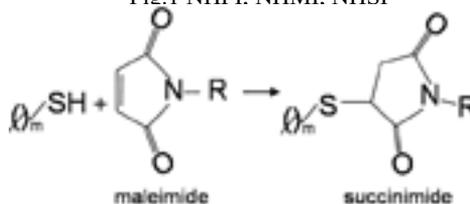
Electroanalysis and Sensors

MicroelectrodeS based on nano dispersed titanium and tungsten oxides for dissolved oxygen sensor

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A microelectrodes for the determination of oxygen dissolved in biologically active liquids have been developed, the operation of which is based on the oxygen electroreduction process. The cathode material is nanoscale titanium and tungsten oxides. Titanium oxide nanoparticles were produced by sol-gel method on a Ti substrate from a solution containing titanium chloride. Tungsten oxide nanoparticles were produced on a Ti-substrate by a method of explosion of the tungsten filament. The mean size of nanoparticles on the electrode surface depended on the conditions of their production, was no more then 5 nm for TiO_2 nanoparticles, and varied between 5 and 50 nm for WO_3 nanoparticles; the average thickness of the layers produced was 500-2000 nm. The thickness of the microelectrodes was 0.2-0.3 mm. It has been found by XPS measurements that the surface of the electrodes is formed from nonstoichiometric tungsten oxide $WO_{2.76} \cdot (OH)_{0.24}$, titanium oxide $TiO_{1.91} \cdot (OH)_{0.09}$, and their hydroxide phases.

The kinetics and mechanism of oxygen electroreduction at electrodes based on nanodispersed titanium and tungsten oxides in blood plasma and a physiological NaCl solution have been investigated. It has been shown that the number of electrons at the discharge stage in the oxygen reduction reaction is n=1, and that the total number of electrons in the reaction is n_s=2, which corresponds to the reduction process which does not include the hydrogen peroxide formation. The maximum sensitivity of the electrodes to dissolved oxygen was achieved at cathodic potentials of -0.6 to -1.0 V (with respect to silver-chloride electrode) and was $(4-5) \cdot 10^{-6}$ g/l. It has been shown that the high electrocatalytic activity of the microelectrodes under investigation in the reduction of oxygen may be due to the formation of catalytically active Ti^{3+}, W^{5+} centers and to the presence of OH groups in the oxide matrix. The WO_3 electrodes possessed a higher stability during the reduction of oxygen in comparison with TiO_2 electrodes.

The microelectrodes were distinguished by a high reproducibility of characteristics in long-time cycling and promise much as reusable electrode materials in the case of developing electrochemical sensors for the determination of oxygen in biologically active liquids.

Electrochemical study of human defense antioxidant system

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This paper reports a new method for total antioxidant activity determination of biological active substances (BAS), enzymes, biological objects using new voltammetric device "Analyzer AOA".

Comprehension of mechanisms of defense antioxidant system and influence biological active substances (BAS) on it could be key for more effective therapy and prophylactic of different diseases. However investigations of this are not effective because of absence of comfortable methods, model systems and devices. This work offers to use effective and convenient voltammetric method for investigation of the mechanisms of interaction of the ROS with enzymes and antioxidants by recording the current of the electrochemical oxygen reduction (ER O_2) at indicator electrode. The latter process has been treated as a "model" reaction because of similar processes of ER O_2 and the oxygen reduction in tissues. Comparison of antioxidant activity determination in vivo and by this method showed identical results [1].

It is known 3 levels of human antioxidant defense system. First level includes superoxide dismutase (SOD), catalase, which catalyses the conversion of $O_2^{\cdot}$ to H_2O_2 and H_2O. Second level is conditioned by polyphenols and vitamins, which protect tissues from the ROS. Third level includes sulphur-containing enzymes such as glutathione (GSH). It has ability to reduce hydroperoxides of phospholipids in cell membranes. We study 3 different mechanisms of interaction enzymes with oxygen and ROS using new voltammetric analyzer.

Applying the above approach, we offered the K as total antioxidant activity (TAA) coefficient of substances, which reflects the quantity of the ROS reacting with antioxidant at μmol l^{-1} min^{-1}:
$$K = (1 - \frac{I}{I_o})\frac{C^0}{t}$$

where C^0 is the oxygen concentration in supporting electrolyte in absence antioxidant in μmol·l^{-1}, I is the ER O_2 current with the investigated substance in A, I_o is the limiting ER O_2 current without antioxidant in the solution in A, t is time of the interaction between ROS and antioxidant at the indicator electrode in min.

Moreover this work includes the calculation of thermodynamic and kinetic parameters of the interaction of different classes of antioxidants with the ROS such as polyphenols, vitamins, pharmaceuticals, enzymes. We have obtained the effective concentration, type of injection and active time of different antioxidants and enzymes. The use of these BAS in prophylactic of different diseases have been recommended.

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Electrochemical screening of enzyme activity in living *saccharomyces cerevisiae* cells

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This work demonstrates the application of a mediated amperometric method for real-time probing of the dynamics of cellular metabolism in genetically modified *S. cerevisiae* strain, EBY44 [ENY.WA-1A *pgi1-1Δ::URA3*]. We investigated the dependence of menadione reducing enzymes on the main metabolic pathways by introducing different carbon sources, glucose and fructose and the consequent effect on dicumarol inhibition of menadione reducing activity.

The amperometric method is based on the ability of menadione, a lipophilic quinone, to freely diffuse through the plasma membrane and accept electrons from certain intracellular NAD(P)H dependent enzymes. The reduced form of menadione is extracellularly oxidized by ferricyanide. The formed ferrocyanide is in turn oxidized at the platinum microband electrode, giving rise to bioelectrocatalytic current proportional to the menadione reducing activity. For each measurement, a controlled number of Ca-alginate-immobilized yeast cells (9.5×10^6) were introduced on silicon microchip surface with integrated Pt-band microelectrodes.

It was found that the amplitude of the yeast-catalyzed amperometric signal was significantly larger when using glucose as the carbon source, primarily resulting in formation of NADPH through the pentose phosphate pathway. Furthermore, the amperometric results showed that the glucose-induced menadione reducing activity was significantly inhibited by dicumarol whereas the fructose-induced menadione reducing activity was not affected. Spectrophotometric assays, performed in crude cell extracts, showed, on the other hand, similar inhibition of menadione reducing activity in the case of added NADPH and NADH.

The obtained results demonstrate the significance of enzyme activity determination in living cells as the source of information on cellular responses, reflecting the different metabolic pathways and regulatory mechanisms.

This gives further emphasis to the potential of mediated amperometry as a tool in metabolic profiling.

Evaluation of a Working Electrode Using the Power Spectral Analysis of Background Current Noise

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A novel technique based on power spectral analysis of background current noise in controlled potential electrolysis at a working electrode was developed to measure the instability of noise and charging current level of the working electrode. This technique was utilized for the evaluation of boron-doped diamond (BDD) and plastic-formed carbon (PFC) electrodes. Since the characteristics of a working electrode in an electrochemical cell often condition the analytical results, the evaluation of the electrode is important for electroanalysis. A comparison of cyclic voltammograms of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ obtained at the electrodes examined is a popular way to select the working electrode material suitable for voltammetric analysis.

The cyclic voltammetry and controlled potential electrolysis were obtained using a system composed of a potentiostat, recorder, and conventional beaker-type electrochemical cell with a PFC (Tsukuba Materials Information Laboratory) or BDD (Fchem) working, an Ag/AgCl reference, and a platinum counter electrodes. The digital data (0.1 s/point) of 1024 data points were converted from background analog signals of current-time curve by an A/D converter, and the power spectrum were obtained from these digital data by Fourier transform. The power spectral analysis was performed by a software (MAY 2000, Hayashi Pure Chemical).

In the cyclic voltammograms of $K_4[Fe(CN)_6]$, the oxidation of $Fe(CN)_6^{4-}$ at the BDD electrode occurred at higher potentials than that at the PFC electrode. The S/B ratios for $K_4[Fe(CN)_6]$ oxidation peak currents were higher for the BDD compared to the PFC. A well-defined oxidation peak was only obtained at the PFC.

The power spectra of background noise in the controlled potential electrolysis at the PFC and BDD electrodes showed the universal feature of natural phenomena that the power density at low frequencies was larger than that at high frequencies. It is often called $1/f$ fluctuation. In the case of the cyclic voltammogram, the background current at BDD electrode was smaller than that at PFC electrode. However, the power density at low frequencies of background current noise using the BDD electrode was larger than that at PFC, indicating that the fluctuation of the noise, i.e. instability of noise level, of the BDD electrode was larger than that of the PFC electrode. The electrochemical double layer at PFC electrode surface would be more stable than that of the BDD electrode surface. Therefore, it was found that the PFC that was elevated lower noise level by power spectral analysis was suitable a working electrode suitable for voltammetry of analyte such as, $K_4[Fe(CN)_6]$.

The present technique using the power spectral analysis would be useful to foresee characteristics of the working electrodes in voltammetry.

Symposium 2 - Poster

Electroanalysis and Sensors

Symposium 2 - Poster

Electroanalysis and Sensors

Platinum Metal Oxides as Mediators in Amperometric Biosensors

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An overview is presented dealing with the development of biosensors based on carbon substrates modified with platinum metal oxides. Procedures for the optimization of sensors are described and their application demonstrated on the determination of hydrogen peroxide and glucose. Such mediators can easily be added to carbon ink, thus forming an amperometric sensor applicable to the determination of hydrogen peroxide under both stationary (bath) and flow conditions. The main field of application is their exploitation as biosensors as they allow very simple, easy and multiple modifications with complex and labile systems, such as enzymes.

Hydrogen peroxide as one of the products of glucose enzymatic oxidation can be determined amperometrically. However, its direct oxidation/reduction at carbon electrodes requires relatively high positive/negative potentials, which in turn causes interferences to many other redox species presented in the sample matrix. Addition of metal oxides leads to a marked decrease in the overvoltage and reduction of negative side reactions [1,2]. The resulting amperometric current can directly be related to the enzymatically liberated H_2O_2 concentration.

In combination with a biocatalyst, such a basic sensor unit can be utilized in the construction of biosensors. Amperometric determination of glucose is realized based on the previously mentioned H_2O_2 sensor adding of a glucose oxidase layer. Glucose is oxidized enzymatically with molecular oxygen forming of gluconolactone and H_2O_2. In screen-printed electrodes, enzyme is entrapped in Nafion, which is a co-polymer facilitating a simple immobilization of enzymes at the electrode surface. Such a modification requires a very small amount of enzyme (ca 100 μg). Interferences and applications in analyses of real food samples are refereed as well.

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Scanning Photo-Induced Impedance Microscopy using Amorphous Silicon Photodiode Structures

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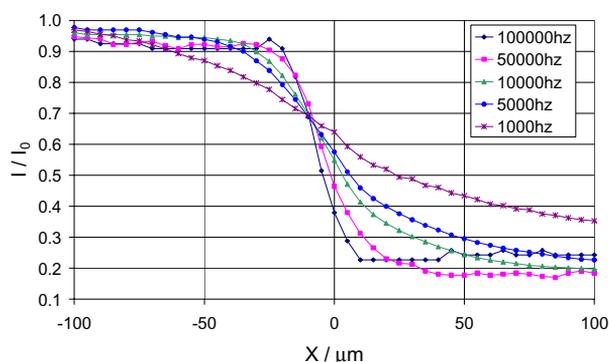
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Scanning photo-induced impedance microscopy (SPIM) is an impedance imaging technique that is based on photocurrent measurements at field-effect structures. The material under investigation is commonly deposited onto a semiconductor-insulator substrate. The lateral resolution of photocurrent measurements is limited by the lateral diffusion of minority charge carriers. Therefore it would be advantageous if semiconductors with a short diffusion length of charge carriers such as amorphous silicon could be employed. However, field-effect capacitors fabricated using amorphous silicon suffered from a large number of interface states, high leakage currents through the insulator and small photocurrents. In this work, it was investigated whether field effect structures could be replaced by p-i-n diode structures in amorphous silicon as this was expected to result in higher photocurrents and eliminate the necessity of a high quality insulator with a small number of interface states.

Amorphous hydrogenated silicon photodiode structures (a-Si:H p^+-i-n^+/SiO_2 or n^+-i-p^+/SiO_2) were deposited by low-power PECVD onto ITO coated glass substrates and characterised by focusing a 405 nm laser through the glass substrate and the ITO layer onto the a-Si:H layer. Cellulose acetate films were deposited and partially peeled off to obtain areas of different impedance. Coated and uncoated areas could be clearly distinguished by the contrast in photocurrent. To investigate the resolution of photocurrent measurements in this arrangement, the focused laser was scanned from the uncoated to the coated part of the sample. The resolution was shown to depend strongly on the modulation frequency (Figure 1). The higher the frequency the better is the resolution. The conductivity of the top a-Si:H layer and the absorption behaviour of the p-i-n structure were also expected to affect the resolution. Hence the influence of the doping concentration and the laser wavelength were investigated.


Figure 1 Photocurrent line scan from uncoated to coated part of the sample on a p^+-i-n^+/SiO_2 sample

Application of self-assembled monolayer modified electrode to a glucose sensor

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In biological fluidic sample containing glucose, such as blood, urine or food, ascorbic acid co-exists with glucose. Although ascorbic acid is indispensable for life as vitamin C, it is easily oxidized electrochemically and interferes the amperometric determination of glucose. The elimination of electrochemical oxidation ascorbic acid is very important to amperometric glucose sensing.

A surface of gold electrode was modified with a self-assembled monolayer (SAM) modified to eliminate the oxidation of co-existing ascorbic acid in biological fluids. Since ascorbic acid is negatively charged at neutral pH, its blocking based on electrostatic repulsion was performed with SAM. Modification of the electrode was done with 7-carboxyheptane thiol (7C) and 8-aminooctanethiol (8A). On the modified electrode, glucose oxidase (GOD) was immobilized with use of ethylenediamine(ED) and/or glutaraldehyde (GA). Oxidation of glucose was mediated by $Co(phen)_3{}^{2+}$. When GOD was immobilized on the 7C SAM modified gold electrode with 0.5% ED and 2.5% GA, the GOD-immobilized electrode showed most selective response to glucose at 200 - 250mV, which was the oxidation potinatial of $Co(phen)_3{}^{2+}$. With the electrode, glucose was determined upto 0.5mM at room temperature.
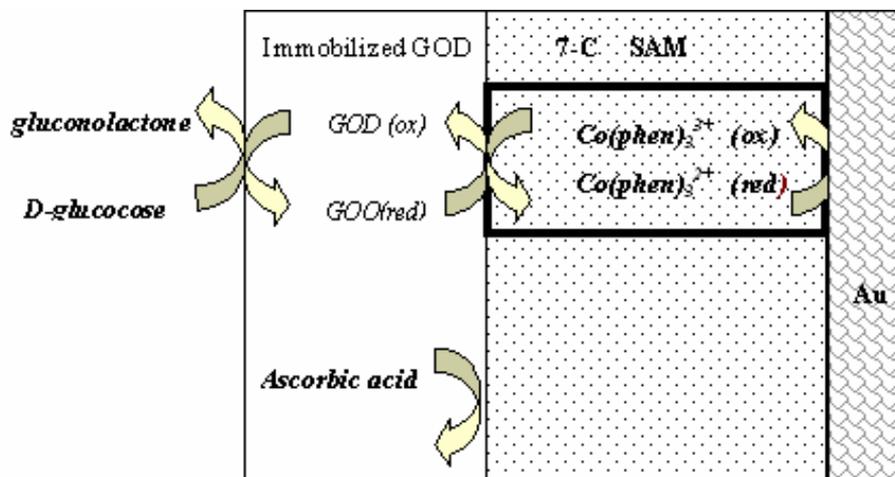
7C SAM modified electrode completely blocks ascorbic acid oxidation and selectively oxidize Co(phen)₃ Mediator.

Fig.1 Principle of 7C SAM glucose sensor

S2·P-55

HPLC with Electrochemcial Detection for Determining the Plasma Free Fatty Acids in Diabetic Rats

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School of Pharmacy, Tokyo University of Pharmacy and Life Science, 1432-1 Horinouchi, Hachioji, Tokyo, Japan;
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Although free fatty acids (FFAs) are less active electrochemically, FFAs are detected electrochemically after the derivatization with electrochemically-active labeling reagents or by mixing FFA with a quinone reagent. In the latter case, the presence of FFA in unbuffered solution causes a prepeak of the quinone reduction wave on the voltammogram, and the prepeak height is increased with the FFA concentration. Based on this catalytic prepeak, we previously developed a new HPLC with electrochemical detection (HPLC-ECD) using 2-methyl-1,4-naphtoquinone as a quinone reagent for determining plasma FFAs. In this study, the HPLC-ECD system has been improved in terms of sensitivity and separation of each FFAs by a C_{30} microbore column and 3,5-di-*t*-butyl-1,2-benzoquinone (DBBQ) as the quinone reagent, and the determination of plasma FFAs in normal and diabetic rats was carried out using the present method.

An ethanol-acetonitrile (10:90) mixture and an ethanol-acetonitrile (10:90) mixture containing 6 mol/l DBBQ and 0.1 mol/l $LiClO_4$ were used as a mobile phase and a quinone solution, respectively, in the HPLC-ECD system. A 5 μl aliquot of test solution was injected into the column, and the elute was allowed to merge with the quinone solution stream to mix together in a mixing tube. The applied potential of the working electrode was fixed at -0.09 V vs. Ag/AgCl for monitoring the FFAs. Blood samples were drawn from the caudal veins of the diabetic rats that were injected intraperitoneally an alloxan solution, and 20 μl and 5 μl of this blood sample were used for the determination of the plasma FFA and the blood glucose level, respectively.

Chromatographic peaks of arachidonic, linoleic, oleic, palmitic, and stearic acids were appeared within 30 min on a chromatogram. The peak heights were found to be linearly related to the amount of acids, ranging from 3.75 to 850 pmol ($r > 0.999$) in all cases. Plasma FFAs were determined using blood from a rat. RSD ($n = 5$) was less than 3.0%. The recovery of FFA in all cases was more than 93% and its RSD ($n = 5$) was less than 2.1%, indicating the present method to be quite adequate for determining plasma FFAs. Plasma FFAs concentrations and blood glucose level were plotted against time after the maltose administration. Blood glucose level in normal rats increased after maltose administration, reaching maximum at 1 h later. In contrast to this, plasma FFAs, particularly palmitic and oleic acids, were decreased. After then reduction in blood glucose and increase of FFAs thus occurred up to each constant level. The plasma FFAs concentrations in the diabetic rats were 2-3 times higher than those in the normal rats, and were unaffected by the maltose administration. When insulin was injected before maltose administration, FFAs concentrations as well as glucose level in the diabetic rats were remarkably decreased.

Therefore, the present method is a reliable, simple, and highly sensitive method for determining each FFA to clarify the pathophysiological role of plasma FFAs.

Symposium 2 - Poster

Electroanalysis and Sensors

Electrochemistry and Microsystems

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Symposium 2: Electroanalysis and Sensors

During the last 30 years, electrochemical research became increasingly concerned with microscopic problems. For example, thanks to the improved sensitivity of electrical equipment, measurements on miniaturized electrodes became possible. Simultaneously, ultramicroelectrodes with a high selectivity for various ions were developed in biology and medicine due to the special requirements of measurements at biological membranes. Finally, electrochemistry profited from the progress in miniaturisation of sensors. In the field of microtechnology, electrochemistry was applied for special deposition or etching processes. The LIGA process and the production of magnetic heads are typical examples.

During the last years, our research group has developed several biosensors combining electrochemistry and microtechnology. Thus, we have developed interdigitated microarray electrodes [1] which were tested as potentiometric pH biosensors using electrosynthesized polymer films sensitive to pH changes. These sensors exhibited linear, reversible and stable in time potential responses to pH changes.

We also realized potentiometric urea biosensors [2]. These enzymatic biosensors were consisted in surfaces coated by a polymer film in which an enzyme (urease) was immobilized. These urea biosensors showed reproductible responses and appeared stable in time during at least 4 weeks.

Currently, we develop a microelectrochemical cell composed of two ultramicroelectrodes: a working ultraelectrode in platinum and a silver reference ultramicroelectrode. The miniaturized electrodes of this cell are fabricated using microsystem technologies and especially a Focused Ion Beam [3].

We also currently work on the elaboration of a bio-nose. In this aim, we have shown that we were able to deposit polymer films on a microsystem by electrochemical way and to extend our previous polymer-based applications to the olfactory cell culture [4-5]. We also fabricate microelectrodes dedicated to the detection of the neuronal activity when a specific odour is introduced into the culture medium.

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Comparative studies of catalytic effects of FDH (formate dehydrogenase) containing microbes in electrochemical conversion of carbon dioxide to organic acid

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We reported that *Moorella thermoactica* has a catalytic effect of electrochemical conversion of CO_2 (Carbon dioxide) to formate with 50-80% of current efficiency which is responsible for the FDH (formate dehydrogenase) in this microbe[1, 2]. Here we compare the catalytic effects of FDH-containing microbes on the electrochemical CO_2 conversion. *Clostridium pasteurianum* showed similar catalytic effect with less than 10% of current efficiency in formate formation which is much lower than that of *M. thermoacetica*. However, either *Saccharomyces cerevisiae* (ATCC 76269) or *Pseudomonas species* (DSMZ 7220) did not show any catalytic effect on electrochemical CO_2 conversion. *Paracoccus species* (DSMZ 12584) could catalyze electrochemical conversion of CO_2 to an unidentified organic acid and the product analysis is underway.
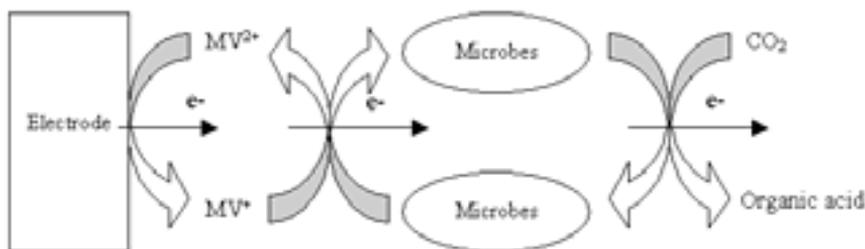
Scheme 1. Electrochemical carbon dioxide conversion using microbes as biocatalysts

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Voltammetric and Gravimetric Studies on the interactions between Cabohydrates and Proteins using Quartz Crystal Microbalance and Gold Nanoparticles

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The quartz crystal microbalance (QCM), as a simple and powerful technique, has been widely employed in chemical and biological analysis. It has been explored as an alternative to biosensors in order to study on the interactions between carbohydrates and proteins. In this work, self-assembled monolayer of thiol-modified carbohydrates have been prepared and used for the interaction studies as well as the quatitation of toxin compounds. A protein, concanavalian A (ConA), from Canavalia ensilformis, which binds specifically to mannoside and glucoside, was used as a model system to study the interactions between the proteins and carbohydrates. The binding constants of the carbohydrates self-assembled on a gold of quartz-crystal and proteins has been determined by this approach. The determined binding constant ($K_a = 2.24 \times 10^7$ M^{-1}) was slightly higher than that in solution due to the cooperative effect. In addition, the detection limit for the Con A was 48 nM.

In order to amlifiy the QCM signal, carbohydrate-modified gold nanoparticles have been employed. Since the Con A has four binding sites, the carbohydrate-modified gold nanoparticles can be binded to the Con A, which is already binded to the carbohydrates self-assembled on the gold electrode of quartz crystal, thus increasing the QCM signal.

Voltammetric methods along with gold nanoparticles also have been employed to study on the interactions between carbohydrates and proteins. In this work, stripping voltammetry of gold nanoparticles have been used to determine the concentration of Con A and cholera toxin.

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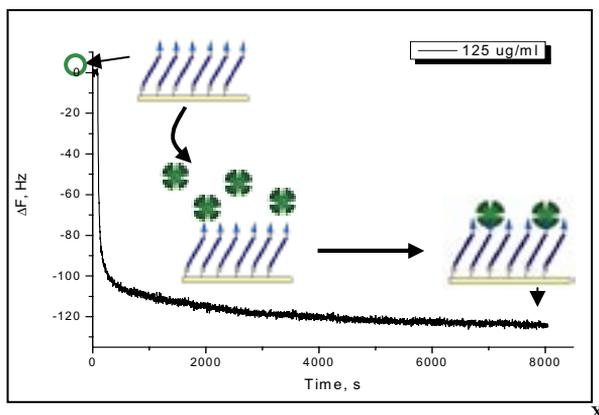
Optical ph measurements based on uv-vis and raman spectroscopy with water dispersion of polyaniline nanoparticles

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A new method for optical pH measurements with a commercially available water dispersion of polyaniline (PANI) nanoparticles (mean particle size: 46 nm) is presented [1,2]. The pH measurements are based on the acid-base equilibrium of PANI and were carried out either by combining the **automated sequential injection analysis system (SIA)** and **UV-vis** or **Raman spectroscopy** (excitation wavelength : 633 nm). The detection was done in continuous mode at λ=800 nm by using the SIA technique for transporting the sample to light path of the UV-vis or Raman instrument. With a fibre-optic lightguide, the UV-vis detection was done in batch mode at λ=400 nm and 580 nm. In both methods, fresh pH reagent (PANI) solution was used in each measurement, thus overcoming the problem with hysteresis (memory effect), which is usually observed with PANI films. Fast pH measurements can be done with the PANI nanoparticles between pH 6-10.5 depending on the measuring technique.

The nanoparticles were characterized with UV-vis spectroscopy in pH buffer solutions between pH 2-12 and a protonation constant of log $K_{H_{0.5}L}^{0.5H,L}$ =4.4 was calculated from these data. The protonation constant provide important information about the pH sensitivity of different types of polyaniline and can therefore be used for choosing right PANI materials for specific applications where either pH sensitivity or insensitivity is required. The acid-base equilibrium is established entirely in the solution phase. The protonation equilibrium is therefore established faster in small nanoparticles than in films, which usually have a thickness of at least several hundreads of nanometers.

Potential application areas of the presented optical pH measurement methods are e.g. automated flow analysis systems where the application of the glass pH electrode is difficult, determination of pH under elevated pressures and pH measurements of sea water where the sodium error may limit the use of the glass pH electrode. The limitations of the absorbance measurements of real samples should, however, be considered when developing new optical methods. It should be stressed, that this is a fundamental study showing the applicability of PANI nanoparticles in optical pH measurements.

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Symposium 2 - Poster

Electroanalysis and Sensors

Symposium 2 - Poster

Electroanalysis and Sensors

The diffusion resistance of gases in ammetric-type electrochemical sensors

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A theoretical and experimental study has been conducted into the mass transfer of the gases determined in ammetric-type electrochemical sensors for monitoring the ambient air. The response of the sensors as current signal, I, is expressed by the equation $I = K P$, where P is the partial pressure of the gas determined; K is the transformation coefficient. It has been shown that K^{-1} is an analogue of diffusion resistance (DR), which comprises inner and outer components. The outer component of DR depends on the conditions of convective diffusion of the gas analysed, in particular, on the rate of the flow and its direction towards the diffusion port of the sensor. The DR of high-resolution sensors is inversely proportional to the flow rate of the gas analysed and increases in going from axial to radial direction of the gas flow towards the diffusion port. It has been shown that whatever the direction of the gas flow, with increasing the flow rate the DR tends to a constant value corresponding to the inner components of the sensor resistance.

The inner components of the DR include time-stable resistances of construction elements, in particular, a porous diaphragm and a calibrated diffusion channel and the reduced diffusion resistance of the indicator electrode of sensor. The latter is a function of catalytic activity, true surface, degree of flooding of open pores, wettability of the indicator electrode to the electrolyte and solubility of the gas determined in the electrolyte. The above parameters can vary with temperature, relative humidity of the gas analysed as well as ageing of the sensors. This causes a change in the reduced resistance of the indicator electrode and, correspondingly, in the performance of the sensors. It has been shown that the scaling parameter for the analysed gas sensors of different types is a relative part of the component resistances in the overall DR of the sensor. With decreasing the part of the outer component resistance and reduced resistance of the indicator electrode the resolution of the sensors deteriorates. In particular, for the chlorine sensors studied with decreasing the part of outer component from 24 to 2 % and that of the indicator electrode from 23 to 1.6 % of the overall DR the resolution of the sensors changed from 0.01 to 0.2 ppm with a relative error of 0.25.

On figure show a part of an outer resistance in total DR (f) from speed a stream (V^{-1}) at radial (1-3) and axial (1´-3´) flow towards the diffusion port of a sensor with inner resistance: 1,1´ - 0,22; 2, 2´ - 1,0; 3, 3´ - 3,0 ppm ·μA^{-1}. A mathematical model for the mass transfer of gases in ammetric-type electrochemical sensors has been worked out which can be used for developing and designing sensors of a required range and resolution as well as for selecting the operation conditions.
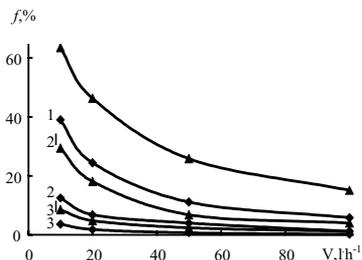
Electrocatalytic reduction of nitric oxide using nickel hexacyanoferrate electrodes

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Nitric oxide (NO) and its derivatives have a function, as either stressors or regulators, in a vast range of processes, including cardiovascular homeostasis, immunity, neurotransmission, glycolysis and apoptosis. It serve also as a marker of a number of respiratory diseases: asthma, chronic obstructive pulmonary disease, cystic fibrosis.

In last two decades transition metal hexacyanoferrates have found application in electrocatalysis, electrochromic display devices, electroanalytical devices, etc. Recently they were also reported to be studied in the detection of biologically relevant species such as NADH and vitamin B6.

Here we propose a new sensor based on nickel hexacyanoferrate (NiHCF) for the detection of NO. NiHCF layer was deposited on a platinum electrode by cyclic voltammetry in a solution of nickel (II) chloride and potassium hexacyanoferrate (III). The electrode exhibited a good stability in buffer, containing at least 100 mM KCl in the pH-rage 2.0 – 6.0 as revealed by continuous voltammetric investigation.

By polarizing the electrode at potentials within the range from 0 mV up to 300 mV vs. Ag/AgCl/1 M KCl the reduction of NO was monitored. The most appropriate potential was determined to be in the range 200-250 mV due to the advantageous signal/noise ratio. The sensor responded fast, its t_{95} value was 3-4 s. The sensitivity of the electrodes was found to be 1.5-1.9 A M^{-1} cm^{-2}. The sensor was characterized for potential interferents: hydrogen peroxide and nitrite. Their signal was measured to be considerably lower than for NO.

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Electroanalysis and Sensors

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Electrochemical behaviour of SOD-electrodes based on a cysteine mutant of a monomeric human Cu,Zn–SOD in mixed organic solvent/buffer solutions

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The harmful properties of reactive oxygen species such as superoxide O_2^- to several biomolecules and thus their involvement in numereous diseases and metabolic disorders have evoked the development of several detection methods for these species. Mainly, the methods based on the photometric detection of reaction products of the radical. In addition biosensors have been developed based on cytochrome c (cyt. C) or superoxide dismutase (SOD). Therefore, the electrochemical behaviour of both protein electrodes has been intensively studied in aqueous buffer. Combined with a radical source the electrodes can be also applied for the characterisation of antioxidants. Particularly for the latter application also organic solvents are important. It could be shown that cyt. c electrodes can be applied in solutions with certain organic solvents such butandiol or dimethyl sulfoxide (DMSO) [1,2]. SOD based electrodes can provide a much higher sensititivity [3,4]. Thus the aim of this study was the characterization of the electrochemical behaviour of SOD electrodes in mixtures of buffer and organic solvent.

For these investigations electrodes were used which are based on a cysteine mutant of a monomeric human Cu,Zn-SOD. The SOD mutant has been immobilised directly onto gold electrodes using the thiol groups of the cysteine residues introduced. The behaviour of the surface confined enzyme was voltammetrically investigated in mixtures of HEPES buffer (50 mM, pH 7.5) and DMSO up to an organic solvent content of 60%. The formal potential E_f was found to be rather independent on the DMSO content. However, half peak width increased and the redox active amount clearly decreased with raising DMSO content. For the kinetic analysis the model of Laviron was used. The kinetics of the heterogeneous electron transfer became slower with increasing organic solvent content. But still a quasi-reversible electrochemical conversion of the immobilised mutant SOD was feasible. Furthermore it was found that the immobilised protein retained its activity for the conversion of superoxide up to concentrations of 40% DMSO.

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Bioelectroanalysis on mesoporous carbon composites

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Effective and reliable strategy both retaining high activity of the immobilized biomolecules and making the direct electron transfer of redox protein feasible is desired. Immobilization of biomolecules on several mesoporous matrices has attracted considerable interest in the fundamental studies of protein and electrode interaction and the development of biosensor devices. Here the structure-tailored and ordered mesoporous carbon composites have been fabricated for enzyme immobilization and bioelectroanalytical applications.

Mesoporous carbon materials, type of nanostructured carbon materials, which provide a rigid, uniform open-pore structure and possess narrow pore size distributions and large surface areas up to 2500 m^2/g, have many valuable applications in diverse fields from catalyst carriers, absorbents to electronic devices. They are attractive candidates to host biomolecules. Different from carbon nanotubes, mesoporous carbons are composed of carbon nanorod with ordered arrays and large porosity. Mesoporous carbon materials can be easily prepared via the hard templating method with low cost and free from any impurities if mold is fully etched away. Several types of ordered one-dimensional, three-dimensional intertwined mesostructured carbons and spiral graphited carbons have been synthesized and applied to study the direct electrochemical behaviour of enzymes. The pore diameter and structural topologies can be readily tuned to match the dimensional size of diverse biomolecules. The experimental results show that mesoporous carbons are ideally effective electrical connectors. In this process, through molecular interactions, this carbon microenvironment maintains binding to intact proteins so as to facilitating the direct electron transfer between the redox active center and electrode surface. Moreover, the remarkable electrocatalytic properties of mesoporous carbon composites make them extremely attractive in direct electrochemical studies of redox proteins and also in the development of the biosensors.

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Electroanalysis and Sensors

Antioxidant redox sensors based on DNA modified carbon screen printed electrodes

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Antioxidant (AO) redox sensors based on DNA modified carbon screen-printed electrodes (SPE) were developed. The carbon ink was doped with TiO_2 nanoparticles, onto which double strand DNA was adsorbed. A redox mediator, namely tris-2, 2′-bipyridine ruthenium (II) $[Ru(bpy)_3^{2+}]$ was electro-oxidised on the SPE surface to subsequently oxidised both the adsorbed ds-DNA and AO in solution. The resulting oxidation damage of ds-DNA was then detected amperometrically in a second solution containing only $Ru(bpy)_3^{2+}$. In the presence of AOs in the first solution during the indirect oxidation of ds-DNA, the extent of ds-DNA damage was reduced. A kinetic model is developed to study the protecting role of AOs in solution. The developed electrochemical sensor can then be applied to the evaluation of AO activity.

Keywords: antioxidant, DNA oxidation, electrochemical sensor.

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Fab-based electrochemical immunosensor for the determination of testosterone in bovine urine

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This work describes the development of an electrochemical immunosensor for the detection of testosterone in bovine urine using anti-testosterone Fab fragment for molecular recognition. The electrochemical immunosensor was fabricated by immobilising the testosterone-bovine serum albumin conjugate on the surface of screen-printed electrodes (SPEs), and followed by the competition between the free testosterone and coating conjugate with anti-testosterone Fab fragment. The use of anti-mouse IgG-horseradish peroxidase conjugate determined the degree of competition. The electrochemical technique chosen was the chronoamperometry, performed at a potential of +100 mV whereby the product of 3, 3', 5, 5'-tetramethylbenzidine undergoes reduction produced by the label horseradish peroxidase. ELISA was primarily used to develop the assay system, prior to transferring to SPEs. The sensor exhibited the linearity range between 0.3 – 40 ng/ml with limit of detection of 90±13 pg/ml. Furthermore, the developed immunosensor allowed for the bovine urine samples determination directly after dilution, omitting extraction and hydrolysis. Comparison of the results of administrated bovine urine samples analysed between GC-MS and immunosensor showed that the quantitative or semi-quantitative analysis obtained from our system enable to find and select suspicious samples for further extensive analysis by established analytical techniques. With simple sample preparation, low limit of detection, and good repeatability, the proposed methods can after alternative advantages as a primary screening tool for meat quality control.

Key word: testosterone; screen-printed electrode; immunoassay; bovine urine

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Electroanalysis of ascorbic acid and dopamine using prussian blue and poly-(3,4-ethylenedioxythiophene) bilayer films on platinum

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Preparation and electrochemical behaviour of bilayer films consisting of iron (III) hexacyanoferrate, well known as Prussian Blue (PB), and of poly-[3,4-ethylenedioxythiophene] (PEDOT), on a platinum electrode, are reported. The PB/PEDOT coverage is prepared electrochemically by a two-step method. Firstly, a PB layer is electrodeposited onto a platinum electrode in aqueous solution. In the second step, the electrochemical deposition of PEDOT film over the Pt/PB modified electrode was carried out. Thereafter, the electrochemical behaviour and the stability of the bilayer coating were studied in aqueous solutions.

The electrochemical features of the PB/PEDOT bilayer system are examined in aqueous solutions. The electrocatalytic activity of the Prussian Blue/conducting polymer bilayer system towards the oxidation of ascorbic acid is examined in aqueous solutions. From differential pulse voltammograms, a linear dependence of the current on the ascorbic acid concentration up to 4 mM has been obtained. The electrochemical behaviour and analytical applications of bilayer films consisting of PEDOT, and subsequently of PB, on a platinum electrode, are also reported. The electrocatalytic activity of the PEDOT/PB bilayer system towards the oxidation of ascorbic acid and dopamine is examined in aqueous solutions. From differential pulse voltammograms a linear response to ascorbic acid and dopamine was observed in the concentration range from 5×10^{-5} to 5.0×10^{-3} M and 1×10^{-4} to 2×10^{-3} M, respectively.

Electrocatalytic Sulfite Determination in a Simple Microfluidic Device

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Microfluidic devices are ideal for many electroanalytical and electrosynthetic processes [1]. This study addresses the effect of interacting electrodes in a microfluidic flow system with a channel height smaller than the diffusion layer thickness. Flowcell devices with several geometries are investigated with ferrocene model redox systems. The effect of the interacting electrodes is confirmed and quantified via numerical simulation.

Sulfite anions are known to be oxidised to sulphate in the presence of ferricinium cations. This process may be described by an overall EC'-type mechanism. The microfluidic system is employed (i) to investigate the mechanism, (ii) to determine sulfite by electrocatalytic oxidation with ferrocene derivatives, and (iii) to demonstrate the effect of supporting electrolyte on the electrocatalytic process. The conditions for the sulfite determination are optimised.

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Electroanalysis and Sensors

Electroless and electrodriven silver deposition on polypyrrole and poly(3,4-ethylenedioxythiophene)

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Processes of metal deposition (either spontaneous or driven by external polarisation [1]) on conducting polymers films are important from the point of view of possible applications in: electrocatalyst production, sensors, recovery of heavy metal ions and manufacturing metal – polymer contacts.

In our work, silver deposition from $AgNO_3$ solutions on electrodes coated by semi-oxidized conducting polymers: polypyrrole and poly(3,4-ethylenedioxythiophene) was studied. It is known that in the case of spontaneous deposition, Ag(I) ions are reduced by the conducting polymer [2,3,4]. In the present work, more detailed kinetic information concerning this redox process was obtained from open circuit potential transients. It was found that for slightly oxidized polymers in quiescent solution the rate of Ag(I) reduction is dependent on Ag(I) ion diffusion in solution. Either in stirred solutions or for more oxidized polymers the initial step of the process is controlled by a new phase (Ag on conducting polymer) formation. The influence of Ag(I) concentration, conditioning time, kind of polymer and its thickness on the amount of deposited silver was analysed.

Comparison of these results with silver deposition studies, carried out under potentiostatic conditions, using chronoamperometry and rotating disk electrode voltammetry, points to similarity of both deposition modes (electroless and electrodriven). The reaction-diffusion balance determines, where the silver is deposited in the polymer. Although both polymers can be penetrated by Ag^+ ions, the highest amount of the metal is detected on the polymer surface, as laser ablation coupled with mass spectrometry experiments have shown.

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High temperature polymer electrolyte fuel cells. Model and experiment

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One of the major issues limiting the introduction of polymer electrolyte fuel cells (PEMFC) is the low temperature of operation which makes platinum-based anode catalysts susceptible to poisoning by trace amount of CO. In order to alleviate the problem of CO poisoning and improve the power density of the cell, operating at temperature above 100 °C is preferred. Nafion[®]-type perfluorosulfonated polymers have been typically used for PEMFCs. However, the conductivity of Nafion[®]-type polymers is not high enough to be used for Fuel Cell operations at higher temperature (>90 ºC) and atmospheric pressure because they dehydrate under these condition. A ne higher temperarature fuel cell is based on polybenzimidazoles; the most widely used acid-doped polymer is poly[2,2-(m-phenylene)-5,5 bibenzimidazole], generically referred to as polybenzimidazole (PBI). PBI fuel cells operate in the temperature range of 120-200ºC and these operating temperatures limit CO poisoning of the platinum catalyst.

This paper presents experimental data on our PBI based PEMFC. A steady-state isothermal model of the fuel cell is also developed to aid in fuel cell performance optimisation.   The governing equations involve the coupling of kinetic, ohmic and mass transport. The open circuit potential, the exchange current density and diffusion coefficients are all functions of temperature and pressure. Mass transport of species is described using the Stefan Maxwell multi-component diffusion equations and Darcy's law. The kinetics are represented by the Butler Volmer expressions and the ionic and electronic resistances using Ohms Law. The model produces polarisation curves which are validated against experimental data.
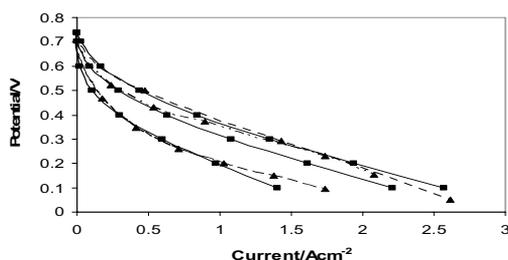

Fig 1 Fuel cell polarisation curves; model and experiment. Loading 0.5 g m^{-2}, Pt/C ratio 30, membrane width 20 μm, atmospheric pressure. Experimental result at temperatures 125ºC. 150 ºC, 175 ºC. Solid lines. Model results at temperature: 125ºC, 150 ºC, 175 **ºC.**

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Assessment of the optimal electrochemical method to develop an immunosensor for steroid

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The reliable identification of illegal growth promoters in cattle is based on expensive gas chromatography-mass spectrophotometric analysis. The use of simple, semi-quantitative electrochemical biosensor may provide a means of screening for the presence of illegal steroids. Until now there is no electrochemical biosensor reported to detect steroids. Development of a biosensor based on appropriate detection technique would be a greater interest. In this work a range of electrochemical detection techniques such as Differential Pulse Voltammetry, Square Wave Voltammetry, Linear Scan Voltammetry, Chronoamperometry and Capacitative techniques were examined to detect testosterone in urine. Chronoamperometry was found to be the optimum technique to detect testosterone in urine. An algorithm was developed to increase the efficiency of the detection technique. It was found that integration of 8 to 10 s in chronoamperogram provided the highest slope and optimal correlation. The substrate TMB and H_2O_2 are stable for 20 mins, a 40% of decrease in the signal was observed after 20 mins. The optimal pH was 6 for the sensor utilizing HRP an the enzyme.

Voltammetric Determination of Acetylsalicylic Acid at a Boron Doped Diamond Electrode

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The paper reports the electrochemical determination of acetylsalicylic acid (ASA), commercially known as aspirin, both in standard aqueous solutions containing only the active substance (pharmaceutical purity) and in solutions resulting from three common aspirin-based pharmaceutical products. Cyclic voltammetry and amperometry were performed on copper, gold and a boron doped diamond electrodes in standard solutions. Comparative assessment allowed highlighting of the distinct aspects offered by the use of determination of ASA under various experimental conditions (different supporting electrolytes, various formulations). Electrochemical measurements were performed by using an AUTOLAB PGstat 20 Eco Chemie and a Metrohm cell and three different electrodes, i.e. the working electrode, platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The amperometric detectors employed were: a BDD disk Windsor electrode, a gold disk Metrohm electrode, and a copper disk home manufactured electrode embedded in Teflon. All disks had a 3mm diameter. The reagents were of analytical grade purity, except the active substance which was of pharmaceutical purity and the three types of aspirin-pharmaceutical commercial products. Standard solutions were prepared from the active substance (neutralized and hydrolyzed, acetylsalicylic, and salycilic acid respectively) dissolved in 0.1 M NaOH. The final concentration range inside the cell was 0.05-10 mM, and below the lower limit under the hydrodynamic and amperometric batch injection conditions, respectively. The supporting electrolytes used were sodium hydroxide, for all electrodes, neutral phosphate buffer, and neutral sodium sulphate solutions for BDDE.. The voltammetric data showed a single pronounced anodic wave and the irreversible behaviour of the all the investigated systems. The good amperometric signal as well as the voltammetric wave for gold and copper (obtained as catalytic response) and the high anodic signal for BDDE in alkaline media corresponded to a potential range of 0.5-0.8 V vs. SCE. The amperometric responses (as cyclic voltammetry CV and chronoamperometry CA) strongly manifested, stable and reproducible were obtained for the BDDE-analyte system at higher anodic potential range (0.9-1.25 V vs.SCE) in quasi-neutral media. The high chemical stability and non-fouling of the electrode, the linearity of the current vs. concentration plot, the very low relative standard deviation (RSD) sustain the use of BDDE for voltammetric determination of acetylsalicylic or salycilic acid.

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Copper electrode-an electrochemical alternative for amperometric organics assay in waste water

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Copper electrode preformed as copper oxide electrode was tested as a catalytic detector and an alternative of classical method for the detection of some electrochemical oxidable organics, conventionally and predominantly considered responsible within chemical oxygen demand (COD) evaluation. Copper oxide electrode was obtained in-situ by five repeated scans in a potential range of –0.221 V to 1 V (first vertex potential) and –1 V (second vertex potential) vs SCE in 0.1 M NaOH as supporting electrolyte. Based upon the voltammetric peak for the organics oxidation, it was found that the copper oxide electrode in the presence of different concentrations of organics using cyclic voltammetry (CV) is suitable for analytical applications. The voltammograms shapes of copper oxide electrode obtained for the studied organics were similarly except those obtained in the presence of sulphur-containing organics. For all situations, a linear relationship between the amperometric responses of a copper electrode and the concentration of certain organics was obtained within the potential range of 0.2-0.6 V vs SCE. The calibration plot was established for the determination of each studied organic compound and concentration range. Under these conditions, the most adequate supporting electrolyte for organics detection was found. The best results were obtained using the mixture of 0.1 M NaOH and 0.01 M Na_2SO_4 solution as supporting electrolyte. The inorganic species, which are usually present in the real waste water (*e.g.*, NO_3^-, NO_2^-, Cl^-, NH_3, SO_4^{2-}) did not interfere organics detection within above-mentioned potential range. Within the selected potential range, the correlation between the overall amperometric response of the copper oxide electrode, as overall equivalent of the concentration of analytes, and COD parameter corresponding to organics overall concentration and determined by classical method was established. It was determined the analytical performance characteristics of the amperometric determination of oxidable organics on the copper oxide electrode in alkaline media regarding the method reproducibility and accuracy, electrode sensitivity and recovery test, and compared with those of the classical method of COD evaluation. Also, data related to the electrode fouling were obtained using chronoamperometry (CA) within the batch injection analysis (BIA) as an easy and fast method of amperometric detection of organics, when the linear relationship between amperometric current magnitude and organic concentration was obtained, without the consistent fouling of the electrode.
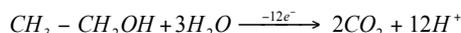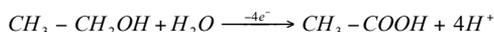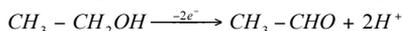
Electrooxidation of ethanol at glassy carbon modified with metallic microparticles

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Modified Glassy carbon (GC) electrodes were tested as electrocatalysts to oxidize ethanol. Mo, Pd, Ru and Pd / Ru / Mo, supported on GC.

Electrooxidation of ethanol is expected to occur following any of these steps or a mixture of them:

$$CH_3 - CH_2OH \xrightarrow{-2e^-} CH_3 - CHO + 2H^+$$

$$CH_3 - CH_2OH + H_2O \xrightarrow{-4e^-} CH_3 - COOH + 4H^+$$

$$CH_3 - CH_2OH + 3H_2O \xrightarrow{-12e^-} 2CO_2 + 12H^+$$

It has been shown that ethanol oxidizes within two potential regions: the first one starts at about 0.5 V vs. SHE and it is attributed to adsorption of ethanol at the catalyst surface and the second one at 0.7 V and it has been assigned to oxidation of adsorbed ethanol to yield acetaldehyde, acetic acid or carbon dioxide or a mixture of them. Results on Ru/Mo/GC and Ru/Pd/Mo/GC are promising and are under study.
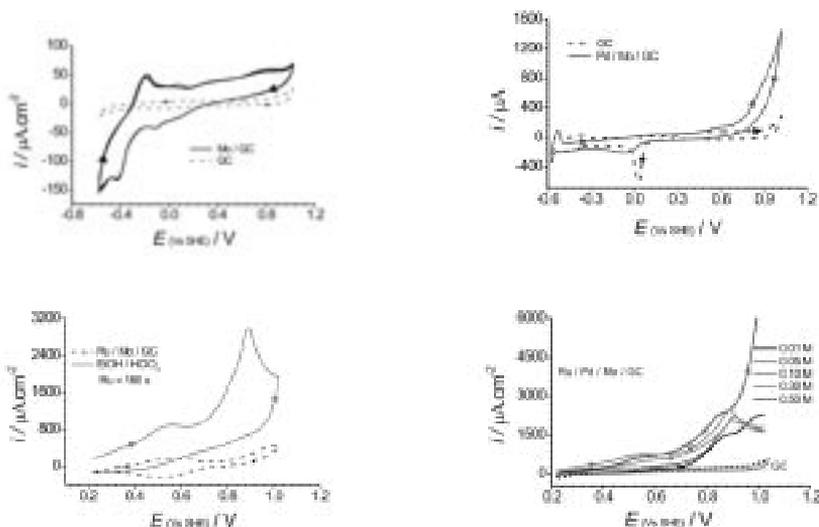
Voltammetric responses of different modified electrodes and at bare GC in ethanol

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Electroanalysis and Sensors

ELECTROCHEMICAL OXIDATION OF METHANOL ON V(ox)/Pt

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Cyclic voltammetric (CV) evaluation of $NaVO_3$ in $HClO_4$ on platinum, within the potential range -0.2V to 1.6V vs Ag/AgCl (KCl$_{sat}$) was initially performed. The formation of vanadium II, III, IV and V along the anodic potential sweep as well as vanadium III and II in the cathodic direction were confirmed by CV and UV-Vis experiments. A voltammetric zone of polyvanadium IV was also defined (fig 1).

The electrochemical oxidation of CO and MeOH on some of these electrodes was performed and electrochemical parameters measured. It was found that the way the electrode was prepared has much to do with its efficiency in the oxidation process. In some cases, the oxidation current was more than five times the value on platinum and this difference was kept along the electrolysis. The FTIR results showed carbon dioxide as the main reaction product and also showed that its production started much earlier on the platinum modified electrode (fig.2). The scanning electronic microscopy (Fig. 3) gave some information about the morphology of deposits, it is amorfous in the zone of low potentials, with an increase in cristalinity when the anodic potential was increased. In this last case, a type of capsules and needles were formed.
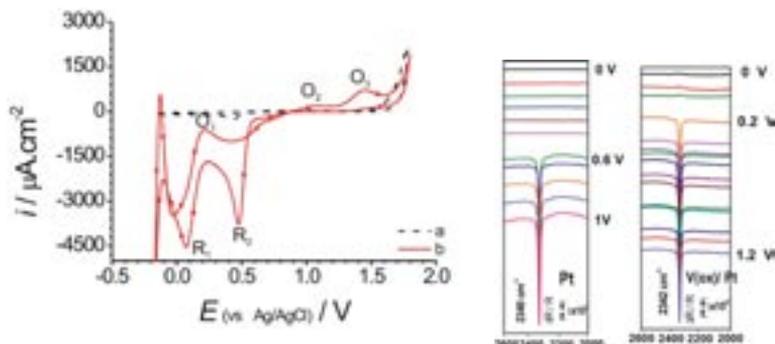
Cyclic voltammetry of platinum on: (a) 1M $HClO_4$ (b) $9x10^{-2}$M $NaVO_3$ in 1M $HClO_4$

Insitu FTIR response of 1 M methanol oxidized in 0.5 M $HClO_4$ at platinum and V(ox)/Pt electrodes

SEM of V(ox)/Pt electrodes prepared by 60 min. pulse potentials: A) 0.3 V, B) 1.2 V y C) 1.5 V

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Amperometric micro biosensors for determination of ATP at the carotid body

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Laterally resolved release of ATP was determined at the carotid body using a miniaturized dual-enzyme biosensor [1] based on the co-immobilization of glucose oxidase and hexokinase under various stimuli to establish the dose-response of the carotid body from rat pups. The carotid body preparations were stimulated by potassium depolarization, hypoxia, and hypercapnia and the thereby induced ATP release in a concentration range of 2.5-10 μM was measured. The carotid body preparation time-response to each stimulus was established using these local micro sensors. Potassium depolarization causes a quick release of ATP in the order of a few seconds followed by a second stage of ATP release at lower concentration. Hypoxic and hypercapnic conditions triggers ATP release in much longer time scale of a few minutes, where ATP concentration increases with extended exposure to either hypoxic or hypercapnic conditions. A novel immobilization scheme based on the covalent attachment of enzymes will be realized at gold ultramicroelectrodes of 25 μm diameter. The enzymes, glucose oxidase and hexokinase, can be covalently linked to the gold surface by using a self-assembled monolayer (SAM) tether. An activated mercaptohexadecanoic acid to allow spontaneous attachment of enzymes and biomolecular receptors to gold surfaces in general was synthesized. Optimization of the immobilization scheme was performed for a glucose microsensor and will be adapted and implemented for ATP sensing. By optimizing the experimental enzyme's reaction conditions such as pH, temperature and reaction time enhanced sensitivity for glucose compared to current state-of-the-art enzyme entrapment in polymer suspensions could be obtained. Furthermore using the covalent attachment to a SAM also yielded superior reproducibility and stability.

In this contribution we present first results on localized ATP measurements above the carotid body along with flow-injection analysis for demonstrating the analytical performance of the novel enzyme's immobilization chemistry. Theoretical modeling of enzymatic biosensors response was performed to corroborate the analytical response obtained with such sensors.

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Symposium 2 - Poster

Electroanalysis and Sensors

Symposium 2 - Poster

Electroanalysis and Sensors

Electrocatalytic oxidation of L-cysteine on the surface of glassy carbon electrodes modified with quinizarine

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Chemically modified electrodes (CMEs) have recently attracted much attention [1-3]. They are characterized by a chemically altered surface displaying new qualities that can be exploited for electrochemical purposes. The preparation and electrochemical characterization of glassy carbon electrodes modified with L-cysteine were investigated by employing cyclic voltammetry, chronoamperometry and rotating disc electrode techniques. The cyclic voltammograms of the electrooxidation of L-cysteine showed an enhanced current peak at approximately 0.725 V in presence of hydrazine in phosphate buffer pH=2 and scan rate 10 mV/s. The thermodynamic and kinetic parameters of the oxidation of L-cysteine at glassy carbon have been evaluated using cyclic voltammetry. The experimental parameters were optimized and the mechanism of the catalytic process was discussed. The obtained values of $E^{o\prime}$ (V vs. Ag/AgCl), the apparent electron transfer rate constant k_s (s^{-1}), n, α (charge transfer coefficient of L-cysteine) and D were as follows: $E^{o\prime}$ (0.725 V vs. Ag/AgCl) at scan rate 10 mV/s (pH 2), k_s=4.44 s^{-1}, n=1, α=0.46 and D=4.5×10^{-6}cm^{2}s^{-1}.

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Voltammetric Behaviour Of Indole And 3-Methyl Indole At Screen-Printed Carbon Electrodes And Its Exploitation For Sensor/Biosensor Applications

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The aim of this investigation was to develop screen-printed carbon electrochemical sensors/biosensors for the measurement of indole and 3-methyl indole which would have potential in oral malodour studies. Screen-printed carbon electrodes (SPCEs) were fabricated using two different ink formulations; an organic solvent based carbon ink and a water-based carbon ink. Two strategies for the measurement of the analytes were investigated: direct oxidation at plain SPCEs and a biosensor containing an enzyme and electrocatalyst cobalt phthalocyanine (CoPC). The latter decreases the required potential for hydrogen peroxide detection which is produced in the enzyme reaction. The water-based carbon ink also incorporates the enzyme and permits the fabrication of the biosensor in one step. Studies were performed using cyclic voltammetry in order to understand the voltammetric behaviour of the two indoles and indicated the possibility of exploiting the redox behaviour of these species in the development of an amperometric sensor using the optimised conditions. In order to simplify the measurement system, chronoamperometry and constant potential amperometry were investigated and were shown to possess the required sensitivity for the proposed application. This poster will describe the results of these investigations.

Symposium 2 - Poster

Electroanalysis and Sensors

Oxygen reduction on Ag/TiO$_2$ composite layer

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Silver is known as a good catalyst for electrochemical oxygen reduction reaction (ORR) in alkaline solutions. Silver dispersed on a fine carbon support was investigated as oxygen reduction catalysts [1]. Following similar investigations of the Pt/TiO$_2$ [2], in the present study, adopting the program of potentiodynamic polarization of titanium in an aqueous AgNO$_3$ solution, an adherent Ag/TiO$_2$ composite layer was synthesized. The method used in this study provided a well adhered silver deposit in a form of silver-enriched TiO$_2$ islands (Fig.1). Within these silver-rich regions, one may distinguish silver agglomerates approx. 50-150 nm in diameter. Silver loading was found to amount to

Fi g. 1 SEM photograph of Ag/TiO$_2$ surface at the magnification 25,000

3. 35 µg cm^{-2}. The voltammetric response of this composite Ag/TiO$_2$ layer was investigated in an oxygen saturated aqueous 0.1 M NaOH solution. The results of various studies are compared in a common diagram in Fig. 2. The Tafel line positions and slopes indicate that Ag/TiO$_2$ displays generally the averaged behavior of pure polycrystalline silver and pure TiO$_2$. In the present case, with very small surface concentration of silver in the composite layer, the Tafel line is much closer to the one of bulk silver, most probably tanks to a good adherence and a high degree short-circuiting betwen silver particles and titanium support. Furthermore, the effectiveness similar to that of 10% Ag/C [1] prepared to simulate industrial catalyst, was achieved.
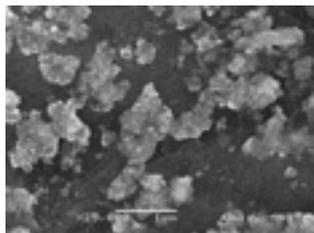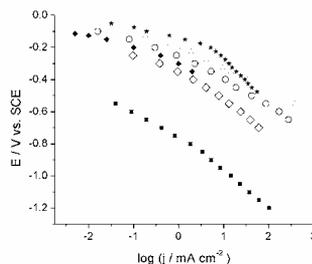

Fig. 2 The diffusion corrected Tafel plots for ORR in 0.1 M alkaline solution at different electrode materials: ($\diamond$) - Ag/TiO$_2$ (this work), ($\star$) - bulk polycrystalline Pt (this work) (Δ) - bulk polycrystalline Ag, activated (this work), (o) - Ag- monocrystal , plane 100, (ref.[3]), ($\blacksquare$) – potentio-dynamically formed TiO$_2$ (this work), ($\blacklozenge$) Ag/C, ref. [1], non-prereduced sample

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Electrochemical Impedance Spectrometry as a Tool for Characterizing Carbon Paste Electrodes

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This contribution includes an overview of achievements and prospects of electrochemical impedance spectrometry (EIS) applications for characterizing the surface of the carbon paste electrodes (CPE). Several general guidelines are pointed out and illustrated by experimental results. EIS determinations have been performed either in the absence or in the presence of a redox couple. In the first case, the surface state is described by the characteristics of the constant phase element only, but the equivalent circuit must take into account the possible occurrence of both basal and edge planes at the carbon-solution interface [1]. In the second case the charge transfer resistance (which is inversely proportional to the apparent standard rate constant) also comes into play. Sometimes, the redox probe may interact with the paste material and react in the adsorbed state as well and relevant elements should be added to the equivalent circuit [2]. In addition, we attempted at applying the theory of the charge transfer reaction at partially blocked electrodes [3] in order to assess the average size and spacing of the active sites on the carbon paste surface. In order to estimate the effect of the probe-carbon paste interaction, various redox probes with different charge and hydrophobicity degrees have been selected and also the effect of the counter ion was scrutinized. The above procedures have been applied to investigate the effect of additives and surface pretreatment, with a particular focus on applications for metal ion determination by stripping voltammetry.

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Symposium 2 - Poster

Electroanalysis and Sensors

Luminol Electrochemiluminescence on Screen Printed Electrodes

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A novel flow cell with screen printed electrodes was tested for its feasibility for heavy metal detection of ions such as copper and cobalt, through the combination of stripping voltammetry as a micro-preconcentration procedure, with electrochemiluminescence (ECL) detection. A dual working electrode system was used with a carbon electrode for metal preconcentration and oxygen reduction and a platinum electrode for luminol electro-oxidation. Each electrode was 50 μm wide and the spacing between them was 125 μm. The reference and counter electrode ; silver/silver chloride and platinum respectively, were each 1mm wide and 500 μm from the working electrodes. All electrodes were screen printed on a ceramic substrate with a printed area of $35x17.5$ mm^2. The ECL flow cell was fabricated in-house using an injection moulding technique.

The performance of several electrode designs were evaluated for carrying out the luminol electrochemiluminescence reaction in borate buffer pH 9 with an applied asymmetric double step (negative and positive) potential. Preliminary results show great potential of such a combination for the enhancement of the performance and selectivity of the electrochemiluminescence technique.

Determination of Azinphos-methyl in Soils With a Gold Ultramicroelectrode

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Organophosphorus compounds are one of the most important classes of insecticides. There are a number of characteristics of these pesticides, including their persistence, degradation and elimination, genetic effects on diverse organisms, and effects on people's health that are of social and scientific interest. Azinphos-methyl ((dihydro-oxobenzo-triazinyl-methyl)-dimethyl-phosphorodithioate) belongs to this group and it is a systemic and general insecticide.

In recent years, modern voltammetric techniques are gaining increasing importance in environmental control. Analytical voltammetry is being significantly influenced by the use of ultramicroelectrodes since they exhibit several attractive and important properties [1].

The main aim of the present study was to investigate the electrochemical behaviour of azinphos-methyl on a gold ultramicrodisk surface (radius = 12.5 x10^{-6} m) and to study the applicability of stripping voltammetry performed by ultramicroelectrodes in order to obtain a simple, fast and highly sensitive procedure for analysis of the selected insecticide in soil extracts.

Preliminary investigations of the electrochemical behaviour of azinphos-methyl were performed by cyclic voltammetry. To get the more appropriate conditions for stripping voltammetric detection at the gold ultramicroelectrode, the square-wave parameters, namely, pH, deposition and conditioning potentials, deposition time, frequency, amplitude and step were optimized. Once the influence of all these variables was studied and their optimum values established, validation of the proposed procedure for quantitative assay of the selected organophosphorus insecticide was examined via evaluation of linear working range, limit of detection, repeatability and recovery.

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Potentiometric sensors for ag+ based on poly(3,4-ethylenedioxythiophene) (pedot) doped with sulfonated thiophenes

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Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most stable conducting polymers available today [1]. PEDOT doped with sulfonated calixarenes and poly(styrene sulfonate) (PSS$^-$) [2] or sulfonated resorcarenes [3] shows high sensitivity and selectivity to Ag^+. Ag^+ is known to interact with sulfur atoms [4] and double bonds(л-coordination) [5] present in the polymer backbone and the doping ion. Previous study showed that the potentiometric response of PEDOT-based ion selective electrodes to Ag^+ seems to be partly due to the interaction between Ag^+ and the sulfur atoms present in the backbone of PEDOT [3].

In this study, two different sulfonated thiophenes were used as doping ions in the synthesis of PEDOT using electrochemical polymerization method. These thiophenes, which are sodium 2-(3-thienyloxy) ethanesulfonate (**a**) and sodium 2-(3-thienyloxy) hexanesulfonate (**b**), differ from each other in the length of the alkyl chain between the covalently bound charge compensator and the thiophene unit.

(**a**)   (**b**)
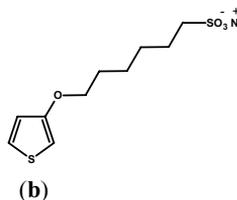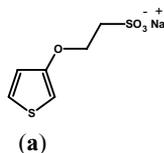
Potentiometric ion sensors were prepared by the galvanostatic electrosynthesis of PEDOT doped with (**a**) or (**b**). The resulting electrodes were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Potentiometric measurements were carried out on the prepared sensors in order to study and compare their sensitivity and selectivity to Ag^+. The film prepared from PEDOT doped with (**a**) was also studied using infrared (IR) spectroscopy, which confirmed that (**a**) acts as a doping ion and it was not irreversibly immobilized in the PEDOT film.

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Symposium 2 - Poster

Electroanalysis and Sensors

Electrocatalytic oxidation of some carbohydrates at ni(ii)-curcumin modified glassy carbon electrode in alkaline media

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Curcumin (1,7-bis[4-hydroxy-3-methoxyphenyl]-1,6-heptadiene-3,5, dione) is an important natural phytochemical found in the rhizomes of *curcuma longa* or turmic, which has been known for its medical properties since ancient times. Recently there have been many reports in the literature on the metal chelating properties of curcumin, employing techniques like potentiometry and spectroscopy [1-2]. Curcumin forms complexes of the type 1:1 and 1:2 with transition metals [3-4]. It was found that such modified electrodes formed by electropolymerization its metal complexes act as very effective catalyst for oxidation of some organic compounds [5].

In our previous work, we reported the electrocatalytic oxidation of glucose at Ni(II)-curcumin modified glassy carbon electrode [6]. In this study, the electrocatalytic behavior of Ni(II)-curcumin complex on electrooxidation of some carbohydrates (monosaccharides: such as fructose and galactose, disaccharide: maltose) were investigated and compared with glucose by using cyclic voltammetry (CV), chronoamperometry (CA) and stationary polarization methods. The cyclic voltammetric studies indicated that in the presence of carbohydrates the anodic peak current was increased, followed by decreasing in the corresponding cathodic current. The oxidation of carbohydrates at Ni(II)-curcumin modified glassy carbon electrode gave approximately 12 electrons. Also, diffusion coefficients, rate constants of the catalytic reaction and electron transfer coefficients of carbohydrates were obtained. The results have been shown that by using the Ni-curcumin modified electrode, yielded low detection limits for determination of carbohydrates in aqueous media.

Keywords: Nickel, Curcumin, Carbohydrates, Modified Electrode, Electrocatalysis.

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Symposium 2 - Poster

Electroanalysis and Sensors

Comparative study of Methylene Blue- and Methylene Green- modified zeolite incorporated in carbon paste as amperometric transducers for H_2O_2 detection

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Zeolites ability to immobilize different redox mediators recommend them as attractive matrices for the preparation of composite electrode materials [1, 2]. Methylene Blue (**MB**) and Methylene Green (**MG**) are water-soluble cationic dies with the redox potential close to the optimal potential window for amperometric detection. They were incorporated in zeolite composite electrodes for amperometric detection of ascorbic acid [2, 3] and of NADH [3].

In this context and continuing our previous preoccupations in the field of zeolite modified electrodes [4], two new composite electrode materials, consisting of **MB** or **MG** (as redox mediators), a synthetic zeolite (as immobilization support) and carbon paste (as conductive material) (**MB-Z-CPEs** or **MG-Z-CPEs**), were prepared. Their electrochemical behavior was investigated by cyclic voltammetry measurements performed at different pH and potential scan rates. Using Laviron's treatment, the rate constant (k_s) of the heterogeneous electron transfer and the transfer coefficients (α) were estimated.

Both electrodes exhibit improved stability and good electrocatalytic activity toward H_2O_2 mediated electro-reduction.
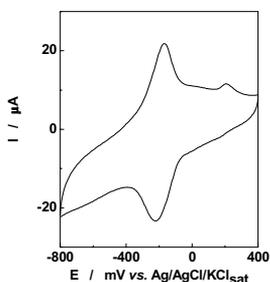
Cyclic voltammograms for **MB-Z-CPEs** recorded in phosphate buffer. Experimental conditions: starting potential, -800 mV *vs.* Ag/AgCl/KCl$_{sat}$; potential scan rate, 10 mVs^{-1}; supporting electrolyte, 0.1 M phosphate buffer, pH 5.0.

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Glucose and Lactate Biomonitoring by Scanning Electrochemical Microscopy (SECM)

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The present work aims the fabrication and visualization of micro-patterned complex biosensor architectures used as sensing chemistries in amperometric glucose and lactate biosensors [1].

Linear enzymatic microstructures with typical dimensions of 100 μm were obtained by micro-dispensing technology and were visualized using SECM to detect the enzymatic produced H_2O_2. Among all the modified surfaces (graphite, glassy carbon, glass, Pt, gold), the gold was found to be the best. The enzymatic structures were immobilised on the gold surface using glutaraldehyde.

Scanning a Pt-ultra microelectrode (25 μm diameter), placed above the modified surface and operated in feedback mode, over a pattern of immobilized glucose oxidase or lactate oxidase, each enzyme could be visualized (as increased current) in the presence of their specific substrate. The amplitude of the currents measured with the SECM tip was found to be proportional to the analyte concentration in the surrounding solution. So, enzyme microstructures combined with SECM could be used for multianalyte monitoring both in qualitative and quantitative ways (see figure below).
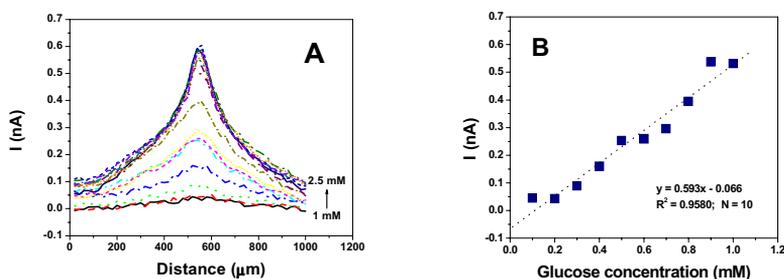
H_2O_2 oxidation currents (**A**) and calibration curve (**B**) obtained over a glucose oxidase line, deposited on a gold surface, for increasing glucose concentration (from 0.1 to 2.5 mM). Experimental conditions: E_{appl}= + 600 mV *vs.* Ag/AgCl pseudo reference

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Electroanalysis and Sensors

Polyelectrolyte-Functionalized ionic liquids and their applications to electroanalytical chemistry

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As low melting organic salts, ionic liquids (ILs) have attracted an increasing amount of interests due to their features such as low volatility, non-flammability, high chemical and thermal stabilities, high ionic conductivity and broad electrochemical windows. The initial investigations have been focused on chemical synthesis, catalysis, and separation as "green" solvents. More recently, ILs have started to emerge for fabrications of ionic devices, analytical chemistry, non-aqueous enzymology, preparation of functional nanostructures, their immobilization, *etc*.

It was noted that polyelectrolyte could be easily immobilized onto many substrates through various methods such as electrophoresis, layer-by-layer (LbL) assembly and casting, etc. Therefore, it would be helpful for us to immobilize IL facilely on general substrates with the aid of polyelectrolyte as carrier. So, the facile immobilization of ionic liquids by using polyelectrolyte as carrier (PFIL) was achieved. As examples, the immobilized PFIL exhibited the direct electrocatalysis activity towards the oxidation of NADH, which was never reported concerning the electrocatalysis of ILs.

Furthermore, a new approach based on a polyelectrolyte-functionalized ionic liquid (PFIL) for supporting electrolytes-free electrochemistry was succeeded. Such a PFIL with high ion conductivity and good compatibility towards a number of inorganic and organic species was immobilized on the electrode, which made it a promising solid polyelectrolyte for supporting electrolytes-free electrochemistry. And, the successful application of PFIL in a flow system was also achieved, suggesting that PFIL would bring a new area for the supporting electrolyte-free electrochemical detection and the HPLC-electrochemical detection (HPLC-ECD) system. This investigation would pave a new and significant way in the field of the supporting electrolyte-free electrochemistry, such as electrochemical synthesis, flow analysis, fuel cells and electrolysis.

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Electroanalysis and Sensors

Electrochemical oxidation and reactivity with superoxide anion of some new C-4 hydroxyphenyl 1,4-dihydropyridines in dimethylsulfoxide

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1,4-dihydropyridines (1,4-DHPs) have been widely used in cardiovascular therapy, due to their modulation of the slow L type Ca^{2+} channels. By this mechanism, 1,4-DHPs modulates the contraction of the vascular smooth muscle, which explains its therapeutic application in the arterial hypertension. Additionally, a large body of evidence obtained from several experimental models and results of clinical trials support that 1,4-DHPs exert antiatherosclerotic actions, which apparently are related with intrinsic structural characteristic of DHPs. This effect seems at least in part independent of the blood-pressure-lowering effect. In the present work the electrochemical oxidation and the reactivity with superoxide anion, $O_2^{\cdot-}$ in dimethylsulfoxide of some new C-4 hidroxyphenyl 1,4-DHPs (phenyl, 3-hydoxyphenyl, 4-hydroxyphenyl) is reported.

From the by cyclic voltammetry studies at different sweep rates it was concluded that the compounds were irreversibly oxidized under these conditions. Results on the reactivity of the synthesized 1,4-DHPs with superoxide anion followed by UV-Vis spectroscopy with diode array detector assembled with stopped flow technique demonstrated that the tested 1,4-DHPs significantly reacted with the radicals. In the figure, the time-course of the reactivity of 0.05 mM 4-phenyl-1,4-DHP in the presence of 0.5 mM of superoxide anion is shown. A decrease in the original absorption at 350 nm and the appearance of a new signal at 450 nm were observed. Finally, the inclusion of an hydroxyphenyl group of the 4-position on the DHP ring produced a significant increase in the kinetic rate constants.

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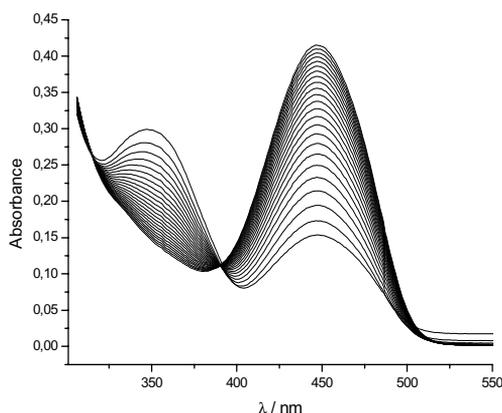
Examination of Solvation Process with Gravity Electrode

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Under a gravity field, an electrode reaction changes solution composition in the neighbourhood of an electrode, so that varied solution density induces a convective flow. Such change in solution density reflects the change in solvation states between product and reactant, which, therefore, can be detected in higher sensitivity by gravity electrode using convection in a high gravity field. Gravity electrode is, as shown in Fig. 1, an electrode system utilizing a centrifugal force as a gravity force, which can easily provide gravitational accelerations 100 times higher than natural gravity acceleration. An electrolysis cell attached on an arm revolving around a rotor is externally controlled by a potentiostat. Using the gravity electrode, diffusion current arising from the convective flow is firstly measured. Then, a density coefficient, a non-dimensional parameter intrinsic to the reaction is calculated. For a gravity field vertical to an electrode surface, the limiting-diffusion current density is expressed by

$$\vec{i}_{\lim} = A_v \left(\gamma \right)_{\lim}^{1/3} \alpha^{1/3} C_s \qquad (1)$$

where A_v is a constant, α is the gravity acceleration, C_s is the bulk concentration and $(\gamma)_{\lim}$ is the density coefficient in the limiting diffusion. From the obtained value of $(\gamma)_{\lim}$, the change in the partial molar volume ΔV during the reaction is calculated; e.g., in the case of a redox reaction, ΔV is given by $\Delta V = -(\gamma)_{\lim} / C_s$. Figure 2 shows the density coefficients measured in copper reduction in $CuCl_2$+KCl solution. $(\gamma_1)_{\lim}$ and $(\gamma_2)_{\lim}$ correspond to the reactions, $Cu^{2+} \rightarrow Cu^+$ and $Cu^{2+} \rightarrow Cu^0$, respectively. For
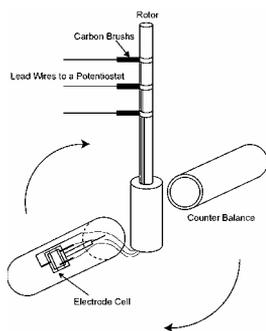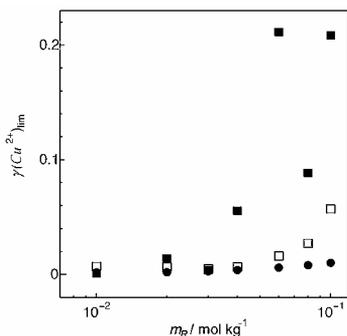

Fig. 1 Gravity Electrode System

Fig. 2 γ vs CuCl$_2$ molality. ■, $(\gamma_1)_{\lim}$; □, $(\gamma_2)_{\lim}$; ●, pycnometer.

Symposium 2 - Poster

Electroanalysis and Sensors

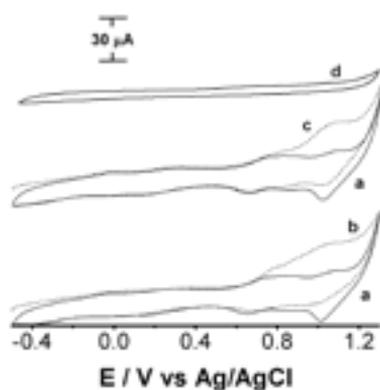# Electrocatalytical Oxidation of Guanine and Guanosine at a Ruthenium Hexacyanoferrate (RuHCF) modified electrode

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Guanine/guanosine are the most easily oxidized DNA base/nucleoside by processes involving ionizing radiation or attack by reactive oxygen species [1]. Hence, there is continuous interest for electrochemical sensors with ability to monitor at real-time conditions DNA damages caused by chemical transformations in the guanine moiety. To this end, in this work the electrochemical properties of a RuHCF modified electrode on the electrocatalytical oxidation of guanine/guanosine are described. Films of RuHCF were electrodeposited onto glassy carbon (GC) electrodes by cycling the potential between 0.0 to 1.2 V at 100 mV s^{-1} (15 cycles) in a fresh solution containing 0.5 M NaNO$_3$, 0.05 M HCl, 1 mM RuCl$_3$ and 1mM Fe(CN)$_6^{3-}$. The stability of the deposited film was investigated in supporting electrolyte solutions and the current decrease was less than 4 % after 15 potential cycles. Figure 1 shows the voltammetric responses of guanine and guanosine at bare GC and GC|RuHCF electrodes. At bare electrodes both substrates are poorly oxidized. The anodic peaks at 0.85 and 1.11 V in supporting electrolyte only are assigned to the consecutive anodic processes involving Fe(II)/Fe(III) and Ru(III)/Ru(IV)[2]. The film is not stable at alkaline conditions. The current enhancement of the anodic component is attributed to an electrocatalytic process when guanine and guanosine are added to the solution. Hydrodynamic studies with rotating disk electrode were performed and the limiting current did not increase linearly with $\omega^{1/2}$, the deviation from linearity being more evidenced at higher rotation rates. This suggests a kinetic limitation in the electron-transfer process and a similar behaviour was also observed at thicker films. However, electrocatalytic currents measured at 1.1 V increased at thicker films, which is an indication that the substrate penetrates into the film and that charge propagation is not restrained by the material deposited on the GC surface. Further investigations will be directed to the evaluation of analytical parameters in order to study DNA damage processes in single cells by using a RuHCF microelectrode.

Figure 1. Cyclic voltammetry of bare (d) and RuHCF modified GC (a,b,c) electrodes in the absence (a) and presence of 1mM guanosine (b,d) and 1 mM guanine (c,d) in a 0.5M NaNO$_3$ + 0.05M HCl solution. Scan rate = 100 mV/s.

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New concept to remove heavy metals from liquid waste based on electrochemical pH-switchable immobilized ligands.

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Absorption on resins is often used as secondary step in the treatment of water-based effluents, in order to reach very low concentrations. The separation of the trapped effluents from the resins and the regeneration of the resins for further use create wide volumes of secondary effluents coming from the washings of the resins with chemical reagents. We propose an alternative solution based on a « surface strategy » through adsorption phenomena and electrical control of the expulsion stage [1, 2]. The final goal is to limit or ideally to avoid the use of chemical reagents at the expulsion (or regeneration) stage of the depolluting process. Heavy metal ions were captured on active filters composed by a conducting surface covered by poly-4-vinylpyridine (P4VP). Due to pyridine groups those polymer films have chelating properties for copper ions. Our strategy for electrical triggering of the copper expulsion in aqueous medium is based on pH sensitive chelating groups. Applying moderate electro-oxidizing conditions generates acidic conditions in the vicinity of the electrode i.e. "inside" the polymer film. This allows a "switch-off" of the complexing properties of the film from the basic form of pyridine to pyridinium. Interestingly, no buffer washing is necessary to restore (or "switch-on") the complexing properties of the polymer film because the pH of the external medium is left unchanged by the electrochemical effect that affects only the vicinity of the electrode. Switch-on/switch-off cycles are followed and attested by IR spectroscopy and EQCM method.

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Medical Applications of a Sensor Technology Using a Microarray of 50-μm Diameter Microcavities with Self-contained Electrochemistry

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We report the development of rapid, sensitive, portable, low-cost, and reliable bioassays with electrochemical detection for medical applications using our technology involving microarray chips (Figure 1) of 50-μm diameter microcavities (depth of 8 μm) with self-contained electrodes (wall microelectrode at 8 μm^2 and bottom microdisk electrode at 2×10^{-5} cm^2). When the RMD is converted into a capture surface, the 4-um distance to the TNB detecting electrode provides close proximity for a rapid response showing the first signal in 30 s after substrate incubation. The smallest volume used with the microarray to date is 100 nL. The microelectrodes in the cavity exhibit lower background signals and zeptomole detection limits.

Our goal is to convert the microarray chips into self-contained microelectrochemical lab-on-a-chip (LOC) assay platforms that will integrate the high specificity of selected antibodies and/or DNA and the sensitivity of the microelectrodes in the microcavity. The self-contained microelectrochemical LOC assay can detect either a single analyte or multiple analyte in an array assay format by using monoclonal antibodies or capture probes to different analytes from a single sample.

Initial results for the detection of antibodies against the protective antigen (anti-PA IgG) from *Bacillus anthracis* will be discussed. Using the TNB microelectrode inside the 50-μm diameter microcavity as the detecting electrode, we have detected as low as 50 ng/mL Anti-PA IgG in a ~30 min total assay time from capture to signal generation. We will also present our preliminary results in the detection and quantification of the pathogen *Plasmodium falciparum* that causes malaria. We will include preliminary results on the solid phase-immunoassay capture of ovarian cancer biomarker CA 125 and TADG 14. We will describe efforts toward portability and automation that will allow use in clinics, hospitals, and research laboratories.
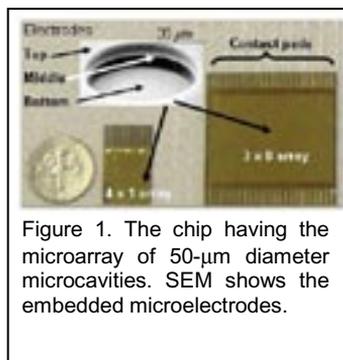

Figure 1. The chip having the microarray of 50-μm diameter microcavities. SEM shows the embedded microelectrodes.

Redox-switched anion binding of meso–tetraferrocenyl–t etramethylcalix[4]pyrrole

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Anion receptors containing electrochemically active groups such as ferrocene [1] are of great interest in supramolecular electrochemistry [2]. Recently, ferrocene amine compounds, based on calix[4]pyrroles and containing one ferrocene unit attached to a calix[4]pyrrole ring, were proved to selectively bind different anions [3].

In this context, the electrochemical behavior of a new organometallic compound, meso–tetraferrocenyl–tetramethylcalix[4]pyrrole (**FC**) [4], was investigated. Cyclic voltammetry measurements were used to examine the **FC** electrochemical response in different experimental conditions (different electrode materials, anion concentrations, pHs and potential scan rates), and in the presence of various anions (F^-, Cl^-, Br^-, SO_4^{2-}, $H_2PO_4^-$, ClO_4^-, AsF_6^-, NO_3^-).

The influence of the anion nature on the **FC** redox behavior was studied using: (i) dissolved **FC**, and (ii) immobilized **FC** by adsorption on different electrode materials. The voltammetric response of the **FC**-modified graphite electrode reveals the **FC** ability to bind selectively different anions. The value of the standard formal potential allows ranging the binding strength between **FC** and the investigated anions in the following sequence: $AsF_6^- < ClO_4^- < SO_4^{2-} < Br^- < F^- < NO_3^- < H_2PO_4^- < Cl^-$.
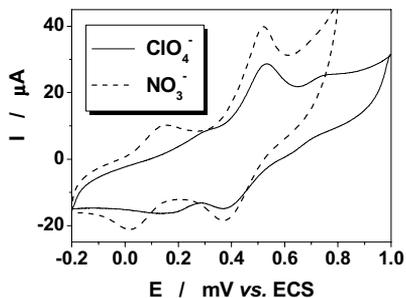
Anion influence on the voltammetric response of **FC** dissolved in DMSO.
Experimental conditions: **FC** 1 mM; working electrode, spectral graphite; potential scan rate, 50 mV/s; initial potential, -0.2 V vs. SCE; 0.1 M Na^+ salts.

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Development of a blood typing impedimetric immunosensor

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The development of methods targeting the direct monitoring of antibody-antigen interactions is particularly attractive. Among these, Electrochemical Impedance Spectroscopy (EIS) represents one of the most powerful methods, especially in terms of simplicity (no labeling is needed) and of its ability to be more easily integrated into multi-array diagnostic tools or microprocessor- controlled implanted sensors.

Here, a brief report on the work done in our laboratory regarding the development of EIS Impedimetric Immunosensors is presented.

The following points will be presented in details:

1) Development and study of Faradaic Impedimetric Immunosensors based on 11-amino-1-undecanethiol or on Dithiobis(succinimidyl) undecanoate SAM's.
2) Development and study of Faradaic Impedimetric Immunosensors based on poly-tyramine glassy carbon electrodes.
3) Analytical performance of the above-modified electrodes on blood-typing tests.

Electroanalysis and Sensors

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Electroanalysis and Sensors

Development of an impedimetric ozone sensor

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Electrochemical Impedance Spectroscopy (EIS), has emerged as a useful analytical tool for the development of sensor devices in a wide variety of configurations. More recently, the study of degradation phenomena taking place at polymer-coated substrates has led to the successful construction of versatile polymer-coated transducers for sensor development.

Here, a brief report on the work done in our laboratory regarding the development of an impedimetric ozone sensor is presented.

The following points will be presented in details:

1) Development and sensing performance of an electropolymerized poly-eugenol glassy carbon electrode.
2) Development and sensing performance of a lignin (organosolv or alkali)–modified glassy carbon and gold electrodes.

Electrochemical study and Application of Quinone/ Hydroquinone redox in unbuffered aqueous solutions

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Since the introduction of the quinhydrone electrode by Biilmann a great deal of experimental work to determine its range of applicability and the factors which limit its use, has been carried out, most of the work being done on well buffered solutions. Kolthoff and Bosch in testing the applicability of the electrode to weakly buffered solutions of pH values ranging from 3.6 to 7.2, prepared by diluting the usual buffer solutions, concluded that the electrode gives values in good agreement with those obtained by the hydrogen electrode over the range investigated. But in unbuffered solutions (pH>5) the electrode gives erroneous values [1]. Also some literatures indicate that"salt error" that is a function of the hydrogen ion concentration as well as mole fraction of the salt [3]

In this work we show that the response of quinhydrone is different in buffered and unbuffered solutions with same value of pHthe . Based on our result voltammograms of hydroquinone and quinone has same value of $E_{1/2}$ in buffered solution but in unbuffered solution $E_{1/2}$ of hydroquinone has a significant difference (0.35 V) with quinone half wave potential. In unbuffered solution with pH range of 5-8 potential of the peak is dependent on basicity and acidity of the strongest base or acid that exists in solution These result are used for investigation of acidity or basicity of weak acid or base in inert aqueous solutions such as aqueous KCl

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Electroanalysis and Sensors

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Electroanalysis and Sensors

Studies Towards a Novel Electrochemical Biosensor System for Real-Time Monitoring of In-Vitro Cell Toxicity

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The aim of this study is to develop novel screen-printed biosensors for application in toxicological analysis. The biosensor system should allow continuous measurements of the cellular metabolites lactate, and lactate dehydrogenase as markers of cellular toxicity. It has been shown that these biomarkers can be linked and monitored via the production of hydrogen peroxide (H_2O_2) [1]. Screen printed carbon electrodes incorporating the electrocatalyst cobalt phthalocyanine have been investigated given their ability to detect H_2O_2. These devices demonstrate that H_2O_2 can be determined over the range $10 \mu M$-1mM with a sensitivity of 0.92 nA μM^{-1}. The results were obtained in 0.25M phosphate buffer at pH 7.3 indicating that the biosensor should operate successfully in tissue culture medium. The data provides proof of principle evidence that cobalt phthalocyanine can be used to detect micromolar levels of H_2O_2. Current research is underway to miniaturise the working electrode, so that toxicity measurements may be performed continuously without significant perturbation of the biological system.

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Fast Response and Selective Perchlorate Polymeric Membrane Electrode Based on Bis(dibenzoylmethanato) nickel(II) Complex as a Neutral carrier

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The traditional anion-selective membrane electrode based on ion exchanger always displays a Hofmeister selectivity sequence, in which a membrane selectivity is controlled by the tree energy of hydration of the ions involved recently have been more concerning on the electrodes using plasticized poly (vinyl chloride) (PVC) membranes incorporating different complexes as a carrier [1].Recent research has shown that chlorate and perchlorate anions may be found at high concentrations (>50 and >1000 mg l^{-1}, respectively) in surface waters and ground waters around the world [2]. Such contamination is due to the perchlorate salts that are used in solid propellants and in a wide variety of industrial situations. Thus, the determination of perchlorate in different samples such as ground water, driver water and urine in presence of other anions is of vital importance [3]. The determination of perchlorate ion has been carried out directly or indirectly by a variety of classical and instrumental methods. These methods include volumetric titration, gravimetery, spectrophotometry, atomic absorption spectrometry and ion chromatography. However, most of these methods are susceptible to interference from different cationic or anionic species and are either time-consuming or need sophisticated instruments. Potentiometric detection based on ion-selective electrodes, as a simple method, has several advantages, for example speed, ease of preparation and procedures, simple instrumentation, short response time, no contamination, nondestructive, unaffected by color or turbidity, wide dynamic range, reasonable selectivity, and the list of available electrodes has grown substantially over the last few years. In this study the feasibility of a synthesized Ni(II) complex $(Ni(DBM)_2)$ as a novel ionophore for the preparation of solid ion selective polymeric membrane (PVC) was tested. The Ionophore has shown with enhanced potentiometric selectivity toward perchlorate compared to other anions. The selectivity sequence of this electrode is as follows: $ClO_4^- > SCN^- > I^- > CN^- > ClO_3^- > NO_3^- > Br^- > SO_3^- > BrO_3^- > F^- > Cl^-$, which is a Hofmeister selectivity sequence. The proposed electrode possesses very wide Nernestian potential linear range to perchlorate from 1.0×10^{-6} to 1.0×10^{-1} M (0.138 µg ml^{-1}-138 mg ml^{-1}), low detection limit (6.6×10^{-7} M) and good perchlorate selectivity over the wide variety of other anions. The developed electrode have especially fast response (<5S) and wide pH independent range (1.2-12.5) in comparison with recent reported electrodes. The proposed electrode was used for the determination of perchlorate in the water samples and human urine with satisfactory results.

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Electroanalysis and Sensors

Application of polydiphenylamine (pdpa) films as potentiometric ph sensors

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The measurement and control of pH in different media are subjects of great importance in numerous fields of science and technology. Several methods have been developed for the determination of pH; among them the potentiometric ones. The glass electrode is the most widely used, nevertheless it presents some disadvantages that justify the increasing interest in the design of new sensors for pH. Chemically modified electrodes, especially by conducting polymer films, have gained considerable attention as pH sensors due to their ease of synthesis and stability under ambient conditions .

It is possible to generate pH sensors for different pH range, using ring substituted or N-substituted PANI derivatives, because it is possibly to tune the pKa of the film. In the present work, a study on the possibility of use of PDPA as a potentiometric pH sensor is reported. Different experimental conditions for electrochemical synthesis of the film are discussed, that allow to obtain adherent films as well as to improve the potentiometric pH response.

PDPA films were deposited on gold wire electrodes by electropolymerization from a deoxygenated 3.7M $HClO_4$ solution containing a variable concentration of the monomer. In order to obtain homogeneous films, with good adherence and sensitivity for pH measurements, different experimental conditions were employed. The influence of monomer concentration, upper potential limit and number of cycles were analyzed. Best results were obtained with the following conditions: saturated monomer solution, potential limits, -0.1 and 0.60 V, and 200 cycles. The potentiometric response of polymer films was measured in the pH range of 0-10.

The results obtained in this work indicate that PDPA modified electrodes are suitable for pH sensing. Stable and adherent films are obtained on gold by electropolymerization in diphenylamine saturated solution and it is possible to improve the linearity of calibration curve by means of an electrochemical conditioning treatment.

Electrochemical Characterization of new 4-indolyl 1,4-dihydropyridines

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1, 4-dihydropyridines (1, 4-DHPs) have been widely used in the treatment of the hypertension.. From the discovery of the pharmacological effects of these compounds, a great interest has been generated to optimize its structure, in the search of new therapeutic and more selective applications with less deleterious effects. From a metabolic point of view, 1, 4-DHPs undergo a fast and extensive biotransformation by hepatic oxidation, giving rise to the pyridine derivative, which is pharmacologically inactive. In addition, it has been established that 1, 4-DHPs exhibit other biological activities, which also contribute to their pharmacological and clinical effects, i.e. its antioxidant effect. In this context, the indol and its derivatives are well-known as powerful protectors of the CNS against the oxidative stress caused by free radicals. In the present work, we report both the synthesis and the electrochemical oxidation on a glassy carbon electrode of two new derivatives (Figure). The electro-oxidation of 1,4-DHPs was studied in different electrolytic media (protic, mixed and aprotic). For the electrochemical characterization different methods (differential pulse and cyclic voltammetry, controlled potential electrolysis) were employed Also, spectroscopic techniques like UV-Visible spectroscopy, ESR and chromatographic techniques (HPLC, GC/MS) to characterize the formation of possible intermediates generated during the oxidation process were used.
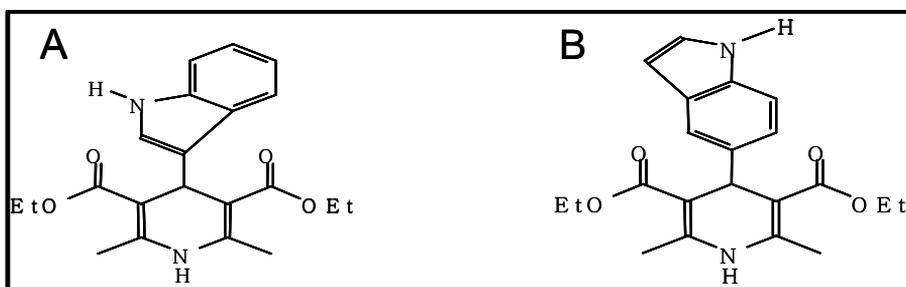
Figure. **(A)** 2, 6-dimethyl-3, 5-diethoxycarbonyl-4-(3-indolyl)-1, 4-DHP and **(B)** 2, 6-dimethyl-3, 5-diethoxycarbonyl-4-(5-indolyl)-1, 4-DHP).

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Modified carbon paste ion-selective electrode for copper(ii) determination

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Some carbon paste electrodes modified with bisthiourea derivatives were developed for potentiometric measurements of copper(II) in aqueous medium. Bisthiourea, phenyl-, bis-phenyl-, bis-alyl-, bisthiourea were the studied ionophores. Best results were obtained using bis-phenyl-bis-thioureea (BTBF) 14,2% (w/w) modified carbon paste sensor. Limit of detection was $2,58 \times 10^{-6}$ mol/L, slope 33,91 mV/decade and response time 2,1 minute. Fixed interferent method was used to determine the selectivity coefficient over Co(II), Pb(II), Zn(II), Ni(II), Cd(II), Mg(II), Ca(II). The potential of the sensor decreases with the increase of the pH, both, in the presence and in the absence of Cu(II), which recommends the use of buffer solutions.

The sensor was used for determination of Cu(II) concentration in alcoholic drinks that are traditionally prepared after fermentation of plums by distillation in copper tanks. The results were compared with the one obtained by staircase anodic stripping voltammetry using hanging mercury drop electrode.

New aspects concerning the electrochemical impedance spectroscopy in the case of charge transfer and diffusion limitations and their implication in drug action testing

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A new approach to the theoretical basis of the Electrochemical Impedance Spectroscopy in the case of redox multielectrodes has been developed by Bonciocat et al. [1,2]. This new approach uses as starting point an integral equation of Volterra type whose solution gives the current density passing trough the redox electrodes when only the CT (charge transfer) and diffusion limitations of electrochemical reaction $O + ne^- \leftrightarrow R$ are present [3].

Based on this approach, new parametric equations of Nyquist diagrams applicable in two extreme domains of frequencies have been deduced. Further this equations have permitted to develop a new way of performing the Nyquist plots, and to get two criteria by which may be estimated the charge transfer and diffusion limitations of reactions occurring simultaneously at the redox multielectrode. One of the redox reaction is taken as reference reaction, the second is due to the physically dissolved oxygen, and the others express the effects of drugs added in solution. In some time the proposed criteria can be used in biocompatible nanostructurated surfaces monitoring.

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Electroanalysis and Sensors

Electrodeposition of silver at disorganised monolayer modified gold electrodes

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The application of voltammetric techniques at solid electrodes for low-level detection of metal ions has proven a challenge in the presence of large surfactant excess. The target analyte in this study was silver, a trace metal pollutant found in photographic waste. As illustrated by earlier studies a disorganised thiol monolayer formed on gold surfaces allows determination of metal concentrations in the presence of surfactants.[1] The excellent electroanalytical abilities of underpotential deposition-stripping voltammetry (UPD-SV) in terms of limit of detection and sensitivity have been noted.[2] The combination of UPD-SV with the simplicity of use of the disorganised monolayer approach for surfactant exclusion has previously allowed determination of copper concentrations in real samples such as soil extracts.[3]

In this work, an investigation of the Ag electrodeposition at gold surfaces modified with a thiol disorganised monolayer was undertaken. The influence of deposition times on the bulk and UPD Ag deposition at both bare and thiol modified electrodes were illustrated using CV studies. UPD-SV was used to investigate the influence of the Ag concentration on the evolution of the stripping signal at both bare and thiol modified electrodes. Surfactant exclusion studies were carried out with gelatin and show the influence of the gelatin concentration on the stripping peak current of Ag at bare and thiol modified electrodes. This investigation provides information on the arrangement of the thiol monolayer when the Ag atoms underpotentially deposit and provides an alternative method of detecting trace metals in sample matrices containing surfactants, proteins or other fouling materials.

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The electrochemical behaviour mechanism of osmium tetroxide

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Electroanalysis and Sensors

Investigation of electrochemical behaviour of osmium tetroxide in the presence of hydrogen peroxide detected the interesting property of system OsO_4 - H_2O_2. At the electrolytic oxidation of precipitate, produced at the electrolytic reduction of osmium tetroxide to metal osmium, reverse peak is observed at the voltammetric curve.

This paper gives the results of reverse peak nature studying and the mechanism of the osmium tetroxide electrochemical reduction and oxidation in the presence of hydrogen peroxide.

As it is known, the hydrogen peroxide in solution can be oxidant or reducer. The effect of different oxidants and reducers on the peaks of this process were investigated in order to determinate the hydrogen peroxide role in the process of osmium tetroxide electrolytic oxidation. Sodium nitrite and sodium sulphite were used as reducers, potassium bromate and potassium chromate ware as oxidants.

The results showed the reverse peak appeared in presence of oxidants (H_2O_2, BrO_3^- and CrO_3^-). Therefore the hydrogen peroxide was determinated to be the oxidant in electrochemical reaction. The comparison of reverse peaks values in presence of different oxidants such as hydrogen peroxide, bromate and chromate showed that the biggest value of reverse peak is observed in presence of hydrogen peroxide.

It should be noted that voltammetric curve of osmium tetroxide electrolytic reduction without hydrogen peroxide can be seen two peaks: one at 0.0 V and the other at –0,15 V. It was established that the sensitivity of osmium tetroxide determination in presence of hydrogen peroxide at the cathode voltammetric curves is higher than in other known backgrounds. This effect can be explained by the chemical reaction influence of osmium dioxide and hydrogen peroxide interaction. During electrolytic reduction on the electrode surface the reduction of osmium tetroxide to osmium dioxide, and later to metal osmium is observed. At the same time, osmium dioxide can be oxidized to osmium tetroxide by chemical reaction (1).

$$OsO_{2s}+4H_2O_2=OsO_{4aq}+4H_2O+O_{2s} \tag{1}$$

As a result of process (1) the current of electrolytic reduction can be higher in presence of hydrogen peroxide. Produced by chemical reaction oxygen is adsorbed on the $Os+OsO_2$ precipitate.

At the voltammetric curve of electrolytic oxidation of precipitate, produced by electrolytic reduction of osmium tetroxide without hydrogen peroxide two anode peaks are observed, one at 0,35 V, and the other at 0,6 V. With the hydrogen peroxide in system two reverse peaks are observed. As the result of investigations it was established that these peaks belong to the process of oxygen electrolytic reduction (2), which is adsorbed on the electrode surface by the Os and OsO_2 precipitates.

$$2O_{2s}+4H^++4e=2H_2O_2 \tag{2}$$

Symposium 2 - Poster

Electroanalysis and Sensors

Direct electrochemistry of laccase covalently immobilized on a dendrimer attached conducting polymer and its application to biosensors

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The direct electron transfer processes of protein or enzyme provide redox mechanisms in biocatalyst and metabolic processes involving electron transfer in biological systems [1] and establish a foundation for constructing the third generation biosensors without using mediators. Among enzymes, laccase catalyzes the various phenolic compounds with the concomitant reduction of oxygen to water [1]. There are only a few publications reporting on the direct electrochemistry of laccase [2]. However, the mechanism of the direct electron transfer of the immobilized laccase has not yet been fully understood. In this respect multilayer films may provide a suitable environment for laccase to transfer electrons with underlying electrodes. The covalent layer-by-layer (LBL) assembly is one of the most perspective methods for the formation of stable multilayer films on solid surfaces [3]. The multilayer formation of an enzyme using dendrimers, which are highly branched, mono-dispersed macromolecules with a high number of surface functionalities are of great interest from the view point of application in biosensing, biocatalyst, etc.

In the present study, laccase from *Rhus vernicifera* was immobilized layer-by-layer on a conducting polymer using dendrimer as a building unit for the multilayer formation. The laccase multilayer was prepared by an alternate covalent LBL deposition of a carboxylic acid terminated polyamidoamine dendrimer (G3-PAMAM) and laccase on a diamine functionalized conducting polymer [4]. The dendrimer/laccase multilayer films were characterized using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), quartz crystal microbalance (QCM), x-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). The direct electron transfer reaction of laccase was studied at the dendrimer attached conducting polymer modified electrode. The dendrimer/laccase multilayer biosensor was used for the detection of catechol and catechin. The immobilized laccase oxidised catechol and catechin in the presence of oxygen and the conducting polymer reduced the oxidized product at about -200 mV and -50 mV, respectively. Amperometric detection of catechol and catechin was studied and their detection limits were evaluated.

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Direct electrochemistry of horseradish peroxidase immobilized on a poly (1, 8-Diaminonaphthalene) film

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The applications of conductive polymers (CPs) to sensors have been received considerable attention due to their unique properties [1]. The CPs serve as an immobilizing matrix and provide a suitable environment for biomolecules in the biosensor systems. Of the many classes of conductive polymers, poly (1,8-diaminonphthalene) (poly-DAN) [2,3] having amine groups can be one of promising immobilizing matrix for biomolecules. Moreover, the conductivity of poly-DAN film can be increased by the electrochemical deposition of metal nanoparticles in or beneath the film. To our knowledge, there is no publication reporting the application of a poly-DAN film with or without metal nanoparticles in the fabrications of sensors or biosensors.

In the present study, amperometric hydrogen peroxide biosensors were fabricated by immobilizing an enzyme, horseradish peroxide (HRP) onto a poly-DAN film on glassy carbon electrode surfaces with or without gold nanoparticles (Au NP). At first, a stable film of poly-DAN was electrochemically grown using cyclic voltammetry (CV) on glassy carbon surfaces with or without prior deposition of Au NP. The enzyme, HRP was then immobilized onto these films through the covalent cross linking using glutaraldehyde as a cross-liker. The immobilized HRP on these films showed a direct electron transfer process in cyclic voltammetric experiments. The surfaces of the HRP/Poly-DAN/Au NP/GCE and HRP/Poly-DAN/GCE were characterized using scanning electron microscope (SEM), x-ray photoelectron spectroscopy (XPS), quartz crystal microbalance (QCM), and electrochemical impedance spectroscopy (EIS) techniques. The electrocatalytic activities of the both electrodes towards hydrogen peroxide detection in a phosphate buffer solution were studied and were compared. The enhanced conductivity of the poly-DAN film by Au NP resulted in the high sensitivity to the detection of hydrogen peroxide compared to our previous result employing a terthiophene based conducting polymer [4]. The linear dyanamic range obtained at the optimized condition was between 0.0001 and 25.0 mM and the detection limit was determined to be 0.1±0.05μM.

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Symposium 2 - Poster

Electroanalysis and Sensors

Genetic Algorithms for the Optimization of Electrodeposition Polymers as Immobilization Matrix in Amperometric Glucose Biosensors

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The rational design of specific biosensor properties in accordance with the prerequisites imposed by the analytical application is important on the way from the principal sensor design to its application in real samples. Previously, we have proposed electrodeposition polymers as immobilization matrix for enzymes in amperometric biosensors, and attempts were made to elucidate the impact of the polymer composition on the sensor properties using combinatorial parallel synthesis of polymer libraries [1]. It was demonstrated that the sensor characteristics varied significantly in dependence from the polymer composition and initial attempts were made towards a rational design of electrodeposition paints for improved biosensors in terms of sensitivity and linear range of response to the analyte.

In most cases the correlation between the polymer composition represented as the impact of the individual monomers used in the polymer synthesis and the biosensor properties are not linear and suitable mathematical models describing the complex parameter space are not available. However, screening of all the possible polymers compositions concerning their impact on the sensor properties could lead to insights into the complex parameter space, although the fabrication and testing of a large number of sensors will be tideous and time consuming. In order to overcome this drawback and finally to develop tools for a fast and straight forward optimization of complex biosensors architectures a strategy is proposed based on genetic algorithms. Premised on the evolutionary ideas of natural selection, genetic algorithms paved way for a significant decrease in time that has to be spent in finding a suitable polymer composition that can be used for fabrication of biosensor with defined characteristics.

As an initial objective for our experiments we have chosen glucose biosensors with simple architecture using cathodic electrodeposition polymers as immobilization matrix and glucose oxidase as biological recognition element. Fabrication and evaluation of biosensors were performed automatically using a previously described [2] electrochemical robotic system. As optimization parameter the maximal current at substrate saturation was used (I_{max}^{app}) aiming on optimized biosensors with high sensitivity. Optimization of the polymer composition using genetic algorithms and automated sensor fabrication and evaluation in an automatic electrochemical robotic system will be presented.

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Electro analysis of heavy metal, cd²⁺ by gold electrode modified with self-assembled monolayers of di-thiols

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The application of self-assembled monolayers (SAMs) in enhancing the selectivity and sensitivity of interfaces towards different species, in particular heavy metals, is well established [1]. SAMs offer a convenient and simple approach for controlling and structuring the interactions between the interface and species in the solution. We will review our recent studies, which will highlight the advantages and prospects of these approaches. The formation of a dithiol monolayer on a polycrystalline Au disk electrode surface has been used for the anodic stripping voltammetry of Cd(II) ions. We found that a monolayer of either 1,6-hexanedithiol or 1,9-nonanedithiol resulted in the appearance of two sharp stripping peaks of Cd(II). The nature of the anodic stripping peaks depends on the deposition time, modification time of the gold electrode. The peaks and the system have been studied by different electrochemical techniques, cyclic voltammetry, linear sweep voltammetry, squarewave voltammetry and differential pulse volttametry, XPS and IR and reveal very interesting interaction of the deposited Cd with the thiol groups. By charactising the Cd deposition onto the gold modified dithiol SAMs at different potential by XPS and IR, we believe that the Cd electrochemically deposit beneath the thiols and therefore continuously interacts with it upon electrochemical dissolution.

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Voltammetric behaviour of a 4-Nitroimidazole derivative: Nitro radical anion formation in presence of surfactants

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Nitroimidazoles have been the source of many investigations because of their properties as antibiotics, radiosensitizers and antiprotozoans wherein the nitro radical anion derivative is a key intermediate in its biological activity. Consequently, the understanding of the nitro radical behaviour is a permanent challenge for this type of compounds and the electrochemistry can play an important role in its study.

In the scope of our current investigations to find new pharmacological important compounds that use the nitro radical anion as the active specie, we synthesized 1-methyl-4-nitro-2-hydroxymethylimidazole (4-MNImOH) a new 4-nitroimidazole derivative substituted in positions 1 and 2. In a previous study (1), we studied the nitro radical anion formation in aqueous, mixed and nonaqueous media, but only in mixed and nonaqueous media the nitro radical anion was capable of being detected in the time scale of the cyclic voltammetric technique. In this work we used a series of surfactants as SDS (anionic), Triton-X (non-ionic), Hyamine (Cationic) and Cetyl Trimethyl Ammonium Bromide (CTAB) (cationic) in order to detect the nitro radical anion from 4-MNImOH in aqueous medium. Cyclic voltammetry (CV), differential pulse polarography (DPP) and tast polarography (TP) were used to study the formation of the nitro radical anion with different surfactants at different pHs in aqueous medium.

The cyclic voltammograms of the nitro radical anion isolated from a solution containing 1 mM of 4-MNImOH in 100 % Britton Robinson Buffer, pH 7.4 with 15 mM of Hyamine at different sweep rates is shown in the figure.

The stability constants of the nitro radical anion were determined at different pHs according to the Olmstead's approach (2).
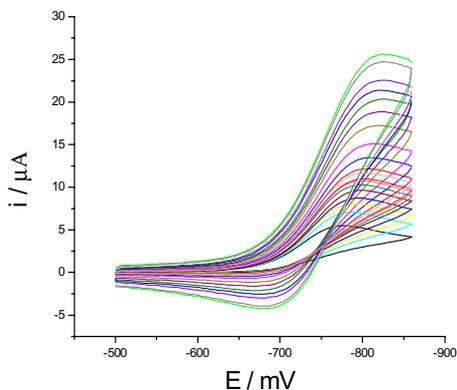
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Electroanalysis and Sensors

A photoelecetrochemical signal chain using cytochrome c and a quantum dot modified gold-electrode

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Generating signal chains on electrodes is a versatile tool to detect specifically various species in solution. The model of such a chain can be found in several biological systems which are often associated with protein interactions on membranes as for example the respiratory chain. Based on that model several systems have been developed in biosensorics by means of protein modified electrodes.

An evolution of the known signal chain framework would be to implement a switch which allows to read out the generated signal in a time and spatially- resolved manner. The photoexcication of so called quantum dots has been shown to be capable of acting as such a switch. An "on" and "off" differentiation can give access to a parallel read out of planar sensor electrodes with different interaction places.

Here we show the application of CdSe/ZnS- quantum dots on gold electrodes in an switchable arrangement based on the light induced generation of electron-hole pairs inside the particles. A light-induced electron transfer from and to the particles could be obtained using light pulses in the range of seconds. The photo current was dependent on the concentration of oxidised/ reduced cytochrome c in the mircromolar range. The formal potential of the protein in our setup was determined. The influence of the excitation wavelength on the signal was examined between 450 and 600 nm.

A signal chain starting from superoxide radicals via cytochrome c to the quantum dot modified electrode could be established. It is based on the electron transfer from the radical to oxidized cytochrome c. Thus, a switchable detection chain for the superoxide radical, a potent marker of oxidative stress, could be developed.

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Electroanalysis and Sensors

Liquid membrane oscillators and lipid, lipid like systems for taste sensing

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The construction of a reliable taste sensor for control of food quality is very important in food industry. Liquid membrane oscillators were proposed for molecular recognition of taste substances. They are composed of two aqueous phases: donor phase (ionic surfactant) and acceptor phase (taste substance) separated by organic solvent phase. The influence of substances belonging to four taste classes on the oscillation of electric potential difference between aqueous phases was examined. The oscillation curves were analyzed by construction of attractors using time delay method. The two-dimensional attractors were different in shape and size for systems investigated. They might be used as fingerprints for identification of responsible substances. However, due to chaotic behavior they can not be applied in taste sensors.

Lipid (elaidic acid, cholesterol) and lipid like (benzylhexadecyldimethylammonium chloride, hexadecylamine, 1-dodecanol) – polymer membrane electrodes were used in five-channel taste sensor. Their responses were sensitive to appropriate bitter, sour and salt substances present in the system and not too sensitive to sucrose concentration. This sensor was successfully applied for discrimination and quality control of different kinds of tonics containing sucrose, quinine hydrochloride and carbon dioxide.

The mixtures of substances belonging to four taste classes have been investigated using potentiometry methods. The five-channel taste sensor was successfully used for recognition of commercial aqueous drinks made up from sucrose, citric acid and carbon dioxide (orangeades).

The characteristics of these membranes and their interactions with taste substances are still poorly recognized. Poly(vinyl chloride) membranes loaded with lipids or lipid like substances in contact with quinine hydrochloride solution were characterized by electrochemical impedance spectroscopy in a frequency range from 100 kHz to 0.1 Hz of the AC signal. Impedance measurements allowed to distinguish three different time constants: high frequency resistance R_{hfr}, medium range frequency resistance and capacitance in series $R_M C_M$, and diffusion impedance Z_W measured as Warburg coefficient σ.

Values R_{hfr} were not sensitive to the outer electrolyte concentration for all membranes. Medium frequency resistance, R_M, was found to be dependent on the outer electrolyte concentration membranes with benzylhexadecyldimethylammonium chloride and hexadecylamine.

S2·P-111

Early fire detection and odor source detection using mobile robot with MOS-type gas sensor

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The objective of this work is to demonstrate a robot with metal oxide semiconductor (MOS)-type gas sensor suitable for early fire detection and odor source detection. It is known that ordinary fire alarm systems respond to smoke, heat and flame in order to detect fire. The detectors, however, can not detect initial stage of fire. Thus, we try to develop an odor sensing system for early fire detection and fire source detection which consist of mobile robot and MOS-type gas sensor array. In this work, five different types of MOS-type gas sensors which are commercially available were used as sensors for early stage detection of fire. A MOS-type gas sensor (Model: CH-Ez from New cosmos Electric Inc.) was used to fire source detection. These sensors can attach to a mobile robot.

Fig.1 Results of the PCA plot

First of all, we measure the odorants generated by burning some materials such as tobacco, cellulose, polyethylene and nylon using MOS-type gas sensor array, as well as disturbed odorants from perfumery and liquid hairdressing in the house. The result of principal component analysis (PCA), which was reduced to the first two principal components for visualization of multidimensional data, is shown in Fig.1, in which outputs of the several sensors for each odorant are plotted. It is clear that the sensor outputs for individual odors tend to cluster in discrete sections of space with well-defined boundaries. This result strongly suggests that proposed sensor array can discriminate the odorants generated by burning materials from

Fig.2 Mobile robot to detect the odor source using four MOS-type gas sensors

disturbing odorants in the initial stage of fire. We also try to detect the fire source using four MOS-type gas sensors attached to a mobile robot as shown in Fig.2. We demonstrate that the robot with MOS-type gas sensors can arrive at the odor source from low concentration to high concentration in the plume by analyzing the sensor outputs using attached microcomputer.
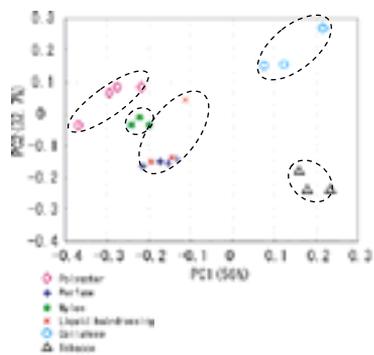
Kinetic analysis of enzymatic hydrolysis of starch granules using an amperometric glucose sensor

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Much attention has been paid to enzymatic hydrolysis of starch granules catalyzed by amylases. In most studies, the reaction has been followed by spectrophotometry of saccharides in the reaction mixture after removing starch granules at different times. In comparison with spectrophotometry, electrochemical measurements have advantages of being free from the influence of turbidity and coloration of a test solution. In this study, an amperometric glucose sensor, in which the oxidation current of the redox mediator reduced by the glucose oxidase (GOx) reaction is monitored, has been introduced to study the kinetics of hydrolysis of starch granules catalyzed by glucoamylase (GA). The dependence of the initial rate of the hydrolysis on the amount of enzyme and substrate and on the specific surface area of substrate is discussed.

Maize starch granules (0.025–1.0 g) were suspended in 5.0 mL of 0.1 M acetate buffer (pH 5.0) for the electrochemical measurement. A film-coated GOx-immobilized benzoquinone (BQ)-mixed carbon paste electrode (CPE) was prepared as described by Ikeda et al. (Agric. Biol. Chem. 49 (1985) 541). GOx (30 units) was trapped by a dialysis membrane on the surface of CPE (3.0 mm diameter) containing 10 wt % of BQ in carbon paste. An oxidation current was recorded at a fixed electrode potential of 0.60 V vs Ag/AgCl/0.1 M KCl without deaeration. The suspension was stirred by a magnetic stirrer at 500 rpm. The film-coated GOx-immobilized BQ-mixed CPE allowed the determination of D-glucose concentration sensitive to levels as low as 0.01 mM, with a linearity of up to 10 mM. The response time was approximately 20 s. Direct and continuous observation of the hydrolysis even in a thick starch suspension can be achieved.

Upon addition of GA to the starch suspension, the current increased linearly. When the supernatant was used in place of the suspension, the current did not change by addition of GA, indicating that dissolution of starch was negligible and that the current increase can be attributed to production of glucose by the surface hydrolysis of starch granules catalyzed by GA. The slope of the linear increase of the current was used to determine the initial rate (v). The v-value increased with increasing concentration of the enzyme to approach a saturation value, whereas it was proportional to the amount of the substrate. Also, the v-value was proportional to the specific surface area of the substrate. The experimental results can be explained well by the rate equations derived from a three-step mechanism, which consists of the adsorption of the free enzyme onto the surface of the substrate, the reaction of the adsorbed enzyme with the substrate, and the liberation of the product.

Structure and potential-dependent properties of electroactive polymeric [Ni(salen)] sensing films

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The quest for novel materials for detection of molecular/ionic solution species is an active research area, with applications as diverse as biology[0] and waste management[0]. A practical sensing system must fulfil (at least) two criteria: (i) selectivity to the target species and (ii) a suitably sensitive detection method. Here we use complexation chemistry to satisfy the former and the electrochemical quartz crystal microbalance (EQCM) to provide the latter.

We have focused on the preparation of electroactive polymer films based on [Ni(*salen*)] units, tuning their properties by altering the substituents. These materials have been extensively characterised in terms of their spectroelectrochemical properties[3], which reveal that polymer redox chemistry is ligand-based and that the metal (here, nickel) has a structural role as a bridge.

We describe how incorporation of macrocyclic ligands (such as crown ethers) in electrochemically-generated poly[Ni(*salen*)] films can endow them with ion recognition capability. We explore this in the context of alkaline and/or earth-alkaline ions, exploiting the selectivity associated with the inherent structural features of the crown ether. Preliminary electrochemical data[0] showed that poly[Ni(salen)(crown)] films were able to detect electroinactive ions, such as Ba^{2+}, at micromolar levels, but provided no insight into the underlying structure and mechanism. Here we show how one can rationalise the binding process and the influence over polymer electronic response on the basis of EXAFS-derived local structural information around the Ni and Ba atoms. Interestingly, the metal-ligand binding and the roles they play are quite different for the two metals.

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Glucose biosensors based on electrodes modified with ferrocene derivatives intercalated into mg/al layered double hydroxides

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The rapid and accurate determination of blood glucose is of fundamental importance for the effective management/treatment of diabetic patients. The monitoring of glucose levels is also very important in industrial applications. In this work, ferrocene-carboxylate ($Fc\text{-}CO_2H$) and ferrocene-sulfonate ($Fc\text{-}SO_3H$) have been used as redox mediators for the oxidation of the enzymatically produced H_2O_2 in amperometric biosensors for glucose determination. Glassy carbon electrodes (GC) have been modified with a biofilm constituted by the ferrocene-derivatives, intercalated into a Mg/Al double layered hydroxide(LDH) and glucose oxidase (GOx) immobilized by crosslinking with glutaraldehyde. The LDH was synthesised by the coprecipitation method in the presence of the anions of the ferrocene mediators [1]. The performances of the two biosensors were evaluated by chronoamperometric tests both in batch and in FIA working at low anodic potentials (0.400 V vs. SCE for $Fc\text{-}CO_2H$ and 0.5 V for $Fc\text{-}SO_3H$). A comparison of the sensitivities to glucose showed that both biosensors have a linearity range extending up to 1.5 mM, in batch and 10 mM in FIA, although the biosensor based on $Fc\text{-}CO_2H$ was more sensitive (6.6 ± 0.3 versus 2.8 ± 0.3 μA $mM^{-1}cm^{-2}$ in batch mode, and 37.1 ± 0.3 versus 15.4 ± 0.4 μA $mM^{-1}cm^{-2}$ in FIA). Long-term stability was about 21 days, if the electrodes were stored in phosphate buffer, pH 7.0 at 4°C. An accurate determination of glucose at a much lower value than the physiological one (0.75 mM) in the presence of the most common interfering compounds (ascorbic acid, uric acid and acetaminophen), at the concentrations usually found in the biological fluids[2], was possible by application of an oxidative membrane, based on MnO_2[3], on the biosensors' surface.

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Reduction of O$_2$ by Bilirubin oxidase at Carbon Nanotube Modified Glassy Carbon Electrodes

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The enzyme Bilirubin oxidase (EC 1.3.3.5, BOD) is an interesting and promising candidate for the bioelectrocatalytic oxygen reduction e.g. in biofuel cells. Thus the investigation of the electroactive properties of BOD is of basic relevance and may open up new ways for creating alternative systems for energy generation.

Recently the possibility of direct electron transfer between BOD and carbon electrodes under anaerobic and aerobic conditions has been shown. In the presence of oxygen a reduction current was detected at several carbon electrodes (spectrographic and highly oriented pyrolytic graphite, glassy carbon) modified with BOD (Shleev et al., 2004; Tsujimura et al., 2004).

Here we present the investigation of oxygen reduction by BOD at carbon nanotube (CNTs) modified electrodes.

During our experiments we used multi walled CNTs (average length <1μm, average diameter 10nm). Glassy carbon electrodes (GCEs) were modified by adsorbing CNTs out of a dispersion in ethanol. This strategy resulted in robust electrodes which yield reproducible results over two weeks.

These optimized CNT modified GCEs and unmodified GCEs were successfully used for electrochemical investigations of BOD. Oxygen reduction was measured with dissolved and adsorbed BOD, under aerobic and anaerobic conditions, at different pH with linear sweep voltammetry. The CNT modification of GCE enhances the oxygen reduction current by about a factor of 10 (at pH 4) in comparison with the signal at an unmodified GCE in the presence of BOD. Highest enzymatic activity was observed at pH 4, but also at neutral pH acitivity could be detected.

It was also demonstrated that BOD can be adsorbed at the CNT surface. Such electrodes showed in protein-free buffer similar oxygen reduction currents compared to the situation in solution (10 μM BOD). Oxygen reduction occurred at a half wave potential of about 0,540 V vs. Ag/AgCl/1M KCl for adsorbed BOD and thus was shifted to more positive values with respect to soluble BOD.

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Symposium 2 - Poster

Electroanalysis and Sensors

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Electroanalysis and Sensors

Elimination voltammetry as a powerful tool for the study of electrodeposition of metals

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Electrode reaction mechanisms of electrolytical coating by metals of paraffin impregnated graphite electrode (PIGE) were investigated by voltamperometric methods including the elimination voltammetry with linear scan (EVLS). The EVLS is based on the fact that the total voltammetric current (LSV) response consists of a set of particular currents, e.g. charging, diffusion, and kinetic currents having different dependences on scan rate. From voltammetric currents measured at different scan rates the elimination procedure enables selected current components to be eliminated, some current components to be conserved and unknown processes to be revealed [1-3]. In aqueous acidic solutions one of these processes is the hydrogen evolution [3,4]. The attention was focused on the interpretation of electrochemical behavior of metals (Cd, Ni, Co, and Cu) from chloride and sulphate electrolytes. Experiments were performed using the AUTOLAB potentiostat (EcoChemie) with three-electrode setting. For the calculation of elimination functions three voltammetric curves at different scan rates were recorded under the same experimental conditions (potential step and range) [5]. The differences in mechanisms of metals deposition from various supporting electrolytes have been observed as a function of metal concentrations, pH, scan rate, and electrode surface roughness. The EVLS helped also to identify the charge carrying species of metals, and the effect of electrode surface roughness. During the deposition processes the EVLS (E4 function) revealed the pre-peak (I_{pp}) reflecting some kinetically controlled surface reactions (e.g. adsorption, surface diffusion, nucleation). The study showed that the EVLS is suitable and powerful tool for the study of reduction processes of metals not only on mercury electrodes but also on solid electrodes.

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Elimination tranformation of irreversible current of an adsorbed electroactive substance

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Ten years ago the theory of elimination voltammetry with linear scan (EVLS) was published and experimentally verified for reversible, quasi-reversible and irreversible electrode systems [1,2]. Up to date this method has found applications not only in electroanalysis, but also in the study of electrode processes of inorganic and organic electroactive substance at mercury, silver or graphite electrodes [3-5]. The EVLS can be considered a mathematical model of the transformation of current-potential curves capable of eliminating some selected current components, and conserving others. This contribution is devoted to the EVLS transformation of irreversible current-potential curves of an adsorbed electroactive substance. The function eliminating charging and kinetic current components, and conserving the diffusion current component, yields specific, sensitive and well developed peak-couterpeak (p-cp) signal [6-7]. This signal was successfully employed in the analysis of nucleic acids and short homo- or hetero-deoxyoligonucleotides (ODNs) containing adenine (A), cytosine (C) and guanine (G). For the calculation of the elimination functions three voltammetric curves at different scan rates were recorded under identical experimental conditions. While only incompletely developed peaks or overlapped reduction peaks of A and C can be seen on LSV or CV curves, the peak-counterpeak signal is able to increase the current sensitivity and to separate two overlapped peaks. The heights and positions of p-cp signals were affected by pH, accumulation time and potential, and by the sequence of bases in ODN chains. It was shown that the EVLS in combination with adsorptive stripping procedure is a promising tool for achieving very good resolution of electrode processes in ODNs, for qualitative and quantitative analysis of ODNs, as well as for identification of neighbouring and non-neighborouring bases.

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Symposium 2 - Poster

Electroanalysis and Sensors

An innovative nanocomposite material for nitrite amperometric detection: electrochemical comparative study

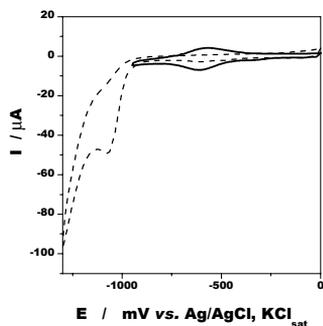G. L. Turdean[1, 2, 3, *], I. C. Popescu[1], A. Curulli[3], G. Palleschi[2]

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Nitrate and nitrite detection gained renewed attention due to their relevance for pollution monitoring and water quality. Usually, the nitrite amperometric detection involves its electrochemical reduction on conventional electrode materials. This process has been found to proceed with high overpotential and low current density, providing evidence that its energy of activation is very high [1].

In this context, the use of a composite electrode material containing: (i) theelectrocatalyst (hemin, a small molecular mimetic enzyme or single-wall carbon nanotubes, SWCNTs), (ii) a polymer film (Nafion or electropolymerized resorcinol) used for the electrocatalyst immobilization on (iii) a conductive material acting as the support of the electrocatalytic matrix (graphite) was proved to be an effective way to carry out the nitrite electrocatalytic reduction [2, 3].

Complete electrochemical studies (using cyclic voltammetry measurements and Laviron's treatment, see figure) provide a quantitative evaluation of the influence of the immobilization matrix on the hemin electrocatalytic activity. The SWCNT presence exerted a beneficial effect on the nitrite reduction at the G/SWCNT-hemin/Nafion electrode.

Electrocatalytic reduction of NO_2^- 1M at G/SWCNT-hemin/Nafion electrode (- - - - -). Experimental conditions: starting potential, 0 mV $vs.$ Ag/AgCl, KCl_{sat}; potential scan rate, 50 mV*s^{-1}; supporting electrolyte, 0.1 M phosphate buffer (pH 7); N_2 saturated solution. For comparison the voltammetric response of G/SWCNT-hemin/Nafion electrode in absence of NO_2^- was included (————).

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# Voltammetric investigations on the oxidation of adenosine-3', 5'-cyclic monophosphate at pyrolytic graphite eletrode

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The voltammetric oxidation of adenosine – 3', 5' – cyclic monophosphate (3',5'-CAMP) has been studied in the pH range 2.13 – 10.07 using pyrolytic graphite electrode (PGE). Voltammetric, coulometric, spectral studies and product characterization indicate that the oxidation of 3',5'-CAMP occurs in an EC reaction involving a $6H^+$, 6e process at pH 7.24. UV/Vis spectral changes were observed during oxidation and the values of psuedo first order rate constants (k) were determined for the intermediate generated and were found in the range $(0.507$ to $0.683) \times 10^{-3}$ s^{-1}. Electrooxidised products were seperated by semipreparative HPLC and were characterized by m.p., ^{1}HNMR, FT-IR and GC-Mass as allantoin cyclic ribose monophosphate as major product and three dimers (-C-C- and -O-O- linked) as the side products.. A detailed interpretation of the redox mechanism of 3',5'-CAMP has also been presented to account for the formation of various products. It has been concluded that the attachment of phosphate groups in adenosine facilitates the free radical pathway leading to the formation of various dimers.

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Electroanalysis and Sensors
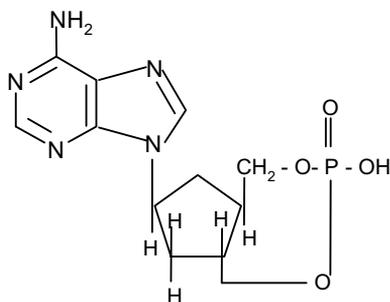
Electrochemistry combined with imaging ellipsometry

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The overall aim of the work presented here is to develop methods to analyze and control reactions and interactions on different artificial substrates for biomimetic applications. In this contribution, we will explore the combination of electrochemical techniques and imaging ellipsometry, allowing for example real time imaging of processes occurring at electrodes. Since electrochemistry is a surface sensitive method, it is very useful in investigating physical-, chemical- and biological phenomena occurring at various metal surfaces. Several electrochemical techniques (i.e. voltammetry, potentiometry, and electrochemical impedance spectroscopy) will be used to obtain information about the structure and behaviour of the system under study. Imaging ellipsometry is, on the other hand, a powerful tool for visualization of the thickness distribution of thin layers on a surface [1]. Using a focusing lens combined with a CCD camera as detector, high contrast ellipsometric images can be obtained with lateral resolution in the μm range and a thickness resolution in the sub-Å range.

The applications of this instrumental set-up mainly focus on the creation and analysis of self-organized biomimetic structures on the molecular level. We will generate gradients of alkanethiol SAMs on gold surfaces, using an electrochemical potential gradient, as described in ref. 2. The formation of the molecular gradient will hence be monitored in real time with the imaging ellipsometer. We will also investigate the effect of potential control of a surface hosting a hydrogel. The idea is that the potential may affect the conformation of the hydrogel, and the ion mobility within the hydrogel matrix. The latter will be investigated by electrochemical impedance spectroscopy.

Preliminary tests using the combination of electrochemistry and imaging ellipsometry have been conducted by depositing copper on a gold surface with constant-current chronopotentiometry. The measuring cell consists of a three electrode set-up, arranged so that the laser beam is reflected on the working electrode. A significant change in the ellipsometric parameters Δ and Ψ were seen upon deposition and oxidation of copper. These parameters could then be used together with a model of the surface system to determine the thickness of different surface layers.

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Electroanalysis and Sensors

Cathodic Behaviour of Cysteine at a Platinum Electrode

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Cysteine is a nonessential amino acid, meaning that it can be synthesized in the human body, for example from methionine. It is one of the few amino acids that contains a thiol group and is found in most proteins, though only in small quantities. Cysteine plays a valuable role by crosslinking proteins in an intramolecular sense. This increases the molecular stability in the harsh extracellular environment, and also functions to confer proteolytic resistance. Intracellularly, disulfide bridges between cysteines within a polypeptide support the protein's secondary structure. Cysteine can also be converted into glucose and used as a source of energy and according to several studies, in people infected with HIV, blood levels of cysteine are low. In addition, this amino acid may play an important role in the communication between immune system cells.

Several methods have been reported for the measurement of cysteine, such as colorimetric and high-performance liquid chromatography followed by spectrophotometric or fluorometric detection. These methods usually require adding a colour-producing or derivatizing reagent that reacts with the free sulfhydryl group. Moreover these methods are easily affected by the colour and turbidity of the sample. Electrochemical studies of cysteine have been performed too, namely using a mercury electrode or amperometric detection following liquid chromatographic separation. These methods present low selectivity and require overpotentials at most conventional electrode surfaces. As an alternative to previous methods reported in literature, electrochemical-based measurements could be considered. They enable quick responses with simple procedures; analysis of samples requires often only a simple dilution with a suitable supporting electrolyte and buffering agent. Other advantages concern the reduced consumption of reagents and emissions of effluents.

In the present work, a detailed study of the electrochemical reduction of Cysteine at platinum electrodes using different voltammetric techniques, namely, cyclic, square wave and differential pulse, has been investigated. The effect of the supporting electrolyte, the pH and the cathodic potential on the reduction curves has been obtained at various scan rates to elucidate the reaction mechanism. The results were applied to the determination of cysteine in pharmaceutical formulations.

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Analysis of metabolism processes by microorganisms in small scale-fermenters

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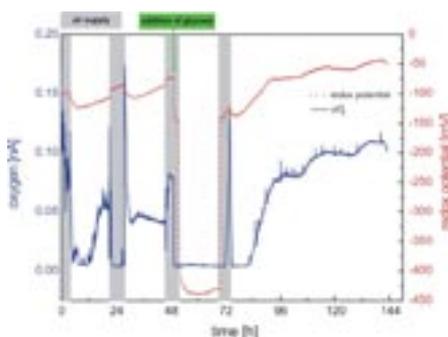[3] *IMM Ingenieurbüro, Leipziger Str. 32, D-09648 Mittweida, Germany*
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It is reported about a chemostatic measuring system for the in situ analysis and clarification of matabolism processes by microorganisms based on the sensory determination of several cultivation parameters and to carry out small-scale fermentative syntheses. Main items of the system are calorimetric and electrochemical sensors for the characterisation of the metabolism processes. The chemostat shown in Fig. 1 contains a small calorimetric reaction cell where the fermentation proceeds. Detecting the thermal power for such processes allows to characterise the physiological condition of cultures not invasive and independent on the composition of the nutrient solution. However, explanations of the causes of the detected behaviour are not yet possible in this way. For this additional parameters, relevant for the growth of the cultures, shall be determined in the chemostat on line, using miniaturised electrochemical sensors. For the aerobic growth, it concerns the oxygen concentration in the nutrient solution. This value delivers important hints about the progress of oxidative processes. Furthermore, in the chemostatic system specific adapted miniaturised sensors are used to measure the redox potential, nitrate and glucose concentration and to clarify microbial metabolism processes. In Fig. 2 the run of the signals of an oxygen sensor and a redox single-rod measuring cell during a cultivation of microorganisms of the type P. denitrificans is to be seen. Addition of air and glucose took place at defined time intervals. The choice of the electrochemical sensors to be integrated, is to be made in dependence on the metabolism process of use. The measuring system is completed by sensor specific circuits, measurement data logging and data interpretation systems as well as electrical actuators to control biotechnological processes.

Fig. 1: Miniature chemostat   **Fig. 2: Cultivation process**

Functionalized mesoporous silica films as ion-permselective pH-switchable electrode layers

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Mesoporous silica films bearing various functional groups in the pore interior can serve as modified electrodes and drastically change the interface properties of the electrode surface. Thus, such films can be used as a matrix for immobilization of discrete redox moieties via ionic or covalent bonds [1]. Polyoxometalate- and hexacyanoferrate-anions were anchored ionically to the alkylaminofunctionalized silica, while ferrocenecarboxylic acid was covalently bonded to amino- and iodo-groups via peptide and ester bonds. The electroactive concentration achieves 90, 260 and 60 μmol/cm^3 for polyoxometalate, hexacyanoferrate and ferrocene, respectively, being several times higher compared to a monolayer on an electrode. Such thin film electrodes with defined texture can be perspective in *e.g.* electrocatalysis or electroanalysis.
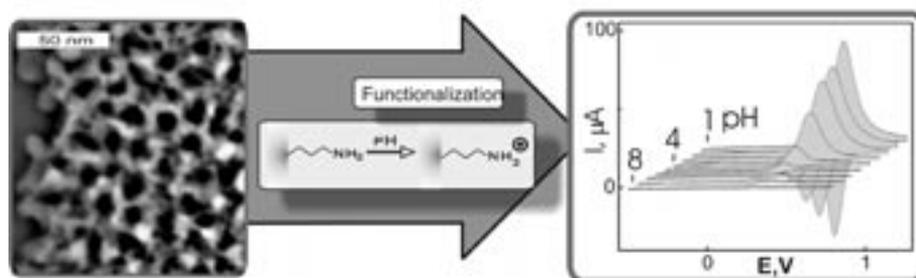

Fig. 1. Functionalization of a mesoporous silica films with amino groups (TEM image, left) and cyclovoltametric response of Fe(CN)$_6$-anions at different pH on an electrode surface covered with such film.

The films functionalized with groups which can be easily protonated act as ion-permselective pH-switchable layers, controlling selectively the flux of ions to the electrode surface with changing pH. Figure 1 shows the effect of the pH value on the permeability of amino functionalized mesoporous silica layer for Fe(CN)$_6$-anions. At pH of 1-6 the film is highly permeable for the anions, showing a linear dependence on the pH. At the same time the film is closed for cations due to the electrostatic barrier of NH$_3^+$ groups. The anion flux to the electrode ceases by increasing pH above 7. So, in spite of their open porous structure, such layers can completely block or enhance the flux of ions, which can be used in permselective or separation analysis of charged species.

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Examination of the Spatially Heterogeneous Electroactivity of Boron Doped Diamond Microarray Electrodes

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Spatial variations in the electrical and electrochemical activity of microarray electrodes, fabricated entirely from diamond with insulating intrinsic diamond surrounding disc-shaped regions of polycrystalline boron doped diamond (BDD), have been investigated and their applicability for electroanalysis assessed.[1] Atomic force microscopy (AFM) imaging of the surface reveals a roughness of no more than ± 10 nm over the array. Each BDD microdisk within the array contains polycrystalline BDD with a variety of different grains exposed. Using conducting-AFM, the conductivity of the different grains was found to vary within a BDD microdisk. Scanning electrochemical microscopy (SECM) operating in substrate generation–tip collection mode revealed that, under apparently diffusion-limited steady-state conditions, there was a small variation in the response between electrodes. However, the majority of electrodes in the array appeared to show predominantly metallic behaviour. For the electrodes which showed a lower activity, all grains within the microdisk supported electron transfer, albeit at different rates, as evidenced by studies on the electrodeposition of metallic silver. The possibility of using these array electrodes for steady-state diffusion-limited measurements in electroanalytical applications is far-reaching. However, caution should be exercised in the kinetic analysis of voltammetric measurements, since wide variations in the electroactivity of individual grains are apparent when the potential is below the diffusion-limited value.

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S2·P-125

An Electrochemical Sensor Based On Phosphomolybdate - Polypyrrole Composite for the Detection of Nitric Oxide in Aqueous Solution

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The short-lived regulatory gas nitric oxide (NO) plays a very important role in a wide variety of biological and cellular functions including the regulation of blood pressure and the immune response. The reliable and specific detection of NO in biological systems and industrial pollution control are of considerable significance.

A new electrochemical NO sensor with bulk-modified carbon paste electrode (CPE) containing polyoxometalate (POM) anion ($[P_2Mo_{18}O_{62}]^{6-}$ or $[PMo_{12}O_{40}]^{3-}$) - polypyrrole (PPy) composite was found to exhibit fine repeatability, short response time, longtime stability and low detection limit for the detection of nitric oxide (NO) in aqueous solution. Response time of such POM-PPy-CPE was less than 6s and the electrode response was linear within a concentration range from 1.9×10^{-6}M to 1.9×10^{-3}M. Detection limit defined as a signal-to-noise ratio of 3 was about 1μM. The amplitude of NO reduction current showed well linear dependence on the NO concentration in 0.5M H_2SO_4. The composition and surface morphology of the electrode were characterized by means of X-ray photoelectron spectroscopy (XPS) and AFM image, respectively.

Additionally, the preparation method of the sensor electrode is convenient, easy, and inexpensive. The creation of such NO sensor not only provided a new device for the detection of NO in aqueous solution, but also suggested that the sensing system based on polyoxometalates will be possible to become promising candidates for developing effective electrochemical sensors of simple molecule detection.
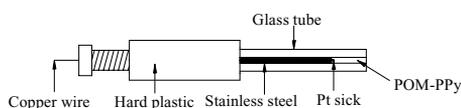
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Electroanalysis and Sensors

Evaluation of thiolated β-cyclodextrin modified electrode towards estradiol electrooxidation

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Cyclodextrins (CDs) are cyclic water-soluble D-glucopyranose oligomers featuring a central hydrophobic cavity capable to form stable inclusion complexes with organic molecules. Among them, thiolated CDs are well known electrode modifiers forming SAMs on electrode surface. We have reported the synthesis of thiolated CDs and the successfully modification of gold electrodes, which were characterized both cyclic voltammetry and scanning electrochemical microscopy (SECM) [1,2]

The aim in the present work is to study electro-oxidation of estradiol using these thiolated CD modified electrodes. The modified electrodes were obtained as was already described [1] by immersion of the gold electrode in an ethanolic solution of thiolated CDs during 12 hrs. The coverage study was performed by both reductive desorption experiments in KOH and cyclic voltammetric experiments using two electroactives probes such as ferricyanide and ferrocenemethanol. The results showed that CDs covered about 95% of the electrode surface. Optimization of the modification time and completely exhaustive washing with ethanol/water mixed are necessary previously use the modified electrodes, because several difficulties were found when we used these completely modified electrodes: no reproducible results were obtained due probably thiol groups of modified-CD in solution already penetrate into cavity of CD fixed on the electrode surface giving a no reproducible multilayer modified electrode. Also, a few cycles in support electrolyte in the interested region of potential were necessary before oxidation of the steroid. Estradiol showed an oxidation peak at 385 mV (versus Ag/AgCl) on bare Au electrode. A shift about 100 mV to more positive potentials was found on modified electrode, but no enhanced of oxidation current of estradiol was observed. However, a current response was obtained indicating association between estradiol and cavity of the CD fixed on the surface. Different concentrations of estradiol were tested with these electrodes. An increase the current according to concentration increase was observed. Treatment of the data using the Langmuir isotherm has been carried out.

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Identification of Acanthopanax Senticosus (Rupr. Et Maxim.) Harms from Different Sources by Capillary Electrophoresis with Electrochemical Detection

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Traditional Chinese Medicines (TCMs) have been used to treat various diseases for over thousand years [1]. Because the active components in herbs are influenced by soil, climate, and the growth stage [2], the analysis of TCMs is very important to ensure authenticity, quality, safety and efficacy. Recently, fingerprint analysis has been accepted as a common method to control herbal quality. Compared with other methods, capillary electrophoresis with electrochemical detection (CE−ED) method possesses many advantages such as high speed, high efficiency, high sensitivity, ultra-small sample volume and low cost. Based on the difference of compositions and their contents of electroactive components in herbs, the unique fingerprint profiles obtained by CE−ED can be applied to distinguish these herbs. The fingerprint analyses of different parts of plant and different species of plants with CE−ED was studied in our previous paper [3]. Here, we would discuss the fingerprint analysis of *Acanthopanax Senticosus* (Rupr. Et Maxim.) Harms from different sources, and investigate the distribution of the bioactive ingredients (isofraxidin, chlorogenic acid and rutin) in the different parts (root, rhizome, stem and leaf) of this herb. The effects of the detection potential, buffer nature, buffer pH, buffer concentration and injection time on the determination were examined. Under the optimized conditions, the analytes were baseline separated within 6 min. The linearity was obtained over 1-3 orders of magnitude. The detection limits (S/N=3) ranged from 1.0×10^{-7} mol L^{-1} to 1.5×10^{-6} mol L^{-1} for all analytes. The results also indicated that the contents of these active components in each part of *Acanthopanax Senticosus* (Rupr. Et Maxim.) Harms were different. Owing to their own unique CE−ED electropherograms fingerprint profiles, the herbs from different sources can be distinguished.

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Symposium 2 - Poster

Electroanalysis and Sensors

Symposium 2 - Poster

Electroanalysis and Sensors

Detection of Cysteine Using Nonionic Fluorosurfactant-Modified Gold Electrode

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Cysteine is of physiological importance as thiol-containing agent and metabolite. Its deficiency is associated with a number of clinical situations, such as liver damage, skin lesions, slowed growth, and AIDS. Many electrochemical and fluorimetric methods have been used for the sensing of aminothiols, and the selective determination could be achieved by conjugating with some separation techniques, such as HPLC and capillary electrophoresis. The development of much simpler methods for the detection of specific thiols in biological samples without separation steps is attractive.

The large overpotential of cysteine oxidation at noble electrodes makes it necessary to apply a high potential (usually ~ 1.0 V vs SCE) for its electrochemical detection. Many biomolecules could be oxidized at this potential, leading to poor detection selectivity. In this study, we used nonionic fluorosurfactant species (Zonyl FSO) to modify gold electrodes, and an oxidation wave of cysteine was observed at a relatively low potential (~ 0.25 V vs SCE at pH 7). It is interesting to note that the adsorption layer of FSO at the electrode generally inhibits the oxidation of other biomolecules, such as glucose, ascorbic acid (AA), uric acid (UA), cystine, glutathione, tyrosine and tryptophan. Although the presence of large excess AA may still interfere the detection of cysteine, the modification of the FSO-gold electrode with a Nafion layer significantly reduced their influences. Therefore, it is possible to detect cysteine selectively in a biosample without separation steps.

The effect of the cation capture on the charge propagation process of poly(o-aminophenol) film electrodes

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Poly-o-aminophenol (POAP) is an electroactive polymer that seems to capture Fe^{+3} ions and further transforms them in Fe^{+2} ions through interaction with its redox sites. In this sense POAP can function as potentiometric ferric ion sensor [1]. It is expected that this cation capture affects the charge propagation process at POAP modified electrodes. In this work it is demonstrated by employing Rotating Disk Electrode Voltammetry (RDEV) [2] and *ac* impedance measurements on POAP films contacting an active redox couple in solution (p- benzoquinone/hydroquinone). A degree of cation capture was defined for POAP [3] by comparing the voltammetric response of freshly prepared POAP films and POAP films after to be subjected to a soaking process in the presence of a solution containing ferric ions. The study of the electron transport by using RDEV allows one to infer the existence of redox sites distributions, which become more extended, as the higher is the content of ferric ions. However, by reducing the amount of ferric ions on POAP by an alkali treatment, the original redox site distribution was not fully recovered. In this way a hysteresis remains on POAP after to eliminate part of ferric ions. Ac impedance measurements were also performed in order to extract the dependencies of the different charge transport and charge transfer parameters of POAP films on the degree of cation capture. Two impedance models [4] were employed in order to interpret the experimental impedance plots. While parameters such as electron (D_e) and ion (D_i) diffusion coefficients and redox capacitance (C_p) as a function of the degree of cation captures (increase and decrease) exhibit hysteresis, other interfacial parameters such as the electron (R_e) and ion (R_i) resistances at the polymer-solution interface and the charge transfer resistance (R_t) and interfacial capacitance (C_H) at the metal/polymer interface, do not exhibit the mentioned hysteresis between the increase and decrease of the amount of captured ferric ions.

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Studies of electron transfer through Self-assembled monolayer on silver electrodes

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Self-assembling of alkanthiols molecules on noble metals provides dense and ordered monolayers under certain conditions depending on the length of the alkyl chain and the choice of the substrate. Such films are found to be useful for several applications including corrosion inhibitions, chemical microsensors and as biomaterials. Alkanthiol films on Ag were also tested for reduction of silver tarnishing and formation of protective films. All of these applications will be significantly dependent on the film stability.

The object of this study to investigate the top surface structure properties and a long range electron-transfer phenomena of such ordered adlayers since it determines the interaction of organic layer with any environments. In the case of self-assembled monolayers (SAM) of alkanthiols on Ag, chemisorbed molecules are bonded by the S head to the Ag surface (as Au) although their tilt angle with respect to the substrate normal ranges from 15º to 0º. The reductive desorption studies of SAMs on Ag single crystal electrodes have been shown the results for the hydrocarbon chain-chain and hydrocarbon chain-solvent interactions similar to those on Au. The significant differences of a given alkanthiolate were observed   in the desorption peak potential which have been shifted on Ag to the more negative potentials. Theoretical calculations are demonstrated also the different space accommodations of water molecules within Ag-supported and Au-supported SAMs.

In   present work the $HS(CH_2)_{10}$ film formations and their stability on different controlled surface poly- and   single crystal Ag electrodes is being systematically investigated   in aqueous $NaNO_3$ solution by means of different capacity and impedance experiments combining with cyclic voltammetry method. The films of decane thiol on Ag electrodes were exposed for prolong periods in atmospheric exposure o/and were conserved under the solutions. Protective effectiveness of two procedures were tested with respect of electron transfer blocking properties and of possibility the oxidant species to penetrate the closely packed alkyl chain structure. The oxidation of rather long chain length alkanthiol SAM on silver electrodes was found rather small in air exposure and generally SAMs on Ag retain their integrity and high stability with atmospheric pollutant elements [1,2].

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Voltammetry of chromium(vi) at liquid|liquid interfaces

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Chemical sensors consist of appropriate recognition and transduction chemistries together with associated devices and systems for electronic measurement. In recent year ion-transfer reactions across the Interface between Two Immiscible Electrolyte Solutions (ITIES) has been investigated as possible recognition tool for sensor development. ITIES has been proved to be a powerful technique for the investigation of the lipophilicity of molecules, mainly drugs. Moreover the use of specific receptors (able to complex target molecules with the aim of improving their lipophilicity) also gives the opportunity of developing new sensor characterized by a strong selectivity [1]. Speciation is one of the major challenges in environmental chemistry, particularly metal speciation. In solutions chromium may exist in Cr(III) and Cr(VI) oxidation states which makes the detection of chromium species a challenging task as these two environmentally relevant valence states of chromium have a contrasting impact in environment and health. Cr(III) is relatively harmless and plays and essential role in biological processes, whereas Cr(IV) is about 100-1000 times more toxic.

The aim of this work was to assess the ability of ITIES voltammetry to perform selective detection of Cr(VI). The selective detection of the Cr(VI) versus Cr(III) is based on charge difference between the two Cr oxidation state being Cr(VI) mostly present as oxo-anion (chromate) and the Cr(III) as cation. The Cr(VI) detection was done by "Transfer by Interfacial Complexation" (TIC) using a polyamine macrocycle 2,5,8,11,14-pentaaza[15]-16,29-phenanthrolinophane (NeoTT) [2] as artificial receptor. Moreover this work is one of the few examples of the use of ITIES voltammetry as a tool for the analytical investigation of anions.

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Symposium 2 - Poster

Electroanalysis and Sensors

Electrochemical and AFM characterization of sulfonated calixarene doped polypyrrole films for the electrochemical detection of cationic iron in seawater

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Iron is an essential actor for the growth and metabolism of all marine organisms [1]. It acts in cytochromes and FeS redox proteins that are involved in key metabolic processes such as photosynthetic and respiratory electron transport, nitrate and nitrite reduction, N_2 fixation and sulfate reduction. It is also present in catalases and peroxidases and in some superoxide dismutases and is thus important in the detoxification of reactive oxygen species such as superoxide anion and hydrogen peroxide. A detailed and exhaustive list of its various roles would be anyway too long to be given here

In seawater, an oxygenated and weakly alkaline aqueous solution, iron II cations are quickly oxidised to provide iron III cations. These latter display a low solubility and thus precipitate rapidly, leading therefore to concentrations as low as 0,1 nM in oceans and 400 nM in estuaries. From these data, one can easily deduce that the cartography of iron distribution in oceans is crucial to understand the oceanic geochemical role of iron but highly compromised due to its very low concentration. Therefore, the elaboration of an analytical device allowing the determination of sub-nanomolar concentrations of iron in seawater is still a challenge nowadays.

In this work, we suggest the use of an amperometric sensor based on hexasulfonated calix[6]arene doped polypyrrole (**PPy:1**) films. The cited anionic calixarene derivative is known to be electroactive [2] and an efficient binding agent towards various currently targeted analytes such as for example uranyle cations [3] and ammonium derivatives. As such, the **PPy:1** functionalised electronically conducting polymer is a fascinating material for the making of amperometric analytic devices aimed at applications in various (biological or natural) analysis media. We thus report hereafter investigations dealing with its electrochemical preparation and properties. A morphological and electrical characterisation carried out with the help of atomic force microscopy (AFM) in several modes is also introduced. Our aim is to establish conductivity/morphology and morphology/ analytical performances type correlations. Preliminary results concerning the validity of a **PPy:1** based sensor for the electrochemical detection of Iron III in seawater will be discussed.

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# Nanostructured Materials Based Electrodes for biofuel cells

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Combination of biologically active components (enzymes, antibodies, nucleic acids and cells) with nanomaterials of unique properties has been promising for biosensing, genome analysis, bioelectric devices, biofuel cells.[1,2] To realize these applications, high stability and function density of the immobilized biologically active components are usually required. We recently focused on the preparation and characterization of biointerfaces based on assembly of nanostructured materials with rigid structure, good conductivity, good biocompatibility and larger active surface area. Glucose oxidation and direct electron transfer of hemoglobin were used as models to demonstrate importance of such materials for the construction of functional electrodes for glucose biosensor and bioelectronic devices with high function density.

The nanostructured gold or platinum films were prepared by using the template techniques of photonic crystals and anodic aluminium oxide membrane and electrochemical deposition. The morphology (figure 1), structure and property of these materials were characterized by using SEM, XRD and electrochemical methods. Then biomolecules of glucose oxidase and hemoglobin were assembled on the nanostructured films by using different methods and their adsorption kinetics was studied. Finally, the direct electron transfer (figure 2) and bioactivity of the assembled biomolecules were systematically investigated.
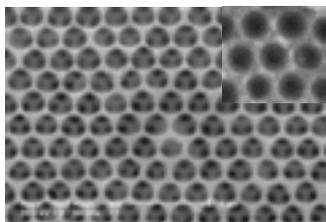
Figure 1. SEM photograph of a 3D macroporous Pt film prepared as described in the text.
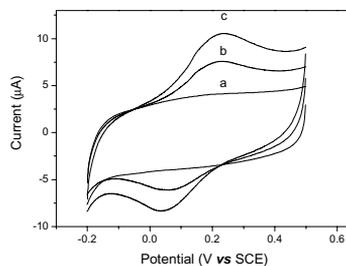
Figure 2. Plot of the charge transfer resistance R_{et} obtained from impedance measurements against incubation time.

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Symposium 2 - Poster

Electroanalysis and Sensors

Symposium 2 - Poster

Electroanalysis and Sensors

Novel Electrochemical Immunosensors and Cytosensing

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Tumor cell has its individual immuno-expression style. The detection of tumor markers both in serum samples and on cell membranes plays an important role in initial diagnostic evaluation and follow-up examination during therapy of cancer diseases. In previous study we presented several immunoassay methods and immunosensors for tumor markers, such as CA125, CA19-9, CEA and AFP, including a disposable immunoassay chip and several flow-injection chemiluminescent immunoassays. This presentation introduced the further development in immunosensors and cytosensing in our laboratory.

Firstly, an amperometric immunosensor for human serum chorionic gonadotrophin (HCG) was constructed by immobilization of HCG in titania sol-gel and the direct electrochemistry of immobilized HRP labeled to HCG antibody. Another electrochemical immunoassay system for HCG was proposed by using a colloidal Au nanoparticles modified chitosan membrane to immobilize immunoconjugate. With encapsulation of HRP labeled HCG antibody in a colloidal gold nanoparticle/titania sol-gel composite architecture, a novel reagentless electrochemical immunosensing approach for sensitive detection of HCG was proposed.

Then, an immunosensor for CA125 was proposed based on the immobilization of CA125 on colloidal gold nanoparticles that was stabilized with cellulose acetate membrane on a glassy carbon electrode. A new simple immunoassay method for CEA detection using a disposable immunosensor coupled with a flow injection system was developed. This system could automatically control the incubation, washing and current measurement steps.

At the same time, a new technique for exogenous effect study of cell viability by immobilization of living cells on nanoparticles was developed. A novel electrochemical anti-tumor drug sensitivity test was proposed with a multi-wall carbon nanotubes-modified glass carbon electrode. Based on the immobilization of leukaemia tumor cell on colloidal gold/chitosan membrane, a novel immunoassay method for directly detecting the protein on the surface of living cell membrane was also developed. The results were comparable to flow cytometric analysis. A new highly hydrophilic zwitterionic monolayer film with good biocompatibility was constructed. It provided an appropriate biomimic interface for attachment and proliferation of cells. Thus monitoring the proliferation and apoptosis of cells on the zwitterionic surface was achieved.

Symposium 3

Enterprise and Innovation

Symposium 3 - Oral

Enterprise and Innovation

The electric vehicles projects and related batteries in China.

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In recent years the rapidly developing electric vehicles (EV) projects in China have attracted more attentions. We (Peking University EV project collaboration team) had carried out related battery materials researches and productions, submitted proposals and suggestions to the authorities concerned and participated in the supervision of EV projects including The huge National EV project (exceeds 2 billions RMB) organized by Chinese Science and Technology Ministry.

China National EV Project includes: 1.Battery operated EV (BEV), works concentrate on Ni-MH batteries and Lithium ion batteries; 2.Hybrid EV (HEV), a pilot HEV public bus team (12 buses) runs on city Wuhan's street, saves 30% fuels. 3.Fuel Cell(PEMFC) EV, including buses, transit buses and sedans. The management of this huge project is unique and regarded as effective, problems will also be discussed.

Other important EV events include: The Demonstration EV Project in 2008 Beijing Olympics (investment 409 M RMB, third largest investment of its kind, 1000 EVs); FCEV Bus Program in 2010 Shanghai World Exposition (which is planning 1000 FCEV buses and taxis on route); National 973 project "The Fundamental Research on New Systems of Green Secondary Batteries" (funding 30 M RMB) is an important support to National Key EV Project; Electric bicycles become a blooming industry (2005 yields ~ 10 million Ebikes) demonstrating the great needs (at an affordable price ~1500 RMB) from people. All above requirements for batteries will be referred to.

The related R&D of quality/cost effective batch productions of $LiFePO_4$ materials and active carbon, EV batteries expert system, VRLA for EV are mentioned. Conclusions and suggestions drawn from the above situations will be discussed.

Symposium 3 - Oral

Enterprise and Innovation

Exploitation of the FFC Cambridge Process

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The FFC Cambridge Process was discovered in 1997 at the University of Cambridge. In 2002, Metalysis was formed to commercially exploit the technology for a range of metals and alloys. Significant funding was secured from the venture capital community in 2005. This paper will describe the steps taken to convert the FFC Cambridge Process from the university bench to a commercial operation and will outline the longer term vision for the company.

S3·O-3

Electroanalysis in Diabetes Management

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My son Ephraim Heller and I founded TheraSense Inc. in 1996 to help diabetic people. The company was acquired by Abbott Laboratories in 2004 for \$ 1.2 billion. TheraSense removed the pain associated with the assay of blood glucose by self-monitoring diabetic people by introducing in 2000 *FreeStyle™*, an accurate thin-layer micro-coulometer in which glucose is rapidly electrooxidized. The blood volume it required was reduced to 300 nL, a volume so small that it is painlessly obtained. About 6 billion glucose assays are performed each year, more than all other medical and non-medical analyses combined. TheraSense also completed clinical tests of a continuously glucose monitoring system, designed to alleviate the worry of diabetic people. The system alerts its user to low and high subcutaneous glucose concentration, as well as to impending low or high glucose concentration. Its core component is a subcutaneously implanted, miniature, amperometric, user replaced, glucose sensor, with a 3-5-day operational life. The implanted sensor is based on electrical wiring of glucose oxidase within an electrically conductive redox hydrogel. The implanted disposable sensor is now hard wired to an external battery-powered non-disposable amplifier transmitter.

Our current work at the University of Texas at Austin is aimed at the integration of the disposable miniature implanted wired glucose sensor and its non-disposable amplifier-transmitter into a miniature disposable sensor-amplifier-transmitter-battery package. The largest and most expensive component of the package is its battery. Batteries comprise corrosive, reactive or toxic components and require a steel case. In collaboration with Woonsup Shin and his co-workers at Sogang University in Seoul, we designed and built a case-less, miniature, implantable Zn│serum│AgCl battery, operating at 1 V. The cell reaction is $3Zn+2H_2PO_4^-+6AgCl+4H_2O \rightarrow Zn_3(PO_4)_2.4H_2O+6Ag+6Cl^-+4H^+$. The enabling breakthrough was the discovery that hopeite-phase lamellae of $Zn_3(PO_4)_2.4H_2O$ grow on Nafion-coated Zn anodes in physiological, phosphate-buffered, pH 7.3, saline electrolytes. The hopeite lamellae are solid Zn^{2+} conductors. They are impermeable to O_2, preventing the non-faradaic (O_2-caused) Zn-corrosion, while allowing the anode to discharge.

A future disposable package might broadcast the subcutaneous glucose concentration to a second package on the skin, containing an RF-receiver, a microprocessor, insulin, an actuator and a pump. Such a system would be the harbinger of other therapeutic drug-delivering feedback loops, with local temperature, pressure, flow and chemical concentration being measured, and with fast-acting drugs being delivered from skin-attached packages in small doses to maintain optimal physiological parameters.

The ITI Energy model for the generation of new technologies

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ITI Energy is an innovative publicly funded company that invests in the development and management of early stage research and development projects across the energy spectrum. Since ITI Energy announced its first R&D project just over a year ago, it has now seven underway with potential investments in excess of £30m. Included in its portfolio of projects is the development of a new cathode material for the next generation of Li-ion rechargeable batteries, a large-scale flow battery technology and a li-ion battery management system for electric vehicles. Ian Edwards and Mike Weston will outline the key principles behind the company s unique model, including the critical areas of market opportunity, technology competitiveness, IP strength and commercialisation strategy as a route to successful commercialisation. They will give insights into their model and its success to date and highlight how the electrochemistry community, academic and commercial, can be a part of the ongoing success.

Symposium 3 - Oral

Enterprise and Innovation

ImmuSpeed: microfluidic electrochemical plateform applied to Enzyme Linked Immunosorbent Assay (ELISA)

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In this presentation, we will explain the different steps that were undertaken to transform a PhD project into a commercial instrument based on electroanalytical principle. Strong physico-chemical bases were applied to provide a system with specific features enabling rapid and small volume immunological test, both for diagnostics and R&D purpose. The description of the different strategic developments that enabled the venturing will be addressed in the presentation and including IP aspects, fabrication of advanced prototype, securisation of production line and transformation from a concept to a product oriented company, etc.

Here after is presented a short description of the microfluidic devices based on electrochemical detection developed by DiagnoSwiss.

The goal of the miniaturization applied to ELISA test is to provide a platform requiring low amount of reagent and sample and a significant reduction in assay time. To this end, the standard micro-well format has been transposed into a microchannel where the typical diffusion distance between reagent and sample is decreased to ~20 micron. At such distances, the time of diffusion is reduced to a few seconds, even for large proteins, thereby diminishing the time to equilibrium of given incubations. Thanks to multi-loading in our 60 nL microchannels, it is possible to pre-concentrate the sample on the microchannel walls and to increase the signal-to-noise ratio, thereby reducing the detection limit. Finally, electrochemistry has been chosen as detection means for its relative easy miniaturization and its ability for multiplexing. The fluidic control unit and detection instrument has been assembled into a platform called *Immuspeed* which uses DiagnoSwiss electrochemical microchips called *Immuchip*, as illustrated in Figure 1.

Symposium 3 - Oral

Enterprise and Innovation

NanoPores to GATTACCA

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Oxford NanoLabs is a recent (June2005) spin out from the University of Oxford Chemistry Department. During the first year the company has successfully completed one international acquisition and two rounds of financing. The presentation will outline the challenges faced by an early stage start up and the process of fund raising. The presentation will also outline the technology behind and the development of the Nanopore Biochip , describing the methodologies for modifying protein pores for detection of analytes ranging from small charged molecules through to proteins, antibodies and DNA.

Symposium 3 - Oral

Enterprise and Innovation

S3·O-7

Symposium 3 - Oral

Enterprise and Innovation

The role of lithium batteries in fighting global warming and in reducing energy consumption

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Batteries play a key role for the progress of modern technology, for a better use of the energy resources and for a more accurate control of the world atmosphere. The continuous evolution of popular   mobile electronics such as cellular phones, laptops and PDAs, requires high power and high energy density microbatteries. The fast decay of oil resources urgently calls for an increased use of renewable energy sources, such as solar and wind which, due to their discontinuity require appropriate storage systems and electrochemical batteries are ideal in this respect. Finally, since transportation represents a significant portion of world energy consumption, the development of zero or low emission battery-operated vehicles, i.e. electric cars, EVs, or hybrid cars, HEVs, is an important issue from both economical and environmental points of view.

To be effective for the electronic market, for energy storage and for powering cars, batteries having specific features such as low-cost, high energy and high power density, as well as safety and long life, have to be selected. This is a challenging task since the above requirements are not commonly met by the existing batteries. Conventional types, such as lead-acid, nickel-cadmium and even nickel-metal hydride, suffer by low values of energy content and also by a certain degree of toxicity which may be undesirable in view of the present environment concern.

The best choice is the lithium-ion battery which in fact, already dominates the portable electronic market. However, although a commercial success, the lithium-ion battery is still open to improvements. In this paper the evolution of this battery from its early stage to the expected development to meet the demands of the modern technology and of the changes in the transportation scenario, will be reported and discussed.

Symposium 3 - Oral

Enterprise and Innovation

Taking Science to Market

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The talk will cover some of the challenges and opportunities around the commercialization of science in the UK. University spinout companies have become a major phenomenon in the UK. The talk will look at their characteristics and why they sometimes work, and sometimes do not. Reference will be made to the US experience also and compare this to the UK.

Symposium 4

Electrochemical Nanotechnology

S4·KN-1

Electrochemical gating: a way to control the orbital occupation of quantum dot solids

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Due to size-quantization, semiconductor nanocrystals possess discrete conduction electron - and valence hole levels, with atom-like symmetry, i.e. S, P, … Semiconductor nanocrystals can be assembled to form artificial solids, also called quantum-dot solids. The opto-electrical properties of such a material will depend on the electronic structure of the nanocrystal building blocks and their mutual quantum mechanical interaction. Of key interst is the occupation of the quantum-dot orbitals by electrons and/or holes. We have shown that it is possible to control this occupation by electrochemical gating : the solid is used as a work electrode in an electrochemical cell; the electron occupation can be varied by the electrochemical potential. The charge of the electrons occupying the orbitals in the quantum dot solid is compensated by ions in the nanovoids of the solid. In such a system electronic (electrochemical) equilibrium prevails. Electronic transport in such a quantum dot solid can be measured for a controlled electron occupation, allowing us to study the physics of artificial metals and insulators. Also the optical properties of quantum dot solids at variable electron occupation can be studied. This may lead, for instance, to the development of a zero-threshold quantum dot laser.

In this key-note lecture I will present the virtues and drawbacks of electrochemical gating, and pay attention to the great possiblities offered for nanoscience.

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Symposium 4 - Keynote

Elecrochemical Nanotechnology

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Elecrochemical Nanotechnology

The Electrochemistry At Nano-Sized Electrodes

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This is the abstract for the **Tajima Prize Lecture**. Monolayer-protected nanoparticles exhibit a series of discrete voltammetric peaks in solutions, which are attributed to the quantized charge transfer of the particle molecular (double-layer) capacitance. This unique charge transfer phenomenon has been very well exemplified by alkanethiolate-protected nanoparticles of several transition metals such as gold, palladium, cupper and ruthenium. Similar quantized charging phenomena can also be observed when the particles are immobilized onto an electrode surface. However, it has been discovered that with these surface assemblies, solvent media play an important role in the regulation of the nanoscale electron transfer processes. For instance, in low-dielectric organic media, the quantized charging features can be seen at both negative and positive potentials (with respect to the particle potential of zero charge). By contrast, in aqueous solutions, the quantized charging responses can be initiated only in the presence of hydrophobic anions and in the positive potential regime; whereas at negative potentials, only featureless responses can be seen and the voltammetric currents are suppressed drastically. Consequently, the overall voltammetric profiles resemble those of a molecular diode. This is interpreted by the manipulation of the electrode interfacial capacitance as a consequence of the ion-pairing between the hydrophobic electrolyte anions and the particle molecules at positive potentials (Randle's equivalent circuit). Detailed studies have been carried out by a systematic variation of the nature and concentration of the anions. It is found that these rectified quantized charging processes are very sensitive to the hydrophobicity of the electrolyte anions which can be correlated very well with their respective solvation interactions with water molecules. Further comparative studies have also been carried out with monolayers and multilayers of particle molecules on the electrode surface within the context of the particle charge transfer kinetics. The interfacial dynamics have also been studied by electrochemical quartz crystal microbalance measurements.

In a more recent study, we investigate the solid-state perspective of the particle single electron transfer. Using Langmuir-Blodgett techniques, we fabricate nanoparticle solid films of monolayers as well as multilayers. By deliberate control of the particle dimensions, interparticle separations and temperature, we are able to observe well-defined single electron transfer across these particle solids. The electron transfer kinetics involved is evaluated voltammetrically and compared to that in solutions. Effects of chemical environments have also been examined which may be exploited as a novel mechanism for chemical sensing.

Electrochemical Tunnelling Spectroscopy Studies on Redox-Active Molecules

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Electrochemical Scanning Tunnelling Microscopy (STM) has proven to be a versatile tool for studying surface structures and dynamics in electrochemical environments. Target systems include small organic molecules, transition metal complexes, proteins, enzymes, DNA fragments, metal nanoparticles and other supramolecular structures. Electrochemical environments offer full potential control of tip and substrate electrodes on an absolute scale. Electrode Fermi levels can independently be aligned with redox levels of immobilized species, inducing tunnelling current modulation and conspicious transistor and switching features. As a unique feature of electrochemical STM, two tunnelling spectroscopic tools are available: current/bias spectroscopy at constant substrate potential and current/overpotential spectroscopy at constant bias.

We use both approaches to study charge transfer processes through individual (or a few) pyridyl-based transition metal complexes with Ru, Os, and Co as central metal ions. These molecules can be brought to display both transistor and diode characteristics. We could show that charge transport occurs via electron hopping, i. e. in two subsequent electron transfer (ET) steps, which is in keeping with expectations from condensed-matter charge transfer theory. Tunnelling current enhancement factors appear to be correlated to monolayer ET rate constants, establishing a direct link between the macroscopic and single-molecule regimes. Under appropriate conditions, the overall tunnelling process is dominated by the substrate/molecule step. Combining experimental data on single-molecule conductivity and theoretical models, a single-molecular tunnelling rate constant could be estimated.

We have successfully extended our tunnelling studies from aqueous solvents to ionic liquids. Ionic liquids are a novel environment in this context and appear to have a number of advantages which we have begun to explore for charge transport measurements at the single-molecular scale.

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Symposium 4 - Keynote

Elecrochemical Nanotechnology

Symposium 4 - Keynote

Elecrochemical Nanotechnology

Oxygen-competition mode of SECM. Application for localized visualization of fuel cell catalyst activity

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One of the principal parameters used to characterise electrocatalysts is their specific activity. In fuel cells the catalyst of choice for the oxygen reduction reaction (ORR) at the cathode is usually platinum deposited in nanoclusters on carbon. Many different electrochemical techniques have been used in the past to elucidate the catalytic activity of various forms and loadings of platinum on a carbon substrate for use as the cathodic catalyst in a fuel cell. However, due to the nature of the techniques employed these results have given more of an overview of catalytic activity rather than divulging information on the local activity of the specific deposits. Analysing local activity enables the quantification of each deposit rather than the sample as a whole, which in turn gives us information regarding which types and loadings of Pt provide the most catalytic activity towards ORR, thus allowing for optimizing the catalytic activity while concomitantly decreasing the amount of noble metal used. Moreover, visualization of catalyst activity with high spatial resolution is important for screening of catalyst libraries, catalyst optimisation and investigation of catalyst/support/membrane assemblies for PEM fuel cells. If a a Pt micro/nano electrode used as SECM tip is moved to
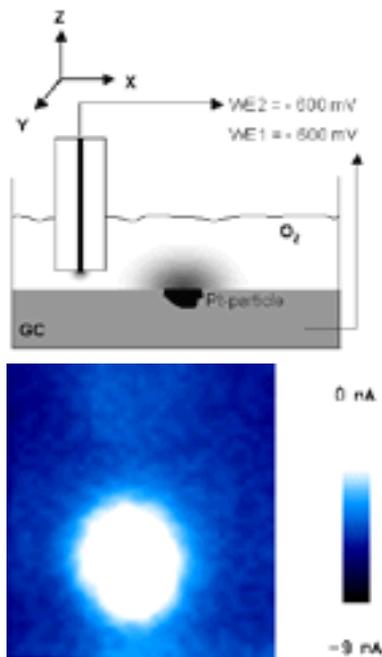
within feedback distance of a Pt deposit and both have potentials applied to them which facilitate oxygen reduction, a competition reaction occurs to reduce the dissolved oxygen in the mediator solution. The current is recorded at the tip and a scan over the Pt deposit produces a map of the electrochemical activity of the Pt deposit. The higher the catalytic activity of the deposit, the lower the recorded current at the tip as there is less dissolved oxygen available for the tip to reduce (Figure 1, 2).

In this communication, evaluation of the proposed oxygen-competition mode of SECM is explained in detail demonstrating its applicability for the visualization of the local activity of Pt clusters deposited under various conditions on glassy carbon surfaces. Specific software tools were developed for recording current decay curves after pulse application of the reduction potential at the SECM tip. In combination with O_2 generation pulses high resolution visualization of the ORR becomes possible.

Electron Transfer at Gold surfaces Modified by Tethered Osmium Complexes

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Molecular junctions using redox molecules such as osmium bipyridine pyridine complexes with fast ET kinetics can be addressed electrochemically and have attracted attention in molecular electronics [1-2]. The linkage of the redox center to the metal contact is an important factor in the electronic coupling and thus in the molecular conductance behaviour. The complexes can be directly adsorbed or chemically bound onto the metal surfaces.

In the present communication we report new binding strategies of an osmium complex by self-assembly via thiols (Au-S bond) and by covalently attachment via aryl radicals (Au-C bond).

Two approaches have been employed to tether the osmium bipyridil pyridine chloride complex ($Os(bpy)_2ClpyCH_2NH-$) to Au surfaces:

a) Post-functionalization of Au/cysteamine SAM by Schiff base reaction with $Os(bpy)_2ClpyCHO)$ and further reduction with cyano borohydride.[3]

b) Electrochemical reduction of the diazonium salt of $Os(bpy)_2ClpyNH_2$ on Au in acetonitrile.[4-6].

The resulting redox modified surfaces have been characterized by cyclic voltammetry, resonant Raman spectroscopy, FTIR, electrochemical quartz crystal microbalance (EQCM), ellipsometry, etc. Spectroscopic and electrochemical evidence show the presence of the Os complex bound to the Au surface but different electronic coupling to Au has been observed.

In both cases, the electron transfer through the osmium complex tethered to Au surfaces has been studied by electrochemical techniques and by the Au/SAM-Os//SAM/Hg method [7].

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Local Electroless Deposition of Nanoparticles by Scanning Electrochemical Microscopy

Y. Yerucham, E. Malel, E. Mekahel and D. Mandler*

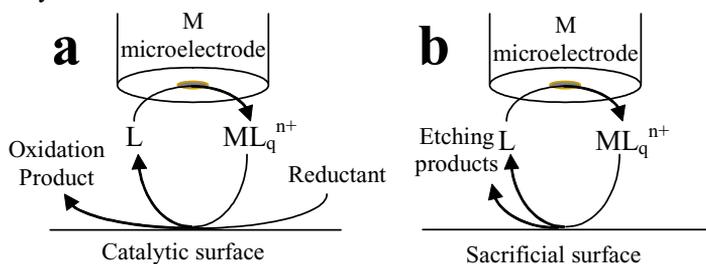*The Hebrew University of Jerusalem, Jerusalem 91904, Israel*
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Electroless deposition (ED) of metals has enormous importance in modern plating technologies and has widely been used in the printed circuit board industry and manufacturing microelectronic devices and structures. ED and electroless displacement (DD) reactions comprise the reduction of metal ions and metal deposition by a reducing agent and not by an external current source. While in ED the reducing agent is in the solution and the surface catalyzes the process, in DD the source of electrons comes from the surface itself which is oxidized. ED offers several advantages depending on the plating metal; however, two major general benefits are its applicability to non-conducting substrates, such as glass and organic polymers, and the uniformity of the deposits, even on complex shapes.

In spite of the fact that ED is well established and widely used, there are only a limited number of successful reports on the ED of metals **locally** on surfaces. Localization of ED has been achieved by either applying lithographic means or by locally activating the surface using mostly laser irradiation or scanning probe microscopy (SPM) techniques.

The scanning electrochemical microscopy (SECM) is probably the most suitable SPM technique for the local ED of metals. We have developed different approaches for the local ED and DD by the SECM (Figure 1). The approaches are based on generating a flux of metal ions, e.g., Ag^+ and $AuCl_4^-$, at the tip, which is held close to a surface. At least four different systems will be presented and discussed: the ED of gold and copper, the DD of silver and the ED of silver by the potential assisted ion-transfer across two immiscible liquids.

Local ED of gold was accomplished by the generation of gold ions in the presence of hydroquinone, while ED of copper was achieved by the generation of copper ions in the presence of tartaric acid, and formaldehyde. On the other hand, the local DD of silver was observed when silver ions electrogenerated at an Ag tip reacted with a copper surface. The structure and distribution of the nanocrystals depend on many parameters, such as the length of the pulse applied to the tip, the surface and the nature of the electrolyte.
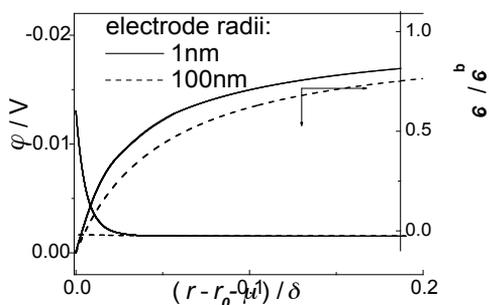

Local electroless deposition (a) and electroless displacement (b) by SECM

The Electrochemistry At Nano-Sized Electrodes

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Electrochemistry at nanometer-sized electrodes has been the subject of extensive studies during the last two decades.[1] As well as the novel applications in SPM and fast kinetics measurement, nano-sized electrodes offer great opportunities to investigate the interfacial electrochemical reaction confined into spatial domains of nanoscales, which is of importance in many areas like electrochemical fabrication of nanomaterials and nanodevices, and nano-electrocatalysis. Recently, several studies have shown that the voltammetric behaviors of nanometer-sized electrodes deviate significantly from the predication of classic electrochemical theories. In this paper, we present some of our recent theoretical and experimental results on the electrochemistry at nanometer-sized electrodes. As shown in Fig.1, there is significant overlap between the potential filed (double layer) and the concentration field (mass transport layer) at the electrochemical interfaces on nanometer electrode, while the thichness of the potential field at large electrode is negligible comparing to the concentration depletion layer. This implies that the electrochemical interface at electrodes of nanoscales is more like an electric-double-layer. It is shown that the double-layer nature of the electrode/electrolyte interface of nanoscales renders that the voltammetric responses vary with electrode size, reactant charge, the value of formal redox potential, and so on. These voltammetric features are novel in comparison to the traditional voltammetric theory based on the transport of redox molecules in the depletion layer. Some experimental results are also shown to compare with the theoretic predications.

Fig.1 The potential and reactant concentration profiles in the interfacial region accompanying one-electron reduction of 5×10^{-3} mol L-1 O^{-} at electrodes of different sizes in the presence of 0.5M supporting electrolyte. k^{0} = 1.0 cm/s, D =1×10^{-5}cm/s^{2}.

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Symposium 4 - Keynote

Elecrochemical Nanotechnology

Local Electroless Deposition of Nanoparticles by Scanning Electrochemical Microscopy

Y. Yerucham, E. Malel, E. Mekahel and <u>D. Mandler</u>*

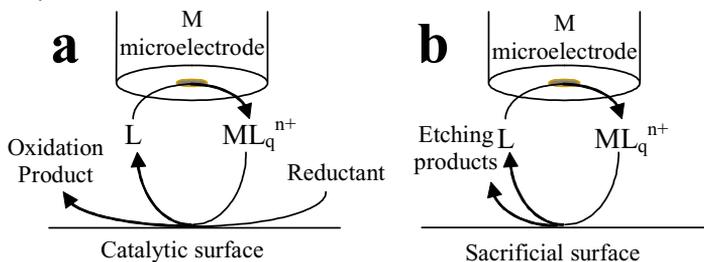*The Hebrew University of Jerusalem, Jerusalem 91904, Israel*
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Electroless deposition (ED) of metals has enormous importance in modern plating technologies and has widely been used in the printed circuit board industry and manufacturing microelectronic devices and structures. ED and electroless displacement (DD) reactions comprise the reduction of metal ions and metal deposition by a reducing agent and not by an external current source. While in ED the reducing agent is in the solution and the surface catalyzes the process, in DD the source of electrons comes from the surface itself which is oxidized. ED offers several advantages depending on the plating metal; however, two major general benefits are its applicability to non-conducting substrates, such as glass and organic polymers, and the uniformity of the deposits, even on complex shapes.

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Local electroless deposition (a) and electroless displacement (b) by SECM

Sers at structured Pt and Pd surfaces

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We have shown that electrodeposition through monolayer colloidal templates can be used to produce stable, reproducible and reusable SERS active silver and gold surfaces that can be used for in situ electrochemical SERS studies [1,2]. Platinum group metals have interesting catalytic properties therefore it would be advantageous to produce SERS active surfaces from these metals. The electrochemical roughening of Pt and Pd, and ultrathin layers of these catalytic metals on a roughened gold produce irreproducible and unstable SERS active surfaces. Here we extend our work to show that templated electrodeposition of platinum and palladium to produce thin (<1 μm) films containing a close packed hexagonal array of uniform sphere segment voids give surfaces which show surface enhancement for Raman scattering from molecules adsorbed at the surface. We report SERS spectra for benzene thiol adsorbed on the structured platinum and palladium surfaces. These SERS spectra for benzene thiol agree well with those in the literature in terms of the band positions and relative intensities. The enhancement depends upon the precise structure of the metal surface and requires the correct choice of template sphere diameter and film thickness. Finally, we report the first example of the use of these surfaces for SERS.

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Application of thin electrolyte layer ATR-FTIR spectroscopy for the surface characterization of synthesized Pt-based nanocatalysts

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Recently, a rapid synthesis method for the preparation of Pt/Ru colloids of controlled size (0.7 – 4 nm) and composition, and their subsequent deposition on high surface area carbons, has been developed [1]. This method uses glycolate as a stabilizer, which is a simple organic molecule that can be oxidatively removed by heat treatment at temperatures as low as 160°C, hence, not alters the catalyst composition [1]. In this work, Pt-based nanoparticles, namely Pt, Ru and Pt/Ru bimetallic catalysts of controlled size are synthesized using this method and deposited on high surface area carbon (Vulcan). The particle size of the single and bi-metallic catalysts can be controlled between 1 and 5 nm. The mechanism of particle size control takes place via the pH dependent ratio of glycolate vs. glycolic acid, the former acting as stabilizer for the colloidal particles and formed as a result of the oxidation of ethylene glycol.

The potential use of the thin electrolyte layer ATR-FTIR spectroscopy [2] to characterize the catalyst particles, size and surface composition such as the Pt to Ru ratio is tested. The main advantage of this technique is that it has good sensibility for studying non-reflecting and porous electrodes and can be applied for in situ investigation of the supported catalysts. The IR spectra of CO adsorbed (CO_{ads}) on the Pt, Ru and bimetallic Pt/Ru colloids are recorded in 0.5 M H_2SO_4. The stretching frequency of CO_{ads} depends on the particle size and composition. Intense IR bands due to the stretching vibration of CO_{ads} are observed between 2010-2050 cm^{-1} for Pt nanoparticles. A shift of the CO_{ads} peak to higher wavenumbers with increasing intensity is observed with increasing Pt particle size. For the Ru particles, two bands for linear bonded CO_{ads} between 2030 and 2060 cm^{-1} and at lower wavenumbers (1980 – 1960 cm^{-1}) for bridged bonded CO_{ads} (Ru(CO)Ru) are observed. The ratio of linear CO to bridging CO decreases as the metal particle size decreases. It seems that for small Ru particles, CO is adsorbed in a predominantly bridging fashion, whereas the linear mode is predominant when the particles size is larger. This variation of intensity possibly can be used for an estimation of particle size. The IR spectra for Pt/Ru particles show complex behaviour. For the larger particles (>2.5 nm) two intensities are observed in the range of 1970-2050 cm^{-1}, while decreasing the particle size leads to the appearance of a third peak around 2020 cm^{-1}. This may indicate that for the larger particles, Ru is only partially dissolved in the Pt lattice and a separate Ru phase is also present. The smaller particles (< 1.5 nm) possibly consist of separate Pt and Ru phases.

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S4·O-3

Nanopore arrays from directionally solidified eutectics as templates for the electrodeposition of gold

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Nanoelectrode arrays are of great interest in electroanalytical chemistry because of their improved S/N ratio when compared to conventional electrodes. Such small-sized electrodes may enable the measurements of very low concentrations of redox active compounds, or even single molecules if they are small enough. Nanoelectrodes are usually fabricated by template-directed synthesis, involving the chemical or electrochemical deposition of the wires.

An alternative route for the fabrication of self-organised nanostructures has been demonstrated with the use of directionally solidified eutectics for the electrodeposition of gold nano- and micro-structures [1, 2]. Pseudo-binary NiAl-X (X = Re, W) eutectics present a structure in which the minor phase (Re or W) is composed of fibres uniformly distributed in a stable NiAl matrix. The selective dissolution of the fibres for the formation of nanopores is accomplished after polarization of the sample at a neutral pH. Under the experimental conditions, the matrix is passivated due to the formation of a stable Al_2O_3 layer for both systems studied.

The mechanism of gold deposition is subsequently studied by examining the current transients recorded after the application of reverse pulses of different lengths to the passivated samples. In an initial stage, the nucleation takes place in the pores, until their complete filling. The application of further pulses results in a diffusion controlled growth of the gold structures [3]. By carefully controlling the duration of the pulses, it is possible to control the electrodeposition of gold to take place exclusively in the pores, thus enabling the fabrication of arrays of gold nanoelectrodes. Gold microelectrodes can be obtained after longer deposition times.

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Symposium 4 - Oral

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Reflectance, Electroreflance and SERS from Au Nanowire Arrays

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In this work, we report on the reflectance, electroreflectance and potential dependence of surface enhanced Raman spectra (SERS) from arrays of Au nanowires electrodeposited in porous alumina templates. The reflectance measurements were conducted using either *p*- or *s*- polarised light. Experiments using *s*- polarised light gave rise to spectra exhibiting the transverse surface plasmon mode of the Au nanowires only whereas with *p*-polarised light, the contribution from the longitudinal plasmon mode was also observed. The reflectance was also measured as a function of the incident angle and of the aspect ratio of the nanorods. A model, based on the calculating the reflectance from a thin uniaxial film, was developed which accounted for the observed effects. In the study using electroreflectance from the arrays, carried out with polarized light, the spectra were again dominated by features corresponding to the surface plasmon modes of the Au nanorods. Modelling of the experimental data here was achieved by calculating the change in the free electron concentration as a function of the applied potential. This is shown in Figure 1.
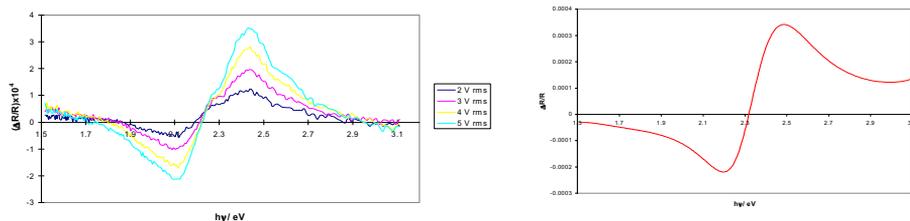
Figure 1
Recorded (left) and modelled (right) electroreflectance spectra using s-polarised light.

The electrochemically grown arrays arrays were utilised as SERS substrates and in our particular fabrication procedure, direct electrical contact to the Au nanowires could be made. SERS spectra were thus recorded as a function of the electrode potential with pyridine employed as the test species. The results obtained (Figure 2) showed the SERS intensity increasing as the potential was made more negative, in agreement with the

Figure 2
SERS Spectra as a function of potential

literature. The more fascinating and unique feature of our data though is that the band associated with the Au-N bond became the dominant feature of the spectra over the potential range examined here.
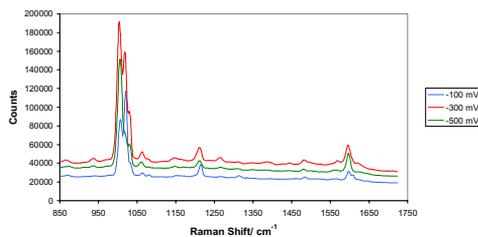
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Quantized Charge Transfer in Nanoparticle Organized Arrays

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This is the abstract for the **Tajima Prize Lecture**. Monolayer-protected nanoparticles exhibit a series of discrete voltammetric peaks in solutions, which are attributed to the quantized charge transfer of the particle molecular (double-layer) capacitance. This unique charge transfer phenomenon has been very well exemplified by alkanethiolate-protected nanoparticles of several transition metals such as gold, palladium, cupper and ruthenium. Similar quantized charging phenomena can also be observed when the particles are immobilized onto an electrode surface. However, it has been discovered that with these surface assemblies, solvent media play an important role in the regulation of the nanoscale electron transfer processes. For instance, in low-dielectric organic media, the quantized charging features can be seen at both negative and positive potentials (with respect to the particle potential of zero charge). By contrast, in aqueous solutions, the quantized charging responses can be initiated only in the presence of hydrophobic anions and in the positive potential regime; whereas at negative potentials, only featureless responses can be seen and the voltammetric currents are suppressed drastically. Consequently, the overall voltammetric profiles resemble those of a molecular diode. This is interpreted by the manipulation of the electrode interfacial capacitance as a consequence of the ion-pairing between the hydrophobic electrolyte anions and the particle molecules at positive potentials (Randle's equivalent circuit). Detailed studies have been carried out by a systematic variation of the nature and concentration of the anions. It is found that these rectified quantized charging processes are very sensitive to the hydrophobicity of the electrolyte anions which can be correlated very well with their respective solvation interactions with water molecules. Further comparative studies have also been carried out with monolayers and multilayers of particle molecules on the electrode surface within the context of the particle charge transfer kinetics. The interfacial dynamics have also been studied by electrochemical quartz crystal microbalance measurements.

In a more recent study, we investigate the solid-state perspective of the particle single electron transfer. Using Langmuir-Blodgett techniques, we fabricate nanoparticle solid films of monolayers as well as multilayers. By deliberate control of the particle dimensions, interparticle separations and temperature, we are able to observe well-defined single electron transfer across these particle solids. The electron transfer kinetics involved is evaluated voltammetrically and compared to that in solutions. Effects of chemical environments have also been examined which may be exploited as a novel mechanism for chemical sensing.

Symposium 4 - Oral

Elecrochemical Nanotechnology

Sensitive Resolution of Electronic Structure and Interfacial Property of Alkanethiol Self-assembled Monolayers at Liquid/Solid Interfaces

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Self-assembled monolayers (SAMs) on various substrates, particularly thiol-gold based SAMs, have provided versatile pathways towards creating functional nanostructures on solid surfaces and liquid/solid interfaces for molecular electronics applications. Further advance of the field is anticipated to rely on rational design and control of SAMs with composite functions. Besides synthesis of "smart" materials, this objective demands increasingly fundamental understanding of electronic structures and interfacial properties of the SAMs. While a great number of efforts have already been devoted to this issue, it remains a challenge to resolve details of microscopic structures and interfacial properties at the nanoscale and single-molecular levels, particularly at liquid/solid interfaces.

In this study, we have chosen three short-chain alkanethiols (i.e. 1-propanethiol, 2-methyl-1-propanethiol, and *tert*-butanethiol) as targets. The structural differences of these alkanethiols are virtually small from a chemical point of view. The alkanethiols are spontaneously assembled on Au(111) surfaces to form highly ordered structures. By a combination of electrochemistry and scanning tunneling microscopy, we have been able to distinguish both electronic structures and interfacial properties of the monolayers at high resolution. Surface microscopic structures are characterized at the single-molecule level. More interestingly, the two branched monolayers show electrochemical rectification toward redox probes. These alkanethiol-modified Au(111) electrodes further offer biologically compatible surfaces for assembly of metalloprotein monolayers where long-range electron transfer is selectively facilitated.

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Symposium 4 - Oral

Elecrochemical Nanotechnology

Electrodeposition of cuprous oxide films and nanowires: growth mechanism and nucleation behavior

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Template-directed synthesis represents a convenient method for generating 1D nanostructures. Oxide could be obtained by this technique and could have important applications such as transparent conducting oxides, sensors, and light emitting devices. Here we report a preparation of Cu_2O nanowires within a porous polycarbonate membrane (pore size = 90 nm) by cathodic reduction of alkaline cupric lactate solution [1].

The experiments were performed in a first step on stainless steel. Chronoamperometry experiments were carried out in order to investigate the copper oxide nucleation growth process. Experimental curves were analysed by means of the model proposed by Scharifker and Hills [2]. Kinetic data of the electrodeposition / nucleation process are compared with progressive and instantaneous nucleation model. A modification of the growth process and the morphology can be suspected when a magnetic field is surimposed in a direction parallel to the electrode surface. This effect can be a new mean to analyse the first moments of the nucleation process.

Finally Cu_2O nanowires have been obtained in polycarbonate membranes by the potentiostatic technique. The morphology analysis and structure characterization of the Cu_2O nanowires were examined by conventional electron microscopy. The electron diffraction pattern of the nanowires confirms the cubic Cu_2O structure previously revealing by X-ray diffraction on thin films. The growth mode of Cu_2O nanowires is discussed and a spiral growth can be hylighted and explained by crystal defect appearance.

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Symposium 4 - Oral

Elecrochemical Nanotechnology

Mixed self-assembled monolayers of 2-mercaptobenzimidazole and 2-mercaptobenzimidazole-5-sulfonate: determination and control of the surface composition

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The present work focus on the formation and characterization of mixed monolayers made of 2-mercaptobenzimidazole (MBI) and 2-mercaptobenzimidazole-5-sulfonate (MBIS) on Au(111).

The behaviour towards electron transfer of self-assembled monolayers of MBI or MBIS was first examined by cyclic voltammetry. The influence of the monolayers was drastically dependent on the charge of the redox probe used. On the MBI modified electrode, no inhibition is observed for $[Fe(CN)_6]^{3-}$ probe, while it is markedly inhibited on the MBIS modified surface. When $[Ru(NH_3)_6]^{3+}$ is used, a post-adsorption peak characteristic of the adsorption of the redox probe is detected only in at the MBIS modified electrode.

Taking advantage of this difference, AC voltammetry has been used to determine the surface composition when mixed monolayers are formed by immersion of the gold substrate in mixtures of different molar fractions of MBI and MBIS. For such a purpose, AC voltammetry is indeed much more sensitive than cyclic voltammetry. The real and imaginary faradaic admittances were extracted from the impedance measurements since, according to the theories dealing with the AC response of adsorbed electroactive species, both are proportional to the surface concentration of the probe.

Results clearly indicate that the ionic strength of the immersion solution plays a key role in the surface composition of the mixed monolayers. At low ionic strength, the adsorption of MBI is largely favoured as compared to that of MBIS. The addition of 0.25 M $CaCl_2$ in the immersion solution significantly increases the amount of MBIS in the monolayers. Such a simple modification as the addition of a concentrated electrolyte to the immersion solution provides an elegant way to modulate the surface composition when a charged surfactant is mixed with a neutral surfactant.

Nanoparticle mediated electron transfer across ultrathin self-assembled films

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Analysis of the reactivity of 2D nanostructured electrodes as a function of the nanoparticle number density is a key approach to rationalising (i) the reactivity of single particles and (ii) the transition from single to collective properties of particle arrays. A convenient strategy to achieve this goal consists in the modification of electrode surfaces by "blocking" self-assembled monolayers and monitoring the changes in the dynamics of electron transfer to a redox probe upon adsorption of nanoparticles. In the present contribution, we shall discuss the electrochemical properties of electrodes modified by ultrathin poly-electrolytes films and the effect of electrostatic adsorption of metal nanoparticles. We have recently shown that the sequential modification of Au electrodes with a self-assembled monolayer of mercapto-undecanoic acid (MUA) and poly-l-lysine (PLYS) generates highly compact films that strongly hinder the electron transfer to the hexacyanoferrate redox couple [1]. As illustrated in figure 1, the electrostatic adsorption of citrate stabilised Au nanoparticles generates monodispersed 2D arrays on the PLYS film in which the particle number density is controlled by the adsorption time. Impedance spectroscopy revealed that the ultrathin film does not substantially affect the rate of electron transfer between the electrode surface and the nanoparticles. On the basis of the electrochemical results, as well as detailed analysis of the film structure by ex-situ and in-situ scanning probe techniques, a model for the electrode-film-nanoparticle architecture is presented. Furthermore, the use of this type of nanostructured electrodes for studying fundamental aspects of electrochemical nucleation is briefly presented.
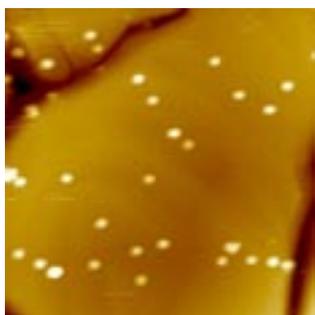
Figure 1. 2μm×2μm AFM image of an electrostatic assembly of 20 nm citrate stabilised Au particle on a Au electrode modified by a self-assembled monolayer of MUA and an ultrathin film of PLYS. The film acts as blocking layer for direct electron transfer to the electrode surface as well as tethers the particles forming monodispersed 2D arrays.

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Synthesis of nanoporous crystalline metals or compounds with superior catalytic and capacitive activity via electrochemical lithiation

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Nanoporous materials have attracted great technological interest during the past two decades essentially due to their wide range of applications: they are used as catalysts, molecular sieves, separators or gas sensors as well as for electronic and electrochemical devices. Most syntheses of nanoporous materials reported so far focused on template-assisted bottom-up processes including soft templating and hard templating methods.

Here we exploit a mechanism implicitly occurring in lithium batteries [1, 2] at extreme discharging in order to develop it into a room temperature template-free method (see Fig. 1) of wide applicability range for the synthesis of transition metals or metal oxides with large surface area and pronounced nanoporosity. The power of this top-down method is demonstrated by the synthesis of nanoporous Pt and RuO_2 both exhibiting superior properties. The nanoporous Pt prepared shows outstanding performance with a peak current density of 186 mA mg^{-1} when used as an electrocatalyst for methanol oxidation. In the case of nanoporous RuO_2, a specific capacitance of 385 F g-1 at a scan rate of 1 mV s^{-1} is obtained when it is used as a supercapacitor electrode material.

The described synthesis strategy is relatively simple (just starting from micrometre-sized transition metal oxides), yet very effective, and owing to its versatility, can also be extended to the synthesis of other nanostructured transition metal oxides and also to sulphides, fluorides, nitrides and phosphides. Also structure-forming chemical agents other than Li (Na, Mg, etc.) could probably be used in order to achieve different pore structures. We anticipate nanoporous materials with increasing richness of inorganic compositions to make a decisive impact in future applications in the various fields such as electrochemical storage, electrocatalysts, photocatalysts, and sensors.
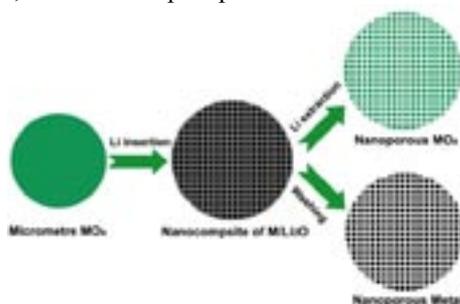
Fig. 1. General scheme for the template-free electrochemical lithiation/delithiation synthesis of nanoporous structures.

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The synthesis of novel nano-structured carbons and their application in direct methanol fuel cells

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The synthesis of a series of novel mesoporous and macroporous carbon structures is demonstrated. These structures are then loaded with platinum and are currently being tested against commercially available equivalent materials in a Direct Methanol Fuel Cell.

The synthesis of mesoporous silicas is a well known process and utilises surfactant templates to produce regular structures with pore sizes in the 20-100Å region. By impregnating these materials with platinum followed by filling of the pores with carbon and dissolution of the silica it has been possible to produce carbon negatives of these materials with the platinum centres incorporated into the walls of the material (Figure 1.) to reduce leaching and sintering of the metal. The structures produced

Figure 1. Platinum particles within a nanoporous carbon structure showing the pores running through the platinum.

have surface areas in the region of 1000m^2/g and the extent of metal loading can be tailored.

Using a similar technique it is possible to produce negatives of a range of porous structures. In addition to mesoporous silica, the use of macroporous diatomaceous earth has produced an open carbon structure which has a surface area of ~300m^2/g (Figure 2.). Diatomaceous earth has the benefit that it is extremely abundant, has a range of pore architectures available and is readily dissolved to produce the negative.

The structures produced have been incorporated into a DMFC membrane and are currently being tested, preliminary results on the efficacy of these materials will be presented.

Keywords: diatomaceous, nano-porous, carbon, platinum

Figure 2. Carbon negative of an individual diatom cell

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Oxygen reduction on nanostructured nIckel in alkaline solution. The effect of alkali metal intercalation

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Nanostructured Ni electrodes were obtained by pulse plating and oxidised in alkaline solution to form a smooth layer of $Ni(OH)_2$ on the surface. The rate of oxygen reduction on such a layer was found to be significantly higher than on bulk Ni. In both cases high yield of hydrogen peroxide was formed. Experimental data clearly show that oxygen reduction depends on both the conductivity in the solid phase and the availability of active sites on the hydroxide surface. Oxygen reduction at Ni(II) sites embedded in a hydroxide matrix has been modelled using quantum chemistry and the results follow closely the previous investigations on similar sites for Co[1], where the coordination of the active site was found to be important. Intercalation of alkali metals in $Ni(OH)_2$ is known to influence its structure and properties[2,3] and hence an investigation on the effect of alkali metal cations on the rate of oxygen reduction was made. The rate of oxygen reduction clearly depends on the type of intercalating cation (see Figure 1a). The disc current decreased in the order $Na^+ > K^+ > Li^+$, while the efficiency for hydrogen peroxide production increased in the opposite

Fig. 1. RRDE data for O_2 reduction (a) and CV for oxidation of $Ni(OH)_2$ to NiOOH (b).

direction. The origin of the difference in activity is believed to be related to the structure of the active surface site. The different properties of the intercalated $Ni(OH)_2$-layers can also be observed in the oxidation process to NiOOH, Fig 1b. The oxidation shifts to more positive potentials as the size of the cation decreases.
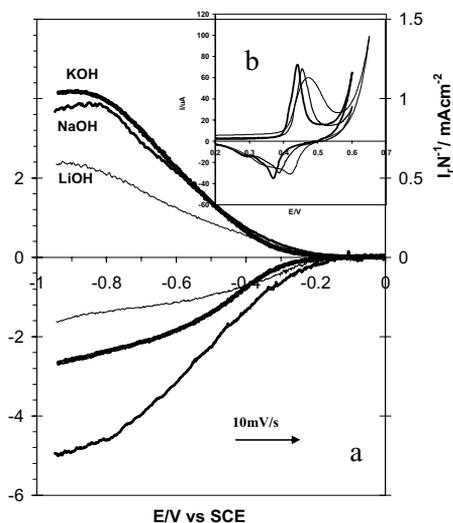
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A new type of *in situ* single molecule rectifier

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"It is only theory that tells us what we actually observe" (Albert Einstein)
We present a theory of in situ tunnelling conductance of a chain molecule controlled by fluctuations of relative conformations between the nearest neighbour units of the molecule. The theory leads to a simple formula for linear conductance. In one regime it reproduces recently reported Arrhenius dependences for alkanedithiols (*Haiss et al*, 2005) with activation energy proportional to the length of the molecule, whereas in other regimes it shows activationless behaviour which corresponds to the tunnelling across more rigid molecules. The general formula covers the transition between the two limits, predicting some new dependencies that could be challenging to verify experimentally. We extend the theory to describe the voltage and electrolyte dependence of the current. We show that the current/voltage characteristics of this junction may provide ***striking rectification and gating features*** at moderate potentials in a purely ***symmetric*** system which without electrolyte will not exhibit such behaviour.

Biological molecules often possess higher lying electron energy levels, so that tunnelling through a molecule is facilitated by the virtual transitions to these states (*superexchange mechanism*). We extend the theory on this case as well, and derive a transparent analytical formula, which exhibit different temperature dependence of the tunnelling conductance, but similar rectification behaviour.

In addition to new horizons in ***electrochemically-based molecular electronics***, the predicted spectacular effects offer new opportunities for the study of polypeptide chains by the methods of *in situ* tunnelling spectroscopy and suggest new design for lab-on-a-chip biosensors. Treating experimental data, this theory can also help to distinguish the mechanisms of electron transport through of single-molecule.

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Bridge-mediated electron tunneling in *in situ* electrochemical junctions: physical mechanisms, rectification, relaxation, hysteresis, and all that

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Studies of electron transfer through single atomic or molecular bridges confined between two metal substrates evolved in a broad field and cover a whole range of the sizes of the mediators, from small atomic groups to large molecules, like polymers, short fragments of DNA, or larger biological macromolecules.

New dimensions are added by studies of single-molecule processes in electrolyte solution. Molecular electronic conductivity and electron transfer in aqueous media have disclosed new ET phenomena of general significance for ET science.

We discuss various physical mechanisms of electron transfer through a bridge molecular group located in an electrochemical scanning tunnelling microscopy (*in situ* STM) gap or in solid-state electrochemical tunnel junction. They involve through-space and through-bond (superexchange) tunneling, and elastic and inelastic tunneling through electron energy levels of a bridge group. A special attention is devoted to electron transfer through the energy levels of a redox bridge group which is called redox-mediated electron tunnelling. Theoretical frames are available [1]. Resulting current-voltage relations show spectroscopic, transistor-like, and diode-like behaviour, attractive for basic research and with technological perspectives. Other features are relaxation, hysteresis and switching

We overview the predicted basic features of the current-voltage plots verified by recent data for transition metal complexes [2,3], organic molecules [4], and redox metalloproteins [5,6].

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Thin film photovoltaic cell with porphyrin-fullerene dyads and gold nanoparticles

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Organic photovoltaic devices have attracted a growing interest in recent years. This contribution presents a thin film photovoltaic cell with an attempt to improve cell performance by introducing gold nanoparticle layers in the structure. One studied scheme of the cell design is given in Figure 1a. The primary charge separation takes place in the covalently linked Porphyrin-Fullerene dyad molecule /1/. The overall cell configuration is planned to enhance this process.
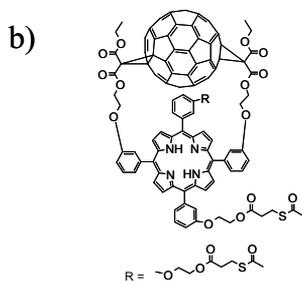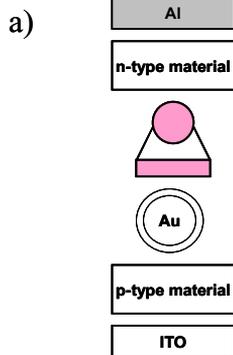
Langmuir-Blodgett (LB) and Langmuir- Schäfer (LS) methods are used to construct well-organized, monomolecular films of metal nanoparticles, dyad molecules and n- and p-type organic semiconductors. The cell structure is fabricated between ITO and Al-electrodes. Thiolate protected gold nanoparticles of different diameters have been prepared by the two-phase method /2/.

The cell function has been studied with time resolved Maxwell displacement charge (TRMDC) method /1/ and by current-voltage measurements. First, TRMDC method is used to study the vectorial electron transfer processes in thin film structures with gold nanoparticles and the dyad. In TRMDC measurements, the sample is excited by a laser pulse and the induced photovoltage and relaxation of charge separated state in time ranges up to 2 ms is measured. Second, the overall perfomance of the PV cell is evaluated by current-voltage measurements and parameters like fill factor, short circuit current and power conversion efficiency are obtained.

Figure 1. a) PC cell design
       b) Porphyrin-Fullerene dyad

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Fabrication of nanobands and nanoband arrays by focused ion beam (FIB) milling and characterisation by voltammetry

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The fabrication of nanoelectrodes has gained increasing interest in recent years [1]. While a number of advantages of such electrodes over conventionally sized macro-electrodes have been proposed, including enhanced mass transport rates and increased signal to noise ratios, a disadvantage associated with their use is the very small current that is generated from them. The use of nanoband geometries, where the width of the band is in the nanometre range, can generate larger currents but still retain non-linear diffusion characteristics, thus enhancing the aforementioned advantages. Using an array of nanobands can further enhance the current, however, non-linear diffusion is also dependant on the inter-electrode spacing.

Nanoband fabrication techniques have incorporated (i) creation of insulator-metal-insulator layers followed by etching or polishing to expose one of the edges, (ii) evaporation of metal films followed by electron beam lithographic patterning and etching, and (iii) deposition of molybdenum oxide (MoO_2) nanowires into Highly Ordered Pyrolytic Graphite (HOPG) trenches followed by polymer film deposition and gold evaporation [2]. Some disadvantages associated with such techniques include difficulties in accurate bandwidth determinations, laborious multi-step procedures and undefined nanoband spacing.

In this work, single nanobands and arrays of nanobands have been created by focused ion beam (FIB) milling through a passivation layer of silicon nitride to an underlying layer of platinum. This technique has provided a simple and rapid means for the fabrication of nanobands and array prototypes, with controlled nanoband dimensions, numbers and inter-band spacing. Voltammetric characterisation has determined the nature of diffusion at the nanoband electrodes, allowing their development and potential application as analytical sensing devices.

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On the stability of modified Au nanowires

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The formation of monoatomic gold chains has awakened particular interest among both experimentalists and theoreticians. Different experimental groups have recently generated linear chains of 3-4 Au atoms between two tips of the same material and have obtained images of the system by means transmission electronic microscopy (TEM) [1-3]. In the last years, it has also became of both theoretical and experimental interest the formation of these chains in the presence of atoms and small molecules. On one side, the unusual interatomic distances observed have been explained through the intercalation of foreign atoms. On the other hand, the existence of fractional conductance values has also been explained in terms of the insertion of hydrogen atoms[4-6]. Furthermore, it has been suggested recently that the intercalation of different molecular entities may serve to control the critical force at which the wires should break.

In the present work we have performed first principles calculations for monoatomic free Au chains and also interacting with diatomic molecules (H_2, O_2) and other species within density functional theory (DFT) using the SIESTA code [8], to which we have added the nudged elastic band technique (NEB) [9]. This has allowed us to obtain information concerning the minimum energy path (MEP) for the elongation and rupture of the nanowires, as well as to obtain information on the dissociation process of the molecules upon nanowire elongation.

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Self-Organized Nanostructure on Silicon by Photoelectrochemical Oscillation

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Oscillatory behaviour of silicon electrodes occurs in fluoride containing solutions at increased anodic potential. Depending on solution composition, pH and illumination level (for n-type samples), regular sustained and damped oscillations with varying frequency can be adjusted. The theoretical description of photocurrent oscillations is based on the assumption of two types of oxides formed during oscillation. Within an oscillatory cycle, earlier formed oxides are less stressed than later formed ones because of the compressive stress in the remaining non-oxidized Si. The later formed oxide contains more cracks and pores and etches faster by three-dimensional attack. Such oxide pores are seen with high resolution scanning electron microscopy (HRSEM) and their width and density depends on the photocurrent phase at the instant of sample emersion. Using the selectivity of alkaline etching, pores in silicon oxide that connect to the silicon substrate can be etched deeper into Si. Selective HF etching of the ~10nm thick oxide prepares an oxide-free surface that shows nanometre-sized pores propagated into Si(100) in an AFM experiment.

The following structure has been further processed: silicon with an oxide that contains nanopores that have been etched deeper into the underlying Si was used for deposition of metals (Pt, for instance) that form a Schottky barrier with n-Si. Pt islands have been electrodeposited at positions on the surface where electrical contact between Si and the electrolyte could be made. Beneath theses metal nano-islands, the insulating oxide covers the Si surface. HRSEM and AFM images and XPS analyses show and identify the Pt islands.

In photoelectrochemical experiments on the nanocomposite structure, photoelectrochemical solar cells and photoelectrocatalysis is investigated. Already initially, a photovoltage of 0.5V on a non-optimized structure was found. It will be shown that the increased propagation of nanopores can be used for the fabrication of novel nanostructures of thin film Si-based photovoltaic solar cells.

Electrodeposition of Mesoporous PbTe Films from Lyotropic Liquid Crystalline Phases

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Lead chalcogenides are very promising materials for infrared detectors, laser diodes and thermophotovoltaic energy converters due to their narrow band gaps and face-centered cubic structure. Both theoretical predictions and experimental studies based on molecular beam epitaxy suggest that large improvements could be achieved in nanostructured systems [1]. Furthermore, recent studies have shown that monodispersed PbSe nanocrystals exhibit the expected size-dependent effects of quantum confinement and offer high photoluminescence quantum yields [2]. It is therefore essential to develop a new approach of fabricating nanophased lead chalcogenide films to extend their application in optical devices. In this paper we will present the first synthesis of mesoporous nanostructured PbTe semiconductor films via direct liquid crystal templating.

The synthesis of mesoporous nanostructured PbTe films was carried out by cathodic electrochemical codeposition of lead acetate and tellurium dioxide dissolved in the aqueous domain of the lyotropic liquid crystalline phases of the non-ionic surfactant octaethyleneglycol monohexadecyl ether ($C_{16}EO_8$). It was found that the electrodeposition conditions have significant effects on the nanostructure and morphology of the deposited PbTe films. By careful control of the deposition conditions and the phase structure of the employed plating mixtures it is possible to produce mesoporous PbTe films with hexagonal and bicontinuous cubic phases. The evidence of the existence of a nanostructure for the films was obtained by TEM and low-angle XRD. In addition quartz crystal microbalance studies provide further evidence for the mesoporosity of the films. Wide-angle XRD spectra revealed that the deposited films are crystalline cubic PbTe (F$m3m$). Optical studies showed that the mesoporous PbTe films deposited from plating mixture with a hexagonal phase exhibit strong birefringence due to the anisotropic characteristic of the hexagonal phase. Since the mesopore dimension and the topology of the nanostructured semiconductors are under direct experimental control, this approach enables us to explore band-gap engineering and quantum size effects of such nanostructured lead chalcogenide semiconductor films.

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Symposium 4 - Oral

Elecrochemical Nanotechnology

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Polypyrrole Based Nano-Electrode Arrays

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The implementation of sensor platforms providing high sensitivity of detection is a crucial step for the design of the new analytical device generation for biosensor developments. Designing platform with active/non-actives region at nanoscale has shown already a drastic increase of sensitivity [1]. Besides, the electrochemical sensitivity can be as well enhanced by using nano-electrode arrays that increase mass transport rate[2]. Polypyrrole (PPy) is a good candidate to fulfil these requirements. Its preferential material for bio-analytical electrochemistry based sensor thanks to its good environmental stability, excellent biocompatibility and higher conductivity [3], together with the possibility of being functionalised with biological relevant functional groups [4]. In this work surfaces with PPy nano pillars were fabricated by electrochemically growing PPy in a nano-template of gold nano-seeds in a silicon oxide (SiO_x) matrix.
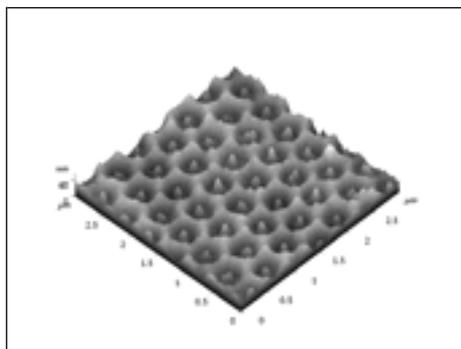
Fig.1. Atomic Force Microscope image: PPy nano pillars growth in SiOx matrix.

Atomic force Microscopy and Scanning Kelvin Microscopy demonstrated that PPy grown only inside the conductive gold seeds, creating nano pillars of conductive material surrounded by an insulating material (Fig. 1). The nano-structured surfaces were studied by Cyclic Voltammetry using hexacyanoferrate and the typical sigmoidal shape voltammogram of nanoelectrodes was obtained [2]. Square Wave Voltammetry was tested in the surface and a well defined peak was obtained which indicates that the nanoarray is a promising surface for use in trace analytical analysis.

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# Combined electrochemical atomic layer epitaxy and microcontact printing techniques

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The attainment of ultrathin films of well ordered II-VI and III-V compound semiconductors has been an active research area of the Electrochemical group in Florence. The method employed was the Electrochemical Atomic Layer Epitaxy (ECALE) which is based on self limiting reactions such as underpotential deposition. Recently, the possibility of combining the electrodeposition at nanometer scale and the self assembling phenomena has been investigated. In particular, the ECALE method was used to deposit CdS on Ag(111) covered by a patterned hexadecanthiol, $C_{16}SH$, SAM. In fact, the deposition of CdS takes only place on the uncovered silver substrate whereas it is prevented on the thiols monolayers, yielding CdS patterned according to the used stamp.

The patterned Ag(111) was obtained by using the microcontact printing technique of a polydimethylsiloxane (PDMS) stamp previously immersed in $C_{16}SH$. The stamp used in this work produced thiol strips approximately 300 nm large, with a 900 nm pitch.
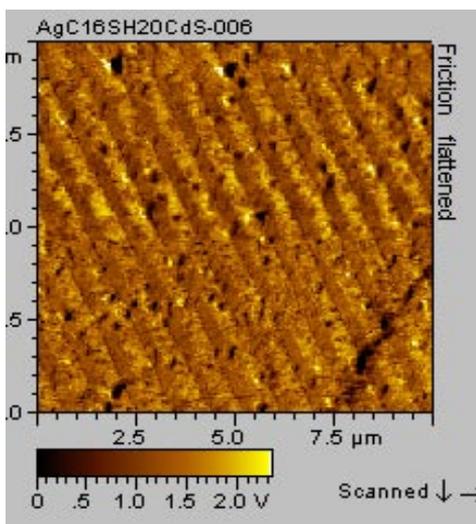
The AFM image shows the final product consisting of 600 nm CdS strips alternated to 300 nm $C_{16}SH$ strips.

Electrochemical measurements showed that the deposition process of CdS on these modified Ag(111) surfaces is similar to that performed on the bare Ag(111), with the obvious decrease in the amount of material obtained, due to the reduced electrode surface. In particular the right 1:1 stoichiometric ratio between Cd and S and the linear increase of the deposit with the number of deposition cycles still indicate the layer-by-layer growth mechanism that is the aim of ECALE method.

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Superconformal film growth: mechanism and quantification

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State of the art manufacturing of semiconductor devices involves electrodeposition of copper for device wiring. The process, pioneered by IBM, depends on the use of electrolyte additives that affect the local deposition rate thereby resulting in superconformal, or bottom–up "superfilling" of trenches and vias. This remarkable growth process is examined in the context of the recently developed curvature enhanced adsorbate coverage (CEAC) mechanism [1]. The model stipulates that 1.) the growth velocity is proportional to the local accelerator, or catalyst, surface coverage and 2.) the catalyst remains segregated at the metal/electrolyte interface during copper deposition. For growth on non-planar geometries this leads to enrichment of the catalyst on advancing concave surfaces and dilution on advancing convex sections; thereby giving rise to bottom-up superfilling of sub-micrometer trenches and vias. The mechanism is applicable to any growth process that is mediated by an interfacial chemical reaction such as electrodeposition, electroless deposition or chemical vapor deposition. The talk will focus on the quantitative application of the CEAC mechanism to connect kinetic measurements performed on planar surfaces with 3-D shape evolution during feature filling. This will be accompanied by a report of recent in situ surface analytical studies of catalyst evolution relevant to the copper Damascene process that is used in the fabrication of microelectronic and MRAM devices.

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Intercalation of cations into TiO$_2$ nanotubes: photoelectrochemical processes

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The ability of TiO$_2$ layers to serve as a host for H$^+$, Li$^+$ and K$^+$ have been the topic of intensive research in various scientific groups due to its potential application as electrode material in rechargeable batteries and photochromic devices. This later effect is based in the change of color generated by the generation of electron traps during the reduction of Ti^{4+} to Ti^{+3} as a consequence of the cation insertion. The kinetics and magnitude of this insertion and the consequent electrochromic reaction is expected to strongly depend on the diffusion length of H$^+$ and therefore on the geometry of the electrode surface. Typically, attempts to produce large area electrodes were made by means of sol–gel deposition or by sintering nanoparticles.

Layers of self-organized TiO2 nanotubes, obtained by anodization in F$^-$ containing electrolytes opens a new opportunity to generate highly defined nanostructure combining the advantage of a high surface area with a very good contact between the TiO2 nanotube structure and the substrate. In this work, we present a study based on cyclic voltammograms and potential step experiments combined with reflectance measurements that show a high storage capacity for H$^+$ and Li$^+$. The nanotube structures present a very high specific optical contrast when switching the layers from the H-loaded to the H-unloaded states (see figure 1), defining a good suitability for its application in the construction of smart windows.

The intercalation kinetics is largely influence by the structure of the oxide. In fact, it was shown that oxide annealing leads to a more defined distribution of the energy distribution of the intercalation sites, it being visualized in more defined potential for intercalation/deintercalation processes.
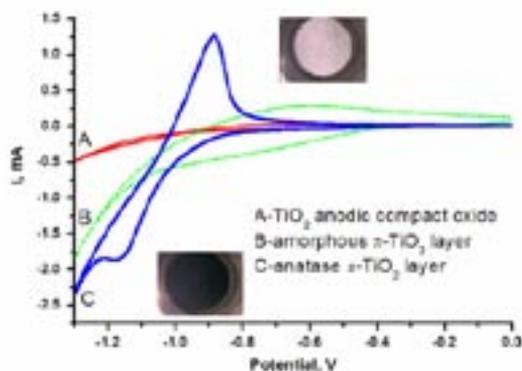

Fig.1 : Cyclic voltammograms performed in 0.1 M HClO$_4$ on different TiO$_2$ substrates. The constrast effect shown in the insets corresponds to the loading and unloading fo the annealed porous layer.

Formation of micro- and nano-sized ordered structures by self-organization in electrochemical systems

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Self-organized formation of ordered micro- and nano-structures of metals and semiconductors at solid surfaces has been attracting keen attention in view of nanotechnology. The self-organization method has an advantage over the photolithography and surface probe method in that it meets both the conditions of atomic-scale fabrication and the adaptability of mass production. Recent studies on non-equilibrium, nonlinear chemical dynamics have proved a large possibility of self-organized formation of a variety of ordered structures such as stripes, dot arrays, and target and spiral patterns. However, most of the patterns thus far reported are limited to those of two dimensions (2-D) lying parallel to the substrate surface. The formation of organized "vertical" structures and further organized 3-D structures will need novel strategy. From this point of view, oscillatory electrodeposition is an interesting target because it has an ability to produce ordered electrodeposits by recording ever-changing self-organized spatiotemporal patterns during oscillations. Here we review our recent studies on the

Figure 1 (a) Potential oscillation observed in Sn electrodeposition. (b) An optical microscopic image of highly ordred latticeworks of Sn produced by the oscillatory electrodeposition.

Figure 2 (a) Current oscillation obtained in SnCu-alloy electrodeposition. (b) SEM (top view) of a bowl-shaped hollow with a slanting cross section, prepared in the deposited alloy film by Ar+ ion etching. (c) Schematic illustration of sample preparation for (b).

structurization by oscillatory electrodeposition[1-3], with a focus placed on the formation of strikingly well-ordered metal latticeworks, standing perpendicular to the substrate, through ingenious cooperation of various processes with long-range spatiotemporal synchronization.
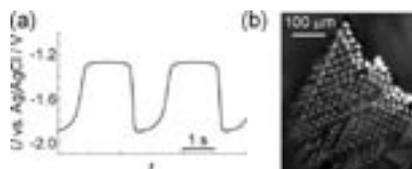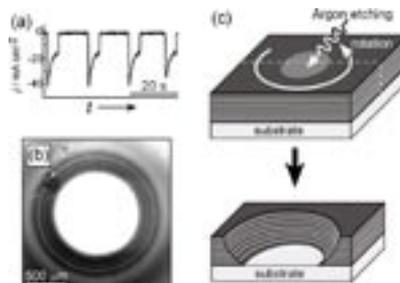
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S4·O-25

Single molecule conductance in ambient conductions and electrolytes

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Methods for forming stable molecular wires between a gold surface and a gold STM tip in both ambient conditions will be discussed and compared in this presentation. The resulting single molecule conductance (SMC) values for a variety of dithiol molecules, including more complex molecules with electrochemically active groups along the molecular wire and DNA will be discussed. Methods for obtaining single molecule conductance during current-distance and current-time experiments will be described. For instance, spontaneous formation of stable molecular wires between a gold scanning tunnelling microscopy (STM) tip and substrate is observed when the sample has a low coverage of dithiol molecules and the tunnelling resistance is made sufficiently small without touching the tip against the surface. The versatility of the techniques is demonstrated on a variety of molecule wires ranging for simple alkanedithiols [3] to redox active molecular wires [1,2,4] and single and double stranded DNA [5].

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Symposium 4 - Oral

Elecrochemical Nanotechnology

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Effects of the seeding conditions on the crystal growth of gold nanoparticles on indium tin oxide surfaces in the seed-mediated growth method

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Gold nanoparticles are the most intensively studied and applied metal nanoparticles in electrochemistry owing to their stable physical and chemical properties, useful catalytic activities and small dimensional size. These attractive properties allow them providing some important functions for electroanalysis and the construction of electrochemical sensors.

In recent years, our group is studying on the fabrication method of gold nanoparticles directly attached indium tin oxide (AuNP/ITO) electrode. By utilizing the seed-mediated growth approach, which was developed for the wet synthesis of gold nanorods by Murphy et al. [1], we successfully attached AuNP onto the ITO surface without using peculiar binding reagents [2]. A characteristic feature of the AuNP/ITO is the reduced charge transfer resistivity due to the nature of the direct attachment, which was verified using the electrochemical impedance measurement [3, 4]. In addition, in our approach, AuNP are weakly capped by cetyltrimethylammonium ions, so that the further modification of the surfaces of AuNP on the ITO would be easily performed [5, 6].

In the seed-mediate growth method for the surface attachment of AuNPs on ITO, the first step is the immersion of a piece of ITO in to the Au colloid solution whose size is ca. 4 nm. We had been using the seed solutions containing the same component in our published works [2-6]. However, recently, the component of the seed solutions, i.e., the concentrations of trisodium citrate and $HAuCl_4$, has been found to affect the grown-up nanostructures of AuNPs, even though the same growth solution was used in the treatment for the growth of AuNPs .

Thus, in the present paper, we would like to present how the nanostructures of AuNPs changes depending the components of the seed solution. Although the Au nano-seed particles were not gathered in the original conditions, some larger AuNPs were found to be formed on the ITO surfaces even just after the seeding process in some peculiar conditions. However, the nanocrystal growth of AuNPs was found to proceed in all the cases reflecting the components of the seed solution. The detailed results will be presented in the meeting together with the electrochemical performances of the AuNP/ITO electrodes having thus formed various nanostructured surfaces.

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Unfolding Electrocatalytic Properties of Carbon Nanotube-Metallophthalocyanine (CNT-MPc) Sensing Platforms

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Carbon nanotubes (CNTs), single-walled (SWCNTs) or multi-walled (MWCNTs), exhibit unusual but excellent electrical conductivity and mechanical properties, possess modifiable sidewalls and functionalisable open-ends, and are ideal for constructing efficient electrochemical sensors.[1,2] Transition metal phthalocyanine (MPc) complexes (e.g., CoPc and its derivatives), versatile class of organic macrocycles with 18 π-electrons, have continued to established themselves as excellent electrocatalysts suitable for the fabrication of electrochemical sensors.[3] We believe that smart coordination of these two remarkable π-electron species may revolutionize their applications as excellent electrocatalysts for the fabrication of high-performance electrochemical sensors for various organic and inorganic species.

Recently, we have been engaged in the rational design and functionalisation of CNT-MPc complexes and exploring their potential applications in the fabrication of electrochemical sensors. This paper will discuss some of our recent findings on the unusual but exciting microscopic, spectroscopic (including electrochemical impedance spectroscopy), electrochemical and electrocatalytic properties of these new complexes and their thin solid films at basal plane pyrolytic graphite electrode (BPPGE) as electrodeposits or gold electrode as self-assembled monolayers (SAMs) towards the detection of pollutants and cheap chemical weapons.

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Symposium 4 - Oral

Elecrochemical Nanotechnology

CS-AFM investigations of iron oxide nanoparticles/ polypyrrole type electrochemically generated hybrid materials

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Among composite materials, organic/inorganic hybrid materials constitute a fascinating research subject. Nevertheless, they have been only poorly investigated from a fundamental point of view, up to now, despite the key applications they can be involved in. Let us cite for example protection against corrosion [1], the conception of positive electrodes for battery materials [2] and electrocatalysis [3]. It appears nevertheless more than likely that their various properties, such as their mixed ionic/ electronic conductivity and their electroactivity, result from an inter-dependence between structural, surface and grain boundaries effects.

Atomic force microscopy (AFM) allows the determination of morphology at the nanometer scale as well as a cartography of the conductivity of the imaged samples on condition that it be carried out using a conductive AFM tip. The so-called current-sensing (CS) mode of AFM thus allows a structure/conductivity/reactivity correlation to be established easily.

In this contribution, we report CS-AFM studies of electrogenerated iron oxide/ polypyrrole hybrid materials as a function of various electrodeposition or CS-AFM imaging parameters. To this purpose, iron oxide particles of hematite, Fe_2O_3 and magnetite, Fe_3O_4 were trapped in tetra-oxalate doped polypyrrole films during the electrodeposition of this latter on gold coated mica substrates. In parallel, transmission electron microscopy (TEM) experiments were performed in order to investigate the spatial distribution of iron oxide particles trapped in the polypyrrole matrix; EQCM measurements allowed characterizing the particle fraction in volume.

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Nanostructured electrodes for methanol electro oxidation

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In the present, two different kinds of nanostructured catalysts are synthesized and evaluated for the application in direct methanol fuel cells (DMFCs). Synthesis is based on the use of nonionic surfactants (Brij 30 and 56) for a common purpose: the improvement of electrode performance by increasing the Pt electroactive area. However, this goal can be achieved following different strategies:

1- By using high concentrated surfactant (Brij 56) as template for the production of monolithic nanostructured metallic catalysts.

2- Using surfactant (Brij 30) in low concentration as part of Pt nanoparticles microemulsion synthesis. After that, the surfactant is also used as capping agent in the deposition process. Deposition of micelles onto Au(111) results in the formation of parallel rows of Pt nanoislands of approx. 0.6 nm height.

The catalyst structure is characterized by scanning tunneling microscopy "STM" (a deep study is performed in the case of synthesis 2), and the electrochemical properties towards methanol oxidation by *in situ* spectroscopic techniques. Thus, Fourier transformed infrared spectroscopy "FTIRS" and differential electrochemical mass spectrometry "DEMS" are used for the characterization of intermediates and products generated in this reaction. Also the CO tolerance of these materials is investigated. The studies are performed at different temperatures. Finally, the possible advantages of the use of each electrode concept are discussed on the basis of their possible applications.
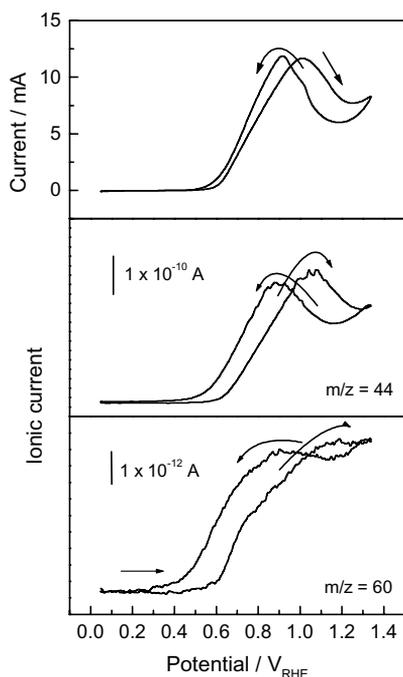
Fig.1. Cyclic voltammogram and DEMS responses for 1 M CH_3OH oxidation in 1 M H_2SO_4 at mesoporous Pt. T = 60ºC, v = 10 mV s^{-1}.

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Characterization of monolayer-protected gold cluster films in aqueous solutions by UV-Vis spectroelectrochemical quartz crystal microbalance

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Au clusters coated with a monolayer of thiolate ligands, so-called *monolayer protected clusters* (MPCs), exhibit very interesting chemical, electronic and optical properties [1]. In particular, it is possible to observe single-electron charging of sub-2 nm Au MPCs at room temperature due to their subattofarad double layer capacitance. We have recently observed the emergence of bands in the UV-Vis absorption spectra of hexanethiolate-protected Au_{147} cluster films concurrently with each single electron charging step in aqueous solutions [2]. The potential-induced spectral changes observed by UV-Vis Absorption Spectroscopy in multilayer films deposited on ITO were linearly dependent on the MPC core charge.

However, the origin of the spectral transitions in charged MPC films is not totally understood yet. In order to shed more light on the origin of this interesting phenomenon, it is essential to assess the influence of key experimental factors. For instance, the role of the electrolyte during charging-discharging of these hydrophobic films in an aqueous environment is crucial. We show here the importance of using multiresponse techniques, and in particular, UV-Vis Spectroelectrochemical Quartz Crystal Microbalance (a combination of UV-Vis Reflectance Spectroelectrochemistry and Electrochemical Quartz Crystal Microbalance) in order to gain knowledge on the interdependence between the electrical charge and the optical properties in this type of Au MPC assemblies. The complementary information provided simultaneously by the three responses (coulometric, gravimetric and optical) facilitates understanding of the processes leading to the observed potential-induced spectral changes.

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Molecular Junctions Incorporating α-Helical Peptides

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Self-assembled monolayers of alpha-helical peptides on gold surface were employed as model systems for the investigations of mediated electron transfer. The peptides contained 14, 15 and 16 amino acid residues. The measurements of electron transfer efficiency through single helical peptide molecules were performed using scanning tunneling spectroscopy (STS). The molecules were trapped between the gold tip and the substrate (see figure below). The electrical contact between the molecule and the gold probe was achieved by the use of peptides containing thiol groups present at each end of the helix. The electron transfer behavior of the peptides was examined as a function of tip-substrate distance at fixed bias voltage. The data obtained from these experiments indicate, that there is a directional dependence of electron transmission through peptide. It is suggested that the observed electron transfer behavior is connected with the electric field generated by the molecular dipole of the helix. The measurements performed with the peptides containing different number of amino acid residues reveal that the distance dependence of electron transfer through α-helix is weaker comparing to simple n-alkyl bridges.
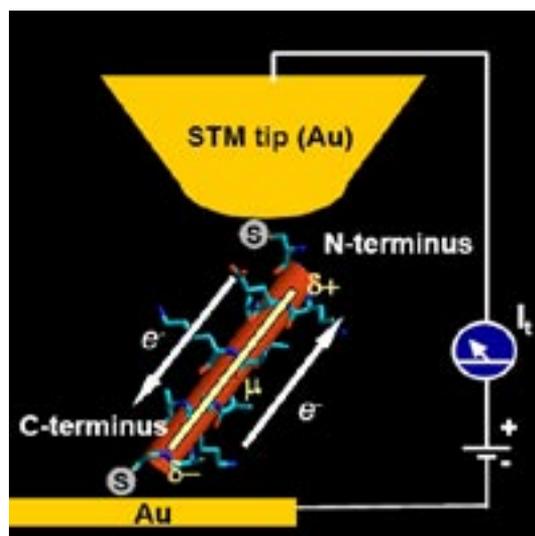
Symposium 4 - Oral

Elecrochemical Nanotechnology

Electrochemical Study of Composite Nanostructures: Contrasting behaviour of two redox pairs on Polyelectrolyte/Gold Nanoparticle Multilayers

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The redox pairs $[Fe(CN)_6]^{-3/-4}$ and $[Ru(NH_3)_6]^{3+/2+}$ were used as electroactive species to gain insight in the mechanism of charge transport through olyelectrolyte/gold nanoparticle multilayers composed of poly(L-lysine) (pLys) and mercaptosuccinic acid (MSA) stabilized gold nanoparticles (Au NPs). The assemblies were characterized using UV-vis absorption spectroscopy, cyclic and square wave voltammetry, electrochemical impedance spectroscopy and atomic force microscopy. We report a large sensitivity to the charge of the outermost layer for the permeability of these assemblies to the probe ions. With the redox pair $[Fe(CN)_6]^{-3+/-4+}$, striking changes in the impedance response were observed for thin multilayers for each new layer deposited. In contrast for the redox pair $[Ru(NH_3)_6]^{3+/2+}$, the multilayer behaves as a conductor exhibiting a noticeable lower impedance response being the electric current enhanced as more layers are added for Au NP terminated multilayers. These results are interpreted quite satisfactorily by means of a capillary membrane model that encompasses the wide variety of behaviors observed. It is concluded that electron transfer through the Au NPs is the dominant mechanism in the case of the $[Ru(NH_3)_6]^{3+/2+}$ pair while nonlinear slow diffusion through defects (pinholes) in the multilayer is the governing mechanism for the $[Fe(CN)_6]^{-3/-4}$ species.

Controlling supramolecular assembly by scanning electrochemical microscopy: Redox active dendrimers at molecular printboards on glass

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Redox-active ferrocenyl (Fc) functionalized polypropylene (PPI) dendrimers were solubilized in aqueous media by complexing all Fc end groups with β-cyclodextrin (βCD). Complexation of all Fc moieties of the dendrimers with βCD at pH = 2 resulted in water soluble dendrimer-βCD assemblies which were characterized by cyclic voltammetry. The Fc dendrimers were immobilized at monolayers of βCD at SiO_2 ("molecular printboards") via multiple host-guest interactions. The directed immobilization of the generation 3 dendrimer-βCD assembly (G3-PPI-(Fc)16-(βCD)16) at the printboard was achieved by supramolecular microcontact printing (µCP). During conformal contact between the stamp and substrate, the dendrimers form multiple host-guest interactions with the printboard resulting in stable patterns of the dendrimers at the molecular printboard. The redox activity of the patterned dendrimers was mapped by scanning electrochemical microscopy (SECM) in the positive feedback mode using $[IrCl6]^{3+}$ as a mediator. The local oxidation of the ferrocenyl-decorated dendrimers resulted in an effective removal of the dendrimers from the host surface since ferrocene in its oxidized form (the ferrocenium cation) is not able to form inclusion complexes with βCD. Thus, SECM provided a way not only to image the surface, but also to control the binding of the Fc-terminated dendrimers at the molecular printboard. Additionally, the desorption process could be followed in time. In addition to that Scanning electrochemical microscopy (SECM) has been used as a means of generating a flux of $[IrCl6]^{4+}$ ions at a Pt disk micro electrode near to ferrocenyl (Fc) functionalized polypropylene (PPI) dendrimers surface by means of potential step chronoamperometry (PSC). By following the chronoamperometric curves, the redox activity of the patterned Fc-functionalized polypropylene (PPI) dendrimers can be evaluated quantitatively.

Preparation and Electrochemical Characterisation of Nanostructured Pt/GC Electrodes Produced by Metal Loaded Micelle Technique

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The ability to produce nanostructured model catalysts by modern nanotechniques opens new possibilities for electrocatalytic studies. The simple geometry of nanostructured samples offers an outstanding possibility for the quantitative description of the reaction and transport processes. We have recently reported results on nanostructured model Pt catalysts prepared by colloid lithography on a polished glassy carbon substrate [1, 2].

We present, for the first time, results on nanostructured Pt/C electrodes produced by deposition of Pt nanoparticles by micellar techniques on a glassy carbon substrate. Electrodes, with monodisperse and homogeneously distributed metallic nano-particles, are formed from a monolayer of diblock copolymers inverse micelles loaded with Pt-salt deposited via dip-coating. The organic matter is removed by subsequent oxygen plasma treatment, followed by hydrogen exposure at elevated temperature, which also reduces the metal ions to a metallic state. Previously, the method has successfully been used on e.g. Si or Ti wafers [3]. Nanoparticles with a diameter in the range of 3 to 12 nm can be formed. The interparticle distances (15-150 nm) can be controlled by the length of the polymers. The nanostructured surfaces were characterised by HRSEM and XPS.

The electrocatalytic properties of the catalysts were studied by Differential Electrochemical Mass Spectrometry (DEMS).
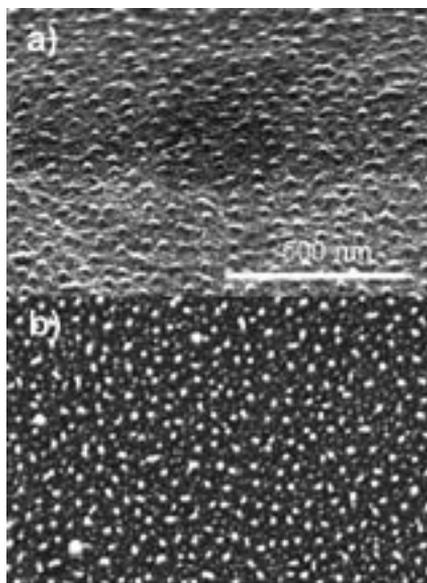
Nanostructured Pt/GC electrodes produced by metal loaded micelle technique. a) Monolayer of metal loaded micelles on GC substrate. b) Surface in a

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Symposium 4 - Oral

Elecrochemical Nanotechnology

Study of electrocatalytic and IR properties of nanomaterials constructed by electrochemical methods

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Owning to the quantum size effect, surface effect, dielectric confinement effect and other particular effects of materials at nanometer scale, the nanomaterials exhibit often novel properties, among which the electrocatalytic and optic properties have attracted extensive attentions. We have investigated systematically, in recent years, the electrocatalytic and anomalous IR properties of metallic nanomaterials including platinum group metals and metals of ion triad. 1-3 Novel IR properties, such as the abnormal infrared effects (AIREs), and high activity in electrocatalysis of these metallic nanomaterials were revealed. It has demonstrated that the study is of particular importance in fundamental studies of multidiscipline, and in applications of electrocatalysis as well as optical sensors and devices.

The present paper reports our recent studies emphasized upon the electrochemical construction of nanostructured materials and the investigation of electrocatalytic and anomalous infrared properties of these nanomaterials. In combination with different technologies, such as surface template, chemical synthesis, interfacial assembly, etc. the electrochemical methods were used to construct different metallic nanomaterials, including nano-films, ordered nanostructure systems and nanoparticles in different states (dispersed, aggregated, confined, etc.). The electrochemical methods present advantages not only in structure control deposition of nano-films but also in shape control inductive growth of nanoparticles. The results obtained by electrochemical investigations and CO-probe in situ FTIR spectroscopic studies revealed the particular electrocatalytic and anomalous IR properties of the constructed nanomaterials, and thrown light upon understanding of the intrinsic law of materials at nano-meter scale and the structural dependence of activity of electrocatalysts.

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Non-spherical Gold Nanoparticles – Synthesis and Optical Properties

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Non-spherical gold nanostructures, particularly rod-shaped and cubes, offer excellent prospects for probing biological systems due to the biochemically inert nature of the material and the unique optical properties from the localized surface plasmon resonances that may extend from the visible to the NIR region. However, production of high quality non-spherical particles in a reproducible manner is quite challenging due to the highly symmetric cubic system that gold exhibits and the requirement of synthetic protocols to induce symmetry-breaking in the growth stages. A variety of synthetic routes have been reported in the literature using either seeded or non-seeded approaches with CTAB acting as the stabilizing agent and growth medium. The advantages and disadvantages of these methods will be discussed. Research in the authors' lab have shown that the seed particles are not stable over extended period of time as reported previously and the role of ascorbic acid in the growth medium needs to be considered further in the growth mechanism. Non-seeded methods developed in the authors' lab, which are reproducible for producing gold nanorods will be discussed and corresponding theoretical simulation of the uv-visible region for suspensions of these nanorods are presented.

The organization of non-spherical nanoparticles into 2-D and 3-D assemblies is of great interest with potential applications in biological sensing by exploiting the shifts in the plasmon bands and interplasmon coupling in the Au nanorods. To apply these gold nanorods to biologically relevant systems, they were functionalised with carboxylic acid-terminated thiols to form chains and the interplasmon coupling was theoretically studied. Testing of the response of the system to glucose molecules is an avenue being explored.

Two-dimensional assembly and local redox-activity of molecular and ionic hybrid structures in an electrochemical environment

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The idea of building an electronic device using individual molecules was first proposed by Aviram and Ratner [i]. The molecular approach bears several unique opportunities: (1) custom-design of nanoscale molecular units, (2) high reproducibility due to self-organization and recognition properties of the molecular building blocks, (3) implementation of localized functions such as charge transfer, π-π - stack conductivity or molecular rectification etc. In the present work we aim to explore the adsorption and electron transport properties of redoxactive molecules at solid/liquid interfaces employing in-situ <u>s</u>canning <u>t</u>unneling <u>m</u>icros-copy (STM), <u>s</u>canning <u>t</u>unneling <u>s</u>pectroscopy (STS) and <u>s</u>urface <u>e</u>nhanced <u>i</u>nfrared <u>r</u>eflec-tion <u>a</u>bsorption <u>s</u>pectroscopy (SEIRAS) in combination with electrical (electrochemical) measurements. We aim to create in-situ metal | molecule | metal (gold) nanobridges, which contain single and/or small numbers of specifically tailored molecules. A vertical STM/STS – based approach is combined with a horizontal nano-electrode based hybrid configuration. Methodological developments towards a nanoscale electrochemistry with bare and redox-molecule tailored electrode assemblies will be presented. The custom-made molecular reactands contain one or two thiole – groups, separated by alkyl or phenylethynylene spacer groups and a redox-active center. Specifically, we will report on the local redox-activity of functionalized viologens and immobilized terpyridines ($Me = Co^{2+/3+}$, $Ru^{2+/3+}$) on "macro" and "nano"-sized gold electrode assemblies. Possible structure changes involved will be discussed based on in-situ SEIRAS investigations. By tuning the Fermi level of the (nano-) electrodes relative to the energy levels of the redox-molecules we aim to explore concepts of redox-gated nanostructures in an electrochemical environment. Working in an electrochemical environment offers the possibility that two potential differences can be controlled individually: the bias voltage between the two working electrodes, and the potential drop between one working electrode and the reference electrode. The latter may be considered as a "gate electrode". The current flow to the external circuit is assisted by a fourth electrode, the counter electrode. An attempt will be made to correlate molecular structure, gap composition and electron transport.

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Symposium 4 - Oral

Elecrochemical Nanotechnology

Research of physical and electrochemical property of single enzyme molecules

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Charge transfer plays key roles in many biological and chemical processes as well as in molecular electronics. The advent of scanning probe microscopies, along with other supersensitive techniques, has made it possible to characterize or directly observe charge transfer through organic molecules down to the nanoscale and single molecule levels. In the present work, we try to study the electron transfer mechanism through the biological molecules and across the interface between molecules and macroscopic electrodes. Protein glucose oxidase (GOx) is studied due to its importance as a model enzyme. In order to immobilize the protein onto the substrates, highly oriented pyrolytic graphite (HOPG) was treated by electrochemical anodic oxidation in 0.1 M $HClO_4$, which changes the hydrophobic surface into hydrophilic surface. It provides a suitable microenvironment for the fixation of GOx molecules while keeping the atomic flat surface. In situ scanning tunneling microscopy (STM) images with single molecular resolution about the protein have been recorded as shown in Fig. 1. A butterfly shape with dimensions of $6\pm1\times9\pm1$ nm^2 was observed, which is assigned to the lying position of the molecule on the substrate. Direct electron transfer between the adsorbed GOx and the electrode has been revealed by voltammetry as shown in Fig. 2.
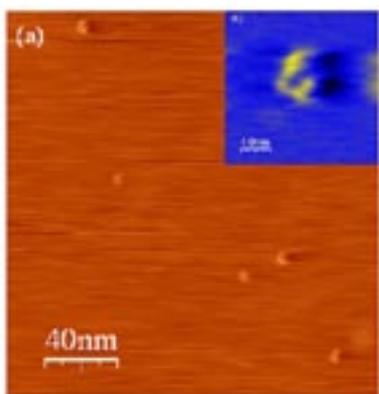

Fig. 1. Typical STM images of GOx molecules observed on HOPG surface: (a) scan range: 200×200 nm^2, (b) 20×20 nm^2. U_{WE}= 400 mV vs. NHE. Bias voltage : –50 mV. Tunnel current: 0.5 nA.
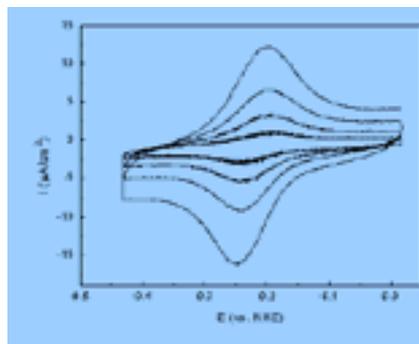
Fig. 2. CVs of the GOx/HOPG electrode in 0.01M phosphate buffer solution (pH 7.2) with N_2-saturated at various scan rates. (from inner to outer curves: 20, 50, 100, 200 mV s^{-1}).

Correlating the electrochemical properties of carbon nanotubes to their electrical characteristics

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Single walled carbon nanotubes have many remarkable properties, but perhaps one of the most overlooked is that every atom is exposed to its environment; there are no surface and bulk atoms, only surface atoms. As a result the delocalised π orbitals that give the nanotubes their well-known electrical properties are all exposed to their environment. We may thus expect the electrical and electrochemical properties of nanotubes to be uniquely intricately linked. Previous studies on the effect of solution on the conductivity of nanotubes have shown that the charge double layer present next to surfaces in solution can electrostatically dope semiconducting nanotubes to be either conducting or non-conducting depending on the solution potential, so called 'wet gating'[1]. A link between electrical 'defect' sites and metal nucleation points at low overpotentials has also been observed[2].

We have fabricated carbon nanotube electrodes that allow both electrical and electrochemical measurements. The nanotubes are grown by chemical vapour deposition onto an insulating surface. Photolithography is then used for patterning electrodes onto the substrates, enabling electrical measurements on individual nanotubes, several nanotubes in parallel or networks of nanotubes. To study the electrochemical properties of these electrodes the final step is a coating of insulation, leaving only the nanotube(s) exposed.

We will present a method for obtaining electrical and electrochemical results simultaneously, which enables a direct correlation between the electrical properties and the electrochemical response[3]. We have also used a variety of standard conductivity measurements, and electrical based scanned probe techniques to investigate the conductivity of the nanotube, e.g. scanned gate microscopy to identify the defect sites along the nanotubes. These results can then be correlated with subsequent electrochemical investigations, e.g. enabling us to comment on the effect of defect sites on electrochemical activity.

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Self-Assembly Dynamics of Surface Layer Proteins on Gold Electrodes

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Two-dimensio¬nal crystalline bacterial cell protein surface layers (S-layers) on solid substrates are of fundamental and technological interest in biotechnology [1], biomineralization [2], bio sensorics [3,4], and bottom-up nanostructuring technologies [5,6]. First electrochemical in-situ quartz microbalance and ex-situ SPM and XPS measurements showed that self-assembly dynamics and surface bonding of the protein molecules dependent strongly on the structure of the electrochemical double layer [7,8]. It could be shown that electropositive metal salts (e.g. aurates) can lead to the autocatalytic formation of metal nanodots on the protein surface [9].

In this context, the role of calcium ions as lateral bridging agent and as competitor for protein-metal bonds has been studied by dynamic quartz-microbalance and scanning force microscopy investigations.

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One Step Fabrication and Characterization of Gold Nanoelectrode Arrays Formed via Amphiphilic Block Copolymer Self-Assembly

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A novel one-step approach to fabricate Au nanoelectrode arrays (NEAs) has been developed by coating a porous amphiphilic block copolymer [polystyrene-block-poly (acrylic acid)] self-assembly with controlled pore size on an Au disk electrode. The morphologies of prepared NEAs were characterized by optical microscope and SEM. The SEM image (Figure 1 (A)) shows that the NEAs had a site density of 1.8×10^7 /cm^2, and pores radii are 420 nm approximately. The mechanism of formation of NEAs was given. The variable scan-rate cyclic voltammetry was conducted on the prepared NEAs to investigate their scan-rate dependent votammogram based on the fundamental theory of NEAs. Figure 1(B) shows the voltammograms is typically sigmoidal waveform and characterization of ultramicroelectrode under steady-state scan. The sealing property between the polymer layer and Au electrode in NEAs was evaluated by measuring the capacitance of the prepared NEAs. There is no leaking from one pore to the next. This procedure of nanoelectrode arrays fabrarction is simple and fast, and requires only conventional, inexpensive instrumentation. These NEAs provide tools for both the understanding of solution properties in nanoscale matrixes as well as the creation of nanoscopic devices. We are currently studying the further electrochemical properties of these arrays, as well as applying these systems to the creation of miniaturized multisensing units for application in vivo and flow processes.
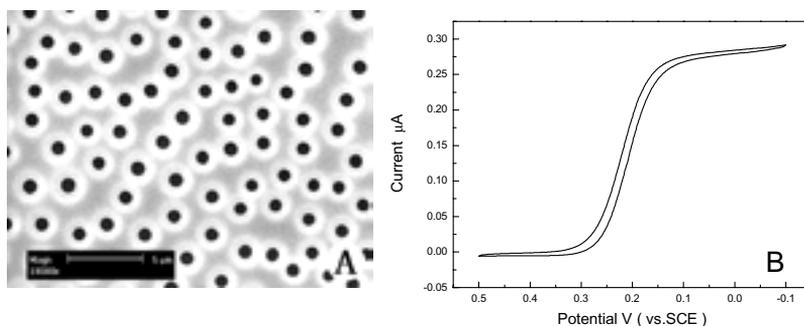

Figure 1. (A) SEM image of PS-b-PAA nanopores membrane on the Au electrode (1 % PS-b-PAA/THF, 90 % r. h humid atmosphere); (B) The cycle voltammograms of the NEAs in 1 mM K$_3$Fe(CN)$_6$ and 1 M KNO3 solution. Scan rate: 5 mV·s^{-1}.

Molecular Scale Electron Transfer and *In Situ* Scanning Tunnelling Spectroscopy of Redox Molecules and Biomolecules

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Molecular spectroscopy and electronic conductivity at the single-molecule level have developed broadly over the last decade. Single-molecule conductivity reports have mostly referred to ultra-high vacuum and/or cryogenic temperatures, but ambient air and aqueous solution environment has come in recent intense focus. Redox molecules have been particularly attractive by their sophisticated electronic function (amplification, negative differential resistance etc.) in electrochemical nanogap and *in situ* STM configurations. Recent experimental studies on single-(redox)molecule conductivity in electrochemical environments have been paralleled by new theoretical concepts and formalism for molecular scale electrochemical electron transfer, sometimes preceding experimental discoveries [1,2].

We provide first a brief overview of some concepts appropriate to two- and multi-step molecular scale electronic conductivity of redox molecules confined between electrochemical nanogap electrodes or in an *in situ* STM gap. We then overview some cases of electrochemical *in situ* STM of redox molecules and biomolecules comprehensively studied in our group over the last couple of years. The systems include transition metal complexes [3] and, notably, both a redox metalloprotein (the blue copper protein azurin) [4] and a redox-functionalized oligonucleotide [5]. The systems display strong tunnelling spectroscopic features resembling molecular electronics function and broadly accord with theoretical frames. In this way they also substantiate new electron transfer phenomena.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Preparation of gold nanoplates modified indium tin oxide surfaces for electrochemical measurements

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Gold nanoparticles have been attracting active attention in the recent years due to their unique optical, electronic, magnetic and catalytic properties that are different from those of the bulk states. In this field, some interests have been focused to the synthesis of anisotropic gold nanostructures, such as gold nanoplates formed via two-dimensional growth, since it may provide another effective strategy to control the properties of the gold nanoparticles over the size. Gold nanoplates, for instance, are characterized by a thin structure of several nanometers in thick and featured dominant certain crystallographic planes, namely {111}, that exposing to outside. Such condition should give rise to their electrochemical activities, in particular, and may create novel characteristics for electroanalysis and electrochemical applications.

Recently, we have grown spherical gold nanoparticles directly on the indium tin oxide (ITO) surface without the use of certain binding molecules, such as aminopropyl-trimethoxysilane, using a seed-mediated growth method [1] for electrochemical applications. Remarkable improve on the electrochemical properties of such gold nanoparticles modified-ITO electrode as a result of effective contact between ITO surface and gold nanoparticles could be obtained [2-4].

In the present paper, we demonstrate a novel effective strategy to grow other types of gold nanostructure, namely nanoplates instead of spherical nanostructures, directly on the ITO surface. By following a consecutive immersion in the seed solution [5] and in the new-developed growth solution, namely the mixed aqueous solution of $HAuCl_4$ and poly(vynilpyrrolidone) (PVP) and without using a certain reducing agent [6], large-scale of gold nanoplates that cover almost 40% of the surface area can be fabricated. The nanoplates feature thin structure of several nanometer in thick with edge-length of $0.5 – 1$ µm and grow parallel to the surface inferring an effective surface coverage.

The electrochemical characterization on gold nanoplates modified-ITO towards the presence of 25 µM cytocrhome c in the PBS (pH. 7) indicated that the gold nanoplates modified-electrode system exhibited remarkable higher electrochemical activity compare to other gold nanostructure modified-ITO systems and even bulk gold electrode. The gold nanoplates modified-electrode system should find use as promising electroanalytical systems and electrochemical sensors.

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Study of the electrogeneration of Ag nanoparticles by Bidimensional Spectroelectrochemistry

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Nanoparticles have become an important research field due to the unusual chemical and physical properties demonstrated by this intermediate state of matter. Silver nanoparticles are very important in the electronic industry because they exhibit the highest electrical and thermal conductivity among all metals. Formation of controlled size nanoparticles depends on the synthetic route. Many techniques, based on chemical and physical principles, have been developed to prepare the metal nanoparticles. The chemical reduction way is the most common method to synthesize metal clusters but, nowadays, a number of attempts using electrochemical reduction have been carried out. The actual size of the particles obtained is not easy to explain, especially in view of the fact that a lot of parameters influence in the final result.

New tools are required for studing *in-situ* the process of formation of this kind of particles. In this work, Bidimensional Spectroelectrochemistry [1] has been used to study the electrogeneration of silver nanoparticles in aqueous solution. Bidimensional Spectroelectrochemistry provides simultaneously one electrochemical and two different spectroscopic signals about the process under study in a single spectroelectrochemical experiment. Here we have used a Bidimensional Spectroelectrochemical cell that is based on the reflection of the normal beam on the electrode surface, and simultaneously, the solution adjacent to the electrode is sampled in parallel configuration. The information provided by each kind of measurements is different because the normal configuration signal accounts for the changes due to the deposition of Ag on the electrode surface, while the parallel configuration response obtains information about the different size silver nanoparticles generated simultaneously in solution. Complementary information supplied by the three signals measured simultaneously helps us to understand the mechanism of electrochemical generation of Ag particles in aqueous solution.

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Synthesis and characterization of alloys ru base produced by mechanical alloying

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Ru-Se and Ru-Mo (1:1 wt %) alloys have been produced by mechanical alloying using commercial Ru, Se and Mo powders. The formation process and structural properties of these nanocrystalline materials were characterized by X-ray diffraction (XRD) and Scanning Electronic Microscopy (SEM). The methods employed for studied the behavior electrocatalytic were cyclic voltammetry (CV) and rotating disc electrode (RDE). The electrocatalytic properties of these nanocrystalline materials were studied for oxygen reduction reaction (ORR) in 0.5 M H_2SO_4 aqueous solution at room temperature. XRD analysis of alloyed powders showed the presence of two phases. Scherrer´s equation was used to calculate average grain size ss an approximation. Ru-Se and Ru-Mo alloyed powders showed greatest catalytic activities for ORR than Ru bulk electrodes. The electrocatalytic behavior was related to characteristics of enhanced solubility, morphology and nanometric grain size exhibited by mechanically alloyed powders.

Elecrochemical Impedance Study of Polycarbazole and Its Derivatives

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Carbon fibre electrodes are microelectrodes using a single carbon fibre (or small group of fibres) as the conducting element. In addition, when electrografting of the conductive polymers such as polycarbazole (PCz) and their derivatives on the surface of carbon fibre micro electrodes (CFMEs), their conductivity properties are improved considerably.

Carbazole (Cz) or its derivatives like carbazole-9-carbonylchloride (Cz-9-COCl) was electropolymerized potentiodynamically on CFME. The polymerization conditions such as solvent, supporting electrolyte, monomer concentration, scan rate or scan number, were changed and determine optimum conditions for each monomer to obtain better electrode. The polymers grafted on CFMEs were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), FTIR-ATR spectroscopy, UV-vis Spectroscopy and Scanning Electron Microscop (SEM), and compared with uncoated CFME.

Figure1. (a) CV of polymer growth and monomer free of PCz in 0,05M TEAP/DCM (b) Bode phase graph of P(Cz-9-COCl)

Cyclic voltammograms of polymerization showed that current density was increased with the thickness of thin film on CFME. Bode phase angle of 75° was obtained from EIS study that means the polymer showed a capacitor behaviour.

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Local Ionic Conductivity Measurements Using Atomic Force Microscopy Tips

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Conventional impedance spectroscopy is a very well known and powerful experimental tool to investigate the electrical and electrochemical properties of ionic conductors. However, due to the usage of large sized electrodes (typically ~ 1cm) the method is handicapped in the context of systems displaying a strong local effects at micrometer or nanometer length scales. This can be vastly improved by using electrodes of smaller dimensions (~ few tens of nm- 1μm). Here we present the study of local ionic conductivity using nanometer-sized AFM tips as electrodes (fig.1) two different systems: a) $PEO-LiCF_3SO_3$ polymer electrolytes and (b) AgI nanoplates.

Polymer electrolytes, formed by dissolving an ionic salt (e.g. LiX) in a polymer solvent (e.g. PEO), comprise an important class of ion conductors. Impedance mapping of $PEO-LiCF_3SO_3$[1] polymer films using AFM conducting tip (radius: 50nm) as an electrode yielded remarkably a two-modal conductivity distribution with positional ionic conductivity varying by four orders of magnitude. The conductivity of insulating regions had similar order of magnitude as obtained using 1cm sized electrodes. The high conducting regions were found to be amorphous (XRD, DSC, AFM topography) but non-percolating at room temperature.

Synthesis of silver iodide (AgI) nanoparticles from aqueous solution routes involving various polyelectrolytes[2] display interesting morphologies and phase compositions and as well striking conductivity properties. The ion conductivities are the highest ever measured at room temperature for binary compounds. The plate-like AgI nanoparticles or nanoplates (using PDADMAC in aq. $AgNO_3$ and KI) with a hexagonal/polygonal face are most important in this context. Topology of AgI nanoplates revealed three different particle morphologies. Ionic conductivity measurements of individual particles having different morphologies with AFM tip as electrode did not reveal any observable anisotropy and conductivity values were very similar to ones obtained from measurements using 0.6cm electrodes on nanoplate films.
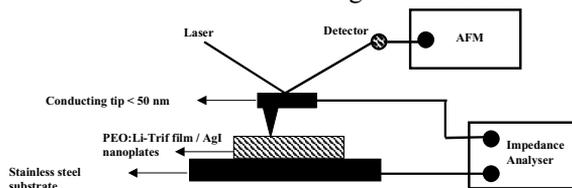

Figure 1: Schematic experimental set up combining impedance spectroscopy and AFM

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Formation of Gold Nanoparticles using Amine Reducing Agents

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We report on the use of amines as reducing agents in the formation of gold nanoparticles. We can predict whether or not the amines will function as reducing agents in this reaction based on their redox properties. The kinetics of AuNP formation can be understood in terms of Marcus electron transfer theory, where the slower reactions proceed in the inverted region owing to the difference between the Au reduction potential and the amine oxidation potential. For certain of the amine reducing agents, following reduction of $HAuCl_4$, a subsequent reaction of the amine radical cation with other reducing agent molecules in solution can form poly(amine)s. These findings point collectively to the utility of amines as reducing agents in AuNP formation and provide information on the conditions under which these reactions will proceed.

We have also used poly(allylamine) (PAH) as a reducing agent for the formation of gold nanoparticles (AuNPs). The formation of AuNPs using this polymer matrix allows for the AuNPs to be imbedded in the polymer matrix, once formed. The kinetics of AuNP formation are shown to be pseudo first-order in $[HAuCl_4]$. The kinetics of AuNP formation are controlled by the ratio of reducing agent to $HAuCl_4$ as well as the overall concentration of the PAH and $HAuCl_4$. Additionally, at low PAH: $HAuCl_4$ ratios, the plasmon resonance wavelength can be controlled through the ratio of the reactants. This plamson resonance shift shown to be related to AuNP size by means of TEM imaging data on the AuNPs.

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Metal-Chalcogen Multilayer Deposition Monitoring by PDEIS

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Dependences of equivalent circuit parameters on electrode potential in potentiodynamic electrochemical impedance spectroscopy (PDEIS) were shown to be useful indicators of nonstationary electrochemical interface dynamics [1,2]. The opportunity of the double layer and Faradaic response parameters simultaneous separate monitoring has been applied recently [3] for atomic bilayer assembling. In this work, we have used PDEIS for characterisation of multilayer assembling in successive surface controlled deposition of metals and chalcogens. Atomic layers of Te, Cu and Pb were sequentially deposited by upd and the frequency response of the interfacial structures was analysed in terms of variable equivalent circuits. All the stages were considerably irreversible and this determined the type of the equivalent circuit shown in Figure 1. There was no adsorption capacitance, and the Faradic part of the response was represented by the charge transfer resistance and the diffusion impedance. Double layer pseudocapacitance, Q_{dl} (a parameter of the constant phase element that represented the nonstationary double layer response), charge transfer resistance, and Warburg constant were obtained as functions of the variable potential. All the three functions have been found to be informative indicators of the multilayer assembling dynamics.
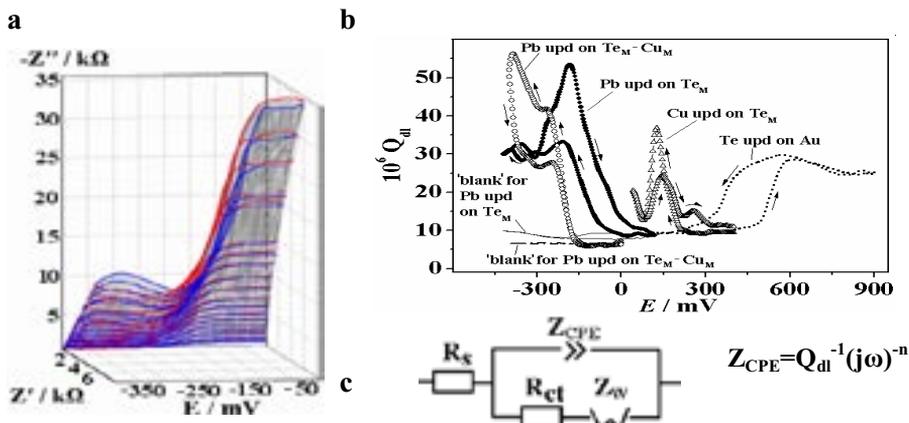

Figure 1. Pb upd on Te-Cu bilayer: (a) cyclic PDEIS spectrum, (b) the best-fit equivalent circuit, (c) double layer pseudocapacitance variation in electrode potential scans in different stages of atomic multilayer assembling.

$$Z_{CPE}=Q_{dl}^{-1}(j\omega)^{-n}$$

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Nanostructured Pt/C electrocatalysts Preparation, size measurement and electrochemical behaviour

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It is well know that electrochemical reactions occurring under fuel cell conditions (electrooxidation of alcohol and carbon monoxide in reformate gas, oxygen electroreduction) are sensitive to the nature and the structure of the electrocatalyst. Therefore the precise characterization of nanostructured catalysts is of great interest in order to optimise the metallic charge and to approach catalytic fundamental processes. Nevertheless, the reproducible method of catalyst preparation has to be developed. The water-in-oil microemulsion was chosen to prepare platinum nanoparticles supported on carbon powder [1]. The weight loading of platinum dispersed on carbon was determined by correlation of thermal gravimetry and XRD measurements. From recent development in crystallography theoretical developments and mathematical tools to determine the nanoparticle size distribution from XRD diffractogramms could be used [2] which led to avoid the problem of statistical representativeness of a particle counting using TEM photographs. This procedure will be presented. The size distribution from DRX measurements will be compared with the size distribution obtained by TEM. At last, the increase of the mean particles size of platinum dispersed on carbon will be studied as a function of temperature under controlled atmosphere. The apparent activation energy of the sintering process of platinum nanoparticles will be discussed [3], which could be a new indicator for the characterization of stability and metal/support interaction of the electrocatalysts. A correlation between XRD results and electrochemical experiments (cyclic voltammetry, CO stripping, RDE measurement in CO saturated solution, *in-situ* InfraRed experiments) used to measure metallic area and catalyst behaviour will be presented.

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Catalytic reduction of H_2O_2 by Horseradish Peroxidase on Au and Pd via direct electron transfer

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It was shown by several groups that HRP can bind directly to Au surfaces and retain its catalytic activity by direct electron transfer from the electrode to the enzyme. The aim of our experiments is to investigate the catalytic reduction of H_2O_2 by Horseradish Peroxidase (HRP) on metal nano-clusters.

Before immobilizing enzymes to nano-clusters, their behaviour should be investigated on extended surfaces. Polycrystalline Au and Pd surfaces were used as substrates; the Pd substrate was obtained by depositing electrochemically three monolayers of Pd on Au.

Current densities of the direct oxidation/reduction of Au and Pd by H_2O_2 at different concentrations show that H_2O_2 is a highly reactive species, which produces undesired background currents. Using a concentration of $[H_2O_2] = 0,1mM$, the addition of HRP to the Au/H_2O_2 system produced cathodic currents at potentials between 100mV and 900mV vs. NHE. In contrast to Au, the same experiment on a Pd surface produced cathodic currents at potentials between 600mV and 900mV vs. NHE, while for potentials between 100mV and 300mV vs. NHE, small anodic currents occurred.

STM experiments are currently done to clarify whether the different behaviour of HRP on Au and Pd can be explained by differences in adsorption.

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Nano- and Micro - Structured Composite Coatings SiC-Nickel: Electrochemical and Structural Studies

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At present the research and development of composite coatings of various types is of great interest. This is explained by their excellent combination of physical-chemical properties, such as low friction coefficient, wear resistance, corrosion resistance and chemical stability, otical properties, etc. This work is focused on: 1) Electrochemical methods (cathodic polarisation and electrochemical impedance spectroscopy diagrams performed at cathodic potential) to study the influence of dispersed nanosized and microsised dispersed phases on the mechanism of nickel reduction; 2) Surface characterisation of composite coatings obtained by SEM and TEM. The composite coatings have been obtained by electrodeposition using a nickel Watts baths and two types of dispersed phases: nanosized SiC (20 nm mean diameter) and microsized SiC (30 μm mean diameter). Influence of nano- and micro- sized SiC particles on nickel electrodeposition was observed by potentiodynamic diagrams and electrochemical impedance spectroscopy measurements performed with and without dispersed particles. The charge transfer resistance calculated from impedance diagrams. The addition of silicon carbide particles displaces the nickel reduction curve to more positive potentials. The shift in reduction potential were attributed to an increase in the active surface area due to the adsorbed particles on the cathode and to a possible increase in ionic transport by dispersed particles with their ionic layers adsorbed. It is supposed that the dispersed particles are surrounded by a thin layer of (Ni^{2+}) and (H_3O^+) ions adsorbed after the particles were introduced in the electrolyte. These positively charged particles could reach the cathode surface. The negatively charged particles will be rejected to the bulk of the solution. The EDS analysis show the presence of nanosized silicon particles in the composite layer by content of carbon and silicon founded. The SEM investigations shows that the composite coatings with nanosized dispersed particles develop in a nodular disturbed surface structure. The EDS spectra of composite coating obtained by codeposition of microsized SiC with nickel show a higher content of dispersed phase. The highest content of silicon carbide is due to bigger SiC particles (30 μm mean diameter). The structure of nickel matrix is also perturbed but seems to have a more regular grain size than that in the case of SiC nanoparticles codeposition. We suppose that the higher density of nucleation sites due to nanosized silicon carbide particles perturb the growth of nickel matrix resulting in smaller grain size and random orientation of nanostructured composite coating.

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Preparation of Anodic Porous Niobium Oxide for DNA biosensor applications

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The research activities for the preparation of new biosensors to detect DNA or protein have dramatically increased over the past decade. Immobilization of a DNA probe on a desired substrate is very important process for the preparation of DNA biosensor since the sensitivity in the detection of target DNA is significantly affected by immobilization step. In this presentation, we will discuss on the preparation of conductive porous niobium oxide by anodization [1] and its application for electrochemical DNA biosensors.

In order to prepare self-ordered porous niobium oxide, anodization was carried out under well-controlled electrochemical oxidation conditions. In respect to the effects of electrolytes on the formation of porous structures, we found that a single HF electrolyte leads to the formation of pores as well as to the destruction of formed pores by the dissolution of pore wall, whereas the dissolution of the formed oxide is significantly retarded by the addition of appropriate amount of H_3PO_4. It is probably due to either the formation of thicker protective oxide films by PO_4^{3-} or competitive adsorption of F^- and PO_4^- on the metal surface, which leads to decrease of electrochemical reaction areas by F^-.

As the same tendency has been reported in the preparation of porous alumina, the interpore distance of porous niobium oxide is determined by anodization potential with a proportional constant of 1.4nm/V (vs. Ag/AgCl/ M KCl). As explained in the previous section, the electrolyte and the applied potential should match each other in order to prepare ordered porous structures. In that respect, it is found from SEM observation that optimized potential is 2.5V (vs. Ag/AgCl/ M KCl) in the mixture of 1wt% HF and 1M H_3PO_4.

After an optimized anodic time (~1h), the pore walls are dissolved, resulting in the formation of interconnected pores at the surface (~2h), or destruction of porous structures (~16h). The density of pores at the surface does not increase after 1h, meaning that we could achieve porous structures with a high aspect ratio if the dissolution of the formed oxide is well controlled.

In addition, immobilization of ssDNA on anodic porous niobium oxide by selective terminus adsorption will be discussed in the presentation in detail.

Electrocatalytic Reduction of CO_2 on Nanocrystalline TiO_2 Film Electrode in aqueous solution

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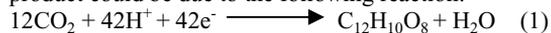
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CO_2 is a cheap and abundant "green carbon source" for production of organic chemicals and fuels. The transformation of CO_2 into organic substances is a promising long-term objective. The electrochemical reduction of CO_2 appears to be an attractive means for removing from the atmosphere and converting it into more valuable chemicals[1]. In this paper, we report, for the first time, the electrocatalytic synthesis of C_{12} organic compound from CO_2 and H_2O on nanocrystalline TiO_2 (nano TiO_2) film electrode by controlled potential electrolysis

Experimental

The nanoTiO$_2$ film modified titanium (Ti/nanoTiO$_2$) electrode was prepared by direct hydrolysis precursor Ti(OEt)$_4$. The electrochemical measurements were carried out using a CHI model 660A (USA CH Instrument) electrochemical workstation with a three-electrode system at room temperature. The electrochemical reduction of CO_2 (purity 99.9%) was performed in a divided H-type cell with an ion exchange membrane by cathodic polarization at –2.0 V *vs* SCE for 9 hours. The product of the catholyte was extracted by using ethylactetate-methanol(8:2, v/v) and the sample of the extracting agent was distilling under reduced pressure at 30℃. The products were characterization by UV-vis and mass spectrum(MS), Fourier transform infrared (FTIR) reflection absorption spectroscopy, ^{1}H NMR and ^{13}C NMR spectrum.
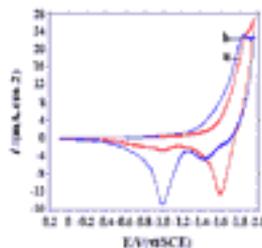
Results and discussion

Fig. 1 shows the cyclic voltammograms of the Ti/nanoTiO$_2$ electrode in 0.5 mol.cm^{-3} K_2SO_4 solutions saturated with N_2 (a) and CO_2 (b), respectively. There were two pairs of well-defined redox peaks for nanoTiO$_2$ film electrode in correspondence with TiO_2/Ti_2O_3 and TiO_2/Ti(OH)$_3$ [2] couple (Fig. 1a). In 0.5 mol.cm^{-3} K_2SO_4 solutions saturated with CO_2 (Fig.1b), the onset (starting) potential of cathode current was shift negative approximately 0.2V and the anodic peak (I_{a2}) of the TiO_2/Ti(OH)$_3$ couple was almost absent. It is evident that heterogeneous elctrocatalytic reduction of CO_2 were carried out by the surface Ti^{IV}/ Ti^{III} redox system and the high oxidative peak at -1.0V (*vs* SCE) was mainly caused by the reoxidation of a product generated in the cathodic reduction of CO_2. The prolonged electrolysis of CO_2 on nanoTiO$_2$ film electrode at – 2.0 V (*vs.* SCE) was performed in 0.5mol.dm^{-3} K_2SO_4 aqueous solution. The products were characterization by UV-vis, MS, FTIR, ^{1}H NMR,^{13}C NMR spectrum with molecular formula $C_{12}H_{10}O_8$ (1,1-diformoyl-2-propenyl oxalate). The process for forming the product could be due to the following reaction:

Fig. 1 Cyclic voltammograms of the Ti/nanoTiO$_2$ electrode in 0.5 mol.cm^{-3} K_2SO_4 solutions saturated with N_2 (a) and CO_2 (b). Scan rate: 100 mVs^{-1}.

$$12CO_2 + 42H^+ + 42e^- \longrightarrow C_{12}H_{10}O_8 + H_2O \quad (1)$$

Acknowledgments

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Electrodeposition of Nanoporous Platinum from the Reverse Micelle Phase of a Nonionic Surfactant

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A new fabrication method of nanoporous platinum thin film by electroplating from reverse micelle (L_2) solution of nonionic surfactant is demonstrated. So far, metallic thin films with nanopores of a few nm scales have been deposited electrochemically in hexagonal (H_1) lyotropic liquid crystalline phase[1], or micelle-type assembly of surfactant formed on the electrode surface by a potential applied[2]. Although the lyotropic liquid crystal or the micelle-type aggregation is one of the dominant phases that the mixtures of water and surfactant can form, there are a few more phases to be exploited as templates for nanostructured materials. One of them is the reverse micelle solution (L_2) phase, which electroplating of nanoporous metal has been hardly reported for. In this presentation, we will demonstrate that nanoporous platinum thin film can be fabricated by electroplating in reverse micelle (L_2) solution, and propose it as a new electroplating method with valuable advantages.

Through this work, nanoporous platinum thin films were successfully electroplated from reverse micelle solutions of a widely used nonionic surfactant, Triton X-100. The resulting platinum film showed a nanoporous structure (pore size 1.29(±0.29) nm and high roughness factor (*ca*. 232 for passed charge of 2.55 C cm^{-2}). The observed pore size is smallest among the nanopores fabricated by electroplating method. The electroplating in L_2 phase shows rapid plating and alleviates the electrode polarization. The high fluidity of the L_2 phase may let itself to be adapted to the electroplating bath acceptable for the automated plating and mass production process. The use of nonionic surfactant is expected to make the structure of electroplated platinum less sensitive to the applied potential. In terms of electroplating nanoporous metals, these results extend the scope that has been limited within liquid crystalline template and potential controlled self-assembly.

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Core-Shell Dendrimer-Au@Prussian Blue Electrode Using Layer-by-Layer Self Assembly Approach

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A novel class of modified electrodes has been prepared using polyelectrolytes and dendrimer-encapsulating metal nanoparticles using the layer-by-layer technique (LbL) [1]. In this work, we report the fabrication of nanostructured films comprising nanoparticle-containing polyamidoamine (G4-PAMAM) dendrimers and poly(vinylsulfonic acid) (PVS) through the LbL technique. Nanosized Au nanoparticles were grown inside PAMAM molecules using formic acid as the reduction agent. The PAMAM-Au hybrids were then assembled onto an indium thin oxide (ITO) electrode for electrochemical characterization. In subsequent electrochemical experiments, Prussian Blue (PB) was employed in order to evaluate the adsorption of a redox mediator onto the Au-nanoparticles (Au@PB), via electrodeposition. The presence of the PB mediator on the nanoparticles is interesting due to its outstanding electrochemical and electrochromic properties. In addition, materials based on PB molecules have been studied in self-organized media mainly because of PB's ferromagnetic properties.

Formation of Au@PB was studied using 5 mmoL L^{-1} Fe(CN)$_6$$^{-3}$ in 0.5 mol L^{-1} H$_2$SO$_4$ electrolyte solution at a 6-bilayer ITO-PVS/PAMAM-Au. The voltammograms obtained corresponding to three stages of formation of the system core-shell Au@PB. During the first potential cycle, a redox pair due to hexacyanoferrate (II)/(III) as well as the oxidation and reduction peaks of the gold nanoparticles are observed. After 10 cycles, the gold nanoparticles' surface is already partially covered by adsorbed PB, as shown by the presence of two new anodic peaks attributable to PB at ca. 0.6 and 0.8 V (Ag/AgCl) as well as that of gold. After two hours in the same solution, at open circuit, the gold oxidation peaks were not observed any more, indicating that the PB film had completely covered the Au nanoparticle surface, with formation of an ITO-PVS/ PAMAM-Au@PB electrode.

This approach could be applied in a number of technological applications such as biosensors and nanoelectronics where a reversible redox mediator is required.

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Modified porous electrodes applied in the detection of heavy metal cations

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Heavy metals represent a serious pollution problem. Several heavy metals cations (Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}) are known as extremely toxic and not biodegradable. Nowadys sensitive electrode materials were developed, capable to detect ppb levels in a very short time and with low cost analytical devices. Besides the detection of heavy metals from diluted solutions their removal became more and more important. The modified graphite felt electrodes were used over 20 years in electrocatalysis or in electro synthesis. Our first approach using these kinds of electrodes was to prepare by an unconventional way new heterocycles having biological activity[1,2]. Lately the covalent attachment of different catalyst on graphite-felt electrode was achieved [3].

The removal of heavy metals from diluted solutions is a research direction with application in drugs quality control, environmental protection and recovery of heavy metals, detection of heavy metals from biological fluids etc.

A new approach regarding porous carbon felt electrodes allowed us to modify by covalent grafting this electrode material. In this purpose some new promising materials from supramolecular chemistry known as water-soluble receptor for heavy metals cations were used [4]. Among these, the aza oxo derivatives play an important role due to their remarkable stability and selectivity over a few heavy metals cations (Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+} etc).

The presentation will discuss about the covalently modified porous electrodes and about the electroanalytical studies showing the detection and the removal of two heavy metal cations (Pb^{2+} and Cu^{2+}) from diluted solution using a divided flow cell.

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Interfacial wetting at nano-scale contoured surfaces

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Development of materials with spatially ordered features and functionality is significant for a range of applications including (bio)sensors, data-storage, microchip reactors and photonics[1]. The fabrication of materials with nano/meso-scale architecture often involves expensive techniques such as electron beam lithography or nanoscale lithography. Recent studies have yielded a simple cost efficient route for the preparation of mesoporous surfaces with pore sizes of a few hundred nanometers, via the formation of close packed arrays of uniform colloidal spherical particles (silica, polystyrene latex microspheres or polymethylmethacrylate) as sacrificial templates. The desired metal/semiconductor is electrochemically deposited in the interstices of the close packed spheres and the template is finally removed to leave the required highly ordered porous film[2]. Spherical particles suitable for template formation are readily available in a wide range of diameters (10 nm – 50 μm). As the pore size is directly related to the sphere diameter used in the template this enables the production of films with various pore sizes. Coupled with appropriate choice of deposited material, this can lead to films with novel electronic, optical, magnetic and chemical properties[2,3].

In many applications, one could anticipate that a critical issue would be the extent of penetration of solution into the porous film. This study sets out to address the extent of fluid penetration using the electrochemical quartz crystal microbalance (EQCM), here using 10 MHz AT-cut quartz resonators with Au electrodes. Copper nano-porous films were prepared by electrochemical deposition from acidified 1×10^{-3} mol dm^{-3} aqueous $CuSO_4$, through polystyrene latex microsphere templates of varying sizes, onto the Au surface of the quartz resonator. Dissolution of the polymer template reveals the ordered porous film. We describe the use of the EQCM as a gravimetric probe of surface composition, providing precise and sensitive *in situ* real time monitoring of film deposition. AFM images also support the success of the deposition strategy. The effects of pore size, fluid properties and surface derivatization on film wetting will be examined and compared to a recent theoretical model for the wetting of idealized corrugated surfaces [4].

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Elecrochemical Nanotechnology

Can Nanomaterials Improve Energy Storage?

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The positive electrode in rechargeable lithium batteries operates by insertion and removal of Li. To achieve high power and hence rate, short diffusion distances for Li^+ and e^- in the electrode are required. We have prepared the first example of a mesoporous alkali transition metal oxide and with highly crystalline walls, namely Low Temperature-$LiCoO_2$ (Fig 1a). The electrolyte can flood the pores and the diffusion distance for Li^+ and e^- removal and insertion within the thin (4nm) crystalline walls is only 2nm. The performance of such an electrode is superior to bulk materials (Fig 1c). The syntheses and characterisation of nanowire (Fig 1b) and mesoporous lithium transition metal oxide will be discussed. A recent attempt to improve energy density involves reacting Li directly with a transition metal oxide, e.g. Li and CoO, converting the latter to a nanocomposite of Li_2O and Co [1]. These conversion reactions differ from classical Li insertion/deinsertion. These oxides may be used as a negative electrode in a rechargeable lithium ion battery. However to obtain high power densities, essential for use in hybrid electric vehicles, high surface areas are required, which leads to poor reversibility of the electrode reaction [2]. Instead of simply using nanoparticles to obtain a high surface area, we have prepared nanostructured transition metal solids including nanowire and mesoporous Co_3O_4 and 3D nanoarray Mn_3O_4. The structural changes that occur on reacting these materials with Li will be discussed. The results show that high rates of reaction may be obtained in the case of Co_3O_4 and with much better reversibility than with nanoparticles of the same surface area, i.e. using an internal surface leads to better performance.
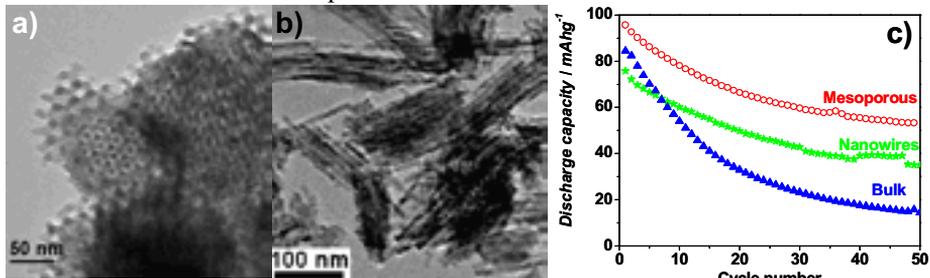
Figure 1: High resolution TEM images of nanostructured transition metal oxides such as (a) mesoporous and (b) nanowire LT-$LiCoO_2$. (c) Discharge capacities for bulk (▲), nanowire (★) and mesoporous (○) forms LT-$LiCoO_2$.

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Ruthenium-Oxide-Based Coatings Formed on Ti$_3$SiC$_2$ support

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This work is dedicated to the memory of Professors Aleksandar Despić

Ruthenium-oxide-based coatings on titanium are used widely as anodes for chlorine production and oxygen evolution [1]. These long-lasting anodes replaced fragile graphite anodes and hence they are known as dimensionally stable anodes (DSA). However, DSAs are also of limited service life, owing to the dissolution of active oxide, but also due to low corrosion stability of titanium, at high anodic potentials and elevated temperatures. These processes lead to the anode deactivation and increase in anode resistance and finally to the end of anode service life [2]. In order to increase DSA service life, it could be advantageous to replace Ti with some similar material that has higher corrosion stability. A new class of solids, $M_{n+1}AX_n$, where M is an early transition metal, A is an A-group (mostly IIIa and IVa) element and X is C and/or N, has a metal-like electrical and thermal conductivity, satisfactory good damage tolerance and are readily machinable [3]. Most important, these materials have excellent corrosion stability in HCl and H_2SO_4 solution at elevated temperature, with five orders of magnitude slower corrosion rate than Ti [4]. In this work, we test ternary MAX phase Ti$_3$SiC$_2$ as the support for RuO$_2$-based electroactive coatings. RuO$_2$ coatings on Ti and Ti$_3$SiC$_2$ were prepared by alkoxide sol-gel procedure [2], which preliminary showed most promising
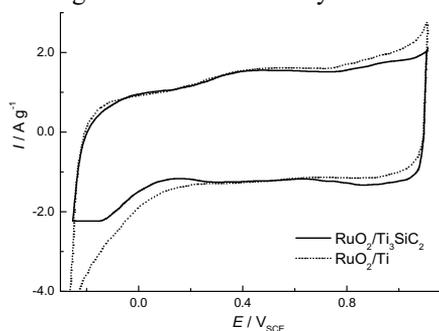

Fig. 1. Cyclic voltammograms of RuO$_2$/Ti and RuO$_2$/Ti$_3$SiC$_2$ electrode registered in 0.50 mol dm^{-3} H$_2$SO$_4$ at 20 mV s^{-1}.

electrochemical properties. The oxide was applied onto the support from ethanol suspension (ink method), which was followed by thermal treatment at 450 °C. The CVs of prepared RuO$_2$/Ti and RuO$_2$/Ti$_3$SiC$_2$ electrode in 0.50 mol dm^{-3} H$_2$SO$_4$ at 20 mV s^{-1}, are shown in Fig. 1. As can be seen, quite similar voltammetric behavior, which is usual for these electrodes [1], was registered for the coatings on different substrates.

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Fabrication of High-order Structured Thin Films by the Liquid Phase Infiltration Method

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Two- (2D) and three-dimensionally (3D) ordered nanomaterials have attracted much interest owing to their potential applications in photonic crystals, data storage, and biosensors. In order to control the highly ordered structure of the thin films, we have recently applied a liquid phase deposition (LPD) method as a novel aqueous solution-based process to prepare metal oxide thin films using ligand-exchange hydrolysis of metal-fluoro complexes and the F^- consumption reaction with H_3BO_3 and Al metal. In this paper, the liquid-phase infiltration (LPI) method for preparing metal oxide thin films with 2D or 3D periodicity using several kinds of template materials.

Surface coating on the narrow interval trenches using deep-RIE method — The silicon wafer was etched by Deep-RIE method with the ultra-high precision electron beam lithography ICP plasma systems. Obtained Si wefer has a narrow intervals and high aspect ratios uo tp 40 as a substrate for LPD process. This substrate was dipped into reaction solution using a solution of $(NH_4)_2TiF_6$ and H_3BO_3. TiO_2 thin film deposited densely as shown in Fig.1.

2D-alley structured thin films --- A novel technique for the direct synthesis of two-dimensional metal oxide films with highly ordered periodic structure has been studied. TiO_2 films with highly nano-ordered architectures were directly deposited on substrates at room temperature by LPI method.[1]   2D arrays of several kinds of metal oxide rods with diameters ranging from ca. 100 to 1000 nm are fabricated by filling the holes in a Si wafer.

Fig.1. LPD surface coating of narrow interval trenches prepeard by Deep-RIE method.

Inversed-opal structured thin films--A novel soft solution process for the direct synthesis of large-area well-crystallized oxides with 3D ordered periodic structure has been developed based on the LPI method as shown in Fig.2.[2] Metal oxide thin films were deposited directly into the nano-space, and thus the nano-space was completely infiltrated with metal oxide. X-ray diffraction studies on samples calcined at temperatures between 200 and 600ºC indicate that crystallite growth is limited to the size of the nano-space. The LPI process provides a direct fabrication route for metal oxide films with highly ordered structures, enabling nanoscale modification of optical properties of photonic crystals.

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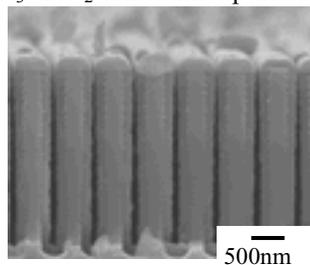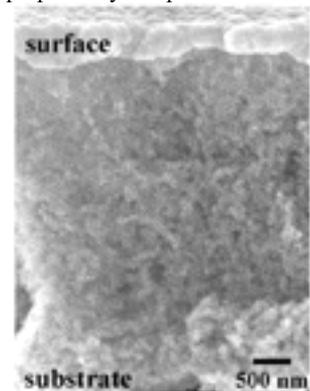[2] S. Iizuka et al., *Electrochim. Acta.*, **51(5)**, 802 (2005).

Fig.2. 3D periodic structured TiO_2 film.

Electrolytic growth of copper pentagonal microcrystals

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Particles with pentagonal symmetry forbidden by the classical laws of crystallography have been investigated intensively during the last decade. In this work the origin and the features of an internal structure of large pentagonal crystals formed during copper electrodeposition are investigated. The geometry and form of these crystals are discussed in order to find evidence for the disclination. Pentagonal crystals with a cross sectional size from 1 to 300 microns and various structures were isolated by varying the current density and substrate type. Eight types of pentagonal crystals that varied in their exterior form, size and internal structure was observed. It should be noted that most of the large pentagonal crystals were formed by electrodeposition – this was a novel procedure.

We assumed that all of these crystals were formed from one crystallization center and have one or six pentagonal symmetry axes. They are all characterized by the presence of twinning boundaries. It is proposed that there is a generic mechanism responsible for the observed self-organizing of the crystal during its growth.

There are two convincing experimental proofs of disclination of the pentagonal crystal growth during electrodeposition. The first observation is the splitting of the central point in large crystals (≈ 50 μm) where five twinning boundaries are converged (Fig. a). The second is the occurrence of the pentagonal point on the periphery of the twinning boundary during the etching of the crystal (Fig. b). It is easy to explain the first observation (Fig. a) as energetically favorable splitting 7-degree partial disclination ($\omega = 7°20'$) on two ($\omega^2 > \omega^2_1 + \omega^2_2$). The splitting is followed by the emission of a dislocation along one of the boundaries $\{111\}<110>$ (Fig. a). The occurrence of the pentagonal point in the crystal during etching (Fig. b and c) is connected with the presence of a high-energy defect as partial disclination.
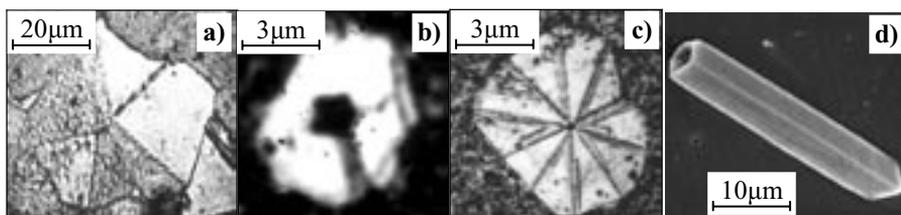
The metallography of pentagonal crystals (a, b and c) and pentagonal microtubules (d)

The opportunity of cavities ("holes") formation in needle-like pentagonal crystals has been predicted from disclination theory. It has been observed that pentagonal microtubules formed during the electrodeposition of copper for the first time (Fig. d).

It is natural to assume that coatings, films and foils made up of such crystals should also have unique properties due to the specific features of their structure.

Electrochemical-chemical fabrication of (Cu,Ag-)oxide – porous indium phosphide nanocomposites

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We investigated the chemical-electrochemical plating techniques as a method of fabrication of nanocomposites on the basis of AIIIBV semiconductor materials (n-InP). The results of fabrication of nanocomposites by means of electroless plating of copper and silver oxide in pores of n-InP on the basis of structures produced by method of electrochemical anodic dissolution are reported. Parallel pores (diameter of pores $\Box$ 80 - 110 nm) stretching perpendicular to the initial surface of the sample were introduced by electrochemical dissolution of bulk n-InP substrates in HCl aqueous solution under conditions of self-arrangement of pores in two-dimensional hexagonal lattice (aspect ratio $A = h/d \sim 500$, where h – depth of pore, d – diameter of pore). The kinetics of metallization and features of distribution of metal oxide in nanopores at high A are described.

We demonstrate the filling degree of nanopores is determined by rate of chemical deposition. Relatively high rate of deposition of copper oxide (from glycerate aqueous solution for chemical coppering) results in nonuniform filling of pores and, as a consequence, low throwing power of electrolyte and low filling degree of pores. Unlike this considerably lower rate of chemical plating of silver oxide (from solution containing triethanolamine) results in higher uniformity. In consequence of this the conditions, under which the filling degree of pores by metal oxide is higher, are realized. At electroless plating of silver oxide the uniform average concentration of metal (from oxide) in pores being equal $\sim$ 50 wt % is reached.

Microscopic studies of organic electrochemical intercalation and Cu electrodeposition on 1T-TaS2

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Transition metal dichalcogenides are ideal host materials for the intercalation of organic molecules, resulting in large changes of structural and electronic properties. Furthermore, vapour deposition on these layered crystal surfaces results in the formation of various metallic nanostructures, in particular metal nanowire networks. In this study the atomic-scale mechanisms of the electrochemical intercalation / deintercalation of pyridine[1] and octylamine[2] in $1T - TaS_2$ and the formation of Cu nanowires by electrodeposition on $1T - TaS_2$ were investigated by in-situ electrochemical STM, AFM, electron microscopy, and cyclic voltammetry.STM studies in 0.01 M pyridine and octylamine solution (pH 3) show characteristic structural changes in the surface morphology at potentials negative of -0.45V vs. SCE, where intercalation commences, indicate an important role of surface defects, such as holes and steps. In particular, the formation of holes, step flow etching and the formation of small islands of submanolayer height were observed. Studies of Cu deposition on TaS_2 reveal that metal nanowires can not only be formed under vacuum conditions [3], but also by electrochemical deposition. Using a combination of ex-situ scanning electron microscopy, and AFM the morphology of these wires and of the TaS_2 substrate was characterized as a function of coverage and deposition rate. These observations indicate characteristic differences to Cu nanowires formed by vacuum deposition and provide details on the growth process.

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Effect of Introducing Oxygen Type Functionalities on the Electrochemical and Conductance Properties of Single Walled Carbon Nanotubes

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Increasingly, the importance of chemically functionalized SWNTs for chemical sensing type applications is becoming recognized.[1] Carboxylate (-COOH) derivatisation of SWNTs, through acid etching, is often the first step in the route to chemically functionalize SWNTs.[2] However, the effects of this process on the electrochemical and solution conductance properties of the SWNTs, which is obviously important for solution-based chemical sensing applications, is still little understood. In this study, we introduce oxygen functionality into the SWNTs in two ways; through (a) acid etching and (b) plasma ashing.[3] The SWNTs are grown in network form on insulating substrates using catalyzed chemical vapour deposition (CVD) and sputtered iron as the catalyst. Modifications to the structure of the SWNTs are studied using various imaging techniques and Raman spectroscopy, whilst changes in conductivity across the networks are investigated using electric force microscopy, two point probe conductance measurements and silver electrodeposition. It is found that the major effect of acid reflux treatment is shortening of the SWNTs leading to a reduced number of tube-tube contacts and decreased network conductivity. In addition, Raman microscopy shows preferential oxidative attack at metallic SWNTs. In contrast, the predominant mechanism during plasma treatment appears to be sidewall functionalisation. The change in the hybridisation of the carbon atom from sp^2 to sp^3 leads to a drastic change in SWNT electronic structures[4], as supported by Raman spectroscopy and conductance measurements. The effect of both treatments on the electrochemical response of inner sphere and outer sphere electron transfer processes at SWNT electrochemical devices has also been explored.

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Diagnostics of nanostructured low-conducting matrix using impedance spectroscopy

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A possibility to use an impedance spectroscopy method to estimate a size of nanoparticle, which form a multilevel structure, has been investigated. Nanostructured materials, namely poorly crystalline Ca hydroxyapatite (Ca-HAP) and amorphous zirconium hydrophosphate (ZHP), were studied in a frequency (f) range of 10^{-2}-10^6 Hz. Values of dielectric permittivity and dielectric losses have been calculated for different frequencies, Contributions, which correspond to: (i) ionic conductivity due to H^+ (ZHP) or OH^- (Ca-HAP) transport, (ii) relaxations cased by OH dipoles, have been separated using Havriliak-Negami functions [1] by means of computer simulation of the experimental dependencies. It was found that relaxations peaks are distorted comparing with Debay ones. According to IR spectroscopy data, this distortion is caused by formation of hydrogen bonds between functional groups on the one hand and between functional groups and water molecules on the other hand.

Values of ac conductivity (σ'), which comply to ionic transport, have been calculated (Fig.1). The σ'-f dependencies were mathematically treated using Almond-West equation, which describe a hopping diffusion model [2]:

$$\sigma' = \sigma'_{dc} + A(2\pi f)^s, \tag{1}$$

where σ'_{dc} is the dc conductivity, A and s are the parameters, which depend on temperature conditions in the case of ionic conductivity. A low-frequency part of the curve corresponds to grain boundary conductivity, while a high-frequency part is connected with a bulk conductivity. The A and s parameters have been found for each part of the curve and the conductivity relaxation time (τ_0) has been calculated as $\tau_0 = \left(\dfrac{A}{\sigma'_{dc}}\right)^{\frac{1}{s}}$. The order of the τ_0 value was found to reach 10^{-5}-10^{-6} s (bulk conductivity) and 10^{-1} s (grain boundary conductivity). The particle size has been calculated from the σ'_{dc} of the low-frequency part of the σ'-f curve using the following equation:

$$\sigma'_{dc} = \frac{C Nq^2 d^2}{6kTt_0}, \tag{2}$$

where C is the mole fraction of charge carriers, N is the Avogadro constant, q is the carrier charge, d is the hopping distance, k is the Boltzman constant, T is the temperature.

The order of particle size for Ca-HAP and ZHP was found to reach 10^{-1}-10^{-2} nm and depend on synthesis conditions. The results obtained with the impedance measurements were confirmed by data of small-angle X-ray scattering technique. It was shown that a presence of water in a structure of the materials decreases an accuracy of the impedance spectroscopy method due to contribution of Grothus mechanism to the conductivity.

Fig. 1 Frequency dependence for real contribution of *ac* conductivity, which corresponds to onic conductivity, for Ca-HAP: experimental (1) and modelling (2, 3) curves. The conductivity corresponds to the bulk (2) and nanoparticle boundaries (3).

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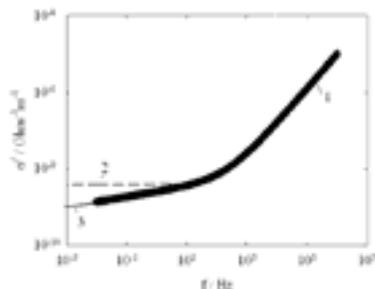3. E. Axelrod, A. Givant, J. Shappir, Y. Feldman, A. Sa'ar, Phys. Rev. B, **65** (2002) 165429.

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Scanning ion conductance microscopy: Development and applications

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Scanning Ion Conductance Microscopy (SICM) [1,2] is a high resolution, non-contact electrochemical imaging technique. Imaging takes place under solution, whereby an electrode containing, micro- or sub-micro- pipette filled with electrolyte is scanned in a raster pattern over the substrate, while a potential is applied between the intra-pipette electrode and a reference electrode. The magnitude of the ionic current varies with the proximity of the substrate and can be calibrated to give a measure of distance between the pipette and the surface. Furthermore, upon scanning over pores one is able to detect current due to ionic flow.

The diameter of the pipette aperture dictates, to a large extent, the resolution of the instrument, thus micro- and sub-micro- resolution is readily attainable. This work will describe the construction and testing of an instrument suitable for both SICM and scanning electrochemical microscopy (SECM). Preliminary findings on a range of substrates are presented, including the imaging of a microporous biological substrate (dentine).

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Effect of minute amount of Cu deposition on zincate substitution reaction of Al alloys

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Double zincate pretreatment has been used for metal plating on Al. For Al-Si alloys used in electronic devices, however, uniform zincation is difficult due to non-unform Zn deposition probably caused by nonuniform Si distribution. On the other hand etching pretreatment preceding double zincate pretreatment in sulfuric acid solution contaning small amount of Cu^{2+} ion provides uniform Zn deposition in the double zincate pretreatment. This phenomenon is considered that small amount of Cu deposits on Al alloy and provides nucleation points of Zn deposition in the zincate pretreatment. However any investigation has not yet been reported. In this study mechanism of Cu pretreatment on magnetron sputter deposited Al-Si films formed on glass plate and its effect on double zincate pretreatment were investigated.

Specimens were Al film and three kind of Al-Si (1), (2), (3) films of 0.5 μm in thickness deposited on glass plates prepared by magnetron sputtering method. From EPMA results, concentration of Si in the films was 1,1, 2.1 and 2.5 wt %, respectively. Each specimen was etched in H_2SO_4 solution or H_2SO_4 + $CuSO_4$ solution at 333 K for 40 s and then prepared by double zincate process. During etching pretreatment and zincate process immersion potential was traced using Ag/AgCl reference electrode or Zn electrode. Immersion potential shift during etching process was interpreted in a term of mixed potential of Cu deposition and Al dissolution. In double zincate process, potential shift corresponding to proceeding substitution reaction shortened for the specimen pretreated with Cu etching due to rapid Zn deposition. Fig. 1 shows FE-SEM images of Al and Al-Si(3) films after the second zincate pretreatment. On Al-Si(3) film Cu pretreatment provides remarkably uniform zincated surface comparing with Al-Si(3) film without Cu pretreated or Al film Cu pretreated.

10μm
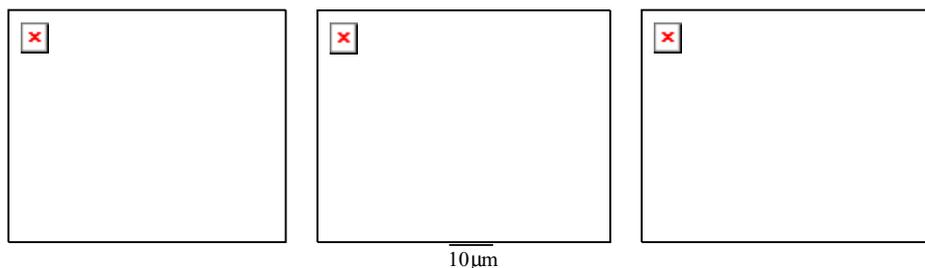
Fig. 1 FE-SEM images of (a,b) Al-Si(3) and (c) Al films after 2nd zincate pre-treatment. Specimens were etched in H_2SO_4 solution with (b,c) or without (a) Cu^{2+} ions before zincate pretreatment.

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Elecrochemical Nanotechnology

On the Origin of the Spontaneous Potential Oscillations Observed during Galvanostatic Deposition of Layers of Cu and Cu_2O in Alkaline Citrate Solutions

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Potential oscillations are demonstrated under reducing galvanostatic conditions in alkaline Cu(II)-citrate solutions containing 0.4 M Cu(II) and 1.2 M citrate at elevated temperatures (see figure 1). The oscillations, which give rise to the deposition of layers of Cu and Cu_2O, originate from local modulations of the pH near the working electrode. Similar potential oscillations obtained with the Cu(II)-lactate system was first described by Switzer et al., (Adv. Mater. 9 (1997) 334-338). Oscillations in the local pH were demonstrated by Leopold et al., (J. Electroanal. Chem., 547 (2003) 45-52) for the Cu(II)-lactate system. In analogy with the Cu(II)-lactate case, a local pH increase is obtained during the deposition of copper from the $[Cu_2H_{-2}Cit_2]^{4-}$ complex predominating in the solution. This increase stems from the protonation of the liberated citrate. As a result of the increase in pH, electrodeposition of Cu_2O at a less negative potential becomes possible at the rate required by the constant current. This reaction is switched on and off as the local pH increases and decreases, respectively.
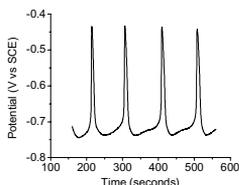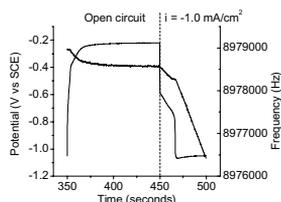

Fig 1

Fig 2

In the present study, electrochemical quartz crystal microbalance (EQCM) data show that the onset of the electrochemical deposition of Cu_2O is accompanied by an electro-less deposition of Cu_2O. This occurs by comproportionation involving deposited Cu and Cu(II) in solution once the local pH is high enough so render Cu_2O the stable phase on the electrode surface. As the comproportionation consumes hydroxide ions, the local pH then decreases rapidly. When the local pH drops, the electrodeposition of Cu_2O becomes unable to sustain the current and the potential shifts negatively. The previously deposited Cu_2O is now reduced to copper, as is seen from the chronopotentiogram and the smaller slope of the frequency curve (see figure 2). This reduction is however incomplete during the oscillation conditions because the remaining Cu_2O becomes coated with a growing layer of copper. Finally, the oscillation cycle is completed by a gradual replacement of the reduction of Cu_2O by that of the $[Cu_2H_{-2}Cit_2]^{4-}$ complex. At this point the local pH starts to increase again. With the present kinetic model in mind, it is also demonstrated how nano-structured layers of Cu and Cu_2O can be fabricated using a galvanostatic pulse technique.

Electrochemical Investigation of Molecular Transport into Nanostructured Silica Thin Films

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The intersection between silica-based mesoporous materials and electrochemistry is very rich. Material science takes advantage of the powerful tools provided by electrochemist community to characterize processes occuring into their materials, especially the monitoring of mass transfer processes [1]. And from the other side, electroanalysts can exploit mesoporous materials for the development of new sensor devices [2].

Since the discovery of mesostructured MCM-41 materials [3], an intense research has been devoted to the control of the porosity of sol-gel materials by use of templated molecules. In particular, important effort has been made to shape the mesoporous material in the appropriate form: particles with varying size and shape, monoliths, fibers and films.

Evaporation Induced Self-Assembly (EISA) has been introduced recently to prepare thin mesoporous films with controlled mesostructure [4]. With using Cetyltrimethyl-ammonium Bromide (CTAB) as template, the EISA method allows to prepare thin films with various textures (p6m, $P6_3/mmc$ and Pm3n) and thicknesses. It is particularly important to control the relative humidity into the deposition chamber during the evaporation process in order to direct the mesostructure [5].

The present work deals with the electrochemical investigation of mass transfer processes into mesostructured silica thin films as deposited by EISA method onto Indium-doped Tin Oxide (ITO) electrodes. The porosity of the different films (with p6m, $P6_3/mmc$ and Pm3n textures) have been characterized by ellipso-porosimetry using water adsorption-desorption cycles. Electrochemical characterizations by cyclic voltammetry and wall-jet electro-chemistry were performed in aqueous solution using electrochemical probes displaying various charges and sizes (I^-, $Fe(CN)_6^{3-}$, $Ru(bpy)_3^{2+}$, FcMeOH).

Strong modification in permeability results from modification of the material texture. This study points out the importance of texture control in thin film technology when considering applications that involve mass transfer through such thin layers, as for example electrochemical sensing devices.

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Modulation of the electrode work function by self-assembled metal nanoparticles
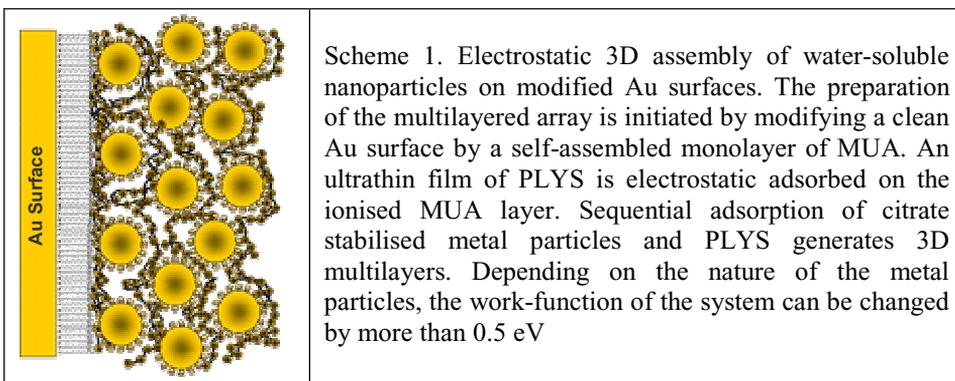
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The modification of the electronic properties of surfaces by self-assembling nanoparticles has important implications in the design of heterogeneous catalysts as well as electrical contacts for hybrid optoelectronic and molecular devices. In the present contribution, we examine the effect of the electrostatic adsorption of metal nanoparticles on the work-function of modified metal surfaces. The evolution of the work-function (Φ) of polycrystalline Au films upon sequential layer-by-layer adsorption of mercapto-undecanoic acid (MUA), poly-l-lysine (PLYS) and metal nanoparticles (NP) was monitored by Kelvin Probe measurements [1]. The NP were synthesised by protocols based on the Turkevich method [2], generating particles in the range of 3 to 40 nm diameter stabilised by a citrate layer. The role of the MUA monolayer is to fix a negative charge at the Au surface for the electrostatic adsorption of PLYS. Furthermore, sequential adsorption steps of PLYS and NP allows growing 3D films of nanoparticles as illustrated in scheme 1. Changes in Φ associated with the adsorption of Au and Pt NP are rationalised in terms of the bulk properties of macroscopic materials. However, the apparent Φ for Ag NP substantially increases above the corresponding macroscopic value as the size decreases. XPS analysis of the Ag NP arrays suggests that the apparent Φ is affected by the presence of an oxide layer. The topography of the self-assembled particle arrays is also examined by atomic force microscopy.

Scheme 1. Electrostatic 3D assembly of water-soluble nanoparticles on modified Au surfaces. The preparation of the multilayered array is initiated by modifying a clean Au surface by a self-assembled monolayer of MUA. An ultrathin film of PLYS is electrostatic adsorbed on the ionised MUA layer. Sequential adsorption of citrate stabilised metal particles and PLYS generates 3D multilayers. Depending on the nature of the metal particles, the work-function of the system can be changed by more than 0.5 eV

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Double template electrochemical deposition and characterization of Zn-Ni alloy nanoparticles

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Nanomaterials have attracted extensive interest in recent years because of their unusual quantum properties and their potential use in nanoscale device. The physical and chemical properties of nanoparticles depend on the composition. The preparation of such alloys in nanoscale could be very interesting in electronic industry and in corrosion protection.

Porous aluminum oxide membrane and the hexagonal phase of lyotropic liquid crystal (containing zinc and nickel ions) were used as templates for preparation of the nanostructured alloy film. Highly ordered Zn-Ni alloys nanoparticles were obtained by direct electrochemical reduction of zinc and nickel ions from aqueous solution within the pore of the alumina membrane (Fig. 1). The combination of the hexagonal phase of liquid crystal and the alumina membrane (double template deposition) lead to the reduction of the size of the nanorods. Particles that grow from the bottom of the pore of alumina membrane have many subdivisions on their surface due to the columns of liquid crystal (Fig. 2 and profile 2a). Potentiodynamic stripping of the deposit confirmed the presence of alloy phases. Electrochemical impedance measurement shows two separated time constant and diffusion in the pore of the nanofilm.
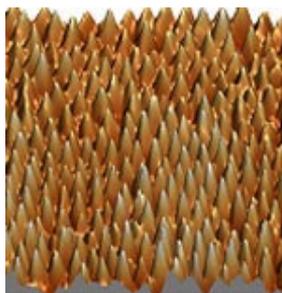

Fig.1. Zn-Ni alloy film deposited from solution; 1.6 x 1.6 x 0.9µm

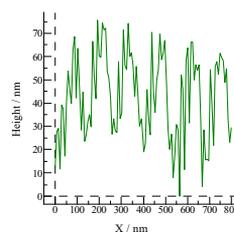Fig. 2. Zn-Ni film deposited from liquid crystal; 1.6 x 1.6 x 0.08µm.

Fig. 2a. Profile

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Template synthesis and examination of cadmium nanostructures

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In this study we have electrochemically produced and examined cadmium nanorods of defined diameters and lengths. As the templates polycarbonate membranes of various porosities (from 50 to 800 nm) were used. These membranes were attached on to a graphite paste electrode and cadmium was electrodeposited electrochemically via cyclic voltammetry or chronoamperommetry. After synthesis the samples were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Cyclic voltammetry was mainly used for prepreparation, wetting and conditioning of membrane template.

Chronoamperometry was realized in different time and potential regimes. The i vs. t plots were used to establish the mechanism of cadmium nucleation and growth within the pores. We have found cadmium to nucleate instantaneously on graphite paste and on template covered graphite. However, the presence of membrane provokes 2D growth of existing nucleus while 3D growth prevails on uncovered graphite.

AFM and SEM images confirmed that Cd deposition starts at the bottom of the pore and provided the deposition time is long enough, nanorods emerge from the pore and eventually cadmium crystals starts to grow over the membrane. The shape of cadmium dendrites covering the template depends on membrane porosity and time of deposition.

Electrochemical investigation of nanostructures built by means of the damascene process for microelectronics

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A microcircuit was designed and built by means of the damascene process used in microelectronics (1). The copper structure were made up 300 nm, 3 µm, and 30 µm nanoelectrodes, which have circular or cubic shapes with various orientations with respect to a line. The electrodes are arranged by pairs in a way that one of the electrodes can be used as a cathode and the other one as an anode. Voltamperometry and impedance measurements were carried out to investigate the coupling between the kinetics and transport in the deposition mechanism of copper in oxalic acid medium.

Reference
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Figure: SEM images of nanoelectrode pairs; circular electrodes are 300 nm in diameter.

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DC electrodeposition of niquel and cobalt on AAO templates with highly ordered pores

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Electrodeposition inside nanoporous membrane templates provides a versatile approach to prepare free-standing nanowires of metals, semiconductors and polymers. Provided the diameter and the density of the pores can be properly controlled, porous anodic aluminum oxide (AAO) is particularly suitable for this purpose. Current work deals with the optimization of the experimental conditions for obtaining AAO templates with pores ordered in a hexagonal structure for further potentiostatic electrodeposition of nickel and cobalt nanowires. In order to obtain a homogenous surface, aluminum was successively pre-treated with annealing, mechanical polishing and electropolishing. Anodization was conducted in two steps in 0.30M oxalic acid at a voltage of 40V and 20°C. V. After the first anodization, the oxide is dissolved in a H_3PO_4 /H_2CrO_4 mixture which leaves a pre-textured aluminum substrate with concave hemi-spheres very well distributed, serving as preferential nucleation sites for the pores formed in the second anodization. This procedure assures a maximum order in the final porous structure as confirmed by AFM images from which a pore diameter and interpore spacing of 30nm and 100nm, respectively, was verified.

The effect of overpotential and pH at room temperature on the structure of Ni and Co nanowires were systematically studied. XRD shows that at -0.900 V (*vs* Ag/AgCl) Ni nanowires present a preferred crystallographic orientation along the [111] direction, changing to [220] at -1.10 V. Possible reasons for this behavior are discussed on the basis of thermodynamics and electrochemistry. In turn, the increase in pH produces a better crystallinity without orientation changes. On the other hand, the XRD of the Co nanowires were more complex, probably due to the fact that this metal can be found either in the cubic or hexagonal phases. The latter is stable at higher temperatures however, some authors have reported its presence in nanowires prepared at room temperature. This behavior should be examined in detail further.

Preparation of Co-Ag nano-heterogeneous films by electrodeposition

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In recent years the development of magnetoresistive materials in which nanometric clusters of ferromagnetic metals are included in a non ferromagnetic matrix has attracted much interest. The possibility to obtain this kind of materials by means of electrodeposition is contrastable. Silver is an excellent matrix to include ferromagnetic metals. In this line, our interest is the design of silver baths to allow the simultaneous electrodeposition of cobalt to prepare magnetoresistive films, taking into account the substantial difference between the standard potentials of cobalt and silver metals.

Electrodeposition of silver films, potentially useful as a matrix for cobalt-silver magnetoresistive materials, is studied in perchlorate bath over vitreous carbon electrode. Acidic baths are used, varying the pH between 2 and 5. Silver electrodeposition at negative potentials is analyzed in order to attain deposition potentials next to those of cobalt using 0.1 mol dm^{-3} of thiourea as complexing agent. Voltammetric experiments show that the presence of thiourea shifts the deposition process to negative potentials and decreases the deposition rate. Thiourea allowls silver electrodeposition in a wide range of potentials in which secondary process of proton reduction is not significant. Scanning electron microscopy analysis of deposits obtained potentiostatically shows that the presence of thiourea in the bath is beneficial, since the silver films coated the substrate completely, as opposed to behaviour observed from a free-thiourea bath. Furthermore, the obtained silver deposits are compact, fine grained but rough. Compositional analysis shows that S is not incorporate in the deposits.

New species as sodium gluconate (0.1-0.3 mol dm^{-3}) and boric acid (0.1-0.3 mol dm^{-3}) are added to the electrolytic bath to improve the quality of deposits. Their presence does not modify the general behaviour of the deposition process. Deposits are fine-grained, smooth and uniform up to more negative deposition potentials, in the same way as the potential range in which coherent deposits are obtained is enlarged. However, when very negative potentials are used, dendrític growth develops. As silver electrodeposition results very sensitive to temperature in the tested bath, low temperature (15ºC) is selected to perform the deposition. The lowering of bath temperature shifts the onset of the deposition process to negative values, close to those of cobalt deposition, maintaining the deposits quality.

Cobalt-silver codeposition is studied in the silver optimized bath, using always a high cobalt (II) : silver (I) ratio in order to obtain nano-heterogeneous Co-Ag deposits with moderate cobalt percentages adequate to magnetoresistive behaviour. Voltammetric experiments allow selecting the more adequate conditions to perform the electrodeposition. Different deposition techniques (single step or multi step), bath composition and several potentials or current densities are tested to delimit the cobalt percentages in the uniform binary Co-Ag deposits.

Electrocatalytic and Magnetic Properties of Ultrathin Nanostructured Melanin Films on Au(111)

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We have prepared ultrathin nanostructured melanin films on Au(111) by using an electrochemical method. Film formation takes place at a noticeable rate at E = –1.0 V (vs SCE) in 0.100 M NaOH. High resolution STM images at the early stages of growth show that the smallest units of the film, 5-8 nm in size and 0.3-0.4 nm in height, form ordered arrays that closely follow the Au(111) topography by electrochemical self-assembly process. These films contain iron species and were characterized by Auger electron spectroscopy, scanning tunneling microscopy, magnetic force microscopy and electrochemical techniques. The inorganic-organic composite exhibits magnetic properties and catalyze the hydrogen peroxide electroreduction in alkaline and neutral electrolyte solutions. Results from this paper can be used for understanding the complex chemistry and electrochemistry of the iron-melanin system that seems to be involved in Parkinson´s pathogenesis.

The influence of a gradient magnetic field on the nickel electrodeposition from the sulphamate electrolytes

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The influence of a magnetic field on electrochemical processes are ascribed to the Lorenz force which acts on the mass transfer of charged particles in electrolytes and results in surface modification of the deposits. From this point of view it is possible to change behavior of the process by means of a magnetic field application only in the case when mass transfer is a determining stage.

In this work influence of a gradient magnetic field on the nickel deposits creation from the sulphamate electrolyte was investigated. Electrodeposition was performed without diffusion limitation namely under high nickel salt concentration and low density of the currents.

It is established that presence of a magnetic field changes structure of the nickel deposits. A great difference between nickel morphologies obtained with and without a magnetic field was observed. The nickel deposits obtained without a magnetic field have a smooth fine-grained structure (fig. 1 a). On the other hand application of a gradient magnetic field initiates formation of the deposits with arborous dendritic structures (fig. 1 b). It is necessary to note that dendrites form only in the regions with the maximal *s*trength and gradient of a magnetic field. The obtained data indicate that a magnetic field acts not only on the mass transfer but and on the crystallization stages. It is possible that a magnetic field disturbs a crystal growth mode of the metals due to the influence of a gradient magnetic force on Ni ions and adatoms.

Also the opportunity of the deposits macro- and microstructure control by changing the strength of a magnetic field and its gradient is investigated. The lattice of arborous dendrites was obtained by spatially periodic magnetic field gradient.
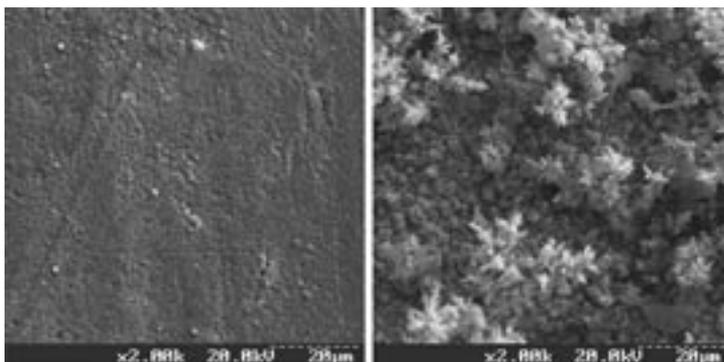

Fig. 1. Microstructures of nickel deposits a) direct current mode; b) direct current mode with gradient magnetic field.

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3D Electron Tomography Characterization of Nickel Foams and Their Electrocatalytic Activity

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Micro- and nano-structured nickel materials are used in rechargeable batteries, fuel cells and supercapacitors either as an active electrode mass or a current collector. One of the most important issues related to the implementation of Ni-based, high surface area materials is a reliable evaluation of their active surface area, mechanical properties, chemical stability and electrical conductivity. Suitable methods should be applied to analyze porous, micro- and nano-structured Ni materials, such as foams, filamentary powders, and polycrystalline sheets or wires. In this contribution, we present results on comprehensive materials science and electrochemical characterization of industrial nickel foams (INCOFOAM$^\square$). 3D electron tomography analysis reveals a fibrous nanostructure within individual micro-fibres of the foam's 3D skeleton. Electrochemical characterization of the foams is performed in aq. KOH solution. We investigate the behaviour of "as-received" foams and compare it to that of the same materials after chemical etching. The results show that the etching reduces the amount of Ni surface oxides/hydroxides formed as well as increases its surface roughness. We analyze different experimental methods to determine the active surface area. The first approach is based on the charge density associated with the reversible oxidation of Ni (to α-Ni(OH)$_2$), whereas the second is based on the double-layer charging current. We observe that the capacitive behaviour of the foams is affected by Mott-Schottky capacitance. The data show that the conditions at which the reversible Ni oxidation is carried out should be carefully selected in order to avoid the possible overlap of the H$_2$ oxidation current and the irreversible transition between various forms of Ni(II) compounds (α-Ni(OH)$_2$ and β-Ni(OH)$_2$). We further study the kinetics and mechanism of the hydrogen evolution reaction (HER) at the Ni foams. We investigate HER at "as-received" and pre-treated Ni foam. The pre-treatment methods include chemical etching, anodic oxidation and cathodic polarization, and lead to an increase of the surface roughness as well as changes in the reduction/formation of Ni surface oxides (such as NiO, Ni(OH)$_2$, or NiOOH). The pre-treatment changes both the Tafel slope (b) and the exchange current density (i_o) of HER, because the reaction is affected by the electronic state of the electrode surface. The chemical etching leads to an increase of b and i_o. We analyze the changes in kinetic parameters of HER on the basis of modification of semiconducting properties of the electrode surface. The results obtained using the Ni foams are compared to those for bulk-type Ni.

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Investigation of the Electrochemical Behaviour of Networks of Pristine Single Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) are unique materials which have many interesting physical and electrical properties. SWNTs consist of a single graphene sheet rolled to form a tube about 1 nm in diameter, which can either be metallic or semiconducting in nature. In any mix of SWNTs about 2/3 will be semiconducting and 1/3 metallic. Traditionally, electrochemical studies of SWNTs have often been made on SWNTs which have been subjected to strong acid treatment resulting in the creation of acid functionalities and then deposited on conducting surfaces or mixed with an inert resin. The variation in the electronic properties is often ignored when interpretating the electrochemical response. In this study we present a fundamental investigation of the factors which control the electrochemical performance of SWNTs. The SWNTs employed here are grown in house using CVD to form networks on an insulating surface. They are not subject to acid treatment and thus remain in their pristine state. Using a variety of techniques and experimental arrangements we are interested in examining the

Figure 1: Field emission-scanning electron microscopy (FE-SEM) image of a network of SWNTs.

relationship between the conductivity and the electrochemistry of the network of SWNTs to a range of redox probes. We will also explore what effects factors such as defect density ; network density ; number of SWNT-SWNT contacts has on the electrochemical response.
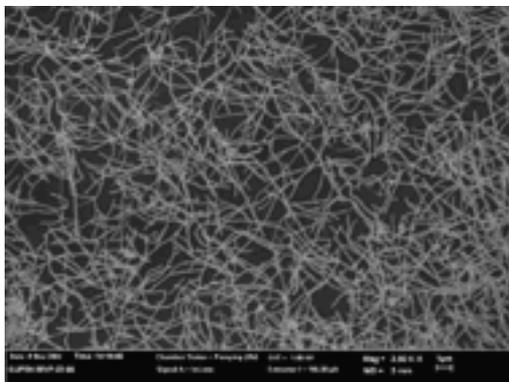
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In-situ Video-STM study of the dynamic behavior of nanoscale metal strings on reconstructed Au(100) electrodes

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The dynamics of the basic elements of the Au(100) surface reconstruction - hexagonally-ordered five atom wide strings, embedded in the topmost atomic Au layer - has been studied by Video-STM in 0.01 M Na_2SO_4 + 0.001 M HCl. These "hex"-strings can be observed during the potential-induced phase transition from Au(100)-(1x1) to the "hex" reconstructed surface.

In this work we will focus on the surprisingly high mobility of isolated "hex"-strings parallel and perpendicular to the string direction [1-3]. In particular, results of a detailed quantitative study of the motion perpendicular to the string direction will be presented, using "hex"-strings which are confined by other, perpendicular running strings on each end (Fig. 1). This study reveals (a) that two elementary processes (jumps by one and by two Au spacings, respectively) contribute approximately equal to this motion and (b) that the perpendicular mobility does not depend on the string length. These observations can be explained within a simple model, where the string moves due to nucleation and propagation of lateral string distortions "kinks". Furthermore, we discuss potential- and temperature-depend measurements, which show that the string mobility increases towards more negative potentials and is thermally activated.
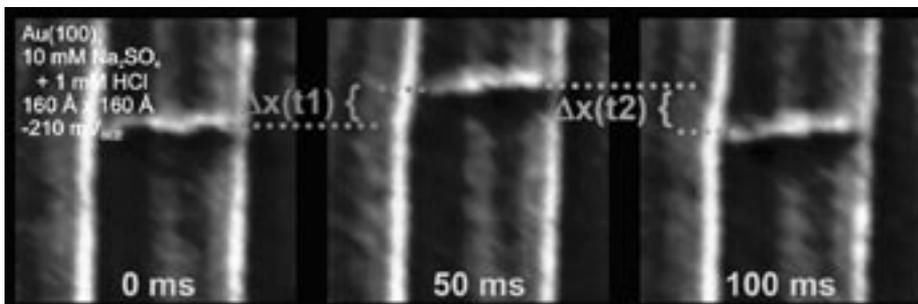

Fig.1: Video-STM sequence showing the motion of confined "hex" strings on Au(100).

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Photoelectrochemical deposition of CdTe thin films on the Te-Modified Au electrode

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Photoelectrochemical deposition of CdTe thin films on the Te-modified Au electrode using electrochemical quartz crystal microgravimetry (EQCM) and voltammetry is described. Corrosion of pre-deposited Te electrodes by illumination at applied potential resulted in Te^{2-} species, which was manifest from the EQCM frequency changes. Te^{2-} species from the photocorrosion were diffused into the bulk solution with stirring. Without stirring, Te^{2-} reacted with Cd^{2+} ions in the electrolyte to form CdTe films/particles on the Te/Au electrode. The effects of light intensity, applied potential and electrolytes on the CdTe formation through the photocorrosion were studied in detail. Also, photoelectrochemistry, XPS, EDX, SEM, Raman spectroscopy were used for the characterization of CdTe/Te heterostructures.
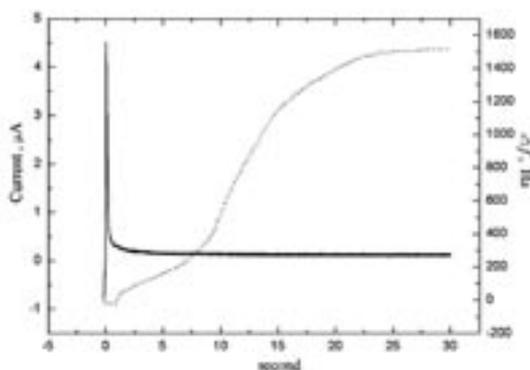

Fig. 1. Current (solid line) and corresponding frequency changes (dash line) during the illumination of white light (~300mW/cm^2) on the Te-modified polycrystalline gold electrode in 0.1M Na_2SO_4 at a fixed potential of - 0.2 V
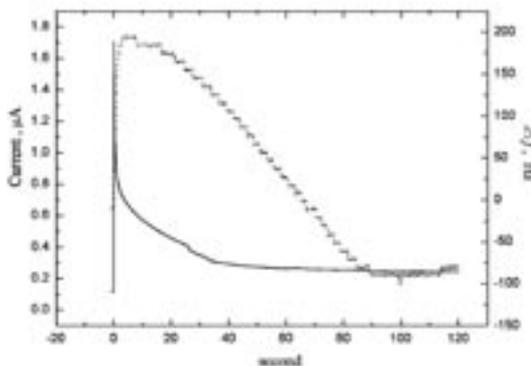

Fig. 2. Current (solid line) and corresponding frequency changes (dash line) during the illumination of white light (~300mW/cm^2) on the Te-modified polycrystalline gold electrode in 30 mM $CdSO_4$ in 0.1M Na_2SO_4 at a fixed potential of - 0.2 V

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Evaluating electron transporting thin films for an organic photovoltaic design

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The organic photovoltaic cell studied in this contribution is based on the idea of vectorial electron transfer in organised thin films of covalently linked porphyrin-fullerene dyads (Fig. 1a) [1]. The primary process is the excitation of the porphyrin moiety in the dyad and the consequential electron transfer from porphyrin to fullerene. The cell structure (Fig. 1c), including a hole transporting layer (HTL) and an electron transporting layer (ETL), is designed to support the charge separation process in the dyad. Finding good candidates for the ETL is somewhat challenging as there are only few available electron accepting materials with desired thin film processing properties. The ETL materials studied in this communication are quinoxaline based polymer PPQ, diacid-fullerene FDA, octanethiol protected gold nanoparticles C_8S-Au and resorcarine-fullerene complex EMR+C_{60}. Films in the cell structure are prepared by Langmuir-Blodgett and Langmuir-Schäfer methods which produce very thin and well organized films. Electron transporting materials are evaluated by time resolved Maxwell displacement charge (TRMDC) [1] and current-voltage (IV) measurements. Studied ETLs were combined with a dyad layer and the electron accepting ability was verified for PPQ, FDA and EMR+C_{60} materials by TRMDC. In TRMDC system (Fig. 1b) the active layers are insulated from the electrodes and excited by a pulsed laser. Induced photovoltage is an indication of charge movement perpendicular to film plane. Performance of the photovoltaic cell (Fig. 1c) is determined by IV curves and incident-photon-to-current-efficiency (IPCE) spectra. Successful photovoltaic cells were prepared with FDA and PPQ as the ETL. IV-curves show that the cell parameters fill factor, short circuit current and power conversion efficiency at the maximum absorption wavelength of the dyad are higher for the FDA cell compared to the PPQ cell. PPQ has favourable effect on the open circuit voltage. For the PPQ cell IPCE spectrum follows the shape of the absorption spectrum of PPQ indicating that the photoconductivity of PPQ is controlling the cell operation. For FDA cell the IPCE and cell absorption spectra have similar shapes demonstrating that FDA can act as an ETL in the designed photovoltaic cell.

Figure 1.
Porphyrin-fullerene dyad (a),
TRMDC system (b) and
photovoltaic cell (c).
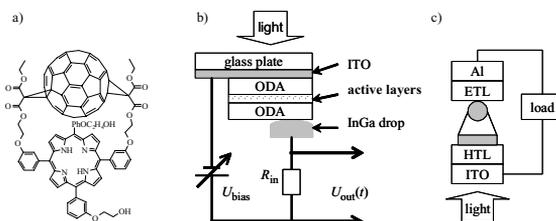
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Effects of surfactants on the crystal growth and electrochemical properties of gold nanoparticles on indium tin oxide surfaces

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Metal nanoparticles have unique optical, electronic, magnetic, and catalytic properties that are often different from those of the bulk metals. These properties are currently under intense study for potential uses as optoelectronic components, spectroscopic enhancers, biological detection labels, and chemical sensing elements. For electrochemical measurements, much attention has been devoted to the modification of electrodes with metal nanoparticles, which is a promising approach to provide nano-structured functional interfaces [1].

In recent years, our group is studying on the fabrication method of gold nanoparticles directly attached indium oxide (AuNP/ITO) electrode. By utilizing the seed-mediated growth approach, which was developed for the wet synthesis of gold nanorods by Murphy et al [2], we successfully attached AuNP onto the ITO surface without using peculiar binding reagents [3]. A characteristic feature of the AuNP/ITO is the reduced charge transfer resistivity due to the nature of the direct attachment, which was verified using the electrochemical impedance measurement.

In our previous works, cetyltrimetylammonium bromide (CTAB) has been used as a capping reagent, which allowed some further modification [4] as well as the electron transfer reactions thorough the weaker capping. However, to know the effects of the capping reagents, we need to observe what happen if we used the different ones.

Thus, in the present work, we tried to attach AuNPs onto ITO in the presence of sodium dodecyl sulfate (SDS). SDS was selected because it is an anionic surfactant though CTAB is cationic. Moreover, it has been reported that, in solution phase, highly faceted pentagonal shaped AuNPs were synthesized in the presence of SDS [5].

As the result for optimizing the reduction conditions to promote the nanostructural growth of AuNPs on ITO, we could fabricate the AuNP/ITO even in the presence of SDS. Thus, the electrochemical properties were compared depending on the nature of the capping reagents, i.e., CTAB or SDS. The results of the electrochemical impedance measurements showed that the electron transfer resistivity was improved to a similar extent for both CTAB and SDS. In the cyclic voltammetric measurements of $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)_6^{3+/2+}$, no dramatic changes were observed due to the charges of the reactants and surfactants, so that it is expected that both surfactants are loosely capping the AuNPs. The detailed results will be presented at the meeting, together with the results of other capping reagents.

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Fabrication and characterizations of macroporous iridium oxide films

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Iridium oxide films are known to have great pH sensitivity, remarkable stability in both acidic and basic solutions, and unique electrochromic properties. In this study, iridium oxide films were anodically deposited on to Pt, glassy carbon and gold electrodes from alkaline solutions. The deposition solution was based on Yamanaka's recipe and consists of iridium tetrachloride, oxalic acid and potassium carbonate (pH 10) [1]. The deposition of iridium oxide film was carried out by cycling the electrode potential. Macroporous iridium oxide films were fabricated through a template made by self assembled polystyrene spheres. The templating procedure followed the method described by Bartlett et al [2] on both Au and ITO surfaces. The structured iridium oxide films were characterized by cyclic voltammetry in the growth solution and subsequentially in acid and base solutions. SEM (Fig 1) was used to assess the texture and morphology of the films while UV spectroscopy was used to probe the electrochromic properties. The presentation will highlight the fabrication and characterizations of these novel films.
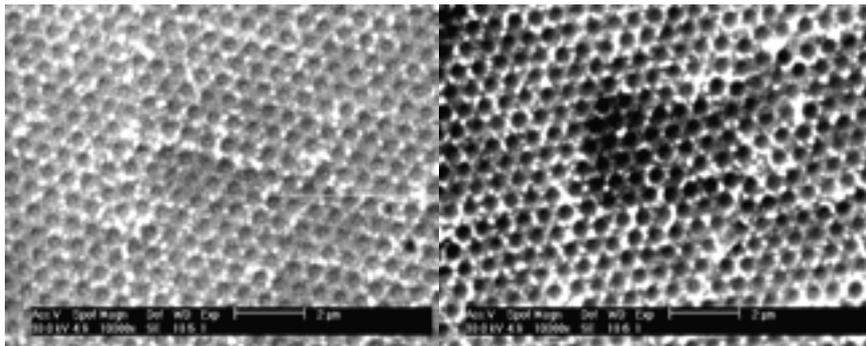

Fig. 1. SEM pictures of macroporous iridium oxide after 60 potential cycles (left) and 100 cycles (right) through a template made by 600nm spheres.

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Innovative Electrochemical Processes towards Industrial Applications

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The authors and coworkers have been extensively challenging to create and develop innovative molten salt electrochemical processes (MSEP), some of which are currently progressing towards commercialization steps.

Functional Nitride Films

Cathodic reduction of nitrogen gas occurs with sufficiently high current density, under moderate condition by using a nitrogen gas electrode in a molten LiCl-KCl system. This reaction can be used as a counter electrode for the electrochemical implantation of nitrogen atom into metal, to form various types of functional nitride film. For instance, in case of the electrochemical surface nitriding of stainless steel (SUS 304), an adhesive coherent nitrided layer was formed on the specimen surface and the hardness in the layer increased up to about 1300 Hv. And the layer can be formed both on the outside and inside surfaces of the thin tube homogeneously. This process is also applicable to synthesize various types of semiconductor and magnetic materials.

Functional Carbon Films

   Carbon film with interesting morphology can be electrochemically formed by a cathodic reduction of CO_3^{2-} ion dissolved in LiCl-KCl eutectic melt at, for instance,   723K. Here, total cathodic reaction is expressed as: $CO_3^{2-} + 4\ e^- \ \square\ C\ +\ 3O^{2-}$ Morphology of the electrodeposited carbon is drastically affected by the electrolytic conditions as well as the substrate metal, and by applying appropriate electrolytic conditions, the carbon film having interesting nano-structured construction can be obtained. Beside the function of surface coating of various substrate, this electrolytically deposited carbon film can be applied for an electrochemical capacitor and/or negative electrode of Li-ion battery. This process is also interesting from the viewpoint of the fixation of CO_2. When CO_2 is bubbled into the melt, it reacts with O^{2-} ion in the melt produced by reaction (1) to become CO_3^{2-}, according to the reaction:

$CO_2 + O^{2-}\ \square\ CO_3^{2-}$. The CO_3^{2-} ion thus produced is cathodically reduced to form functional carbon film. The remaining oxide ion can be oxidized at the anode to evolve oxygen gas according to the reaction: $2\ O^{2-}\ \square\ O_2\ +\ 4\ e^-$. As a result, CO_2 is electrochemically fixed in the form of 'valuable' functional carbon. On the other hand, when sufficiently reactive carbon is used as an anode, alternative reaction is the anodic dissolution of carbon. Thus, low quality carbon can be transformed to the valuable functional carbon film.

Plasma-induced Electrolysis to Form Fine Particles

Even in the case where one electrode is positioned outside over the electrolyte surface, plasma-induced stationary discharge makes continuous electrolysis possible under some appropriate conditions even under atmospheric pressure. By this process, various kinds of fine particles have been formed; Ag, Cu, Ni, Nb, Ta, C, TiO_2, WS_2, MoS_2 and C_3N_4. Especially, the fine particles of Nb and Ta thus obtained are attracting much attention from the viewpoints of commercialization. The bench-scale experiments have been conducted in success by the authors.

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Improved Potentiostatic Polymerization of Aniline in the Presence of Carbon Nanotubes

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Within the family of conductive polymers, polyaniline, because of its inexpensive monomer and diverse polymerization reaction, has attracted a special attention. Beside the mentioned reasons, electropolymerization can be processed from aqueous solutions. On the other hand, carbon nanotubes (CNTs) due to their uniqueness in nanomaterials are appropriate candidates for the development of novel polymer-based nanocomposite materials with enhanced functionality. Here, potentiostatic technique as an efficient electrochemical technique for electropolymerization was, but the key point is just exploiting the superb characteristic of CNTs within the electrochemical cell. As the matter of fact, this forthcoming conclusion comes from the comparative study of current transient curves in the presence and absence of CNTs (curves a and b, respectively). Beside the major difference in potentiostatic polymerization of two

discussed cases, SEM images also predicate a quite distinct morphology from what which has always been known as polyaniline morphology. It means that no individual carbon nanotube in the porous nanostructure of the film is observable, which according to solubility of CNTs in aniline does not sound unbelievable, so it could be easily guessed that CNTs do play their role in electropolymerization enhancement in a rather hidden trick. Consequently, the pores responsible for most of the surface area correspond to the void space between the particles. Because the resultaning product is a film of PANI/CNTs nanocomposites, through this classification increasing the strength of the bonding between the nanotubes and the polymer matrix in order to gain the overall strength, toughness and electrochemical properties of the composite material are worth of further discussion.
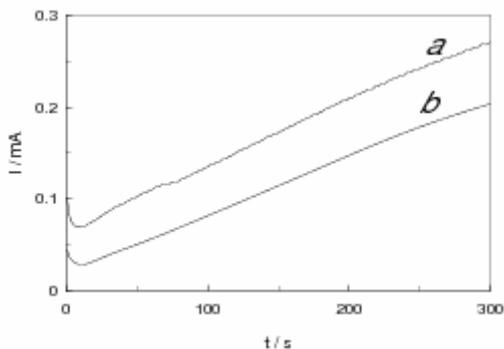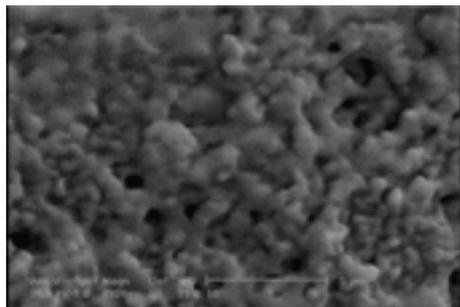
Interactive supported electrocatalysts for hydrogen and oxygen electrode reactions

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Since cohesive and free surface energy are linearly correlated with each other and with electrocatalysis for hydrogen electrode reactions, the stronger the intermetallic bonding, the less strong the adsorptive interaction of rate determining intermediates and the more active such a composite electrocatalyst arises. The same effect imposes the Strong Metal Support Interaction (SMSI) between the individual or prevailing hyper-*d*-interelectronic catalyst and usually hypo-*d*-oxide supports. Besides the strong *d-d*-bonding effect, there also arises the interactive spillover effect of primary oxides (M-OH), these being decisive for both cathodic CO oxidation and oxygen reduction (ORR). The present paper is primarily based on and introduces highly electronic conductive and SMSI Magneli phases (in average Ti_4O_7) along with their anatase titania surface modification as interactive supports for Low Temperature PEM Fuel Cells (LT PEM FC) and membrane-type hydrogen generator in water splitting. Since nanostructured electrocatalysts usually feature the SMSI effect only along the circumference of two phase interactive contacts, such an effect tends to its maximum when metallic catalyst distribution approaches monoatomic network dispersion and almost individual interatomic strong bonding with the interactive support. Such a SMSI Au upon anatase titania and Magneli phases has been shown to be interactively brought to feature the reversible properties of hydrogen electrode along with advanced CO tolerance. At the same time a monoatomic network of Pt dispersion upon Magneli phases exceeds all results achieved so far in electrocatalysis for the ORR and promises to approach the reversible oxygen electrode properties upon both acidic and even more so alkaline membranes. New trends towards higher middle temperatures (above 160 ºC), in particular with OH-conductive alkaline membranes, promise to reduce dramatically the corrosion requirements and even the significance of electrocatalysts based on noble metals, so that the entire phenomenon shrinks upon thermodynamic or thermal effects. Since in heterogeneous catalysis every single nanoparticle forms an independent and mutually integrated micro-reactor for the overall efficiency, the current collection represents a substantial problem in electrocatalytic systems where all particles should be current collected, but carbon carriers can not satisfy with about 30% of particles missing to be current collected. In such a respect high electronic conductive (1,000 S cm^{-1}) and rather strong *d-d*-bonding Magneli phases arose as an ideal and unrepeatable supporting material in electrocatalysis both for the LT PEM FC and water electrolysis. Unfortunately, at the present time Magneli phases expose a rather low surface per mass area (~ 1.2 m^2 g^{-1}) and the main intention has been to increase the latter to about 50 m^2 g^{-1}. Modification of Magneli phases by submonolayer of anatase titania (TiO_2) upon its exposed surface already satisfies such requirements and keeps conductivity almost unaltered, while a new approach with direct reduction of TiO_2 promises to resolve all problems..

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Electrocatalytic activity of platinum nanoparticles on oxidized support

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It has been shown that at least three factors: particle size, exposed crystal faces and oxidation state of carbon support determined specific activity of platinum supported on high area carbon materials including glassy carbon (GC). The aim of this work is to examine in detail the influence of the pretreatment of glassy carbon on the properties of electrodeposited Pt particles and their activity for methanol and formic acid oxidation in sulphuric acid.

Platinum was electrochemically deposited under the same conditions and similar loadings on polished or on GC substrate oxidized in sulphuric acid at different potentials and during 35 s and 95 s. The change of voltammetric charge, roughness, fraction of different functional groups and morphology of the electrode surface depends on the potential and time of polarization and proceeds through the three stages in the electrochemical activation process. The higher the potential and/or the longer the time of polarization of GC prior to Pt deposition is, the smaller are Pt agglomerates as well as particles. However, if GC is oxidized at higher potential during longer time than, as the roughness is also higher, low number of agglomerates are observed on the surface while majority of smaller agglomerates are in the cracks. The electrocatalytic activity of the GC/Pt electrodes for oxidation of methanol as well as formic acid oxidation depends on the conditions applied in the oxidation of the support (Fig. 1).
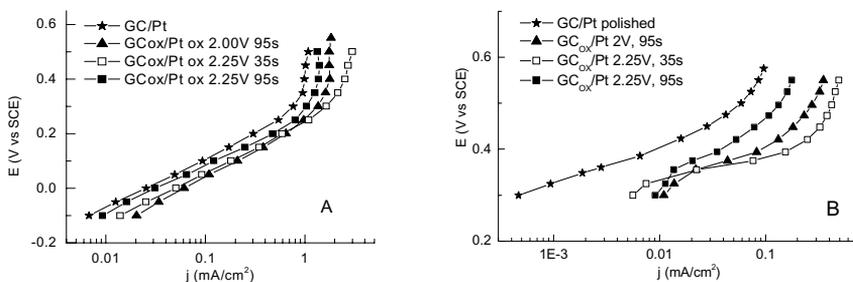

Fig.1: Tafel plots for the methanol (A) and formic acid (B) oxidation in 0.5 M H_2SO_4 solution at GC/Pt and GC_{OX}/Pt electrodes. Sweep rate: 1 mV s^{-1}.

The activity is increasing as the roughness of GC increases upon oxidation up to some optimal state after which further increase in roughness of GC is too high and the consequence is the decrease in electrocatalytic activity of GC_{OX}/Pt electrode.

The reduction of oxygen on multi-walled carbon nanotubes modified highly oriented pyrolytic graphite electrodes

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Carbon nanotubes (CNTs) are novel nanomaterials, which reveal unique electronic, chemical and mechanical properties. The electronic behaviour of CNTs reveals that they have the ability to promote electron-transfer reactions, which is the main reason why they possess a remarkable electrocatalytic activity toward O_2 reduction in alkaline media [1, 2]. This makes CNTs very promising in electrochemical applications [3,4]. The aim of the present work was to study the applicability of multi-walled carbon nanotubes (MWCNT) for the electrochemical generation of H_2O_2. The electrochemical reduction of oxygen has been studied on MWCNT modified highly oriented pyrolytic graphite (HOPG) electrodes in 0.1 M KOH solution using the rotating disk electrode (RDE) technique. HOPG was used as an electrode substrate due to its inactivity toward O_2 reduction [5]. We investigated the O_2 reduction behaviour of MWCNT/HOPG electrodes of various modifications. As the first method, MWCNTs were dispersed in water in the presence of an anionic surfactant dihexadecyl phosphate (DHP) achieving the MWCNT-DHP film-coated HOPG electrode. It was found that a stable and uniform MWCNT-DHP film formed. The RDE data showed that O_2 reduction occurs via two steps, first to HO_2^- and then to OH^-. Alternatively, MWCNTs were dispersed in DMF and MWCNT coated HOPG electrodes were achieved. To obtain a stable MWCNT film, the electrode was finally covered with a Nafion layer. According to the RDE results the number of electrons exchanged (n) was close to 3.5. As the third procedure, multilayer film of MWCNTs was assembled on HOPG electrode with layer-by-layer (LBL) method, based on electrostatic interaction of poly(diallyldimethylammonium chloride) and MWCNTs. These electrodes showed a lower activity as compared to the previous ones and the value of n was close to 2.5. Finally, MWCNTs were abrasively immobilised onto HOPG surface. An activity decrease was observed during the RDE measurements, which is probably related to the desorption of MWCNTs from HOPG. Apparently, the abrasive immobilisation of MWCNTs is not a suitable method for the preparation of electrodes for the oxygen reduction electrocatalysis.

On the basis of the results obtained with variously modified MWCNT/HOPG electrodes it is concluded that these electrodes are active catalysts for O_2 reduction.

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Elecrochemical Impedance Study of Polyaniline on carbon fiber microelectrode.

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The electrochemical (EC) capacitor is an important device in energy storage and conversion systems. This device attracts significant attention due to its promising application in high pulse power devices of energy storage systems. Recent interest in EC capacitors has been stimulated by their potential application in parallel with batteries in hybrid electric and electric vehicles. The capacitance of an EC capacitor arises mainly from the redox reaction on/within the electrode materials[1,2] Current attention has been focused on conducting polymers especially, polyaniline(PANI), due to the existence of several oxidation structures, the intrinsically chemical stability, and a low preparation.
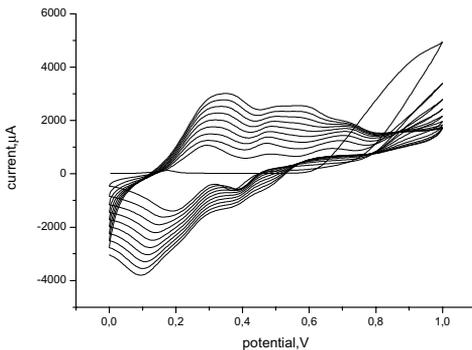

Figure1. Electropolymerization of An on CFME in 0.5M H_2SO_4.at 100mVs^{-1} +0.1M aniline aqueous solution.

In this study, Aniline (An) was electropolymerized on carbon fiber microelecrode(CFME) in 0.5 M H_2SO_4. The characterization of Polyaniline(PAN) thin film was achieved with cyclic voltametry(Figure1) and electrochemical impedance spectroscopy(Figure2). Also potential effect of PANI on capacitor behavior was studied.

Nano-structured electrocatalyst as nano-electrode array with superior analytical performances

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Miniaturization to nano-scale usually creates new scientific and technological fields, and electroanalysis is not an exception. Improved analytical characteristics of amperometric sensors can be achieved by decrease of electrode dimensions resulting in hemi-spherical profile of analyte diffusion. In case of single electrode, however, this causes requirements to measure very low currents. To overcome this problem it is convenient to use micro-electrode arrays.

To form nano-electrode arrays we propose nano-structuring of electrocatalyst onto inert electrode support. Indeed, if background electrode reaction is negligible, analyte fluxes are directed to islands of electrocatalyst, which thus behave as nano-electrodes. The highest signal-to-background ratio has been achieved for deposition of Prussian Blue (a superior electrocatalyst for hydrogen peroxide reduction) through sol-gel templates based on vinyltriethoxysilane. As compared to unstructured electrocatalyst the signal-to-background ratio was improved by an order of magnitude.

AFM investigation confirmed nano-structuring of the electrocatalyst.

Except for improved signal-to-background ratio, nano-electrode arrays are expected to be characterized by much faster equilibration of diffusion fluxes at the electrode surface. This may cause flow-injection response to ultra-low analyte concentrations.

Indeed, hydrogen peroxide sensor based on nano-structured Prussian Blue in FIA mode displayed: (i) sensitivity similar to unstructured electrocatalyst (0.7 A L mol^{-1} cm^{-2}), (ii) linear calibration range prolonged over 7 orders of magnitude of H_2O_2 concentration with (iii) its lower limit of 10^{-9} mol L^{-1} (0.03 ppb) H_2O_2; the latter is two orders of magnitude lower as compared to the sensor based on conventional (unstructured) Prussian Blue. The 100 times decreased detection limit without loss of sensitivity seems to be at the limiting level for sensor improvement by forming of micro- or nano-electrode arrays.

The linear calibration range prolonged over 7 orders of magnitude of analyte concentration with its lower limit of 10^{-9} mol L^{-1} (0.03 ppb) H_2O_2 achieved for the Prussian Blue based nano-electrode arrays are record in electroanalysis.

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Effect of annealing on electrodeposited Ni-Cu/Cu superlattices

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In this work a large number of Ni-Cu/Cu metallic superlattices were grown on strongly (100)-textured polycrystalline Cu substrates using electrodeposition. The structure of the superlattices was investigated using XRD. In most of the diffraction patterns satellite peaks, due to the existence of a superlattice structure, were observed. The XRD results show that the superlattices also have a strong (100)-texture, probably indicating epitaxial growth. Figure 1 shows a part of a high angle x-ray diffraction pattern measured for a 130×[Ni-Cu(60Å)/Cu(20Å)] multilayer. The fact that up to second order satellite peaks are observed corresponding to the period of the multilayer demonstrates that a sharp interface has been achieved.
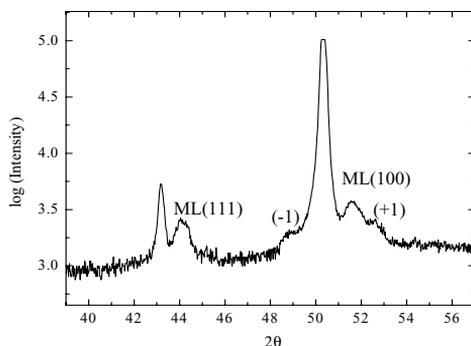

Figure 1. A part of high angle x-ray diffraction pattern of a 130×[Ni-Cu(60Å)/Cu(20Å)] multilayer before annealing.

In order to study the effect of annealing temperature on the interface structure of the bilayers a number of the electrodeposited Ni-Cu/Cu multilayers were annealed for different times and temperatures under a vacuum of 10^{-3}torr. The results show that the amplitude of the satellite peaks begins to decrease at 300 ^{o}C after an hour and disappears at 600 ^{o}C after 3 hours. Figure 2 shows the high angle x-ray diffraction pattern for the latter case.

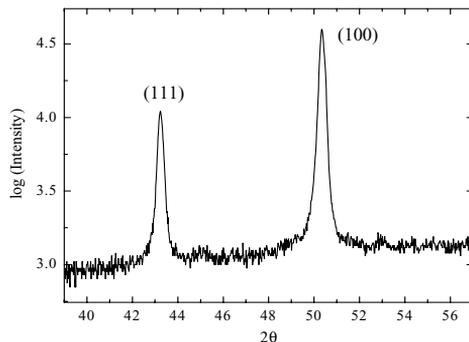Figure 2. A part of high angle x-ray diffraction pattern of a 130×[Ni-Cu(60Å)/Cu(20Å)] multilayer after annealing at 600 ^{o}C for 3 hours.

Effect of substrate cleaning on the growth of MgO nanowires

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CO_2 is a cheap and abundant "green carbon source" for production of organic chemicals and fuels. The transformation of CO_2 into organic substances is a promising long-term objective. The electrochemical reduction of CO_2 appears to be an attractive means for removing from the atmosphere and converting it into more valuable chemicals[1]. In this paper, we report, for the first time, the electrocatalytic synthesis of C_{12} organic compound from CO_2 and H_2O on nanocrystalline TiO_2 (nano TiO_2) film electrode by controlled potential electrolysis

Experimental

The nanoTiO_2 film modified titanium (Ti/nanoTiO_2) electrode was prepared by direct hydrolysis precursor $Ti(OEt)_4$. The electrochemical measurements were carried out using a CHI model 660A (USA CH Instrument) electrochemical workstation with a three-electrode system at room temperature. The electrochemical reduction of CO_2 (purity 99.9%)was performed in a divided H-type cell with an ion exchange membrane by cathodic polarization at –2.0 V *vs* SCE for 9 hours. The product of the catholyte was extracted by using ethylactetate-methanol(8:2, v/v) and the sample of the extracting agent was distilling under reduced pressure at 30℃. The products were characterization by UV-vis and mass spectrum(MS), Fourier transform infrared (FTIR) reflection absorption spectroscopy, ^{1}H NMR and ^{13}C NMR spectrum.
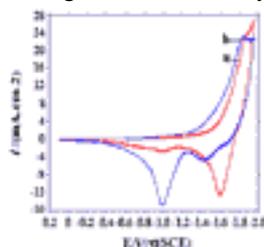
Results and discussion

Fig. 1 shows the cyclic voltammograms of the Ti/nanoTiO_2 electrode in 0.5 mol.cm^{-3} K_2SO_4 solutions saturated with N_2 (a) and CO_2 (b), respectively. There were two pairs of well-defined redox peaks for nanoTiO_2 film electrode in correspondence with TiO_2/Ti_2O_3 and $TiO_2/Ti(OH)_3$ [2] couple (Fig. 1a). In 0.5 mol.cm^{-3} K_2SO_4 solutions saturated with CO_2 (Fig.1b), the onset (starting) potential of cathode current was shift negative approximately 0.2V and the anodic peak (I_{a2}) of the $TiO_2/Ti(OH)_3$ couple was almost absent. It is evident that heterogeneous elctrocatalytic reduction of CO_2 were carried out by the surface Ti^{IV}/Ti^{III} redox system and the high oxidative peak at -1.0V (*vs* SCE) was mainly caused by the reoxidation of a product generated in the cathodic reduction of CO_2.The prolonged electrolysis of CO_2 on nanoTiO_2 film electrode at – 2.0 V (*vs.* SCE) was performed in 0.5mol.dm^{-3} K_2SO_4 aqueous solution. The products were characterization by UV-vis, MS, FTIR, ^{1}H NMR,^{13}C NMR spectrum with molecular formula $C_{12}H_{10}O_8$ (1,1-diformoyl-2-propenyl oxalate). The process for forming the product could be due to the following reaction:

$$12CO_2 + 42H^+ + 42e^- \longrightarrow C_{12}H_{10}O_8 + H_2O \quad (1)$$

Fig. 1 Cyclic voltammograms of the Ti/nanoTiO_2 electrode in 0.5 mol.cm^{-3} K_2SO_4 solutions saturated with N_2 (a) and CO_2 (b). Scan rate: 100 mVs^{-1}.

Acknowledgments

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Elecrochemical Nanotechnology

Mesoporous metal oxide electrode materials for pseudocapacitors

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Interests in the development of electrochemical capacitors for high power applications have greatly intensified in recent years. On the basis of the electrode material and the charge storage mechanism, electrochemical capacitors are classified into: (a) electrical double-layer capacitors (EDLCs) that employ carbon electrode materials with high surface area, and (b) pseudocapacitors (or supercapacitors) in which electroactive materials such as transition metal oxides or conducting polymers are employed as electrodes.

Among several transition metal oxide electrode materials for pseudocapacitors, hydrous ruthenium oxide shows a high capacity over 700F/g and excellent cyclability in aqueous H_2SO_4. Because of its high cost, alternative metal oxide electrode materials are being searched to replace ruthenium oxide, e.g. NiO_x, CoO_x, MnO_2, etc. Compared with RuO_2, however, these transition metal oxides exhibit lower electrochemical capacitive performance.

Electrode materials with a large surface area and a highly porous structure would effectively combine high energy with high power characteristics required forpseudocapacitors. Materials characterized by a bicontinuous structure of a solid phase surrounding pores in the range of a few tens of nanometers would be excellent candidate materials for high-performance pseudocapacitors.

It is well known that mainly the micropores (<2 nm) are not easily accessed by the liquid electrolyte and the exposed surface in micropores may not be utilized for charge storage whereas the mesopores (2~50nm) can play an adsorption and transporting role, especially for high rate condition in EDLC.

High surface area metal oxide materials containing regularly interconnected mesopores are highly desirable for the pseudocapacitor electrodes. Mesoporous electrode materials would allow the electrolyte to deeply penetrate within the solid phase. And very thin solid phase of the material would further reduce the length of the ionic diffusion paths for the ions participating in electrochemical reaction. In addition, increased electric conductivity of the electroactive material in the electrode is very important to improve rate capability of a pseudocapacitor.

We tried to improve the electrochemical performance of the electrodes based on metal oxides introducing an ordered mesoporous structure into metal oxide materials. For this propose, we prepared mesopoous metal oxides and meporous metal oxide/carbon composite electrode materials by liquid template method.

More details about mesoporous metal oxides and/or mesoporous metal oxide/carbon composite synthesis and their structural and electrochemical properties will be presented at the meeting.

The effect of charge and counter ions on the stability and thiol exchange of MUA-capped Au-nanoparticles

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Water-soluble nanoparticles are becoming more important due to their possible applications in biosciences. Therefore the stability and functionalisation of these particles is a highly relevant topic for research. They very often have charged acid-groups on the surface, which are very sensitive to ionic strength and the type of counter-ions present in the system. Small counter ions can induce bridging and aggregation through ion pairing. It is postulated that this could be avoided by using larger counter-ions, giving a larger charge separation. Zeta potential measurements offer a means to study thiol exchange reactions on a nanoparticle surface when charged species is exchanged to a neutral one.
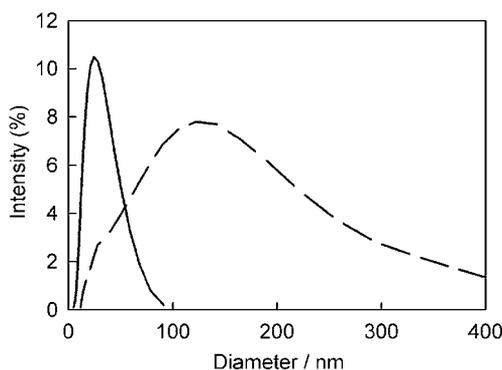
Figure 1. Size distributions of MUA-capped Au-nanoparticles in 10 mM NaOH (dashed) and 5 mM TEAOH (solid) measured with dynamic light scattering. In presence of Na^+ large nanoparticle aggregates are formed.

Place exchange and particle stability were investigated using mercaptoundecanoic acid (MUA) stabilized gold-nanoparticless as a model system. It was clear from the experimental data obtained that the counter-ion has a marked influence on the stability of the nanoparticles as is seen in figure 1. Small cations such as Na^+ caused the particles to form >50 nm aggregates in solution due to electrostatic coupling of the ligand shells and could induce particle precipitation at relatively low concentrations. This effect, however, was not seen with larger cations e.g. the tetraethylammonium (TEA^+) ion, which gives a better charge separation and limits particle cross-linking. Place exchange was studied by exchanging MUA-groups to mercaptoethylamine groups.

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Electrosynthesis of Metal Oxide Nanorods

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One dimensional (1D) nanostructures have been attracting intense scientific interest owing to their novel properties and potential applications for the development of nanodevices. For example, 1D ZnO nanostructures exhibit near-UV emission, UV absorption and field-emission capabilities.[1] Electrochemistry plays a vital role in nano-science and nano-technology. It offers novel routes to create nanostructures. We have successfully developed one electrochemical method to fabricate metal oxide nanorods.

Templated electrosynthesis has been employed widely to prepare solids of defined dimension.[2] Here we illustrate how electrochemistry can be employed to manage the pH within the pores of a template and demonstrate that controlled growth of continuous metal oxide nanorods can be achieved. The strategy is exemplified by the growth of zinc oxide nanorods and tin oxide nanotubes. At room temperature, the reduction of hydrogen peroxide within pores was employed to electrogenerate hydroxide ions and drive local precipitation of polycrystalline zinc oxide nanorods. Rods shown in Fig. 1, which displayed the same growth direction along their entire length, were obtained when growth was performed at 90 $^{\circ}$C using the reduction of nitrate as the electrochemical source of hydroxide. The relationship between the length of ZnO rods and the integrated charge passed has been studied.
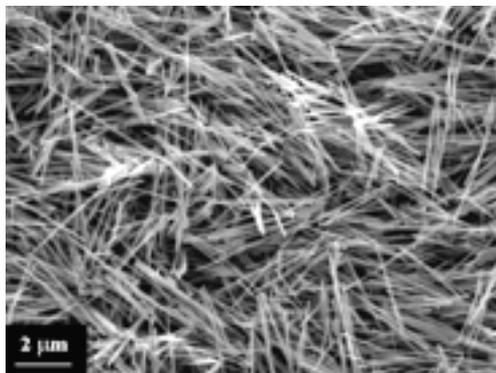

Fig. 1. FE-SEM images of ZnO nanorods prepared at 90 $^{\circ}$C using nitrate ions as hydroxide precursor.

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Single Molecule Conductivity of Aromatic Bridged Alkanedithiols

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The drive to move away from silicon as the base of all electronic devices is being spearheaded by research into organic compounds. The aim is to understand better the processes of electron transport through organic molecules and investigate structures with the potential to serve as alternatives to current technology. In our study we have looked at linear hydrocarbon molecules terminated by thiol groups at both ends. Specifically we have investigated the phenomenon of electron hopping through molecules consisting of alkyl chains bridged by conjugated aromatic groups, such as benzene and 4,4'-bipyridyl. Synthesis of these molecules was followed by conductance measurements on an STM (scanning tunnelling microscopy) machine, which involved a gold tip being brought into close proximity to a gold (111) surface having a low phase coverage of adsorbed organic molecules. When a molecule bridges the tip-substrate junction a change in the tunnelling current is observed. The tunnelling current between tip and substrate is measured as either a function of distance, (I_s), or as a function of time, (I_t). This change is understood to be due to the presence of an organic molecule. STM conductivity measurements reveal that electronic transport through the molecules is facilitated by the presence of the aromatic groups when compared to alkanedithiols of similar length. We believe these groups act as 'hopping centres', providing a less resistive pathway for the electrons to tunnel along.

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Synthesis of FexOy nanostructures by the HF dipping of Fe foils

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In the past decade, considerable attention has been drawn towards nanostructured materials, including nanotubes, nanorods, nanoparticles, nanosheets, and nanowires, becasue of their interesting physical properties and their wide range of potential applications in nanodevices. Much effort has been made to understand the magnetic, electronic, and optical properties of these nanostructures because they exhibit novel physical and chemical properties, differeing from those of their bulk counterparts, due to their reduced size and large surface-to-volume ratios. To date, various approaches, including thermal evaporation, chemical vapor deposition, laser ablation, and solution-based process, have been developed for the preparation of nanostructured magnetic materials such as magnetic metals, alloys, and metal oxides. To the best of our knowledge, there are rare reports on the growth of 1D nanostructures or related nanostructures by simple dipping the metal foil into the chemical solution. Iron oxides are widely used as semiconductor, recording material and photocatalysts. Accordingly, in the present work, we report the successful production of FexOy nanostructures by the simple dipping of Fe foil onto the HF solution. We have discussed the possible growth mechanisms. The as-synthesized products were characterized by X-ray diffraction, field emission scanning electron microscopy, and transmission electron microscopy.

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Elecrochemical Nanotechnology

Nano-porous Titanium Oxide Thin Films on Copper Cladded Polymers for Embedded Capacitors

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Embedded capacitor technology can improve electrical performance and reduce assembly cost compared with traditional discrete capacitor technology. Nano-porous TiO_2 thin films on Cu cladded polymers have been of great interest as embedded capacitor material because they has the following benefits: better electrical performance, higher reliability, lower cost and improved design options.

Embedded capacitors refers to capacitors as passive devices which are mounted as parts of a printed circuit board(PCB). The most important advantage of the embedded capacitor PCB is that since the capacitors are mounted as parts of the PCB, there is no need to mount the capacitors on the surfaces of the PCB.

To improve the capacitance density of the TiO_2 embedded capacitor on Cu cladded fiber reinforced plastics(FR-4), the specific surface area of TiO_2 thin films were enlarged and the morphologies were controlled by anodization process parameter variations.

Nano-porous TiO_2 thin films were grown from the titanium metal films using an anodic oxidation process, from which high capacitance density embedded capacitors were fabricated. Titanium films sputter deposited on Cu cladded polymer were anodized in a fluorine containing electrolyte to obtain the nano-porous morphologies. The current changes during the anodization were observed to control the microstructures of the nano-porous TiO_2 layers. The crystal structure of titanium oxide films prepared in the H_2SO_4 solution was a mixture of Anatase and Rutile and contained nano-sized pores. Nano-porous TiO_2 thin films with Pt top electrode show the capacitance density of 244 nF/cm^2 at 1 MHz, the breakdown voltage of 9 Volts, and the leakage current of 20 μA/cm^2 at 3.3V.

Herein, we will discuss the morphologies, structure and electrical characterizations of the nano-porous TiO_2 layers which is fabricated by the anodic oxidation in the electrolyte and with the external biases.

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Elecrochemical Nanotechnology

MODELLING NANOSTRUCTURE STABILITY: FROM NANODOTS TO NANORIPLES

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The fabrication of metal and semiconductor nanostructures with a given size and spatial order on metal or semiconductor surfaces is a key point in many fields of nanotechnology [1]. In particular, the preparation of dots and ripples in different materials has attracted considerable attention. Metallic ripples have been used as platforms to build anisotropic magnetic nanostructures by deposition of ultrathin layers of transition metals [2]. Metal electrodeposition is a well known technique involving relatively low cost equipments and it is currently used in many technological applications. Electrodeposition on patterned templates is particularly attractive to build metallic, oxide and semiconductor nano/microstructures [3] because extremely low amounts of material can be deposited in a controlled way by changing the applied potential (or current). Recently, we have performed experiments where silver nanodots and nanoripples were grown on nanocavity-patterned Au templates by controlled electrodeposition [4]. By controlling the amount of deposited Ag dots ≈ 40 nm in average size and ≈ 4 nm in average height can be grown with spatial and size distributions dictated by the template. The dots were found to be in a metastable state. Further Ag deposition turned the dot surface structure into nanoripples formation.

In the present work we tackle the transition from dots to ripple regime by means of computer simulations. We model this type of phenomena by means of the Ising model [5] and analyze the metal deposition of different surface structures with this type of defects under different conditions.

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Electrochemistry of Low Dimensional Metallic Nanostructures. Monte Carlo Simulations and Phenomenological Approach.

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The formation of metallic nanostructures on foreign metal and semiconductor surfaces plays an important role in modern nanotechnology. The usual fabrication procedure is carried out at solid/vacuum interfaces under UHV conditions. However, electrochemical nanostructuring at solid/liquid interfaces has great advantages in this field because local supersaturation or undersaturation can be precisely adjusted and rapidly changed via the electrode potential [1]. Super and undersaturation determine the number of metal atoms in the critical nuclei and growth mode of the subsequent electrochemical growth process. On the other hand, surface defects may serve as nucleation centers, from which the new phase emerges. In the present work the energetic stability of a set of 36 adsorbate/substrate(111) couples involving Au, Ag, Cu, Ni, Pt and Pd is analyzed for perfect metal surfaces and for metal surfaces with different types of defects. A Monte Carlo annealing at low temperatures is performed to obtain the minimum energy configurations. The results of the simulation are used to check some theories employed to calculate the binding energy of atoms on surfaces from simple energetic considerations, and a new phenomenological formulation is developed. The latter can be employed to predict the existence of underpotential deposition in the case of several types of 0-dimensional structures.

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Elecrochemical Nanotechnology

DFT study of oxygen and water adsorption onto a graphite layer modified with titanium

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Recent studies have shown that titanium decoration of carbon nanotubes remarkably increases the capacity of the latter for hydrogen storage from the gas phase [1]. In the present study, the behavior of a single carbon layer (SCL) modified with titanium is studied in presence of oxygen and water. The blocking of hydrogen adsorption sites by the adsorption of oxygen molecules is analyzed. Furthermore, the interaction of the substrate with water is considered. The present results are relevant for electrochemical hydrogen storage, since in the latter case the hydrogen stored comes from water electrolysis.

The SCL was considered as an infinite system by means of periodic boundary conditions in x and y directions. For oxygen and water adsorption, the minimum energy path was found by means of the nudged elastic band method and density functional theory (DFT) calculations employing the SIESTA computer code [2], which uses a localized basis set to represent the Kohn-Sham orbital. Exchange and correlation effects were described using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [3]. The basis set used was a double-ζ one plus polarization quality.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Formation and Characterization of Metal Nanoparticles at Interfaces using Scanning Electrochemical Microscopy

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Scanning electrochemical microscopy (SECM) offers a novel approach for the formation of micrometer- and nanometer-sized metal structures at interfaces beneath an ultramicroelectrode (UME) tip [1] and for the characterization of reactions at nanostructured interfaces [2]. Here, we present the first study using SECM to deposit metal structures at liquid/liquid interfaces and to determine the underlying kinetics. Ag particles have been electrodeposited at the 1,2-dichloroethane (DCE)/water interface by anodic dissolution of an Ag UME positioned in the aqueous phase close to the liquid/liquid interface [3]. Ag^+ ions diffuse to the liquid/liquid interface and undergo reduction by an electron donor (decamethyl ferrocene) which is confined to the DCE phase. We show how the resulting current-time behaviour for potentiostatic experiments provides information on the nucleation and growth kinetics. The use of the method to study other metal deposition processes is also considered. In a separate aspect, the use of SECM to investigate nanoparticle-catalyzed processes has been examined. The hydrogen evolution reaction (HER) catalyzed by Pd and Pt nanoparticles supported on solid substrates has been characterized and investigated by SECM. The dependence of the kinetics on pH and the effective particle concentration has been studied thoroughly; the catalytic efficiency of these nanoparticles for hydrogen generation has been demonstrated.

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Photocatalytic Oxidation of Methyl Orange Using a Silver Loaded Ti/TiO$_2$ Nanostructure Electrode

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The photocatalytic oxidation and reduction reactions on the surface of TiO$_2$ have been widely investigated as an effective method to environmental purification since the Honda-Fujishima effect [1] was discovered. Many efforts have been made to solve the problem of low photocatalytic efficiency and the difficulty of separationg particles from aqueous solution.[2,3]

In this paper, a novel Ti/TiO$_2$ nanostructure electrode as a new type of electrode was produced by electrochemical anodization process.[4] To evaluate the photocatalytic efficiency, methyl orange (MO) was used as dye pollutants for photoelectrocatalytic oxidation under UV irradiation. The effects of structure, surface morphology and anodic bias on its photocatalytic activity were investigated in the lab. The photocatalytic (PC) oxidation and PEC oxidation of MO in aqueous solution were investigated. It is found that the highest MO photocatalytic activity is achieved by the 5 min photochemical reduction with silver content around 0.16 wt% on Ti/TiO$_2$ nanostructure electrode with 450^{0}C pretreatment. The photocatalytic activities are strongly dependent on the amount of deposited silver nanoparticle. The lower loaded silver can increase the color removal efficiencies, while higher silver content decreases the color removal efficiencies due to the blocking of UV light by the over-coated silver grains. The kinetic constant of MO degradation on the optimal content silver loaded on the Ti/TiO$_2$ (0.16 wt%) nanostructure electrode is four times faster than that without silver nanoparticle doping. Moreover, it is demonstrated that the PEC oxidation by applying an anodic bias between the Ti/TiO$_2$ electrode and Pt electrode can also significantly enhance the MO degradation rate compared with the PC oxidation. It is attributed to the extension in lifetime of the active photoholes and the reducing sites of photoelectro-hole recombination in the degradation reaction.

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In-situ FTIR Spectroscopy Studies of Hypermec Catalysts for Ethanol Fuel Cell

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Hypermec anode and cathode catalysts are platinum-free and designed for use in anionic fuel cells. These catalysts offer a low-cost alternative to those traditionally used and for the first time allow the use of ethanol, a renewable material, as fuel.

These catalysts are nano-fabricated using a patented templating technology which organises stable nano-sized metal alloys and controls their size to below one nanometre on the surface of a support, typically carbon. In this case the anode uses an equal mixture of iron, cobalt and nickel while the cathode is based on cobalt and iron.

The reactivity of the Hypermec catalyst towards the electro-oxidation of ethanol in alkaline solution has been studied by in-situ FTIR spectroscopy as a function of potential and concentrations of ethanol and electrolytes. It has been shown clearly that the complete oxidation of ethanol on the anode catalyst to CO_2 and bicarbonate (see figure 1a) has been achieved and that no reaction of ethanol on the cathode catalyst over a wide range of potential (e.g., up to 1.400 V vs Ag/AgCl in 0.2 M NaOH + 0.5 M EtOH) detected (see figure 1b) which indicates a high tolerance towards ethanol.
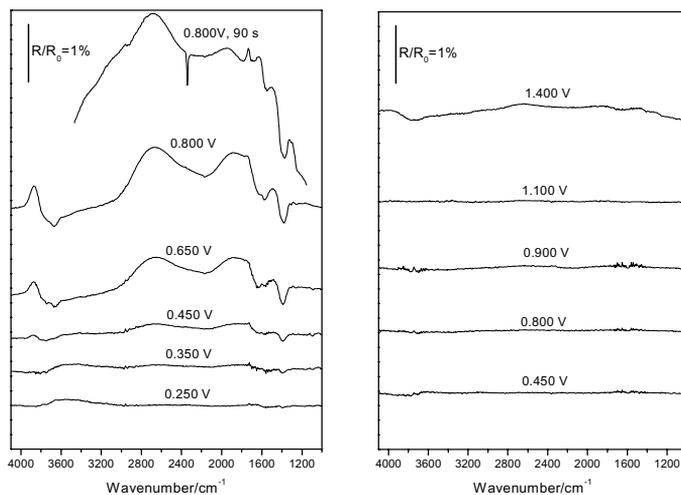
Figures 1a and 1b. In-situ FTIR Spectra (100 co-added and averaged scans at 8 cm^{-1} resolution, 16 s per scanset) collected from the anode catalyst (a ,left) and cathode catalyst (b, right) supported on Ti electrodes in 0.5 M C_2H_5OH + 0.2 M NaOH at room temperature. The spectra were calculated against a reference spectrum taken at -0.150 V vs Ag/AgCl.

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Size effects of Pt and Pt-Ru particles on ethanol oxidation

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In recent years ethanol has attracted increasing research attention as an alternative fuel for fuel cells. [1] Although a number of materials were studied for their catalytic activity toward ethanol oxidation, the particle size effects of the catalyst has not been found in the literature, to the authors' best knowledge. This paper presents our experimental data for the size effects of Pt and PtRu (atomic ratio 1:1) nanoparticles on deposited Au microdisk electrodes (φ30 µm). The nanoparticles were electrochemically deposited using the double-pulse method. The particle size was estimated according to SEM images and the deposited mass was calculated according to the charge passed during deposition. The total surface area of Pt nanoparticles was calculated from the charge of adsorbed hydrogen on the CV curves in background solution and the surface area of a PtRu particle was assumed to be equal to that of a Pt particle of the same size. Polarization curves of ethanol oxidation were recorded in 0.5 M H_2SO_4 + 1 M ethanol, at a potential scan rate 10 mV/s.

The results obtained at 60°C are given in Figure 1. The specific activity j per unit surface area of the PtRu nanoparticles increases with particle diameter d up to 5 nm and levels off when the size grows further. In contrast, Pt shows a maximum specific activity near 4 nm. The trend was found to be similar at 25°C. More data will be presented at the meeting and discussed together with the saturated adsorption coverage θ_s of oxygen and ethanol on Pt particles obtained using programmed polarization method (Fig. 2).

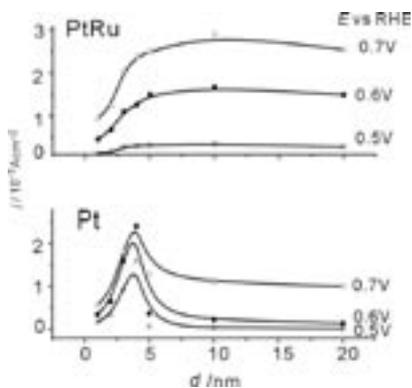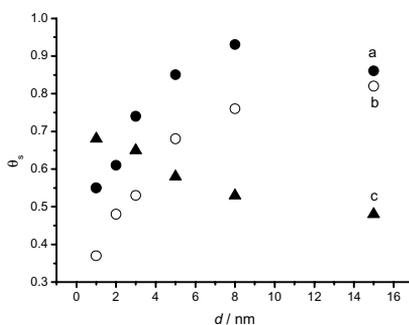

Fig. 1 Plot, j vs. d

Fig. 2 Plot, θ_s vs. d . a and b: θ_s of ethanol at 25^{0}C and 60^{0}C. c: θ_s of oxygen atom on Pt particles.

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Size effects of Au nano particles on borohydride oxidation

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The size effects of Au nano-particles deposited on Au micro disk electrodes (diameter 30 μm) for BH_4^- oxidation in KOH solution is presented in this abstract.

The nano Au particles were electrodeposited by the double pulse potential step method. The particle size was estimated by SEM observation.

In order to know the behaviours of BH_4^- oxidation on the nano-particles, the current generated by the substrate Au surface not covered by particles was subtracted. When the coverage of nano-particles was low, the nano-particles can be considered to be independent to each other. As a result, the nano-particle modified microelectrode is equivalent to an assembly of a large number of nano-electrodes (denoted as NEA).

In Fig.1, the anodic peaks (A1 and A2) and the cathodic peak (B) correspond to BH_4^- direct oxidation on NEA, the oxidation of intermediates on partially oxidized Au surface and the adsorption of intermediate BH_3OH^-, respectively [1]. The current density of peak A1 increases and peak potential shifts negatively with decrease of the particle size. The specific activity (per surface area), the mass activity and the electron number (n) of peak A1 increases with the decrease of particle diameter, d, and n approaches 8 when the particle diameter goes down to 5nm. When diameters are below 10 nm the currents increase rapidly, as shown in Fig. 2. The ratios of anodic peak A2 and cathodic peak B to A1 decrease with the decrease of particle diameter. The possible reason for these phenomena will be discussed.
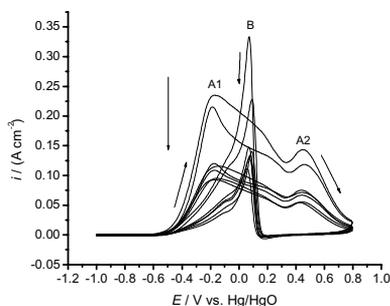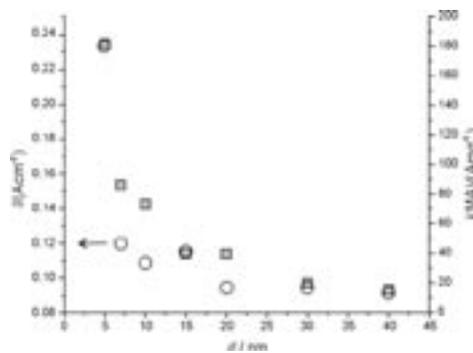
Fig. 1

Fig. 2

Fig 1 CV on nano Au assembles at 20Vs⁻¹ in 0.012M NaBH₄+2M NaOH. The leftest arrow indicates the sequence of diameter decrease : 5, 7,10, 25,20, 30, 40 nm.

Fig. 2 Plot of i_p vs. d. circles: surface specific activity; squares: mass specific activity.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Electrodeposited nanostructured substrates for NIR-SERS

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Surface-enhanced Raman spectroscopy (SERS) is a very sensitive and selective technique for detecting surface species. Mostly ultra-violet (UV) and visible excitation laser sources are used in SERS experiments. This can cause photochemical reactions on the surface apart from fluorescence from the adsorbed molecules, which could be particularly disadvantageous with biomolecules. A way to circumvent this possibility is the use of near infra-red (NIR) laser sources. However, this would warrant appropriate design of substrates for NIR-SERS for obtaining maximum enhancement of signals from analytes.

Colloidal crystal templated 'inverse opal' nanostructured gold films have been demonstrated to be excellent SERS substrates [1, 2]. Most reports in the literature use UV-visible laser excitation. Also, though the optical and enhancement properties of SERS substrates have been found to be structure dependent [3, 4], no reports exist wherein such substrates are targetted and tailored for use with a particular excitation wavelength, especially in the NIR region, for SERS. In the present study, we use variation in sphere size of colloidal templates and electrochemical control over film height to tune substrates for NIR-SERS for use with a 1064 nm laser source. Proper combination of the two parameters of sphere size and film height resulted in significant enhancement of signals from the adsorbed analyte. We demonstrate the effect of matching incident and scattered radiation with plasmonic resonances on the enhancement of Raman bands of benzene thiol adsorbed on our nanostructured gold substrates. Our study proves the feasibility of design and empirical fruition of reproducible NIR-SERS substrates.

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Characterization of ZnSe thin films prepared by electrodeposition

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Thin films of semiconductors are commonly used for the fabrication of cost-effective solar cells. The ability to grow compact and device quality semiconducting films using electrodeposition is of considerable technological interest. ZnSe is a wide band gap (2.7 eV) semiconducting material, which finds application as a promising material for the optical devices such as LED in the short wavelength region. Also it has been identified as an important alternative material to CdS, as a window material in hetero-junction solar cells, resulting in a higher efficiency by means of admission of more photons to the absorber layer, which finds application in the area of PEC solar cell devices also. The aim of the present study is to analyze the different experimental conditions to prepare ZnSe films using electrodeposition process.

Electrodeposition of ZnSe was studied in a bath containing $ZnSO_4$, SeO_2 and $HClO_4$ using cyclic voltammetry. ZnSe thin films were grown by electrodeposition technique by using potentiostatic method on the Pt substrates at different potentials (0.03 and 0.6 V vs. NHE) to obtain the co-deposition of Zn and Se. Following electrodeposition, the ZnSe films were removed by anodic sweep at same deposition solution. Voltammetric cyclic experiments were performed using a microcomputer controlled potentiostat/galvanostat, EG&G PARC mod. 263. The deposits were characterised by SEM and AFM.

Figure 1shows voltammograms for Se, Zn and Zn-Se systems and it is possible to observe the anodic peaks corresponding Zn and Se dissolution formed from underpotential deposition. The difference observed during anodic sweep indicates that Zn-Se thin films were formed at different deposition conditions and the Zn presence favored the Se deposition. The atomic force microscopic examination of the ZnSe films indicated compact and close packed granular growth.
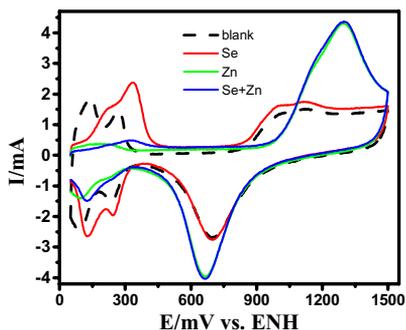

Figure 1. Voltammograms recorded for the Zn, Se and Zn-Se systems 1,0 x 10^{-2} molL^{-1} de $ZnSO_4$ and 1,0 x 10^{-5} molL^{-1} de SeO_2 at 4Vs^{-1}.

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Elecrochemical Nanotechnology

Qualitative interpretations for the optimal composition of the bath used for the electrochemical deposition of the permalloy layers

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A lot of previous experiments have shown that $Ni_{100-x}Fe_x$ alloys exhibit magnetic properties which could be of interest in the industrial field, especially for data storage.

We have focused our attention on the electrolytic procedures in order to define simple technological methods of preparation; in most of previous experiments the electrolytical   procedures were running at temperature higher than the ambient temperature and implemented solutions whose concentration in metallic ions take higher values; the solutions were either basic or acid.

Starting from the previous experiments and the technological ways, which has been identified, it has been attempted to define optimal conditions for the reproducible electrolytical deposition of Ni-Fe alloys; an exhaustive analysis of the influence of the physical and chemical parameters has been examined for Ni-Fe layers whose atomic percentage in Fe is situated in the 10-50% range.

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Elecrochemical Nanotechnology

Formation and Characterisation of Mesoporous TiO$_2$ – Gold Nanocomposite Film Electrodes

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Structured films of TiO$_2$ (anatase) nanoparticles (ca. 6 nm diameter) and gold nanoparticles are formed via a layer-by-layer deposition procedure [1]. TiO$_2$ nanoparticles are deposited with a Nafion polyelectrolyte binder followed by calcination to give a well-defined mesoporous thin film electrode. Gold nanoparticles (ca. 20 nm diameter) are incorporated into this film with a poly(diallyl-dimethylammonium chloride) polyelectrolyte binder followed by calcination to give a mesoporous TiO$_2$ – gold "cermet". Finally, a film composed of TiO$_2$ nanoparticles is coated with a TiO$_2$ – Au film to give (after calcination) a structured two-component film.

Electrochemical experiments with these films show that the gold nanoparticles cause a considerable change in conductivity, electrically connecting effectively through many layers of TiO$_2$ – Au nanocomposite. With a partially insulating TiO$_2$ sub-layer, two types of indirect electron transfer from the electrode to the gold nanoparticle layer are demonstrated based on (i) a Ru(bpy)$_3^{3+/2+}$ solution phase redox mediator system and (ii) the surface immobilised FAD/FADH redox mediator system

200 nm
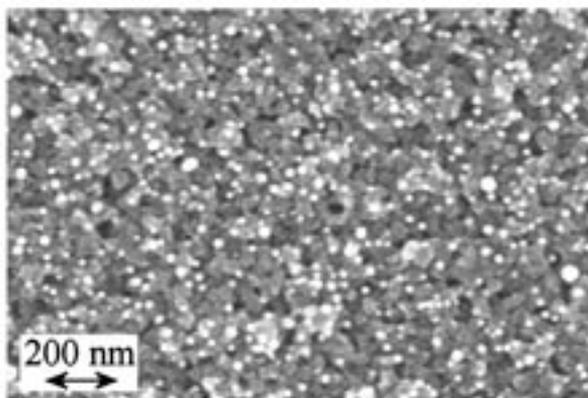
[1] E.V. Milsom, H.R. Perrott, L.M. Peter, F. Marken, Redox processes in mesoporous oxide membranes: Layered TiO$_2$ phytate and TiO$_2$ flavin adenine dinucleotide films, Langmuir, 21 (2005) 9482-9487.

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Elecrochemical Nanotechnology

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Elecrochemical Nanotechnology

Elecrochemical Impedance Study of Polycarbazole and Its Derivatives

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Carbon fibre electrodes are microelectrodes using a single carbon fibre (or small group of fibres) as the conducting element. In addition, when electrografting of the conductive polymers such as polycarbazole (PCz) and their derivatives on the surface of carbon fibre micro electrodes (CFMEs), their conductivity properties are improved considerably.

Carbazole (Cz) or its derivatives like carbazole-9-carbonylchloride (Cz-9-COCl) was electropolymerized potentiodynamically on CFME. The polymerization conditions such as solvent, supporting electrolyte, monomer concentration, scan rate or scan number, were changed and determine optimum conditions for each monomer to obtain better electrode. The polymers grafted on CFMEs were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), FTIR-ATR spectroscopy, UV-vis Spectroscopy and Scanning Electron Microscop (SEM), and compared with uncoated CFME.
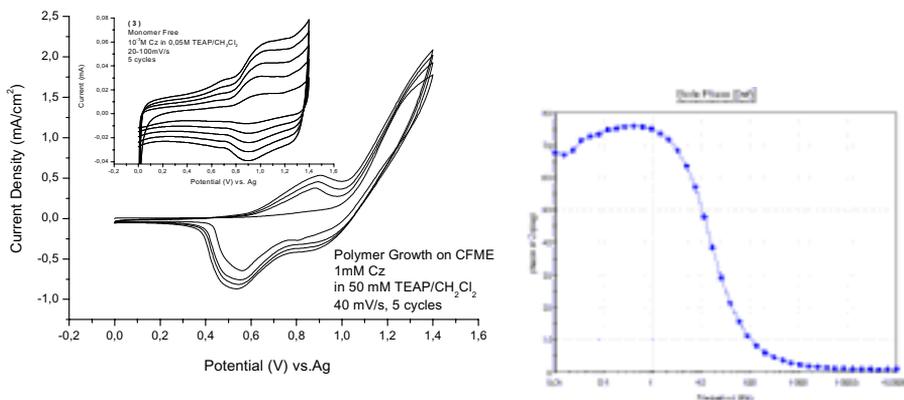

Figure1. (a) CV of polymer growth and monomer free of PCz in 0,05M TEAP/DCM (b) Bode phase graph of P(Cz-9-COCl)

Cyclic voltammograms of polymerization showed that current density was increased with the thickness of thin film on CFME. Bode phase angle of 75° was obtained from EIS study that means the polymer showed a capacitor behaviour.

AlOOH/Al$_2$O$_3$ Ceramic Coatings Prepared by Electrophoretic Deposition from Aqueous Sol

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Electrophoretic deposition (EPD) of ceramic coatings has become very interesting because this method has allowed the formation of thin films or multilayer films of controlled thickness, enabling the formation of films on substrates of complex geometry. The use of sol-gel routes in ceramic processing has many advantages in comparison to conventional powder-based processing techniques: greater purity, higher homogeneity and ultrafine grain size distribution, while the sintering temperatures can be lowered by several hundred degrees.

The aim of this work was to prepare boehmite coatings of lower sintering temperature using electrophoretic deposition from boehmite aqueous sol.

Boehmite aqueous sol was prepared by the peptization of Al(OH)$_3$. The boehmite powder, obtained by drying the prepared aqueous sol, was characterized by infrared (IR) spectroscopy, X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The thermal properties of the boehmite powder, i.e. water desorption and phase transformation from pseudoboehmite to α-alumina, were analyzed by thermogravimetric analysis (TGA). The starting formula of pseudoboehmite was calculated from TGA to be Al$_2$O$_3$□1.82H$_2$O, while XRD analysis confirmed pseudoboehmite structure.

The influence of the applied voltage and deposition time on the electrophoretic deposition of boehmite coatings on titanium from aqueous sol was investigated. The deposition was performed at constant voltage between 1.0 and 10 V and for a constant deposition time between 10 and 30 min. An increase in the applied voltage and deposition time increased the mass of the boehmite deposit, as well as the amount of evolved hydrogen, causing a more porous structure. It was shown that boehmite coatings of maximum thickness, low porosity and good adhesion can be formed at lower deposition voltage (4.0 V) and longer deposition time (30 min).

A coating electrodeposited at 4.0 V and for a deposition time of 30 min was treated at 1300 °C and α-alumina was confirmed. This indicates the significantly lower sintering temperature of the boehmite coating obtained by the EPD process from aqueous sol compared to sintering temperature of 1600 °C for boehmite coating obtained by classical forming methods.

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Elecrochemical Nanotechnology

preparation of tungsten oxide nanorod arrays with gas sensing properties by anodic oxidation of Al/W bilayers

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Tungsten oxide (TO) is an indirect band gap semiconductor that exhibits excellent electrochromic, photochromic and gas sensing properties. Recently, TO nanopowders, nanoparticles and porous structures have been synthesized via various routs. In this paper, we describe a novel, electrochemical approach for the fabrication of large-area arrays of self-organized, closely packed nanorods of tungsten oxide semiconductor by anodizing and subsequent annealing of a specimen consisting of a layer of aluminum deposited upon a layer of tungsten.

Commercially available alumina plates (Rubalite 710) and microscopically flat oxidized Si wafers were used as a substrate. Magnetron sputtering-deposited Al(1 μm)/W(0.3 μm) bilayers were firstly anodized in 0.1-0.9 M $H_2C_2O_4$ solutions at a constant current of 10 mA cm^{-2} and a steady-state voltage ranging 30 to 53 V. During this stage a porous alumina film was formed from the aluminium layer and the underlying tungsten was partly and locally oxidised through the alumina pores. Then the specimens were reanodised to a higher voltage ranging 90-250 V and subjected to selective chemical dissolution of the alumina part in the anodic films. Finally, the films were annealed in a vacuum at 200-800^{0}C. The specimens were examined by SEM, XPS and XRD. Gas sensing properties of the films were assessed by measuring the in-plane electrical resistivity in the presence of either pure air or NO_2 (CO) gases of various concentrations in a temperature range of 100 - 300°C.
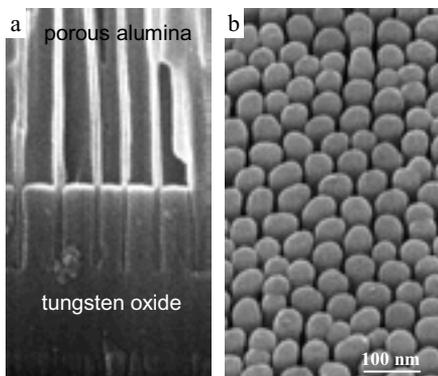
Fig.1 SEM of an anodised Al/W bilayer (a) before and (b) after dissolution of the porous alumina

As an example, fragments of TO vertical 'rods', of 150 mn high, 50 nm thick and up to 10^{10} cm^{-2} population density, penetrating the pores and then released from the pores are shown in SEMs of Fig. 1. It was found that the as anodized nanorods have amorphous structure and a mixed composition of WO_3 and tungsten suboxides. Further, a thin, continuous layer of oxygen-deficient tungsten oxide forms between the rods and substrate. The annealing leads to the formation of $W_{32}O_{84}$ nanocrystals with orthorombic symmetry, stable at room temperature. Simultaneously, the measured resistance of the films droped from an unmesured value down to 22 kOm. Test sensors employing the annealed TO nanorods as the active material showed clear responses to NO_2 already at 130^{0}C, the sensitivity depending upon the formation conditions.

Impedance Spectroscopy of TiO$_2$ nanotubes

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In the last years, a great renewed interest was focused in a better understanding of the electrochemical behavior of metal oxide semiconductors due to their potential applications in the construction of photo-catalytic devices, lithium-ion batteries, dielectrics in integrated circuits and dye-sensitized solar cells. Especially, the n-semiconductor behavior of TiO$_2$ with a comparatively low band gap justifies the numerous investigations performed on this material. Recently, the achievement of large self organized tubular structures by anodization opened a new and wide application spectrum due to the new specific functional properties of this type of material.

Impedance studies were performed on porous layers generated in 1 M Na$_2$SO$_4$ + 0.5 % NaF (see morphology in Fig.1). Preliminary results have shown that the potential dependence of capacitance can be described by a Mott-Schottky behavior at low band bending for compact and porous layers. Then, a different behavior was observed in the porous layer that cannot be only attributed to a surface increase. Here, the resistance of the electrolyte inside the pores seems to play a key role in the impedance response. On the other hand, the previous polarization of the layer at U > 1 V conducts to structural changes reflected in a change of the donor concentration. Different surface chemistries in the compact and porous oxides are revealed by different potential dependences of the capacitance at high band bending.
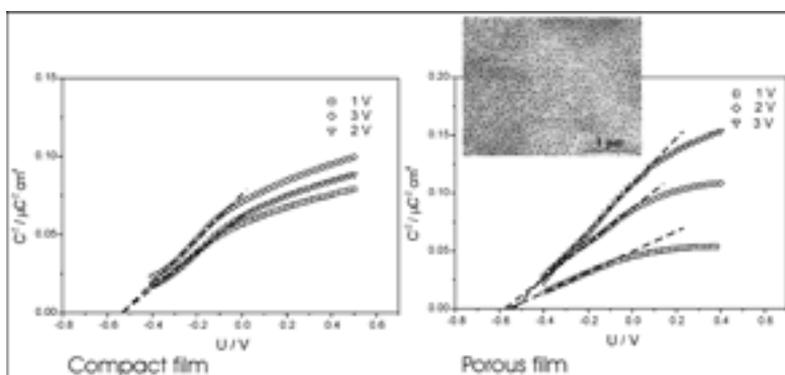

Fig.1 : Potential dependence of capacitance obtained on annealed compact and porous TiO$_2$ films in Na$_2$SO$_4$. f = 1 kHz.

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Elecrochemical Nanotechnology

Electrochemical Multilayer Assembly of Methylviologen/ Manganese Oxide Composite

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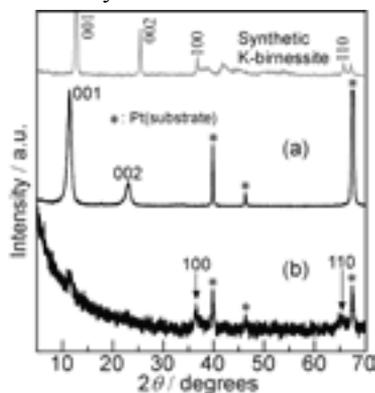**nkymm@yamaguchi-u.ac.jp*

N,N'-dimethyl-4,4'-bipyridium dication commonly known as methylviologen has been widely used as an electron acceptor for artificial photoredox systems. Interest is particularly high in the incorporation of MV^{2+} into inorganic solids because such a host-guest approach may offer improved efficiencies of photoinduced charge separation. In 2004, we present a new strategy for constructing birnessite-type layered manganese oxides intercalated with alkaline metal and alkylammonium ions in a thin film form.[1] The process involves a potentiostatic oxidation of aqueous Mn^{2+} ions in the presence of the guest cations. This methodology is remarkably versatile because the inorganic host can adjust itself to accommodate guest molecules upon electrodeposition.[2,3] In this study, electrolysis was similarly performed with MV^{2+} ions to confine them between Mn oxide multilayers.

Electrodeposition was made on a polycrystalline Pt plate by applying a constant potential of +1.0 V in a 2 mM $MnSO_4$ solution containing 5 mM $MVCl_2$. Conventional and in-plane XRD analyses were performed to elucidate the layered structure.

Fig. 1 shows the conventional (a) and in-plane (b) patterns of the film deposited on a Pt electrode, along with the pattern of synthetic K-*birnessite* powder. Peaks at 11.4º and 22.8º in pattern a are indexable to 001 and 002 reflections of Mn oxide layers, respectively, and the d_{001} value, 0.78 nm, corresponds to the interlayer distance. Considering the size of the planner molecule MV (1.35×0.6 nm), the pyridine rings orient parallel to the Mn oxide layers. In pattern b, the above two peaks are dramatically weakened. Instead, two diffraction peaks assigned as 100 and 110 are observed at 36.5º and 65.5º, suggesting that these faces are perpendicular to the substrate direction, i.e. the Mn oxide sheets are electrochemically assembled dominantly parallel to the electrode surface.

Fig. 1 Conventional (a) and in-plane (b) XRD patterns of the deposited film (along with the pattern of synthetic K-*birnessite*).

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Electrochemical Multilayer Assembly of Methylviologen/Manganese Oxide Composite

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Layered nanocomposites are usually composed of an organic polymer included between layers of an inorganic host having a nanoscale repeated unit. Great efforts has been made to develop synthetic routes for these materials, e.g. (i) *in situ* polymerization of intercalated monomers; (ii) exfoliation of a layered host and subsequent adsorption of polymer and reaggregation; (iii) template synthesis of host structures in polymer-containing solutions. In 2004, we presented a direct electrochemical route to construct a polymer/manganese oxide layered structure. The product is crystallized from a homogeneous aqueous solution of a strong polyelectrolyte and Mn^{2+} ion precursors by a potentiostatic oxidation at +1.0 V vs Ag/AgCl. In the present study, such an anodic methodology was extended with the use of a weak polyelectrolyte (poly(allylamine hydrochloride), PAH).

A layered manganese oxide film with PAH was prepared on a Pt plate electrode by applying a constant potential of +1.0 V in a 2 mM $MnSO_4$ solution containing 200 mM PAH. The resulting Pt-supported film was characterized by XRD, XPS, and CV. A typical CV of the layered PAH/MnO_x film in 0.1 M KCl solution is depicted in Fig. 1A, along with that of the amorphous counterpart. Moreover, XRD measurements were made for the films being polarized at oxidizing (+0.8 V) and reducing (0 V) potentials for 20 min after the voltammetric steady state had been reached (Fig. 1B). Clearly, the CV of the layered product is much larger in size than that of the amorphous one, while the layered structure is maintained during the potential cycling and further polarization. These results strongly suggest that the electrochemical process including the redox of Mn^{3+}/Mn^{4+} takes place at the interior surface of the multilayered PAH/MnO_x film.
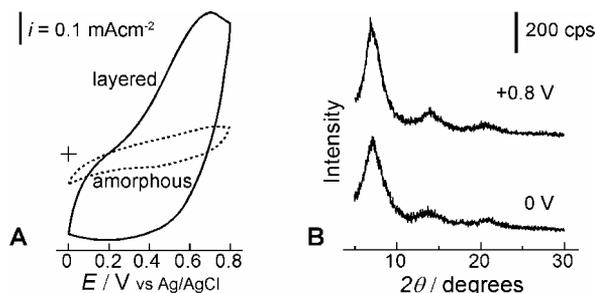
Fig. 1 (A) CVs of layered and amorphous films of PAH/MnO_x taken in a 0.1 M KCl solution at 20 mV/s. (B) XRD patterns of the layered PAH/MnO_x after polarization at +0.8 and 0 V.

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Electrochemical Nanotechnology

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Elecrochemical Nanotechnology

Electroanalysis of [Zn $^{2+}$] During the Growth of ZnO Nanostructure

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 ZnO nanorods were synthesised on a substrate via the decomposition of hexamethylenetetramine in an aqueous solution containing zinc nitrate hexahydrate. SEM investigation indicated that nanorod morphology changed significantly over the course of a reaction run, 9- 12 hours. The roles of pH, temperature and zinc ion concentration on morphology were studied. It was shown that in the first 30 minutes the pH fell rapidly and then remained constant throughout the run. The zinc ion concentration in the reaction mixture at varying times throughout growth was determined electroanalytically using anodic stripping voltammetry with polished mercury- plated glassy carbon electrode. It was established that the changes in the concentration profile coincided with the observed morphological changes. A concentration of 0.01M zinc ions was established to be suitable for nanorod formation while a concentration of 0.001M zinc ions was suitable for nanotube formation. These established concentrations for nanorods and nanotubes were in agreement with the empirical work of Vayssieres [1].
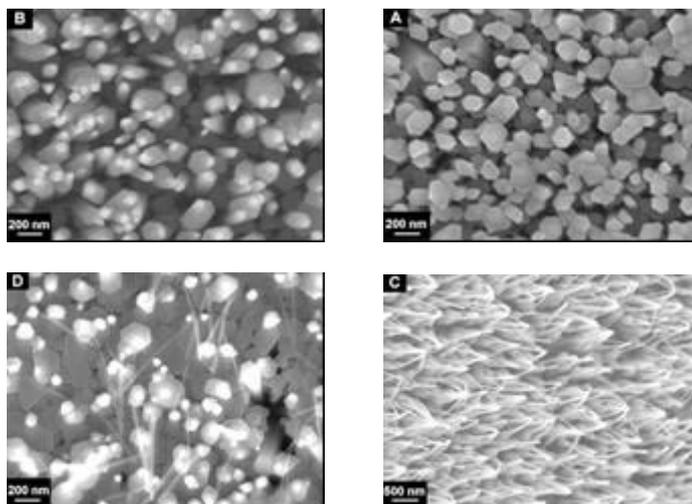
Figures A, B, C and D are SEM images of ZnO nanostructures grown on silicon coated surface after 3 hours, 6 hours, 9 hours and 12 hours.

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Electrochemical deposition of Au nanorod and its application to fuel cells

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For the aromatic thiols having relatively large cross sectional area, the Au(100) or Au(110) surface has advantages to construct arranged structures. [1] However, the Au(100) or Au(110) surface is metastable state in thermodynamics, therefore, it is impossible for us to prepare the surfaces by vacuum evaporation or sputtering. Recently, nanoparticles including Au nanorods having Au(110) surface for a long axis have been studied from view points of practical applications.

In this study, the electrochemical deposition of Au nanorod having the (110) surface and the application of the prepared surface to the catalytic reaction for oxidation of sugars are reported. The electrochemical deposition carried at room temp. may maintain the properties of nanorods.

Figure 1 shows change in the current ratios (Ii: initial current)

Fig. 1 Change in the current ratios (I/Ii) of the initial currents (Ii) and currents(I) acquired during electrolysis at -0.3 V for a) an Au NRs-modified PFC electrode treated with piranha solution, b) an Au NPs electrode, c) a Ru/Au NRs-modified electrode, d) a gold plated electrode, and e) an Au NRs- modified electrode heated at 573 K for 20 min.

during the electrolysis of glucose at (a) Au nanorod, (b) Au nanoparticle, (c) Ru-modified Au nanorod, (d) Au plate, and (e) Au nanorod (heat treated) electrodes at -0.3 V. For all the cases, the current ratios decreased with the increase of electrolysis time. At gold plate electrode (d), the oxidation current stopped around 25 min, however, at the other nanostructured Au electrodes, the currents continued to flow. Especially, the Au nanorod modified electrode (a) was most effective to the oxidation of glucose among the electrode evaluated in the study. [2] The crystallographic surface structure and morphology of the electrode may play important roles for the oxidation of glucose and prevent from inhibition.

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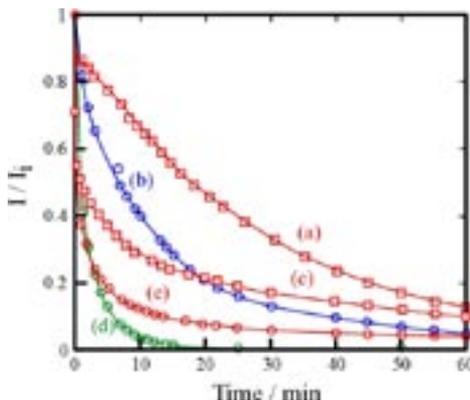(2) K. Nishiyama, R. Ishibashi, K. Toyota, and I. Taniguchi, *to be submitted.*

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Elecrochemical Nanotechnology

Effects of the seeding conditions on the crystal growth of gold nanoparticles on indium tin oxide surfaces in the seed-mediated growth method

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Gold nanoparticles are the most intensively studied and applied metal nanoparticles in electrochemistry owing to their stable physical and chemical properties, useful catalytic activities and small dimensional size. These attractive properties allow them providing some important functions for electroanalysis and the construction of electrochemical sensors.

In recent years, our group is studying on the fabrication method of gold nanoparticles directly attached indium tin oxide (AuNP/ITO) electrode. By utilizing the seed-mediated growth approach, which was developed for the wet synthesis of gold nanorods by Murphy et al. [1], we successfully attached AuNP onto the ITO surface without using peculiar binding reagents [2]. A characteristic feature of the AuNP/ITO is the reduced charge transfer resistivity due to the nature of the direct attachment, which was verified using the electrochemical impedance measurement [3, 4]. In addition, in our approach, AuNP are weakly capped by cetyltrimethylammonium ions, so that the further modification of the surfaces of AuNP on the ITO would be easily performed [5, 6].

In the seed-mediate growth method for the surface attachment of AuNPs on ITO, the first step is the immersion of a piece of ITO in to the Au colloid solution whose size is ca. 4 nm. We had been using the seed solutions containing the same component in published works [2-6]. However, recently, the component of the seed solutions, i.e., the concentrations of trisodium citrate and $HAuCl_4$, has been found to affect the grown-up nanostructures of AuNPs, even though the same growth solution was used in the treatment for the growth of AuNPs .

Thus, in the present paper, we would like to present how the nanostructures of AuNPs changes depending the components of the seed solution. Although the Au nano-seed particles were not gathered in the original conditions, some larger AuNPs were found to be formed on the ITO surfaces even just after the seeding process in some peculiar conditions. However, the nanocrystal growth of AuNPs was found to proceed in all the cases reflecting the components of the seed solution. The detailed results will be presented in the meeting together with the electrochemical performances of the AuNP/ITO electrodes having thus formed various nanostructured surfaces.

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Adhesion of electrografted nitrobenzene films on silicon surfaces as a function of the final applied potential. An AFM study

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Electrochemical reduction of the diazonium salt of 4-nitrobenzene was investigated *in situ* in DMF medium at silicon surfaces in the environment of an AFM microscope.

Generation of an aryl radical and formation of a covalent bond with a surface species is the well-accepted mechanism for the grafting reaction. However, several factors appear to significantly influence the structure and the adhesion of films formed on the substrate in particular the final potential applied for the electrochemical reaction. The average film thickness increases with the number of cyclic potential scans indicating the formation of multilayers. AFM investigations clearly reveal that, depending on the final potential applied, those layers are not completely anchored onto the substrate as they can be easily removed by the mechanical erosion of the tip. A microscale pattern can then be obtained this way.

It is likely that strongly cathodic potentials promote very efficient formation of radicals from the diazonium solution. Those radicals can eventually react either wit the already grafted nitrophenyl moieties to increase the grafted film thickness, or between them thus forming compounds which are not chemically anchored to the surface of the sample. That latter phenomenon is likely to increase with the number of radical species generated in the vicinity of the electrode. A polynitrophenylene film can thus precipitate of the surface without any chemical linkage with the grafted polynitrophenyl film. That polymer can be removed (or displaced), by simple mechanical effect, with the successive scans of the tip. Starting from a final potential cathodic enough for the first cycle, or beyond a threshold potential (<-0.8V/Ag wire) for the following cycles, one notes the drive of the matter in contact with the tip even on surfaces said "new", visible on the images by the formation of a square on the surface, corresponding in dimensions, with the previous scanning.
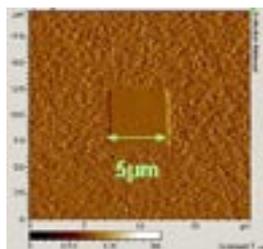
Microscale pattern of the polynitrophenylene film obtained by AFM contact mode.

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Elecrochemical Nanotechnology

Elecrochemical Impedance Study of Poly EDOT-ECZ-EDOT copolymer

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Conducting and redox active polymers have attracted some attention for use as electrochromic materials due to their inexpensive and potentially processable nature[1]. In this extend, 3,4-ethylenedioxythiophene (EDOT) has recently come out as a new thiophene derivative combining high conductivity of its polymer, low band gap, good electrochemical properties, exceptional thermal stability in the oxidized state.
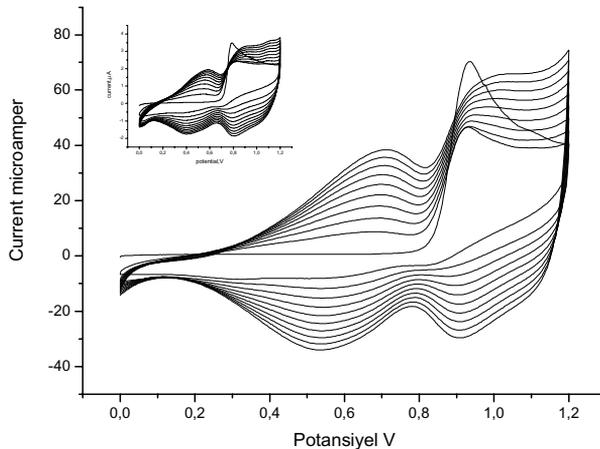

Figure1. EEE polymer growth in LiClO$_4$/PC at 50mV/s scan rate on CFME el, Inset : EEE polymer growth in LiClO$_4$/PC at 50mV/s scan rate on Pt electrode.

Electrodeposition of Zinc Oxide Films in the Presence of Organic Additives

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Electrodeposition is a low temperature growth method in solution, which offers the possibility of using organic additives as growth conducting agents. Of special interest are the oxides since a large variety of functional groups in organic molecules are able to interact to their surface. Zinc oxide illustrates spectacularly the possibilities offered by surface-additives interactions during the growth process not only for controlling the shape of the deposits but also to include organic compounds in the films and bring additional properties to them.

Specific interactions between different ZnO crystallographic planes and additives are considered at the origin of morphological control by influencing the associated growth rates. Polarity of the faces (Zn or O terminations) can also control the adsorption processes. At the moment there is a great demand to better understand these processes and curiosity to explore these interplays in new experimental systems.

The growth of zinc oxide by electrodeposition can be easily obtained by using dissolved oxygen as a reactant according to the overall reaction [1]:

$Zn(II) + 0.5 O_2 + 2e \circledR ZnO$
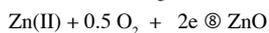
Hydrogen peroxide [2] or nitrate ions can be also used as oxygen precursors. Films of zinc oxide of high crystalline quality are prepared at temperatures as low as 50-60°C. Epitaxial growth has been achieved on single crystalline substrates [3].

A large variety of organic molecules and ligands containing carboxylate, sulfonate or phosphonate groups were shown in recent years to interact with ZnO during deposition and to modify the structure of the films. Most often the films become nanostructured with a very fine porosity. Moreover the organic component is included in the film, anchored to the zinc oxide by means of the functional group. For instance by an ester bond in the case of the carboxylate group.

Impressive are the structural changes observed with eosin [4,5]. Eosin and Zinc (II) ions are strongly interacting, especially for the reduced form of eosin, with the formation of complexes (via the carboxylate group). This leads to remarkable shape controlling processes, with under some conditions, the formation of porous structures with interconnected pores filled with eosin.

Similarly, the formation of highly porous structures are observed with another carboxylate groups containing organic ligand : the bipyridine dicarboxylate (dcbpy). Morphological transitions are observed not only with increasing the dcbpy concentration in the deposition bath, but also with the deposition time. If the initial zinc oxide layer is dense and poor with dcbpy, within a few minutes pores appear and the layer is finally made of entangled fibers containing both zinc oxide and dcbpy with a fibrous aspect.

dcbpy ligand contained in the film can be complexed with different cations by an activation treatment and the films obtained show remarkable luminescent properties under UV illumination . The color of the luminescent emission can be tailored by changing the ion.

Phthalocynine complexes functionalized with sulfonate groups are soluble in the zinc oxide deposition bath [6]. When codeposited with ZnO, the films are blue colored. They are also porous and the porosity is a function of the deposition potential and the metal in the complex (Ni, Co or Fe). These films present voltage monitored color changes when placed in an electrochemical cell. If all the films in their oxidized initial state are blue, their color transitions when polarized negatively, depend on the metal in the complex. The film spectroelectrochemical analysis shows a full color transition. Almost all the Pc molecules included in the films are thus accessible to the electrolytic solution and an open porosity is developed. The color changes observed can be analysed in term of redox state transition of the different Pc complexes

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Nanostructured ZnO Thin Films with a Controlled Wettability

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Electrodeposition is an interesting low temperature, low-cost method for the preparation of zinc oxide with a high structural quality [1]. By this method in solution, it is possible to control finely the thin film morphology by adjusting the deposition bath composition and the deposition time. In this way, a transition between a smooth dense layer towards arrays of nanorods can be observed for instance. Another approach for obtaining nanostructured films is to add organic molecules in the deposition bath which will act as structure directing agents. By the method, well-crystallized large single crystals with mesopores can be prepared [2,3].

The aim of this work was to study the influence of ZnO thin film morphology on the wettability of the layer. Electrodeposited films with different morphologies have been prepared and studied with the contact angle method. The effect of sample heating has also been investigated. If flat films present a contact angle ranging between 40 and 70°, depending on the pH of the drop, the porous films are found hyperhydrophilic. The deposited drop rapidly disappears and wets the layer. The ZnO wetting properties can be tailored and transitions to a hydrophobic or a hyperhydrophobic ($\theta > 140°$) behavior can be obtained by adsorbing *ad hoc* molecules such as alkylsilanes. The adsorption is due to the anchoring of the organic molecule on the ZnO surface by its silane function [4]

Interestingly, the property is reversible: under UV light illumination, the organic component can be oxidized by the hole generated at the ZnO surface and transition towards hydrophilicity is observed.

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Electrophoretic Fabrication of a Nanostructured TiO$_2$/Carbon Photocatalyst for Oxidative Wastewater Treatment

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In recent years, heterogeneous photocatalytic water-treatment technologies have attracted the attention of many research groups around the world [1]. Among advanced oxidation processes (AOPs), photocatalytic treatment offers high capacity for destroying organic contaminants by oxidation with hydroxyl radicals ˙OH that are generated under mild conditions [2]. Organic dyes represent a major pollution problem for the textile industry. Highly colored discharges of water to the ecosystem represent a serious environmental problem. The dye compounds, which are present in high concentrations, have very stable structures. For this reason, standard physicochemical and biological treatments are ineffective for their degradation and decolorization [3]. Photocatalytic oxidation with TiO$_2$ offers a potentially effective technique for treating such wastewaters.

Recent studies show that the light-absorption and photocatalytic efficiency of TiO$_2$ can be improved by coupling TiO$_2$ nanoparticles with non-metallic dopants, such as carbon [4]. In this paper we describe the electrophoretic preparation of a novel TiO$_2$/Carbon composite photocatalyst on a glass substrate. The objective is to take better advantage of the e$^-$/h$^+$-pair generated by photoexcitation of semiconducting TiO$_2$ particles. The transfer of the e$^-$ electrons into adjacent carbon nanoparticles promotes oxidation of oxygen to produce H$_2$O$_2$, which can subsequently in the presence of iron ions form ˙OH via the Fenton reaction. At the same time, adsorbed ˙OH is formed from water by the h$^+$ holes in the TiO$_2$. Thus, the ˙OH oxidant is produced by two routes.

Our results indicate that it is possible to generate H$_2$O$_2$ photochemically on the composite TiO$_2$/Carbon catalyst, increasing the production of H$_2$O$_2$ by a factor of two with respect to TiO$_2$ without carbon. With the objective of evaluating the capacity of this system to destroy target organic compounds, a 50 mgL^{-1} solution of Orange-II dye was treated with UV illumination of the catalyst. We observed 30% removal of color within 2-3 hours, which was three times as effective as a TiO$_2$ photocatalyst in the absence of carbon.

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Elecrochemical Nanotechnology

Pt-Ru-Pt metallic multilayers for small organic molecules oxidation

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Metallic multilayers, in which each layer are few monolayers thick, can have unusual mechanic, electrical, optical and magnetical properties compared to the bulk metals or their alloys. Since the giant magnetic resistance effect was described for the first time, in 1988, several groups have investigated their magnetic and electronic properties. From a different point of view, there are few papers in the literature concerning the use of noble metals multilayers as electrocatalysts[1,2]. Considering these facts, we present here the preparation and electrochemical characterization of Pt-Ru-Pt bilayers systems for the oxidation of small organic molecules.

The preparation of the bilayers system were perfomed using a two step procedure. First, it was electrodeposited one monolayer of metallic ruthenium over a platinum substrate from a 1 mMolL^{-1} RuCl$_3$ in 0.1 MolL^{-1} H$_2$SO$_4$ solution at 0.05 V (vs. Hydrogen Electrode in the Same Solution, HESS) during 300 s. Over the Ru layer, 1.1 monolayer of Platinum was electrodeposited from 0.5 mMolL^{-1} H$_2$PtCl$_6$ in 0.1 MolL^{-1} HClO$_4$ solution at 0.05 V during 20 s. The electrochemical oxidation of the methanol, ethanol and formic acid were investigated in 0.1 HClO$_4$ solution using cyclic voltammetry and chronoamperometric curves. Finally, the electrode properties were characterized using XPS, SEM and AFM measurements.

The Pt-Ru-Pt electrode were characterized in 01. MolL^{-1} HClO$_4$ solution and it has the characteristics of a bulk platinum electrode. The electrochemical active area were calculated for both the Pt substrate and the Pt-Ru-Pt are the results are equal indicating that the bilayer system is thin enough to not change the surface area. The average roughness factor from AFM data confirmed this result. Only one important difference can be observed in the Pt-Ru-Pt electrode which is the decrease of the potential for oxygen evolution reaction which started at 1.42 V. A complete different behavior is observed when small organic molecules are added to the solution. In this case, an important increase in the current density oxidation peaks is observed for the bilayer electrode. This increase is about 320 %, 340 % and 430 % for the methanol, ethanol and formic acid, respectively, compared to the bulk Platinum substrate. It is important to stress that all the data are normalized to the electrochemical surface area and then the observed effect can't be attributed to a change in the real surface area. The ratio among the current density peak during the direct (more positive potentials) and reverse sweeps also changed for the Pt-Ru-Pt electrodes. Finally, it was observed also a potentital displacement towards more negative potential of the beginning of the oxidation for ethanol (100 mV) and formic acid (70 mV). Considering the results obtained, we concluded that it was prepared a new material for small organic molecules oxidation.

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Templating of Electrodeposited Pd by Poly(ethylene glycol)

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Additives of water-soluble polymers are usually used to regulate chemical and electrochemical metal deposition. We applied electrochemical techniques, SEM, STM, TG and XRD to demonstrate the pronounced effect of poly(ethylene glycol) (PEG) molecular mass and concentration in $[PdCl_4]^{2-}$ plating solution on nano- and microstructural properties of electrodeposited palladium.

For diluted PEG solutions, we observed the phenomena we name quasi-templating effect [1,2]. Quasi-templating effect results from adsorption of polymer molecules on growing Pd nanocrystals. Adsorption is responsible for the decreased surface concentration of secondary nucleation centres as well as for more slow growth. The presence of adsorption products in thus formed deposits stabilizes Pd nanoparticles.

A number of electrochemical experiments on PEG adsorption on dispersed electrodeposited Pt (as a model system) are reported, giving better understanding of quasi-templating peculiarities. It is found that PEGs tend to dissociative adsorption and hydrogenation, and the rate of dissociative adsorption decreases with PEG molecular mass. Terminal groups of PEG take part in this process. PEG adsorbates can be imagined as collapsed spherical globules of PEG molecules. PEG adsorption behaviour differs strongly for the behaviour of monomeric ethylene glycol. The effect of adsorbed PEGs and inorganic polyanions on hydrogen and oxygen adsorption is compared, and a model of permeable adsorption layer is proposed to explain experimental data.

For the most concentrated PEG solutions, the process of Pd electrodeposition can be considered as a classical template deposition [3,4]. It is regulated by sieving the reagent species across polymer solution.

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A Reusable Glucose Biosensor Based On Insoluble Meldola`s Blue And Glucose Dehydrogenase

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The aim of this study is to produce a reusable glucose sensor that is oxygen independent, and is based upon a novel mediator system.

Our method is based on a screen-printed 2 electrode system, using an insoluble mediator incorporated into the carbon working electrode. A traditional screen-printed silver/silver chloride electrode is used as the reference/counter electrode, and a new modified carbon ink as a working electrode.

The bio cocktail includes stabilised glucose dehydrogenase, and NAD^+ cofactor which was deposited onto the working electrode via an automatic positive displacement syringe system.

An exclusion membrane was deposited onto the biosensor to avoid interference with ascorbic acid, uric acid, paracetamol.

The prototype biosensor was based upon an insoluble meldola`s blue mediated electrode.

A biosensor based on soluble meldola`s blue mediated electrode was used as a reference against the work carried out on the insoluble salt.

This poster will describe the results of our studies.

Single Molecular Conductivity at Electrified Solid/ Liquid Interfaces – An in-situ STM approach

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We have performed macroscopic, microscopic and single molecule studies of a series of alkanedithiols (C_5, C_6, C_8, C_9, C_{10}) at solid/liquid interface employing various techniques (single crystal electrochemistry and STM/STS) in different environments (aqueous electrolyte, non-polar organic solvent, argon atmosphere).

Single molecule studies were carried out employing an STM – based stretching technique at room temperature [1,2,3]. The approach involves the repeated formation and breaking of molecular junctions between a polyethylene coated gold tip, capable for atomic resolution, and a Au(111)-(1 x 1) substrate electrode modified with the appropriate alkanedithiol. Individual current – distance traces were acquired according to the following loop: (1) feedback disabled at z_o (defined by starting conditions), (2) approach with a maximum rate to z_{min}, (3) dwelling time of 100 ms at z_{min} to form molecular junctions, (4) recording of the current vs. distance characteristics upon retraction from z_{min} to z_{max} ($> z_o$) with a pulling rate of 2 to 4 nm s^{-1}, (5) stabilizing of the tip at z_o and switching on the feedback, (6) repetition of the cycle, and inspection of the surface by in-situ STM imaging. The recorded current – distance traces are non-exponential and exhibit single or a series of plateaus which are separated by characteristic steps. The statistical analysis of the plateau currents (typically from more than 500 individual traces) enabled the construction of histograms. Single molecular conductivities were determined and will be compared with relevant data obtained by other groups. The estimated single molecular conductaivities are linearly dependent on the applied bias voltage in $E_{bias} < \square 0.2$ V$\square$ and exhibit an exponential dependence on the chain length. The conductance properties of alkandithiol – junctions will be complemented with results obtained for the bifunctionalized alkans having selenol and pyridyl anchor groups. The experimental data will be compared with results and predictions of first principle quantum chemical calculations.

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Elecrochemical Nanotechnology

Formation of Phenylene Multilayers Films on Metal Electrodes by Electrochemical Reduction of Benzenediazonium Salt

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We describe a fast and very easy electrochemical method to form, in organic medium, polyphenylene (PP) films onto metallic surfaces.[1] This is achieved through the electrochemical reduction of benzenediazonium salt onto iron, copper and gold surfaces at – 0.8 V / SCE by cyclic voltammetry or chronoamperometry. Phenylene multilayers are strongly bonded to the metal since they resist sustained rinsing under sonication in acetone.
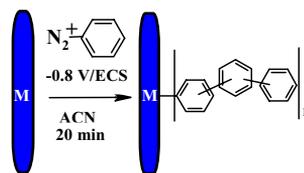
Scheme 1. Electrochemical formation of PP film onto metals.

Films of micrometer thickness are obtained on iron and copper, they are analyzed by IR, Tof-SIMS and HRSEM. IR results permit to evidence the grafting of a polyphenylene film and indicate the presence of different types of aromatic substitutions of benzene rings. There is no adsorption of the diazonium salts on the surface after rinsing. Tof-SIMS spectra prove the polyphenylene character of the film through the presence of phenyl monomer, dimer, trimer and tetramer fragments. HRSEM images indicate that the coating is uniform without pinholes.

Film thicknesses from 50 to 2200 nm are measured by profilometry and ellipsometry. Film resistance is measured by contacting the PP layer with a carbon paper or with a mercury drop at the end of a capillary. From the resistance and thickness of the PP film on copper, it is possible to estimate its conductivity ($2.5 \pm 0.5 \ 10^{-6}$ S cm^{-1}).

Cyclic voltammetry of redox probes shows that there is little difference between a bare gold or copper electrode and the same electrode modified by a micrometer PP film.

As the PP film is fairly conductive, it is possible to further derivatize its surface by reduction of another diazonium salt (4- bromobenzene or 4- nitrobenzene diazonium) in an organic medium. The presence of bromophenyl groups after the film derivatization is confirmed by Tof-SIMS analyses while that of nitrophenyl groups is shown by CV. When the PP film onto iron is used as a cathode for the electrolysis a 20 mM CuSO$_4$ solution in ACN, a bright homogeneous copper film is obtained on the top of the PP film.

Analysis of the transient chronoamperometric curves permits to estimate an order of magnitude of the attack of phenyl radicals on the PP film (~ 5 cm s^{-1}), which is also an upper limit for the attack of the same radical on iron.

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Electrolyte Effects on polymethoxyphenylpyrole grafted CFME's Electrochemical Impedance Spectroscopy

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The choice of an electrolyte is made by considering its solubility and nucleophilicity. Moreover the anion oxidation potential should be higher than the monomer. The nature of the anion has an impact on the quality of the film produced which depends on the hydrophobic character of the anion and the interaction between the polymer and the anion. On the other hand, anion nucleophilicity interferes with the reaction by increasing the formation of soluble products. The polymer of the highest conductivity is produced when elevated concentrations of electrolyte are used
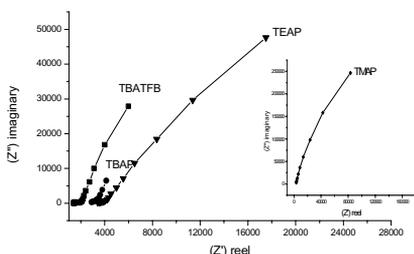
Figure 1. The electrolyte effects on impedance measurements of modified CFMEs

Potentiostatic conditions were used to obtain the modified carbon fiber micro electrodes by applying 0.8V. All of the polymerizations were performed in 30 minutes and methoxyphenylpyrole was used as monomer.

As it is seen from the plot TBATFB effect the polymerization in the best way and it become more capasitive. TBAP and TEAP have again capasitive behavior but not as much as TBATFB. Still, TMAP has the lowest capasitive feature but it has the best resistance. Consequently, we could say that long alkyl groups increase the conductivity of the structure by supplying long chain.

Figure 2. Comparison of the FT-IR spectrum of poly 1[4-methoxyphenyl]pyrrole polymer films prepared in different electrolytes containing CH_2Cl_2

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Studying Local Etching by Scanning Electrochemical Microscopy

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High resolution etching of semiconductor and metal surfaces is of technological importance in the production of microelectronic devices and is usually carried out by photolithography through several consecutive steps. Localized etching can be achieved in one step by a scanning probe microscopy technique, such as the scanning electrochemical microscopy [1-2]. This is typically accomplished by electrochemical generating a strong oxidant at the tip, which is held close above the active substrate, e.g., GaAs or Cu.

In the first part of this work we show that by varying the shape and size of the approaching microelectrode it is possible to generate an anisotropic flux of etchant and as a result to imprint the shape of the microelectrode. Several shapes of microelectrodes were constructed, which formed identical etching structures on the surface. The etched structures were characterized by optical and scanning electron microscopy as well as by profilometry.

In the second part of the research, we studied the copper etching by the feedback mode of the SECM. The major question, which we have considered was why copper is etched upon injection of holes. It is not trivial that injection of holes locally onto a highly conducting surface would cause metal dissolution. Hence, we conducted a series of experiments where the thickness of the copper (evaporated on glass) and the amount of charge injected by a platinum microelectrode, were systematically varied. We found that the etching efficiency depended on the thickness and the flux of injected holes. We are currently developing a model, which accounts for the etching efficiency. Briefly, the total current of the tip is the sum of the hindered current, the etching current and the current due to lateral conductivity. The latter depends on the thickness of the copper.

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microelectrode   *Etching structures*
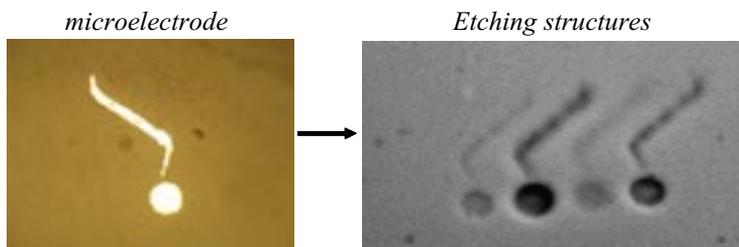
Detection of Hydrogen Peroxide Produced during Electrochemical Oxygen Reduction

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Generally, to establish the stoichiometry of the catalytic reduction of O_2 on macroelectrodes, rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) voltammetric methods are used [1]. This has the disadvantage that for each new electrocatalyst an new ring-disk electrode must be prepared. Here we try to investigate the kinetic parameters and the electron transfer number of oxygen reduction by scanning electrochemical microscopy (SECM). The method is tested that is based on the substrate-generation/tip collection mode (SG/TC)[2]. The method is illustrated with three electrocatalysts showing different behavior as oxygen reduction catalysts. Both, O_2 and H_2O_2 are reduced at Pt, while at Au only the reduction of O_2 to H_2O_2 occurs. The alloy of PdCo alloy (including 8.75 atom % Co) is known to produce both H_2O and H_2O_2 as the reaction product in a fixed amount. This method has the advantage that different substrates can be examined easily, i.e., without the need to construct RRDEs which are rather difficult to fabricate, and higher intere-lectrode fluxes are available without the need to rotate the electrode or otherwise cause convection in the solution. This is very useful for the selection of electrocatalyst in fuel cell.

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Production of Gold Nanoparticles by Electrodeposition: Control of Particle Density & Size Distribution

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The production of nanometre sized gold deposits at interfaces with high particle density and small particle size distribution is an area of intense research. This interest is driven in part by the production of nanostructured electrode surfaces with the aim of creating high sensitivity amperometric sensors, as well as Surface Enhanced Raman Scattering (SERS) and, surface plasmon resonance (SPR) substrates. In this contribution, we report on the production of immobilised gold nanoparticles by applying a potentiostatic transient to an optically transparent Fluorine-Doped Tin Oxide (FDTO) electrode.
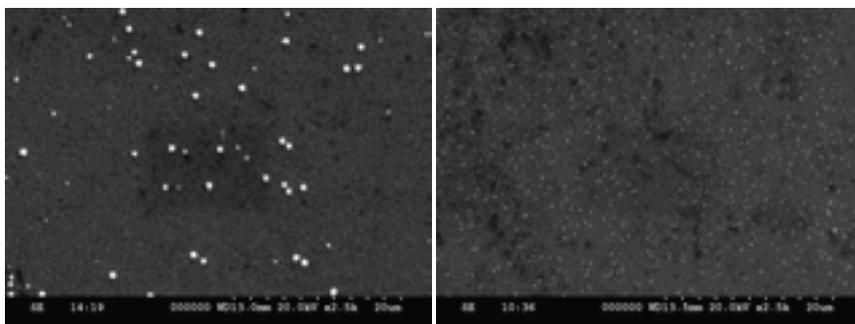
Figure 1: SEM images of metal deposits obtained using 0.001M $HAuCl_4$ in 0.1M KCl at a deposition potential of 400mV on Bare FDTO (left) and ADMMS modified FDTO modified with a 100ms nucleation pulse at -300mV (right).

To achieve the desired small particle size distribution, diffusion controlled growth with instantaneous nucleation must be achieved, and growth must proceed at low overpotentials to reduce diffusion zone coupling[1]. Here, we discuss the impact of the nucleation and growth potentials and times as well the effect of additives. For example, our work has shown that modification of the FDTO surface with an amino-terminated methoxysilane modifier (3-Aminopropyldimethylmethoxysilane) encourages instantaneous nucleation at significantly lower overpotentials compared to electrodeposition on the bare surface. We have shown that by applying a two-pulse potential programme to the 3-Aminopropyldimethylmethoxysilane modified FDTO surface we can significantly increase particle density and reduce particle size distribution.

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Fabrication of ZnO nanotubes with silicon oxide templates by atomic layer deposition

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Nanotechnolgy has now been recognized to have the potential to revolutionize a host of industries. One-dimensioanl hollow nanostructures, also called nanotubes or nanotubules, have attracted much attention owing to their potential applications in optoelectronics, biosensors, catalysts, and the separation of chiral compounds. Zinc oxide is a well-known direct wide band-gap wurtzite-type semiconductor with a large band-gap energy of 3.37 eV at room temperature. It is an excellent semiconductor material as a potential replacement for other wide band-gap materials like GaN and SiC. Furthermore, due to its large exciton binding energy of 60 meV, the excitons in ZnO are thermally stable at room temperature, and thus ZnO has significant advantages in optoelectronic applications, such as UV lasing. Owing to their promising uses in electronic and optical devices, various one-dimensional nanomaterials of ZnO with different morphologies, including nanotubes, nanowires, nanorods and nanobelts have increasing drawn attention. Among them, because of their unique structural characteristics, the preparation of nanotubes is relatively difficult, and fewer synthetic technology have been developed. In this study, we have employed the silicon oxide nanowires as a template for the growth of ZnO nanotubes. Although the silicon oxide nanowires are easily removable after the deposition of ZnO outer layers, the silicon oxide with the amorphous structure is usually not amenable for the formation of a continuous ZnO layer by most of synthesizing methods. Accordingly, we have generated the ZnO films on the silicon oxide nanowires by the atomic layer deposition technique. Pure ZnO nanotubes were formed readily by etching the silicon oxide nanowires as a template. In addition, large-scale production of ZnO nanotubes could be realized with this method without complicated preparation procedures.

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Si(111) Self-Organisiation on a Nanometer Scale: Accumulation Layer on Step Bunched Surface.

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Wet chemical treatments with alkaline solutions are of central importance for miniaturization on the nanometre scale. Despite widespread use of alkaline etching, several aspects of silicon dissolution are still not fully understood. Detailed knowledge of (electro)chemical dissolution steps in combination with a refined control of the (electro)chemical parameters can provide new strategies for directed nanostructuring.

We will report on nanostructure formation and a free standing accumulation layer on n-Si(111) after cathodic polarization in 2M NaOH thus forming a two-dimensional electron gas (2DEG). 2DEGs are of considerable interest for basic research (Quantum Hall effect) and applications, e.g., high electron mobility transistors.

Experiments were done in-situ at SoLiAs, the combined chemistry/ultra high vacuum (UHV) analysis system, were synchrotron radiation photoelectron spectroscopy (SRPES) at the U49/2 beamline at Bessy II was performed.

It will be shown that SRPES experiment allows indicating reaction intermediates and more probably reaction path. Further inspection of the SRPES data reveals a shift of the Si 2p core level of about 0.2 eV towards lower binding energy for higher excitation energy (i.e. lager escape depth). The high surface sensitivity x-ray photoelectron valence band spectrum shows that the energetic position of the valence band w.r.t. the Fermi level is extrapolated to be located at 1.06 eV. From the band diagram we can learn that an accumulation condition at the surface is responsible for the observed 0.2eV shift in the SRPE spectra.

For surface nanotopography analysis ex-situ experiments using contact mode atomic force microscope and Si_3N_4 tips were performed. After electrochemical treatment, the Si surface developed step bunching. Accumulated steps are present; they are about 0.3 μm wide and from 9 to 12 BL high.

SRPES data deconvolution showed that almost 30% of surface species are non (111) species. The AFM images and dissolution model show that the sample topography is built by the surface of {111} terraces but also by the side walls of bunched steps which are likely made of (100) oriented facets where the non-(111) species are localized. Evidences for this theory we will try to find in in-situ LEED (Low Energy Electron Dyffraction) experiment that can bring information about surface symmetry and position of atoms in elementary crystallographic cell.

Recent approaches on immobilization of proteins on semiconductor will be transferred to investigate protein absorption on this Si surface structure.

Stability and Electrocatalytical Properties of Nanostructured Pt/GC Electrodes Produced by Colloidal Lithography

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We recently introduced colloid lithography (CL) as a tool for the controlled preparation of nanostructured model Pt/GC electrodes with well-defined particle sizes and interparticle distances [1]. The simple and controlled geometry of nanostructured samples offers an outstanding possibility to study mass transport effects on electrochemical reactions. The nanostructured surfaces are prepared from a Pt thin film deposited on the substrate. Subsequently, a layer of polystyrene (PS) particles is adsorbed as a mask prior to Ar sputtering. In previous works, electron beam evaporation was used as the deposition technique. However, it was shown that Pt nanodiscs, produced from the evaporated film had poor adhesion to the GC substrate and detached from the surface during electrochemical measurements under continuous electrolyte flow. Pre-treatment of the polished GC by Ar plasma slightly improved the adhesion, but more importantly, the adhesion was significantly enhanced through the use of sputter deposition instead of e-beam evaporation. No damage of the nanostructured electrodes was observed after the experiments where sputter deposition technique had been employed [2].

Previously, we have shown that the nanostructured Pt/C model catalysts have comparable electrochemical and catalytic characteristics with polycrystalline Pt and conventional Pt/C catalysts in CO and HCHO oxidation [3]. However, effects of surface morphology on the product distribution (HCOOH and CO_2) in the HCHO oxidation reaction were registered that can be attributed to re-adsorption and mesoscopic transport effects.

Here, we show recent results comparing the electrocatalytic properties for different nanostructured Pt/GC surfaces produced by the CL technique, now with sputter deposition. The influence of particle size (~130 and ~80 nm diameter) and distribution (from 20 to 40 % coverage) on the CO and HCHO oxidation reactions are investigated by means of Differential Electrochemical Mass Spectrometry (DEMS) using a thin-layer flow-cell under controlled flow conditions.

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2. R. Lindström, M. Gustavsson, Z. Jusys, B. Kasemo and R. J. Behm, "Stability of nanostructured Pt/GC electrodes prepared by colloidal lithography" in preparation.
3. R. Lindström, Z. Jusys, M. Heinen, Y. X. Chen, M. Gustavsson, B. Kasemo and

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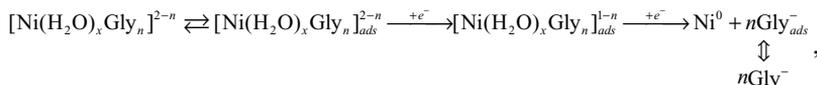# Kinetics of Nickel Electrodeposition from Aqueous Solutions Containing Glycine

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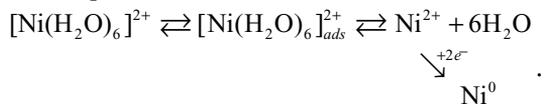**NVS@chem.vsu.ru*

Nickel coatings have a number of useful functional properties. Solutions of complex salts are widely used in modern electroplating technologies in order to prepare such coatings. One of the most promising ligands are aminoacids because they are non-toxic and allow to direct the deposition process in wide spectra of technological regimes. As long as in 1967 α-aminoacetic acid (glycine) was proposed by N.T. Kudryavtsev as effective additive for the electrolytes for nickel deposition since it has buffer and complexing properties along with anti-pitting and leveling action. After that a number of publications were devoted to the investigation of peculiarities of nickel deposition from glycine-containing solutions. However, complex composition of the electrolyte sufficiently impedes revelation of phenomena taking place during the electrolysis. Thus, the relevant data are noticeably differ one from another.

In this work thermodynamic analysis of ionic equilibriums in the Ni-Gly$^-$-H$_2$O system was carried out in order to know the solution composition at different pH and glycine concentration. The kinetics of nickel electrodeposition from aqueous electrolyte containing glycine was investigated depending on aminoacid concentration, solution pH, temperature, potential scan rate and rotational frequency of rotating disk electrode which were changed in wide range of values. On the basis of experimental data mechanism of considered process was proposed with the help of diagnostic criteria of voltammetry with linear potential sweep and RDE techniques. This mechanism implies that complexes of all possible types are reduced simultaneously excepting [NiGly$_3$]$^-$ and cathodic current is defined by fracture of each of them. Reduction of Ni(II) complexes is irreversible and controlled by the step of charge transfer. In neutral and alkaline media existing complexes are directly reduced on the electrode without any previous chemical reactions:

$$[\mathrm{Ni(H_2O)}_x\mathrm{Gly}_n]^{2-n} \rightleftarrows [\mathrm{Ni(H_2O)}_x\mathrm{Gly}_n]^{2-n}_{ads} \xrightarrow{+e^-} [\mathrm{Ni(H_2O)}_x\mathrm{Gly}_n]^{1-n}_{ads} \xrightarrow{+e^-} \mathrm{Ni}^0 + n\mathrm{Gly}^-_{ads}$$
$$\Updownarrow$$
$$n\mathrm{Gly}^-$$

where $x = 4$; $n = 1$ at pH 4.0 ..5.5 and $x = 2$; $n = 2$ at pH 6.0 .. 7.5.

In acidic media (pH 2.5) charge transfer is preceded by dissociation of aquacomplex that is manifested by appearance of additional current maximum at potentials more positive than potential of main peak.

$$[\mathrm{Ni(H_2O)_6}]^{2+} \rightleftarrows [\mathrm{Ni(H_2O)_6}]^{2+}_{ads} \rightleftarrows \mathrm{Ni}^{2+} + 6\mathrm{H_2O}$$
$$\searrow^{+2e^-}$$
$$\mathrm{Ni}^0$$

Keywords: nickel; glycine; electrodeposition; kinetics.

Synthesis of silver nanoparticles in ethanol environment

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Silver polarisation in unhydrous ethanol solution containing 0.1M $NaNO_3$ was investigated by means of potentiodynamic and potentiostatic method. Voltammetric studies revealed that anodic silver dissolution occurs above 0.4 V (all potentials are given vs Ag/AgCl). For potentials higher than 0.6V oxidation of ethanol takes place, what was confirmed by an experiment on platinum electrode and by theoretical calculations.

In a course of chronoamperometric polarisation a precipitate was obtained for potential higher then 0.6 V, what suggests that ethanol oxidation plays a role in the process. The precipitate was investigated by transmission electron microscopy (TEM) with energy dispersive X-ray analysis (EDX), by electron diffraction and X-ray photoelectron spectrosopy (XPS). These studies revealed that the precipitate consists of metallic silver nanoparticles and their size is of the order of approximately 20 nm (Fig. 1a). The electron diffraction studies on single nanoparticles confirmed their face centered cubic crystal structure (Fig. 1b).

The proposed mechanism, assumes that both Ag dissolution and oxidation of ethanol to aldehyde takes place on anodic surface. The reaction of aldehyde with Ag_2O leads to formation of silver nanoparticles.
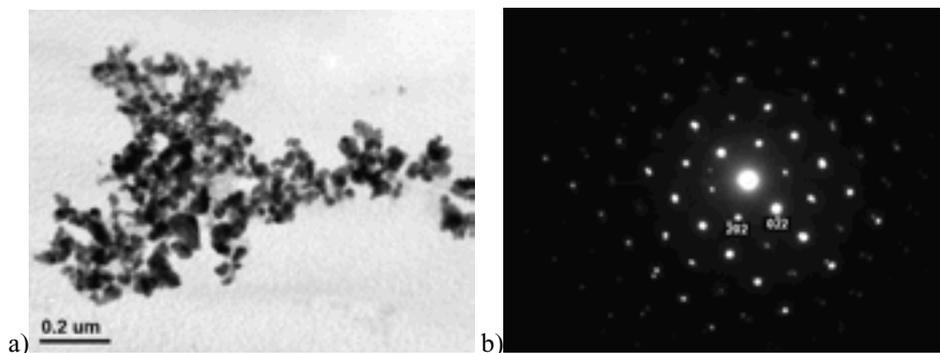
Figure 1. (a) TEM analysis of silver nanoparticles, (b) electron diffraction on a single nanoparticle.

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The characterisation of inorganic fullerene-like WS$_2$ as an electrocatalyst in the sulfide/polysulfide redox couple

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Since their discovery in 1992, inorganic fullerenes have been investigated for a wide range of applications, including solid state lubricants, electrode materials for Li ion batteries, materials for hydrogen storage, and catalysts for methanation. Experiments are underway to characterise inorganic fullerene-like WS$_2$ as an electrocatalyst in the sulfide/polysulfide redox couple, with the aim of improving the efficiency of redox flow batteries which employ this couple. Characterisation techniques to be employed include cyclic voltammetery, BET surface area analysis and high resolution transmission electron microscopy.

Preparation of Platinum Monolayer Islands on Au(111) and Their Electrocatalytic Activities on Oxygen Reduction

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Nanoparticles of metal or semiconductor are receiving intense scientific interest because of their specific properties compared with those of bulk materials. The geometric structure, electronic and magnetic properties as well as their catalytic activity depend on size of the particles. However, difficulty in preparing metal clusters having uniform quality with less lattice defects and small size distribution is a reason of contradictions between results obtained by different research groups. Such complicated parameters can be excluded by utilizing two-dimensional materials.

We have previously examined reactivity of Ag monolayer islands against oxygen reduction reaction (ORR) and found that the reaction path is very sensitive to the average size of the islands.[1] It was shown that monolayer islands of metal are a powerful material to intensively investigate nanoparticles and their catalysis. In polymer electrolyte fuel cells, expensive Pt is the dominant electrocatalyst of which loading must be reduced for fuel cell to become practical. Ultimate use of Pt can be obtained at Pt monolayer island where all Pt atoms are exposed to the reactants.

Recently, we have developed a new method to prepare monolayer islands of noble metals including Pt, using self-assembled property of thiols and replacement deposition technique of noble metal (Fig. 1).[2] This method allows change in island size from 3-15 nm. Electrochemical investigation of the prepared electrodes has revealed that the size of Pt monolayer islands affects the stability of surface oxide species and the relevance of surface oxide species on catalytic activity against ORP. As a result, the Pt monolyaer islands show size-dependence for electrocatalytic activities on ORR, giving the highest activity at 5 nm size.[3]

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2 A. Kongkanand, S. Kuwabata, *Electrochemistry*, **72**, 412 (2004).
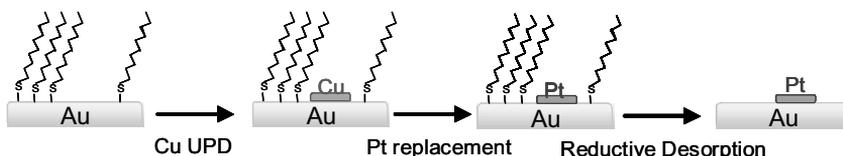3 A. Kongkanand, S. Kuwabata, *J. Phys. Chem*. B **109**, 23190 (2005).

Figure 1 Schematic illustration of procedures for preparation of Pt monolayer islands.

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Redox properties of 1-hexanethiol protected gold nanoparticles

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The alkanethiolate monolayer-protected gold nanoclusters (MPCs) demonstrate fascinating electronic properties and can be formally equivalent to multivalent redox species.[1-2] Their redox properties have been studied at the both solid|liquid and liquid|liquid interfaces.[3-4] Recently, by taking the bulk solvent effect into account, we have derived the absolute standard redox potential of hexanethiolate monolayer-protected gold nanoclusters (MPCs) in solutions theoretically from electrostatic considerations. In terms of this derivation, the valence state of MPCs at a given potential can be estimated by employing an internal redox molecular reference, such as ferrocenium/ferrocene. Importantly, the significant effect of the solvent on the redox properties of MPCs was verified experimentally by studies in various organic solvents. Furthermore, the redox properties of MPCs self-assembled on the gold electrode surface through dithiol linkers were studied. The effect of the electrostatic interaction between MPCs and substrate electrode on the redox behavior of MPCs was theoretically considered in terms of the method of images in classical electrostatics and justified experimentally.

MPCs were also used as redox quechers at the polarizable water|1,2-dichloroethane (DCE) interface. Photocurrent responses originating from the heterogeneous quenching of photoexcited porphyrin species by MPCs dissolved in the DCE phase were observed. As MPCs can function as both electron acceptors and electron donors, the photocurrent results from the superposition of two simultaneous processes, which correspond to the oxidation and reduction of MPCs. The magnitude of the net photocurrent is essentially determined by the balance of the kinetics of these two processes, which can be controlled by tuning the Galvani potential difference between the two phases. We show that, within the available potential window, the apparent electron transfer rate constants follow the classical Butler-Volmer dependence on the applied potential difference. The rate of the electron transfer reaction was found to be faster than those previously reported in the case of conventional redox molecules at liquid|liquid interfaces.

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In-situ STS of self-assembled biphenyl-type monolayers on Au(111)-(1x1)

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Studies on tailored functionalized structures and local electronic properties are challenging because of fundamental and applied reasons. We present macroscopic, microscopic and single molecule model studies of aromatic thiols (self-assembled monolayers or SAM`s) of a homologous series of ω-(4□-methylbiphenyl-4-yl) alkanethiols, $CH_3(C_6H_4)_2(CH_2)nSH$ (BPn, n=3,4,5,6)) at Au(111)-(1x1)/liquid interfaces using single crystal electrochemistry, in-situ STM and in-situ STS.

The electrochemical results reveal an "odd-even" effect with the alternating number of -CH_2- units for the reductive and the oxidative desorption potentials as well as for the barrier properties of the monolayers. The effect is correlated with the structure of the various adlayers. The BP units with an odd number of -CH_2 units exhibit a 25% higher packing density than those molecules with an even number of -CH_2 units [1,2]. Local electronic properties of BP3 and BP4 SAM´s were explored by current (respective conductance) – distance spectroscopy (IS, Iσ) and current-voltage (IV) spectroscopy in Au(111)-(1x1)-BPn/mesitylene-gold junctions. The junctions were created in a vertical SPM - configuration employing gold tips, which are capable for atomic resolution. The tunneling barrier heights were calculated from the statistical analysis of current-distance (IS) and conductance-distance (σS) measurements. Current-voltage spectros-copy (IV) revealed a wide stability window (∼ 5V) and characteristics of the dielectric breakdown of the various BPn adlayers. The importance of the tip position on the estimated conductance characteristics of the molecule-modified tunneling gaps will be illustrated. The structural integrity of the SAM`s during the STS-experiment was ensured by simultaneous monitoring high-resolution adlayer images.

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Effect of the complexing agents on chrome plating from trivalent electrolytes

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This work provides a new insight into the interaction of urea with formate during the chromium electrodeposition from a sulphate-based Cr(III) solution. The influence of solution chemistry on chromium electrodeposition in a Cr(III) bath containing complexing agents was studied by FT-IR, XPS and AFM.

To identify the species in the studied formate-urea electrolyte FT-IR spectra for both electrolyte and deposit were recorded. The deposit was analysed after coating removal from the plated sample. The data obtained suggest that the secondary ligand containing carbamidic groups was formed in the Cr(III) formate-urea electrolyte. The following reaction was considered as possible:

The results show that good quality Cr coatings may be obtained only in those cases when the secondary ligand with the carbamidic group predominates over urea in the electrolyte. It is suggested that the active chromium-carbamid complexes $[Cr(carbamid)_n(H_2O)_{6-n}]^{3+}$ delay the formation of the stable oligomeric species, and thus provide a prolonged working lifetime in the Cr(III) formate-urea electrolyte.

IR spectra recorded for Cr deposited from formate-urea baths containing hydroxylaminophosphate or hydrazine show the presence of $[Cr(carbamide)_n(H_2O)_{6-n}]^{3+}$ in first case and $[Cr(hydrazide)_n(H_2O)_{6-n}]^{3+}$ with contamination of $[Cr(carbamide)_n(H_2O)_{6-n}]^{3+}$ in last case. FT-IR and XPS spectra testify that hydroxylaminophosphate is not incorporated in Cr deposit This suggests that hydroxylaminophosphate acts as a stabilizer for active complexes bringing a balance between the stability and reactivity and, thus, effectively prevents the formation and precipitation of Cr(III) hydroxides.. In the case of hydrazine, on the contrary, the formation of Cr(III) hydroxide occurs seemingly due to the presence of $[Cr(hydrazide)_n(H_2O)_{6-n}]^{3+}$ complexes..

The morphology of Cr coatings obtained from these solutions is typical nodular structure. Cr deposited from bath containing hydroxylaminophosphate has the best quality and shows a less nodular and smoother fine-grained structure unlike the poor quality deposits with the higher percentage of both oxygen and nitrogen obtained in the presence of hydrazine.

Nano-fablication of the Surface Layers of Diamond and Boron-doped Diamond Electrode with Metal Nanoparticles

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Modification of surface morphology of diamond has been tried by many research groups. Chemical etching of pure diamond with KNO_3 [1], catalytic etching of diamond for the polishing, thinning or patterning of the surfaces by metal films or plates in a hydrogen atmosphere [2, 3], and oxygen plasma etching through an alumina mask to create well-ordered nanoporous honeycomb diamond films [4] have so far been reported; however, catalytic formation of nano-scale channels and holes, *nanochannels and nanoholes*, in the surface layers of diamond has not yet been reported.

This paper presents the catalytic formation of nanochannels and nanoholes in the surface layers of both pure diamond crystallites and conductive boron-doped diamond (BDD) electrodes using metal nanoparticles in a hydrogen atmosphere. A thermogravimetry in the hydrogen atmosphere showed the consumption of diamond begins at temperatures higher than ca. 700 °C. Although the etch pits have a characteristic morphology consisted of flat walls perpendicular to the flat base on the (111) planes, the etched surface formed on the (100) plane was rough. Only methane was detected as the gaseous product of the etching of the diamonds with metal particles under the hydrogen atmosphere. The metal particles, such as Fe, Co and Ni, used for the etching of the diamonds were easily removed by acid. Cyclic voltammetry showed that a surface area of the BDD was increased more than ten fold by the formation of the nanochannels and nanoholes.

This simple method to increase the surface area of diamond materials is useful for introducing several new functionalities, including the attainment of high current density BDD electrodes, and production of loading-sites for fine catalyst metals or compounds. Figure 1 shows an example of the loading of metal catalysts on a diamond substrate. Fine platinum particles are embedded on the (100) plane of a synthetic diamond crystallite.
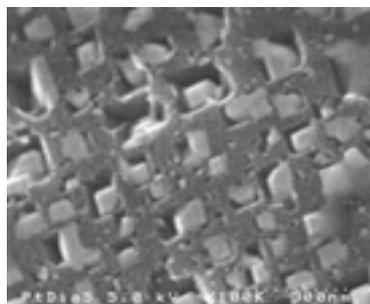

Fig.1 SEM micrograph showing Pt particles embedded on a (100) plane of a synthetic diamond crystallite.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Tailored nano particles for batteries made by flame spray pyrolysis

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Nanotechnology is becoming important for battery applications. It is well known that with decreasing size, nano particles can change their characteristics compared to micron-sized particles. Therefore, electroactive materials such as $LiMn_2O_4$ are of great interest for the improvement of lithium-ion batteries: Small dimensions reduce diffusion lengths within the particles and the high specific surface area increases the number of active sites for surface reactions leading to decreased current densities during charging and discharging processes. For the same reason, the overpotential should be lowered and therefore higher charging/discharging rates are expected. Production of these nano particles can be performed by flame spray pyrolysis process. .
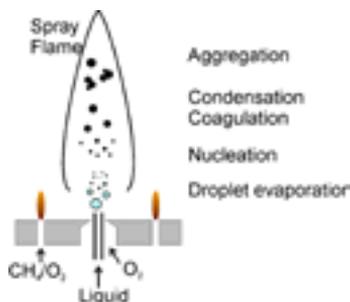
Figure 1: Experimental setup of the flame spray pyrolysis process (FSP).

Organometallic precursors were dissolved in an organic solvent with a certain metal ion concentration. This precursor was fed into the reactor by a syringe pump and dispersed into fine droplets by a gas-assist nozzle. The spray was ignited and maintained by a flame ring of a methane/oxygen mixture surrounding the spray capillary. In addition, an oxygen sheath surrounds the setup to assure the complete conversion of the reactants. A number of electroactive materials such as $LiMn_2O_4$, $Li_4Ti_5O_{12}$, and $LiFe_5O_8$ were successfully synthesized by flame spray pyrolysis. Their electrochemical activity was confirmed by cyclic voltammetry and charge/discharge cycling tests.

Our work demonstrated that electrochemical active nano particles produced by FSP, which is a fast and versatile process, could be used in lithium-ion batteries.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Nanostructured films base copper prepared by electrodeposition

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Electrodeposition is tested as a useful method to prepare nanostructured copper coatings with new magnetic or magnetoresistive properties. Firstly, the possibility of embedding magnetite nanoparticles in a copper matrix to develop magnetic nanocomposite films is studied. Secondly, the possibility of obtaining magnetoresistive granular films from simultaneous electrodeposition of Cu, Co and Ni and a later segregation of ferromagnetic clusters in the copper matrix is analysed.

Magnetite (Fe_3O_4) prepared in our laboratory with 80% yield is characterised by Field Emission (FE-SEM) that reveals agglomerates of rounded particles of nanometric size. X-ray diffraction analysis shows a particle size of 20-30 nm. Magnetic characterization shows a saturation magnetization of 83 emu g^{-1} and a coercivity of 85 Oe.

Magnetite is added to an electrolytic copper acidic bath. Cationic surfactant is used to maintain nanoparticles in suspension and favour their incorporation into the deposit. The magnetite incorporation is analysed as a function of the bath composition, stirring of the solution, electrodeposition method, deposition potential and temperature. Copper-magnetite samples are analysed after dissolution of deposits with aqua regia. Moderate stirring rates, low temperature of the electrolytic bath (15ºC) and pulse-plating method become the better conditions for an incorporation of 5-20 wt% magnetite in copper deposits. Copper-magnetite composites exhibit ferromagnetic response, with magnetic properties depending on the coating composition.

An electrolytic bath containing copper, cobalt and nickel is chosen to electrodeposit ternary Cu-Co-Ni alloy. Citrate is used as a complexing agent to bring the deposition of copper and ferromagnetic metals close. Electrochemical study of the ternary system electrodeposition process over different substrata is performed. Composition of the electrolytic bath is optimized to favour the formation of copper-rich alloys with 10-30 wt% of Co + Ni.

Ternary alloy is deposited. The composition can be adjusted as a function of the deposition potential. The system responds to solid solution behaviour, both from electrochemical and X-ray diffraction experiments. Homogeneous ternary deposits are obtained. Annealing of the samples under vacuum conditions induces segregation of ferromagnetic clusters in the matrix. Magnetoresistive behaviour of the annealed samples is observed, at room temperature (293 K) and especially at low temperature (45 K). Different values of magnetoresistance (MR) can be obtained as a function of the composition and the annealing temperature.

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Elecrochemical Nanotechnology

Magnetic properties of CoNi films prepared by electrodeposition in the presence of surfactants

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CoNi electrodeposits have been demonstrated useful to be used as mobile elements under magnetic fields applied in MEMS devices [1]. Our interest is now the developing of a deposition process of hard-magnetic materials compatible with MEMS processing. Previous studies reveal that presence of surfactants is able to drastically modify the structural properties of the alloy. Then, the electrodeposition of magnetic alloys in the presence of some surfactants is proposed as a method of obtaining metallic films with magnetic properties clearly modified.

CoNi electrodeposition is performed using an optimized chloride solution containing boric acid and saccharin at 55 ºC. The influence of two cationic surfactants on the electrodeposition process of the alloy is analysed. The dodecyltrimethylammonium chloride (DTAC) is not electrochemically active in the range of potentials useful to perform the deposition. 4-butylazobenzene-4'-(oxyethyl)-trimethylammonium iodide (AZTMAI) reduces at potentials previous to those corresponding to CoNi electrodeposition. The presence of surfactant shifts the onset of the deposition process to more negative potentials as a consequence of their adsorption.

Deposits of several microns are prepared over silicon/seed-layer substrates from solutions containing surfactant. CoNi deposits obtained exhibit noticeable morphological and structural changes respect to those prepared in absence of the surfactants. However, cobalt-rich deposits are obtained both in the absence and in the presence of surfactant as corresponds to anomalous codeposition. DTAC or AZTMAI presence favours the formation of CoNi deposits of acicular morphology. Crystalline structure evolves from fcc to hcp as a function of the additive concentration.

Magnetic properties of coatings are drastically changed when they are deposited from additive-containing bath. A drastic increase of the coercivity, as well as a decrease of the remanence and permeability is observed. In the presence of DTAC, the maximum coercivity obtained is from solutions containing low concentrations of additive. However, the coercivity of CoNi deposits prepared in AZTMAI–containing baths is gradually increased as a function of additive concentrations.

CoNi deposits obtained in the presence of DTAC are coherent and uniform only when they are prepared from solutions containing low concentrations of additive. At higher concentrations, deposits are fragile and fluffy as a consequence of the additive incorporation. On the contrary, CoNi deposits obtained from AZTMAI baths are more consistent and uniform because there is no incorporation during the electrodeposition.

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Immobilisation of Alkane(di)thiols on Nickel Surfaces

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It has been previously shown through XPS characterisation that alkanethiols can adsorb on nickel surfaces. [1-4] The homogeneity of monolayers of alkanethiols on nickel could be improved by ensuring that the surface was oxide free. It has also been shown by Suzuki *et al*. that oxide free nickel surfaces can be imaged with STM in low pH Na_2SO_4 aqueous electrolytes under potential control. [5] There is, however, very little detailed knowledge of the adsorption behaviour of alkanethiols on nickel at low pH electrolytes.

Here we show the effect of the pH on the adsorption of alkanethiols. In order to characterise the degree of adsorption of alkanethiols several experimental techniques have been used. Electrochemistry has been used to measure the electrochemical desorption of the molecule. In addition PM-IRRAS has been used to determine the orientation and packing of the molecular adlayer.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Highly-dispersed pt particles on carbon support as a catalyst for oxygen reduction

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Pt/C catalyst prepared by a modified polyol synthesis method in an ethylene glycol (EG) solution, with home made carbon cryogel synthesized by sol-gel polycondensation and freeze-drying was tested for oxygen reduction in 0.1 mol dm^{-3} NaOH solution. Specific surface area of carbon support was determined from nitrogen adsorption isotherm, without and after addition of nano-sized Pt particles. The adsorption isotherm is characterized with a hysteresis loop in the desorption branch indicative of a significant mesoporosity of a support. Specific surface area of carbon support, calculated by BET equation, was found to be 517 m^2 g^{-1}.

X-ray diffraction (XRD) with characteristic diffraction peaks of the fcc Pt demonstrate that a successful reduction of Pt precursor to metallic form has been achieved. Transmission electron microscopy (TEM) images show very uniform Pt particle size distribution with a mean particle size of about 2.65 nm of the catalyst.

Cyclic voltammetry (CV) was used for the determination of the actual exposed surface area of catalyst particles.

The rotating disk electrode measurements of O$_2$ reduction reaction were done to test the behaviour of the Pt/C catalyst and compare it with the same of pure Pt, for oxygen reduction reaction, in 0.1 mol dm^{-3} NaOH solution. By analysing these results the differences in activities of these two electrodes are obvious. The onset of O$_2$ reduction and the half-wave potential are significantly moved to the positive potentials in case of Pt/C electrode indicating its higher catalytic activity for the reduction of oxygen, compared to the same on pure Pt.

The Tafel plots for Pt/C (5μg) and pure Pt, obtained from the kinetic currents show that both electrodes are characterized with two Tafel slopes: one close to -2.3 2RT/F Vdec^{-1} at high current densities and the other close to -2.3 RT/F V dec^{-1} at low current densities usually referred for polycrystalline Pt in alkaline solution. These results show that the kinetics of oxygen reduction on Pt/C electrode, in alkaline solution is described by the same equations as those on pure Pt.

The increase in activity of Pt/C catalyst is analysed through: the increase of active Pt surface area by reduction of Pt particles size even below 1 nm, and increase of the number of active sites for oxygen reduction through simply geometric effects, as well as, through the change of electronic structure of the catalyst, connected to the electronic interactions between platinum and the supportive material.

Electrochemical study of specific binding behavior of the anticancer drug to dna based on the blending of nano tio$_2$ and pla nanofiber

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The binding study of antitumor drugs with DNA may lead to the revealing of the important mechanisms of the antitumor or antiviral components. Recently, nanomaterials have been utilized to facilitate the specific binding and improve the detection sensitivity of biomolecular recognition. As one of the most promising nanomaterials capable of a wide variety of applications in medicine and life science, the high reactivity of nano titanium dioxide (TiO$_2$) makes it possible to apply as a new strategy in the photodynamic therapies of some kind of cancers. Especially, as one of the good biocompatible nanomaterials, the TiO$_2$ nanoparticles could be utilized as an effective agent to accompany with other anticancer agents to facilitate the relative biomolecular recognition. On the other hand, some biodegradable nano polymers can carry the relative bioactive molecules to tissues of interest, due to the potential for the control of the release rate of the drug, and to the well-established methods of the preparation. Among these biocompatibility and biodegradable nano polymers, polylactide (PLA) has attracted intensive interest pertaining to drug delivery, tissue engineering and temporary therapeutic applications in pharmacology and surgery. Considering all of these above, we have explored the possibility of the application of the blending of TiO$_2$ nanoparticles and PLA nanofiber to biomolecular recognition of anticancer drug daunorubicin by using electrochemical methods. Our observations illustrate that the blending of TiO$_2$ nanoparticles and PLA nanofiber could be utilized as a new nanomaterial to improve the detection sensitivity for the relative biomolecular recognition of daunorubicin to nucleic acid. This blending may be also valuable to operate particularly in the field of controlled drug delivery.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Fabrication of carbon nanotube electrodes

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The remarkable electrical properties of carbon nanotubes have been extensively studied since their discovery in 1991. It is well known that single walled carbon nanotubes can either be metallic or semiconducting with a band gap inversely proportional to their diameter. Although the majority of research has focussed on studying the electrical properties of individual nanotubes, with possible applications as diverse as interconnects and sensors, more recently the benefits of nanotube networks as a macroelectronic material have been recognised[1]. Due to their high aspect ratio nanotubes can form highly interconnected networks at very low surface coverage. At low densities, i.e. just above the percolation limit, the networks behave as semiconductors, while at higher densities (although still only ~ 1% surface coverage) they behave as highly conducting thin films. We are interested in studying the electrochemical properties of these nanotube electrodes, the first step in which is, by necessity, the fabrication of carbon nanotube electrodes.

In this work we describe the catalysed chemical vapour deposition growth of carbon nanotubes on an insulating substrate. We can vary the density of nanotubes from below the percolation threshold to well above it, and by varying the size of catalyst particle we can vary the diameter of nanotube produced from ~ 1 –10 nm. Using photolithography we can pattern the nanotubes onto selected areas on the substrate, either by positioning of the catalyst before growth, or by selective removal of nanotubes after growth. Photolithography is also used for patterning electrodes onto the substrates, enabling electrical measurements on individual nanotubes, several nanotubes in parallel or networks of nanotubes. To study the electrochemical properties of these electrodes the final step is a coating of insulation, leaving only the nanotube(s) exposed.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Rapid patterning with cells based on the negative dielectrophoresis in a culture medium

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In this presentation, we describe a rapid fabrication method of two-dimensional micropatterns with biological cells in a culture medium, based on negative DEP (n-DEP) and cultivation of the patterned cells on the cell culture slide. The dielectrophoretic force directs the particles toward the weakest region of the non-uniform electric field by applying ac voltage to IDA electrode. Since the regions of the lowest electric field strength are formed just upper the microelecrode bands, cell patterns are a reproduction of the pattern of the IDA electrode.

The template IDA electrode with 50 µm widths and 100 µm gaps was fabricated by photolithographic methods on glass substrates deposited with indium tin-oxide. A polyester film with 30 µm thickness was sandwiched by the IDA electrode and cell culture polystyrene (PSt) slide. Mouse fibroblasts (3T3 swiss-albino) were cultured in RPMI 1640 medium containing 10 % fatal bovine serum (conductivity: 1.32 S/m). A 10 µL of the cell suspension (1×10^7 cells/mL) was injected into the device, and an alternating (sinusoidal) electric field (typically 3 MHz, 14 Vpp) was applied to the IDA electrode with a function generator. The separated culture slide is immersed in a medium to culture the cells, the IDA electrode is ready for another patterning.

On applying the ac signal to the IDA electrode, the cells suspended in the device are forced to move rapidly to the culture slide and formed lines on it within a minute. Since the cell pattern formed at the slide is a projection shadow of the array pattern of the IDA electrode, the IDA electrode acted as a template for the cell patterning. Incubation for 3 min under the voltage application permits to adsorb the patterned cells on the substrate. The resulting adsorbed cells with the line pattern were cultured for several days. Figure shows an optical microscope image of the patterned cells that are cultured for 4 hr. The shape and number of cells depended on the cultivation time. The teardrop shape was observed after 4 hr. The increase of the cell number by growth gradually disintegrated the line patterns. This result suggests that n-DEP patterning does not cause significant acute damage to cell for growth. We believe that this patterning method provides a novel tool for use in fundamentals studies of cell biology based on cell-cell interactions.
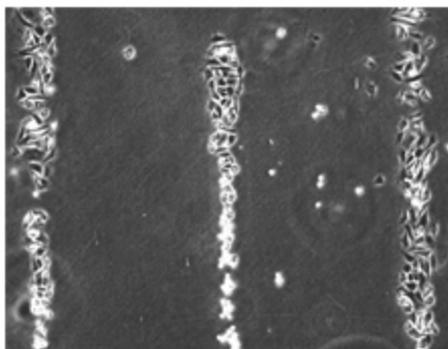

Figure. Optical micrograph of the patterned 3T3 cells on the cell culture slide. Patterend cells were cultured for 4 hr in the medium.

Electrocrystallization and properties of nanostructured gold

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The preparation and the investigation of nanostructured materials are interesting because of the possibility to control their physical and chemical properties by changing the experiment conditions. Nanocrystalline gold was electrodeposited from a solution where Au^+ was stabilized by complex formation with thiol groups. The change of the deposition parameters and the electrolyte composition leads to the change of physical properties of gold. The crystallite size was decreased down to 10 nm by means of pulse techniques and the amount of arsenic containing additive [1]. The structural properties were investigated in situ by high-temperature X-ray diffraction. Nanocrystalline gold exhibits thermal stability up to 573 K and the activation energy of surface diffusion was determined to be E_A=29.5 kJ*mol^{-1} [2]. The surface morphology was investigated by means of AFM and REM. Nanostructured gold exhibits roughness of 13 nm (50×50 μm surface). The hardness of the deposit was estimated to be about 2,26 GPa by means of nanoindentation. The cauliflower-like growth of gold was observed what can be used in applications where big surface area is needed.

The initial stages of gold electrodeposition on a glassy carbon electrode were studied in the above mentioned electrolyte using potentiostatically operated linear sweep voltammetric and chronoamperometric electrochemical techniques. The comparison between theoretical models for electrochemical nucleation and growth and experimental results for gold was made. The experimentally derived current-time transients were analyzed using nonlinear least-squares approximations by various models [3,4,5] of instantaneous and progressive nucleation and three-dimensional crystal growth with overlap. Different electrodeposition mechanisms are observed depending on the deposition potential. A potential dependent inhibition phenomenon was observed during gold electrocrystallization.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Antibacterial Surfaces– Formation and Characterization of Ag-nanoparticle Ultra-thin Films

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The bacterial colonalization has caused an increasing need for the developing efficient and long-term resistant antibacterial surfaces at low cost; biofouling does not only cause enormous economical losses worldwide annually but it has created a huge health risk for example in the form of hospital infections.

The traditional way for preparing antibacterial coatings is to use sol-gel films where antibacterial materials (e.g. silver, copper) are embedded for example in silica matrixes. This approach has several advantages such as homogeneity of the films and low temperature synthesis. However, the presence of a highly crosslinked matrix has also some disadvantages such as the limited formability and the change of the original properties of the surface (such as colour, conductivity). Thus a novel approach for the creating of antibacterial films is needed.

The formation of an extremely thin – monolayer thick – antibacterial film directly on the surface of interest has been studied using both glass and stainless steel substrates. The films containing silver nanoparticles were prepared successfully by immersing the samples into solutions of amino functionalized trimethoxy silane, methanol and silver nitrate similar to the layer-by-layer technique. A final annealing step at 120°C in which the reduction of Ag-ions to silver nanoparticles takes place completes the process.

The effect of both of the immersing and annealing time were studied with UV/Vis spectroscopy (transmittance spectra and reflectance spectra using the integrating sphere) and the mechanism of the growth of the particles as a function of the annealing time was studied by means of scanning electron microscopy.

The plasmon resonance could be well correlated with the size, shape and matrix of the adsorbed Ag-nanoparticle. The adsorption of the protective self-assembled monolayer on the nanoparticles was done to increase the stability of the nanoparticles.

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Study of size effect of conductivity of polyaniline nanowires by conducting AFM

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The template method is regarded as a simple and very effective way for preparing micro and nanomaterial. By different nanoporous template, the conductive polymer nanotubes or nanowires with different nanoscale were fabricated. Our new strategy to modify the diameter of nanowire is to make a hydrophobic AAO wall by assembling surfactants on AAO wall. Because of positive charge of AAO surface, negatively charged hydrophilic head-groups of surfactant are absorbed onto the AAO surface through electrostatic attraction or both electrostatic attraction and chemical binding, and hydrophobic end-groups construct a hydrophobic surface layer. Consequently, a hydrophilic solution will be confined in a smaller space than that of the template pore. The hydrophobic AAO inwall and the hydrophilic solution result in the size reduction of polymer nanowires or nanotubes synthesized in the AAO template. We have synthesized PANI nanotubes and nanowires with smaller diameter by the AAO template of which pore walls were modified by surfactant, as shown in fig.1. We studied the conductivity of fabricated PANI nanowires in the array by conducting AFM（fig.2）,   and found that there is size effect of conductivity of the PANI nanowires: the conductivity increases when the diameter decreases(Table 1).
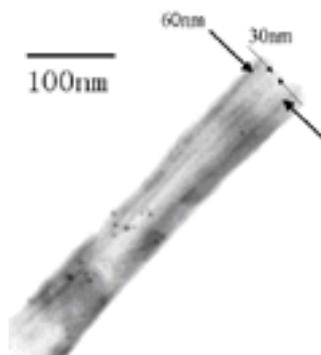

Fig. 1   TEM image of PANI polymerized in AAO modified by surfactant octadecanoic acid

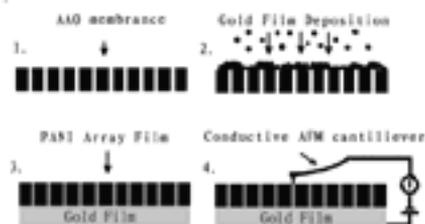
Fig.2 Schematic of the preparation of PANI nanowires embedded within AAO

Table 1 Conductivities of PANI nanowires in terms of the diameter

d/nm	60	40	30	24	20
σ/S·cm⁻¹	0.3369	0.5518	0.6837	0.7508	1.0601

Localization of electrochemical reactions in electrocatalytic processes at nanocompositions

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Electrochemical reactions underlie any electrocatalytic process that leads to electric current generation. In the electrode-electrolyte system, a compromise potential sets up in the electrode-electrolyte system, which depends on the potential value of the reactions that proceed in it at the same time. Using a catalyst-support nanocomposition, one can localize one reaction at the support and another reaction at the catalyst and influence there by the compromise potential. The main criterion for the selection of constituents is different energy barrier to the occurrence of these reactions at the catalyst and support.

For oxygen reduction reaction, which is employed in electrochemical generators with the use of a composition of carbon nanomaterials and catalysts, a localization of the reactions can be achieved. In this case oxygen adsorption will take place at the carbon nanomaterials, and for the catalyst a material with high oxygen evolution overpotential, at which electron attachment with bond rupture in the molecule will take place, must be used. Approximate activity order of metals-catalysts for alkaline solutions:

Co <Fe <Ni <Cd <Pb <Au <Pt

For the hydride electrodes of nickel-metal hydride batteries, the reaction of electron attachment to the water molecule involving adsorbed hydrogen formation at the catalyst with high hydrogen evolution overpotential can be localized during hydride electrode charging making use of the reaction localization principle. In this case, the hydride formation reaction involving adsorbed hydrogen is localized at the hydride-forming alloy. This leads to an increase in charge capacity and cycle life. The preferable activity order of catalysts is:

Pt <Pd <Co <Ni <Fe <Ag <Cu <Zn <Sn <Pb

For the hydrogen electrodes of fuel cells and hydrogen sensors, a catalyst with low hydrogen evolution overpotential must be introduced to localize the reactions. At the catalyst, adsorbed atoms are formed with bond rupture in the hydrogen molecule, and at the carbon nanomaterials, electron detachment takes place with desorption of hydrogen ions. The activity order of catalysts is:

Pb <Sn <Zn <Cu <Ag <Fe <Ni <Co <Pd <Pt

Thus, thanks to the localization of reactions, the catalytic properties of materials can be explained and predicted. The localization of reactions manifests itself best in the case of nanoscale catalysts, which may be accounted for by the spillover of the reactant across the catalyst-support interface.

Symposium 4 - Poster

Elecrochemical Nanotechnology

Symposium 4 - Poster

Elecrochemical Nanotechnology

Mesoporous metal oxide electrode material for supercapacitors

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Interests in the development of electrochemical capacitors for high power applications have greatly intensified in recent years. On the basis of electrode materials used and the charge storage mechanisms, electrochemical capacitors are classified as: (a) electrical double-layer capacitors (EDLCs) that employ carbon material with high surface area, and (b) pseudocapacitors (supercapacitors) in which electroactive materials such as transition metal oxide or conducting polymers are employed as electrodes.

Among several transition metal oxide electrode materials for supercapacitors, hydrous ruthenium oxide shows a high capacity of over 700F/g and excellent cyclability in aqueous H_2SO_4. Because of its high cost, alternative metal oxide electrode materials are being developed to replace ruthenium oxide. e.g. NiO_x, CoO_x, MnO_2, etc. However, comparing with RuO_2, these transition metal oxides exhibit lower electrochemical capacitance performance. Thus, improving the capacitance performance of these materials is the next logical step.

Electrode materials with a large surface area and a highly porous structure would effectively combine high energy with high power characteristics required for supercapacitors. Materials characterized by a bicontinuous structure of a solid phase surrounding pores in the range of a few tens of nanometers, would be excellent candidate materials for high-performance supercapacitors.

It is well known that mainly the micropores (<2 nm) are not easily accessed by the liquid electrolyte and the exposed surface in micropores may not be utilized for charge storage whereas the mesopores (2~50nm) can play an adsorption and transporting role, especially for high rate condition.

Mesoporous electrode materials would allow the electrolyte to deeply penetrate within the solid phase. And very thin solid phase of the material would further reduce the length of the ionic diffusion paths for the ions participating in electrochemical reaction. In addition, increased electric conductivity of the electroactive material in the electrode is very important to improve rate capability of a supercapacitor.

Therefore, high surface area metal oxide materials containing regularly interconnected mesopores are highly desirable for the supercapacitor electrodes.

We have made an attempt to improve the electrochemical performance of the electrodes based on metal oxides introducing a ordered mesoporous structured metal oxides electrode materials. For this propose, we prepared mesopoous metal oxide and meporous metal oxide/carbon composite electrode materials by liquid template method.

More details about mesoporous metal oxides and/or mesoporous metal oxide/carbon composite synthesis and their structural and electrochemical properties will be presented at the meeting.

Surface Movements of Finger-like Islands in Electrochemical Environment

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On the basis of time–dependent in situ scanning tunneling microscopy with electrochemistry, we demonstrate that a group of needle-like long islands move from the step edges of a Au surface to another neighboring step site, which is driven by the electrodeposition of submonolayered thallium metal. A flame-annealed Au(111) surface has large and flat terraces composed of alternating hexagonal close packing and face-centered-cubic stacking connected by partial dislocations that lead to the well-known (22 x √3) reconstruction. When a little amount of thallium is decorated at step edges, Au atoms at hcp jump to the neighboring fcc position because fcc is the more stable than hcp. The lateral spacing between long islands is 6.5 nm, indicating that the surface movement is rooted in reconstructed Au surface. Moving stuffs diffuse at the speed of 0.2 nm/s that is similar to the self-diffusion rate of Au. Through a variety of experimental conditions such as the changes of electrochemical potentials, scanning speeds, tunneling currents, samples biases, and the fixing of the scanning tip after the introduction of thallium to Au surfaces, we conclude that a major agent is thallium for the migration of a bunch of chopstick-like islands even under the interference of aqueous components.

Symposium 4 - Poster

Elecrochemical Nanotechnology

Fabrication of carbon nanotube electrodes

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The remarkable electrical properties of carbon nanotubes have been extensively studied since their discovery in 1991. It is well known that single walled carbon nanotubes can either be metallic or semiconducting with a band gap inversely proportional to their diameter. Although the majority of research has focussed on studying the electrical properties of individual nanotubes, with possible applications as diverse as interconnects and sensors, more recently the benefits of nanotube networks as a macroelectronic material have been recognised[1]. Due to their high aspect ratio nanotubes can form highly interconnected networks at very low surface coverage. At low densities, i.e. just above the percolation limit, the networks behave as semiconductors, while at higher densities (although still only ~ 1% surface coverage) they behave as highly conducting thin films. We are interested in studying the electrochemical properties of these nanotube electrodes, the first step in which is, by necessity, the fabrication of carbon nanotube electrodes.

In this work we describe the catalysed chemical vapour deposition growth of carbon nanotubes on an insulating substrate. We can vary the density of nanotubes from below the percolation threshold to well above it, and by varying the size of catalyst particle we can vary the diameter of nanotube produced from ~ 1 –10 nm. Using photolithography we can pattern the nanotubes onto selected areas on the substrate, either by positioning of the catalyst before growth, or by selective removal of nanotubes after growth. Photolithography is also used for patterning electrodes onto the substrates, enabling electrical measurements on individual nanotubes, several nanotubes in parallel or networks of nanotubes. To study the electrochemical properties of these electrodes the final step is a coating of insulation, leaving only the nanotube(s) exposed.

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Symposium 4 - Poster

Elecrochemical Nanotechnology

Preparation and conductivity staircase behavior of polyaniline nano-dots at room temperature

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The template method is regarded as a simple and very effective way for preparing micro and nanomaterial. By different nanoporous template, the conductive polymer nanotubes or nanowires with different nanoscale were fabricated. Our new strategy to modify the diameter of nanowire is to make a hydrophobic AAO wall by assembling surfactants on AAO wall. Because of positive charge of AAO surface, negatively charged hydrophilic head-groups of surfactant are absorbed onto the AAO surface through electrostatic attraction or both electrostatic attraction and chemical binding, and hydrophobic end-groups construct a hydrophobic surface layer. Consequently, a hydrophilic solution will be confined in a smaller space than that of the template pore. The hydrophobic AAO inwall and the hydrophilic solution result in the size reduction of polymer nanowires or nanotubes synthesized in the AAO template. We have synthesized PANI nanotubes and nanowires with smaller diameter by the AAO template of which pore walls were modified by surfactant, as shown in fig.1. We studied the conductivity of fabricated PANI nanowires in the array by conducting AFM（fig.2）, and found that there is size effect of conductivity of the PANI nanowires: the conductivity increases when the diameter decreases(Table 1).

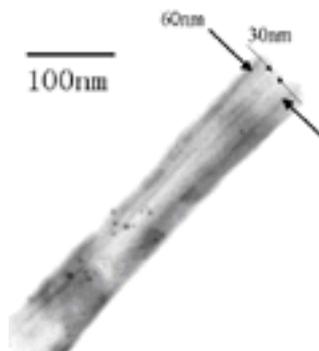Fig. 1 TEM image of PANI polymerized in AAO modified by surfactant octadecanoic acid
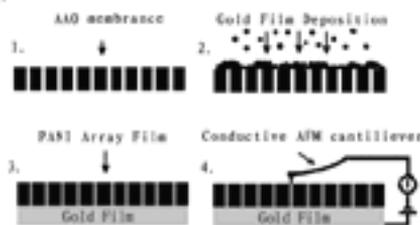

Fig.2 Schematic of the preparation of PANI nanowires embedded within AAO

Table 1 Conductivities of PANI nanowires in terms of the diameter

d/nm	60	40	30	24	20
σ/S·cm^{-1}	0.3369	0.5518	0.6837	0.7508	1.0601

Symposium 5

Electrochemical Engineering & Technology

S5·KN-1

Development and Scale up of the FFC Cambridge Process

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The FFC Cambridge Process was discovered in 1997 at the University of Cambridge. The process is very elegant and environmentally friendly in that an oxide is made the cathode in a bath of a molten chloride of a very electropositive element. Under these conditions, the favoured cathodic reaction is the ionisation of the oxygen in the oxide to from oxygen ions that dissolve in the salt. The final result is a finely divided metal product. Metalysis Ltd has a world-wide exclusive license to exploit the technology for all materials containing less than 40% titanium.

The process starts with a metal oxide powder that is formed into a mechnically stable, porous pellet. A collection of pellets is made the cathode in a bath of molten salt (typically $CaCl_2$) and reduction of the oxide occurs under potential control. The process has wide applicability and a number of materials have been produced in kg quantities.

This paper will describe the basics of the process, illustrate how the process is being scaled and will discuss the nature of a range of metals produced to date.

Symposium 5 - Keynote

Electrochemical Engineering & Technology

Symposium 5 - Keynote

Electrochemical Engineering & Technology

Electrodeposition of nanomaterials in air and water stable ionic liquids

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Ionic liquids, especially air and water stable, have attracted considerable attention since they have extraordinary physical properties superior to those of water or organic solvents. They have extremely large electrochemical windows, more than five volts, and hence they give access to elements which cannot be electrodeposited from aqueous solutions such as, e.g., Al, Mg, Ta, Ge and Si. Moreover, the problems associated with hydrogen ions in conventional protic solvents can be eliminated in ionic liquids because ionic liquids are normally aprotic. In this paper, we report on the electrodeposition of tantalum on different substrates such as, single crystalline gold Au(111), polycrystalline platinum, NiTi alloy and stainless steel in the water and air stable ionic liquid 1-butyl-1-methyl-pyrrolidinium bis (tri-fluoromethylsulfonyl) imide ([BMP]Tf_2N) containing TaF_5 as a source of tantalum. The results show that, in addition to the formation of insoluble compounds, Ta can be electrodeposited in the ionic liquid ([BMP]Tf_2N) containing 0.5 M TaF_5 at 200 °C. The XRD patterns of the electrodeposit show the characteristic patterns of crystalline tantalum. Moreover, it was found that the deposition of an only 500 nm thick film of Ta on NiTi alloy improves its corrosion resistance which, in turn, enhances its biocompatibility. We report also the first results of the electrodeposition of nano- and microcrystalline aluminium in some water and air stable ionic liquids namely, 1-butyl-1-methylpyrrolidinium bis(tr ifluoromethylsulfonyl) imide [BMP]Tf_2N, 1-ethyl-3-methylimidazolium bis(trifluoro methylsulfonyl) imide [EMIm] Tf_2N and trihexyl-tetradecyl phosphonium bis(trifluo romethylsulfonyl) imide ($P_{14,6,6,6}$ Tf_2N).

Electrochemical oxidation of synthetic dyes

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The textile and paper industries require large volumes of water and produce effluents that contain large quantities of organic compounds and inorganic salts and have high COD and colour levels. In particular, due to the presence of reactive dyes, colour removal is the major problem in dealing with these effluents. In fact, synthetic dyes contain one or more functional groups and complex aromatic structures which make them very difficult to biodegrade. Commonly employed methods for colour removal are adsorption, coagulation, chemical oxidation with ozone or Fenton's reagent and advanced oxidation processes; however these processes are quite expensive and have operational problems. For these reasons there has been increasing interest in the use of new methods such as electrochemical oxidation.

Many studies have been carried out on electrochemical treatment of organic compounds and several anode materials have been tested; however several of these have demonstrated a rapid decline in activity due to surface fouling (glassy carbon, and others have performed only selective oxidation of pollutants without obtaining their complete incineration (Ti/IrO_2, Pt). The complete mineralisation of the organics to CO_2 has only been obtained using high oxygen overvoltage anodes such as SnO_2, PbO_2 and boron-doped diamond because during electrolysis at high potentials these electrodes produce hydroxyl radicals from the water discharge on their surfaces. Among these electrodes BDD anodes exhibit good chemical and electrochemical stability even in strong aggressive media, a long life and a wide potential window for water discharge, and are thus promising anodes for industrial-scale wastewater treatment.

The aim of this work was to study the electrochemical oxidation of a model wastewaters containing dyes with different structures: aniline blue ($C_{32}H_{25}N_3O_9S_3Na_2$) a triarylmethane dye, or alizarin red ($C_{14}H_7O_7SNa$) an anthraquinone dye. The influence of the main operating parameters, such as current density, flow-rate and temperature, affecting COD and colour removal was investigated in order to find the optimum experimental conditions.

The results of the electrolysis revealed the suitability of the electrochemical process for completely removing the COD and effectively decolourising the wastewaters due to the production of hydroxyl radicals on the diamond surface. In particular, the oxidation was favoured by a low temperature, a low current density and a high flow-rate meaning that the oxidation was a diffusion-controlled process.

Symposium 5 - Keynote

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Electroreduction of polychloroethanes at silver electrodes

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Recent studies [1-2] on the electroreduction of volatile organic halides on Ag cathodes have highlighted the role of silver as powerful electrocatalyst for the hydrodehalogenation of volatile organic halides, namely polychloro-methanes and –ethanes, in non-aqueous and mixed solvents. The extended cyclic voltammetry experiments on both C1 and C2 derivatives, together with the preparative electrolyses performed on model compounds ($CHCl_3$ and CH_2Cl_2), not only confirm that significant energy saving can be achieved by the use of silver as electrode material, as in all the other electroreductions of organic halides investigated so far, but also suggest that the reaction pathway(s) might once again differ from the one observed on less active materials, as in the case of glassy carbon.

In the present work the investigations have been focussed on polychloro-ethanes and extended from non-aqueous to pure aqueous media to confirm the applicability of the degradation procedure to any H_2O-organic solvent composition, up to 100% H_2O. The results point to a preferential pathway toward the total hydrodehalogenation of the substrates

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Symposium 5 - Keynote

Electrochemical Engineering & Technology

Electrochemical mass transfer modelling of a complex two phase heat transfer problem: case of a prototype slagging gasifier

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This paper describes the modelling of heat transfer in the hearth of a prototype slagging gasifier using the electrochemical limiting diffusion current technique and subsequent application of the Chilton-Colburn analogy between heat and mass transfer. The apparatus used was based on a quarter scale model of the British Gas Westfield gasifier and was manufactured in the form of a large conical vessel with top diameter of 0.61 m fabricated from nickel sheet. The half angle at the cone base, where gas could be introduced through nozzles of various diameters, was 43 degrees. To provide suitable cathode and anode portions for the electrochemical cell the cone was cut vertically into two sections in the area ratio 1:5 and 32 nickel mini cathodes of diameter 1 mm were flush mounted with the inside surface of the cone at various distances from the nozzle blocks at the cone base. The mini cathodes were fixed and isolated from the main cathode surface using Araldite adhesive. The well known electrochemical equimolar ferri-ferro cyanide redox system in excess supporting electrolyte was used for the limiting current mass transfer measurements eg [1]. However, here we had to simulate the properties of a molten slag and CMC in various concentrations was used as additive to increase viscosity. This precluded the use of the strong alkali NaOH, the usual supporting electrolyte, and a buffer solution of sodium carbonate and sodium bicarbonate was used. The full range of solution compositions provided a comprehensive range of Schmidt numbers between 1624 and 3,800,000.

Initially gas flow tests were carried out using water and air as fluids, the air being injected from the gas plenum through the vertical nozzles and into the conical model gasifier vessel. The bubble frequency was measured using a pressure tapping in the wall of the gas plenum and plots of bubble frequency against flow rate yielded excellent agreement with British Gas data obtained using a wide variety of liquids.

Polarisation curves with very well defined limiting current plateaus were obtained in natural convection conditions (no gas flow into the electrolyte), but as soon as gas was injected through the nozzles fluctuation of the limiting currents occurred, in some cases giving very unsteady readings. To avoid the electrolyte sloshing about in the conical vessel and to more accurately simulate conditions in the real gasifier a flow dampener was introduced in the form of table tennis balls glued together and situated on the top surface of the liquid. The chart recordings of current fluctuations showed lower amplitudes and more regular waveforms when compared with flows under similar but undamped conditions.

Plots of time averaged limiting currents from the mini-electrodes with the macrocathode simultaneously active allowed the distribution of mass transfer along the sides of the conical vessel to be determined. These distributions produced high values at the top where there is considerable surface motion and also near the base where there are intense liquid recirculation eddies associated with the emergence of the gas stream from the nozzles – a complex gas jet flow pattern. The form of the distribution of local mass transfer coefficient was found to be sensitive to liquid viscosity and also to gas velocity. Spatially average mass transfer coefficients based on macrocathode data and on integration of the mini electrode data with appropriate weighting for the varying cone area gave agreement within a few percent.

Plots of modified mass transfer j-factor against gas nozzle Reynolds number provided excellent correlations both for the 16 mm and 19 mm nozzles and for CMC concentrations between 0 and 3%.

Use of the Chilton-Colburn analogy between mass and heat transfer allowed the calculation of heat transfer coefficients, h, for the model gasifier using slag properties provided by Rhine et al [2]. Values of h thus calculated ranged between 160 and 200 W/m^2 K. These values might be somewhat enhanced by contributions from natural convection and agree remarkably with the value of 170 W/m^2 K suggested by British Gas [3].

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Nanostructured SnO_2-IrO_2 sol-gel composite electrocatalysts: from powders to electrodes

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The research and development on new electrocatalytic composite materials entails a wide spectrum of parallel investigations on the electrochemical performance, the morphological features, the bulk and surface compositions, and their possible modifications in connection with the use of supporting materials and additives as required by cell and electrode design.

The supporting material and techniques become of critical importance when dealing with nanostructured composite materials [1-3] prepared *via* sol-gel, a technique which allows the accurate tailoring of the powder morphology and composition, but implies the adoption of appropriate current collectors.

In this context, the present work focuses on the role played by the support on the observed properties of nanostructured mixed Sn-Ir oxides, prepared by a low temperature sol-gel method, and used as electrocatalysts for the oxygen evolution reaction in acid water electrolyzers.

The materials are investigated by both ex-situ techniques (XRD, XPS, SEM and BET) and in-situ electrochemical characterizations (typically, voltammetric techniques and impedance spectroscopy). The results obtained for a $Sn_{0.85}Ir_{0.15}O_2$ model powder are discussed in terms of different supporting materials and procedures, also in the presence of selected additives (carbon, proton conducting polymer).

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Advanced modelling of 3D electrochemical machining with time dependent imposed current or potential

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Most of the time the non-symmetrical and complicated tool/work piece configurations encountered in ElectroChemical Machining (ECM) can only be approached by real 3D modelling. In addition to that the imposed current or potential is often changing during the process in order to gently start or to optimise the process. Finally the high current densities applied can involve local ohmic drops in resistive work pieces (e.g. made of stainless steel) that influence the final shape.

This paper presents the basics of an integrated approach solving an electrical network that is coupled with three dimensional potential distributions in tool and work piece and three dimensional secondary current density distributions in the electrolyte. This model is coupled with three dimensional electrode shape change simulations with moving tools.

The electrical network consists of resistors and time dependent current and/or potential sources. The electrochemical process model assumes that the electrolyte is well stirred and refreshed such that the current density in the electrolyte and the electrodes is governed by the Laplace equation. At the interfaces between electrodes and electrolyte non-linear boundary conditions model the electrode reactions. The whole geometry is discretised in tetrahedra and the Finite Element Method (FEM) is applied to discretise the potential field. The electrode shape is found by displacing the nodes on the anode surface proportional with, and in the direction of the local current density and efficiency according to Faraday's law.

The mathematical modelling of the whole ECM process is integrated in the CAD package SolidWorks®. This enables to perform ECM design directly starting from scratch or by reading in existing CAD files (STEP, AutoCad, IGES, …). The software can visualise results at different stages of the electrode shape process using color plots, isolines and streamlines.

In the examples the effects of the metal resistivity, different contacting methods, different power supply sources and different moving rates of the work tool will be demonstrated.

Symposium 5 - Keynote

Electrochemical Engineering & Technology

Formation of micro- and nano-sized ordered structures by self-organization in electrochemical systems

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Self-organized formation of ordered micro- and nano-structures of metals and semiconductors at solid surfaces has been attracting keen attention in view of nanotechnology. The self-organization method has an advantage over the photolithography and surface probe method in that it meets both the conditions of atomic-scale fabrication and the adaptability of mass production. Recent studies on non-equilibrium, nonlinear chemical dynamics have proved a large possibility of self-organized formation of a variety of ordered structures such as stripes, dot arrays, and target and spiral patterns. However, most of the patterns thus far reported are limited to those of two dimensions (2-D) lying parallel to the substrate surface. The formation of organized "vertical" structures and further organized 3-D structures will need novel strategy. From this point of view, oscillatory electrodeposition is an interesting target because it has an ability to produce ordered electrodeposits by recording ever-changing self-organized spatiotemporal patterns during oscillations. Here we review our recent studies on the

Figure 1 (a) Potential oscillation observed in Sn electrodeposition. (b) An optical microscopic image of highly ordred latticeworks of Sn produced by the oscillatory electrodeposition.

Figure 2 (a) Current oscillation obtained in SnCu-alloy electrodeposition. (b) SEM (top view) of a bowl-shaped hollow with a slanting cross section, prepared in the deposited alloy film by Ar+ ion etching. (c) Schematic illustration of sample preparation for (b).

structurization by oscillatory electrodeposition[1-3], with a focus placed on the formation of strikingly well-ordered metal latticeworks, standing perpendicular to the substrate, through ingenious cooperation of various processes with long-range spatiotemporal synchronization.
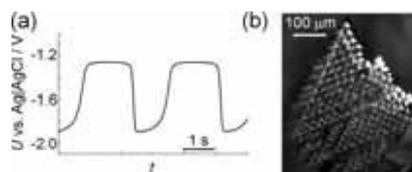
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Visibile – Light Photoelectrochemical Degradation of Pollutants on Co-Doped TiO$_2$

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Semiconductors photocatalysis has reached a high maturity level, and the discipline is now credited as one of the most promising within the so-called "Advanced oxidation technologies" (AOT) for applications in depollution processes or in clean syntheses (Green Chemistry). [1, 2] . As now well known, TiO$_2$ has unique properties as a photocatalyst for applied purposes such as stability, low cost and ecological compatibility. On the other hand, the disadvantage of absorbing a small fraction of the solar light is a weighty one. Doping and surface derivatization of the oxide are two widely explored routes presently adopted by researchers with the aim to increase the response of the material to visible light and/or increase its efficiency in photo-oxidation processes [2]. The use of TiO$_2$ doped with low quantities of foreign species represents, on the one hand, a possible strategy to extend the absorption of the oxide to the visible region. [3].

In this work we examine the photocatalytic activity and characterization of Co doped commercial TiO$_2$. Cobalt-doped TiO$_2$ is a somewhat controversial system in that, compared to undoped TiO$_2$, it is reported as photocatalytically more active [5] and less active [6], respectively. We assessed the photocatalytic activity of the different Co-TiO$_2$ samples in the photodegradation of 4-chlorophenol and bisphenol A. Independently from parameters such as the calcination time and temperature, doped TiO$_2$ were always more active than TiO$_2$ with the same thermal history. Furthermore, the absorption spectrum of TiO$_2$ is red shifted on increasing the amount of dopant. This fact prompted us to investigate the photoactivity of the samples using visible light ($\lambda > 420$ nm and $\lambda > 450$ nm). We observed that while doped samples still had a photocatalytic efficiency, undoped TiO$_2$ was practically inactive in this wavelength range. This enhanced photoactivity of Co-TiO$_2$ reaches a maximum for 0.5% Co (w/w).
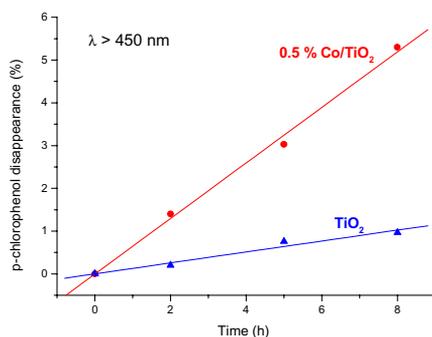
Photodegradation of p-chlorophenol on Cobalt-doped TiO$_2$
with visible light ($\lambda > 450$ nm)

The photocatalysts were characterized with DTA, XRD, XPS, surface area (BET) and TEM. XRD, DTA measurements did not reveal any change in the phase distribution of the TiO$_2$ doped compared to undoped TiO$_2$ samples. Likewise, the measured surface area remains the same within experimental error. XPS measurements showed that for low doping levels (< 1 %) only Co (II) is present in doped material.

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Symposium 5 - Oral

Electrochemical Engineering & Technology

Electrochemistry of the anodic oxidation of 4-methoxytoluene: mechanism and selectivity

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In the frame of the European programme IMPULSE, the anodic oxidation of 4-methoxytoluene into acetal and aldehyde in methanol has been considered as the test reaction for the design of micro-structured electrochemical cells because of its industrial relevancy and the selectivity issues.

The electrochemistry of the reaction was thoroughly investigated at RDE using either sodium/lithium perchlorate or potassium fluoride, and varying the carbon material employed: in addition to graphite, the glassy carbon (GC) was either polished by the supplier or cut in its cross-section in the preparation of the RDE. The "cut" surface was observed to be far less smooth than the polished one. The concentration of anisole was kept below 0.01M to reduce the cell current and the ohmic drop contribution in electrode potential. The residual current was subtracted from the global current, and the potential was corrected for ohmic drop. Low-scan rate voltammetry and impedance spectroscopy were applied. On polished GC surfaces, i-E curves exhibited a fairly defined plateau between 1.5 and 1.65 V/SCE; in contrast, the current increased steadily over 1.5V on "cut" GC, suggesting the occurrence of a further oxidation. Acetal oxidation was actually shown to occur at approx. 1.55V on graphite and cut GC, and near 1.7V on the other surface. Fitting the experimental variations to the Koutecki-Levich equation yielded estimates for anisole diffusivity and the kinetic parameters. The diffusion coefficient, of the order of 10^{-9} $m^2 s^{-1}$ is in agreement with values obtained from published correlations. Besides, the Tafel slope of the overall reduction was of the order of 70 mV/decade with graphite and the "cut" surface, while the polished surface was far less active, with a Tafel slope twice as large: such a slope value indicates that one electron only should be involved in the rate-controlling process, as for the formation of ether.

Batch experiments were carried out in stirred vessel at constant current density. The anisole conversion calculated depending on the charge passed (in F/mole), suggested the significance of the two-step oxidation in acetal formation, in particular for GC surfaces. The intermediate ether species evoked above and formed globally with two electrons likely accumulated in the first period of the run, and the selectivity in acetal/aldehyde, formed with four electrons exchanged was typically low. Use of KF instead of perchlorate salts resulted in slower anisole conversions and significantly higher selectivity. For the all surfaces tested, the potential increased slightly with time: ether oxidation became faster after sufficient conversion, as shown by the increasing selectivity, and later for higher anisole conversions, the potential attained the value of half-wave oxidation of acetal oxidation: this was confirmed by the decreasing selectivity in the final period of the run, especially with Na or Li perchlorates.

Hard Chromium deposition using ionic liquids as a potential substitute to hexavalent chromium plating: First results in European IONMET programme.

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Hexavalent chromium (CrVI) solution are worldwide largely used for hard chromium plating. But CrVI is reputed as a carcinogenic and highly toxic agent, so regulations through the world are becoming more and more drastic. As consequences, studies on hard chromium plating alternative processes are extensively developed : HVOF, PVD, electrolytic and electroless metal deposition (Ni or Co - with and without particles inclusions), trivalent chromium solutions…. But at the moment no processes are able to really industrially substitute the "old - good - simple" hard hexavalent chromium plating in all its applications.

Due to highly specific characteristics and used in special conditions, Ionic Liquids formed with metal salts (as halide) could allow electrolytic deposition of metal which can be investigated as potential substitute of aqueous deposition in some applications.

Experiments and results obtained in the course of hard chromium deposition during IONMET programme using ionic liquids formed with trivalent chromium salts will be presented. In particular influence of temperature, current density, additive elements and surface preparation will be disclosed. Potential industrial application of the process as alternative to hard chromium plating will be considered in particular in engineering (wear and corrosion resistance, friction coefficient) and in environmental aspects.

Symposium 5 - Oral

Electrochemical Engineering & Technology

What is the Ominous Chlorine Consumption in the Disinfectant Production by Drinking Water Electrolysis?

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Discussing the behaviour of several electrode materials or arrangements, very often ominous chlorine consumption is cited to explain discrepancies between the results. This underlines the fact, that the process of direct drinking water electrolysis is studied insufficiently so far. To close the gap, special experiments were carried out using IrO_2/RuO_2 and boron doped diamond electrodes for the drinking water electrolysis in a non-divided cell. The experimental settings of the discontinuous electrolysis at 20 °C are similar to those described in [1]. It was found that in absence of irregular electrolysis conditions [2] at least six influence factors are responsible for remarkable chlorine consumption, thus lowering the disinfection efficiency of the process. These influence factors are

- the cathodic production of hydrogen peroxide from dissolved oxygen
- the cathodic production of nitrite and ammonium from nitrate ions
- the anodic formation of chlorate
- the enlarged oxidant production on boron doped diamond anodes
- chlorine reaction with organic components
- interference effects during the analysis.

Hydrogen peroxide can be formed easily on the mixed oxide cathode and, in much larger scale, on the diamond anode. The consecutive fast reaction with active chlorine may reduce the chlorine content in the ppm range of concentration. The reaction mechanisms are well understood.

The formation of nitrite and ammonium could be clearly demonstrated using ion chromatography. Both products can react with chlorine species. In the case of ammonium, the formation of chloramines occurs. This is in contradictions to drinking water regulations in several countries. In all discontinuous processes, a rapid formation of chlorate was observed. Using a diamond anode, even a consecutive destruction of chlorate ions was apparent. Extending the electrolysis time to larger values, a total removal of chloride and hypochlorite is possible.

It was found recently [3] that monochloramine may disturb the analysis of active chlorine by the DPD method. Also, amperometric methods often show enlarged analysis values with respect to active chlorine. When the monochloramine takes part in additional electrode or chemical reactions a highly complicate analysis situation exists resulting into wrong results and interpretation.

The authors are convinced that a chlorine formation is possible even for extreme small chloride concentrations. However, side reactions with relatively high reaction rate reduce the chlorine production immediately. For example, in a solution containing chloride and nitrate ions a minimum chloride concentration of 10 ppm was found for the detection of active chlorine on the diamond anode. It is a conclusion of the presented studies, that a more sophisticated discussion is necessary to discuss experimental results from drinking water electrolysis.

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Electrochemical synthesis of hydrogen peroxide on o₂ fed graphite/ptfe electrodes modified by 2-ethylanthraquinone

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This paper reports an investigation on the performance of a catalyzed H_2O_2 electrogeneration process using a modified O_2 fed graphite/PTFE (MGDE) electrodes modified by 0.5 % to 10% of 2-ethylanthraquinone (EAQ). H_2O_2 electrogeneration rate was optimized relative to cell potential and catalyst concentration. The MGDE precursor mass was prepared from Degussa Printex 6L graphitic pigment and a 60% PTFE dispersion as hydrophobic binder. Sintered 3 mm thick MGDE (60 mm diameter) was obtained after 2 h at 320 ^{o}C, under load of 18 MPa. Voltammetric responses showed increasing current values for oxygen reduction as EAQ concentration increased. Electrolysis in sulfate medium, pH 3, at potential of –0.6 V vs. Ag/AgCl, produced a 250 mg L^{-1} H_2O_2 solution in an 1 hour controlled potential experiment, using the MGDE with 5% EAQ. Kinetics of the H_2O_2 electrogeneration process followed a zero-order kinetic and apparent rate constants were calculated as a function of cell potential and concentration of the catalyst which is shown in figure 1. The presence of EAQ in the MGDE shifted the optimal potential for H_2O_2 electrogeneration by 300 mV more positive when compared to the performance of a non-catalyzed electrode. For the electrodes containing 10% of EAQ, apparent rate constant were 35% higher compared to non-catalyzed electrode.
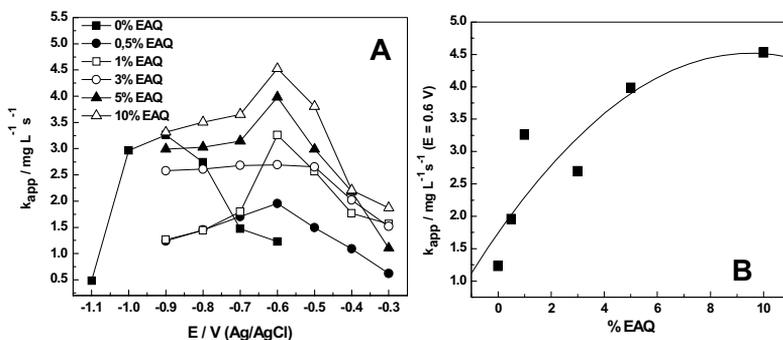
Figure 1 – (A) Apparent rate constants for H_2O_2 electrogeneration as a function of applied cell potential. (B) Apparent rate constants at – 0.6 V as a function of EAQ concentration.

Symposium 5 - Oral

Electrochemical Engineering & Technology

Electrochemistry in Conservation

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Environments rich in chloride ions pose threats to the stability of historic monuments and artefacts particularly where iron, or its alloy steel, are present as construction materials [1]. Chloride ions may disrupt protective layers on the metal surface, and corrosion of the metal object can then occur. Wood/iron composites and assemblies represent another group of materials particularly vulnerable to degradation when chloride ion penetration is possible. Thus, removal or reduction in levels of chloride ions present in metallic and non-metallic substrata and/or associated corrosion products, followed by protection of the metal surface will reduce the amount of deterioration and prolong the lifetime of the structure or artefact.

This paper describes the use of electrolysis in the removal of chloride ions from two large-scale conservation projects involving the World War I monitor, the M33 [2] and the *s.v.Cutty Sark* [3-4] The pre-treatment procedures and electroytic experiments are described. In the case of the M33, a total of 52 kg of sodium chloride was ultimately removed from crevices present in a surface area of 250 m^2 in the lower regions of the ship. The electrolysis was carried out over a two-year period with areas treated sequentially; average electrolysis times were approximately 12-14 months. The second example involves the electrolysis of composite structures of wood and iron from the *Cutty Sark*. The laboratory experiments carried out to confirm the applicability of this method to treatment of a composite assembly are described. In particlular, the electrochemical and microbiological aspects of a complex system are discussed together with the subsequent pilot study in the Aft Peak area of the ship confirming the feasibility of using electrolysis to remove chloride ions from the wood/iron matrix [5].

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First stages of CIS electrodeposition from Cu(II)-In(III)-Se(IV) acidic solutions on polycrystalline Mo films

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Copper-indium diselenide (CIS) is a recent material in development for thin film photovoltaic solar cells [1 and references therein]. Electrodeposition is a low-cost method, which allows the coverage of large areas and has been recently applied to CIS deposition [2]. To get a better knowledge of the electrocrystallization process, we are investigating the first stages of CIS electrochemical deposition from acidic solutions on molybdenum covered glass plates (standard contact on CIS layers [3]).

CIS layers were deposited at constant potential for increasing durations. The current time transients were recorded, the film morphology was examined by SEM-FEG, the surface was analysed by XPS. Raman spectroscopy, X-ray diffraction and X-ray fluorescence analysis were also carried out.

SEM examination shows a 3D quasi-instantaneous nucleation occurring mainly on the ridges of the Mo grains, with a high density of nuclei ($> 10^{11}$ cm^{-2}) (Fig. 1). With increasing deposition time, the diameter of the nuclei increases as a function of $t^{0.5}$ until coalescence occurs for an electrical charge, Q_2, close to 0.25 C.cm^{-2}. XPS analysis indicates an evolution of the surface composition (Fig. 2) and of the chemical environment of selenium. For short deposition times, the Se/Cu atomic ratio is very low. The composition tends to stabilize for much longer deposition times than the current density which reaches a steady-state value after a few seconds (Q_1). This behaviour may indicate that, in addition to the electrochemical reduction of the electroactive specie, chemical reactions, which do not contribute to the current response, with slower rate constants, are involved in the growth process.
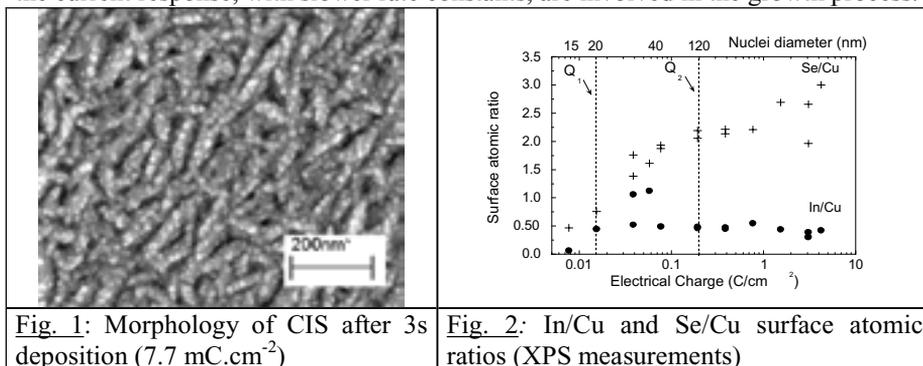
| Fig. 1: Morphology of CIS after 3s deposition (7.7 mC.cm^{-2}) | Fig. 2: In/Cu and Se/Cu surface atomic ratios (XPS measurements) |

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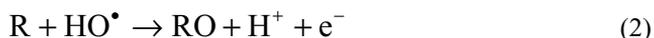[3] O. Ramdani, B. Canava, E. Chassaing et al., 209th ECS meeting (2006)

Symposium 5 - Oral

Electrochemical Engineering & Technology

Symposium 5 - Oral

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Investigations of Electrochemical Oxygen Transfer Reaction on BDD using Microelectrodes-array

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Boron-doped diamond (BDD) electrodes exhibit interesting electrochemical properties like a high anodic stability and a wide potential window for hydrogen and oxygen evolution. The previous studies of electrochemical oxygen transfer reactions on BDD electrodes bring to evidence that hydroxyl radicals are the main intermediates formed during EOTR[1]. They are produced by water discharge according to the equation 1. Oxygen transfer reactions can proceed via electrochemical (Eq.2) or chemical reaction (Eq.3).

$$H_2O \rightarrow HO^\bullet + H^+ + e^- \tag{1}$$

$$R + HO^\bullet \rightarrow RO + H^+ + e^- \tag{2}$$

$$R + 2HO^\bullet \rightarrow RO + H_2O \tag{3}$$

In this study EOTR is investigated on boron doped diamond microelectrodes-array. Due to the small dimension of the microelectrodes (5µm) and appropriate spacing (150 µm) the spherical diffusion dominates enhancing the mass transfer. The superior mass transportation away from the electrode surface allows to work without nucleation of bubbles on the surface[2]. Moreover, microelectrodes have a small ohmic drop, small capacitive background current, high signal to noise ratio, access to steady state conditions and short equilibration time[3].

The oxygen evolution reactions were studied in 1M $HClO_4$. The mechanism of oxygen evolution on BDD and assumptions of the rate determining step are presented. The voltammetric response of BDD microelectrode-array in presence of organic compounds was also studied and compared with planar BDD anode.

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Electrodeposition of Zn, Ni, Sn and Fe Alloys From Deep Eutectic Solvents Based on Choline Chloride

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Research at C-Tech Innovation as part of the EU FP6 IONMET project, has been conducted on electrodeposition of a range of metal alloys from eutectic mixtures (ionic liquids) as an alternative to conventional aqueous techniques. Here we describe the electrolytic deposition of Zn, Sn, Ni and Fe alloys from solutions of the metal chloride salts separately in urea and ethylene glycol / choline chloride based ionic liquids. We examine the effects of solution composition (metal concentration, ionic liquid and additives), temperature, current density and mass transport on the composition, morphology and adhesion of the deposits. We show that a wide range of alloy compositions can be obtained from ionic liquids and that suitable operating windows exist to alloy scale up beyond the laboratory to pilot plant scale.

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Electrochemical Engineering & Technology

Symposium 5 - Oral

Electrochemical Engineering & Technology

Electrochemical investigation of the oxoacidic properties of zirconium(IV) in The LiF-NaF-KF eutectic melt at 500°C eutectic?

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The molten salt reactor was one of the concepts retained in the international forum Generation IV (2001) for the future nuclear energy systems. In this concept, the ThF_4-UF_4 fuel is dissolved in a molten fluoride mixture whose composition is not yet totally defined. In order to prevent any ThO_2 or UO_2 precipitation, ZrF_4 is strongly envisaged as a component (from 5 to 20 mol%) of these future mixtures. Moreover, fuel salt reprocessing usually considered involves some steps based on electrochemical methods particularly liquid metal/molten salt extraction. Therefore, the electrochemical behaviour and the oxoacidic properties of the molten salt have to be very well known. Oxoacidic properties of Zr(IV) - which govern the ability to form either zirconium oxyfluoride or oxide - were thermodynamically determined with an oxide amperometric titration technique using a calibrated gold working electrode. The electrochemical redox potential were determined using voltametric measurements. The required equilibrium data necessary to precise oxoacidic and potential ranges of zirconium(IV)-based molten fluoride salts were so determined.

One of the major investigation lines for the development of the molten salt nuclear reactor (concept which was retained in 2001 at the international forum Generation IV for the future nuclear energy systems) is the formulation of the molten nuclear fuel. In particular, use of $ZrF4$ as an extra component is more and more considered because of its oxoacidic properties which enable to prevent any precipitation of $ThO2$ or $UO2$. In this frame, we have developed electrochemical techniques both for in situ accurate determination of the free oxide anion content of melt and for the obtention of the thermodynamic data relevant to the stabilities and solubilities of the zirconium(IV) oxyfluoride and oxide. The resulting data confirm the positive role of $ZrF4$ as a melt component.

A new process for electroplating of magnesium

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The use of magnesium in aviation industry will increase due to the fact that weight reduction is becoming increasingly important. However, magnesium suffers from a lot of severe corrosion problems and an effective corrosion protection for manifold applications is demanded.

A new coating system for Mg alloys based on electroless deposited zinc has been developed in the EC-funded project *"Integrated Design and Product Development for the Eco-efficient Production of Low-weight Aeroplane Equipment" (IDEA)*. The coating was first applied to well known alloys (e.g. AZ91) and was then transferred to new Mg alloys with improved mechanical properties and casting qualities.

State of the art of Mg metallization is an electroless deposited starting layer on the substrate with an autocatalytic electroless nickel/phosphorus coating and a subsequently electrodeposited reinforcement. However, this system suffers from the large electrochemical potential difference between magnesium and nickel causing dramatic corrosion damages.

A more favourable process is the deposition of electroless zinc on magnesium which is, however, not an autocatalytic, but a cementation process (1, 2). The deposition rate and consequently the quality of the zinc layer is adjustable by the use of special complexing agents which control the concentration of free zinc ions in the electrolyte.

The described process produces close layers with some pores due to the hydrogen evolution caused by the magnesium dissolution in the electrolyte. Thus, the magnesium has contact to the electrolyte up to a Zn thickness of about 2 microns, when the zinc layer will close and the hydrogen evolution stops.

The starting layer is reinforced with an electrodeposited coating of zinc or zinc/iron alloy, passivated with a chromium[VI]-free passivation. If demanded, the corrosion protection can be improved further by an organic sealing.

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Symposium 5 - Oral

Electrochemical Engineering & Technology

Electrodeposition of iron from molten salts

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The steel industry in Europe has initiated a research program to study possibilities for developing new processes for the production of iron and steel by eliminating or greatly reduce CO_2 emissions. Electrowinning of iron from molten salts using an oxygen evolving anode is an attractive alternative. Controlled laboratory experiments were conducted to study the electrochemical behaviour of dissolved iron oxide in molten salt electrolytes at medium temperatures ranging from ~ 500 - 1000 ℃. The cathode process during reduction of iron complexes was studied on substrates of carbon, tungsten, molybdenum and nickel. Laboratory scale bulk electrolysis experiments to deposit iron were also performed, and the cathode product was examined by XRD, SEM/EDA and SEM/EPMA. The solubility of hematite, Fe_2O_3, was determined by ICP and LECO of electrolyte samples or by using an in-situ emf method.

The major challenges have been to find an electrolyte which dissolves enough hematite to allow for a high current density for electrodeposition of iron and to obtain smooth electrodeposits of iron. Several electrolytes were tested, including molten chloride mixtures based on $CaCl_2$, pure fluoride and mixed chloride/fluoride electrolytes. The performance of candidate inert anode materials to evolve oxygen was tested during electrolysis. Electrodeposits of pure iron were obtained in many electrolytes. The most promising results were obtained in the molten system KF-NaF-$CaCl_2$. The solubility of Fe_2O_3 was determined to be of the order of 0.5 - 1 mol% in melts containing ~10 mol% $CaCl_2$. In these electrolytes pure iron was deposited at current densities exceeding 0.5 A/cm^2 using a rotating Fe cathode to increase the rate of mass transfer of Fe(III) species. The current efficiency with respect to iron was consistently found to be above 95%.

Symposium 5 - Oral

Electrochemical Engineering & Technology

Effect of polyethylene glycol as an inhibiting additive on electroless copper deposition in submicrometer trenches

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Electroless copper deposition is a promising trench filling process for the fabrication of ULSI copper interconnections as an alternative to electrodeposition because it is capable of achieving uniform copper deposition on high aspect-ratio nano-structures fabricated even on large-area substrates. We recently investigated the filling of trenches with electroless copper deposited from the conventional electroless copper plating bath containing formaldehyde as the reducing agent (bath A), and found that void-free filling was achieved with the bath containing polyethylene glycol (PEG) as an inhibiting additive and 8-hydroxy-7-iodo-5-quinoline sulfonic acid (HIQSA) as an accelerating additive [1]. In the present study, we examined effects of these additives on the performance of the bath containing glyoxylic acid as the reducing agent (bath B), which is preferred to bath A for environmental reasons.

The baths used in this study (bath B) contained $CuSO_4$, glyoxylic acid, EDTA, and various concentrations of PEG (Mw4000) and HIQSA, and they were operated at $70^\circ C$ and pH of 12.5 (adjusted with TMAH).

The formation of voids in trenches was completely suppressed when 1ppm of PEG was added to the bath (Fig. 1b). The improvement of filling property brought about by PEG is attributed to a decrease in PEG concentration in the interior of the trenches resulting from the low rate of diffusion of PEG molecules into the narrow trenches. The decrease in PEG concentration in trenches should lead to a higher deposition rate inside the trenches than at the trench openings. For this bath, the addition of HIQSA, was insignificant for trench filling, in contrast to the case of bath A,

Fig. 1. SEM images of copper deposited in trenches from (a) additive-free and (b) PEG-containing baths. Deposition time, 3min.

in which improved filling property was observed when HIQSA was added together with PEG. This study thus demonstrates that the effect of additives depends strongly on the reducing agent used in the bath.
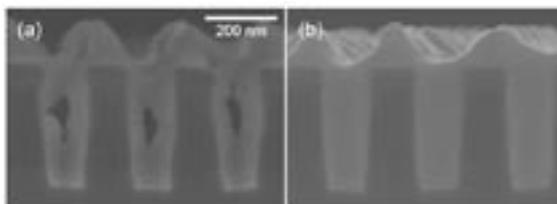
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Symposium 5 - Oral

Electrochemical Engineering & Technology

Synthesis and electrochemical behaviour of benzo[b]- and dibenzothiophenes, their S- oxides and metacyclo[2](2,5)-thiophenophanes with extended systems

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Dibenzothiophene (**2**), benzo[b]thiophene (**1**) and alkylated derivatives are ubiquitous and persistent components in crude oil. The consumption of these fuels contributes a significant release of SO_2 into the environment. Many different polyaromatic sulphur heterocycles are present in hydrotreated diesel fuel and the different alkyl side chains in these compounds affect their reactivity towards both inorganic and enzymatic catalysts, and thus complicates the search for suitable desulfurization catalysts and for suitable desulphurisation conditions. Presently, two different approaches are studied, - hydrodesulphurisation and biodesulphurization, with intensive research in both areas, but still with different important drawbacks.

Recently, the authors have found that certain thiophene-*S*-oxides, which are oxidation products of thiophenes, can be desulfurized electrochemically. This finding has prompted us to study the electro-oxidative behaviour of benzo[b]thiophenes and dibenzothiophenes and their *S*-oxides as well as thiophene systems containing other modes of pi-conjugation such as π-conjugated metacyclo[2](2,5)thiophenophanes (**3**). The electrochemical behaviour of these compounds has been studied by cyclic voltammetry in an acetonitrile/Bu_4NBF_4 system. , and preparative electrolyses have been carried out. The authors have found distinct differences in the behaviour of these conjugated thiophene structures with reactions leading to oxidized S-containing products and in certain instances also to *S*-extruded molecules.
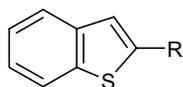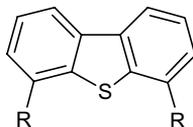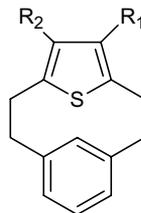
(1)   (2)   (3)

Electro-Reduction of Solid SiO_2 in Molten $CaCl_2$

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Pure silicon is urgently needed in large quantity, not only in the traditional metallurgical processes but also in many modern semiconductor and solar energy devices. This industrial product through the carbothermic reduction of SiO_2 at about 1700 ℃, known as the metallurgical grade silicon (MGS), only has a purity about 97~99%, which can not be used directly to manufacture most high-tech products such as solar cells, where at least 99.99 % in purity of silicon is required. The industrial purification of the MGS is a multi-step process, which is too expensive to the growing application of silicon in solar cells industry. New method is highly desired especially for the production of low cost solar grade silicon (SG-Si).

Historically, high purity silicon was successfully prepared in laboratory by electro-deposition from molten chlorides (99.999% purity claimed) [1] or from molten oxides (reported 99.98% purity, 1450 ℃) [2]. It was reported recently that when solid metal oxides are made into an electrode, respective metals or alloys can be directly prepared by the electrolysis in molten $CaCl_2$ [3]. This leads to a great possibility for the production of silicon directly from solid SiO_2 [4-6].

This presentation introduces our recent experimental and fundamental findings in relation with the electro-reduction of solid SiO_2 in molten $CaCl_2$. It was found that the reduction of SiO_2 is much earlier than the reduction of Ca^{2+} in the molten salt to Ca, providing a large potential range for the preparation of the silicon. Silicon has been achieved either by electrolysis of quartz glass plate or cylindrical pellets of pressed and sintered fine SiO_2 powders. The reduction has been qualitatively confirmed to proceed via the propagation of the $Si \,|\, SiO_2 \,|\, CaCl_2$ three phase interlines (3PIs) [7]. Special attention is given to the lower reduction rate in the depth direction, which is progressively slower as a result of the ohmic and concentration polarisations.

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Electrodeposition and morphology of ni and co powders

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This work is dedicated to the memory of Prof. Aleksandar Despi

Polarization characteristics for Ni and Co powders electrodeposition from $(NH_4)_2SO_4$ and NH_4Cl supporting electrolytes, as well as their morphology (SEM) are investigated. It is shown that measured polarization curves must be corrected for the IR drop and that hydrogen evolution current must be subtracted from the corrected polarization curves in order to obtain real j-E curves for powders electrodeposition [1]. In Fig. 1a are shown j-E curves for Co powder electrodeposition (j_m) and (j_{comp}) recorded in sulfate supporting electrolyte and j-E curves for hydrogen evolution onto pure glassy carbon substrate (j_H(sulfate) and j_H(chloride)), while in Fig. 1b real j-E curves for powders electrodeposition are presented . In the case of Ni powder cauliflower type of particles are detected, while in the case of Co powder different types of particles are detected, depending on the conditions of powder electrodeposition and the supporting electrolyte used: (*i*) Dendrite particles and (*ii*) Different types of agglomerates, compact, spongy-like and ball-like ones. Characteristic of almost all agglomerates is the presence of deep cavities on their surface and the fern-like dendrites on the bottom for most of these cavities.
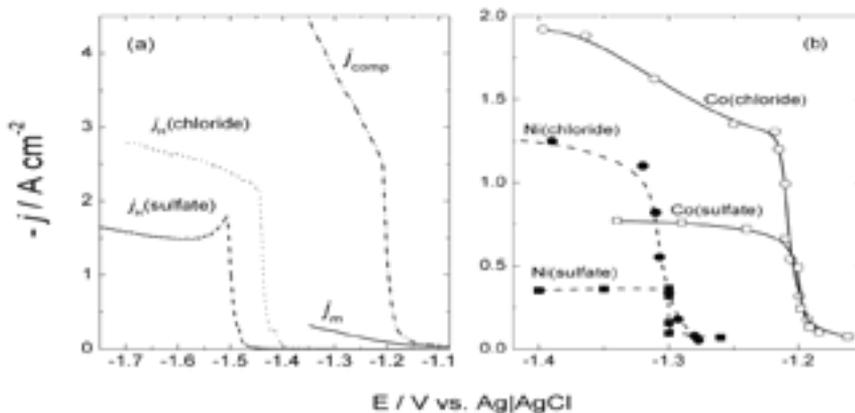
Fig. 1. (a) j-E curves for Co powder deposition without (j_m) and with IR drop compensation (j_{comp}) in the solution 0.1 M $CoSO_4$ + 1 M $(NH_4)_2SO_4$ + 0.7 M NH_4OH and j-E curves for H_2 evolution in corresponding supporting electrolytes. (b) Real polarization curves for Ni and Co powders electrodeposition.

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Circulating Particulate Bed Cathode for Metal Recovery

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Applications of electrochemical technology involving low reactant concentrations often require electrodes with high mass transport rates and specific surface areas to increase cross-sectional current densities and optimise capital and operating costs. For electrodeposition of metals from dilute solutions, cathode feeder electrodes contacting unconsolidated beds of moving, conducting particles that can grow, achieve these requirements, and enable continual harvesting of the metallic product by hydraulic transport from the bed of the particles, the relative motion of which may facilitate adherent and coherent deposit morphologies. One design option, shown schematically in Fig.1, is a circulating particulate bed electrode [1,2], for which experimental results will be reported and compared with model predictions for recovery of:

1. low concentrations of platinum from aqueous iodide solutions with simultaneous generation of tri-iodide on a carbon felt anode (Fig.1);

2. metals from acidic aqueous chloride solutions, produced by the leaching of waste electrical and electronic equipment (WEEE), containing precious metals (Ag, Au, Pd) in low concentrations and base metals (Cu, Pb, Sn etc.) in high concentrations.
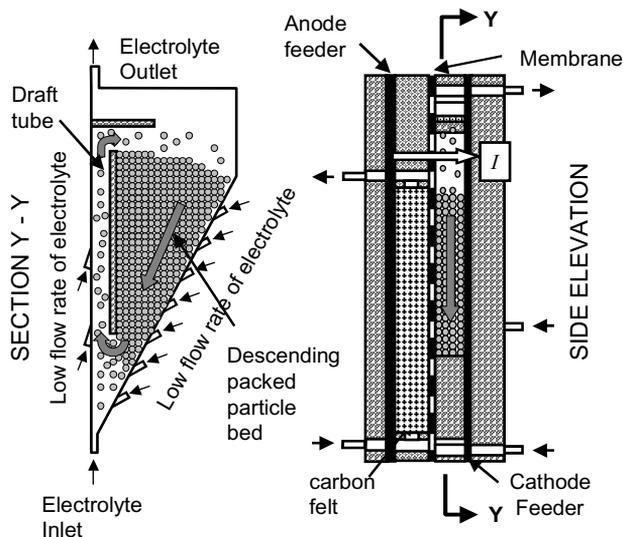

Fig.1. Electrochemical reactor incorporating circulating particulate bed cathode

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Quenching of h$_2$ evolution at boron-doped diamond electrode in nitrate solutions

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BDD electrodes exhibit a slow kinetics for H$_2$ evolution illustrated by a very high overvoltage for water decomposition. This property has been used to efficiently reduce nitrate at boron-doped diamond (BDD) electrode in neutral [1] and acidic solutions at negative potential (>-1.5 V/SCE). We found that H$_2$ evolution and nitrate reduction occur simultaneously which is not the case for Pt electrode on which H$_2$ evolution impedes the reduction of nitrate. With the goal to get further knowledge on the parameters that favor or impede the reduction of nitrate at BDD electrodes, cyclic voltammetry, electrolysis under constant potential and gas chromatography analysis of the gas formed have been investigated in various electrolytes (KCl, KNO$_3$, HCl and HNO$_3$).
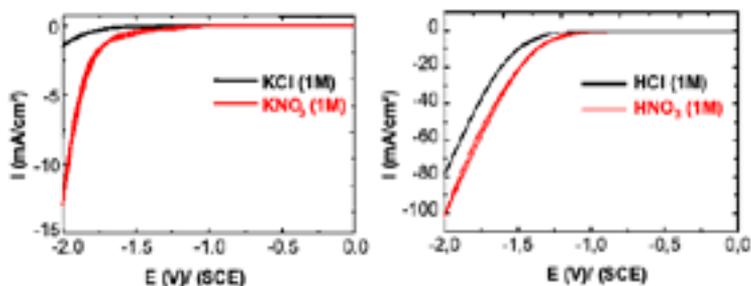
Fig. 1 Voltammograms of a BDD electrode in various electrolytes

In KCl and HCl the reduction reaction is water decomposition and only H$_2$ is formed. In KNO$_3$ and HNO$_3$ there is competition between water and nitrate reduction. Comparison of the voltammograms shows that in KNO$_3$ and HNO$_3$, 90 and 20 % of the current seems to be used to reduce the nitrate. In fact, quantitative analysis of the H$_2$ formed during the electrolysis in the various electrolytes shows that H$_2$ evolution is slightly and strongly impeded in neutral and acidic nitrate solutions, respectively. Meaning that 95-98 and 85 % of the charge is used to reduce at –2 V/SCE NO$_3^-$ ions in KNO$_3$ and HNO$_3$, respectively, confirming that competition between H$_2$ formation and NO$_3^-$ reduction at BBD electrode is weak. The mechanism of NO$_3^-$ reduction will be discussed in term of diamond surface termination and adsorption.

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High current density cathode for electrorefining of spent nuclear fuel in molten electrolyte

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Pyrochemical processing is a promising technology for closing the nuclear fuel cycle for next generation nuclear reactors. At Idaho National Laboratory (INL), such a pyrochemical process has been implemented for the treatment of spent nuclear fuel from the Experimental Breeder Reactor (EBR-II) [1]. Electrorefining is considered to be the signature or central technology for pyrochemical processing. This paper summarizes the technical characteristics of a novel design high current density cathode aimed at improving the throughput of the existing electrorefiner to treat spent EBR-II fuel. The experimental conditions, results, and technical discussions are also provided in the paper.

Experiments and Results

Two engineering scale experiments with the high current density cathode were performed in the Mark-V electrorefiner, which is located in the hot cell of Fuel Cycle Facility in INL. The electrolyte was LiCl-KCl eutectic with actinide chlorides. The anode material was uranium/plutonium ingots of approximately 14 kg each. The highest achieved current density at the cathode was ~ 1A/cm^2. The morphology of the deposit was fine particles or mud like due to high percentage of adhering salt.

The material collected by the high current density cathode experiments was run through a Cathode Processor (CP) to distillate adhering salt. Based on the amount of distillate recovered, the salt fraction in the cathode product was 59 wt%. After the CP run the material was consolidated in a Casting Furnace, where pin samples were taken for chemical analysis. Samples were also taken from the electrolyte before and after the experiments to confirm the partitions of the actinides in the salt and in the cathode product.

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Cathodic inhibition and anomalous electrodeposition of zn-co alloys

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Electrodeposition of Zn-Co alloy is considered complex and is usually divided into two potential regions i.e. a normal deposition range (positive to Zn equilibrium potential E^0_{Zn} = -1.06V vs. SCE) and an anomalous deposition range (negative to E^0_{Zn}).

The electrodeposition of Zn-Co alloys from Chloride electrolytes is compared on both steel and Ni covered steel substrates. In order to elucidate the deposition mechanism a complementary approach was used based on the combination of various electrochemical techniques (such as potentiodynamic cathodic polarization, potentiostatic deposition and anodic stripping) and surface analytical techniques (SEM, EDS and GDOES.

It is found that a critical potential exists in the so-called normal deposition range. More positive to this critical potential the phase of Co-Zn (Zn up to max.30%) is favored. Further negative to the critical potential a severe mitigation of deposition occurs which corresponds to the under potential deposition (UPD) of a monolayer of Zn on the substrate and on active Co sites. The critical potential and UPD shifts to more negative values with the increase in Co^{+2}/Zn^{+2} ratio in the electrolyte.

Beyond E^0_{Zn} potential the deposition is considered anomalous due to the fact that a higher amount of Zn is detected than more noble Co. This anomalism is explained by the faster deposition kinetics of Zn as compared to Co on steel and Ni covered layer. The anomalism can be overcome by increasing the Co^{+2}/Zn^{+2} ratio in the electrolyte or by carrying out the deposition at higher temperature. Both higher concentration of Co and temperature assist in increasing the amount of Co^{+2} in cathodic double layer and as a result recover the noble nature of Co during deposition. The results confirm that the hydroxide suppression mechanism that is usually associated with this anomalism is not responsible for this inhibition.

Biphasic electrolysis modelling: coupling between phenomena and scales

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During water electrolysis for hydrogen there are bubbles which are created at the two electrodes which imply a great hydrodynamic acceleration but also a quite important electrical field and electrochemical processes disturbance. This disturbance can lead to the modification of the local current density and to anode effects for example. There is few works concerning the local modelling of coupled electroactive species transport and electrochemical processes in a biphasic electrolyte. There are also few local experimental measurements in term of chemical composition, temperature or current density which will allow the numerical calculations validation. Nevertheless, effects like the anode effect, particularly expensive on the point of the process efficiency, should need a better understanding. Nowadays, the respective roles of the local temperature increases, the electroactive specie composition or the transport properties modification due to bubbles are not known.

The goal of the present work is the modelling and the numerical simulation of the hydrogen production process for a vertical electrode configuration. Bubbles presence is supposed to modify the electrical properties, the thermal properties and then the electroactive specie diffusive transport and the current density. Bubbles are also motion sources for the electrolysis cell flow, and then hydrodynamic properties are strongly coupled with specie transport and electrical field [1,2]. The present work shows hydrodynamic, electrical, thermal and chemical composition properties in a laboratory scale electrolysis cell with a vertical electrode. The numerical algorithm used was the finite volume used in the computational fluid dynamic software Fluent®.

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Coagulation and electrocoagulation with aluminium hydrolyzing salts

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In the literature, it is widely reported that the conventional coagulation and the electrocoagulation processes yield different efficiencies in the treatment of wastewaters [1-4]. However, very few works are focussed on the fundamentals of these processes, and thus, the cause of these differences is still unclear.

The objective of this work is to study the differences that exist between the conventional and the electrochemical technologies, in terms of the hydrolizing metal species formed in both treatments. To do this, the characterization of aluminium species generated under conditions of coagulation and electrocoagulation have been studied by Al–Ferron complexation timed spectrophotometry [5]. The results obtained by this technique had allowed to distinguish among four different species of aluminium: monomeric, oligomeric, polymeric and precipitate. The total aluminium concentration and the pH were found to be the most significant parameters in this speciation. On the contrary, for the same value of both parameters, the way of adding aluminium (dosing or electrochemical) did not influence the results.

The speciation of the hydrolizing aluminium products have been used to explain the differences between several chemical and electrochemical experiments carried out in bench scale plants. Different wastes (colloidal suspensions, oil in water emulsions and solutions of dyes) have been studied for this purpose, and in every experiment, the efficiency in the removal of pollutants, the aluminium species formed and the Z potential have been monitored. In every case, operating results were satisfactorily explained in terms of the species of aluminium. This better understanding can help to improve the design of electrocoagulation processes and to optimize its operation conditions.

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Real time imaging of the growth of anodic oxide coatings on titanium under sparking conditions

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Plasma electrolytic oxidation (PEO) is a method of surface modification of valve metals. It involves anodizing at potentials above the dielectric breakdown voltage of an oxide film, which leads to the development of thick (typically of the order of 10 μm) ceramic coatings. The coatings are composed of crystalline and amorphous phases derived from constituents of the metal and of the electrolyte. The composition and structure of the coatings can be controlled and tailored by the process parameters. The coatings provide improved surface performance, such as increased hardness, wear resistance, corrosion resistance, and bioactivity. The areas of potential application of PEO coatings on titanium include aerospace, automotive, oil and gas and biomedical industries.

PEO involves continuous random spark or arc micro-discharges over the surface of the anode, accompanied by gas liberation, under the regimes of DC, pulsed unipolar or bipolar current or amplitude modulated AC. The development of the coatings involves discrete thickening at sites of dielectric breakdown, local growth at the metal/oxide interface and destruction of earlier formed oxide [1, 2]. The characteristics of the discharge process and their relation to the mechanism of coating growth are not well established, largely due to experimental difficulty of probing processes at individual discharge channels, occurring over dimensions of a few microns with durations of < 1 s.

Here, the microdischarge characteristics during DC PEO of titanium are disclosed by real time imaging at 25 Hz frame rate. The dynamic development of the microdischarges, their population density and fractional distributions in size and time are related to the corresponding stages of development of coating morphology, composition and topography, determined by SEM, EDX and AFM. The aspects affecting coating efficiency - a critical feature in a relatively high cost technology - are revealed, offering a new perspective on coating processes.

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Advanced PEM water electrolysers for the production of pressurized hydrogen and oxygen

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Water electrolysers are key components in hydrogen-based energy systems powered by renewable sources of energy. Potential applications cover the fields of re-filling stations for transport needs, autonomous power stations for radio transmission and energy supply units for remote sites. For such applications, the proton exchange membrane (PEM) technology is of particular interest for the production of hydrogen and oxygen of electrolytic grade, offering several advantages over the more mature alkaline process: higher reliability and lower on-site maintenance, higher gas purity (more than 99.99% for hydrogen, oxygen being the main impurity), higher security including the possibility of producing compressed gases (up to 200 bar) for direct pressurized storage without additional power inputs, and ecological safety.

GenHyPEM[1] is a three-year long international research program coordinated by the University of Paris XI, launched by October 1st 2005. The project which is gathering partners from Russia, Romania, Germany, Belgium and France has received the financial support of the European Commission. Its main goal is to develop advanced PEM hydrogen generators in the medium power range, with reduced cost and improved operating performances.

This communication is aimed at presenting different results obtained recently. Concerning electrocatalysis, different techniques aimed at developing new electrode structures with quite large roughness factors and small amounts of noble metals (< 0.1 mg cm^{-2}) have been developed. Alternatively, new non-noble compounds have been synthetized, characterized and tested. Various membrane materials have been used to prepare different membrane–electrode assemblies and their electrochemical performances have been compared. Different stack design have been tested for high pressure operation and a prototype generator which can produce H_2 up to 1000 Nl/hour has been constructed and tested.

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The Electrochemical Characterisation of Electrochemical Machining (ECM)

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The fundamental basis of ECM is the contactless removal of metal through anodic dissolution. Unlike many competing metal machining processes, ECM can machine a material irrespective of hardness and is able to produce complex shapes at relatively high removal rates. The process also has the potential to produce a high quality machined surface free from residual stresses or microstructural damage. However, a significant constraint is the lack of characterisation of the high current, high electrolyte velocity (up to 100 Acm^{-2} and 50 ms^{-1}) workpiece dissolution characteristics applicable to ECM. As these determine ECM dissolution parameterisation and tool shape, this hinders process specification such that ECM generally requires expensive and time-consuming iterative trials and tool design to enable precise control.

This paper presents electrochemical characterisation using a novel segmented tool planar ECM system:
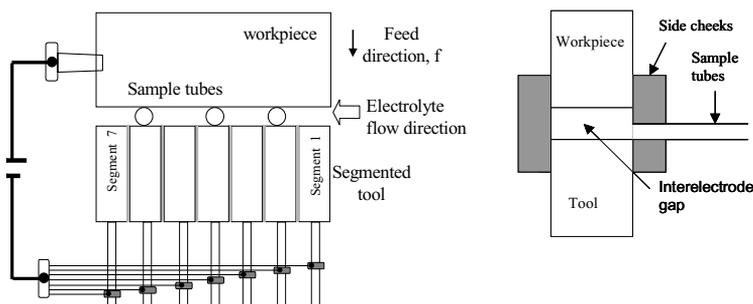
An ultrasound probe applied to the back face of the workpiece has been used to measure *in situ* dissolution characteristics under a variety of flow, voltage and feed rate conditions applicable to ECM for Ti6/4, In718 and stainless steels in chloride electrolytes. These give real insight into the high current-high flow electrochemical dissolution processes occurring in the surface oxide during ECM; they also enable process parameterisation. This parameter base has been used in enhanced finite difference simulation of the ECM process, enabling more accurate simulation of the time–dependent current transients and tool and workpiece configurations for the non-planar configurations more applicable to industrial ECM. This approach forms an integrated strategy for materials characterisation, enabling accurate process simulation and tool design in ECM.

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NO Reduction in the NO, CH$_4$,Ar/Pt/C// Polybenzimidazole-H$_3$PO$_4$//Pt/C/H$_2$,Ar at 135°C

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Catalytic reduction of NO$_x$ plays a very important role in pollution control. The use of hydrocarbons as reducing agents in this process has recently attracted much attention.

This study is a continuation of our previous research where Pt/C// Polybenzimidazole-H$_3$PO$_4$//Pt/C was used in a catalytic methane oxidation and NO reduction[1,2]. In these two cases the electrochemically produced hydrogen promoted the partial catalytic oxidation of CH$_4$ by oxygen to C$_2$H$_2$ and the catalytic reduction of NO by hydrogen. The present investigation revealed a more complex mechanism of the NO reduction in a mixture with methane.

It has been found that, without any reducing agent (like CH$_4$), NO can be electrochemically reduced in the NO, Ar/Pt/C// Polybenzimidazole-H$_3$PO$_4$//Pt/C/H$_2$,Ar fuel cell with participation of H$^+$ or electrochemically produced hydrogen.

When added, methane has partially suppressed the electrochemical reduction of NO. Methane outlet concentration monitoring has shown the CH$_4$ participation in the chemical catalytic reduction, i.e. methane co-adsorption with NO inhibited the electrochemical NO reduction and introduced a chemical path of the NO reduction.

The products of the NO reduction were N$_2$, CO and CO$_2$. The catalytic NO reduction by methane was promoted when the catalyst was negatively polarized (-0.25V vs. hydrogen counter electrode). Maximum NO conversion was around 90%.

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Development in Direct Borohydride Fuel Cells (DBFCs)

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The rapid development of different types of fuel cells has created the need for alternative source of energy to fossil fuels. It is likely that within the next decade or two, power generation for some portable electronic equipment and transportation will rely on fuel cells for energy the source. Serious questions remain about the reliability of these systems, safety during storage and supply of inflammable gaseous fuels. These concerns have stimulated research into alternative fuels. Liquid methanol has been widely studied, an alternative is sodium borohydride, which is typically available as a solid or as a 30% solution in concentrated, aqueous sodium hydroxide.

The formal potential of the oxidation of borohydride ions is –1.24 V *vs*. SHE. In combination with the reduction of oxygen in a fuel cell, this provides an equilibrium cell voltage of around 1.6 V. This compares well with H_2/O_2 and CH_3OH/O_2 fuel cells, which have equilibrium cell voltages of 1.24, V and 1.21 V, respectively. Higher cell voltage can be achieved if H_2O_2 is used instead of O_2. In addition, the energy density of solid sodium borohydride is 9.3 kWh kg^{-1}, which is attractive in comparison with 6.2 kWh kg^{-1} of pure methanol.

A fuel cell operating with sodium borohydride and hydrogen peroxide using the FM01-LC electrochemical cell is reported. The borohydride oxidation was carried out on Au/C electrode while the reduction of hydrogen peroxide was carried out on Pt/C electrode at various temperatures. Results are shown for a single cell and for a four-stack cell operating in the bipolar mode. Problems caused by low current densities and decomposition of the reactants are considered and an alternative cell design is proposed. Current challenges to the development of DBFCs are considered.

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Modelling of a large scale redox flow battery system

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Redox flow battery systems offer flexible storage of electrical energy with relatively high efficiency and have the potential for application at a very large (utility) scale. Such systems could offer a solution to the problems of matching supply with demand for renewable energy generation such as wind power. In addition such systems can be used to manage the electricity supply network to improve security of supply and minimise the need for excess generation capacity for periods of high demand.

We have developed a model of a large scale redox flow battery system to enable evaluation of alternative redox flow battery electrolyte systems. For a given electrolyte systems and operating conditions the model estimates the losses associated with electrode overpotentials, ohmic losses (in the electrolytes and membrane), and pumping energy. In addition, the model can estimate the size of plant required for a given application and estimate the process costs. The model can be used to optimise the operating conditions (current density and flow velocity) to minimise the cost of energy storage, and to determine the sensitivity of the process costs to features of the electrolyte system, such as electrochemical kinetics, solubility etc. The model will be used to identify the features of electrolyte system that are needed to deliver a viable large scale redox flow battery system, and to compare the currently available electrolyte systems.

S5·O-29

Symposium 5 - Oral

Electrochemical Engineering & Technology

Anodic oxidation of the blue reactive 19 dye on pure or fe,f-doped lead dioxide electrodes

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The widespread conscientiousness of the necessity to avoid environmental contamination has greatly increased the interest on the elimination of toxic organic compounds present in industrial effluents. Because a very large quantity of dyes is industrially used each year, they are a type of organic compound commonly present in industrial effluents, mainly from textile plants. To avoid problems associated to the chemical and biological treatments, like the transport/storage of the chemical reactants and sludge formation, respectively, the use of electrochemical technologies has also been investigated for the removal of dyes from effluents [1,2]. Considering that the electrocatalytical activity as well as the stability of PbO_2 can be significantly improved by the incorporation of dopants [3], in the present study we investigated the performance of Fe- or Fe and F-doped Ti-Pt/PbO_2 electrodes in the electrooxidation of the Reactive Blue 19 dye (BR-19) in a filter-press cell. The PbO_2 electrodes were electrodeposited (20 mA cm^{-2}) on Ti-Pt using a four-electrode one-compartment cell; the amount of deposited PbO_2 was 50 mg cm^{-2}. The electrodeposition solution (magnetically-stirred, at 65 °C) was: 100 mmol L^{-1} Pb(NO$_3$)$_2$ + 0.5 g L^{-1} sodium lauryl sulfate, in 0.1 mol L^{-1} HNO$_3$. To obtain the doped electrodes, 1.0, 10 or 100 mmol L^{-1} Fe(NO$_3$)$_3$ and/or 30 mmol L^{-1} NaF were added to that solution. The results obtained in this work using pure or doped Ti-Pt/β-PbO_2 electrodes indicate that they are interesting alternatives for the electrooxidation of dyes. When 100 mL of 25 mg L^{-1} BR-19 in 0.5 mol L^{-1} Na$_2$SO$_4$ was electrolyzed (50 mA cm^{-2}), good results weree obtained for its decolorization simply using a pure Ti-Pt/β-PbO_2 electrode: 90 % decolorization after passing a faradaic charge per unit solution volume of about 0.3 A h L^{-1} (8 min of electrolysis). However, from the point of view of mineralizing the BR-19 dye in the solution (125 mL), Fe and F-doped Ti-Pt/β-PbO_2 electrodes were the best performers: TOC decreased to only 5% after 2 h of electrolysis (8 A h L^{-1}). The above results for the pure or Fe and F-doped Ti-Pt/β-PbO_2 electrodes were better than the ones attained by carrying out the electrolysis using a boron-doped diamond anode, indicating that the lead dioxide electrodes might be excellent options for the electrooxidation of dyes.

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Symposium 5 - Oral

Electrochemical Engineering & Technology

Electrodeposition of Zinc-Tin Alloys, Bright Metal Coatings and Composites From Deep Eutectic Solvents Based on Choline Chloride

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Our research has focused on developing eutectic mixtures (ionic liquids) as alternatives to established technologies that utilize harsh and often very toxic aqueous environments. Here we describe the electrolytic deposition of Zn, Sn and Zn/Sn alloys from a solution of the metal chloride salts separately in urea and ethylene glycol / choline chloride based ionic liquids [1]. We show that the deposition kinetics and thermodynamics differ from the aqueous processes and that qualitatively different phases, compositions and morphologies are obtained for the metal coatings in the different ionic liquid systems. We have quantified the electrochemical stripping responses using cyclic voltammetry together with compositional analysis using SEM/EDAX and x-ray diffraction. The differences in electrochemical responses are rationalized in terms of the speciation of both Zn and Sn chlorides in the ionic liquids that have been identified using FAB mass spectrometry. We demonstrate that composite metal coatings, *e.g.* containing Al_2O_3 particles, can be obtained from these liquid systems by virtue of the stable liquid suspensions. This novel feature of these liquids is a function of their relatively high viscosity. In addition we show that surface morphology of the metal deposits can be controlled by using metal ion coordinating agents such as EDTA, ethylenediamine or acetonitrile in the electroplating liquid. This has made it possible to produce optically bright coatings of several metals including Cu. We will present the results of morphological studies, using atomic force microscopy (AFM), on these systems.

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Optimization of the electrosyntesis industrial process of peroxodiphosphate with conductive diamond electrodes

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Peroxodiphosphate salts are strong oxidizing agents which presently can be used as reagents in a great variety of industrial processes (organics synthesis, cosmetic, agriculture, polluted water treatment…), and also they have potential uses as persulphates substitutes. However, only few synthesis industrial processes have been developed, and most of them required the addition of reagents (whose later removal increases the manufacture costs largely) to obtain efficient processes [1,2]. In this work, the optimization of a new method for the synthesis of peroxodiphosphate [3] based on the use of boron-doped diamond electrodes was carried out. The procedure developed is able to produce high-purity peroxodiphosphate (no reagents different than phosphate salts are used as raw materials) with a high current efficiency. Results show that the conversion of phosphate to peroxodiphosphate and the efficiencies of the process strongly depend on the pH and on the operating conditions (temperature and current density). It was observed that the pH does not seem to influence the electrochemical process but the chemical stability of the oxidant generated. Thus, the control of the pH (around pH 12.5) seems to be one of the main operating constrains. Low temperatures are required during the electrosyntesis process to minimize the thermal decomposition of peroxodiphoshphate and to guaranty high current efficiencies and product conversions. In addition, two marked trends in the conversion and efficiency obtained (that only seem to depend on the current density used) are observed. This fact can be explained in terms of the contribution of hydroxyl radicals in the oxidation mechanisms that occur on diamond surfaces. In that essays carried out below the water oxidation potential, the generation of hydroxyl radical does not take place. In these cases, the direct mechanism is the only responsible of the peroxodiphosphate generation and, therefore, lower efficiencies are obtained. On the other hand, at higher potentials, both direct and hydroxyl radical mediated mechanisms contribute to the oxidant generation and the process is more efficient. However, for a given range of current densities, an increase in the current density does not lead to higher efficiencies and increases unnecessarily the specific energy consumption. Thus, a current density of 1000 A m^{-2} can be considered as the optimum value. In the search of industrial applications of this oxidant the procedure to obtain solid salts of peroxodiphosphate has a great importance. Moreover, it has been observed that the amount of oxidant recover as solid depends on the pH. For this reason, the procedure to obtain solid salts has been optimized.

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Electrochemical studies of the interfaces with ionic liquids

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Ionic liquids, ILs, have received considerable attention particularly as solvents for chemical reactions and in electrochemical applications as on lithium rechargeable batteries, electrical double layer capacitors, dye sensitized solar cells, electrodeposition or electropolishing. Most of the studies have concentrated on imidazolium or piridinum based liquids but a different type of ILs have been developed using eutectic mixtures of quaternary ammonium halides and hydrogen proton donors. Despite the increasing number of studies the information related to interfacial properties of electrodes in contact with ionic liquids is scarce.

Inserted in a project aiming to understand the double layer properties of Ils cyclic voltammetry and electrochemical impedance spectroscopy data obtained for Au, Pt and Glassy Carbon electrodes in contact with [CnMIM] PF6, n=2,4,6 and choline chloride +urea mixtures will be presented and discussed. The influence of electrode material and size of the imidazolium cation on the interfacial capacity potential curve will be discussed.

Electrochemistry of tantalum (V) in the mixtures 1-butyl-1-methyl-pyrrolidinium chloride-TaCl$_5$

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Low-temperature molten salts, or ionic liquids, are very attractive alternative media for electrochemical deposition of refractory metals at ambient temperatures.

We succeeded in obtaining a series of ionic liquids consisting of 1-butyl-1-methyl-pyrrolidinium chloride (Pyr$_{14}$Cl) and TaCl$_5$ at molar fraction of Pyr$_{14}$Cl in the range 0.85-0.20 and all mixtures were studied using cyclic voltammetry. By means of differential scanning calorimetry (DSC) the phase behavior of the mixtures Pyr$_{14}$Cl-TaCl$_5$ was investigated and the optimal compositions of electrolytes for electrochemical trials were found at molar fraction of Pyr$_{14}$Cl equal 0.63 and 0.40.
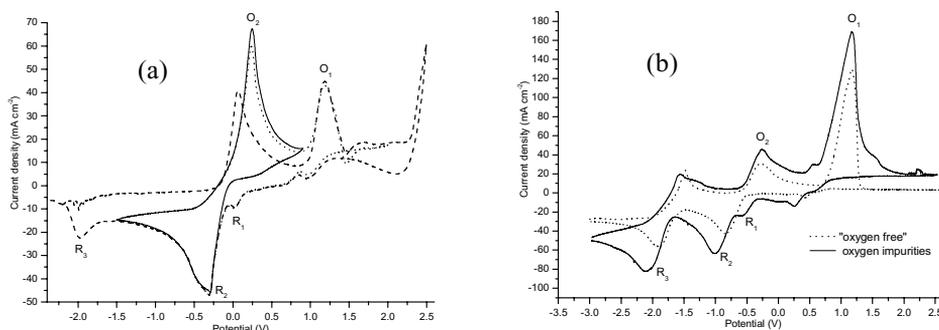

Figure 1. Cyclic voltammograms of Pyr$_{14}$Cl-TaCl$_5$ at the molar ratio 63:37 (a) and 40:60 (b) obtained at 140^{0}C (sweep rate 100 mVs^{-1}, WE-Pt disk, quasi RE-Pt wire, CE-GC)

Cyclic voltammograms of [TaCl$_6$]$^-$ exhibit three reduction waves for both compositions (Figure 1, a and b) observed at different peak potentials. The first minor reduction peak (R$_1$) was identified as a reduction of oxochloride complexes of tantalum (V) (Figure 1, b). The second reduction peak (R$_2$) is due to a reversible and diffusion controlled process attributed to the reaction [TaCl$_6$]$^-$ + e$^-$ ↔ [TaCl$_6$]$^{2-}$. The peaks observed at -0.3V (a) and -1.0 V (b) reflect the reduction of different species of tantalum (V) formed at various concentrations of TaCl$_5$. The third reduction peak (R$_3$) could be assigned to the further reduction of tantalum (IV). Using pulse plating, electrodeposition of tantalum was achieved on Au substrate at -2.3 V but with oxygen impurities.

The formation of oxochloride complexes and the changes of the structural units of tantalum (V) depending on molar ratio of the components were confirmed by FTIR-spectroscopic measurements.

Study of the electrochemical 4-methylanisole methoxylation on the glassy carbon electrode

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4-methoxybenzaldehyde (4-MBA) is an important intermediate in the production of semi-synthetic antibiotics. 4-MBA can be synthetized chemically, however this synthesis is not very selective. Much more convenient is the electrochemical synthesis which can be carried out with the selectivity near 100% and substantially higher space time yields. The electrochemical synthesis is based on the anodic methoxylation of 4-methylanisole (4-MA). An intermediate 4-methoxybenzylmethyl ether is once more methoxylated and yields 4-methoxybenzaldehyde dimethyl acetal (4-MBA DMA), that is acidically hydrolyzed to 4-MA. This study is a part of extensive project dealing with the development of more efficient process of 4-MA production. The main objective of our project is to increase the efficiency of 4-MBA production by using the microstructured reactor technology. In this report are presented results of the study of the anodic methoxylation reaction kinetics and mechanism in a methanol environment with $NaClO_4$ as a supporting electrolyte. The results of this work serve as an input data for the mathematical modelling and optimisation of a design of the novel industrial microstructured electrochemical reactor.

Three-electrode RDE set-up was used with the glassy carbon (GC) and SCE as a working and reference electrodes, respectively. Platinized Ti or Pt grid served as a counter electrode. The linear voltammograms of 4-MA methoxylation reaction were recorded on GC electrode. Recorded polarization curves were corrected for the uncompensated Ohmic resistance of the solution and the simultaneous methanol oxidation. The Tafel slopes and the rate constants of the reactions, and the diffusion coefficients of the involved species were determined.

It follows from the previous experiments, that in the presence of $NaClO_4$ in the solution the reaction mechanism is influenced by the electrode material, as the electrode reaction is of the direct type. Two partially overlapped oxidation waves in the voltammogram can be seen on the GC electrode. The first oxidation wave corresponds to the 4-electron oxidation of 4-MA to 4-MBA DMA. The second wave is related to 4-MBA DMA overoxidation. All the electrode reactions are followed by the chemical ones. Thus the system was found to behave like totally irreversible. This is confirmed by the fact, that no cathodic current was observed even at high cathodic overpotentials.

Investigation of the Electrochemical Impedance of Copper in Acid Plating Solutions

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Polycrystalline metal surfaces are heterogeneous [1]; they contain defects, e.g. terraces, ledges, kinks and adatoms; these correspond to surface atoms of different lattice coordination states, different energies, different redox potentials and even different types of electrochemistries. As discussed recently for gold [2], low energy and high energy metal atoms, at the same surface, exhibit different types of electrochemistries, the low energy (or conventional, EMS state) response, e.g. the Cu/Cu^{2+} transition of copper (at ca. -0.4V SMSE) being irrelevant from an electrocatalytic viewpoint. Copper also exhibits a very low level, virtually subliminal, transition at ca. -0.7 V (SMSE). The latter transition, apparently involving a Cu^*/Cu^+_{ads} couple (Cu^* being an active, protruding, copper atom, i.e. an MMS State), dominates the electrocatalytic and bath additive behavior of copper surfaces in acid solution.

Electrochemical impedance spectroscopy (EIS) is a powerful technique for the characterization of electrochemical systems. Most EIS studies of the copper electrode system [3, 4] in acid assume that the electrode process involved is simply

$$Cu^{2+} + 2e^- = Cu$$

and concentrate on the mechanism of this reaction based on impedance data recorded at either a fixed potential or a narrow range of potentials close to the equilibrium value. The effect of additives [3, 4] in the plating solution on the reaction kinetics has also been discussed. Glarum and Marshall [5] measured the admittance of copper in the plating bath as a function of frequency, potential and concentration.

It appears that there are three important potentials or redox systems involved: $E_1 \approx -0.4$ V (Cu/Cu^{2+}), $E_2 \approx -0.75$ V (Cu^*/Cu^+_{surf}) and $E_3 \approx -1.0$ V (H_2/H^+): the potential scale involved here is SMSE i.e. saturated mercury/mercurous sulphate. E_2 is associated with a rapid, but non-equilibrium, i.e. quasi-reversible or active state, transition. Non-equilibrium (metastable) states play a central role in metallurgy; their role as catalytic centres [2] and in some cases as inhibitors [6] in the surface electrochemistry of solids was outlined recently; their central role in electrocatalysis and bath additive behaviour of copper in acid will be discussed.

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Influence of accelerator consumption to the filling of copper by electroplating

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Recently, via-filling technology is one of most important methods used for layer-to-layer interconnections in the build-up process. Today, via holes must be filled with copper metal in order to get good reliability and fabricate a high-density package. Generally, to achieve via-filling without voids by copper electroplating, some additives, such as polyethylene glycol (PEG), bis-(3-sulfopropyl)-disulfide (SPS), and Janus Green B (JGB), are used to control the copper deposition. It is known that PEG and JGB are adsorbed and therefore suppress the copper deposition on the surface substrate and at the outside corner of the via hole opening. On the other hand, SPS works to accelerate the copper deposition at the bottom of the via-holes. However, its filling ability is decreased with increased plating time. This phenomenon suggested that SPS was being decomposed by the application of the current.

In this study, we compared and investigated SPS and 3-mercapto-1-propanesulfonate (MPS), known as the oxidation product of SPS, as accelerators. We used a conventional decorative bath (high copper concentration). The filling ability was evaluated by inspection of the cross sectional image and filling ratio (Figure 1). The apertures of the via-holes were 60, 90 and 150μm in diameter. They were 50μm in depth.

Images taken during the first stage of the plating are shown in Figure 2. The SPS image shows increased deposition at the bottom while the MPS image shows uniform plating. Furthermore, using MPS, the thickness on the surface of the PCBs is thicker than when SPS was used. Therefore, it is suggested that MPS can penetrate under the PEG and accelerate the deposition on the entire substrate.
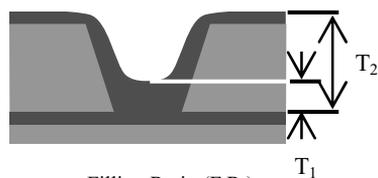
Filling Ratio (F.R.)
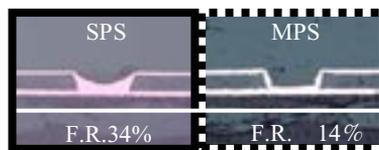$= T_1 / T_2 \times 100$ (%)
Figure 1 Evaluation method

Figure 2   The cross sectional image

Through-Hole Filling by Copper Electroplating Using Two Step Method

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Miniaturization of printed circuit boards(PCB) and the semiconductor devices have been progressed, because the electronic devices are sharply downsized. In PCB application, the buildup process by fullfilling blind micro via holes (BVH) has been paid attention as a processing technology corresponding to the downsizing trends. In addition to BVH filling, today, through-hole fullfill technology is also emerging as a more reliable processing for electric and thermal characteristics. In other applications such as 3D packaging and RF technology, also, the connection of both sides by fullfilling through-wafer vias is a crucial component for the electrical and thermal reliability.

In this study, the copper filling for 80 μm through-holes with the aspect ratio of 3.5 was examined with controlling the current density in the high copper concentration bath. To achieve high aspect ratio of through-hole filled, two step methods of copper plating were applied, where the currents were allowed on both or on the only one side in each step. The structures of the through-hole after the first step and the fullfilled step were shown in Fig.1. The plugged positions in the through-hole were dependent on the current and the seed layer conditions. The effects of plugging position were investigated as well as those of the hole size and the concentration of the copper. And the uniformity of via filling over the whole wafer was also considered with the aid of the current distribution simulation.

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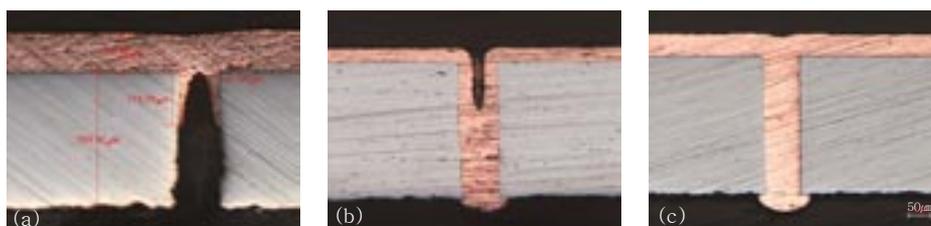

Fig. 1. Cross sectional images after the first steps (a) with one-side current or (b) with both-side current and (c) after the second step.

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Copper Deposition within High Aspect Ratio Vias for 3D Through-Silicon-Via Interconnects

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The continuous pressure to reduce size, weight, and cost, while increasing the functionality of portable products, has created innovative 3D packaging concepts. Through-silicon-via (TSV) interconnects can provide the shortest and the most plentiful connections with reduced signal delay and power consumption. The enabling technologies include via hole etching, insulator/barrier/seed deposition, via filling with copper, top metal removal, annealing, redistribution, wafer thinning and bonding. Copper deposition within high aspect ratio vias is one of the most important technologies to make TSV chip stacking manufacturable. Two approaches have been generally adopted for TSV interconnect formation. One is the blind-via filling with 3D seed layer followed by top metal removal and wafer thinning, and the other is the through-via filling with 2D seed layer after wafer thinning. Till now, the first approach looks more popular than the second approach due to difficulty in handling and plating thin wafers.

We examined the impact of various deposition conditions on the overall filling capability. We tested the effects of bath composition (organic and inorganic components), waveform, current density, and flow conditions. Depending upon deposition conditions, three types of filling profiles were observed; sub-conformal profile leaving a large void at the bottom, conformal profile leaving a seam void, and super-conformal profile leading to void-free, bottom-up filling. With optimized conditions, we can achieve void-free, bottom-up filling with a variety of via sizes (3-80µm wide and 45-160µm deep). Figure 1 shows the super-conformal growth with an optimized condition. Currently we are working on improving the filling rate.

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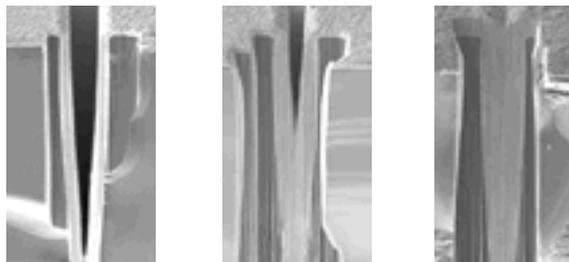2. B. Kim, *et al.*, Semicon Korea 2006, Proceedings of SEMI Technical Symposium (STS), p. 269 (2006).

Figure 1. The change of via filling profile over time with an optimized condition, where the via is 12µm wide and 100µm deep.

Formation of micro- and nano-sized ordered structures by self-organization in electrochemical systems

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Self-organized formation of ordered micro- and nano-structures of metals and semiconductors at solid surfaces has been attracting keen attention in view of nanotechnology. The self-organization method has an advantage over the photolithography and surface probe method in that it meets both the conditions of atomic-scale fabrication and the adaptability of mass production. Recent studies on non-equilibrium, nonlinear chemical dynamics have proved a large possibility of self-organized formation of a variety of ordered structures such as stripes, dot arrays, and target and spiral patterns. However, most of the patterns thus far reported are limited to those of two dimensions (2-D) lying parallel to the substrate surface. The formation of organized "vertical" structures and further organized 3-D structures will need novel strategy. From this point of view, oscillatory electrodeposition is an interesting target because it has an ability to produce ordered electrodeposits by recording ever-changing self-organized spatiotemporal patterns during oscillations. Here we review our recent studies on the

Figure 1 (a) Potential oscillation observed in Sn electrodeposition. (b) An optical microscopic image of highly ordred latticeworks of Sn produced by the oscillatory electrodeposition.

Figure 2 (a) Current oscillation obtained in SnCu-alloy electrodeposition. (b) SEM (top view) of a bowl-shaped hollow with a slanting cross section, prepared in the deposited alloy film by Ar+ ion etching. (c) Schematic illustration of sample preparation for (b).

structurization by oscillatory electrodeposition[1-3], with a focus placed on the formation of strikingly well-ordered metal latticeworks, standing perpendicular to the substrate, through ingenious cooperation of various processes with long-range spatiotemporal synchronization.

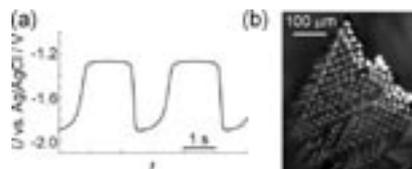1. S. Nakanishi, et al., *J. Am. Chem. Soc.*, **126**, 9556 (2004).
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Electrowinning of iron in alkaline media from iron ore suspensions

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In view to reducing greenhouse effects in the steel industry, European steelmakers are screening various technologies in the frame of the five-year European programme ULCOS. As evidenced in the 70's, the electrochemical reduction of iron ore particles, e.g. hematite in strong alkaline media over 100°C can be a promising route for such purpose: as a matter of fact, compact Fe deposits could be produced at 0.1 A cm^{-2} with high faradaic yields at the surface of a rotating disk electrode. The present work was aimed at highlighting the mechanism of the complex deposition conduced in the presence of concentrated suspensions of particles

First, a software was developed for the prediction of the E-pH diagrams depending on temperature and the concentration of sodium hydroxide. Pourbaix diagrams yielded by the software showed that the concentration of ferric ions in the considered media was below 10^{-3}M, as confirmed by experimental work: the reduction of dissolved Fe(III) cannot correspond to the experimental deposition current mentioned above, and more complex mechanisms had to be considered. Hematite, the ore phase considered here leads to the formation of ferric ions and magnetite, which is unstable at cathodic potentials and dissolves into ferrous and ferric species. Ferrous species, mainly in the form of $Fe(OH)_3^-$ appears to have a significant role in the overall deposition of iron.

Secondly, original experiments were designed to highlight the role of Fe(II) species. This species could be stabilised at approx. 0.1M by continuous anodic dissolution of iron; its reduction was shown to yield iron whose morphology is the same as what is observed for hematite reduction. The kinetics of Fe(II) reduction could not be drawn from the i-E variations, because of the absence of defined diffusion plateau and the likely side evolution of hydrogen. Fe(II) species was therefore shown to be an intermediate that can be easily reduced to metal Fe in the investigated conditions.

In order to understand how iron oxide particles can lead to metal in the process various pathways have been considered. Because hematite is a non-conducting phase, the polarisation of particles and the occurrence of core electrochemical reactions are questionable. A more likely mechanism involves the transformation of hematite to an intermediate phase at the surface of the suspended particles through a complex equilibrium with magnetite together with ferrous and ferric species in the reductive environment: this intermediate phase could be reduced to metal via its dissolution into ferrous ions. The planned electrochemical investigation of magnetite reduction in alkaline media should reveal whether it would be the searched intermediate species between hematite particles and iron, via ferrous species. The physical consistency of the overall mechanism is thoroughly discussed in the paper.

Arsenic electro-removal from drinking underground water

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Arsenic (As) is a highly toxic element that has been released into the environment by anthropogenic processes and weathering of As bearing minerals. Arsenic drinking water contamination is a worldwide problem concern and in the central part of northern of México (La Laguna (LA)) this problem is severe, recently underground sources of water in this region have presented an approximate arsenic content of 120 μg L^{-1}, which is approximately a magnitude order higher than the maximum value admissible for drinking water (<10 μg L^{-1}). Exist several methods for As removal from drinking water, however among them the electrochemical method of electrocoagulation (EC) presents important advantages respect the others, owing to the low sludge amount produced and not requirement of chemicals reagents addition. This study compares the arsenic removal degree by EC process between model water with an As content of 120 μg L^{-1} and LA underground water contaminated with a similar As content and other ions normally found in small amounts in this type of water. The experiments were carried out using iron electrodes in galvanostatic conditions for 1 hour and two current densities, 1.5 and 3 mA cm^{-2}, three temperatures, 30, 45 and 85°C and three pH values, about of 6, 8 and 12. The results have shown that for the model solution, near all As content was removed reaching values lower than 10 μg L^{-1} at the end of the EC process whereas for LA underground water no As was removed. This difference between the model solution and LA underground water, was attributed to the interference of the multiple ions present in LA underground water on the As removal. This study shows a procedure to surmount this interference in order to promote the As removal up to percentages higher than 70%.

On the activation and physical degradation of boron-doped diamond electrodes after cathodic polarizations

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Previous studies [1] showed that cathodic polarizations at –3.0 V *vs.* HESS for 30 min are a simple and very efficient way for generating highly active electrochemical surfaces on boron-doped diamond (BDD) electrodes. This pre-treatment is accompanied by an intense hydrogen evolution and renders more precise analytical measurements as well as reproducible electrochemical responses. On the other hand, a recent work [2] describes the loss of such activity with time of exposure of the BDD surface to the atmosphere, which is recovered by further cathodic polarisations. Meanwhile, those repeated polarisations have other effects on the BDD behaviour, such as an apparent increase in the number of active sites as well as a physical degradation of the electrode surface probably due to erosion (as observed by SEM and AFM measurements) and will be described here.

Tafel plots obtained for the hydrogen evolution reaction in acid medium are shifted towards higher current densities as the BDD doping level increases from 300 to 8000 ppm, an effect associated to a larger amount of active sites when the boron content increases. However, an extensively pre-treated 800-ppm electrode shows current densities higher than those of a 2000-ppm surface. This clearly indicates an increase in active (or conductive) sites brought-on by the pre-treatment since the electrochemical area remains constant for outer-sphere redox reactions ($Fe(CN)_6^{4-/3}$) studied by cyclic voltammetry. In a sense, the surface behaves as an array of microelectrodes of variable number but sufficiently close to each other to produce an overlapping of the diffusion regions.

To minimize the physical degradation of the surface but retain the beneficial effects of the cathodic pre-treatments, experiments were carried out with the aid of EIS measurements. It was established that a minimum charge density value of -4 C cm^{-2} using 1 A cm^{-2} allowed a totally reversible CV response for the couple $Fe(CN)_6^{4-/3-}$ without producing any physical degradation of the surface. Under those conditions, the resistance associated to a high-frequency element was similar to the one attained previously (4 Ω cm^2) after –3.0 V for 30 min on a 4500-ppm BDD electrode [1].

These results show the way for proper activation of the BDD surfaces that avoid unwanted degradation of the material as well as some problems that may arise in industrial applications of cathodic processes using BDD electrodes.

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Electrochemical Engineering & Technology

Electrochemistry of tantalum (V) in the mixtures 1-butyl-1-methyl-pyrrolidinium chloride-TaCl$_5$

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Low-temperature molten salts, or ionic liquids, are very attractive alternative media for electrochemical deposition of refractory metals at ambient temperatures.

We succeeded in obtaining a series of ionic liquids consisting of 1-butyl-1-methyl-pyrrolidinium chloride (Pyr$_{14}$Cl) and TaCl$_5$ at molar fraction of Pyr$_{14}$Cl in the range 0.85-0.20 and all mixtures were studied using cyclic voltammetry. By means of differential scanning calorimetry (DSC) the phase behavior of the mixtures Pyr$_{14}$Cl-TaCl$_5$ was investigated and the optimal compositions of electrolytes for electrochemical trials were found at molar fraction of Pyr$_{14}$Cl equal 0.63 and 0.40.

Figure 1. Cyclic voltammograms of Pyr$_{14}$Cl-TaCl$_5$ at the molar ratio 63:37 (a) and 40:60 (b) obtained at 140^{0}C (sweep rate 100 mVs^{-1}, WE-Pt disk, quasi RE-Pt wire, CE-GC)

Cyclic voltammograms of [TaCl$_6$]$^-$ exhibit three reduction waves for both compositions (Figure 1, a and b) observed at different peak potentials. The first minor reduction peak (R$_1$) was identified as a reduction of oxochloride complexes of tantalum (V) (Figure 1, b). The second reduction peak (R$_2$) is due to a reversible and diffusion controlled process attributed to the reaction [TaCl$_6$]$^-$ + e$^-$ $\leftrightarrow$ [TaCl$_6$]$^{2-}$. The peaks observed at -0.3V (a) and -1.0 V (b) reflect the reduction of different species of tantalum (V) formed at various concentrations of TaCl$_5$. The third reduction peak (R$_3$) could be assigned to the further reduction of tantalum (IV). Using pulse plating, electrodeposition of tantalum was achieved on Au substrate at -2.3 V but with oxygen impurities.

The formation of oxochloride complexes and the changes of the structural units of tantalum (V) depending on molar ratio of the components were confirmed by FTIR-spectroscopic measurements.

Electrochemistry and spectroscopy of niobium (V) and tantalum (V) in 1-butyl-1-methyl-pyrrolidinium trifluoro methanesulfonate

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Low temperature molten salts, or ionic liquids, have the potential to deposit refractory metals that cannot be deposited from aqueous solutions.

Electrochemical behavior of niobium (V) and tantalum (V) was investigated in 1-butyl-1-methyl-pyrrolidinium trifluoromethanesulfonate ($Pyr_{14}TFMS$). Cyclic voltammograms and electroconductivity of $Pyr_{14}TFMS$ with the additives of $NbCl_5$ and $TaCl_5$ (up to 35 mole %) were measured in the temperature range $60\text{-}170^0C$. The structure and compositions of electrochemical active species were investigated using FTIR-, FTIR-emission, and UV-VIS spectroscopy. The thermal behavior was studied by means of differential scanning calorimetry (DSC).
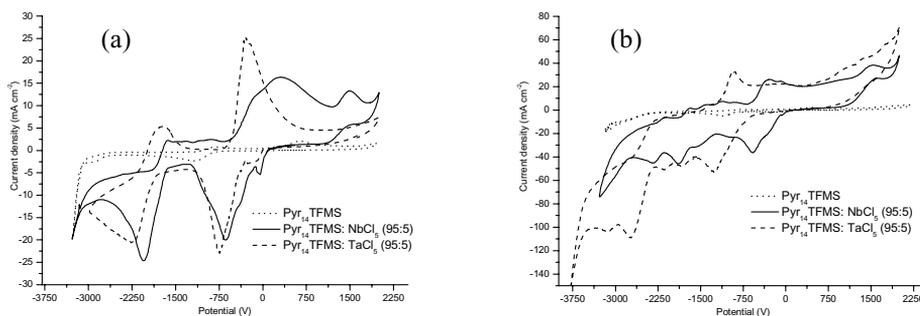
Figure 1. Cyclic voltammograms of $Pyr_{14}TFMS$-$NbCl_5$ (5 mole %) and
$Pyr_{14}TFMS$-$TaCl_5$ (5 mole %) obtained at 60^0C (a) and 120^0C (b)
at sweep rate 100 mVs^{-1} (WE-Pt disk, quasi RE-Pt wire, CE-GC)

Cyclic voltammograms of niobium(V) and tantalum(V) at 60^0C exhibit two reduction waves and the behavior is similar to that one in ionic liquids on the base of 1-butyl-1-methyl-pyrrrolidinium chloride [1]. Increase of the temperature up to 120^0C leads to the appearance of additional reduction waves caused by the formation of new electrochemical active species due to the interaction of $NbCl_5$ and $TaCl_5$ with the $[CF_3O_3S]^-$ anions.

In the FTIR- and FTIR-emission spectra new vibrational features confirm the formation of new species of niobium(V) and tantalum(V) and their evolution depends on the temperature.

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Symposium 5 - Poster

Electrochemical Engineering & Technology

An electrochemical method for the treatment of diary industry wastewater

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Milk is composed of a complex mixture of lipids, proteins, carbohydrates, vitamins, and minerals. Therefore, these wastewaters are rich in biodegradable organics and nutrients. If not treated, they cause gross pollution of land and water with their high BOD and COD. The dairy industry wastewaters are generated primarily from the cleaning and washing operations in the milk processing plants and are estimated to be 2.5 times the volume of the milk processed. Thus, because of high organic content, these kinds of effluents need to be treated prior to discharge.

In this study electrochemical treatment of dairy industry wastewater was investigated and over 95% of COD removal was obtained in a few minutes. Although there are some studies interested in the application of electrochemical methods to the dairy industry, this study can be evaluated as an innovating study for the treatment of dairy industry wastewater. There is a review [1] about the application of electrodialysis to the dairy industry, mentioned that the usage of electrodialysis for the transform, purify, or separate milk components. Also, in the other study [2] electrocoagulation was performed with the aim of protein extraction from whey.

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Electrodeposition of Fe-Zn and Zn-Fe alloys from air and water stable ionic liquids

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In addition to their good corrosion resistance, Zn-Fe alloys have good weldability and ductility and suitability for deep black chromate coating.

An ionic liquid bath composed of choline chloride/urea has been used to dissolve $ZnCl_2$, $FeCl_2$ and $FeCl_3$. Voltammetry at a platinum electrode and low carbon steel substrate has been used to study the electrochemical deposition of Zn-Fe alloys in open-to-air conditions and under vacuum system. Samples of electrodeposits were prepared and characterised by optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). A liquid mixture containing 1:1 $ZnCl_2/FeCl_3$ produced a Zn-Fe alloy with a constant Fe content (around 7 %) independent on the applied current density. On the contrary, 1:1 $ZnCl_2/FeCl_2$ produced a Fe-15 % Zn alloy deposit.

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Application of solid polymer electrolytes based onlithium salts in electrochromic devices

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Solid-state electrochromic devices have been the subject of an increasing research investment during the last decade. Smart windows and reactive labels are just two examples of potential markets where electrochromic materials may find application in commercial devices with high production volumes. Very promising results have already been reported describing the use of polymer electrolytes as dual-function electrolyte/adhesive components in electrochromic devices [1-3]. In this domain the transparency, flexibility, ready processibility and low cost of solid polymer electrolytes are attractive properties.

In this presentation the fabrication of a prototype solid-state electrochromic device based on poly(trimethylene carbonate) incorporating lithium salts is described. The results of characterization of the device performance as a function of the nature of the guest salt, the salt concentration and the polymer component layer thickness are reported.

Figure: Prototype electrochromic devices in bleached and written states

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Green Chemistry Approach to the Electroorganic Synthesis of New 1,3-Indandione Derivatives

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Ortho- and *para-* dihydroxybenzenes and their quinone derivatives are abundant in nature and play important roles in many biological systems. Due to the presence of two exchangeable hydrogen atoms capable of exhibiting both anti- and pro-oxidant behaviour [1], and 1,3-indandione has anticoagulant properties [2], this is the reason that motivate the present investigation. In this work we investigate the electrochemical oxidation of 2,3-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 2,3-dihydroxybenzaldehyde, 3,4- dihydroxybenzaldehyde, 4-methylcatechol and 4-*tert*-butylcatechol in the presence of   2-phenyl 1,3-indandione as a nucleophile in aqueous solution (H_2O:AcCN, 90:10) has been studied. This is an environmentally friendly method on the electrochemicalsynthesis in two step of EC mechanism reaction involving alternatively: electrochemical oxidation and chemical reaction. The research in this work, using a variety of experimental technique, including cyclic voltammetry, controlled-potential electrolysis, spectroelectrochemistry, and spectroscopic identification of products, and delineates application of the electrochemical and spectroelectrochemical studies in the design of an electrochemical method for synthesis of new 1,3-indandione derivatives.

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Symposium 5 - Poster

Electrochemical Engineering & Technology

The phenomenon of post-polarization of titanium self-dissolution in acid liquor

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The purpose of present work was the study of influence of preliminary polarization duration by an alternating current, initial concentration of an acid, current density and frequency on speed of chemical dissolution of metal after electrolysis.

The study was carried out in electrolytic cell consisting of three sections; in middle section titanic shavings were working as bipolar electrodes. In extreme sections two titanic plates connected to alternating current source were used as the basic electrodes.

At polarization of titanic electrode by alternating current with frequency from 30 up to 80 Hz in cathodic half-cycle the reduction of oxide layer of metal and uncovering of titanium surface take place:

$$TiO_2 + 4H^+ + 4e \rightarrow Ti + 2H_2O$$

At further polarization of electrode metallic titanium not having protective oxide film on surfaces begins to dissolve anodically by reaction:

$$Ti \rightarrow Ti^{+3} + 3e$$

and as the result of chemical interaction with electrolytic solution:

$$2Ti + 2H^+ \rightarrow 2Ti^{+3} + H_2$$

Obviously constant and intensive emitted hydrogen on titanium surface and near-electrode layer of certain structure prevent to formation of new oxide film. Due to this thing there is continuous titanium dissolution with formation of its trivalent ions. It is known that on titanium surface hydride layer can be formed which apparently also prevents to formation of oxide film.

As is shown by results of study at increase of time of preliminary polarization by alternating current the rate of chemical dissolution begins to grow. At preliminary treatment of metal during 30 minutes and more the rate of further chemical dissolution of titanium practically remains constant.

At increase of initial concentration of acid after electrochemical activation of electrodes (τ = const) the rate of post-electrolytic self-dissolution of titanium raises. As the result of titanium self-dissolution with time crystal sediments of titanium (III) chloride and sulfate begin to precipitate. Also is shown that the increase of solution temperature essentially accelerates the rate of titanium self-dissolution that will be quite in accordance with thermodynamics of chemical processes.

The frequency of alternating current at electrochemical activation essentially effects on process of post-electrolytic self-dissolution of titanium. It was established that the maximal rate of chemical dissolution of titanic electrodes was observed at frequency of alternating current ≈ 50 Hz.

Electrochemical modification of the catalytic activity for propane combustion of Pt/β''-Al$_2$o$_3$ electrodes

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The effect of electrochemical promotion or non-faradaic electrochemical modification of catalytic activity (NEMCA) [1] was studied in the reaction of propane combustion over a Pt film catalyst interfaced to sodium β''-Al$_2$O$_3$, a Na$^+$ conductor, in the temperature range 320 to 440°C. It was found that electrochemical pumping of sodium to the platinum surface markedly modifies its catalytic properties. For stoichiometric oxygen to propane ratio the system exhibited electrophobic NEMCA behavior, i.e. addition of sodium (negative current application or decrease in catalyst potential) resulted in decrease of the CO$_2$ production rate (Fig. 1). Relative changes in the catalytic rate typically by up to 60 times larger than the corresponding change in sodium coverage were observed implying a pronounced electronic poisoning effect of sodium. The formation/decomposition of the sodium phases on the catalyst surface were followed by linear sweep voltammetry (Fig.2).The observed electrochemical promotion behavior is in agreement with the recently described [1, 2] rules of promotion and can be explained by taking into account the reaction mechanism and the effect of the electrochemically controlled sodium coverage on the bonding of coadsorbed reactant species.
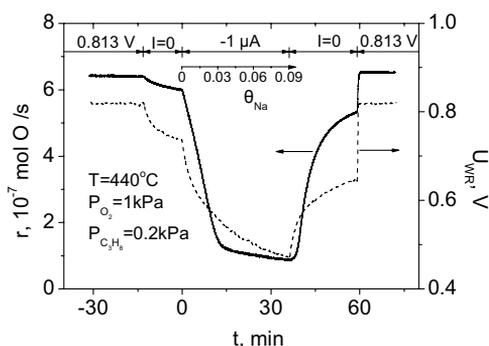
Fig.1. Rate r and potential U$_{WR}$ response to application of a current I= -1µA. Sodium coverage change θ$_{Na}$ is calculated by using Faraday's law.
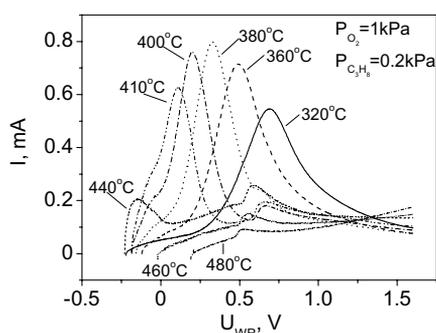
Fig.2. Linear sweep voltammograms at different temperatures after previous application of -50µA for 20 min. Scan rate 20 mV s^{-1}.

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Comparative Analysis of Measuring Techniques to Investigate the Scaling of the Cathode in Direct Water Disinfection Electrolysis

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The direct electrochemical water disinfection in non-divided cells has been known for many years to be a subject of intensive studies. One of the main problems related to this method is the blocking of the cathode due to calcareous and other deposits. To remove these deposits, a periodical exchange of the electrode polarization is used.

Within this work, different electrochemical methods were compared to study the scaling process at the cathode: linear sweep voltammetry, chronopotentiometry, chronoamperometry, potential decay measurements, electrochemical impedance spectroscopy and electrogravimetry using Electrochemical Quartz Crystal Nanobalance technology. EG&G potentiostat 283, HEKA bipotentiostat and ELCHEMA model EQCN-700 were used in the experiments with synthetic and tap water systems. Isothermal experiments were carried out on Pt, RuO_2, IrO_2 and IrO_2/RuO_2 rotating disc electrodes of 1 cm² at 20°C.

With anodic linear sweep voltammetry it was not possible to characterize the scaling after cathodic prepolarization. Changes in the surface state of the electrodes and IR corrections by calculation (HEKA) were additional error sources. Surface re-oxidation could also be observed in chronopotentiometric experiments and overlaid effects from scaling in discontinuous experiments. Potential decay experiments resulted in measured curves, at which the existence of a scale layer could be clearly observed. Nevertheless, this method only led to a statement about the existence of a scale layer, but no conclusions about structure, morphology etc. of the precipitated layer could be made. However, the method provides information for a mode of changing polarization without damaging the electrodes from shocking them in rapid double layer discharge and charge. With the impedance spectroscopy, it was possible to measure the characteristics of the precipitated scale layer in-situ. No influence of the IR drop occurs when the measurements are carried out at equilibrium potential. An electrical equivalent circuit was derived to describe the layer. During cathodic electrode polarization of a gold electrode, EQCN technology was applied. Both potentiostatic and galvanostatic experiments showed clear dependences of deposited mass on the chosen electrode parameters. Besides $CaCO_3$ also other water components were able to be deposited or form film-like structures, while sulphate ions had even hindering effects on the layer formation.

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Continuation of Discussion on Chlorine Dioxide Formation in Direct Drinking Water Electrolysis

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Chlorine dioxide is known for being an effective disinfectant with respect to immobilized microorganisms and biofilms. ClO_2 can be formed chemically or electrochemically from chlorate at a cathode or from chlorite at an anode. Additionally, electrochemical formation starting from chloride is reported in literature but no detailed data exist. Using UV spectrophotometry we found unexpectedly that ClO_2 may occur as by-product in low concentrated chloride electrolysis. A first discussion was given in [1]. The undefined presence of ClO_2 may result in a formation of other by-products such as chlorate or chlorite, limiting concentrations of them is usually restricted by regulations. Chlorite is also discussed as an intermediate of the electrochemical chlorate process.

The results presented here are based on experiments in ppm range (0-50 ppm) of components' concentration using IrO_2/RuO_2 anodes in three types of electrolytic cell. The first cell was a 150 ml cell with rotating plate anode (diameter 35 mm) above an expanded mesh cathode made from IrO_2. The second cell was a flow-through cell with two parallel plate electrodes (20mm x 50 mm) at a distance of some mm. Both were made from IrO_2/RuO_2. In a third case, this cell was divided by a cation exchange membrane. All cells were used in discontinuous operation at 20 °C. Concentrations were measured using spectrophotometrical methods of *Macherey&Nagel* and UV spectrophotometry (*Analytik Jena*). Varied main parameters were several concentrations, pH, temperature and current density (100 A m^{-2} - 500 A m^{-2}). Buffers may suppress reactions, for example the anodic of chloride reduction. Thus, mostly non-buffered solutions were electrolyzed.

In the electrolysis of chloride solutions only small amounts of chlorine dioxide, usually below 1 ppm, were measured, except the case of disturbed experiments with changed flow fields or probably enlarged local current densities. The ClO_2 concentrations were nearly independent on the rotation rate of anode and pH, whereas lower temperature, higher chloride concentration and higher current densities resulted in higher chlorine dioxide concentrations.

When chlorite was added to deionized water the increase of ClO_2 concentration was significant and proportional to the added chlorite concentration. Adding of chloride to a chlorite solution lead also to higher chlorine dioxide concentrations - both at low pH and medium pH conditions. Chlorite disappeared in anolyte and catholyte during electrolysis. Chlorate was a main product in chloride electrolysis in the anolyte and in electrolytes of the non-divided cell. ClO_2 concentration was very small reacting hypochlorite and chlorite in the range of 20 ppm. Chlorate electrolysis did not result in ClO_2 in the catholyte but chlorate can be slightly decomposed. Hypochlorite could more ore less react at the cathode and anode in dependence on the chosen current density. In acid media hypochlorite reacted rapidly but only small amounts of ClO_2 were detected. No higher ClO_2 concentration was measured when active chlorine concentration increased during other experiments. Summarizing the experimental results it can be concluded that most of chlorine dioxide is formed electrochemically from chloride ions or corresponding intermediates, however more studies in divided cells are necessary.

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Electrochemical Engineering & Technology

About the potential risk of forming nitrite and ammonium using diamond electrodes in water electrolysis for disinfection

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There are many new advertisements of electrodes for disinfection electrolysis of waters poor in chloride ions [1]. Mostly, boron-doped anodes are described for several oxidation and disinfection purposes. In these cases, a disinfection activity may be caused by oxidants such as peroxides, ozone and radicals - often called reactive oxygen species. In fact, also our studies [2] showed a disinfecting ability of electrolysed waters, which contained only traces of chloride. However, in comparison with anodes producing chlorine the disinfecting ability is much lower.

The aim of studies described in the present work was the assessment of species formation resulting from nitrate reactions in non-divided cells for flow-through disinfection. Drinking water may include nitrate up to 50 ppm according to the corresponding regulations. A cell with rotating anode above a cathode was used for the discontinuous experiments at 20 °C. Current density was varied between 50 Am^{-2} and 200 A m^{-2}. A second cell was of semi-industrial type using stack electrodes for drinking water in single pass operation. Several cathodic materials such as IrO_2 , IrO_2/RuO_2, Ti and stainless steel were used. Boron-doped diamond and IrO_2/RuO_2 were typical anode material. Research studies were focused on the use of diamond anodes in combinations with other cathode materials. Waters containing nitrate, nitrite, chloride and sulphate ions in ppm range of concentrations were used in the experiments. Analysis was carried out using test sets of spectrophotometry, UV spectrophotometry and ion chromatography.

Results show that a very complex mechanism of possible reactions exists. Both concentration ratios and electrode material combination are of decisive influence on the obtained product spectrum. Reactions mentioned as follows were identified in discontinuous electrolysis: anodic chlorine and chlorate production, chemical chlorate production, anodic chlorate oxidation, anodic and cathodic H_2O_2 formation, cathodic nitrite and ammonium formation, anodic ammonium oxidation, chemical and anodic nitrite oxidation. At mixed oxides electrodes, ammonium and nitrite are mainly formed from nitrate in the considered range of current density. Products may react each with other: peroxide with chlorine, chlorine with ammonium etc.. Obviously, adsorption of sulphate ions may suppress anodic reactions and thus influence by-product yields. The formation of chloramines is possible. All mentioned products are clearly detectable but usually in concentrations lower than 1 ppm. However, addition of some products is not allowed according to the rules for drinking water. It is interesting to note that the non-catalytic properties of diamond favour the presence of ammonium and nitrite, which can accumulate in the treated solution. The obtained results underline the fact that water electrolysis is significantly controlled by mass transfer, migration, adsorption and electrocatalytic electrode behaviour. Prediction of reaction results is very complicate.

Pseudomonas inactivation with electrolyzed water poor in chloride ions using BDD electrodes

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Numerous cell configurations and electrode materials have been investigated in electrochemical water disinfection with respect to various microorganisms. The inactivation efficacy is largely dependent on cell configuration, electrode material, electrolyte composition, the microorganisms used, and other parameters such as current density. The presence of chloride in the electrolyte will increase the cells inactivation efficacy generating highly germicidal active chlorine species.

The aim of the studies presented here was the assessment of disinfection abilities of different waters low in chloride concentration. A cell with rotating anode above a cathode was used in discontinuous experiments at 20 °C. Current density was varied between 100 A m^{-2} and 300 A m^{-2}. The cathode was made from IrO$_2$ and Boron Doped Diamond (BDD) alternatively. IrO$_2$/RuO$_2$ was used as anode material. Research studies were focused on the use of diamond anodes. Waters containing nitrate, sulphate, carbonate, hydrogen carbonate and chloride ions in ppm range of concentrations were used in the experiments. Disinfection analysis was carried out using *Pseudomonas fluorescens*, an ubiquitous Gram-negative aerobic bacterium.

It was found that *Pseudomonas fluorescens* can be killed by electrolysed water containing 240 ppm sulphate and chloride below 0.5 ppm using BDD electrode. Lower sulphate concentrations, lower current densities and the use of mixed oxides electrodes did not show any effect (Fig. 1). Nitrate, carbonate and hydrogen carbonate did not provide any disinfection ability at 50 ppm in single component electrolysis applying both types of electrodes.

A complete inactivation was achieved for electrolytes containing 25 ppm chloride and 50 ppm nitrate when BDD was used. At lower chloride concentrations, no or only slight effects were measured. Better results were obtained with IrO$_2$/RuO$_2$ as anode material in the same solution. Already samples from 3-5 ppm chloride electrolysis inactivated *Pseudomonas fluorescens* completely within 10 minutes. Also, at lower current densities a complete reduction within 30 minutes was possible.

The obtained results show that electrolysis at low-chloride concentration level is significantly controlled by the electrolyte composition, type of electrode and current density.

The concentration range considered in the studies is in accordance with the rules for drinking water. Further research will be focused on the use of higher current densities.
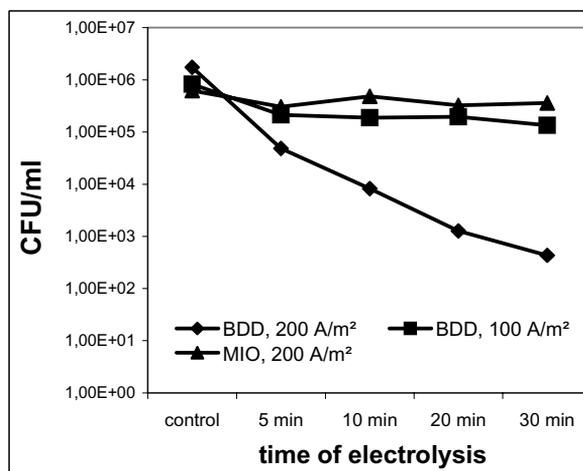

Fig. 1 Disinfection efficacy of electrolysed water (240 ppm sulphate, BDD and mixed oxides (MIO) anode).

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Electrochemical Engineering & Technology

The study of geometrical factors of the electrolysis cell for direct drinking water disinfection with respect to chlorine evolution efficiency

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The main idea of direct drinking water disinfection (DDWD) is based on water electrolysis under formation of chlorine as the main electrodisinfection product from the natural chloride content in drinking water. Although the principle of the method is known for several decades, the knowledge on the electrode reaction kinetics is insufficient. Also, the complex reaction mechanisms of produced chlorine with constituents of the drinking water [1-3] are not yet fully understood. Several factors such as chloride concentration, current density and the presence of other ions affect the resulting chlorine production rate. Geometrical factors are usually connected with current density distributions and they are considered to have a certain, so far unspecified influence on product and by-product formation.

The aim of the presented work was to develop a mathematical model of the DDWD electrochemical cell. The presented model of the rectangular cell equipped with plate or expanded mesh electrodes allows assessing influence of the geometrical factors and problems in cell design in dependence on the chlorine formation efficiency. The secondary current density distribution is considered. The electrode reaction kinetics as well as current efficiency values in dependence on the current density and chloride concentration were determined experimentally. An artificial drinking water with varied chloride concentration and a semi-technical cell with parallel plate electrodes were used. The *Laplace* equation was solved using the finite element method in the Femlab© environment [4].

The main attention has focused on the indication of inhomogenities in the local current density distribution and theirs impact on the process efficiency. It was demonstrated that because of the irregularities on the electrode edges, the expanded mesh electrode provides in this particular application less favourable results than simple planar electrodes.

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Aplication of electrochemical techniques in pyrochemical processes. Chemical and electrochemical behaviour of Eu(III) and Yb(III) in the eutectic LiCl-KCl

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Partitioning and transmutation (P&T) is one of the powerful strategies for reducing the radiotoxicity and volume of nuclear wastes. In this strategy, the separation (partitioning) of long-lived radionucleides, i.e. minor actinides (MAs), from other fission products especially lanthanides (Lns), is required before transmuting them into other stable or lower-level nuclides, otherwise the Lns absorb neutrons effectively and hence prevent neutron capture by the transmutable actinides. However, the separation of MAs from Lns is not simple due to the amount of Lns in the fission products and the similarity of their chemical properties.

This work is concerned with the electrochemistry of europium and ytterbium, a light and a heavy lanthanide respectively. The study has been carried out in the eutectic LiCl-KCl mixture at temperatures between 673 and 823 K using inert (i.e. GC, W) and reactive (i.e. Al) electrodes.

The stable oxidation states are (III) and (II). Eu and Yb metals react with the melt to displace lithium, so electrodeposition of metals cannot be observed within the electrochemical potential window. The electrochemical systems Eu(III)/Eu(II) and Yb(III)/Yb(II) are quasi-reversible and the values of the $E_{1/2}$ and the kinetic parameters, k^0 and α, have been calculated by simulation of the cyclic voltammograms or logarithmic analysis of the convoluted curves. Mass transport towards the electrode are simple diffusion processes, and the diffusion coefficient of Eu(III) and Yb(III) ions have been calculated. The validity of the Arrhenius law was also verified in both cases.

Cyclic voltammetry, open-circuit chronopotentiometry and potentiostatic electrolysis pointed out that both Eu(III) and Yb(III) can be reduced on an aluminium electrode to form Eu-Al and Yb-Al alloys. Therefore, the use of a reactive cathode made of aluminium for the extraction of europium and ytterbium from chloride media could be the use of a pertinent route.

Potentiometric titrations of Eu(III) and Yb(III) solutions with oxide donors, using a yttria stabilized zirconia membrane electrode "YSZE" as a pO^{2-} indicator electrode, have shown the formation of EuOCl, YbOCl and Yb_2O_3 compounds, and their solubility products have been determined at 723K. E-pO^{2-} predominance diagrams of Eu and Yb in the studied melt have been constructed.

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Biomass valorisation: electrochemical oxidation of lignin

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The low cost of lignin associated with its availability makes it an interesting raw material for fine chemistry. The estimated annual production of lignin as a by product of paper industry is about 30 millions tons. However most of it is burned or dumped as polluting effluent and only 5% is used to produce useful compounds. The aim of this work is to use electrochemical methods to perform oxidative degradation of lignin producing high valued compounds such as vanillin.

Previous studies [1,2] indicate that production of vanillin and vanilic acid is accomplished by electrochemical methods but the yields are quite low. In an attempt to increase the yields on vanillin and vanillic acid, the electrochemical oxidative degradation of Kraft lignin was studied on different experimental conditions.

A systematic study of the experimental parameters that could have an effect on the yields and selectivity towards vanillin and vanillic acid was carried on. Exhaustive electrolyses of lignin solutions in alkaline medium were performed at both controlled potential and constant current, in a flow cell (FM01-LC) and in a batch cell. The following experimental parameters were studied: applied potential and current, anode material (Ni, Cu and PbO_2) and lignin concentration.

Direct quantitative analyses of the electrolyses solutions were performed after precipitation and centrifugation. The electrolyses products were identified and quantified by GLC and HPLC after comparison with commercial reference compounds.

Conversion and chemical yields were found to be dependent mainly on the applied current density and the partial pressure of oxygen at the interface. It was also noticed that the nature of the electrode influenced mainly the reaction rates.

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Chromium (VI) Reduction Processes in Competition

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The problem of chromium (VI) compounds in industrial waste water is found in different technical processes. The most common sources of effluents containing chromate ions are chromium plating shops working with electrolytes based on aqueous solutions of chromic acid, metallurgical plants producing or processing chromium alloyed steels and running acidic pickling baths, and – last but not least – factories for vanadium oxide production. The main fraction of this material is subsequently converted into ferro-vanadium and sold to steel industry.

The reason for a chromium problem in this process is the inevitable chromium content of all available vanadium raw materials (ores or slags) and the usual roasting procedure with soda under oxidising conditions. Hereby vanadium compounds are transformed to water-soluble alkali vanadate but simultaneously chromium oxide reacts to equally water-soluble alkali chromate (VI).

To fulfil the legal waste water regulations all this chromate has to be reduced to chromium (III) ions later and finally eliminated as barely soluble hydrous chromium (III) oxide. For this purpose waste water streams charged with significant amounts of chromate ions are frequently treated with reducing agents, e.g. sulphur dioxide.

All the chemical reduction processes are charged with one or more of the following drawbacks:
• handling of hazardous chemicals (e.g. liquid sulphur dioxide);
• raising the content of neutral salts (particularly sulphates) in effluents;
• supply of costly reducing agents in considerable amounts.

Consequently, electrolytic conversion of chromium (VI) to chromium (III) has to be seen as a reasonable alternative including the option of a combined electrochemical and chemical reduction if the legal concentration limit of chromate ions (0.1 mg/l) in waste water could not be reached economically by only one of them.

In the case of cathodic reduction divided cells have to be used in order to prevent anodic re-oxidation of previously formed Cr (III)-ions. This means automatically the installation of two separate electrolyte loops (catholyte and anolyte will have different composition) and dimensions of industrial waste water streams require an active cathode area in the range of some square meters.

For this reason the advantage of avoiding hazardous or costly chemicals and the benefit of preventing the spill of additional salts is partly compensated by cost for investment (cells, pumps, electrodes, separators…) and for electrical energy.

A comparison of some chemical reduction methods and at least two different electrochemical cell modules with all their particular advantages and drawbacks is given.

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Convective instability of binary electrolyte between ion-exchange membranes

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In the electrochemical systems with binary electrolyte, where ion-selective membranes with low resistance serve as the electrodes, the emergence of periodical convective structures at the near-limiting current is commonly explained by the electro-convective effects. However, in these systems, convective instability similar to the Rayleigh-Benard convective instability can also arise. It is associated with the buoyancy forces that are caused by the nonuniform distribution of concentration, when a current is passed through the electrolyte. It was frequently assumed that the convective instability in the binary system is similar to the Rayleigh-Benard convective instability. However, as was indicated in [V.M. Volgin, A.D. Davydov, Russia J. Electrochem., 2006, vol. 42, no. 6], fluctuations of electric potential should be taken into account when instabilities in the binary electrolyte are analyzed.

In this work, the numerical analysis of convective stability of binary electrolyte is performed taking into account fluctuations of electrochemical potential of both types of ions.

This approach enables us to take into account not only the fluctuations of concentration, but also the fluctuations of electric potential. This makes a considerable contribution to the net result. In addition, electro-convective effects are taken into consideration. These effects arise in the binary electrolyte at the currents, which are not very close to the limiting current. The relationship between the conditions of convective structures origination and the current passing through the system are determined. It is shown that the fluctuations of electric potential and electroconvection have an additional destabilizing effect on the system, and also have a pronounced effect on the geometry of arising periodical convective structure. These results are obtained for the model and several particular electrochemical systems.

Synthesis and characterization of a surface modified cation exchange membrane with preferential selectivity for monovalent cations

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The synthesis of a cation exchange membrane with preferential selectivity for monovalent cations is of particular interest to treat acid effluents containing metallic salt produced by several industries in order to re-use and recycle the chemicals.

Among the various ways of modifying a membrane, we have chosen to confer a monovalent cation permselectivity to a cationic membrane by chemically grafting positive charges on the membrane surface.

A thin positively charged layer was formed on the membrane surface after reaction between SO_2Cl groups of a styrene-divinylbenzene copolymer membrane and a diamine. The diamine used in this work is the 3-dimethylaminopropylamine (3-DMAPA). The membrane surface was modified during a predetermined period of time in the presence of various diamine concentrations. After the amination reaction, the SO_2Cl groups remaining in the inert part of the membrane were hydrolyzed by an aqueous sodium hydroxide solution. The terminal amine groups were protonated in acidic media.

ATR-IR measurements on the membrane surface reveal that the intensity of the band associated to $– SO_2Cl$ decreased with increasing the diamine concentration. The cation capacity exchange is not significantly affected by the presence of the cationic layer on the surface of the membrane.

The influence of the surface modification on the resistivity and selectivity of the membrane will be discussed. Current-voltage curves and impedance measurements were performed to determine the membrane electric resistance while separation tests were based the Hittorf's method. The results showed that a membrane modified with a low concentration of the diamine showed a high membrane resistance with a low limiting current and an excellent permeselectivity. In contrast, a membrane modified with a high concentration of the diamine showed a low membrane resistance but a high leaking of the divalent cations.

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Electrocrystallization of ZnSe on porous titanium oxide

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The electrochemical growth of microcrystalline zinc selenide II-VI semiconductor compound on microporous TiO_x substrates is discussed, in terms of nucleation properties and microstructure of the resulting samples. The products of the process may be evaluated as semiconductor heterojunctions with large interface area dictated by the extended inner surface of the substrate.

Porous oxide layers of variable thickness were prepared by anodizing Ti discs in acidic solutions. The structuring of the oxide overlayer was controlled through the type of the anodization bath and the oxidation overpotential used. Electrodeposition was performed cathodically in both potentio- and galvano-static manner, either in acidic or in alkaline baths of zinc and selenium precursors, under a mixed ionic transfer and chalcogen diffusion control [1, 2]. The as prepared substrate and deposit microstructures were identified down to very thin surface layers by Low Angle Incidence X-ray Diffraction (LIXD). The topology of the pores, their size distribution and the morphology of the deposits were determined by Scanning Electron Microscopy (SEM). Electrolytic current transients were recorded in the deposition baths in order to account for the nucleation and growth of the ZnSe clusters.

Thin layers fitting the pore depth as well as over-grown epilayers up to 0.5 µm in thickness were formed and the composition variation for the pore-filling and coating material was investigated. The full coverage of the substrate led to coatings consisted of ZnSe equiaxed microcrystals inhomogeneously dispersed in a, rich in Se, Se(ZnSe) matrix. Compared to non passive Ti substrates, the anodized Ti promoted the formation of deposits with improved ZnSe to Se atom ratio, i.e. with lower excess of elemental Se and higher content of cubic, (111) oriented ZnSe crystallites. It is shown that the increased ZnSe rather than elemental Se nuclei formation principally occurs at a high rate within the micropores, as a consequence of the specific nucleation environment at the interior of the oxide layer. The in-depth electric potential profile and the diffusion limitation of Se inside the pores were invoked to explain this behaviour, while the effect of crystallographic misfit is also discussed. Reflectance spectroscopy showed that the electrolytic coatings exhibit, after annealing at temperatures as low as 200°C in air for 30 min, the typical for bulk ZnSe band gap width of 2.7 eV. The assessment of the electrical contact between the oxide substrate and deposited ZnSe remains to be accomplished.

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Electrodeposition of Lu and electrochemical formation of Lu-Al alloys from the eutectic LiCl-KCl.

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The operation of nuclear fission reactors give rise to long-lived radionulcides, which may be considered a potential risk born by future generation that must be minimized. To achieved this goal the most radiotoxic elements present in spent nuclear fuels, i.e. minor actinides, must be efficiently separated from the fission products, specially lanthanides, and destroyed by transmutation. Assessment of feasibility of pyrochemical separation processes requires a good knowledge of molten salt chemistry of actinides and lanthanides and therefore basic data of these elements need to be obtained.

This work takes part of a project related to the electrochemical behaviour of lanthanides, and its concerned with the electrochemistry of lutetium. The study has been carried out with, a solution of $LuCl_3$ in the eutectic LiCl-KCl mixture at temperatures between 673 and 823 K using inert and reactive electrodes.

Transient electrochemical techniques, such as cyclic voltammetry, chronopotentiometry and chronoamperometry were used in order to study the reaction mechanism and the transport parameters of electroactive species at a tungsten electrode. The electroreduction of Lu(III) proceeds in a single step and electrocrystalization plays an important role in the electrodeposition process. Experimental current-time transients has been compared with the theoretical models based on instantaneous and progressive nucleation. Mass transport towards the electrode is a simple diffusion process, and the diffusion coefficient of the electroactive specie Lu(III) has been calculated. The validity of the Arrhenius law was also verified.

The electrode reactions of the $LiCl-KCl-LuCl_3$ solutions at an Al wire were also investigated by cyclic voltammetry and open circuit chronopotentiometry. The reduction signal of Lu(III) at the Al electrode was observed at more positive potentials values than those at the inert electrode. This potential shift was due to a lowering of the activity of Lu in the metal phase due to the formation of intermetallic compounds. Lu-Al alloy films were obtained using potentiostatic electrolysis, and the samples were characterized by X-ray diffraction analysis and scanning electron microscopy (SEM). The activities of Lu in the Al phase, as well as the standard Gibbs energies, enthalpies and entropies of formation for the Lu-Al interermetallic compounds were estimated from the open circuit chronopotentiometric measurements.

A quartz sealed Ag/AgCl reference electrode for high temperature molten salts

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High temperature molten salts play important roles in modern electrochemical research and industrial practices. Recently, in molten $CaCl_2$ at ~900°C, electrochemical deoxygenation of metals, such as titanium, was investigated[1]. It was also reported that when a solid metal oxide, e.g. TiO_2, was made into an cathode, regardless of the electronic conductivity, the oxide could be electrochemically reduced in the same melt directly to the metal[2]. The possibility of using this new electro-deoxidation method has been acclaimed for the economical and environmentally friendly production of many useful but currently expensive metals and semi-metals, typically Ti, Si, Nb and Cr, and their alloys[2,3-6]. However, in previous studies, except for some voltammetric observations from using a metal based pseudo-reference electrode coupled with a known electrode reaction as the internal reference[3], most results and analyses were linked with electrolysis in a two-electrode cell which only allowed the control of cell voltage or current. In this laboratory, a quartz sealed Ag/AgCl reference electrode was fabricated and studied in $CaCl_2$ based molten salts[7]. It performed satisfactorily in terms of reproducibility, reusability and stability in experiments that varied the temperature (700°C ~ 950°C) and service time (from hours to days). The electric resistance of the reference electrode decreased from 10^5 Ω to 10^3 Ω when increasing the molten salt temperature from 600°C to 950°C, following well Arrhenius' Law. The potential variation of the electrode upon changing the electrolyte composition ($CaCl_2$, NaCl, KCl, and/or AgCl) suggested the selective conduction of Na^+ ions and possibly Ca^{2+} ions through the thin-wall of the sealed quartz tube. Prolonged use (2~3 days) of the reference electrode in the presence of both oxygen and molten chloride salt led to noticeable erosion of the quartz tube, particularly at the *molten salt-quartz-gas* triple phase boundary, which is attributable to the formation of calcium and/or sodium silicates under the influence of oxygen in the liquid and gas phases, respectively.

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Influence of pH-values on electrochemical stripping of chromium nitride films

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Chromium nitride (CrN) films which exhibit superior thermal stability and wear resistance are widely used in tribological applications. Reworks of CrN films are usually needed to improve the yield rate of the coatings. Electrochemical techniques are the most feasible and efficient method to remove the hard-coatings, which has drawn much attention in industry. Here, CrN films were stripped in electrolytes with a wide pH values under galvanostatic conditions. Figure 1 shows the removed thickness of CrN films, which was measuring by field emission scanning electron microscopy, as a function of stripping time under 10 mA cm^{-2} at various pH values. The removed thickness (ΔL) decreased linearly with time (t) in all cases. The relation can be fitted by $\Delta L = -kt$, where k is a rate constant (nm s^{-1}). Figure 2 displays the rate constant (k) as a function of pH value. As shown in the figure, the rate constant of such an electrochemical stripping process remains with pH value. The pH and time dependence of the removed thickness of the coatings is further analyzed and discussed.

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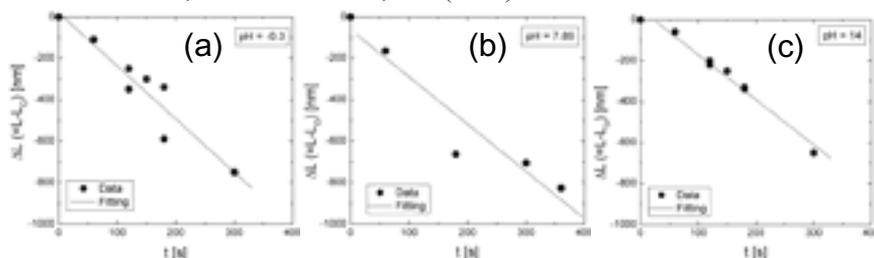
Figure 1. The removed thickness of CrN films as a function of pH-value: (a) -0.3, (b) 7.89, and (c) 14.
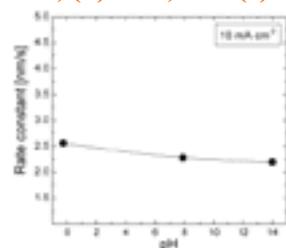
Figure 2. The rate constant of electrochemical stripping of CrN films under 10 mA cm^{-2} in electrolytes with different pH value.

Electrochemical Behave of Nitrobenzene in Room Temperature Ionic Liquid: BMIMPF$_6$

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Many researches on the electrochemical reduction of aromatic nitro compounds have been done in water [1], acetonirile, dimethyl formamide [2], as important green methods. RTILS [3] with several desirable properties including negligible volatility, strong solubility, wide electrochemical window, good conductivity and catalysis, could be used as green media and electrolyte in electrochemical systems [4,5]. Our group systemly investigated the electrochemistry of nitrobenzene in BMIMPF$_6$.

Cyclic voltammograms and steady-state polarization curves were carried out on CHI 660B electrochemical work station. The work electrode was a micro disc of platinum and its area was 2.8×10^{-9} m^2, the reference and auxiliary electrode was a large area platinum plate. BMIMPF$_6$ was synthesized according to reference [6] (containing negligible amount of residual water).
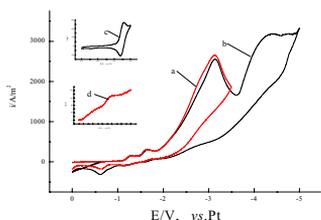

Fig.1 Cyclic voltammograms of 0.01 mol/L nitrobenzene in BMIMPF$_6$,353 K, v=0.1V/s,scanning range:
(a) 0~-3.5V,(b) 0~-5V,(c) insert,0~-1.5V,
(d) Quasi steady-state curve, v=0.0001V/s, 0~-2.3V.

There are four electrochemical steps in the course of cyclic voltamograms (Fig. 1). The first peak (E=-1.30 V) is related to a reversible reduction to nitrobenzene radical anion (Fig. 1, insert), the number of electron transfer calculated by measuring quasi steady-state curve is one (Fig.2). The scond peak (E=-1.67 V, Fig. 1a) mainly shows a irreversible reduction to dianion, and a chemical reaction with 2H$^+$ produces subsequently nitrosobenzene and water, the number of electron transfer is one also. At third peak (E=-3.14 V), a irreversible reduction to nitrosobenzene radical anion arises, the number of electron transfer is one, correspondly. The radical anion couples and reacts with 1H$^+$ subsequently, producing azoxy[2], In this step, there are some more complex reaction furtherly, producing azobenzene, hydrazobenzene, etc. The fourth peak shows the reduction of BMIM$^+$ [7]. The cursory exchange current density of aforementioned three step calculated by quasi steady-state curve are 8.5, 4.0, 1.7 A/m^2, respectively (Fig.2).

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BaA$_{0.9}$Sb$_{0.1}$O$_{3-\delta}$ (A=Pb, Sn) as anode material for catechol electrodegradation

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Wastewaters produced by the pulp and paper industries contain a wide range of phenolic compounds, which can include lignin degradation products, and modified products such as chlorinated species like chloroguaiacol and chorocatechol. Some of these compounds are quite toxic and resistant to biodegradation by most microorganisms. Recent work has studied successfully the electrodegradation of guaiacol using as anode material an oxide with a perovskite like structure BaPb$_{0.9}$Sb$_{0.1}$O$_{3-\square}$. The chemical composition of the electrode is an important parameter in the electrochemical oxidation. In this work, we have studied the oxidation of a phenolic lignin model compound, catechol. The electrochemical oxidation of catechol was performed using as anode material, BaPb$_{0.9}$Sb$_{0.1}$O$_{3-\square}$ and BaSn$_{0.9}$Sb$_{0.1}$O$_{3-\square}$; these oxides were sinthesised by the ceramic method at 1123 K and 1523 K, respectively, and the obtained powders was sinterized in the pellet form to prepare electrodes. Bulk electrolysis was studied using Na$_2$SO$_4$ as electrolyte, during 96 h at current densities of 2.5, 5 and 10 mA cm^{-2}, and different initial catechol concentrations of 50, 100 and 200 mg L^{-1}.

UV-Visible absorbance measurements, Chemical Oxygen Demand (COD) tests and Total Organic Carbon (TOC) analysis were performed, in order to follow the organic load removal and the mineralization index. Results have shown COD removals between 40 - 60% and reduced TOC removals, corresponding to the oxidation of catechol mainly by a conversion mechanism, rather than combustion, which is corroborated by the formation of dark solutions that are compatible with the presence of polymers. The assays with higher organic load removal were performed with the electrode made of BaPb$_{0.9}$Sb$_{0.1}$O$_{3-\delta}$, maybe due to the fact that this oxide is made of a fine powder, comprising smaller crystallites, which increases the surface area of the electrode.

Symposium 5 - Poster

Electrochemical Engineering & Technology

"*In situ* Raman spectroscopy as applied to the characterization of sulfur-containing electroactive films"

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During the last years a number of new cathode materials have been investigated for their application in lithium rechargeable batteries [1]. Apart from the lithium intercalation compounds, the broad family of Organic Conducting Polymers (OCPs) constitutes a subject matter of intensive research in this area owing to their particular electron-conducting properties. Among the postulated OCPs, aniline derivatives seem to offer both the environmental stability and the high charge density required for their implementation in commercial devices.

Naoi et al [2] investigated the redox process of poly(2,2'-dithiodianline) and concluded that the unusually high charge storage ability shown by this material is due to the participation of the interchain disulfide bond on the whole redox response of the polymer. Thus, the reversible charge-discharge process of this polyaniline derivative implies the well-known benzenoid-to-quinoid transformation as well as the formation and rupture of the disulfide link. Both processes were postulated to occur under the same voltammetric peak as shown in the scheme.
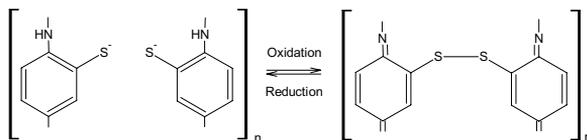
In the present study, the *in situ* Raman spectroscopy technique has been employed to monitor the integrity of the S-S link as a function of the potential applied to the polymeric material. The results obtained disagree with Naoi's hypothesis, therefore the participation of the disulfide bond in the charge-discharge process of this cathode material can be completely ruled out. We concluded that the high storage ability of poly(2,2'-dithiodianilithe) as compared with that of polyaniline should be explained in terms of the structural changes induced in the polyaniline backbone by the presence of the disulfide link.

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Natural-convective instability of stagnate electrolyte between horizontal electrodes: effect of external magnetic field

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The external magnetic field has a considerable effect on the natural convection of electrolyte solution and in particular on its natural-convective-instability. For heat convection in the liquid with a constant conductivity in the uniform magnetic field, it is known that the critical Rayleigh number is quadratic in the Hartmann number, which is defined as a ratio between the magnetic and viscous forces. The available solutions were obtained in the absence of external electric field and ignoring the variations in the liquid conductivity. Under these conditions, the electric current in the stagnant liquid is absent. Obviously, this does not take place in the electrochemical systems, where, under the action of external electric field, the electric current flows even in stagnant electrolyte. In addition, the current disturbs the uniform distribution of concentrations that have an effect on the electrolyte conductivity. Therefore, when solving the stability problem for electrochemical systems, the variations in the electrolyte conductivity should be taken into account.

In this work, the effect of an external uniform magnetic field on the monotonic and oscillatory natural-convective instability of stagnate binary and multi-ion (containing three or more types of ions) electrolyte between two horizontal electrodes is studied using a set of equations involving the Navier-Stokes equations for incompressible viscous liquid to the Boussinesq approximation that account for the buoyancy and Lorentz forces, the ion-transfer equations that account for diffusion, migration, and convection, and the electroneutrality condition. A set of nonlinear equations for the undisturbed steady state and a set of linear equations for amplitudes of small perturbations were solved numerically. The dependences of critical Rayleigh number on the Hartmann number and on the system's parameters (the diffusion coefficients and the mass coefficients) for monotonic and oscillatory instabilities are obtained for the case that the electrochemical reaction proceeds under the conditions of limiting current. It is found that magnetic field not only provides a strong stabilizing effect, but can change oscillatory instability to monotonic one for the electrolytes with three or more types of ions. Stability diagrams are presented and stability of several electrochemical systems is analyzed.

Symposium 5 - Poster

Electrochemical Engineering & Technology

Passivating treatment of mild steel in molibdate containing solutions

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The ecological problems connected with application of chromates as passivating inhibitors of corrosion, have put a task to find the alternative not toxic passivators. Molibdates and their mixtures with some organic or inorganic substances are appeared acceptable replacement of chromates for corrosion protection of steel in neutral environments. In the present work the stability of passive films, generated on middle steel in solutions with molibdate's additive, was investigated. The corrosion rate and potentials of previously passivated samples were measured in water not containing passivators.

It was determined, that the application of molibdate as passivator allows to obtain the stable passive films in solutions which contain such components as metal nitrate salts, borax or some organic acids. The optimum value of pH of passivating solutions is within the limits of   3 - 4.

The essential displacement of potential to the positive values and reduction of steel dissolution rate in 10 - 100 times, testifies to transition of steel in a passive state under the action of molibdate and other various additives. At carry of passivated steel in water without the additives one of three types of dependence potential - time is observed: 1 - potential has negative value which is closed to steel potential in water without inhibitors; 2 - the initial value of potential corresponds to the passive state of steel, but then a displacement of potential in the negative site and activation of steel occur; 3 - potential of steel changes in time a little and remains in zone of a passive state of steel.
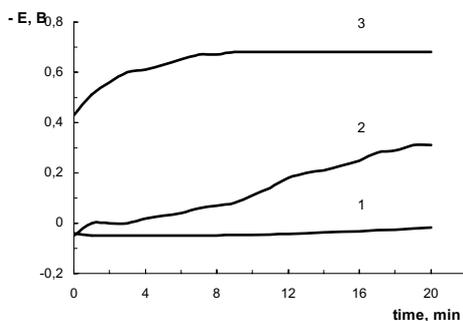
Fig. 1. Change in time of steel corrosion potential in distilled water with (1,2) and without (3) preliminary passivation in nitrate solutions which contained: (1) 2 g/l Na_2MoO_4; (2) 0,5 g/l Na_2MoO_4 .

In last cases the corrosion of steel in water is reduced essentially. The using of treatment in proposed passivating solutions providing the subsequent protection of steel from corrosion in water without the inhibitors is perspective method of steel protection against atmospheric corrosion.

Extreme Artificial Engineering

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Extreme Artificial Engineering:

This will look to be quite a futuristic talk but it will come live one day- The extreme artificial intelligence.

I don't want to go deep into AI but let me give you an idea AI stands for Artificial Intelligence and science dealing with this is Artificial Engineering. It basically deals with the simulating the ideal human reaction for a particular action ie. it can be stated in simpler terms as making the machines to act on preset of conditions by making them think artificially. This is achieved by solving complex mathematical equations. But Extreme Artificial engineering goes ahead of it, It will be humans controlling the machines with there minds and making them to act as per the thoughts coming to your mind.

It will deal with human brain interaction with a device which can read those pulses or signal and interpret them to machine language. Let me explain it with an example

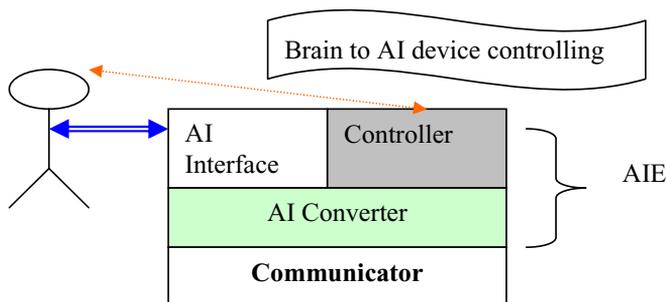This above diagram explains X Artificial engineering. It is like this a human being will be having a AIE which is artificial intelligence equipment which consist of hardware as well as embedded software(will explain latter) so this AIE is controlled by the brain waves. This device will be very small in size and as technology advances the device will change it size from a gadget to a ring or IC which can be implanted in your body itself. So this device will get the signals from brain through AI interface this will convert those signals to machine language and can be transferred through a communicator to anywhere in the universe. The communicator can connect to blue tooth, WAN or old pstn lines.
This process can be reversed ie. the communicator can receive the signal from the network and pass it on to the AI converter which will convert it back to brain pulses and pass it back to human brain.

Removal of Ni^{2+} ions from diluted solutions with an electrodeionization method using ion-exchangers of different nature

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Electrodeionization, which provides a discontinuous purification of solutions simultaneously with electroregeneration of ion-exchanger and concentration of the component being removed, is a perspective method for purification of waste waters. Traditionally this method is used for removal of alkaline metal ions and also some divalent cations, particularly Ni^{2+}. For Ni^{2+} removal a flexible ion-exchange resin, which is low selective in regards to nickel, is used. Unfortunately this resin is chemically unstable and nonselective in regards to Ni^{2+}. It is known that inorganic ion-exchangers based on zirconium hydrophosphate (ZHP) are stable in aggressive media and rather highly selective towards heavy metal cations. Efficiency of use of any ion-exchanger in electrodeionization process is determined by a mobility of sorbed ions. Ion mobility in ZHP depends on a composition of this ion-exchanger: concentration of functional group per volume unit and water content. Thus the ion-exchanger, which is characterised by high mobility of sorbed ions, could be obtained by regulating of its composition during synthesis process.

Sorptive and kinetic characteristics of the ZHP samples with different water content were studied. Ni^{2+} и H$^+$ self-diffusion coefficients and also the effective diffusion coefficients of Ni^{2+} ions, which correspond to Ni^{2+}→H$^+$ exchange, were determined using sorption method. In the case of the sample containing 85 % water (hydrogel) the self-diffusion coefficients were found to reach $4.17·10^{-11}$ (Ni^{2+}) and $5.06·10^{-10}$ (H$^+$) m^2 s^{-1}. It was shown that drying of the ion-exchanger (hydrogel-xerogel transition) results in a decrease of ion-exchange rate (decrease of ion mobility).

Ni^{2+} transport in ZHP hydrogel was investigated with electromigration method using cation-exchange membranes: Ni^{2+}-loaded ion-exchanger was regenerated under potentiostatic conditions. It was revealed that the dependence of Ni^{2+} flux through the membrane on the potential gradient through the ion-exchanger bed could be fitted with a linear function. The effective diffusion coefficient of Ni^{2+} found using Nernst-Planck and Nernst-Einstein equations was estimated as $1.14·10^{-11}$ m^2 s^{-1}. It is in a good agreement with the self-diffusion coefficient obtained by sorption method.

It was shown that ZHP can be used for nickel removal from diluted solutions containing 40 ppm Ni^{2+}, 40 ppm Ca^{2+} and 12 ppm Mg^{2+}. The highest purification degree is reached for nickel (70 %) and does not exceed 35 % for other cations (Fig. 1). Use of inert glass particles instead of ZHP results in a deterioration of the purification. The Ni^{2+} transport is realised not only through the solution, but also through the ion-exchanger (Fig. 2). Some amount of Ni^{2+} is transported to the anode compartment due to formation of concentration gradient through the ion-exchanger bed. In order to prevent a fouling of the membranes and ion-exchanger due to Ni(OH)$_2$ deposition a small amount of strongly acidic flexible resin (a quarter of total volume) was added. The limiting current through the cation-exchange membrane has been calculated using correlation equations. It was found that a fouling of the

membranes and ion-exchanger, which is caused by deposition of insoluble oxide compounds, can be minimised, if a mix of ZHP and flexible cation-exchange is used. In this case the inorganic component provides selectivity towards Ni^{2+}, at the same time the resin increases the current efficiency for Ni^{2+} transport due to deposition minimization.

Optimal conditions of the electrodeionization process (flow rate of the solution, current, ratio of the organic and inorganic components etc.) were found. A simple model, which allows use to predict the condition of steady state has been proposed.
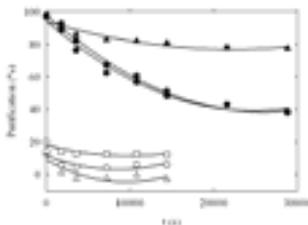

Fig.1. Purification degree of the combined solution over time of electrodeionization using ZHP (■,●,▲) and glass (,○,□) for ions: Ni^{2+} (▲,), Ca^{2+} (●, ○) and Mg^{2+} (■, □).

Electrochemical synthesis of 5,6-dihydroxy-2-methyl-1-benzofuran-3-carboxylate derivatives

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Electrochemical oxidation of catechols (**1a-c**) has been studied in the presence of methyl acetoacetate (**2a**) and ethyl acetoacetate (**2b**) as nucleophiles in aqueous solution using cyclic voltammetry and controlled-potential coulometry. The results indicate that the quinones derived from catechols (**1a-c**) participate in Michael addition reactions to form the corresponding benzofuran derivatives (**3a-f**). The electrochemical synthesis of (**3a-f**) has been successfully performed in an undivided cell in good yield and purity. The oxidation mechanism was deduced from voltammetric data and by coulometry at controlled-potential. The products have been characterized after purification by IR, ^{1}H NMR, ^{13}C NMR and MS.
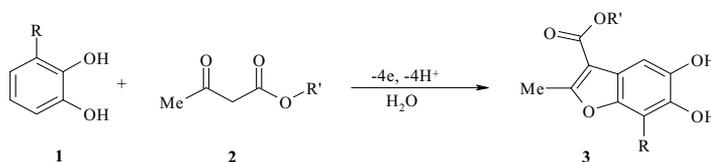
1	R	**2**	R'	**3**	R	R'	%Yield of **3**
a	H	**a**	Me	**a**	H	Me	60
b	Me	**b**	Et	**b**	Me	Me	70
c	OMe			**c**	OMe	Me	55

Electrosynthesis on BDD anodes in non aqueous media

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The interest in fundamental electrochemistry and its applications to industrial processes have known a second breath with the use of boron-doped diamond (BDD) as electrode material. It has shown interesting properties like wide electrochemical window, a low background current and a chemically stable surface, which have been intensively studied in the wastewater treatment [1, 2] and more recently in non aqueous solvents for organic synthesis. In fact it has been shown that using BDD anodes in methanol, new pathways are available compared to classical electrodes like graphite [3-5].

The present work has the aim to study the use of a BDD anode in glacial acetic acid. Therefore by using electrochemical characterization methods like cyclic voltrammetry, chronoamperometry, galvanostatic transient and comparing the results with preparative electrolysis it is possible to develop reactions mechanisms for the acetoxylation and the methylation of aromatic compounds. Ultramicroelectrodes (UME) have been used for the electrochemical characterization in order to get rid of the huge ohmic drop due to the low conductivity of glacial acetic acid. The use of UME enables very accurate measurements and allows getting a lot of mechanistic information; concerning the oxidation potential, the rate determining step or the surface poisoning.

The advantage of BDD over classic electrode has been proven by the enhancement of current efficiencies for the acetoxylation of toluene. Another advantage of this electrode material is the ability it has to oxidize very stable compounds like nitrobenzene, which is nearly completely inert on classical electrodes like platinum or graphite. Polymeric products have also been observed in preparative analysis with BDD anodes that were not found on Pt and graphite, thus it indicates a clear difference in the mechanisms.

The very low conductivity of glacial acetic acid may be overcome in preparative electrolyses by using a reactor with a very small distance between the anode and the cathode (typically $200 - 400$ µm). Moreover for increasing the capacity of such a reactor, a series of reactor may be constructed using the dipolar reactor theory. The advantages are a very high ratio surface to volume and reasonable ohmic drop, beyond the specific advantages of the dipolar reactor.

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Potential activation in the initial process of the copper deposited on iron substrate

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'Potential Activation' phenomenon was put forwarded firstly by author, which is a theory concept about explaining the adhesion between electrodeposition layer and substrate metal, and it is the 'activating by oneself' process of substrate metal surface in the initial process of electrodeposition. When the deposition potential of adhesive metal is negative than the activation potential of substrate metal, the cathode potential is polarized to activation potential firstly, and the substrate metal has been activated, then adhesive metal was deposited on the activated substrate, so the adhesion is good; whereas it is bad. The potential-time curves under the constant current and cyclic voltammetry curves of iron electrode were measured in cuprous cyanide solution and in common cupric pyrophosphate solution. The results indicated that the iron electrode has been activation at -1.2V versus SHE in cyanide electrolyte, and copper is deposited on the activated iron substrate at -1.3V versus SHE, therefore, the adhesion between layer and iron substrate is good. But in the common cupric pyrophosphate solution, the reduction reaction of Cu^{2+} to $Cu(s)$ was occurred at -0.5V versus SHE which is positive than the activation potential of iron electrode, hence the copper was deposited on the inactive iron substrate and the adhesion is bad, furthermore, the existence of oxide between plating layer and iron substrate has been validated by Ar ion sputtering and X-ray photoelectron spectroscopy. Through adding assistant complexing agent and controlling initial current density, cathodal polarization was intensified in cyanide-free electrolyte. When the deposition potential of copper is less than activation potential of iron substrate, the potential activation process was shown, so the adhesion of plating layer can reaches $7180N/cm^2$ and it is close to that of cyanide copper plating. The transformation of component on the iron electrode surface in 5% KCl solution was determined by Enhanced Raman Spectroscopy. The result showed that the reduction process of each oxide on iron substrate under different potential.

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A comparative microelectrode voltammetric study of the diffusion of surfactant aggregates in aqueous solutions

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Voltammetry with platinum disc microelectrodes was employed to gain information on the diffusion coefficient, D, of two different surfactants (CTAB and Triton X-100) in water and NaBr aqueous solutions. Microelectrodes have a unique ability to measure mass-transport steady-state currents in the presence or absence of supporting electrolytes [1]. This makes them particularly suitable for studying the dependence of the micellar diffusion coefficient on solution composition. Studies were carried out by using ferrocene as hydrophobic probe, provided that this electroactive specie does not perturb the micelle, its rates of entrance/exit into the aggregate are, at least, comparable to those of surfactant monomers and the electron transfer involved is fast and reversible. The dependence of D on surfactant concentration was employed to extract the diffusion coefficient at the critical micellar concentration, i. e. where the interaction between micelles is negligible [2]. Data were obtained at several NaBr concentrations to investigate the influence of electrolyte concentration on the properties of micelles (dimension and/or morphology of the aggregate). Diffusion coefficient data were calculated by using the steady-state current obtained in voltammetric experiments as described elsewhere [3]

Figure 1 shows that the behaviour of charged and uncharged surfactant aggregates in solution is quite different. The diffusion of charged micelles (CTAB) is strongly affected by the electrolyte concentration because of the atennuation of repulsion among the surfactant head-groups and the increase of aggregation number caused by the reduction of micellar double layer. On the other hand, the influence of electrolyte concentration on neutral aggregates (Triton X-100) is less pronounced, showing that electrostatic repulsion among charged micelles plays an important role on intermicellar interactions.
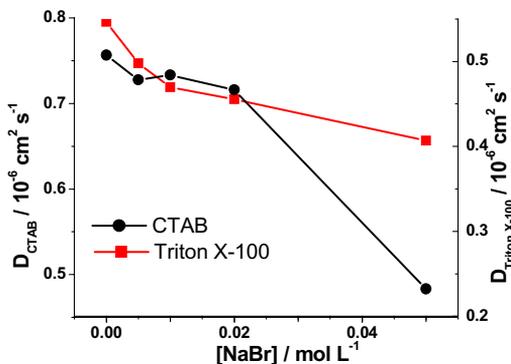
Figure 1 – Dependence of the diffusion coefficients of CTAB and Triton X-100 on the concentration of NaBr. D values were measured in solutions containing 0.15 mol L^{-1} surfactant and 0.0015 mol L^{-1} ferrocene.

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Corrosion mechanism of a non-chromate conversion coating for magnesium alloys and magnesium-based metal matrix composites in nacl at different ph using eis.

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The use of magnesium alloys in applications requiring a combination of high strength, stiffness and lightweight has been applied in the automotive and transport industry nowadays. Despite of all of these achievements, one of the main problem that limits the use of magnesium and its alloys in many structural applications, is the poor corrosion resistance of these materials, especially in comparison with aluminium and its alloys.

In order to overcome this problem, surface treatments, such as chemical and electrochemical anodising, surface sealing, painting and electroplating have been routinely used. [1, 2, 3]

In the present work, Electrochemical Impedance Spectroscopy (EIS) was used to evaluate and characterize the corrosion mechanism of a non-chromate conversion coating used to protect Mg^{comm}, ZC71 Mg alloy, WE43 Mg alloy and a $12\%SiC_p/ZC71$ Mg alloy MMC. Evaluation of the coating was carried out by immersion of coated specimens in a 3.5 wt. % NaCl solution at room temperature and three pH values, namely 3.5, 7 and 12.

Key Words: Mg_{comm}, ZC71, WE43, $12\%SiC_p/ZC71$ Magnesium alloys MMC.

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Palladium as electrocatalyst for PEM applications

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Today Pt is widely used as an electrocatalyst for proton exchange membrane (PEM) fuel cells and water electrolysers. But because of elevated price and limited resources, Pt cannot be used for large-scale applications and alternative materials are needed. The goal of present study is development and investigation of nano-structured Pd-based electrocatalysts for hydrogen reduction and evolution in PEM systems.

Various Pd-based electrocatalysts (Pd, Pd-Pt, Pd-Pt-Ru and so on) including supported by different carbon carriers have been synthesized and characterized using physical and electrochemical techniques. Electro-active metallic structures were obtained by chemical reduction of precursor salts using ethylene glycol with addition of formaldehyde and polyvinylpyrrolidone (synthesis on carbon carrier) or using sodium borohydride (for metal black synthesis). Vulcan XC-72, acetylene carbon black, Sibunit, carbon nano-tubes and nano-fibers and other carbons have been used as catalyst carriers. Alternatively, Pd nano-clusters have been obtained from chemical reduction of precursor salts in perfluorinated polymer materials such as Nafion membrane materials. The electrocatalytic activity of these catalysts with regard to hydrogen reduction and evolution has been investigated for PEM applications. In particular, Pd catalysts (40% wt) on Vulcan XC-72 have specific electrochemical active surface > 33 $m^2 g^{-1}$, particle size 14.9 ± 2.1 nm. PEM fuel cell with this catalyst on the anode has shown a current density of ca. 0.7 A cm^{-2} at a voltage of 0.7 V. The typical voltage of PEM electrolysis cell with Pd-based catalyst on the cathode is ca. 1.65 V at a current density of 1 A cm^{-2}. One can see from comparison of obtained results, in general, the performances of PEM systems with Pd electrocatalysts (including on the carbon carrier) on hydrogen electrode is comparable to that with the Pt-based electrocatalysts. Thus, Pd could be potentially used as an electrocatalyst for PEM systems.

Beneficiation of industrial solid waste composed of zinc oxide by electroremediation

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Industrial activity generates large amounts of solid waste containing heavy metals. This work deals with zinc beneficiation of industrial solid waste by an electrochemical process: the electroremediation. This technique is based on application of an electric field to the solid waste to be treated. Protons generated at the anode by water oxidation, migrate towards the cathode: they react with metal oxides or salts contained in the solid placed between the electrodes. Metal ions are formed and migrate to the cathode where they form a deposit.

A laboratory cell was built for testing the method. It consisted of three compartments, two electrode compartments and a solid waste chamber placed between these. Catholyte and anolyte – sulphuric acid solutions - were separated from the waste by a polypropylene cloth. Experiments were carried out using a synthetic waste prepared by dispersing zinc oxide at 10% in silicon dioxide. Preliminary tests of the cell yielded encouraging results with 90% leaching conversion within eight hours at 4.5 A dm^{-2}. The initial H$^+$ concentration was at 0.1M at the anode side and 1M at the cathode: the occurrence of electrode reactions tended to increase the concentration at the anode, and to decrease the acid content in the cathode chamber, because of the side hydrogen evolution at the cathode. Zn species extracted from the solid was recovered only to 40% in form of metal, the rest accumulated in the cathode chamber and the central compartment.

The preliminary results showed the significant coupling between electrode processes, leaching chemical equilibrium and transport processes of H$^+$ and Zn^{2+} by migration. Additional work has been done for better understanding of the process, in view to optimal design of experiments and cells. First, zinc electrodeposition has been investigated in a Hull cell. The influence of the proton/zinc ratio on the deposit morphology and the current efficiency have been studied: whatever the Zn^{2+} concentration, H$^+$ concentration has to be kept in the range 0.25 – 0.5M for the sake of high current yields. Besides, the cell design has been improved with forced convection of the liquid in the cathode chamber, and gas sparging in the particle bed, for more regular dissolution of zinc oxide, and enhanced diffusion-convection of dissolved zinc to the cathode compartment. Finally the transport of Zn^{2+} ions from the central compartment by migration appeared to be rate-controlling in most cases: the competition of H$^+$/Zn^{2+} transport in the cell depending on their relative concentrations is thoroughly discussed.

Electroremediation designed and carried out using the methods developed, will be applied to metal ores of industrial significance.

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Electrochemical Engineering & Technology

Electrochemical Reduction Characteristics of m-Nitrobenzene Sulfonic Sodium at Cu Electrode

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Nitroaromatic compounds are an extremely important class of compounds, which are widely used in the pharmacal and chemical industries. The electrochemical behavior of the nitroaromatic compounds has been intensively investigated in different media. Due to the poor solubility of nitroaromatic compounds in the aqeuous solution, the electrochemical reduction of nitroaromatic compounds are usually controlled by the diffusion of the reactant. In order to eliminate the effects of diffusion process on elucidation of electrochemical reduction characteristics of nitrobenzene, a sulfonic group which is a good leaving group was introduced into the benzene ring to improve the solubility of nitrobenzene in the aqueous solution. In this paper, the electrochemical reduction behavior of m-nitrobenzene sulfonic sodium (m-NO$_2$C$_6$H$_6$SO$_3$Na) at Cu electrode was reported .
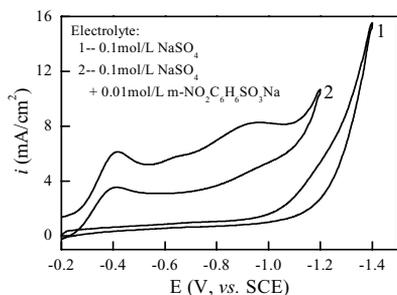
Fig.1 Cyclic voltammograms of m-NO$_2$C$_6$H$_6$SO$_3$Na at Cu electrode. Scan rate : 20 mV/s.
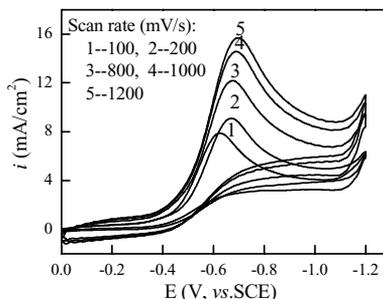
Fig.2 Cyclic voltammograms of m-NO$_2$C$_6$H$_6$SO$_3$Na at Cu electrode at various scan rate

Figure1 shows the cyclic voltammograms of m-NO$_2$C$_6$H$_6$SO$_3$Na at Cu electrode. At curve 2, the reduction peak at –0.4 V can be ascribed to the reduction of nitro group, while the reduction peaks at more negative potential are identical to the reduction of benzene sulfonic acid. Hence, these peaks can be ascribed to the reducion of sulfonic group. Figure 2 depicts the cyclic voltammograms of m-NO$_2$C$_6$H$_6$SO$_3$Na at Cu electrode at various scan rate. It can be seen from figure 2 that the peak potential shifts negatively with the increasing of scan rate. This indicates that the reduction of nitro group at Cu electrode is an irreversible process. Moreover, the peak current increases linearly with the increasing of scan rate. This illuminates that the electrochemical reduction of nitro group of m-NO$_2$C$_6$H$_6$SO$_3$Na is controlled by the adsorption process. The preliminary results show that the introduction of an good leaving group into benzene ring to improve the solubility of nitrobenzene may be one of the feasible ways to enhance the mass transfer process during the electrolytic preparation of p-aminophenol from nitrobenzene.

Electrodeposition of ZnTe Compound Semiconductor in Propylene Carbonate Bath

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Compound semiconductors are used for solar cell material because of their high optical absorption coefficient and high conversion efficiency. Dry processes were widely used for produce the compound semiconductor. But some compound semiconductors such as CdTe, ZnTe, ZnSe and so on, can be formed by wet processes. In this study, we have investigated the electrodeposition of ZnTe compound semiconductor in propylene carbonate bath. In case of the ZnTe electrodeposition in organic solvents such as methanol, propylene carbonate, acetonitrile and so on, we have obtained the results that it formed by the normal co-deposition of Te and Zn in methanol solvent, and by UPD of Zn in acetonitrile solvent and propylene carbonate solvent, which is similar mechanisms to that in the aqueous solution. A good ZnTe films were obtained in the propylene carbonate solvent among them. We have investigated the more suitable electrolytic conditions for ZnTe electrodeposition and studied the effect of Cu co-deposition as a dopant in ZnTe films.

The electrolytic solutions contained $TeCl_4$ (0.2 - 2 mM), $ZnCl_2$ (2 - 20 mM), and $NaClO_4$ (100 mM) as a supporting electrolyte. The working electrode was an Au electrode (1 cm^2), a Pt foil was used as the counter electrode and an Ag/AgCl electrode immersed in saturated NaCl solution as the reference electrode. The potentiostatic electrodeposition of ZnTe was carried out for 1 C in electricity at 423 K.

A single-phase ZnTe film close to the ideal stoichiometric composition of ZnTe was obtained at -0.4 ~ -0.6 V vs. Ag/AgCl in the solution with a molar ratio of Zn(II)/Te(IV) = 10 and a low Te(IV) concentration. This ZnTe film had a smooth and dense granular crystal morphology and an n-type property. Current efficiency was about 85 %. As for the other potentials and molar ratio in this study, Te was also deposited with ZnTe.

The ZnTe film, which was electrodeposited at –0.4 V in 0.2 mM $TeCl_4$, 2 mM $ZnCl_2$ and 0.001 mM $CuCl_2$ solution, had a more smooth and dense granular crystal morphology than that in the bath without $CuCl_2$. Cu was co-deposited in ZnTe films obtained in the bath containing more than 0.05 mM $CuCl_2$ and this Cu could not play any role as a dopant. The current efficiency was similar to that without Cu, but the deposition time for 1 C was reduced. This Cu-doped ZnTe film had a resistivity of 1.5×10^4 Ωcm and a carrier concentration of 1.5×10^{15} n/cm^{-3}.

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Electrochemical Engineering & Technology

Surface Modification of Polyimide Using UV for the Metallization

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In recent years, for portable terminals, particularly, downsized electronic devices have been requested with various functions and in various configurations. Therefore, flexible printed circuit boards (FPC) have been used for these electronic devices. FPCs are composed of a conductive layer on an insulating material. Generally, FPCs are made of polyimide (PI), because PI has excellent heat resistance, flexibility, and size stability.

There are three conventional methods used to form the conductive layer on PI films: lamination, casting or spattering. However, these methods all have problems, in that the surface of the insulating resin has to be roughened to achieve adhesion between the PI and metal. In this paper we report that good adhesion strength, without roughening of the PI surface, can be obtained by ultraviolet light irradiation, and electroless plating. Following the irradiation of the PI surface with UV, a conductive diffusion barrier layer was made by electroless nickel plating, followed by electro copper plating. In this way, even while retaining a smooth PI surface, adhesion strength of over 1.0 kN/m was achieved without etching between the conductive layer and PI substrate. Moreover, patterns on the PI were generated by irradiation through a photo mask, and then the PI film was immersed in a high pH (12) solution containing an anionic surfactant and followed by the electrolss nickel plating. The fine patterns as shown in Fig. 1 can be generated by this surface modification process .
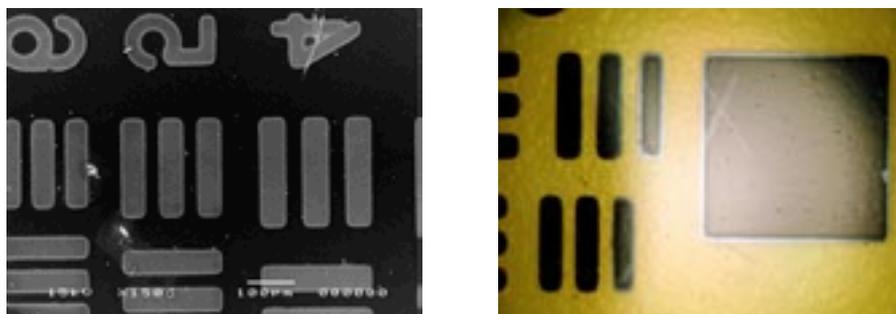

Fig.1 Example of the fine patterns using surface modification process

Electrochemical Disinfection Cells for Use of Drinking Water and Endoscope Using Carbon Fiber Electrodes

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The electrochemical disinfection brings less secondary pollution than the ordinary disinfection using toxic agents. High efficiency electrochemical disinfection cell using palladium coated carbon cloth electrodes was reported previously*. The cell consisted of two electrode system where the electrolytic solution passed through the gappy electrodes that were aligned in pallarel. The disinfection was carried out on two microorganism, *E. coli* and *B. subtilis* and the efficiency was almost complete only by one passage of the electrolytic solution containing a small amount of NaCl. In this study, the palladium coated carbon cloth electrodes was applied to the disinfection of endoscope.

Experimental

A rubber rod on which *E. coli* was fixed was surrounded by a palladium coated carbon cloth electrode. It was then surrounded by a low resistance porous membrane sheet and separated from the outside. The electrolysis was carried out in the electrolyte solution containing 0.9 % NaCl using the palladium coated carbon cloth electrode and ferrite counter electrodes that were set outside the porous membrane. Another rubber rod daubed by lard was prepared to examine the ability to peel off fatty compounds.

Results and Discussion

Figure 1(a) shows the viability of *E. coli* vs. current in the ordinary palladium coated carbon cloth electrode cell for the disinfection of tap water in the solution contaning 0.9 % NaCl. In the anode compartment, the disinfection was complete at 5 mA current suggesting the effect of ClO$^-$ generated at the anode. Figure 1(b) shows the viability of *E. coli* that was fixed on a rubber rod in the disinfection cell for endoscope. It was found that the disinfection was complete at currrents higher than 500 mA.
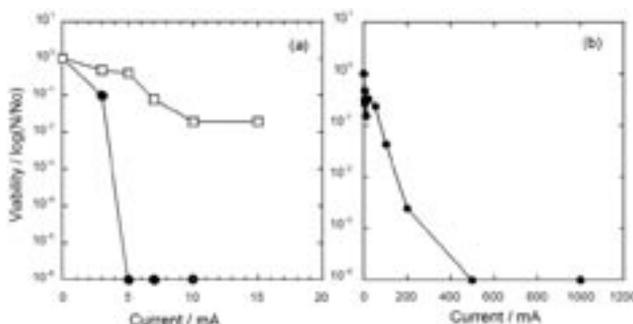
* H. Sadamura, et. al., *Electrochemistry*, **68**, 321 (2000).

Figure 1: (a) Viability *vs.* current curve at palladium coated carbon cloth electrodes in solution containing 0.9 % NaCl. Separator area was 4 cm x 10 cm. Closed circles: in anode compartment, open squares: in cathode compartment. (b) Viability *vs.* current curve in the cell for endoscope disinfection. Viability of 10^{-6} (a) and 10^{-4} (b) mean zero viablity.

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Polypyrrole-supported Graphite Felt for C-C Bond Formation Reactions in Solid Phase Synthesis

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The solid phase synthesis has attracted much interest in organic synthesis, because it can improve the reaction yield by using an excessive reagent and the used reagent can easily be removed by washing. Here we report the first efficient, C-C bond formation reactions in solid phase chemistry with a graphite felt (GF) electrode as a solid support. The preparation of substrate-modified GF electrodes for C-C bond formation reactions in the presence of Pd catalyst is shown in Scheme 1. The substrate precursors containing a pyrrole side chain were synthesized from 3-(pyrrol-1-yl)propionic acid and 4-iodobenzyl alcohol. This pyrrole-based monomer was modified on a GF electrode by electrochemical polymerization at repeated cyclic voltammetric scans between 0 and +1.5 V vs. Ag/AgCl. The amount of substrate on the GF electrode surface was determined by the amount of recovered 4-iodobenzyl alcohol that was yielded by the treatment of iodobenzene-modified GF electrode with $NaOCH_3$. The amount of substrate on the GF electrode surface increased with the increasing number of repeated cyclic voltammetric scannings. The loading of substrate on the GF electrode of 20-times scanning was ca. 80 $\mu mol\ g^{-1}$. Preparative Sonogashira reaction was performed on the iodobenzene-modified GF electrode (3.0 x 1.0 x 0.5 cm) in DMF (10 ml) containing Et_3N (10 mmol), terminal acetylene (5 mmol), $Pd(PPh_3)_4$ (0.25 mmol) and CuI (0.5 mmol) (Scheme 1). The coupling products yield was 72-94% when the substrate-modified GF electrode of 5-times scanning (loading 15 $\mu mol\ g^{-1}$) was used. In addition, the homogeneous Sonogashira reaction was carried out with lower yield (30%) than the solid phase system using the substrate-modified GF electrode. We also tried under standard polymerization and reaction conditions on a Pt plate electrode instead of a GF electrode, however, the generated polymer film was not strongly attached to the Pt electrode surface and solid phase synthesis could not be used. The coupling product yield decreased with the increasing immobilized substrate on the GF electrode surface. This observation suggests that a thick polymer film was formed on the GF electrode surface with the increasing repeated cyclic voltammetric scanning and did not infiltrate the terminal acetylene and catalyst into a polymer layer.
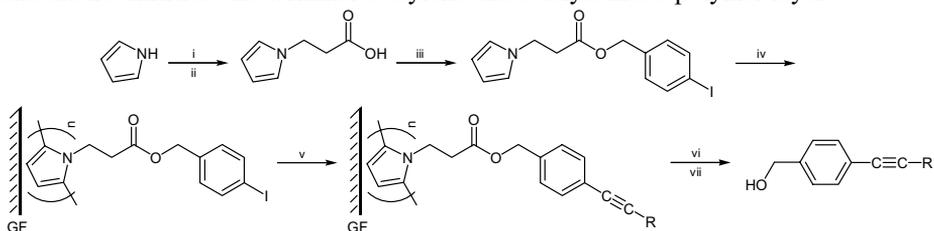
Scheme 1 *Reagent and conditions*: i, acrylonitrile (1.0 equiv.), *n*-Bu$_4$NOH (0.1 equiv.), -78°C; ii, KOH, H$_2$O, Δ; iii, 4-iodobenzyl alcohol (1.0 equiv.), 4-dimethylaminopyridine (5 mol%), DCC (1.5 equiv.), CH$_2$Cl$_2$, 0 °C; iv, electrochemical polymerization; v, terminal acetylene (5 mmol), Et$_3$N (10 mmol), Pd(PPh$_3$)$_4$ (0.1 mmol), CuI (0.2 mmol), DMF; vi, THF, NaOCH$_3$; vii, HCl.

Development of the Cu-Sn alloy plating as an alternative to Ni plating

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A nickel plating has been widely applied in industry due to its high hardness and excellent corrosion resistance. However, allergic dermatitis occurs on a human body caused by physical contact with a decorative Ni plating, which is the important subject to be overcome for plating industry. Thus, the development of nickel-free decorative plating is greatly demanded. The speculum alloy (Cu-Sn alloy with the Sn content of around 40wt%) plating is proposed as an alternative to bright Ni plating.

Although the speculum alloy plating bath containing cyanide as a complexing agent has been already put to practical use, a cyanide-based bath is not recommended because of its toxicity. Kume and Oki revealed that Cu was codeposited with Sn in a weak alkaline bath containing sodium tripolyphosphate as a complexing agent[1]. The tripolyphosphate-based bath is further improved by considering the following points, (i) to build up with benign agents to environment and workers: all components are food additives (except metal salts), (ii) to obtain the speculum alloy plating in a wide range of current density. Furthermore, we tried to refine the crystal grain to a nanometer level by adding an organic compound in order to obtain a film with luster, higher strength and excellent corrosion resistance.

The color and the Sn content of the deposit from a tripolyphosphate-based bath depend on a current density. When the current density was lower than $0.8 A/dm^2$, the deposit showed a golden yellow color and its Sn content was about 20 wt%. When the current density was higher than $0.8 A/dm^2$, the Sn content increased rapidly up to about 37 wt.% and the deposit showed bright and silvery white color. The Sn content was approximately constant in the current density range of 0.8-$2.0 A/dm^2$. Thus, we succeeded in producing the speculum alloy plating using our bath under the wide current density range.

XRD studies showed the speculum alloy plating consisted of a single-phase of NiAs-type crystal structure same as η phase (Cu_6Sn_5) in the phase diagram. The Vickers hardness of the speculum alloy plating was 450 - 500HV, which was comparable to bright Ni plating. According to surface observation by SEM, the average crystal grain size was about 40nm. The high hardness was attributed to grain refinement.

The corrosion resistance was evaluated by soaking in an artificial sweat solution for five days. Neither tarnish nor corrosion was observed with the speculum alloy plating, whereas bright Ni plating obviously tarnished and corroded. Therefore, the speculum plating prepared using the modified tripolyphosphate-based bath was concluded to be equivalent or even better in the properties as compared with Ni plating.

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Electrochemical characterisation of nickel cobalt electrolytes for pulse reverse plating

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Nickel-based alloys such as Ni-Co are used in a wide variety of applications for aerospace, energy generation, corrosion protection, but also magnetic materials and as electro-catalysts in hydrometallurgy, and are considered as hard chromium replacement. Their electrodeposition [1] and pulse reverse plating [2] from aqueous media has been demonstrated recently. In hard chromium replacement the corrosion protective properties of deposited Ni-Co layers are of great importance. Fundamental electrochemical properties of electrolyte systems are the prerequisite for the development of a successful pulse deposition process. Three different electrolyte systems for the galvanic deposition of nickel cobalt alloys (chloride, Watts and sulfamate type) have been investigated in order to unravel underlying deposition mechanisms and rate determining factors [3]. The influence of the deposited micro structure, varying with the pulse plating conditions, on the corrosion stability of the alloy layers are investigated using impedance spectroscopy.

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Electrorefining of Silver in Mixed Electrolytes of Nitric Acid Solution and Acetonitrile

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Electrorefining of silver from the silver source with high copper content was investigated in mixed electrolytes of nitric acid solution and acetonitrile. Large deposition potential difference between silver and impurity metal is required for an effective electrorefining. Electrodeposition potentials of silver and copper were controlled by mixing nitric acid solution with acetonitrile, which has a donor number and a dielectric constant smaller than those of water. Electrodeposition potential difference between silver and copper was 455 mV at room temperature in 0.5 $molL^{-1}$ nitric acid solutions with 0.1 $molL^{-1}$ metal content. Both deposition potentials moved toward negative direction and the potential difference was increased to 671mV in a mixed electrolyte of 1 $molL^{-1}$ nitric acid solution and acetonitrile in a same volume ratio. Raising the temperature of the mixed electrolyte shifted the deposition potential of copper distinctively toward positive direction and reduced the potential difference. For producing 4N silver, the effects of mixing ratio, temperature, and current density were examined to optimise the electrorefining process using factorial design.

Recycle of waste etching acids from semiconductor manufacturing process

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The mixture consisting of nitric acid, Hydrofluoric acid and acetic acid are conventionally used as etchant to dissolve the Si in manufacturing process of silicon wafer and semiconductor devices. The amount of discharged waste acid from one factory is estimated to be about 32,000 tons per year. Conventional neutralization method for the waste acid treatment has many problems such as the high cost of neutralization and inevitable residual of sludge. From an environmental viewpoint, it is important to develop technology for the separation and purification of each acid from the waste acid mixture. In this regard, we attempt to separate the mixed waste acids by using solvent extraction method. A separation process for acid in a waste acid mixture was established by using solvent extraction and the extraction mechanism for nitric, hydrofluoric and acetic acids was investigated. By analyzing the extraction, scrubbing and stripping isotherms in terms of the McCabe-Thiele method, a separation process was proposed for acetic acid recovery from the waste acid mixture. Also, this work involves use of recovered acetic acid as a pickling acid solution of stainless steel. The corrosion characteristics of stainless steel have been investigated in stainless pickling acid originating from recovered acetic acid

Influence of under layer on proerties of electroless deposited gold

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Gold plating is necessary to produce a good wire bonding connection between the PCB and IC. In general, a gold plating thickness of more than 0.2 μm is required. The gold displacement reaction progresses by dissolving the under layer of nickel. Therefore, when serious dissolution of the nickel is proceeded on the under layer of deposited nickel, solder joint strength and wire bonding strength would be decreased. Accordingly, to avoid the dissolution of the nickel, palladium is plated as an interlayer between the nickel and the gold[1]. Figure 1 shows the effect of nickel plating bath pH on wire bonding strength : under as-plated and after 1 hour heat treatment of 200°C. In the case of pH6.0, wire bonding strength deteriorates significantly after heat treatment. Figure 2 shows typical cross-sectional SEM images of both nickel films. The film plated from a 4.5 pH bath shows no clear grain, on the other hand that of pH 6.0 shows quite different structure: a columnar structure. Therefore, the structure of the under layer nickel film greatly affects on the wire bonding strength. It is concluded that control of the structure of the under layer nickel is necessary for high reliability of the connection.
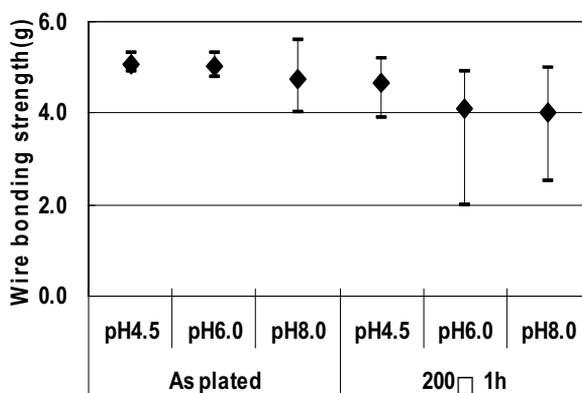

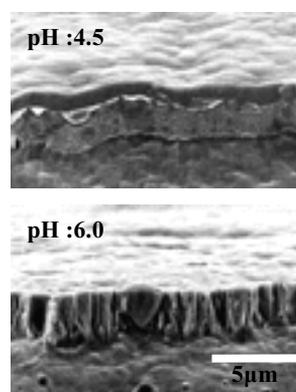Fig.1 Effect of under layer Ni film on the wire bonding strength.

Fig.2 Cross-sectional SEM images of Ni film on copper.

Reference
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Electrochemical Engineering & Technology

Electrochemical oxidation of nitrile herbicide bromoxynil in aqueous methanol media

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Bromoxynil (3,5-dibromo-4-hydroxy-benzonitrile) is a halogenated aromatic nitrile herbicide widely used for post-emergent control of annual broadleaf weeds. Oxidation, together with biodegradation, is one of the main ways of bromoxynil decomposition in the environment. Thus, study of oxidative pathway and intermediate products can give valuable information about fate of bromoxynil in the environment.

The partial oxidation of bromoxynil was studied at potentials between 2.2V and 2.8V by constant potential electrolysis on the Pt net electrode (1 cm^2) in aqueous methanol media (55% vol. of MeOH). As a supporting electrolyte, sodium sulfate (0.04M) was used. Electrolysis were carried out in a two-compartment glass electrochemical cell with an anodic compartment volume of 30 mL. The reference electrode was Ag/AgCl, while the counter electrode was a Pt foil (0.5 cm^2). The compartments were separated by the cation exchange membrane. Concentration of bromoxynil and products of its oxidation was measured by GC-MS.

At potentials less than 2.2V the rate of disappearance of bromoxynil was slow, with no significant quantities of products detected in the reaction mixture. Between 2.2 and 2.6V the rate of disappearance accelerated, reached maximum at 2.6V, and remain constant till the largest possible working potential of 2.8V. The higher potentials were prevented by the sharp increase of oxygen evolution. Rate of disappearance was described by the pseudo-first order rate equation $-d[bromoxynil]/dt = k_{app}[bromoxynil]$, with maximum reached $k_{app} = 0.58$ h^{-1}. It corresponds to 90% of destruction for 4 h treatment at 2.6V. Eleven individual products of partial oxidation were identified by the GC-MS. Three main products were 3,5-dibromohydroquinone, 2-methoxy-4-hydroxy-3,5-dibromobenzonitrile and 2,4-dihydroxy-3,5-dibromobenzo-nitrile. Five products with smaller concentrations were identified as futher methoxylated and /or hydroxylated di-bromobenzonitriles and mono-bromobenzonitriles. The oxidation routes based on the products identification can be described through existence of two concurrent two-electron reactions – hydroxylation and methoxylation, which give a variety of hydroxylated and methoxylated products. Three other identified substances found in significant quantities were products of aromatic ring cleavage; dibromoacetonitrile, 1,1-dibromo-3-nitrile-propene-2 and methyl ester of dibromoacetic acid. Existence of those products can be explained through radical benzene ring cleavage, with consequent oxidation of initial dibromoacetonitrile into dibromoacetic acid and esterification of the acid with MeOH.   No totally debrominated substances were found in the reaction mixture. However, from the quantitative analysis, we accounted for about 40% of the products. Unaccounted for were volatile products, such as bromoform and tetrabromocarbon (for which only traces were found in the reaction mixture), and possibly other light products. We also can not exclude totally the probability of oxidative coupling reactions, commonly seen at oxidation of halogenated aromatic compounds.

Treatment of oil suspensions by electrocoagulation

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Oil suspensions usually consist of complex dispersions hydrocarbon chains in aqueous solutions with surface active agents and other partially soluble compounds. Used suspensions issued by mechanical workshops can be efficiently treated by electrocoagulation under the action of dissolved Al(III) species. The present investigation was carried aimed at highlighting the effect of the oil suspensions and the pH conditions on the treatment efficiency, in terms of maximal abatement, the amount of Al species required, and variation of COD with the Al(III) concentration.

Three oils were considered here. Tests were carried out using a flat electrode cell inserted in a flow rig provided with a pump and a reservoir. The area of the each electrode was 50cm^2 and 1 litre suspension was treated in the batch runs.

The pH of the dispersions introduced in the cell was either at its natural level, i.e. near 9.0, or adjusted at 7 before the run. The pH slightly increased during the run because of the electrolytic formation of hydroxide ions. Treatment of one of the oil was easier at pH 9, whereas the two others were more rapidly treated at pH 7. In particular, Metacoup ® oil was observed to separate from the suspension upon dissolution of very low Al amounts.

The relationship between the oil nature and composition with the treatment – linked to the oil stability - is now under investigation. It seems that two suspensions studied are of moderate stability in comparison to the third one which could be a positive point with concern its treatment by the electrolytic technique.

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Electrotransport of sulfuric acid through AMV anion exchange membrane

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AMV anion exchange membranes were frequently used in electrodialysis to separate and recover acids, in treatment of metals or battery applications. Surprisingly few fundamental studies were devoted to the study of the AMV membrane. It is known that sulfuric acid is utilized in many industrial processes and in particular in plating procedures.

This work focussed on the transport phenomenon of sulfuric acid through AMV membrane used in electrodialysis for the plating water treatment. The transport phenomenon consists in the concentration polarization when the current density changes with time (current-voltage characteristic) and in the transport process of sulfuric acid through the membrane at a given current density (chronopotentiometry). The concentration polarization was characterized by the value of the limiting current density. The relation between external acid concentration and acid concentration in the membrane solution was expressed by means of the equilibrium partition constant K (in this work, K = 2.91). The linear change of the limiting current density as a function of external acid concentration is due to the change of the external solution conductivity. In fact, our impedance spectroscopy results pointed out the influence of external acid concentrations on the membrane conductivity. Like the equilibrium partition study, the membrane conductivity study also allowed confirming the heterogeneity theory (two phase model) given by Zabolotsky and Nikonenko. The interstitial phase fraction of 15,2 % determined from the two phase model is reasonable in comparison with the influence of H_2SO_4 concentration on the water swelling of AMV membrane which changes from 14 % to 15.5 % in sulfuric acid concentration range from 0.0 M to 0.5 M. However it seems to be in conflict with the value of conducting fraction (97.8%) determined from chronopotentometric data using the Sand equation. This contradiction has been discussed and explained by the heterogeneity of the membrane surface and the validity of the assumption of a total dissociation of sulfuric acid in the bulk solution.

The Effects of Polyethylene glycols on the Trivalent Chromium Electrodeposition

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The effects of polyethylene glycol (PEG) molecules added in the solution on the reduction process of trivalent chromium ion were investigated by using potentiodynamic polarization, electrochemical impedance spectroscopy, scanning electron microscopy and x-ray photospectroscopy. It was observed from the potentiodynamic polarization that PEG molecules reduced the hydrogen evolution reactions by shifting onset potential of reduction of proton ions in the low overpotential region. From the open circuit measurements, PEG molecules were supposed to be adsorbed at the surface of cathode in the stationary solution at least for 30 minutes. Microscopic measurements showed that PEG molecules modified the deposits structure of trivalent chromium layers probably with the occurrence of additional overpotential of *ca.* 400 mV for the reduction of trivalent chromium ions. XPS data confirmed that the electrochemical deposition process of trivalent chromium was dependent upon the molecular weight of PEG molecules and so the most inclusion contents of carbon were detected in the presence of PEG of molecular weight of 1,500 in the solution (Fig. 1) .
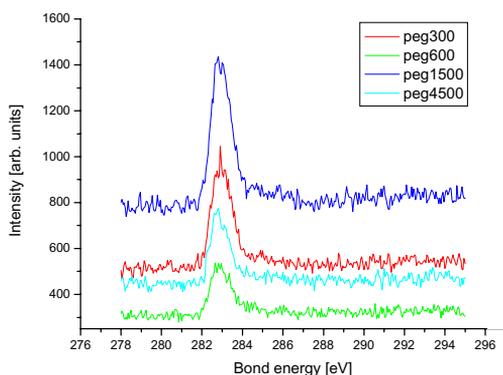

Fig. 1. XPS data of the trivalent chromium layers after etching the surface about 400 nm

Effect of Pulsed Electrodeposition on Soft Magnetic Properties of CoFe Film

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The $Co_{35}Fe_{65}$ binary alloy is known as a material with high saturation magnetic flux density (B_s), which shows a value of about 2.4 T close to the maximum value achievable with ferromagnetic alloys. The $Co_{35}Fe_{65}$ alloy films are promising candidates for a core material of magnetic recording head for realizing ultrahigh-density magnetic recording. We have succeeded in preparing the electrodeposited B_s = 2.4 T $Co_{35}Fe_{65}$ alloy films by use of the bath containing the additive known as reducing agent (trimethylamineborane: TMAB) and the Dual-cell system separated into anode bath and cathode bath [1,2]. Both were effective techniques to prevent the oxidation of ferrous ion to ferric ion in the plating bath. However, the coercivity (H_c) of the films showed too high value to be applied for a core material of magnetic recording head. Furthermore, by annealing for 1 h at an annealing temperature of 400 ºC in vacuum with an external magnetic field, low value of H_c less than 10 Oe were obtained. However, the annealing temperature of 400 ºC was so high that it would damage other write-head components.

In order to decrease H_c of as-deposited film, a pulsed reversed electrodeposition, which is well known as feasible method for obtaining nano-crystallized film, was applied. The effects of operating conditions on the magnetic properties and microstructure of CoFe films were investigated.

The duty cycle defined as t_{on} / (t_{on} + t_{off}), where t_{on} is the cathodic current pulse on period and t_{off} is the relaxation time or anodic current pulse on period, was effective for decreasing H_c value. The H_c value of CoFe films decreased with increase in the pulse reverse current density (i_{pr}), and with i_{pr} = 20 mA cm^{-2}, the H_c value in easy-axis direction (H_{ce}) and that in hard-axis direction (H_{ch}) of the film were approximately 1 Oe (B_s = 2 T). On the other hand, the H_c value of the film which has the same composition prepared by the direct current method was 15 Oe. Additionally, the CoFe film prepared by the pulse reveresed method showed low film stress and smooth deposit surface.

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Influence of the chemical structure of dyes on the redox potential and rate of electrodegradation

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Azo and anthraquinone sulphonate dyes are the two largest groups of synthetic colorants, being responsible for the majority of the coloured effluents in paper and textile industries. Although the biological degradation is the most economic process for organic pollutants, it is not a viable solution for all kind of dyes. In the cases were biological technologies fail, a tertiary treatment has to be performed and electrodegradation has been receiving great attention in the last years.

One of the problems associated with electrochemical degradation of recalcitrant pollutants is the energy cost and, in order to minimize its effect, is very important to understand the electrooxidation process and be capable of predicting the best experimental conditions to perform the degradation.

The aim of this work was to obtain data from cyclic voltammetry (CV) and electrodegradation assays (EA), performed in potentiostatic and galvanostatic conditions, that can be correlated with the chemical structure of the dye molecule and used to predict the best experimental conditions to perform the conversion/combustion of the dyes by electrochemical techniques.

The electrochemical experiments (CV and EA) were conducted using as anode a boron doped diamond electrode, obtained from CSEM (now Adamant Technologies). Six different dyes were tested, 3 belonging to anthraquinone class (sodium anthraquinone-2-sulphonate, sodium anthraquinone-1,5-disulphonate and C.I. Acid Green 25) and 3 from azo type (C.I. Acid Orange 7, C.I. Direct Red 254 and C.I. Brilliant Black BN, respectively, monoazo monosulphonate, diazo disulphonate and diazo tetrasulphonate). Results were followed by UV-Visible spectrophotometry and Chemical Oxygen Demand.

For the studied dyes, the following conclusions can be pointed out: the potential of the oxidation peaks associated to decolourisation increases with the complexity of the chemical structure of the anthraquinone dyes and with the number of azo bonds for the azo dyes; anthraquinone dyes have higher rate of electrodegradation, in diffusion controlled experiments, which increases with the number of sulphonate groups and decreases with the number of aromatic rings in the structure; for the azo dyes, an increase in the number of azo bonds or benzenic rings doesn't have a critical effect on the rate of degradation performed in diffusion controlled assays, but an increase in naphthalenic groups strongly decreases the rate of oxidation.

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A green electro-synthesis of 3,6-dichloropicolinic Acid

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3,6-dichloropicolinic acid(3,6-DCP) as a highly active plant growth regulator was mainly prepared by the reduction of 3,4,5,6-tetrachloropicolinic acid(3,4,5,6-TCP) with hydrazine[1], which was unfriendly to the environment. In this work, 3,6-DCP was prepared by selective electro-dechlorination of 3,4,5,6-TCP on silver electrode.

The silver electrode was treated by the ORC process and its surface morphology of the silver electrodes was characterized by Atomic Force Microscopy (AFM-SII4000) [2-4]. The roughness of the electrode surface were measured by chronoamperometry and shown in table 1. It could be seen that the roughness of the roughened electrodes (b and c) was about 21 times as that of the original silver electrode (a).

Table1 The roughness of the three silver electrodes

The silver electrode	original electrode (a)	1st ORC electrode (b)	2nd ORC electrode (c)
$R(e)(cm^2/cm^2)$	10.7	201.8	222.7

The cyclic voltammogram curves of 3,4,5,6-TCP showed that the dechlorination reaction was irreversible. The conversion of 3,4,5,6-TCP and the current efficiency of dechlorination were studied on different silver electrodes (a, b and c), and the results showed that the roughened silver electrode (b,c) had much greater electrocatalytic activity than that of the original electrode (a).

The change of the concentration of the various dechlorinated products and the substrate were detected as the reaction carrying out. And the possible pathways of the electro-reduction of 3,4,5,6-TCP in basic aqueous solution was Proposed.

The pilot plant scale experimental results further confirmed it is a promising method to prepare 3,6-DCP through electrocatalytic dechlorination.

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The electrochemical reduction of nitrobenzenes at Pt Micro-disk Electrode in aprotic media

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The reduction properties of the aromatic nitrocompounds are of prime importance, and their reduction products are of great applied value[1]. In this paper, the electrochemical reduction of nitrobenzenes in aprotic media was studied.

The experiments were performed on CHI660 electrochemical system. Nitrobenzene and *o, m, p*-nitrotoluene (0.01 M) were dissolved in dimethylformamide (DMF) containing 0.1 M tetrabutylperchlorateamine (TBPA). All chemicals used were of analytical reagents grade.

Fig.1 shows the cyclic voltammograms for the reduction of nitrobenzene (a) and *o, m, p*-nitrotoluene (d, b, c) at platinum micro-diske electrode in aprotic media. Each of the cyclic voltammogram gives one pair of redox peaks. The I_{pc}/I_{pa} ratio of them is calculated to be approximately 1 and $|Epa−Epc|$ value approximately 60 mV, so they are the reversible systems. According to the Nernst equation, these reversible reactions

Fig 1 cyclic voltammograms of 0.01M nitrobenzene (a), *m*-nitrotoluene (b), *p*-nitrotoluene(c) and *o*- nitrotoluene(d)

correspond to the one-electron transfer to the formation of nitro radical anion. Peaks of nitrotoluenes were shifted to more cathodic potentials, in other words, they were harder to reduce directly at the Pt micro-diske electrode. These results could be ascribed to the electron-donating effect of the methyl group on the electron density of the nitro moiety.

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Impact of Grain-Dependent Boron Uptake on the Electrochemical and Electrical Properties of Boron Doped Polycrystalline Diamond Electrodes

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Polycrystalline boron doped diamond (BDD) has been touted as an interesting electrode material. This is as a consequence of its very wide potential window in aqueous solution compared to traditional electrodes, low background currents and corrosion stability in aggressive media. However, given the polycrystalline nature of the surface, the electrochemical behavior of the material is expected to be heterogeneous. Using a combination of high resolution electrical and electrochemical imaging techniques, in conjunction with cathodoluminescence (CL) the electrochemical behavior of oxygen-terminated highly doped polycrystalline BDD was investigated.[1] CL imaging demonstrates that boron uptake is non-uniform across the surface of BDD and conducting-atomic force microscopy (C-AFM) highlights how this impacts on the local conductivity. Whilst C-AFM shows *no* evidence for enhanced grain boundary conductivity, two characteristic conductivity domains are found with resistances of ca. 100 kΩ and ca. 50 MΩ. Using scanning electrochemical microscopy (SECM) local heterogeneities are also observed in the electroactivity of the BDD surface, consistent with the two different types of conducting regions. Local currents of the magnitude expected for metal-like behavior are observed in some regions, suggesting degenerative doping of the grains (supported by CL studies). In other regions, slower electron transfer is apparent. However, even for the reduction of $Ru(NH_3)_6^{3+}$, which occurs at potentials far negative of the flat band potential for oxygen-terminated BDD, all areas of the surface show some electroactivity.

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ANALYSIS OF THE MORPHOLOGY AND COMPOSITION OF Fe-Ni-W ELECTRODEPOSITS

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The electrodeposition of Fe-Ni-W alloys is an example of the so-called induced codeposition mechanism. These alloys can be applied as protective coatings and cathode electrode for hydrogen evolution due to their high corrosion resistance and low hydrogen overpotential. The main goal of this paper is characterize the deposits obtained from ions Ni, Fe and W solutions as your morphology and composition.

Fe-Ni-W deposits were prepared from a 0.2 M sodium citrate electrolyte containing $NiSO_4$, $FeSO_4$ and Na_2WO_4 at different molar ratio. The pH of the plating solutions was adjusted to 5.0. Voltammetric cyclic experiments were performed using a microcomputer controlled potentiostat/galvanostat, EG&G PARC mod. 283. The deposits were obtained at different potentials and galvanostatically at 30 mA/cm^2. The deposits were characterised by SEM, EDX and XPS.

The cyclic voltammetry results showed that peaks current and potentials depend on molar ratio. For molar ratio 10:1:1 two cathodic peaks are observed in the voltammograms, at -0.7 and -1.1 V. These peaks can be related to oxide tungsten and alloy deposition, respectively. For this solution, the anodic sweep revealed a well-defined peak at -0.6 V attributed to iron dissolution. The voltammetric curves show no oxidation and reduction peaks for all another conditions studied. In order to characterise the coatings formed under the different conditions; deposits at long deposition times were prepared by potentiostatic and galvanostatic techniques. SEM micrographs showed smooth and cracked films, for all deposits obtained. The compositions of alloys, evaluated by XPS, are presented in Table below.

Fe Ni W 1:1:1 % at/at			
	Fe	Ni	W	*O*
-1.5 V	20.4	0.03	17.1	62.4
30 mA/cm^2	26.9	0.9	7.0	63.2
Fe Ni W 1:10:1 % at/at			
-1.5 V	18.9	7.7	5.6	67.8
30 mA/cm^2	13.3	13.0	1.8	71.8

The oxygen amount is high at different molar ratio and deposition technique used. The presence of oxygen in the coatings corroborates the voltammetric results showing that oxides mixture were obtained during electrodeposition processes and the deposits is formed by a oxide matrix with low metal content .

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Mathematical model of bulk and surface reactions during electrochemical oxidation at BDD anodes

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Electrochemical oxidation of several organic compounds at Boron doped diamond (BDD) anodes may be achieved with high removal rates and high values of the faradaic yield.

It is well established that the oxidation of organics at BDD anodes takes place in the potential region of oxygen evolution, through reaction steps in which OH radicals are involved. These radicals can react with organic compounds to give more oxidised substances, but can also react with each other, with water or inorganic compounds present in the solution to give oxygen and long-life oxidising agents. Because of the high reactivity of OH radicals the volume in which these reactions can occur is a thin film adjacent to the electrode surface. On the other hand, the electro-generated oxidising agents may diffuse towards the bulk of the solution where they can oxidise the organic matter.

The resulting process is a combination of bulk and surface reactions, the occurrence of each mechanism depending on the operative conditions, such as current density, configuration and hydrodynamic of the reactor and chemistry of the solution.

Depending on the particular application, the contribution of bulk or surface reactions should be maximised: to this purpose, a mathematical model which accounts for the effect of the different operative parameters may be an useful tool in reactor design. This paper presents the results of a numerical study on the electrochemical oxidation of organic substances at BDD anodes. Following the approach successfully utilised in a previous work to describe the surface reactions, surface and bulk reactions were modelled by considering the mass balances of each compound (organic, OH radicals and bulk oxidants) involved in the process. Second order kinetics were adopted to describe the reactions between organics and oxidising agents, both in the reaction film and in the bulk of the solution.

The numerical solution of the model allows to calculate the concentration of the different organic species, as well as of the oxidising agents, during the electrolyses.

The numerical prediction were compared with experimental results obtained in different experimental conditions: electrolyses of aqueous solutions containing aromatic hydrocarbons, characterised by different behaviour towards electrochemical oxidations, were utilised. Different cell configurations, hydrodynamic conditions, current densities and electrolyte compositions were adopted to validate the model.

Influence of Additives on the Formation of Nickel Oxalate Nanoparticles

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Interest in synthesizing nickel nanoparticles has increased considerably with growing applications in recent years. Synthesis of size- and morphology-controlled nickel particle was developed by two-step process. The first step is synthesis of nickel oxalate as precursor by precipitation in aqueous solution, and the second one is thermal decomposition of the precursor. The morphology and size of final products are determined by those of the precursor. In this study, we investigated the influence of the additives in the aqueous solution on the formation of nickel oxalate particles.

The nickel oxalate particles were synthesized as precursor by mixing solutions A and B with 0.05 dm^3 each at 298 K. Solution A consists of 0.2 mol dm^{-3} nickel chloride hexahydrate and 1.2 mol dm^{-3} ammonia. Solution B consists of 0.2 mol dm^{-3} sodium oxalate and additives such as polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and polyethyleneglycol (PEG). After mixing A and B, the solution was agitated continuously for 4 hours for ripening. The precursor particles obtained after ripening were separated by filtration, rinsed with distilled water, and dried for 24 hours at room temperature.

The nickel oxalate particles obtained from the mixed solution without additive were granular aggregates of a few micrometer sizes. Well-dispersed needle-like particles with 530 nm long and 40 nm wide were obtained from the solutions including 1 mmol dm^{-3} PVP with 10 k in molecular mass and 0.2 mmol dm^{-3} with 25 k. A zeta potential for particles prepared from the solutions with and without additives showed a similar value, c.a. -10 mV.

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Electropolishing of stainless steel using ionic liquids

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Electropolishing is a process studied extensively since the 1930s. The majority of processes carried out commercially utilise mixtures of phosphoric and sulphuric acids. The use of these highly corrosive liquids is not only hazardous, but there is poor current efficiency and extensive gas evolution during the process. In this work, efficient electropolishing of stainless steel grade 316 is demonstrated in an ionic liquid [1] composed of ethylene glycol ($HOCH_2CH_2OH$) and choline chloride ($HOC_2H_4N(CH_3)_3{}^+Cl^-$). Significant improvements in process efficiency are demonstrated and data from a 1000 litre scale trial process are shown. Linear Sweep Voltammetry, Scanning Electron Microscopy, Atomic Force Microscopy and AC Impedance methods were used to investigate the steel dissolution mechanism and the results are compared to polishing done in aqueous acidic solutions [2]. It is shown that negligible gas evolution occurs at the anode and the quality of the polish is related to the breakdown of the oxide film. The effects of ageing on the polishing bath are also demonstrated together with a simple, effective recycling protocol for the ionic liquid.

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Composite SnO$_2$-based binary and ternary electrocatalysts

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Oxygen evolution in acid environment represents a very severe test for electrocatalysts. Only precious metal oxides are relatively stable. Among these, IrO$_2$ is, in principle, the most resistant. However the application of pure iridium oxide coatings is strongly restricted by high costs and limited electrode lifetime. Consequently composite materials, where the precious compound is dispersed in a less active but more stable matrix, are being intensively studied to offer less expensive electrodes which might show, at the same time, a good electrocatalytic activity, stability toward anodic dissolution and electronic conductivity.

In the general case of composite materials the electrocatalytic behaviour is the result of a delicate balance between different, often diverging, effects as the coating actual composition, the layer morphology, the crystallite sizes and the overall electrical conductance. The control of these aspects can be obtained, primarily, by modulating the synthetic route of the material.

We have recently started a research concerning the investigation of nanostructured SnO$_2$+IrO$_2$ and SnO$_2$+IrO$_2$+Ta$_2$O$_5$ composites, obtained by a common synthetic path, both as particles and as electrodes. The materials are prepared by a low-temperature sol-gel synthetic process, starting from the appropriate metal salts, combined with thermal treatments in the range 400-600°C. The calcined samples are characterized with respect to the structural and morphological features (XRD, Raman, electronic microscopies, BET). The chemical state of iridium and oxygen in the materials is examined by XPS. The electrochemical behaviour of the electrodes was investigated by cyclic voltammetry combined with electrochemical impedance spectroscopy.

The different characterizations adopted for the electrodes and for the particles point to common features that are determined by the preparation procedure and can be further modulated by the choice of the operating conditions.

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Characterization of Corrosion Resistance for Anodic Films Formed on Aluminum by Electrochemical Impedance

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Aluminum and its alloys have been used in a lot of fields such as electronics, automobiles, beverage cans, etc. Anodizing is one of the common treatments in surface coating for corrosive protection. However, it is easy to corrode in acidic, basic environments and in the solution with corrosive salts. In this paper, aluminum of 99.99 mass% in purity was anodized in aqueous solutions at various pH and with various salts. The corrosion property was also examined in the solution at pH between neutral and alkaline by using electrochemical impedance spectroscopy, EIS.

The specimens were electrochemically polished in 0.1 dm^3 $HClO_4$ + 0.4 dm^3 CH_3OH solution at 18 V, degreased in 10 mass% NaOH solution, pickled in 30 mass% HNO_3, before anodizing. Anodizing was performed in the solutions with sulfate, phosphate, tartrate and carbonate. The anodizing time was controlled to obtain a constant film thickness of ca. 300 nm.

The corrosion test in sodium hydroxide at pH 13 showed that the specimen anodized in carbonate solution at pH 11.5 had the highest corrosion resistance and maintained high corrosion resistance for the longest time in all specimens. The capacitance of an electric double layer for the specimen with good corrosion resistance indicated the low value in any time. Oppositely, the sample anodized in sulfuric acid at pH 0 showed the lowest corrosion resistance and high capacitance value in the corrosion test of alkaline solution, where the dissolved oxygen did not affect corrosion property. The specimen anodized in tartrate solution at pH 6.7 had comparatively low resistance in sodium chloride solution at pH 7, in which corrosion resistances showed larger values than that in alkaline solution. Corrosion behavior was discussed using the mixed potential diagram, consisting of the changes in corrosion current calculated from corrosion resistance in EIS, and corrosion potential measured during corrosion test.

A Simulation Study on the Optimization of ECM Processes: Prerequisites for the Localization of the Current Density Distribution

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Electrochemical machining (ECM) of hard materials has some important advantages over conventional procedures, because it leads to a high quality surface without residual stresses or damage to the microstructure. Since the desired shape of the working piece is dependent on a multiplicity of parameters (shape and movement of the cathodic tool, width of the inter-electrode gap, current density, flow rate, electrolyte composition), there is a strong need for suitable simulation software. In this contribution, moving boundary simulations based on the Potential Model (under the assumption of secondary current density distributions) have been chosen, which consider the movement of the cathodic tool [1] and, therefore, yield the temporal development of the work-piece as a function of the feed rate.

In order to impress the geometrical tool characteristics efficiently on the work-piece, the anodic current density distribution has to be strongly localized. To elaborate the prerequisites for such localization, the variance of the initial current density on an infinitely extended planar anode has been evaluated for different (finite) cathode geometries as a function of typical machining parameters (minimum distance between the electrodes, electrode kinetics, conductivity). It will be demonstrated, that the variance is closely related with the well-known Wagner number, which represents a measure for the inhomogeneity of secondary current distributions.

It is demonstrated, that the machining procedure of distinct work piece domains in the micrometer range would require an extremely pronounced localization (i.e., a variance in the micrometer-range) of the current density distribution corresponding to extremely small inter-electrode distances. Therefore, for technical reasons, ECM in a narrow sense is not possible and one has to switch over to modified techniques, which are based on a localization of the anodic current density distribution independently of the distance between the electrodes. On one hand, one can take advantage of the edge-effect, which corresponds to a localization of the current density distribution, too. A typical example is the sharpening of metal strips with rectangle cross-sections (thickness in the micrometer-range). On the other hand, one can use insulating masks which force the current density to be restricted on selected domains in the micrometer-range. Such techniques are applied in the production of PCB's and will be discussed for the case of electrochemical pattern etching processes.

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Electrochemical Engineering & Technology

Optimization of Technical Processes in Terms of Current Density-, Concentration- and Flow-Distributions

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The simulation-algorithm applied in this contribution [1, 2] is based on the numerical solution of a mathematical model describing the influences of diffusion, migration and convection on the movement of all the ions in diluted electrolyte solutions (system of coupled Nernst Planck transport equations for the ion flux densities). In the framework of this model (Dilute Ion Solution Model), the velocity field of the solvent is not affected by the ionic concentrations, which allows for an independent treatment of the hydrodynamic and electrochemical problem, respectively. As a consequence, the Navier-Stokes equation can be decoupled from the system of transport equations and numerically solved to yield the *flow distribution* for special reactor geometry.

To tackle the electrochemical problem, one, first of all, has to propose a reasonable reaction mechanism to set up the system of transport equations for all ionic species involved. This is, in general, a difficult task which can be solved very efficiently by modelling rotating disk or cylinder electrode experiments by means of a special simulation software [1]. Since, additionally to the elucidation of the reaction mechanism, this software allows for the determination of an optimized set of electrochemical parameters, i.e. it delivers a data base for the solution of the electrochemical problem. In using this data base and inserting the velocity field into the system of transport equations, it can be numerically solved [1] to yield the *concentration distributions* and (tertiary) *current density distributions*.

The combination of (i) modelling rotating disk experiments to extract the basic electrochemical information about the technical process under consideration and (ii) inserting this information into the Nernst Planck equation represents an algorithm which allows for a discussion of technical processes in terms of flow-, concentration- and current-density distributions. As a demonstration, the influence of hydrodynamic flow patterns on the concentration- and current density distributions will be discussed for some technical important processes. In case of through foil etching processes, three typical situations have been selected: (i) the initial unetched assembly (eddies in the interior corners of the cavity), (ii) a situation before the support is exposed to the electrolyte (eddies in the undercut-region), (iii) a situation after the support is first exposed to the electrolyte.

[1, 2] Pirode, Miotras (see, www.elsyca.com)

On the Modelling of Pulsed Current and High-Speed Deposition Processes: Role of the Ion-Surface Concentration

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Pulsed current and high-speed deposition processes represent promising techniques for the realization of high-quality deposits with special properties. In order to propose suitable operating conditions, a computer simulation [1] has been chosen, which is based on the Nernst Planck transport equation for diluted electrolyte solutions. The determination of the electrochemical input-parameters for a numerical solution of this equation by modelling rotating disk electrode experiments will be demonstrated for some selected deposition processes.

Since the transport equation contains contributions of diffusion, convection, and migration, it yields a complete description of the electrochemical deposition process (ion concentration fields, local ion surface concentrations, local current density distributions, layer thickness distributions). Especially the ion surface concentration will be a quantity of interest in this contribution, because it allows for predictions on the deposit quality (e.g. control of mass transfer in the vicinity of the electrode to avoid dendritic structures). In general, a high surface concentration near to the bulk concentration enlarges the number of crystallisation centres, and, therefore, yields a high deposit quality.

In the case of pulsed current (PC) and pulsed reverse current (PRC) depositions, the imposed transient signal causes periodic fluctuations in the ion surface concentrations corresponding to alternating regimes of cathodic deposition, equilibration (via diffusion during the off-times), and anodic dissolution. It will be demonstrated, that – in systems without efficient stirring - the off-times necessary to recover the bulk-concentration by means of diffusion would have to be extremely long, whereas the ion surface concentration can be lifted up very efficiently via convection, i.e. the flow field has to be optimized together with the pulse parameters.

In the case of high-speed DC processes, the pronounced decrease in the ion surface concentration at high current densities is to be compensated by choosing proper convection conditions. It will be demonstrated, that high-speed deposition processes yielding excellent deposit qualities can be realized by an optimization of the flow rate/current density ratio.

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On the Modelling of Deposition Processes from Molten Salts: Layer Thickness Distributions

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The electrochemical deposition of refractory metals and compounds from molten salts is a promising surface modification method for protecting substrates against wear, corrosion and high temperature oxidation. Contrary to physical vapour deposition (PVD), a good coverage of complex geometries without preferable directions can be achieved. But, as will be demonstrated in this contribution by discussing the electro-deposition of TiB_2, the layer thickness distribution is not homogeneous in the case of electrodeposition on complex-shaped substrates. In order to investigate the deposit profile especially near to edges, the coating process of two different geometries has been modelled by moving-boundary simulations in the framework of the Potential Model [1]:

 (I) a strip with rectangle cross-section
 (II) a rod with quadratic cross-section

Up to now, the Potential Model has been successfully used for modelling plating procedures and etching procedures from/in aqueous solutions. As demonstrated in this contribution, it allows for a description of deposition processes from molten salts, too, and yields excellent agreement with the experimental layer thickness distributions when assuming secondary current density distributions, i.e. the kinetic resistance of the interfacial reaction is considered to be not negligible compared to the ohmic resistance which corresponds to a non-zero Wagner number. A linear current-density / overpotential relation with slopes derived from the experimental polarization curve have been used to model the charge transfer polarization behaviour. The model assumption of secondary current density distributions seems to be justified because of the high temperature in molten salt electrolytes causing the concentration gradients to equilibrate very fast.

Furthermore, modelling of the layer thickness distributions near to edges in a current density regime where the deposit becomes powdery again resulted in a good agreement with the experiment by introducing a current density dependent efficiency $E(J)$ into the Potential Model. A strategy to determine $E(J)$ is proposed, which is based on a combination of experiments and simulations with axisymmetrical cells containing truncated cones with different semivertical angles as cathodes. This topic is currently under investigation and some first results will be presented.

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Preparation and Characterization of Copper-Doped Cobalt Oxide Electrodes (Ti/Cu$_x$Co$_{3-x}$O$_4$)

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Transition metallic oxides present a series of exceptional electronic, magnetic and catalytic properties. Cobalt oxides (Co$_3$O$_4$) or cobalt containing mixed oxides with spinel structure, (M$_x$Co$_{3-x}$O$_4$ with M = Cu, Ni, Mg, Zn, etc) have been extensively applied to the electrochemical treatment of wastewater [1,2]. We report the electrochemical characterization and a surface composition study of cobalt oxide (Co$_3$O$_4$) and copper-doped cobalt oxide (Cu$_x$Co$_{3-x}$O$_4$) electrodes, which have been prepared onto titanium support by the thermal decomposition method. The cyclic voltammograms of Ti/Co$_3$O$_4$ and Ti/Cu$_{0.5}$Co$_{2.5}$O$_4$ electrodes in 0.1M NaOH solution show the two characteristic redox couples of a typical Co$_3$O$_4$ electrode. As copper concentration grows, the first couple (Co^{II}/Co^{III}) vanishes. The shift of the second redox transition (Co^{III}/ Co^{IV}) and the OER to lower positive potentials, indicate a modification of the electrocatalytic features induced by Cu incorporation. When x exceeds 1.0, the characteristic features for Co$_3$O$_4$ electroactivity are lost.

The bulk and surface atomic composition were determined by EDX and XPS, respectively and are shown in Table 1. The Cu/Co ratio in the surface is rather close to the bulk ratio and to the nominal composition of the precursor solution. However, the copper over-saturated cobalt spinel (x > 1) exhibits a surface copper enrichment. Moreover, the similar bulk composition of the copper saturated (x = 1) and the copper over-saturated cobalt spinel

Table 1

Bulk and surface composition of Ti / Cu$_x$Co$_{3-x}$O$_4$ electrode

Cu$_x$Co$_{3-x}$O$_4$ / Ti Electrode	Atomic Ratio		
	Nominal Cu/Co	$\left(\dfrac{Cu}{Co}\right)_{EDX}$	$\left(\dfrac{Cu}{Co}\right)_{XPS}$
Cu$_{0.2}$Co$_{2.8}$O$_4$	0.07	0.04	0.07
Cu$_{0.5}$Co$_{2.5}$O$_4$	0.20	0.19	0.23
Cu$_{0.8}$Co$_{2.2}$O$_4$	0.36	0.37	0.49
Cu Co$_2$O$_4$	0.50	0.51	0.50
Cu Co$_2$O$_4$ (+ Cu$_y$O)	1.00	0.56	4.55

(x > 1) suggests the existence of two well-defined phases in the latter oxide: a deeper copper cobaltite phase and a surface segregated CuO phase. This surface phase segregation is probably at the origin of the drastic change of the voltammetric profile at x>1.0.

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2. A. Stavart, A. Van Lierde, J. Appl. Electrochem. 31 (2001) 469.

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Durability of IrO_2-Ta_2O_5/Ti electrodes prepared at low thermal decomposition temperature

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A titanium electrode coated with an IrO_2-Ta_2O_5 catalytic layer has been widely used as an insoluble oxygen evolution anode in electroplating processes of zinc, tin, or copper. The electrode preparation proceeds through the thermal decomposition of the precursor solution containing Ir(IV) and Ta(V) on a titanium substrate. The oxygen evolution behaviors strongly depend on the oxide composition, typically 70 mol% to 80 mol% of IrO_2, and the thermal decomposition temperature.

Our previous work has revealed that the active surface area for OER on the IrO_2-Ta_2O_5/Ti electrode increases with decreasing thermal decomposition temperature from 470 °C to 340 °C. This is because IrO_2 in the catalytic layer becomes amorphous as the thermal decomposition temperature decreases. We have also found that the amorphization of IrO_2 is beneficial to suppress the unfavorable side reaction when the electrode is applied in copper foil production; *i.e.*, copper foil production uses copper sulfate solutions containing Pb(II) ions as impurity, and the oxidation of Pb(II) to PbO_2 can occur on the electrode of crystalline IrO_2, resulting in the formation of PbO_2 layer with low catalysis for OER, but can not occur on that of amorphous IrO_2. The inhibition of PbO_2 formation on amorphous IrO_2 is due to the increase in the nucleation overpotential for the anodic deposition of PbO_2 on amorphous IrO_2 [1].

In this work, we investigated the durability of IrO_2-Ta_2O_5/Ti electrodes at different thermal decomposition temperature. The electrode's lifetime for OER in a sulfuric acid solution was measured, and the effects of thermal decomposition temperature on the lifetime and the deterioration mechanism were examined. The electrode's lifetime became short with decreasing thermal decomposition temperature; especially, the lifetime of the electrode of amorphous IrO_2 was quite short compared to those of crystalline IrO_2. SEM observations of the catalytic layers before and after the lifetime test indicated that many cracks were made on the electrode of amorphous IrO_2 even on the early stage of the lifetime test, inducing the substrate corrosion by the penetration of the acidic solution. However, we revealed that this rapid degradation could be suppressed by an interlayer between the substrate and the catalytic layer, and the electrode's lifetime could be more prolonged.

[1] M. Morimitsu, 55th Annual Meeting of ISE, Abst# S6FP5(KL), 19-24 September, 2004, Thessaloniki, Greece.

Surface Modification of Titanium by Anodizing and Pulse Electrolysis and Bioactivity Evaluation on the Surface

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Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) coating is one of the most popular methods for improving the osseointegration of titanium implants. It is also well known that TiO_2 layer has good biocompatibility. It is easy to produce HAp coatings on Ti substrates by cathodic electrolysis in the aqueous solution including Ca^{2+} and PO_4^{3-}, and TiO_2 films on the substrates by anodic electrolysis. Therefore, we intended to form composite films with HAp and TiO_2 on Ti substrates by a single process, pulse electrolysis, in the aqueous solutions, and to evaluate the bioactivity of them in *in vitro* and *in vivo* methods.

The anodizing was conducted at +9.0 V for 15 min. in the 0.6 mM H_2SO_4, 0.6 mM H_3PO_4, 0.6 mM HCl and 0.6 mM HNO_3 solutions and the solution including both 0.3 mM $Ca(H_2PO_4)_2$ and 0.7 mM $CaCl_2$ at 120°C. The pH value was adjusted to 5.5. Titanium plate was used as a working electrode. The pulse electrolysis was performed in the aqueous solution with $Ca(H_2PO_4)_2$ and $CaCl_2$. The anodic-cathodic rectangular pulse waves were applied for 30 min., in parameter of the electrolysis cycle, the anodic and cathodic potentials, and the duty ratio. The coatings were evaluated by the SEM observation and XRD. In *in vitro* examination, the MC3T3-E1 cells were cultured on the specimen in the CO_2-incubator, and the number of cells was counted and the ALP activity was measured. In *in vivo*, the coated specimens were implanted in the rats tibiae and evaluate the rate of calcification on them.

Anodizing in acidic solutions gave TiO_2 (anatase) film on Ti substrates. The anodic-cathodic pulse electrolysis (+9.0V□-9.0V, 60s□60s) result in the composite coating with HAp and TiO_2. The TiO_2 specimens anodized in the solution including PO_4^{3-}, phosphoric acid solution and $Ca(H_2PO_4)_2$ and $CaCl_2$ solution, result in a high ALP activity. It would be thought that these TiO_2 coating contained PO_4^{3-} slightly, which was the constituent element of the natural bone. The composite films by pulse electrolysis, in the same reason, had a high ALP activity. On the other hand, in *in vivo* examination, the rate of calcification on the pulse electrolysis specimen was higher than that anodized only, because of the synergy effects of HAp and TiO_2.

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Electroreductiion of aliphatic esters using magnesium and lanthanide metal ions as mediators III

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The electroreduction of aliphatic esters **1** is hardly attainable since their reduction potential is highly negative.   On the other hand, we have already reported that the electroreduction of organic compounds using Mg electrodes promotes a variety of unique reactions which can not be attainable under the usual conditions of electroreduction .[1-3]

In the course of these studies, we have recently found that use of Mg cathode and anode makes the reduction of **1** to the corresponding alcohols **2** possible (Scheme 1).[4,5]   The use of Mg electrodes is essential in this reaction since **1** was not reducible with other electrode materials such as C, Pt, Zn, and Pb.

Scheme 1

In the mechanistic study of this reaction, it was appeared that the existence of a catalytic amount of Mg(II) ion promoted the electroreduction of **1** affording the corresponding alcohol-THF adducts **3** (Scheme 2).

M_{red} * = Mg(0) or Mg(I), Ln(0) or Ln(II)
M_{ox} = Mg(II), Ln (III)
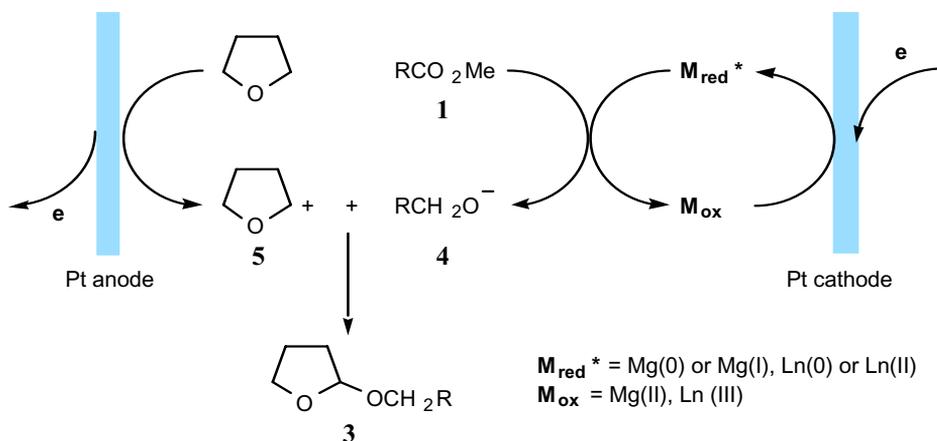
Scheme 2

Electrochemical Formation of Cu-Sn Alloy Layer Using Ionic Liquid as an Electrolyte

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The electrodeposition of alloys is a key technology for thin layer processing in the field of surface finishing, for example. Although the technology is generally considered to be a soft-solution process, the treatment of the waste bath, the entropy of which is high since the bath contains two or more metal components, is energy-consuming in some cases. In contrast, we recently demonstrated that a Cu-Sn alloy layers mainly composed of Cu_6Sn_5 (61 wt.% Sn) and Cu_3Sn (38 wt.% Sn) phases can be formed on a Cu plate through a simple galvanic contact process [1]. Here, we used an electrolytic bath containing only Sn(II) ions and found that the use of ionic liquid, trimethyl-*n*-hexylammonium bis[(trifluoromethyl)sulfonyl]amide (TMHA-Tf$_2$N), as a solvent rendered it possible to raise the processing temperature beyond 100 ˚C so as to form the alloy layers faster than in the case of an aqueous media. The Cu-Sn alloy coating with a composition of 40–60 wt.% Sn, called "speculum metal," appears silver-grey and has been investigated as a promising alternative to an allergenic nickel coating.

In the present study, we tried using a thin Cu layer (electrodeposited from aqueous solution) as a substrate for the Cu-Sn alloying and discuss the thermodynamics of the alloy formation.

In the case of the galvanic contact method at 130 ˚C (Fig. 1a), resulting Cu-Sn layer appears dark-grey involving a β-Sn phase with a trace amount of copper, while the alloying under potentiostatic conditions at +5 to +20 mV *vs.* Sn^{2+}/Sn (Fig. 1b and 1c) resulted in the formation of silver-grey intermetallic phases, Cu_6Sn_5, Cu_3Sn, and Cu_6Sn_5, without the β-Sn phase. The abundance of Sn-rich phase, *i.e.* Cu_6Sn_5 whose tin activity is the highest of the three, increased with decreasing the potential for the alloying. In all cases, diffraction due to elemental fcc-Cu phase was not detected, indicating that the whole layer was converted to Cu-Sn alloy. These demonstrated that a Cu-Sn alloy layer can be prepared through successive electrochemical deposition using two baths, each containing different metal ions, Cu^{2+} and Sn^{2+}.

[1] T. Katase *et al.*, *Electrochem. Solid-State Lett.*, **9**, C69 (2006).
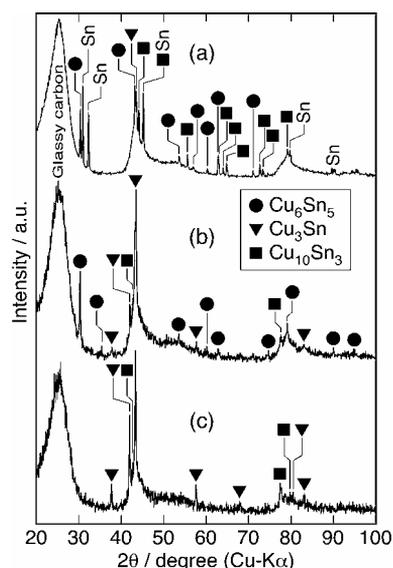
Fig. 1 XRD patterns of Cu-Sn layers prepared from Cu layer on glassy carbon substrate by (a) galvanic contact and (b,c) potentiostatic methods at 130 ˚C. Potentials were (b) +5 and (c) +20 mV *vs.* Sn^{2+}/Sn.

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Electrochemical incineration of p-cresol and o-cresol in a FM01-LC reactor using BDD electrodes

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This work shows a comparative study of the incineration of *p*-cresol and *o*-cresol 2 mM in H_2SO_4 1M in aqueous media. Microelectrolysis studies indicated that the oxidation of *p*-cresol and *o*-cresol, both, were carried out *via* hydroxyl radicals formed by the oxidation of water in the BDD-H_2O-H_2SO_4-*p* and *o*-cresol interface. In both cases, the range of potential and current density, where great amounts of OH$^\bullet$ are formed were between 1.7 V ≤ E ≤ 2.2 V versus SSE and J =10 mA cm^{-2}. Electrolysis in FM01-LC reactor were performed at different Reynolds between 27129 ≤ Re ≤ 42631 and at a current density of 10 mA cm^{-2}. In both substances the mineralization and its current efficiency were function of the Re. For *p*-cresol the mineralization was carried out to 90 % with a current efficiency of 71% and an energy consumption of 1.96 kW h m^{-3}; whereas o-cresol was mineralized to 84%, with a current efficiency of 67% and an energy consumption of 1.64 kW h m^{-3}. The results obtained in this work demonstrated that *o*-cresol is more recalcitrant than p-cresol.

Fabrication of a Tensile Rig for in-situ Studies of the Repassivation Kinetics of thin Oxide Films on Valve Metals

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Thin brittle oxide films formed on metallic substrates have diverse applications, such as in abrasion-resistant coatings, corrosion protection, and for biocompatibility. In order to improve the mechanical reliability of these thin film coatings the fracture and adhesion of the coatings are of major consideration for mechanical engineers. From the electrochemistry and corrosion point of view the focus lays on understanding the repassivation kinetics. Studies on the repassivation kinetics are established by the use of conventional scratch and indentation tests under static load or even under dynamic conditions based on impingement of abrasive particle.

However, all these methods are based on rupturing of the oxide by contact. This study aims at understanding the breakdown of thin passive films under dynamic condition by application of a tensile load. To visualise these effects a tensile rig coupled with an electrochemical setup was fabricated. This allows studying the breakdown of thin oxide films under tensile loading and hence to record the corresponding current transients. Here, the first results carried out on aluminium wires are presented. Initial results reveal the breakdown of the oxide formed on alumiunium wires upon application of the tensile load. This is confirmed by tensile loading of the passivated aluminium surface in an acidified $CuSO_4$ solution. Fig.1. shows the Cu deposits at cracks forming during these conditions.

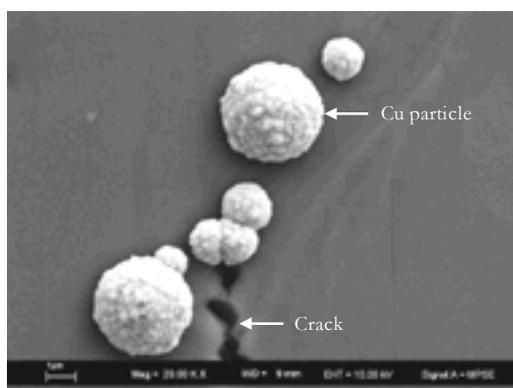Fig 1. SEM micrograph of passivated Al surface showing Cu deposits at cracks during tensile loading in acidified $CuSO_4$ solution.

Mechanism of a formation of honeycomb-like copper structures

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Copper electrodeposition at high overpotentials at which copper electrodeposition is competitive with hydrogen evolution leads to the formation of honeycomb – like copper structures. These structures show the extremely high surface area which is relevant for evaluating electrochemical reactions, and copper electrodes with the stated characteristics can be used as electrodes in many electronic devices such as fuel cells, batteries and sensors [1].

It was shown that a honeycomb – like copper structure is possible to get by a potentiostatic electrodeposition at overpotential of 1000 mV from 0.15 M $CuSO_4$ in 0.50 M H_2SO_4 [2]. Electrodepositions were performed onto copper electrodes, and reference and counter electrodes were of a pure copper. The average current efficiency of hydrogen evolution at this overpotential was 30.0 %. The main characteristics of a honeycomb – like structure were craters or holes with agglomerates of copper grains between them.

The examination of a formation of the honeycomb – like structure reveals a double origin of a formation of these craters or holes.

The one group of craters or holes were craters formed due to the attachment of hydrogen bubbles as a consequence of the intensive hydrogen evolution at this overpotential. These craters had regular cyclic shapes. The diameter of these craters increased with a time of electrolysis due to a growth of the formed hydrogen bubbles. In the later stage of electrodeposition, the increase of a diameter of craters or holes was primarily due to a coalescence of the formed hydrogen bubbles.

The origin of the other group of craters or holes is of agglomerates of copper grains formed in the initial stage of electrodeposition. These craters had irregular shapes. Current distribution at growing surface of copper electrode was a very important for a formation of craters or holes from this group.

The preparation of copper electrodes for copper electrodepositions also affected on a number, size and distribution of craters or holes formed onto the surface area of electrode.

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Electrochemical Properties of the Sol-Gel Prepared Ternary TiO$_2$-RuO$_2$-IrO$_2$ Coatings on Titanium[+]

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Electroactive oxide coatings on titanium have wide application in electrochemical industry, due to good electrocatalytic properties for many processes [1]. Electrochemical properties of activated titanium electrodes are considerably influenced by the oxides and the coatings preparation procedure. The sol-gel coating processing appears to be very promising [2]. The aim of this work is to report the results obtained with the sol-gel prepared ternary TiO$_2$-RuO$_2$-IrO$_2$ coating on titanium. The oxides sols were obtained by forced hydrolysis of metal chlorides in HCl solution at boiling temperature [2]. The mixture of oxide sols was applied on Ti support and the coatings were annealed at the temperature of 450 °C. The properties of Ti/TiO$_2$-RuO$_2$-IrO$_2$ electrodes are compared to Ti/TiO$_2$-RuO$_2$ electrodes, especially with respect to oxygen evolution reaction (OER) and stability during a long-term electrolysis in a diluted chloride solution.
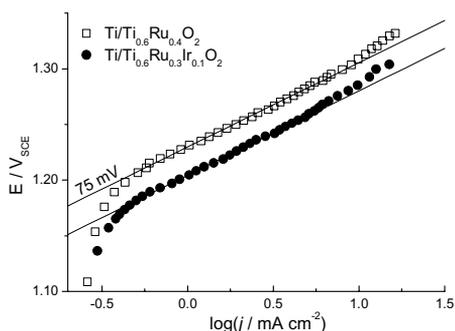
Fig. 1. Polarization curves of prepared anodes, registered in 1.0 mol dm^{-3} H$_2$SO$_4$ at room temperature.

The OER activity of Ti/Ti$_{0.6}$Ru$_{0.3}$Ir$_{0.1}$O$_2$ and Ti/Ti$_{0.6}$Ru$_{0.4}$O$_2$ anodes, registered in H$_2$SO$_4$ solution, is illustrated by polarization curves in Fig. 1. The curves show the Tafel slope of 75 mV dec^{-1}, which is a usual value for OER on these types of anodes [1]. It is seen that Ti/Ti$_{0.6}$Ru$_{0.3}$Ir$_{0.1}$O$_2$ anode shows higher activity in OER if compared to Ti/Ti$_{0.6}$Ru$_{0.4}$O$_2$ anode. It is also known that IrO$_2$ is more stable than RuO$_2$ at high anodic potentials, so it can be expected that Ti/Ti$_{0.6}$Ru$_{0.3}$Ir$_{0.1}$O$_2$ last longer than Ti/Ti$_{0.6}$Ru$_{0.4}$O$_2$ anode. The paths for the loss of electrocatalytic activity of the coatings are discussed.

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+ Dedicated to the memory of Professor Aleksandar Despi .

Symposium 5 - Poster

Electrochemical Engineering & Technology

Effect of Chromate Buffering on Oxygen Evolution

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The impact of chromate on oxygen evolution on a ruthenium based DSA® has been investigated. The system was studied experimentally in a rotating disk electrode (RDE) cell, and by modelling taking into account mass transport, homogenous reactions and electrode reactions. In the model, electrode reactions evolving oxygen from OH$^-$ and H$_2$O were considered. The experimental results, exemplified by Figure 1, showed that the polarisation curve for oxygen evolution at a DSA® had two regions. One was pH dependent (low c.d.), while the other region was independent of pH (high c.d.). The transition between these two regions was found to be a limiting current.
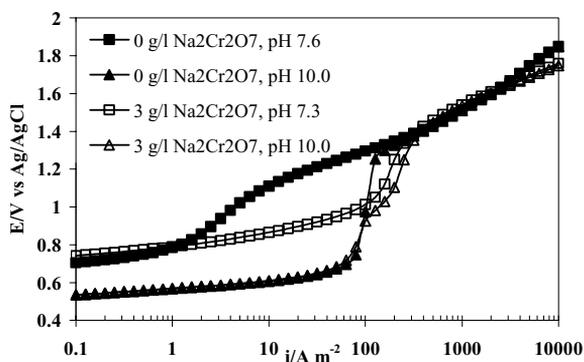
Figure 1. Oxygen evolution on a Ru based DSA® in 5M NaClO$_4$, 70°C, 3000 rpm.

An addition of chromate gave a significant increase of the limiting current for pH values around 7 (Figure 1). However, at pH 10, the effect of chromate was not seen until the limiting current plateau had reached a potential of approximately 0.9 V vs Ag/AgCl. At this point an increase in current was observed and a second plateau was reached. Model simulations showed that the effect of chromate on the limiting current was due to its buffering action at neutral pHs. At bulk pH 10, the first limiting current plateau was related to the mass transport limitation of OH$^-$ from the bulk, while the second plateau was controlled by the rate of the chromate buffering.

Copper recovery from electronic scraps

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Since copper is one of the most important metals for industries and is used in large quantities, development of copper recycling processes is an important issue. Among wastes that contains copper, one of the most complex recycling material is electronic scraps like printed circuit board (PCB). From this background, our research group has proposed an energy-saving copper recycling process using ammoniacal alkaline solutions that is applicable to copper recovery from electronic scraps [1]. Figure 1 shows a schematic drawing of this process. In the leaching stage, electronic wastes are dipped into the solution containing $Cu(NH_3)_4^{2+}$ ions (Cu(II)), and copper in the wastes reacts with the Cu(II) and is dissolved as $Cu(NH_3)_2^+$ ions (Cu(I)). Impurities dissolved into the solution should be separated in the purification stage by solvent extraction etc. Metallic copper is then electrowon from the pure Cu(I) solution in the electrowinning stage. Cu(I) is simultaneously oxidized to Cu(II) on the anode, and the produced Cu(II) is reused in the leaching stage. Concerning this process, we have presented an outline and effective conditions for each stage using synthetic solutions. In this study, a grounded PCB was employed as a real electronic scrap, and copper recovery from the PCB was examined using the solutions containing 5 M NH_3, 0.5 M CuO and either 4 M NH_4Cl or 1 M $(NH_3)_2SO_4$. ICP-AES measurement of the solutions before and after each stage revealed that the sulfate system is superior to the chloride system from the view points of selective leaching and impurity removal in the examined condition. On the other hand, the impurity content of the copper plate obtained from the chloride system (<10ppm) was lower than that from the sulfate sytem.
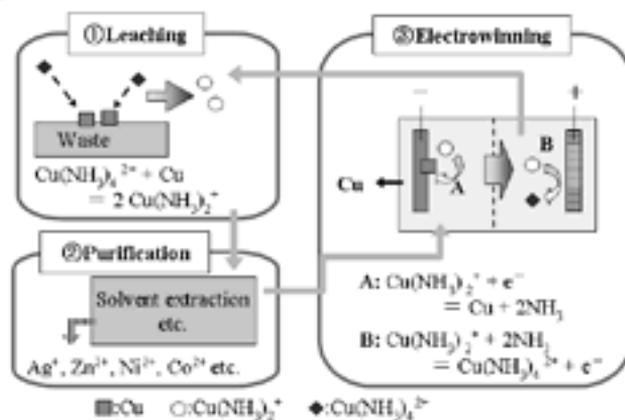
Fig. 1 Schematic drawing of copper recycling process

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Symposium 5 - Poster

Electrochemical Engineering & Technology

Concentration polarization phenomena in cation exchange membrane

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The ion transfer process across cation exchange membrane (CMV) was investigated by analysis of the current density –voltage responses. The limiting –current density was obtained from the polarization curve in a four electrode system. Compared with other electrochemical method such as voltammetry the current-voltage technique(curve I-V) is very popular and useful for the study of membrane transfer process, concentration polarization, water dissociation, overlimiting current.

We then investigated how the limiting current- density was affected by the parameters; Scan rate, concentration of the solution, ionic species and the distance of the wire from the membrane surface.

The agreement of the experimental results with the equation (Randles Sevcik…) of the limiting-current density for the electrode process were discussed.

The Influence of Complexation on the Electrodeposition of Metals and Alloys from Citrate Solutions

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Citrate electrolytes are especially attractive as the non-toxic baths for electrodeposition of metals, alloys and semiconductor materials [1-3]. Citrates form a lot of various metal complexes : different monomeric, dimeric, heternonuclear as also sparingly soluble polymeric complexes. Hence, the analysis of stability of citrate solutions and the analysis of electrodepositon of metals and alloys from citrate solutions is not simple. In the present work, influence of complexation on the electrodeposition of Cu, Ni, Zn, Sn, In, Cu-Ni, Cu-Zn, Ni-Zn and In-Sn from citrate solution was analysed. The ionic strenght in real baths for electrodeposition is high. In these conditions, the methods for calculating activity constants based on the Davies equation or Debye-Hückel theory have very limited reliability hence conditional stability constants were used. The potentiometric titration experiments were performed for determination of conditional stability constants of complex species. Analysis of thermodynamic models built on the base of conditional stability constants allows to determine the predominant citrate complexes. This analysis allows also to indicate ranges of solution parameters within which the stable citrate electrolytes exist (sparingly soluble polymeric citrate complexes, hydrooxides and hydroxysulphates of metals are not formed). Analysis of thermodynamic models of solutions allows also to determine the ranges of parameters within which the little change of concentration of component is causing the great change in properties of electrolyte (e.g. pH, concentrations of the predominant species). The electrodeposition proceeds with wrong reproducibility in these ranges of solution parameters. The kinetics of electroreduction of citrate complexes was studied in the solutions which contain the different predominant citrate complexes. Voltammetric curves and partial polarization curves were determined under various hydrodynamic conditions by the rotating disc electrode technique. No deposit is formed on the cathode in solutions in which the predominant are Ni(II) citrate complexes with charge z<0 and Zn(II) citrate complexes with charge z<-1. The characteristic link between the partial current density of copper and evolution of hydrogen was found in the solutions in which the predominant species were dimeric and heternonuclear citrate complexes of Cu(II). On the partial polarization curves of metals, the maxima were observed in solutions in which heteronuclear complexes were predominant. The model with mixed labile and inert species (LISM, [1]), as also semiempirical quantum method (AM1/d) were used to explain the results.

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Symposium 5 - Poster

Electrochemical Engineering & Technology

Electrocrystallization of silver powder from aqueous solutions

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This work is devoted to the memory of Professor Aleksandar Despić

The various phenomena related to silver electrodeposition under various experimental conditions, producing different deposit morphologies (mostly dendritic), have been studied. In this paper the effect of different deposition regimes (reversing current and pulsating overpotential), on the powdered and dendritic silver electrodeposits morphology were investigated. The size of dendrites decreased strongly with increased overpotential or current. In all investigated samples three main types of particles appear, i.e. dendrites, regular crystals (independent and/or agglomerates) and rods. In some cases of deposition, macro-crystalline deposits can be formed as well as ideal silver grains e.g. in the case of silver deposition it depends on deposition regimes. In the case of pulsating overpotential (Fig. 1), the effect of increasing the pause at one and the same pulse duration on the morphology and particle grain size leads to a formation of smaller particles with a regular crystal structure. In the reversing current deposition (Fig.2), there is no formation of aglomerates, but fine powder particles are obtained directly. It is clear that the morphology and grain size of silver powder particles are strongly influenced in electrodeposition by different deposition regimes.
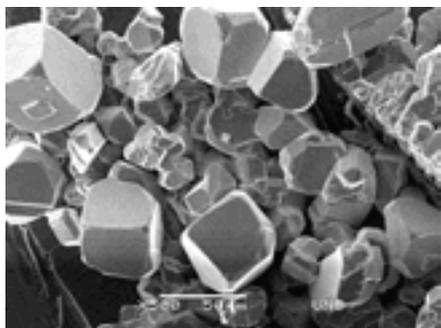

Fig. 1. Silver powder particles obtained by square-wave pulsating overpotential. Overpotential amplitude 300 mV. Pulse duration 50 ms. Pulse to pause ratio 1:5.
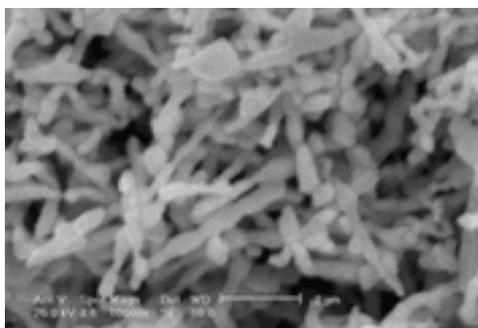

Fig. 2. Silver powder particles obtained by reversing current electrodeposition (j_c= 70mA, j_a= 38.5mA, t_c : t_a = 5 : 1, pulse duration 10 ms, average current density: 51.92 mAcm^{-2}).

Electrodes of Synthetic Diamond: Effects of Surface Microroughness on the Electrode Kinetics at CVD-Diamond Films on Titanium

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The electrochemical behavior of B-doped diamond films on Ti substrates subjected to different pretreatment procedures (annealing, sand-blasting, and etching in hot HCl) is evaluated as a function of surface microroughness. The diamond films deposited onto the pretreated Ti substrates were characterized by surface profiling using interferometer microscope, Raman spectroscopy, and SEM. The roughness varied from 0.1 to ~10 μm; the true-to-geometrical surface area ratio, up to ~3. Generally, the differential capacitance followed the true surface area of the electrodes. The width of the potential window in indifferent electrolyte (2.5 M H_2SO_4) also increased, but slightly, with the roughness, reaching a value of 2.9 V. The electrode reversibility in the $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ redox system increased with increasing surface roughness: the transfer coefficients increase, the potential difference for the anodic and cathodic current peaks in cyclic voltammograms decreases. The apparent increase in the reversibility of the reaction can be explained by the decrease in the true current density. Although the variations of the electrochemical parameters are not strongly pronounced, the tendencies observed can be used for optimizing the electrode properties.

(a)   (b)

SEM pictures showing the surface morphology: (a) Ti-substrate and (b) boron-doped diamond electrode deposited thereon.

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Electrochemical Engineering & Technology

Coalloying Carbide Coatings based on Titanium and Chromium

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The correlation between microhardness and microbrightless of carbide phases, prepared by complex saturation of carbon steels by titanium and chromium have been established in this work. The influence of be alloying for titanium and chromium carbides on the dispersity of phases formed at alloying was shown.

Carbide coatings have a big microhardness and microbrightless, absolute values of which have been determined, as a rule, by type and composition of formed phases. These characteristics reflected a high level of atomic bonding in carbide phases are in direct correlation connections with different mechanical properties (elastic constants, modulus, yield stress and so on). These mechanical characteristics determine efficiency of work of details and instrument with carbide coatings.

The saturation has been carried out in closed atmosphere at the low pressure of gas at wide temperature-time interval. Powders of titanium, chromium, CCl_4 and charcoal have been used as initial reagents.

As established by x-ray diffraction the diffusion layers consisted from two zones are formed on the surfaces of all the steels in such conditions. Zones consist of external layer, based on titanium carbide (TiC). Crystal lattice spacing of compounds prepared at simultaneous complex-component saturation by titanium and chromium distinguish from once prepared at single-component saturation. It can be supposed that coalloying of formed phases can be taken place at complex saturation of steels by titanium and chromium.

(Ti,Cr)C phase are formed at coalloying. It result in microhardness of (Ti,Cr)C decreases. It connects with appearance of the added bonds as Ti-Cr, Cr-Fe being weaker than bond like Ti-Ti and Ti-Fe. Atomic bonding of complex carbides can be increased due to added impairment of crystal lattice.

A microbrightless is decreased on 10-15 % simultaneously with a microhardness of (Ti,Cr)C phase lowering. Grain structure decrease influences on the microbrightless decrease a great extent.

The results of the studies performed shoved that applying of the coatings permits to decrease a corrosion rate of the 20, 45, Y8A steels in the solutions of sulphuric and nitric acids. The complex saturation of steels by the above elements gives rise to an inhibition in the cathodic reaction rate of the corrosive processes. It leads to a minor effect of steel dissolution in the active area, and it leads to a noticeable inhibition in the area of its passive state. At the high anodic polarization the steel re-passivation appears due to dissolution of the chromium. An increase in the effectiveness of the protective action of coatings is reached by a way of introduction of the corrosion inhibitors into the aggressive medium.

Oxidation of the pesticide atrazine at oxide electrodes

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Almost every stage of pesticide use involves the formation of pesticide waste, which contains substances that are strictly controlled by regulatory bodies. It is argued that there is a need for the development of treatment systems that can be used by small-scale users or at least as a mobile treatment system that can be shared between various users. A relatively unexplored treatment method for pesticide waste is electrochemical oxidation. Of the possible electrode materials, dimensionally stable anodes (DSA) have been widely studied for use in the oxidation of a variety of organic compounds, however, to the best of our knowledge, no published work deals with the electrooxidation of pesticides at DSA materials.
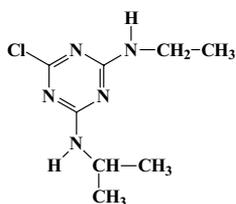
(Left) Fig. 1: Structure of the herbicide *Atrazine*.

(Right) Fig 2: Variation of atrazine concentration with time for electrolysis at 40 mA cm^{-2} in diferent electrolytes.

This paper presents the study of a prospective electrochemical treatment of atrazine (Fig. 1), a widely used a triazine herbicide, using a $Ru_{0.3}Ti_{0.7}O_2$ DSA anode ($\phi = 1.56$ cm^2). Experiments wer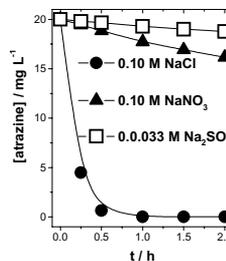e performed in a single compartment glass cell and the effect of using different supporting electrolytes (NaCl, NaOH, NaNO$_3$, NaClO$_4$, H$_2$SO$_4$ and Na$_2$SO$_4$), for galvanostatic electrolysis at 40 mA cm^{-2}, is discussed. The effects of varying the concentration of NaCl, the current density (10 to 120 mA cm^{-2}) and the solution temperature on the efficiency of the electro-oxidation process are presented. Additionally, a comparison of different electrode materials (Ti/Ir$_{0.005}$Ru$_{0.005}$Sn$_{0.99}$O$_2$ and Ti/Ir$_{0.01}$Sn$_{0.99}$O$_2$) is made.

The results demonstrate that the electrochemical removal at 40 mA cm^{-2} of atrazine is pH-dependent in electrolytes where no species (e.g. Cl$_2$, ClO$^-$) that results in oxidation in the bulk of the solution, is formed. In such electrolytes, the removal of atrazine (Fig. 2) and total organic carbon (TOC) is limited. In the presence of NaCl, atrazine removal is observed to rapidly reach completion, independent of the NaCl concentration. On the other hand, TOC removal is directly dependent on NaCl concentration, with 0.10 mol L^{-1} NaCl (highest concentration used) giving the best results. Increasing the current density results in a maximum level of TOC removal at 60 mA cm^{-2}. The use of Ti/Ir$_{0.005}$Ru$_{0.005}$Sn$_{0.99}$O$_2$ and Ti/Ir$_{0.01}$Sn$_{0.99}$O$_2$ indicates that there is little advantage in using these materials over the Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode.

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Electrochemical treatment of Cu(II)-complexed Humic acid

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The presence of humic acid (HA) in drinking water is of considerable concern, complicating treatment procedures and even leading to the formation of carcinogenic compounds. In addition, HA presents a strong coloration and is known to complex with metal ions and may cause microbiological corrosion in pipelines.

This paper presents the study of the degradation of commercial HA (100 mg/L) complexed with Cu^{2+} (10 mg/L). The simultaneous degradation of humic acid with Cu^{2+} removal was performed at different current densities using a filter-press cell with a $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode and a stainless steel cathode. All galvanostatic electrolyses were performed at pH = 5 and NaCl (0.05 M) was used as the supporting electrolyte. Electrolyses were performed with and without a membrane separating the cathodic and anodic compartments of the cell. The effects of different types of membrane (anionic and cationic) were also investigated. The products formed were monitored by liquid chromatography (HPLC) and UV-vis spectroscopy and the concentration of Cu^{2+} monitored by atomic absorption spectroscopy (AAS). Initial cyclic voltammetry (CV) investigations of the Cu-HA system were performed using a Pt electrode.
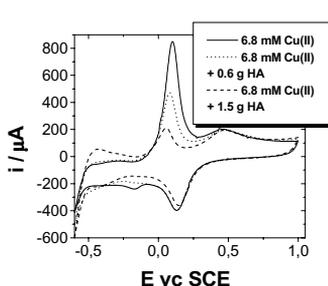
(Left) Fig. 1: VC profile of Pt in the presence of AH, with the addition of Cu(II),

(Right) Fig 2: Variation of UV profile during electrolysis (50 mA cm^{-2}) of Cu-complexed HÁ using an anionic membrane.
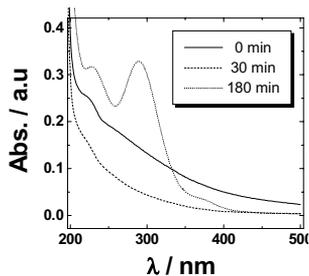
Cyclic voltammetry investigations indicate that the Cu^{2+} in solution is rapidly complexed with the addition of AH to the electrolyte (Fig. 1). For galvanostatic electrolysis at 50 mA cm^{-2}, the results obtained demonstrate the efficiency of the electrochemical process for the removal of the dark coloration of AH-containing solutions in all instances. Under all the conditions employed, the formation of solid residues was not observed. Degradation with and without a membrane resulted in different products and efficiencies. When an anionic exchange membrane (IONAC – Fig. 2) was used, the oxidation of Cu-complexed humic acid, followed by the subsequent reductive removal of Cu(II), the highest efficiencies were observed. The rapid removal of HA and the color is probably due to the formation of Cl_2 at the anode and the subsequent formation of hypochlorite (⁻OCl) in solution (peak observable in Fig. 2 at. ~300 nm). Overall, the results demonstrate that the simultaneous removal of humic acid and complexed Cu(II) is possible, reaching up to 90% Cu(II) and 100 % colour removal, depending on the applied conditions.

Removal of heavy metal ions from waste waters using electrodeposition - ion exchange coupled methods

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Electrochemical Engineering & Technology

The actual environmental legislation imposes extremely low values for the concentration of heavy metal ions (HMI) in waste waters. In order to remove and recover HMI, modern and efficient methods should be used [1, 2]. In this context, in the present work we propose a coupling between the electrochemical and ion-exchange methods for HMI removal from waste waters.

Previous results [3] concerning the electrodeposition of Cu from synthetic neutral diluted solutions confirmed that the efficiency of this method decreases significantly when the Cu^{2+} ions concentration becomes very low. The use of an ion-exchange preliminary step allows an efficient preconcentration of Cu^{2+} ions (over 90 % recovery of initial amount of Cu^{2+}, even if an unselective ion-exchanger was used). Moreover, the highly concentrated acid used during the elution step increases the solution conductivity, diminishing the electrochemical reactor (ER) voltage.

The experimental set-up for the electrodeposition tests includes a home-made cylindrical ER equipped with a cylindrical working electrode of reticulated vitreous carbon and a concentric cylindrical sieve of lead (with 1% Ag), acting as a counter electrode. Potentiostatic measurements at room temperature were performed using a computer controlled potentiostat. The electrolyte solution (1 g L^{-1} Cu^{2+}, 25°C) was recycled with a centrifugal pump and the concentration of copper ions was estimated volumetrically. An example of data evaluated during the cathodic extractions of Cu^{2+}, performed in potentiostatic conditions (E_W = -0.600 V / Ag/AgCl KCl_{SAT}) is presented in the following table.

Time (min)	Q (C)	$[Cu^{2+}]$ (ppm)	ER voltage (V)	Current efficiency (%)
11	195	609	2,29	81,1
22	187	324	2,27	55,6
33	151	130	2,27	46,9
45	117	16	2,27	35,5

The results showed that it is possible to decrease the Cu^{2+} concentration with one order of magnitude, preserving a reasonable current efficiency.

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Symposium 5 - Poster

Electrochemical Engineering & Technology

Preparing Ionic Liquids for Electrolytes

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Our main focus is on preparation and characterisation of novel ionic liquids and their cationic and anionic precursors. After screening over a wide range of possible candidates we have been developing different routes of preparation to find the best methods for cost-efficient synthesis and obtaining high quality products. The substances are tested for suitability as electrolytes and organic solvents.

Most of synthesis undertaken utilises similar basic types of chemistry, but the routes for preparation of ionic liquids are far from being exhausted. Optimum yields and product purity can still be improved by choosing the right pathways. The cationic precursors are prepared by quaternisation reaction with haloalkanes or dialkylsulphates. The ionic liquid of interest is subsequently formed by anion exchange via anion metathesis with alkaline salts. The cation can also be transformed into the hydroxide and the ionic liquid is prepared by a corresponding acid-base reaction. Our work concentrates on nitrogen based ionic liquids such as ammonium, imidazolium, pyrrolidinium, pyridinium and piperidinium to ensure a compact study.

In the scope of this conference we aim to present our data on electrochemical stability by determining the electrochemical windows via cyclic voltammetry. Especially ammonium type ionic liquids will be presented and data of other nitrogen containing species will be set in relation. The chemical structures of ionic liquids shown are manifold: residues attached to the cationic part are simple alkyl chains or aromatic rings, anions are either of inorganic or organic origin and hydrophilic or hydrophobic by nature. Altering the structure and composition of cation and anion alters thermal- and electrochemical stabilities: the cathodic limiting reaction is determined by the cations reduction, the anodic limit is set by the anions oxidation respectively. Electrochemical and thermal data will be presented in respect to the chemical composition of the corresponding ionic liquids.

Electrochemical oxidation in the presence of halides at BDD electrode

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Abstract

In a previous work, the influence of halides in the anodic oxidation of oxalic acid (OA) was studied [1]. These experiments were initially carried out at a Pt electrode in alkaline media, where a quite slow electro-oxidation was found in the absence of any mediator. However, in the presence of a halogen salt, the rate of the electrochemical incineration is significantly increased, following the order $F^- \geq Br^- > Cl^-$. To further enrich the research, investigations were carried out at boron-doped diamond (BDD) electrode in presence of halides. The case of BDD electrode is interesting, in that the very poor adsorptive ability of their surface and their great stability toward oxidation allow the reaction to take place with reactant and intermediates in a non-adsorbed state. The OA anodic oxidation experiments were carried out in the presence of 5 g dm^{-3} of halides in the solution and performed under galvanostatic conditions at 300 and 600 A m^{-2}. The OA incineration at the BDD electrode is significantly fastened by the presence of a halogen salt in solution; interestingly, the mediated process does not depend on applied current density. Based on the results, bromide was selected as a suitable mediator during OA oxidation at BDD. Br^- primarily acts in the volume of the solution, with the formation of strong oxidants; while Cl^- action shown lower improvements in the OA oxidation rate at BDD respect to Pt electrode [1].
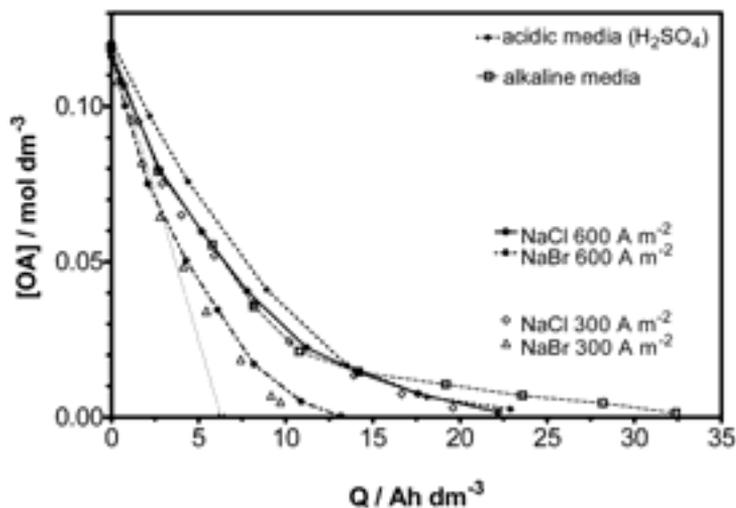
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Elaboration of a chemical decontamination technology: preliminary results

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In the VVER-type pressurized water reactors, various versions of the the so-called AP-CITROX method (AP: alkaline permanganate, CITROX: citric and oxalic acids) have been widely used for the chemical decontamination of the of steam generators (SGs). During the period of 1993-2001 chemical decontaminations of 24 SGs in the blocks 1-3 of the Paks NPP were carried out by a non-regenerative version of AP-CITROX technology, even in 2 or 3 consecutive cycles. Based on the above decontamination procedures a database of characteristic parameters was compiled. The analysis of these data and the explanation of the corrosion effects of the technology reveal that fundamental issues of analytical chemistry and corrosion science were not taken into consideration during the elaboration of AP-CITROX procedure, suggested in steam generator manual, and utilized at Paks NPP. The non-regenerative version of the AP-CITOX technology is not an adequate method for the chemical decontamination of any reactor equipments having large steel surfaces (e.g. SGs). As a consequence of the lack of the appropriate decontamination method, a R&D project focused on the elaboration of the required technology has been initiated in 2005.

The fundamental demands, which must be realized in the course of above R&D project, are as follows: (i) The decontamination method has to be suitable simultaneously for the effective removal of radionuclides (dose reduction) and for the conditioning of steel surfaces. (ii) The procedure has to provide optimal technological parameters for the homogeneous dissolution of oxide layers formed on the steel surfaces originating from both SGs never decontaminated (block 4) and SGs decontaminated earlier (blocks 1-3). The inner surfaces of the heat exchanger tubes of the latter SGs are covered by a special oxide layer ("hybrid" structure with a thickness of several micrometers). (iii) The method has to be able to utilize the technological background and knowledge evolved at Paks NPP in the course of the chemical decontamination. As a consequence of the long-established achievements, it is practical to develop a procedure based on the methodology of the AP-CITROX (or CORD) technology. It should, however, be noted that the comprehensive analysis of the risk factors, which may be emerged during the application of oxalic acid is unavoidable. In this talk, we will present a brief overview on the fundamental issues of the R&D project focused on the elaboration of the required technology and – based on the results of some recent studies in the fields of solution chemistry, electrochemistry and surface science - summarize the main characteristics of an optimal decontamination procedure.

Application of a rotating cylinder electrode reactor (rce) for the copper removal contained in rinsing water generated by a metal finishing industry

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This work shows a methodology that allowed removing copper by electrolysis contained in a rinsing water of a metal finishing industry (Cu(II) 0.866 gr dm^{-3}, Ni(II) 0.033 gr dm^{-3}, Cr_{total} 0.005 gr dm^{-3} at pH 1.86) in a RCE laboratory cell. This methodology consists in characterizing the mass transport for the Cu(II)/Cu process, using a model solution that contained Cu (II) 1,2 gr dm^{-3} in 167 gr dm^{-3} H_2SO_4, obtaining a Sh = $0.014Re^{0.913}Sc^{0.356}$ correlation. From this correlation a current density J = 1.7 A dm^{-2} at Re = 52925 was selected in order to make electrolysis in the rinsing water in batch mode of operation. The Cu(II) depletion was 0.013g dm^{-3} in twenty minutes of electrolysis, with a current efficiency of 90% and energy consumption of 0.002 KWh dm^{-3}. The treated water has the quality to be re-used in the same process of rinsing. The results obtained in this work showed the convenience of the use of RCE for in-situ cleaning of rinsing water, preserving the environment and diminishing costs with regard to the traditional process employed for this kind of industry.

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On the role of the current density in the electrochemical oxidation of aqueous wastes with diamond electrodes

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In mass-transfer-controlled direct-electrochemical processes, an increase in the current density leads to a decrease in the current efficiency. Thus, it could be assumed that a model based on mass-transfer considerations could be used to improve the efficiency of these processes. This kind of model can be used to obtain the optimum current density in every moment, and thus it can allow to work around maximum current efficiencies. One of these models was proposed by Gherardini et al., 2001 [1]. This model summarizes the results obtained in the conductive-diamond electrolysis of several organics [2,3] . It has been verified that this model fits well the experimental data for high current densities (higher than 150 A m^{-2}), although slight differences are observed for the electrolyses of compounds in which the cathodic processes have a marked importance. On the bases of theses results, and with the aim of obtaining a good procedure for operation of electrochemical wastewater treatment processes, a model-based predictive control system (MBPCS) has been developed. The goal of this operation procedure was to maintain optimum operating conditions in terms of maximum current efficiency (ICE value of 1). The performance of this control system has been validated in the treatment of an actual industrial wastewater (coming from a fine-chemical manufacturing factory) and also with synthetic wastewaters. A comparison with the galvanostatic operating mode in the electrolyses of both kinds of wastewaters was also carried out. The results obtained were not those expected, as it has been observed that the presence of salts in the waste leads to the generation of great amount oxidant reagents including persulphates, hypochlorite and hydrogen peroxide, depending on the waste composition and on the operation conditions [4]. This fact causes that the controlling mechanism in conductive-diamond electrolyses was not the mass transfer but the mediated oxidation by these reagents. In spite of this, the use of the MBPCS allows to improve the results obtained (in terms of energy consumptions) if they are compared with those obtained working in galvanostatic conditions.

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The electrochemical property and strain relaxation of strained Si studied by quantum chemistry calculation

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Strained Si wafers are fabricated by laminated Si layer on SiGe in order to induce lattice strain, which increases the carrier mobility and attract much attention as a key material for the ULSI devices[1]. From the results of our previous study using quantum chemistry analysis, it was suggested that strain condition of the Si surface changes surface reactivity[2]. In this study, the change of strain condition in terms of lamination layer thickness was investigated at atomic level by using Periodic Boundary Conditions (PBC) calculation with gaussian basis set. In addition, calculation of redox potentials of Si and strained Si were attempted in order to estimate the surface (electro) chemical properties.

The calculations were operated by using Density Functional Theory of Gaussian03. For the structural analysis, we used strained Si model as shown in Fig. 1. Si layers were wrapped on the fixed structure layer, whose lattice constant was extended.
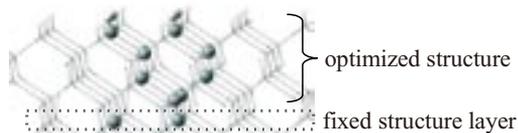
Fig. 1 The model of strained Si of PBC calculation

In order to calculate the redox potential, Nernst equation was applied with the calculated chemical potential values. As the model of SiO_2 and Si, we used cluster model ($SiO_2:Si_{17}O_{16}H_{36}$, $Si:Si_{26}H_{12}$). Lattice constant of Si model $a (= b)$ was extended with keeping bond length constant as shown in Fig. 2.
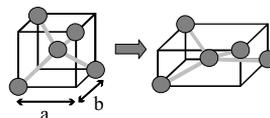
Fig. 2 The model to explain the strained condition of Si in this work

As a result of the geometry optimized calculation, it was indicated that the degree of strain was decreased layer by layer, from the initial (bottom) layer. In addition, the partial density of state of each layer was analyzed to investigate the effect of the strain for the electric structure.

In the calculation of the redox potential of Si, the estimated value was -0.58 V vs. NHE, and it was suggested that the potential was shifted to negative with an increase in the strain. It is suggested that the negative potential shift of strained Si was caused by an increase in Si HOMO energy due to the lattice strain.

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Influence of operative parameters on the electrocarboxylation of benzyl halides at silver cathodes

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In the last years many efforts have been devoted to the mechanistic and preparative aspects of electrocarboxylation of organic halides and pseudo-halides, some of them having led to pilot plants for industrial application, particularly for the production of anti-inflammatory drugs. However, under some circumstances (for example, when the carbon-halogen bond is not activated enough by the proximity of a π^* system, or because the organic moiety bears electrondonating groups, or when the halide is a poor leaving group as a chloride, *etc*.), the reduction of the halide may require too negative potentials, so that it becomes less attractive from an industrial point of view, and may even lead to several by-products resulting from the fact that carbon dioxide may be reduced concurrently. Furthermore, it has been shown that the direct reduction can lead to the passivation of carbon cathodes. Two catalytic ways have been proposed for allowing the electrocarboxylation at a much less negative electrode potential than that required for RX reduction. One consists in using a transition metal catalyst, so that now the process takes place at its facile overall two-electron reduction potential. The second alternative consisting in using redox catalysis has been, recently, widely investigated (1). In the case of direct processes, it has been recently shown in micro scale syntheses that the use of silver cathode allows one to work at more positive potential (2-3) even if the long term activity of the electrode surface at the preparative scale has still to be tested.

In the present work, the electrocarboxylation of 1-chloro, 1-phenylethane oxidation has been investigated on silver cathodes in undivided cells equipped with aluminium sacrificial anodes with the aim to evaluate and discuss the influence of different operative parameters on the performances of the process. Experiments were performed in two different systems: the system I was constituted by a bench scale batch undivided tank glass cell with cylindrical geometry while the system II was constituted by a continuous batch recirculation reaction system equipped with a filter press undivided micro flow cell ElectroCell AB.

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Influence of operative parameters on the electrochemical incineration of oxalic acid at boron-doped diamond electrodes

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The electrochemistry offers an attractive alternative to traditional methods for treating wastewaters containing organic compounds. In particular, synthetic boron-doped diamond (BDD), with its high anodic stability and wide potential window for water discharge, is a very promising material for the complete combustion of organics in wastewater treatment and water disinfection (1). Recently, different works have been devoted to the study of the electrochemical incineration of carboxylic acids on BDD since these compounds are very resistant to oxidation (2-4). In the present work the anodic oxidation of oxalic acid has been investigated on synthetic diamond film with both potentiostatic and galvanostatic alimentation with the aim to evaluate and discuss the influence of different operative parameters on the performances of the process. Experiments were performed both at high (0.2 and 0.3 M) and low (0.01M) oxalic acid concentration in two different systems: the system I was constituted by a bench scale batch undivided tank glass cell with cylindrical geometry while the system II was constituted by a continuous batch recirculation reaction system equipped with a filter press undivided micro flow cell ElectroCell AB. A drastic influence of the potential, in the potentiostatic experiments, and of current, in the galvanostatic ones, on the process was observed both at high and low concentration of the acid. The influence of flow dynamic regime, of temperature and of the electrolyte composition was, furthermore, investigated.

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Electrochemical Kinetics of Nitrobenzene on Pt Micro-disk Electrode in Aprotic Medium

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The electrochemical reduction synthesis of aromatic phenol compounds plays an important role in the field of organic electrochemical synthesis. In this paper, using dimethylformamide (DMF) and tetrabutyl ammonium perchlorate (TBAP) as solvent and supporting electrolyte in aprotic medium, the electrochemical kinetics of nitrobenzene on Pt micro-disk electrode was investigated.
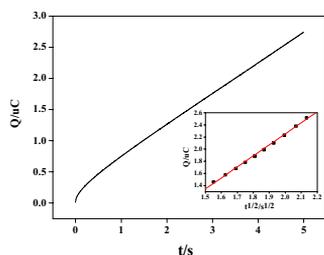
Fig.1 Charge-time curve for chronocoulometry with 10 mM NB in DMF solution.
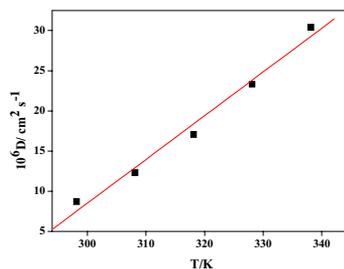
Fig.2 Diffusion coefficients of NB in DMF at different temperatures

In order to quantitative estimate the diffusion coefficient, the electrode reaction should be controlled by diffusion process where the current is direct proportion to the square root of diffusion coefficient. The applicant condition is suitable for Anson equation. Fig.1 shows the charge-square root of time curve for chronocoulometry. Based on the results of the asymptote equation as $Q=-1.3805\times10^{-3}+1.8131\times10^{-3}t^{1/2}$, the diffusion coefficient of NB in DMF at 298.15 K is calculated to be 8.71×10^{-6} cm^2·s^{-1}. The diffusion coefficients of NB in DMF at the different temperatures between 298.15 K and 338.15 K by chronocoulometry are shown in Fig.2. These results suggest that the diffusion coefficient increased with the increasing temperature with the reason of accelerative thermal activity of NB in DMF.

The different step potentials are carried out in our experiment, which are in the ascending part of CV curve. The forward rate constants (k_f) of NB in DMF at different potentials at 298.15 K are obtained. With the increasing electrode surface potential, the value of k_f increased. When the potential is changed from -1.06 V to -1.14 V, the value of k_f increased from 2.51×10^{-5} m·s^{-1} to 3.93×10^{-5} m·s^{-1}, accordingly. The values of k_f at different potentials at other temperatures are also calculated by the same method. The relationship between k^0 and k_f is described. The values of k^0 of the different temperatures are evaluated. Activation energy of electron transfer process can be calculated by Arrhenius equation. The lnk^0 versus T^{-1} dependence is plotted. The pre-exponential factor (A) and the activation energy (E_a) are calculated to be 2.38 m·s^{-1} and 11.3 kJ·mol^{-1}, respectively.

Density functional theory study on adsorption and hydrogen atom elimination reactions of hypophosphite for electroless deposition processes

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Hypophosphite ion ($H_2PO_2^-$) is widely applied as a reducing agent for electroless deposition process to deposit metals, such as Ni, Co, etc. However, it does not work for the deposition of Cu, since the Cu surface does not have catalytic activity for the reaction of $H_2PO_2^-$. In the present work, the origin of the catalytic activity is investigated by theoretical calculations, which have a capability to estimate the elementary reaction step of the oxidation mechanism of $H_2PO_2^-$ [1]. Energy profiles of every step such as adsorption and hydrogen atom elimination reactions were calculated by Density Functional Theory (DFT).

In the case of the adsorption step prior to the oxidation reaction, calculated results indicated that the adsorption energy of $H_2PO_2^-$ on the Cu surface is smaller than that on the Ni surface. It is suggested that the Cu surface is unfavorable for the following oxidation reaction of $H_2PO_2^-$, compared with the Ni surface.

Figure 1 shows the energy profiles for hydrogen atom elimination reaction on the metal surface, which is considered as the rate-limiting step, indicating that the energy barrier on the Cu surface is the highest among other metal surfaces.

These results suggest that the catalytic activity of the metal surface is originated from the energy change at each reaction step, such as the small adsorption energy and the high energy barrier on the Cu surface.
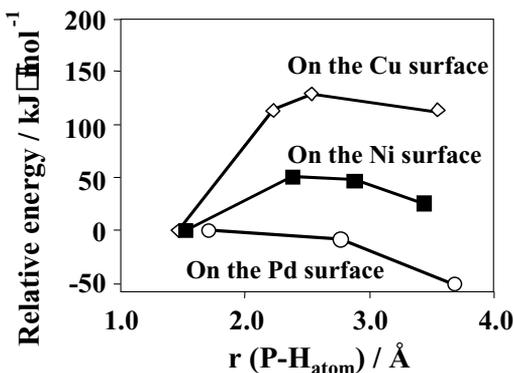

Fig. 1. Relative energy diagrams for hydrogen atom elimination reaction of $H_2PO_2^-$ on the Cu surface, on the Ni surface, and on the Pd surface.

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Effects of Drive Voltage and Electrode Material on the Performance of Polymer Light-Emitting Electrochemical Cells

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Polymer light-emitting electrochemical cells (LEC) are of potential interest for various display applications due to attractive advantages such as low turn-on voltage, high quantum efficiency and high brightness. Such advantages are directly related to the unique operational mechanism of LECs, which involves an initial in-situ electrochemical doping of the conjugated polymer at the electrode interfaces (p-type at the positive electrode and n-type at the negative electrode) followed by the formation of a light-emitting p-i-n junction in the bulk of the active material.

In this study, we have utilized planar LECs with extremely large interelectrode gaps of 1 mm to investigate the effects of different electrode materials (Al and Au), position of the electrodes (bottom and top contact configuration), and drive voltage. The active material of our LECs consisted of three components: (i) an electroactive and luminescent conjugated polymer poly(2-methoxy,5-(2'-ethylhexyloxy)-p-phenylene vinylene) (MEH-PPV) (ii) an ion-conducting polymer poly(ethylene oxide) (PEO), and (iii) an alkaline salt XCF_3SO_3 (X = Li, K and Rb). The LEC devices were prepared in Ar-filled glove boxes and all device characterization was performed in a cryostat under vacuum (<10^{-3} Pa) at 360 K. Images of doping progression and light-emission were recorded using a digital camera under UV illumination.

We have made the following observations: (i) Al-electrode devices exhibit a more balanced doping progression than Au-electrode devices, which results in a more centered emission zone (and p-i-n junction) in the interelectrode gap for Al-electrode devices, (ii) Au-electrode devices are sensitive to whether the electrodes are in a top or bottom contact configuration, and we find that top contact devices exhibits a lower maximum current and that the emission zone is positioned closer to the negative electrode, (iii) a higher drive voltage generally allows for a higher maximum current and brightness, but the quantum efficiency (defined as light intensity divided by current) is lower, and (iv) the emission zone becomes more centered in the interelectrode gap at higher drive voltages, as the larger n-type doping concentration appears to decrease while the lower p-type doping concentration is essentially constant.

We are also currently investigating a number of other characteristics (e.g., rectification ratio, turn-on voltage, frozen-junction behavior) of these extremely wide-gap LEC, and the results of this ongoing study will also be presented.

Highly nonlinear rate & transfer phenomena in chemical and electrochemical systems

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Begin of abstract textFor chemical and/or electrochemical systems we display nonlinear kinetics that describe fluxes of matter, energy and electric current in intense transport or rate processes undergoing in chemical and electrochemical reactors. The traditional mass action approach to rate equations is compared with a new one represented by the so-called potential action formalism in which rate or transfer kinetics are expressed in terms of potential-type quantities instead of concentrations. The essence of the description is a rate equation for an elementary chemical step, with two competing fluxes, forward and backward. By analysis of two competing directions in elementary chemical or transport steps we achieve extended equations of nonlinear kinetics of Marcelin-Kohnstamm–de Donder type that contain terms exponential with respect to the Planck potentials and temperature reciprocal.

$$r_j = r_j^f - r_j^b = r_j^0\left(\exp(-\sum_i \nu_{ji}^f F_i^f) - \exp(-\sum_i \nu_{ji}^b F_i^b)\right) \qquad (1)$$

We regard kinetics of this sort as potential representations of a generalized mass action law that includes effect of transfer phenomena and external fields. We also consider the physics of these kinetics closely and far from equilibrium and point out the significance of nonlinear symmetries and of a generalized affinity. As implied by equation (1), the kinetics is in terms the potential quantities rather than concentrations. Potentials $F_i = (-\mu_i/T, 1/T)$ in (1) are partial derivatives of the entropy with respect to the extensive variables appearing in the (Gibbs) equation for the entropy differential. In fact, the set of F_i comprises all Gibbs intensities: Planck potentials and temperature reciprocal. In the kinetic regime (fast transport; $F_i^f = F_i^b = F_i^{eq}$) the classical chemical kinetics is recovered in the Marcelin-Kohnstamm-de Donder form. On the other hand, in the diffusive regime (fast reactions) the system behalves typically as a nonlinear diffusion system.

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Preparation and electrocatalytic performance of Pt deposits prepared on glassy carbon by an electrodeposition / electroless deposition two-step process

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Electrodeposition of precious metal catalysts on electrode substrates provides accurate control of catalyst loading even for very small deposited quantities but it requires large solution volumes and relatively high concentrations. Most electrocatalysts are thus formed by chemical methods, usually impregnation of the support with the metal ion followed by reduction. In this work we present results of a two-step method for Pt deposition on glassy carbon (GC) electrodes: electrodeposition of metallic Cu or Pb onto glassy carbon, followed by spontaneous replacement of the Cu or Pb deposits by Pt upon their immersion in a small volume of dilute chloroplatinate solution. The resulting Pt(Cu)/GC and Pt(Pb)/GC electrodes were tested for their catalytic activity in the hydrogen evolution, oxygen reduction and methanol oxidation reactions. The effect of Cu or Pb electrodeposit thickness as well as that of substrate treatment (anodisation) was also studied. *Figure (A)* shows an SEM micrograph of a typical Pt(Pb)/GC deposit and *Figure (B)* its voltammetric response to methanol oxidation. It has been found that Pt deposits prepared on a Pb electrodeposited layer show better catalytic activity for methanol oxidation than smooth Pt (both per geometric and real electrode area).
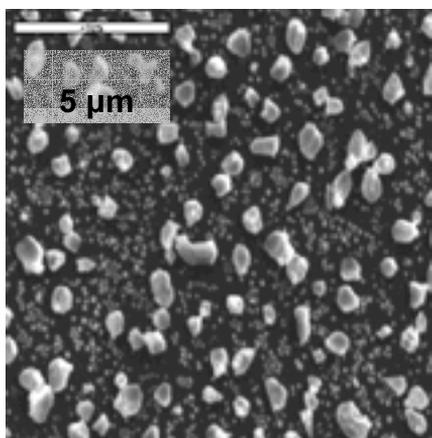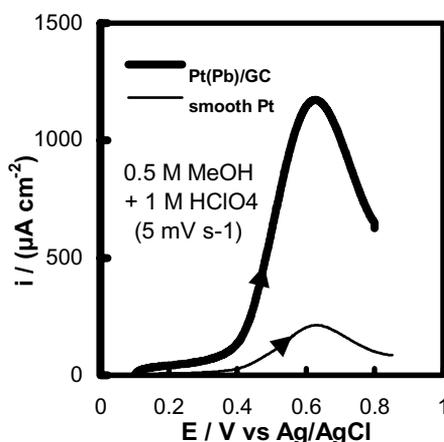
| *Figure (A)* | *Figure (B)* |

Photoelectrochemical degradation of oxalate and malachite green at electrosynthesised TiO$_2$/WO$_3$/stainless steel electrodes

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The activity of photocatalyst films supported on conducting substrates can be enhanced by the application of a positive bias on the catalyst that minimises recombination of photogenerated holes and electrons. In this work, bi-layer WO$_3$/TiO$_2$ coatings have been prepared on stainless steel 304 (SS 304) substrates, by potentiostatic cathodic electrosynthesis from acidic aqueous solutions of peroxytungstate and titanium oxosulfate [1, 2]. The deposits had a particulate, cracked mud, structure characterised by 5-20 μm large patches *(Figure A)*. Photovoltammetry and photoamperometry of small composite TiO$_2$/WO$_3$/SS 304 electrodes under UV or visible light illumination has recently proved [2] the feasibility of using practical and economical SS 304 substrates (since the coating protects them from corrosion) and confirmed high photocurrents at the bi-component electrodes (due to the presence of WO$_3$ which reduces recombination rates and shifts light absorption to the visible range). We report here the photodegradation of oxalate (a model organic) and of malachite green (MG; a typical dye) at large TiO$_2$/WO$_3$/SS 304 photoelectrodes during bulk photoelectrolysis from their 10^{-3} M and 10 ppm solutions respectively. At +0.4 V vs. Ag/AgCl, 21.4% (or 19.8%) removal of oxalate and 85% (or 66.8%) removal of MG *(Figure B)* was observed after 2h of UV (or vis) llumination.
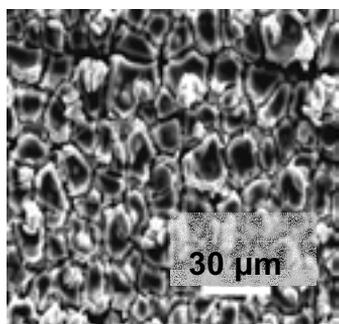
Figure (A)
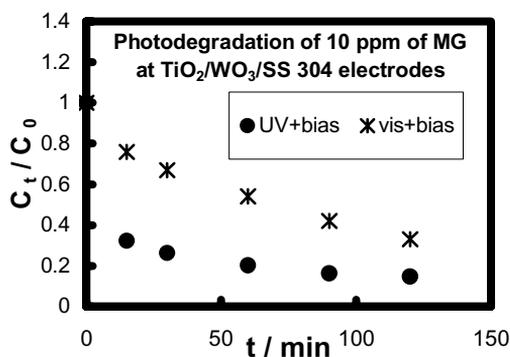
Figure (B)

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Influence of the Reactor Configuration and Operation Conditions on Electro-oxidation of the Spent Dyeing Bath

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There is an increase of the interest in unconventional methods of purification of industrial wastewater, particularly when biologically recalcitrant pollutants are present Among these advanced oxidation processes, electrochemical technologies gain in popularity as, under ideal conditions, they do not require addition of chemical reagents and, hence, can be considered as "environmentally friendly" methods. The paper presents the results of a study on application of the electrochemical reactor for treatment of synthetic textile wastewater. The kinetics of decolourisation, which was chosen as the priority of the process, was followed for a single-cell and a membrane electrochemical reactors, equipped with Ti/Pt-Ir anodes (10^{-2} m^2 area). The reactors were operated under different conditions; in particular the influence of the temperature, type and intensity of stirring and current density are investigated. The experiments were performed under galvanostatic conditions, varying the temperature in the rage 10 to 60°C ± 1 and changing the current density within the interval 100 and 800 A/m^2. Different hydrodynamic conditions were provided by pumping by means of a peristaltic pump (Watson Marlow Mod. 313 F/D), equipped with one or two heads, operating with flow rates in the range 1.6×10^{-7} to 2.40×10^{-5} m^3 s^{-1}. Moreover the possibility of the cathodic reduction of O_2 to produce H_2O_2, which could react with the dye, influencing its overall conversion during electrolysis, was studied. In these experiments the solution to be electrolysed was enriched with oxygen using a Sodemas^R device, and obtaining a fine dispersion of the gas in the liquid phase and the dissolved oxygen concentration exceeding the saturation value. The reaction of colour removal proved to follow the second order kinetics and depended on the type of stirring, temperature (Fig. 1) and current density (Fig 2).
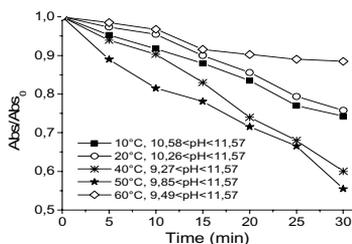
Fig. 1. Anodic compartment: influence of temperature on colour removal.

Fig. 2. Single-cell reactor: colour removal for different current densities.

The regime which controlled the reaction was defined from the Hatta number: Ha=$(k[R]D_{Cl2})^{1/2}/k_m$, where k - reaction rate constant (mol^{-1} m^3 s^{-1}), [R] – initial concentration of the dye (mol m^{-3}), k_m - mass transfer coefficient (m s^{-1}), D_{Cl2} - diffusivity of [OCl$^-$] (m^2 s^{-1}).

Role of dimensional stable anodes in textile wastewater treatment

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In this work two types of Dimensional Stable Anodes (DSA) one coated with Ir and another with a mixture of Ir-Sn provided by ELTECH Systems Corporation, have been used in treatment of synthetic textile wastewater corresponding to a color bath for proteinic fibres (acid orange 24) and another for cellulosic fibres (blue indigo). Both baths have been prepared according to industrial formulations. In order to get an insight of how the removal is affected by the presence of surfactant agents, the electrolytic reactions were conducted in baths which include/exclude them.

Obtained results show that:

A) In absence of surfactant agents, the anode made of Ir provides 95% color removal ; while the Ir-Sn gives a 75% removal. In presence of surfactant agents, color removal is very similar for both electrodes, reaching up 75%.

B) Although color removal is good, the chemical oxygen demand (COD) exhibits an irregular response with highs and lows. Based on COD results, it is observed that the Ir acts decreasing the COD in 30%, while the Ir-Sn increases the COD up to 250%.In presence of surfactant agents COD results exhibit a " regular pattern", in which the Ir-Sn shows a COD increase of up to 20%, while the Ir shows a COD reduction of about 40% in the first hour.

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Electrochemical Engineering & Technology
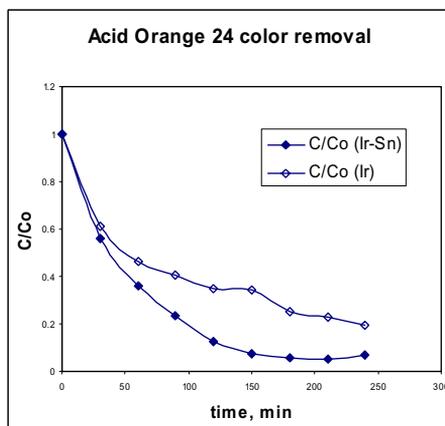
The limiting currents of hydrogen evolution in aqueous electrolytes

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In electrochemistry the large attention was paid to the cathode hydrogen evolution (CHE) from the aqueous electrolytes, because this process is one of the most widespread and important for majority of electrochemical technology. However the issue is under discussion till now, whether the limiting current of CHE can be practically achieved. Some electrochemists consider that limiting current of CHE can not be achieved in general, but they may not take into account schemes of CHE and type of particles hydrogen appears from. In addition the concepts of «protons limiting current» and «water limiting currents» often do not differentiate. «Protons limiting current» can appear due to slow delivery of protons (hydroxonium ions) to the electrode surface, and «water limiting currents» – due to slow delivery of molecules of water to the electrode surface. Both in first and in second case the product of cathode process is hydrogen regardless different schemes of electrochemical. In first case cathode process runs in accordance with a scheme

$$H_3O^+ + e = 0, 5\ H_2 + H_2O \tag{1}$$

And in the second case – in accordance with a scheme

$$H_2O + e = 0, 5\ H_2 + OH^- . \tag{2}$$

The possibility of achieving CHE limiting current in process (2) in common water solutions of electrolytes is extremely low. The reasons for this are: - concentration of water molecules in such solutions is about 50 mol/l; - registrations of limiting current in such electrolyte mixtures becomes complicated because of gas bubbles formation. According to [1], the limiting currents of CHE in process (1) can be practically obtained only in acid solutions with pH range $(2 \div 4)$. For our opinion, bottom limit of pH range, at which the limiting currents are obtained, can be substantially changed to smaller pH values. To prove this thesis special experimental works were provided with platinum electrodes at the temperature of 20 ^{0}C. The working surface of such electrodes was 0,2 cm^2. Polarization curves were obtained at the rate of potential changes 1,0 mV/s. During work with dilute solutions of sulphuric acid the total concentration of sulfate ions (1, 0 mol/l) was supported by addition of sodium sulfate. It is possible to select areas with a practically unchanging current on parts of obtained polarization curves, which corresponds to delivering of hydrogen ions. We consider these areas as the areas of limiting current. Polarization curve with limiting currents are reliably experimentally reproduced in very acid solutions (for example, with pH 2,54, pH 1,44 and pH 0,3). Thus limiting currents were revealed in solutions with the concentration of protons far higher, than it was forecasted on the basis of calculations (pH 2 in [1]). The range of potentials with limiting current can be spread for several hundreds of milivolts.

1. Stezerjanskiy E.A. // Russian Electrochemistry.- 2004.- V.40, №6. – P. 759-763.

Model of secondary current distribution in the segmented thin-gap flow-through reactor for 4-methylanisole methoxylation

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The aim of this study is to provide a tool for the optimisation of the microstructured laboratory electrochemical cell with segmented anode. At the same time a deeper insight into the influence of the cell microstructuring on its performance, especially the current density distribution, will be attained. To fulfill this task, secondary potential and current density distribution inside the cell has to be calculated for various sets of input parameters.

In order to keep relevance to the industrial praxis, the electrochemical 4-methoxybenzaldehyde (4-MBA) synthesis has been chosen as a model system. 4-MBA is an important intermediate in the production of semi-synthetic antibiotics. Its synthesis is based on the anodic methoxylation of 4-methylanisole (4-MA). The kinetics of this electrode reaction is unknown. Therefore it has been determined experimentaly.

The electrode reaction kinetics of 4-MA methoxylation was studied in the three-electrode arrangement. RDE made of glassy carbon was employed as a working electrode. The 0.8 mol dm^{-3} NaClO$_4$ solution in methanol served as an electrolyte. The concentration of 4-MA was kept below 0.01 mol dm^{-3}. It was found that the reaction kinetics is well described by the Tafel type equation. The rate constants of the methoxylation reactions occurring on the glassy carbon electrode as well as the diffusion coefficients of the species involved were determined. Since the equilibrium redox potential of this reaction is not known, it was set arbitrary as 1.35 V vs. SCE. Kinetic equation obtained has been implemented into the mathematical model of the segmented reactor.

The kinetic equation proposed within this study has proven to fulfill requirements of the model designed. The calculations performed have suggested that the interelectrode gap of 0.1 mm introduced in order to reduce the energy losses caused by the electrolyte resistance leads at the same time to an important reduction of the edge effects. It supports, together with thin insulation strips between the anode segments, the homogenous current distribution across the electrodes. The presented model represents a good base for the future extension to a complex model considering tertiary current distribution and an effective cell scale-up.

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Electrochemical Engineering & Technology

Electrochemistry for New Generation of Aluminum Production Processes

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The original data are reported on the electrochemical behaviour of metals and binary alloys in cryolite-alumina melts of 1.3 – 2.7 cryolite ratios. The redox potentials of (metal/metal ion) systems are estimated and discussed, as well as metal oxide and metal aluminate solubilities. XRD analysis of solid degradation products formed under various polarization modes and product distribution along metal/film boundary are reviewed in the context of self-formation of the protective layers of satisfactory conductivity on metallic anodes [1]. Some original data for ceramic [2] and carbon anodes are involved for comparison. The results are reported related to the prospects of in situ deposition of various solid protective coatings directly from the bath under usual operating modes. The disadvantages and profits resulting from low-temperature aluminium production from strongly acidic melts are summarized.

The report is focused on the basic problems of melt electrochemistry related to electrometallurgy, as well and their fast application for solving current and more distant technological problems, like environmental perfection and decrease of energy consumption.

1. E.V.Antipov, A.G.Borzenko, V.M.Denisov, A.Yu.Filatov, V.V.Ivanov, S.M.Kazakov, P.V.Mazin, V.M.Mazin, V.I.Shtanov, D.A.Simakov, G.A.Tsirlina, S.Yu.Vassiliev, Yu.A.Velikodny, TMS-2006 Proceedings; accepted to Light metals.
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Electrochemical investigations of the imidazolium based ionic liquid containing dicyanamide anion

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Imidazolium based room temperature ionic liquids containing dicyanamide anions are hygroscopic and are completely water miscible. Smaller size of anion helps them to have low viscosity. They have stable thermal window [1-3].

Electrochemical behaviour of 1-butyl-3-methylimidazolium dicyanamide, IL was investigated using different working electrodes namely Au, Pt and GC. Electrochemical window of 3V vs Pt quasi reference electrode was observed.

Electrochemistry of chloride salts of Cu(I) and Cu(II) was studied in the 1-butyl-3-methylimidazolium dicyanamide, IL

Experimental results to discuss the electrochemical behaviour of 1-butyl-3-methylimidazolium dicyanamide and to show the redox behaviour of Cu(I) and Cu(II) and the electrodeposition of Cu on different electrodes will be presented.

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Electrochemical investigations of the Cu(I) and Cu(II) ions in trialkylimidazolium based ionic liquid

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1,2,3-trialkylimidazolium based ILs have been found more electrochemically stable then 1,3-dialkylimidazolium based ILs where lower reduction potential has been attributed to the H(2) acidity. [1,2]

Electrochemical investigations of chloride salts of Cu(I) and Cu(II) were performed in the 1-butyl-2,3-dimethylimidazoliumtetrafluoroborate, IL using different working electrodes. Experiments were performed outside the glove box maintaining the constant supply of dry argon gas inside the electrochemical cell.

Electrochemical results were reproducible and dense and well adhered deposits of copper were obtained on different electrodes. It was observed that comparatively better Cu deposits were obtained from Cu(I) than Cu(II).

Comparative redox behaviour of Cu(I) and Cu(II) ions and the electrodeposition of Cu on different electrodes will be presented.

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Electrochemical Engineering & Technology

Electrochemical investigations of the Pd(II) in an imidazolium based ionic liquid

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Electrochemistry and electro-deposition of Pd(II) was studied in the $BMMIBF_4$ and Pd complex, tetrakis(acetonitrile)palladium(II)tetrafluoroborate $[Pd[CH_3CN]_4(BF_4)_2$, was dissolved in the dried $BMMIBF_4$ for the purpose. Experiments were performed outside the glove box and EC cell was kept under argon blanket.

Quasi reversible cyclic voltammograms were obtained on the Au, Pt and GC working electrodes. Thin layers of Pd were deposited on brass and steel working electrodes. At -1.8V deposit layer had scattered Pd particles and at -2.0V fine grained structure were obtained. At -2.5V a thick black deposit layer was obtained but the deposit layer was weakly adhered to the substrate material and after several washings some parts of the deposit layer was peeled off (Fig.1c).

a   *b*   *c*
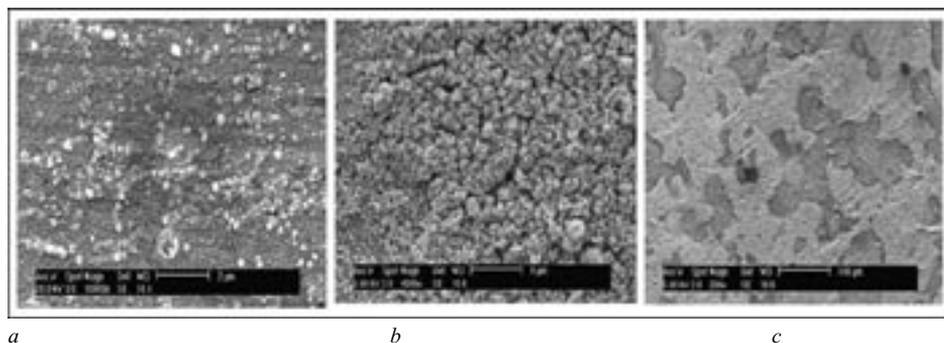
Fig.1 SEM micrographs of Pd deposits on brass,(90°C), through constant potentials of
(a) -1.8V for 80 minutes, (b) -2.0V for 80 minutes, (c) -2.5V for 80 minutes

Redox behaviour of Pd(II) ions and kinetics of electrodeposition process of Pd will be discussed.

Acknowledgements

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Electrochemical Engineering & Technology

Active chlorine formation in the electrochemical treatment of natural waters for disinfection

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The production of drinking water from natural waters necessitates the removal of numerous compounds such as inorganic species, humic substances and toxic micropollutants as well as the inactivation of microorganisms which may be pathogen. Different methods of drinking water disinfection are utilised, such as chlorination or treatment by chlorine compounds. Recent developments show that the trend is to use less chlorine, because of the problems caused by overchlorination, odour, by-product formation, transport and storage risks.

Advanced oxidation processes are considered to have great potential in this area. As it is well known, all the advanced oxidation processes (AOP) are mainly based on the oxidative capacity of OH° radicals originated from different sources. Anodic oxidation of water can be a good source of OH° radicals provided that a suitable anode material is selected.

When oxidation is performed at non-active electrodes such as boron-doped-diamond (BDD) or fully oxidised metal oxides (such as SnO_2 or PbO_2) oxidation of organic compounds occurs at the electrode/solution interface mediated by physisorbed (OH°) radicals from which oxygen can also be produced. Partial degradation of organic compounds can be also achieved by bulk reaction mediated by oxidising agents, generated at the electrode surface, the transfer of which, towards the solution bulk, is under mass transfer control.

OH radicals can also be responsible for the production of active chlorine by oxidation of chlorides which are always present in natural waters, therefore the formation of active chlorine when a natural water is treated by direct electrolysis must be studied.

In the present work the role of chlorides during the electrochemical treatment of waters was considered: the anodic reaction was investigated in the presence of low concentrations of chlorides (20-100ppm) at BDD anode. Experiments were performed using synthetic and real natural waters in undivided cells with different configurations: well mixed batch tank and plug-flow filter press reactor.

The effect of the cell configuration and its hydrodynamic behaviour, the applied current density and other parameters on the nature and concentrations of the oxidizing species detected in the solution bulk is presented.

S5·P-111

Modelling of the influence of gas evolution on mass transfer in electrochemical processes

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The study of electrochemically formed gas bubbles on an electrode surface and its influence on mass transfer are of great industrial importance. The formation of these gas bubbles can have several effects on the electrode behaviour that have to be taken into consideration. For example, if gas evolution takes place on the electrode surface, not only will it consume part of the current, it will also have an important effect on the local process parameters and current distribution. Although indispensable for reactor design and optimization of new and existing industrial processes, no general model has yet been developed to describe the influence of gas bubbles on mass transport. The aim of this study is to develop a quantitative model that describes mass transport in electrodeposition processes with simultaneous gas evolution.

Before the effect of gas evolution can be considered, a representative system has to be chosen in which it is possible to vary the contribution of the gas evolution reaction. The zinc deposition system with simultaneous hydrogen evolution was considered to be the best choice. According to the settings of the process parameters 2 to 65% of the total current is consumed by the hydrogen evolution reaction. A special reactor is designed which allows to study the hydrogen reaction under controlled hydrodynamic conditions.

This study is divided into two building blocks, namely an experimental part and a modelling part where the reaction mechanism and model parameters (rate constants, transfer coefficients and diffusion coefficients) are quantitatively determined. The kinetics of the zinc electrodeposition has been investigated by means of linear voltammetry. Also the interfacial pH is monitored during the electrodeposition process as this gives an important insight into the deposition mechanism.

Next a steady-state model for the zinc deposition mechanism in acid solutions will be proposed. Therefore the possibilities of the numerical simulation tool PIRoDE [1] and an analytical approach recently developed in our group [2], will be explored.

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Hydrodynamic and electrochemical characterisation of porous electrodes

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Internal recycling is very important for the industry, which tries to minimize its environmental impacts.

In order to treat dilute solutions containing metallic ions, porous electrodes (or 3-D electrodes) are used. The aim of the project is the designing of a flexible cell for directly treating effluents in industrial processes. With this method, the metal is recovered and the solution recycled. Potential applications of this cell are rinse water treatment in surface treatment industry and local wastewaters treatment in copper hydrometallurgy. To obtain a good flexibility, it is necessary to characterize and study the porous electrode's electrochemical and hydrodynamic behaviour.

The studied electrode consists of a stainless steel fibre network. The fibre's diameter is very small, between 8 and 20 microns.

The following parameters have been shown to have an influence on the faradic yield of copper electrodeposition from dilute solutions (figure 1): electrolyte flow velocity at the entrance of the porous electrode, concentration of the bath and intensity of the applied current. The correlation between dimensionless numbers ($Sh = A.Re^a.Sc^{1/3}$) for different porous electrodes was established.

The current distribution (under diffusion control) inside the porous electrode was also studied. After copper electrodeposition, the electrode was analysed by EDX in scanning electron microscopy. X-ray analysis made possible to obtain a cartographic distribution of iron (substrate) and copper on the electrode vertical section. The current distribution dependency with time of electrolysis is discussed.

The mathematical modelling of flow and current distribution within the porous electrode was established and compared with experimental results.

The electrode physical parameters effects and the hydrodynamics influence on its electrochemical behaviour enable us to optimise the use of this type of electrode for treating dilute solutions.
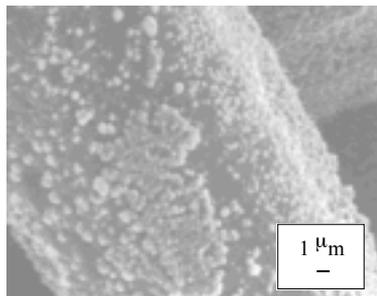
Figure 1 : copper deposit on 3-D electrode

Electrochemical codeposition of pmma particles with zinc

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Zinc matrix composite coatings with PMMA (polymethyl methacrylate) polymeric particles (326.8 nm mean size) were prepared by electrodeposition on low-carbon steel (316L) electrodes under galvanostatic, either stationary or pulse current, plating conditions. The electrolyte was a typical, for zinc electrodeposition, acidic sulfate bath thermostatically controlled at 50 ºC. Sodium lignosulfonate was added in the solution as an anionic surfactant, in order to prevent latexes aggregation and enhance the codeposition process. Mass transfer in the bath was controlled by a rotating cathode setup. The effect of bath pH, deposition current density and pulse electrolysis parameters on the morphology and texture of the as grown deposits was investigated by means of scanning electron microscopy (SEM) and X-ray diffraction.

According to high-resolution SEM imaging and subsequent electron probe (EDS) analysis the present procedure could be effectively applied to attain codeposition of PMMA particles anchored in the Zn matrix, their distribution depending on hydrodynamic, mainly, conditions. The volume fraction of PMMA in the solid film was determined gravimetrically after dissolution of the deposit in sulfuric acid and vacuum filtration. The estimates were compared to the particles' surface fraction as determined by SEM-mapping technique.

Optically smooth deposits were produced due to the leveling action of the surfactant, while the incorporation of polymeric particles led to texture modifications, as compared to single phase Zn electrocrystallized from additive free baths. Namely, a strong inhibition of the typical basal (00.2) texture, accompanied with preferential emergence of prismatic and pyramidal orientations was observed. Regarding the samples' morphology, the PMMA-induced inhibition was associated, in certain cases, to a network structure of needle-like Zn crystallites whose coherence could be controlled by varying the duty cycle of the current pulse. Low duty cycles resulted to open structured films, while higher ones led to structures with shorter intergranular distances, similar to deposits obtained by direct current electrolysis. An attempt was made to relate the verified microstructural features with the engineering properties of the coatings, in terms of corrosion resistance.

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Electrosynthesis and Physicochemical Properties of Composite Electrocatalysts Based on PbO$_2$

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There is a great interest in the improvement of lead dioxide as an anode material for use as an electrocatalyst with a high activity for oxygen transfer processes. In the present work we used some polyelectrolytes and surfactants as electrolyte additives for electrosynthesis of composite materials oxide-polyelectrolyte and oxide-surfactant. Mainly polyelectrolytes and surfactants inhibit the lead dioxide electrodeposition due to their adsorption on the PbO$_2$ coating with blocking some centers on the electrode surface for further reaction. It is interesting to note that both polyelectrolytes and surfactants are incorporated into the deposited lead dioxide forming a composite material. The additive content in the lead dioxide can change from 1 wt. % to 20 wt. % depending from the electrodeposition conditions and the electrolyte composition. The colloidal-electrochemical mechanism of the composite formation was proposed, which include electrochemical formation of oxide particles in the solutions volume, adsorption of polyelectrolyte and surfactants on the oxide particles, their electrophoresis to the electrode (for particles with negative ξ-potential) with further crystallization on the anode surface. It is important to note that in the presence of polyelectrolytes and surfactants submicro- and nano-crystalline coatings are formed. An examination of the XRD spectra shows that peak intensities generally decrease with increasing surfactants and polyeletrolytes content in the composite. This indicates that the grain size is smaller for the lead dioxide films in the composite materials. Difference in intensity provides sufficient evidence of the existence of an amorphous phase and it is a good agreement with SEM data. It was shown that electrocatalytic activity of the materials depends from nature and content of additive in the composites.

Investigations of Iron Disulphide Electrode Kinectics in Molten Salts

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In this work the measurement of the critical kinetics parameters of iron disulphide electrochemical reduction in molten chloride halides mixture was made. The metal sulphide cathode is being tested in new configurations together with several electrolytes especially molten salts in thermal batteries and organic polymers in hybrid / electrical vehicles [1]. Because of strict voltage requirements for thermal batteries, the most viable electrochemical system is FeS_2 with molten chloride halides [2]. This cathodic material has a very low environmental impact, is non-toxic and low cost, besides many mineral sources and synthetic form can be applied.

The applied methodology was the cyclic linear voltammetry at slow sweep rate (2 mVs^{-1}), ensuring quasi equilibrium conditions, in the range of 770 K. For the thermodynamical equilibrium the standard potential determinations for open circuit resulted 0.3306 ± 0.014 V (773 K) with respect to the Ag / AgCl reference. The cathodic transfer coefficient measured 0.48, indicating the reversibility of the electrode process and points at its possible application as secondary battery. The FeS_2 electrocatalytical behaviour was evaluated through the Tafel curves extracted from the voltammograms. The indicating parameter for this reaction spontaneity, the transfer currents, was measured to be $14.75 \pm 2.73 \text{ kA m}^{-2}$. The evaluation of the reaction intermediaries and products were made allying electrochemical data and characterization techniques. The proposed reaction mechanism is initiated by the reduction of FeS_2 to metallic iron as the controlling step, followed by two reactions involving sulphur ions and terminated by the chemical formation of Li_2S [3]. A series of chemical and electrochemical processes are proposed to explain formation of intermediary polisulphides, being the most important Li_2FeS_2 (phase X) spotted here through micrographies displaying it's characteristic crystals of needle-like morphology.

The experiments carried out permitted the specification of the main kinetics parameters of FeS_2 electrochemical reduction in molten chloride halides mixture. Further, the methodology used in this work open grounds for future research in comparing the behaviour of a wide range of cathode materials in molten salt electrochemical systems.

Keywords: Iron disulphide; Molten salts; Electrode kinetics

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About role of metalocomplexes at corrosion protection of metals by organic inhibitors in acid solutions

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The use of organic surfactants (inhibitors) is one of the most effective methods of corrosion protection of metals in different active environments. According numerous works inhibitive activity of such substances appears due adsorption on protected metal surface (Fe, Zn, Cd). Physical adsorption of inhibitors appears due to electrostatic interaction with charged metal surface, because in this case for prediction of inhibitive activity the ϕ-scale of L.I. Antropov used very successfully. According today representation the specific adsorption of first type appears as a result of π-electron interaction with positive charge of metal surface. At specific adsorption of second type, which takes place in presence of heterocyclic compounds, containing N, P or S atoms in heterocycle, mentioned atoms can produce coordination bounds via donor-acceptor interaction with surface metal atoms, that have unsaturation outer electron shell. In our opinion, at organic compound chemosorption between adsorbate molecules and adsorbent surface atoms chemical reaction occurs with new chemical compound producing. We carried out the special experiments to reveal nature of such interaction, as adsorbate used decylpyridiniumchloride (DPC). Results of such experiments showed that ability of heterocycle compounds (for example DPC) to reduce rate of iron dissolution is a result of ability to give complex compounds with cations (not atoms) of metal, which dissolve during corrosion process. The main condition at which inhibition effect can be achieved is low solubility of such metalocomplexes in water. Corrosion protection of metals rises at addition of I^- -ions in corrosive media. It is possible to consider that it takes place to due to very low dissolubility of compound products which include metal cations and I^- anions. From such positions we can explain synergetic effect which are observed in solutions, containing bough iodide anions and heterocycle compounds (DPC). It was shown that in organic solvents (for instance dimethylsulphoxide (DMSO)) such metalocomplexes dissolve, because addition of small quantities of DMSO in water solution diminish the inhibiting influencing of heterocyclic compounds.

It is known that DPC forms more stable complexes with cations Fe^{3+} than with cations Fe^{2+}. Because the dissolved oxygen has indirect influence on the corrosive behavior of iron. Indeed, in presence oxygen the cations Fe^{2+} is easy oxidize to cations Fe^{3+}. Such oxidizing process is accompanied formation of more stable complexes. Being in the system of anions I^- promotes appearance of the catalytic redox-system I^-/I_2, which facilitates oxidization of iron.cations. Therefore in presence of iodide-ions the formation of metalocomplexes DPC with cations Fe^{3+} takes place with greater rate and, as a result, a corrosive process is braked in a greater degree. Thus, it was shown by us, that in examined cases the braking of corrosive process is conditioned blocking of metal surface by the layer of little soluble metalocomplexes, which appear as a result of co-operating of heterocyclic compounds with cations of metal near surface of dissolving metal.

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Natural-convective instability of the stagnate electrolyte between horizontal electrodes: effect of migration and kinetics of electrochemical reactions

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The mechanical equilibrium of density-stratified stagnant fluid between horizontal electrodes is stable provided the Rayleigh number does not exceed a certain critical value Ra_c. For heat systems the Rayleigh number is the sole parameter determining natural-convective instability ($Ra_c=1707.6$). By contrast to the heat systems, analysis of convective instability in electrochemical systems is a more general problem, because the electrolyte contains several sorts of ions with different charges and diffusion coefficients, and the gradient of concentration of each of them has an effect on the density of buoyant forces. In addition, migration of ions in solutions of electrolytes proceeds concurrently with diffusion. This results in a complex pattern of nonlinear interactions between the concentration, hydrodynamic, and electric fields. The character of these interactions depends on the kinetics of electrochemical reaction. However, the available methods of investivation of the effect of ions migration and kinetics of electrochemical reactions on natural-convective instability have some drawbacks: the perturbations of electrode potential and current density are determined taking into account the properties of outer circuit or the perturbations of electrode potential are taken to be zero; the convective stability is taken to be dependent on the electrolysis conditions (potentiostatic or galvanostatic electrolysis).

In this work, we study the convective stability of binary electrolyte and the electrolyte containing three or more types of ions taking into account the kinetic characteristics of discharge-ionization stage of electrode reactions, and the interrelation between the fields of concentration and electric potential. The equations of incompressible viscous liquid flow in the Boussinesq approximation and the equations of material balance with the electroneutrality condition are used as the mathematical model. Stability of the system's steady-state is studied within a linear stability theory. The boundary eigenvalue problem for amplitudes of perturbations of vertical component of hydrodynamic velocity, concentrations, and electric potential was solved numerically. The dependences of critical Rayleigh number on the transport properties of electrolyte and the current density for reversible and irreversible reactions on the electrodes were obtained using the computational experiments. The effect of kinetic parameters (the exchange current density, the transfer coefficient) on the critical Rayleigh number is studied.

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Can changes in the interfacial layer in turbine pipes increase hydro power production?

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Results from laboratory experiments show a reduction in pressure loss due to friction, for water flow in pipes when electric potentials are applied to the pipe wall [1,2,3]. The Norwegian hydro power industry has shown great interest in these experiments, and permission has been given to carry out field experiments in a hydroelectric power plant in order to examine whether application of an electric potential to the turbine pipe reduces the head loss. The chosen power plant, Vrenga power station located in Southern Norway, produces 12.5 MW (85 GWh) and is equipped with a Pelton turbine. Water flows through the single turbine pipe made of carbon steel and coated inside with an epoxy polymer (Jotamastic 87, thickness: 150-200 μm). The length of the turbine pipe is 1562 m, and the average inside diameter is 1 m. The heigth difference between the surface of the water reservoir and the turbine inlet is regulated between 366 and 379 m. The maximum flow rate is 4.68 m^3s^{-1}. The electric potential has been applied between upper manlock and the turbine pipe itself at the turbine inlet. The manlock is made of stainless steel with uncoated inner surface, and is electric insolated from the pipe. The head loss has been measured before applying the electric potential and during a period of 54 months. The head loss measurements were carried out by the Norwegian company Norconsult AS, which speciality is efficiency measurements for hydroelectric power plants. The head loss was calculated by a standard procedure including measurements of water level at the water reservoir outlet, pressures at the inlet and outlet of the turbine pipe, needle stroke for the Pelton turbine, and efficiencies for the generator and turbine. The results show a reduction in the head loss after applying the electric potential, and the results are given in figures 1 and 2. In fig. 1, the measured head loss as a function of square flow rate is given. The upper curve is head loss before applying the potential; the lower curves are results from later measurements. In fig. 2, the measured head loss at maximum flow rate (4.68 m^3s^{-1}) during the period of 54 months of exposure, are given. The head loss before starting the experiments was 45.05 m at maximum flow rate.
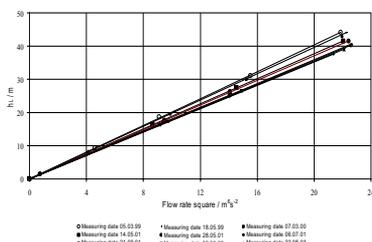
Figure 1. Measured head loss as a function of square flow rate.The upper curve is head loss before applied the potential; the lower curves are results from later measurements.
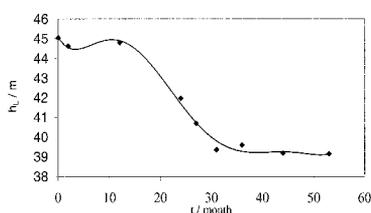
Fig. 2. Measured head loss during a period of 54 months at maximum flow rate (4.68 m^3s^{-1}).

Up to present, a reduction in the headloss of approximately 6 m (13.6% reduction) has been observed. The experiments are still in progress.

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Tetraazamacrocyclic complexes as conductive units of organothiol monolayers

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Tetraazamacrocyclic complexes of Ni^{II} and Cu^{II} can be used as components of catenanes or rotaxanes showing electrochemically switched intramolecular motion in solution [1, 2].

In our present studies, we modify these compounds with organothiol chains to attach them to the surface of the electrode using self-assembly method and use them as molecular switches, which change conductivity by applying appropriate potential.

We focused on investigation of electrochemical properties of these compounds in solution and in case of thiol-derivative on the surface of the electrode. We immobilized macrocyclic complex of nickel(II), which is the axis of the rotaxane, on the gold surface. As shown on the figure, this compound can be anchored to the surface by one or two thiol-groups. The data obtained from STM experiments using colloidal gold confirm that the orientation normal to the surface dominates. The electrochemical experiments reveal reversible one electron oxidation of metal centre from +2 to +3. Most importantly, the conductivity through the single molecule is larger than that obtained for the same length thiol.
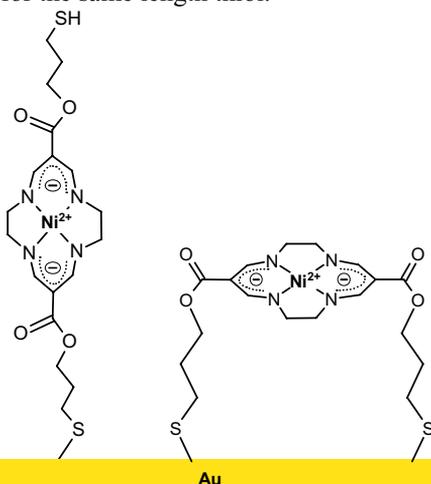
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Electrochemical Engineering & Technology

Mass Transfer between Electrodes using Multijets of Electrolyte

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Generally, the industrial applications of jets in liquid-to-wall mass exchanges use multijets which can be unsubmerged or submerged depending on the process (e.g. chemical dissolution in the printed circuit industry, electropolishing, electrodeposition).

The mean mass-transfer coefficient should have produced high values, but the general correlation is difficult due to the numerous process design parameters (e.g. jet diameter, distance between jets, exit velocity, etc…) and to the complexity of the hydrodynamics over the surface receiving the jets. Indeed the interactions between neighbouring jets generate vortex structures, the number and the size of which depend on these parameters. As a result of the interactions between jets, there is a nonuniform spatial distribution of local mass-transfer coefficients.

The first aim of this work is to investigate the influence of several parameters (jet height, distributor geometry, impingement angle, etc…) on the global and the local mass transfer between submerged and unsubmerged multijets and a plane surface. The second aim is to find the distributor geometry that gives the best mass transfer. To test all these parameters, an experimental cell was built (fig. 1) as well as a series of distributors (slot jets, nozzles, pipe injectors, ...). The mass transfer coefficient at the surface impinged by the jets is measured electrochemically using the tracer method. Then, the experimental results are compared with those obtained by modelling. The electrochemical process modelling tool used is MIoTraS (developed by ElSyCa). The simulations include the calculation of the electrolyte flow profile, the electrical potential and the current density in the cell. After that, we can determine news distributors geometries that give a better mass transfer.
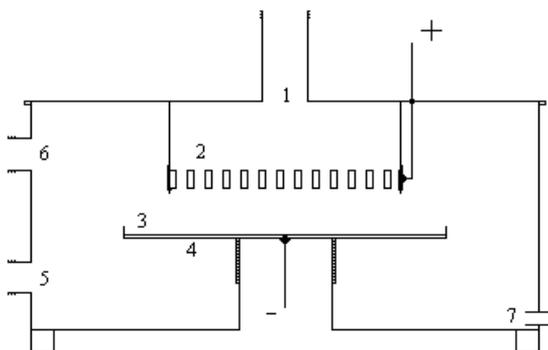
Figure 1: Electrolyte inlet, 2. Distributor = anode, 3. Cathode, 4. Cathode holder, 5. Electrolyte outlet for unsubmerged jets, 6. Electrolyte outlet for submerged jets, 7. Tube for the reference electrode connection

The Effects of Surface Overpotential
on the Current Distribution of the Cathode

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In electroplating, it is, generally, desirable to achieve a maximum uniformity of the deposit thickness, which depends largely on the current distribution over the cathode. The current distribution in the cell is primarily determined by the geometrical characteristics of the electrodes and the cell. Non-conducting shields or auxiliary electrodes are often used to achieve a uniform current distribution in the electroplating on the cathode of complicated shapes. On the other hand, in PCB(printed circuit boards) applications, some products have needs to be electroplated with a different thickness on each side, which is preferable because the functions of each side is different, for example, soldering vs. wirebonding.

In this study, the current distributions were investigated when different current was applied on each side of PCBs to achieve different electrodeposit thickness. The current densities on each side were shown in Fig.1, where the current was concentrated in the center region on the higher current side and in the outer region on the lower current side, because of some current flow from the higher to the lower current side. And it was also found that the ratio of the average current density on each side highly depends on the surface overvoltage of the plating solution (For example, in cyanide Au electrolyte, there were little difference in deposit thickness with the similar conditions). To understand the effects of the surface overvoltage compared with the IR drop in the plating solution, the current distributions were simulated according to solution conductivity, Tafel slope (charge transfer coefficient), current density, plated area, and plating bath size.
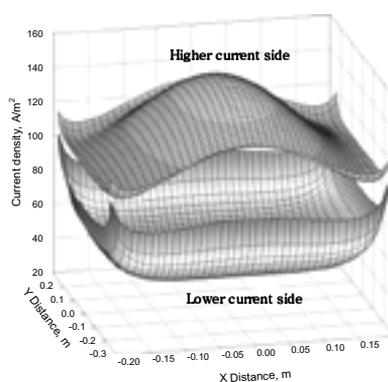
Fig. 1. Current density profiles on the flat cathode, where the ratio of the applied currents was 5:1 in sulfamate Ni bath.

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Micro-electrochemical reactor
with internal recirculation using gas lift

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In the last decades, miniaturization of chemical reactors and more recently of electrochemical ones, gained a great interest. The motivations for this miniaturization are various. Besides others can be cited the gain in response time, the possibility to use extremely small quantities and the chance to minimize drastically the ohmic drop in low conductive media.

The principle of gas lift is well known, as well in chemical and in electrochemical industrial applications. In this contribution we apply this phenomena to a micro electrochemical reactor for product pumping. As application is presented the acetoxylation of aromatic compounds in glacial acetic acid. This medium is known to have a very low conductivity and thus the ohmic drop is an important problem encountered during this process. The very small gap between the cathode and the anode (only a few 100 μm) allows one to overcome this problematic.

Figure 1 shows one of the realized prototypes consisting of a micro-electrolyser and a reservoir for recirculation. Characterization of the device has been done by measuring the average velocity versus the applied current using micro-particles in suspension in the liquid. The possibilities of development offered by such a system are various. For example miniaturisation to a scale of a few mm is under discussion in the light of being used as a micro-pump for micro fluidic devices. Another development under investigation is a dipolar reactor.
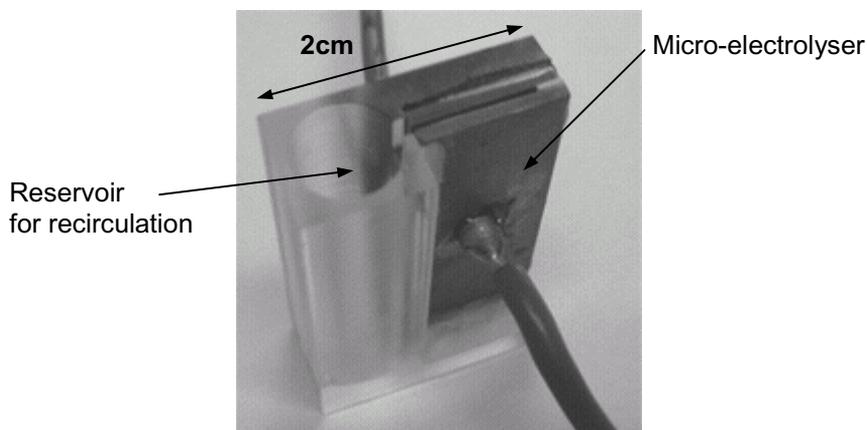
Figure 1 : Prototype of a micro-electrochemical reactor incorporating gas lift for product pumping

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Treatment of alcohol distillery wastewater by electrochemical method

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Distillery waste is one of the most complex, troublesome and strongest industrial organic effluents. Because of this high refractory organic content, treatment of this wastewater, unless performing any pretreatment is not possible using conventional treatment methods, also sometimes it is not possible even performing pretreatment.

In the distillery, ethanol is manufactured by the fermentation of molasses. The origin of molasses is from a sugar-manufacturing unit, which is either based on the beet sugar or sugar cane. The molasses is fermented by yeast after suitable dilution. The fermented solution contains about 6–12% ethyl alcohol, which is recovered by distillation [1]. The undesired bottom product of distillation is called stillage, spentwash, vinasses or alcohol distillery waste. Plant from which the wastewater was supplied has a vinasses evaluating plant to manufacture potassium carbonate. Wastewater used in the study was taken from the outlet point of this evaluating plant and had 5000mg/L of COD.

In this study, electrochemical treatment of alcohol industry wastewater was studied and over 95% of COD removal was achieved.

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Electrochemical treatment of dye wastewater containing basic red 46, maxilon blue, basic yellow 21

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It is now appreciated that the electrolytic oxidation is a very powerful tool for oxidatively breaking up the certain organic compounds. Using the adequate anode materials for electrolysis is essential, because the efficiencies of degradation of organic materials depend on the nature of anode materials. Pt/Ti electrode, which was fabricated by the Pt thin film deposited on the Ti substrate using the r.f. sputtering, and synthetic boron-doped diamond (BDD) thin film electrode were chosen to investigate the effective anodic materials for the electrochemical treatment of refractory organic dyes. The dye wastewater containing Basic Red 46, Maxilon Blue, Basic Yellow 21 was treated by an electrochemical method using a BDD and Pt/Ti as anodes and Cu plate as cathode. In this technique, no electrolyte was added to the test solution and the mixture was passed through an electrolytic cell. Operating variables on the process efficiency including current input, pH, reaction time, reaction temperature and flow rate were optimized for the controlled current electrolysis of aqueous dye wastewater. . Depending on the values of applied current, reaction time, and concentration of solutions, the complete degradation or the partial oxidation of the compounds to other intermediates were obtained. For both the BDD electrode and Pt/Ti electrode, the removal efficiency of dyes in aqueous solution increased with increasing the applied current and reaction time. The color removal efficiencies were reached as high as 92.4 % and 98.3 %, respectively, at the applied current of 100 mA for 1 hr reaction using the flow rate of test solution of 5mL/min. We found that BDD electrode was much effective for the oxidation of the dyes than Pt/Ti electrode. TOC was reduced by 92.2 % at the optimized conditions including the input current of 200 mA for 1 hr reaction for with a BDD electrode.

Newly Developed Magnetic Abrasive Finishing with Nano-sized Diamond Dispersed Nickel-Cobalt Electroless Plated Plastic Ball for Post CMP Process

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Magnetic abrasive particles (MAPs) are crucial to ensure finishing quality and accuracy in magnetic abrasive finishing (MAF) processing[1]. In this research a new bounded MAP based on the electroless nickel-cobalt boron plating, nano-sized diamond composite plating to micro-sized plastic ball was prepared. Plastic ball was used as support here for MAPs growth due to its lightweight and globular form. The aim of the paper is to develop a lightweight and forceful MAP and its application to post CMP process. Magnetic filed assisted finishing was performed to examine the fabricated MAPs. The copper "Damascene" samples were supplied from Selete Co. Ltd.. The finished surface was shown in the figure bellow. The smooth surface was obtained after finishing by the nickel-cobalt diamond composite plated plastic ball. In conclusion, a new MAFs based on the nickel diamond composite plated plastic ball have been prepared successfully. The finishing results have shown that the powerful ability of the new MAFs in the magnetic filed assisted finishing process.

(a)   (b)
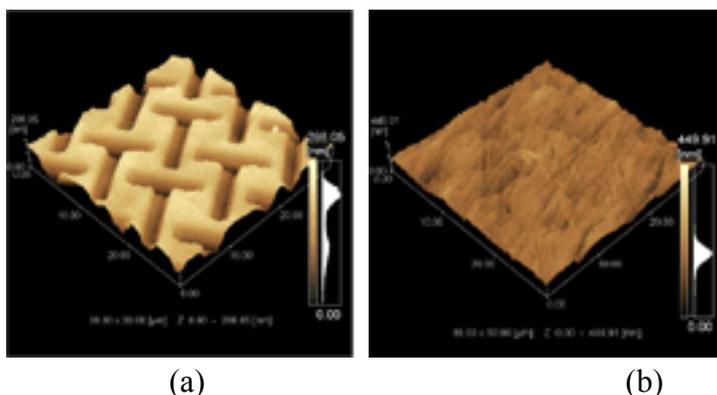
Figure AFM images for the Damascene copper samples
(a)Before Magnetic Abrasive Finishing(MAF) (b)After MAF

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The optimization of an "all wet" process for metal barrier layers for Cu metallization

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A novel formation process using Self-Assembled Monolayer (SAM) and electroless deposition technique for diffusion barrier layer on both inter-level dielectric films and on Cu lines has been developed [1-2]. Barrier layer that suppresses the Cu diffusion are a key technique for the current ULSI fabrication process. High thermal stability, Cu diffusion resistance and film thinness are the properties required for a reliable diffusion barrier layer. It has already been reported that electrolessly deposited NiB is a candidate for such barrier layer materials [2-3]. However, 40 nm thickness of the NiB layer is needed to obtain the stable performance as a reliable diffusion barrier layer. This thickness is far too much as critical dimensions of the interconnect today is in the range of 65-90 nm in manufacturing and it will reach 32-45 nm in few years. To realize ultra thin diffusion barrier layer, the optimization of the surface condition of SAM modified substrate such as catalyst condition has been investigated. In this paper, adsorption and valency condition of catalyst "Pd" on the SAM and its effect on film morphology were discussed. An organic low-k dielectric film (Tokyo Ohka Kogyo Co. Ltd.,) modified by SAM of APS (3-aminopropyltriethoxy silane) was used as a starting material. The catalyst solution contained $PdCl_2$ and HCl. To estimate the condition of the catalyst, TEM (Transmission Electron Microscope) and XPS (X-ray Photo-electron Spectroscopy) were used. The film surface, just after the catalyst process was confirmed by XPS spectrum ($Pd\text{-}3d_{5/2}$). The peak of the spectrum obtained from the specimen merely immersed into the catalyst solution appeared near oxidized Pd area. The peak was shifted to peak of metallic Pd area by immersed into the solution containing reducing agent. TEM measurement was applied to estimate the condition and morphology of Pd. From the specimen after reduction, small metal particles (under 5 nm) were observed. Moreover, it was indicated that the particles were Pd metals by electron diffraction. We believe the uniform particle size and location of Pd particles on the SAM are important factors on the process to make thin films. On the presentation, we will report the details of the Pd catalyst chemical state and its effects on film the conditions.

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Electrodeposited Cobalt-Boron Alloys for Hydrogen Evolution in 8 M Hot NaOH

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Tailoring of active cobalt alloy cathodes for hydrogen evolution in a hot concentrated sodium hydroxide solution was attempted by electrodeposition. Enhancement of cathodic activity of cobalt for electrolytic hydrogen evolution has been carried out by the formation of cobalt alloys containing different content of boron.

The present work aims to obtain nanocrystalline and amorphous Co-B alloys with high cathodic activity for hydrogen evolution by electrodeposition. We try to clarify the effect of the boron addition in enhancing the activity for hydrogen evolution and in changing the morphology of electrodeposits. The addition of boron to Co alloys significantly increased the activity for hydrogen evolution in 8 M NaOH at 90°C. In particular, Co-B alloys with high concentrations of boron showed the Tafel slope of about 36 mV/dec, suggesting the rate-determining step of recombination of adsorbed hydrogen atoms. In spite of the high activity for hydrogen evolution, open circuit immersion during shutdown period in 8 M NaOH at 90°C resulted in dealloing and hence the durability of the electrodes was insufficient. In order to improve the durability the carbon addition was performed to form Co-B-C alloys. Although the carbon addition was effective to suppress the dealloing process, complete prevention of dealloing during open circuit immersion was not attained. Even after open circuit immersion of the Co-B-C alloys in 8 M NaOH at 90°C for long time high activity for hydrogen production was maintained.

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Co-W Alloys for Hydrogen Evolution Electrodeposited Under External Magnetic Field

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There has been known a variety of nickel alloy electrodes for hydrogen evolution in chlor alkali industries. Among them, the electrodeposited Ni-Fe-C alloys showed the highest activity for hydrogen evolution in hot alkaline solutions and excellent durability: The overpotential for hydrogen evolution at the current density of 1000 Am^{-2} in 8 M NaOH at 90 ^{o}C was less than 100 mV. The activity did not decrease and no iron dissolution occurred during open circuit immersion in the same hot alkaline solution. As has been found for Ni-Fe-C alloys, the additions of electronegative elements such as oxygen and carbon are quite effective in preventing dissolution of iron in the form of oxyanions during open circuit immersion.

Tailoring of active cobalt alloy cathodes for hydrogen evolution in a hot concentrated sodium hydroxide solution was attempted by electrodeposition. Enhancement of cathodic activity of cobalt for electrolytic hydrogen evolution has been carried out by the formation of cobalt alloys containing different content of tungsten.

The present work aims to obtain nanocrystalline and amorphous Co-W alloys with high cathodic activity for hydrogen evolution by electrodeposition. We try to clarify the effect of the tungsten addition in enhancing the activity for hydrogen evolution and in changing the morphology of electrodeposits. External magnetic field generated by permanent magnet was used in order to modify composition and morphology of alloy. The changes in morphology and composition of alloys was searched in order to determine influence of magnetic field on alloys` electrodeposition.

Production of electroplated Ni-ZrO$_2$ nanocomposite coatings for tribological applications

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Composite coatings produced by electrodeposition of particles within a metal matrix are widely used in order to enhance specific properties, i.e. mechanical and chemical stability, of materials. Different types of particles, e.g. pure metals, sulfides, oxides, ceramics, or organic materials, with diverse properties can be used for the incorporation into the metallic matrix.

In the present work, Ni-ZrO$_2$ nano-composite coatings were produced for tribological applications. The composite coatings were electrodeposited from a Watts bath with nano zirconia particles (5 nm and 40 nm particle size) dispersed.

The deposition of nano zirconia particles into a nickel matrix using direct current and pulse plating techniques was studied. High current densities were possible to apply with the help of a rotating cylinder electrode by changing the streaming conditions. Also the temperature, pH and concentration of particles in the electrolyte were optimized with the help of zeta potential measurements in order to obtain a maximum in particle incorporation.

The concentration of zirconia in all layers was determined by means of EDX analyses, and the structure of the composite layers was studied by ESEM and FIB. The variation of the microhardness and the friction coefficient with the incorporation of zirconia in these layers was tested.

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A comparative study of ni-w alloys electrodeposition from aqueous electrolytes and ionic liquids

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Among electrochemical processes having a considerable impact on technical development in a large range of industrial areas and including implications from environmental viewpoints, electrodeposition and electroforming play an important role.

Under the frame of the efforts to find ecological alternatives to chromium plating, alloyed Ni with tungsten or molybdenum as well as boron or SiC based composites are showing promise for specific applications.

With this in view, several comparative experiments dealing with electrodeposition of Ni-W alloys (5-25%W) from aqueous electrolytes and ionic liquids based on choline chloride [1] are presented. The influence of some plating parameters on Ni-W metallic alloys electrodeposition from an aqueous ammonium-citrate electrolyte has been investigated.

Cathodic potentiodynamic polarization curves, cathodic current efficiency and alloy composition have been studied against hydrodinamic regime, pH value and current density. Ordered, compact Ni-W electrodeposits containing 15-25% W were obtained. The strong effect of citrate concentration both on the deposit quality and alloy composition has been evidenced.

Preliminary results dealing both with choline chloride based system preparation and Ni-W alloy electrodeposition are discussed.

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Sn-Pb alloys flexible foils produced by electroforming

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Among electrochemical processes having a considerable impact on development within microcomponents/microsystems area, electrodeposition and electroforming play an important role. Because electrochemical deposition represents a process that occurs at atomic/molecular level the formed metallic layer follows entirely the tri-dimensional shape of the support with a very good accuracy of micron or submicron order.

Sn–Pb alloys have specific applications in electronics and microelectronics and recently, due to their flexibility they showed to be suitable as building element for biological structures [1]. Electrochemical deposition of Sn-Pb alloys with a lower Pb content is also of an increased interest under the frame of concerted efforts to reduce the use of toxic/pollutant elements – in this case of Pb- which is intensely involved in SnPb welding alloys.

With this in view, several results will be presented dealing with electroformation and characterization of Sn-Pb (30-55% Sn) alloys thin metallic foils (thicknesses of min.10 μm) from fluoborate type electrolytes. The influence of operating parameters e.g. current density, electrolyte composition, hydrodynamic regime, temperature is discussed, as well as the correlation between alloy composition and electrical, mechanical characteristics in close connection with potential applications.

According to the obtained results the electroformed foils have been characterized by an excellent maleability and flexibility. XRD measurementS showed the presence of non-stoichiometric solid solutions, different from thermally obtained alloys, with cristallites having sizes of 60-70 nm. The electrical resistivities varied between 15-20 μΩ.cm against alloys composition.

Some aspects regarding corrosion protection performance involving electrochemical methods, such as: potentiodynamic polarization curves and impedance spectra at open circuit potential in 0.5M NaCl, are also presented.

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Palladium as electrocatalyst for PEM applications

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Today Pt is widely used as an electrocatalyst for proton exchange membrane (PEM) fuel cells and water electrolysers. But because of elevated price and limited resources, Pt cannot be used for large-scale applications and alternative materials are needed. The goal of present study is development and investigation of nano-structured Pd-based electrocatalysts for hydrogen reduction and evolution in PEM systems.

Various Pd-based electrocatalysts (Pd, Pd-Pt, Pd-Pt-Ru and so on) including supported by different carbon carriers have been synthesized and characterized using physical and electrochemical techniques. Electro-active metallic structures were obtained by chemical reduction of precursor salts using ethylene glycol with addition of formaldehyde and polyvinylpyrrolidone (synthesis on carbon carrier) or using sodium borohydride (for metal black synthesis). Vulcan XC-72, acetylene carbon black, Sibunit, carbon nano-tubes and nano-fibers and other carbons have been used as catalyst carriers. Alternatively, Pd nano-clusters have been obtained from chemical reduction of precursor salts in perfluorinated polymer materials such as Nafion membrane materials. The electrocatalytic activity of these catalysts with regard to hydrogen reduction and evolution has been investigated for PEM applications. In particular, Pd catalysts (40% wt) on Vulcan XC-72 have specific electrochemical active surface > 33 $m^2 g^{-1}$, particle size 14.9 ± 2.1 nm. PEM fuel cell with this catalyst on the anode has shown a current density of ca. 0.7 A cm^{-2} at a voltage of 0.7 V. The typical voltage of PEM electrolysis cell with Pd-based catalyst on the cathode is ca. 1.65 V at a current density of 1 A cm^{-2}. One can see from comparison of obtained results, in general, the performances of PEM systems with Pd electrocatalysts (including on the carbon carrier) on hydrogen electrode is comparable to that with the Pt-based electrocatalysts. Thus, Pd could be potentially used as an electrocatalyst for PEM systems.

Electroreductiion of aliphatic esters using magnesium and lanthanide metal ions as mediators iii

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The electroreduction of aliphatic esters **1** is hardly attainable since their reduction potential is highly negative. On the other hand, we have already reported that the electroreduction of organic compounds using Mg electrodes promotes a variety of unique reactions which can not be attainable under the usual conditions of electroreduction.[1-3]

In the course of these studies, we have recently found that use of Mg cathode and anode makes the reduction of **1** to the corresponding alcohols **2** possible (Scheme 1).[4,5] The use of Mg electrodes is essential in this reaction since **1** was not reducible with other electrode materials such as C, Pt, Zn, and Pb.

$$RCO_2Me \quad \xrightarrow[\textbf{LiClO}_4 \text{ / } t\textbf{-BuOH / THF}]{\textbf{+e}} \quad RCH_2OH$$

1   **Mg** cathode and anode   **2**

Scheme 1

In the mechanistic study of this reaction, it was appeared that the existence of a catalytic amount of Mg(II) ion promoted the electroreduction of **1** affording the corresponding alcohol-THF adducts **3** (Scheme 2).

M_{red}^* = Mg(0) or Mg(I), Ln(0) or Ln(II)
M_{ox} = Mg(II), Ln (III)

Scheme 2

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Electrodes of Synthetic Diamond: Effects of Surface Microroughness on the Electrode Kinetics at CVD-Diamond Films on Titanium

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The electrochemical behavior of B-doped diamond films on Ti substrates subjected to different pretreatment procedures (annealing, sand-blasting, and etching in hot HCl) is evaluated as a function of surface microroughness. The diamond films deposited onto the pretreated Ti substrates were characterized by surface profiling using interferometer microscope, Raman spectroscopy, and SEM. The roughness varied from 0.1 to ~10 _m; the true-to-geometrical surface area ratio, up to ~3. Generally, the differential capacitance followed the true surface area of the electrodes. The width of the potential window in indifferent electrolyte (2.5 M H_2SO_4) also increased, but slightly, with the roughness, reaching a value of 2.9 V. The electrode reversibility in the $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ redox system increased with increasing surface roughness: the transfer coefficients increase, the potential difference for the anodic and cathodic current peaks in cyclic voltammograms decreases. The apparent increase in the reversibility of the reaction can be explained by the decrease in the true current density. Although the variations of the electrochemical parameters are not strongly pronounced, the tendencies observed can be used for optimizing the electrode properties.

(a)   (b)

Model of secondary current distribution in the segmented thin-gap flow-through reactor for 4-methylanisole methoxylation

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An application of microstructured systems is supposed to be a promising way to improve chemical reactors performance. The main advantage of these systems consists in a local control of the process parameters. From the electrochemical point of view this approach allows to control locally the electrode current density and thus operate the electrochemical cell near to the optimal process conditions. Such behaviour can be attained by segmentation of the working electrode. It leads to the process with higher single-pass conversion and due to the higher process efficiency to easier products separation. The first theoretical analysis of this approach has been provided by Rode et al [1].

This study represents first results of numerical computation of a local current density in a single-pass high-conversion electrochemical structured reactor. The aim is to provide a tool for the cell design optimisation. At the same time a deeper insight into the influence of the cell microstructuring on its performance, especially the current density distribution, will be attained. To fulfil this task, secondary potential and current density distribution inside the cell has to be calculated for a various sets of input parameters.

In order to keep relevance to the industrial praxis, the electrochemical 4-methoxybenzaldehyde (4-MBA) synthesis has been chosen as a model system. 4-MBA is an important intermediate in the production of semi-synthetic antibiotics. Its synthesis is based on the anodic methoxylation of 4-methylanisole (4-MA). The kinetics of this electrode reaction was, however, not known. Therefore it has been determined experimentaly.

The electrode reaction kinetics of 4-MA methoxylation was studied in the three-electrode arrangement. RDE made of glassy carbon was employed as a working electrode. The 0.8 mol dm^{-3} $NaClO_4$ solution in methanol served as an electrolyte. In order to avoid overlaping of the methoxylation reaction by the methanol oxidation on the anodic part of the polarisation curve the concentration of 4-MA was kept below 0.01 mol dm^{-3}. The polarisation curves were corrected for an Ohmic potential drop. Corresponding electrolyte resistance was determined by means of electrochemical impedance spectroscopy. It was found that the reaction kinetics is well described by the Tafel type equation. The rate constants of the methoxylation reactions occurring on the glassy carbon electrode as well as the diffusion coefficients of the species involved were determined. Since the equilibrium redox potential of this reaction is not known, it was set arbitrary as 1.35 V vs. SCE. Kinetic equation obtained has been implemented into the mathematical model of the segmented reactor.

The examined reactor consists of the rectangular channel. Its upper side is formed by the segmented anode. This anode is divided into 10 sections of identical dimensions (10 x 10 mm^2), separated by the insulating strips 0.1 mm thick. The cathode forms the cell wall opposite to the anode. Both electrodes are of the same length.

The kinetic equation proposed within this study has proven to fulfill the requirements of the model designed. The calculations performed have suggested that the interelectrode gap of 0.1 mm introduced in order to reduce the energy losses caused by the electrolyte resistance leads at the same time to an important reduction of the edge effects. Together with thin insulation strips between the anode segments it supports the homogenous current distribution across the electrodes. The presented model represents a good base for the future extension to a complex model considering tertiary current distribution and effective cell scale-up.

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Electrochemical investigations of the Cu(I) and Cu(II) ions in trialkylimidazolium based ionic liquid

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1,2,3-trialkylimidazolium based ILs have been found more electrochemically stable then 1,3-dialkylimidazolium based ILs where lower reduction potential has been attributed to the H(2) acidity. [1,2]

Electrochemical investigations of chloride salts of Cu(I) and Cu(II) were performed in the 1-butyl-2,3-dimethylimidazoliumtetrafluoroborate, IL using different working electrodes. Experiments were performed outside the glove box maintaining the constant supply of dry argon gas inside the electrochemical cell.

Electrochemical results were reproducible and dense and well adhered deposits of copper were obtained on different electrodes. It was observed that comparatively better Cu deposits were obtained from Cu(I) than Cu(II).

Comparative redox behaviour of Cu(I) and Cu(II) ions and the electrodeposition of Cu on different electrodes will be presented.

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Corrosion Inhibition of Steel and Copper Water Pipes by Ammonium Pyrrolidine Dithiocarbamate

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Corrosion inhibition of steel and copper water pipes, used in Jordan National Water Supply Network (JNWSN), is studied in different corrosive media by adsorption of ammonium pyrrolidine dithiocarbamate (APDTC) on the surface of the pipes. APDTC is a nontoxic material widely used in agricultural applications.

The experimental work utilized mainly electrochemical impedance spectroscopy (EIS), weight loss techniques and UV-visible spectrophotometeric analysis. The effect of the corrosive solution concentration, APDTC concentration and immersion period on the corrosion inhibition efficiency of APDTC are studied and fully interpreted.

The results indicate that inhibitor efficiency (%P) increases with increasing the inhibitor concentration and immersion period. The inhibitor efficiency decreases with increasing the concentration of the corrosive solutions. The inhibitor efficiency is checked determining the concentrations of Fe^{2+} and APDTC in the solutions.

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Electrochemical Treatment of Chlorinated Petrochemical Effluents and Wastewater in lab cell and pilot plant

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Petroleum exploitation is one the most important sources of contaminants in the industrial sector. The fact that this activity is often practised near (or inside) seas or important water receptacles makes its contamination even more preoccupying. Even if some compounds of the petroleum waste can be partially destroyed at light exposition, it is to notice that most of them are cancer suspect agents, as resulting from the combination of hydrocarbons and chlorine, and their direct or indirect destruction processes can lead to even more dangerous products. Among the constituents of these effluents are some aliphatic compounds with one or two carbons which are volatile and susceptible to further transformation. Some of these products are trichloroethylene (TCE), Tetrachloroethylene, 1,2-dichormethan, tetrachloromethane, the oxidative study of which is presented in this work in solutions of lone or mixed components. Individual components were studied to determine the own behaviour and, further, mixture of the same were electrolysed to approach the destruction process of a petroleum wastewater containing these products. Trials were performed using the direct oxidative electrochemical degradation methods with a boron doped diamond (BDD) anode coupled with a titanium platinised cathode and also using indirect electrochemical oxidation with Fenton-based processes, such as Electro- and Photoelectro-Fenton with the use of an oxygen diffusion (O_2-D) cathode that provides hydrogen peroxide in the bulk solution. Other trials were done with single Fenton process to compare the opportunities given by the studied oxidation treatments. Preliminary results on TCE have shown a quick disappearance of this product from the electrolysed media during Fenton-based oxidations. This is enhanced in the case of Electro- and Photoelectro-Fenton. The combination of BDD with O_2-D, in Electro- and Photoelectro-Fenton, gives a most profitable effect due to the higher over tension at the BDD anode and the efficient generation of hydroxyl radicals in the bulk from the electrogenerated H_2O_2 at the O_2-D cathode.

Ni²⁺ REMOVAL from diluted solutions with an electrodeionization method using ion-exchangers of different nature

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Electrodeionization method, which provides a discontinuous purification of solutions simultaneously with electroregeneration of ion-exchanger and concentration of the component being removed, is a perspective method for purification of waste waters. Inorganic ion-exchanger based on zirconium hydrophosphate (ZHP), which is are stable in aggressive media and rather highly selective towards heavy metal cations are proposed for Ni²⁺ removal.

Sorptive and kinetic characteristics of the ZHP samples with different water content were studied. Ni²⁺ и H⁺ self-diffusion coefficients and also the effective diffusion coefficients of Ni²⁺ ions, which correspond to Ni²⁺→H⁺ exchange, were determined using sorption method. In the case of the sample containing 85 % water (hydrogel) the self-diffusion coefficients were found to reach $4.17 \cdot 10^{-11}$ (Ni²⁺) and $5.06 \cdot 10^{-10}$ (H⁺) m² s⁻¹. It was shown that drying of the ion-exchanger (hydrogel-xerogel transition) results in a decrease of ion-exchange rate (decrease of ion mobility). Ni²⁺ transport in ZHP hydrogel was investigated with electromigration method using cation-exchange membranes: Ni²⁺-loaded ion-exchanger was regenerated under potentiostatic conditions. It was revealed that the dependence of Ni²⁺ flux through the membrane on the potential gradient through the ion-exchanger bed could be fitted with a linear function. The effective diffusion coefficient of Ni²⁺ found using Nernst-Planck and Nernst-Einstein equations was estimated as $1.14 \cdot 10^{-11}$ m² s⁻¹. It is in a good agreement with the self-diffusion coefficient obtained by sorption method. It was shown that ZHP can be used for nickel removal from diluted solutions containing 40 ppm Ni²⁺, 40 ppm Ca²⁺ and 12 ppm Mg²⁺. The highest purification degree is reached for nickel (70 %) and does not exceed 35 % for other cations. Use of inert glass particles instead of ZHP results in a deterioration of the purification. The Ni²⁺ transport is realised not only through the solution, but also through the ion-exchanger. In order to prevent a fouling of the membranes and ion-exchanger due to Ni(OH)₂ deposition a small amount of strongly acidic flexible resin (a quarter of total volume) was added. In this case the inorganic component provides selectivity towards Ni²⁺ , at the same time the resin increases the current efficiency for Ni²⁺ transport due to deposition minimization. The limiting current through the cation-exchange membrane has been calculated using correlation equations. Optimal conditions of the electrodeionization process (flow rate of the solution, current, ratio of the organic and inorganic components etc.) were found. A simple model, which allows use to predict the condition of steady state has been proposed

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The electrode processes in sulphate-containing chloride and fluoride melts

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The behaviour of sulphate under anodic polarization in sodium chloride and sodium fluoride melts was investigated by chronopotentiometry at the temperatures 820 °C and 1000 °C, respectively. By using a platinum working electrode two waves were observed on chronopotentiograms in the system $NaCl-Na_2SO_4$. The first wave was attributed to the formation of oxygen. Sodium sulphate partly decomposes thermally according to the reaction $Na_2SO_4(l) = Na_2O(l) + SO_3(g)$. The second wave may originate from the oxidation of the decomposition products of SO_3, which is unstable at high temperatures, or from a reaction between oxygen and platinum under the formation of PtO, and/or PtO_2. The proposed mechanism of the anode reaction was supported by an investigation of the anodic process in the molten $NaCl-Na_2SO_4$ system by using a gold working electrode. In this case no waves were observed on the chronopotentiometric curves. Thus the sulphate ion is electrochemically inactive when a gold electrode is used as anode.

The cathodic reduction of sulphate in chloride and fluoride melts was investigated by cyclic voltammetry and chronopotentiometry in the temperature range 820 °C – 1000 °C. It was found that the numerical value of the chronopotentiometric term $j\tau^{1/2}/c^0$ increased with increasing cathodic current density. This behaviour was explained by chemical decomposition of sodium sulphate into SO_3 and Na_2O, followed by electrochemical reduction of SO_3. The decomposition of sodium sulphate is enhanced with increasing temperature, resulting in an increase in the chronopotentiometric transition time. Numerical simulation of this electrode process supported this interpretation of the electrode process. It is not a classical CE mechanism as described in the literature, because the formation of SO_3 is suppressed by the presence of Na_2O in the melt.

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Electrodeposition process: coupling between continuous scale and mesoscopic scale

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During electrodeposition process, electrochemical reactions are related in the electrode vicinity with a mixed hydrodynamic regime, natural and often forced. It is due to the reactive species transport step using diffusion, convection and electromigration. Composition heterogeneities can also induce thermo-physical properties variations due to the local chemical coupling. The modelling of these coupled phenomena using numerical method like finite differences, elements or volumes is of a great interest for both the fundamental and the applied electrochemistry.

The present work is in this research field, with the goal to calculate chemical processes coupled with transport mechanic, homogeneously or heterogeneously at interfaces for the rotating cylinder electrode geometrical configuration. The numerical method used for this work is the finite volume method programmed in software like Fluidyn® or Fluent® with C language user defined functions. The efficiency of the use of this numerical tool in the electrochemical field has already been presented in the most popular electrochemical configuration, the confined rotating disk electrode [1].

The present work focuses its interest on the second more used electrochemical configuration, the rotating cylinder configuration, which is very used in the industrial applications. We particularly will show the hydrodynamic regime changes which occur due to the free convection flow induced during the electrodeposition process. The flow regime becomes mixed and the coupling between flow and electrochemical processes becomes strong [2]. The mass transport properties are then not yet well correlated.

The complete hydrodynamic and mass transport properties in term of Sherwood number are correlated with the classical parameters and compared with success with experimentally obtained correlations and also with limiting current density measurements [3].

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Symposium 5 - Poster

Electrochemical Engineering & Technology

Distributed impedance modelling and analysis of reactions and charge transport in Au-YSZ composite electrodes

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Electrochemical membrane reactors (EMR) have been suggested as a new reactor type to conduct selective partial oxidations of hydrocarbons in a controlled way [1]. Their functional principle is similar to the Direct Hydrocarbon SOFC. Yet the primary goal is the synthesis of a valuable chemical compound rather than electro-energy generation. Au-YSZ composite anodes are used in the EMR to provide a sufficiently large reaction surface. Electrochemical techniques can be applied to investigate the mechanism of the desired reaction as well as of possible electrochemical side reactions. Impedance measurements of composite electrodes, however, often exhibit (one or multiple) depressed semicircles [2] indicating a frequency dependend inhomogeneous current distribution. In composite electrodes, a pronounced inhomogenous current distribution exists across the electrode thickness, which could be the dominating reason for the observed frequency dispersion. Therefore, it has to be taken into account in the interpretation of impedance spectra.

In our contribution a detailed analysis of the effect of charge transport within the electrolyte subphase and of reaction kinetics on the impedance of Au-YSZ composite electrodes will be presented.

A 1D macrohomogeneous model of the composite electrode was derived which accounts for radial current and concentration distributions across the electrode as well as for local electrode reactions. Fourier transformation was used for model-based simulations of impedance spectra. We show that even for simple one-step electrochemical oxygen evolution the typical depressed semicircles arise (Fig.1). Different reaction mechanisms including adsorption, two charge transfer steps or parallel electrochemical reactions are tested. It can be shown that reaction mechanisms, which have a specific shape of the impedance plot in the concentrated parameter range, are as well distinguishable under distributed conditions. Experiments, which are currently carried out in our group to validate these model predictions will be shown.
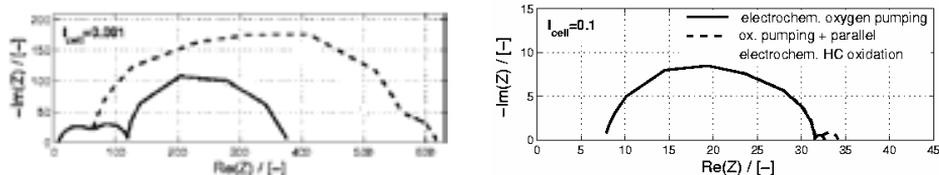
Fig.1: Simulated dimensionless impedance spectra of composite electrodes at different dc-currents

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Symposium 6

Liquid-liquid Electochemistry

Voltammetry of ion transfer across the micro liquid-liquid interface formed at the orifice of a micropipette in the room-temperature ionic liquid

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The ion transfer across the interface between a hydrophobic room-temperature ionic liquid (RTIL) and an aqueous solution (W) is important in elucidating the partition properties of ionic species between the RTIL and W. We proposed a voltammetric approach in studying the ion transfer across the polarized RTIL|W interface [1]. One of the difficulties in dealing with RTILs is the high viscosity. To circumvent this problem, we have been using a micro RTIL|W interface formed at the orifice of a glass micropipette. When the current is limited by the diffusion of analyte ions from the bulk RTIL phase into the W phase inside the capillary, the steady-state voltammograms are usually obtained. However, even when the diffusion of the ions in W limits the current, voltammograms also show steady-state behavior [2,3], which is at odd with a simple expectation that the linear diffusion of the ions inside the glass capillary determines the current. Similar steady-state voltammograms have been observed for the ion transfer at the conventional liquid|liquid interface [4,5]. Such steady-state voltammograms are unusual in that the current of the limiting current region is much smaller than what is expected in the case of the radial diffusion of the analyte ions to an interface of hemispherical or inlaid-disk type [3]. It is obvious that the actual shape of the tip of a micropipette, which is drawn out to have a tapered shape, gives rise to augmented transfer due to the radial diffusion inside the micropipette. We will show that the numerical simulation of voltammograms taking account of the actual shape of the micropipette well reproduces the shape of experimentally observed voltammograms. The limiting current and the half-wave potential ($E_{1/2}$) are both functions of the tile angle. The shift of $E_{1/2}$ with the tilt angle of the inner wall is considerable at the RTIL|W interface due to the high viscosity of RTIL. Given values of the tip radius and the tilt angle, the concentration and the formal potential for ion transfer of the analyte ions can be determined. The values of $E_{1/2}$ for the ion transfer across the RTIL|W interface are compared with those at nitrobenzene|W and 1,2-dichloroethane|W interfaces. In the case of facilitated ion transfer, steady–state voltammograms allows us to determine the formation constant in RTIL.

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Membrane-Mimetic Shuttling Mechanism of Ion Transfer at the Liquid-Liquid Interface

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The transfers of hydrophilic ions from aqueous and organic phases are ubiquitous in biological and technological systems. These energetically unfavorable processes can be facilitated either by small molecules (ionophores) or by ion-transport proteins. In absence of a facilitating agent, unassisted ion transfer (IT) reactions are assumed to be "simple", one-step processes. In our recent study of IT at nanometer-sized interfaces between aqueous solutions and neat organic solvents, some anions (e.g., chloride) and relatively hydrophobic cations (e.g., tetraalkylammonium ions) were readily transferred from water to less polar neat solvents such as 1,2-dichlotoethane. However, the transfers of strongly hydrated alkali metal cations occurred only in the presence of organic supporting electrolyte. Li^+, Na^+, K^+, and Cs^+ could be transferred by adding as little as 0.1 nM of hydrophobic electrolyte to neat organic solvent.[1] This phenomenon is quite general: the transfers of all metal cations we have tested, as well as protons, and F^-, require a hydrophobic counter-ion to be present in organic phase. Our results suggest that a number of "simple" ion transfers are actually facilitated by organic counterions. This finding is incompatible with the generally accepted one-step IT mechanism. A new shuttling mechanism of ion transfer is proposed to explain the observed phenomena. While shuttling is a well-known pathway of transport of ionic species across biomembranes and artificial liquid membranes,[2,3] it has not yet been discussed with regard to IT processes at the liquid-liquid interface.

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Electrocatalysis of oxygen reduction at a polarised liquid-liquid interface by electrodeposited metal particles

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Electrodeposition of noble metals, e.g. Au, Pd, Pt and Ag, at the polarised interface between two immiscible electrolytes solutions (ITIES) has attracted a great deal of interest mainly for two reasons. First, ITIES has been considered to be an ideal background for metal nucleation studies because of the absence of a solid support comprising permanent nucleation sites. Second, the controlled metal deposition at ITIES could represent a novel approach to preparation of metal catalysts or photocatalyst, as a viable alternative to traditional chemical and electrochemical methods.

Here we present first evidence and evaluation of electrocatalysis of the interfacial oxygen reduction at the polarised water_1,2-dichloroethane (DCE) interface by *in-situ* deposited Pt particles. The electrochemical process involved the reduction of oxygen in the aqueous phase by decamethylferrocene (DCMFc) as an electron donor in DCE, and was investigated in a broad range of interfacial potential differences and the aqueous solution pH (3-10). The Pt particles were deposited at the interface by reducing ammonium tetrachloroplatinate in the aqueous phase by the same organic-phase electron donor. It is shown that the diffusion equations for an irreversible interfacial oxygen reduction coupled with the reversible partition of oxygen between the aqueous and DCE phase can be solved by using the convolution principle. Convolution analysis of voltammograms made it possible to consider the stoichiometry of the overall electron transfer reaction, and to infer kinetic data (Tafel plots). This analysis indicated that: (a) the catalytic oxygen reduction proceeds as a four-electron transfer reaction; (b) the rate of the oxygen reduction by DCMFc increases by more than one order of magnitude in the presence of the interfacial Pt particles; (c) the rate-determining step is the first electron uptake not including the concerted proton transfer; and (d) a transition from the normal (α= 0.26 – 0.39) to the activationless (α < 0.1) region occurs, which is probably associated with a high overpotential for the rate-determining step.

Symposium 6 - Keynote

Liquid-liquid Electrochemistry

Unravelling ITIES: Theory update

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This keynote will give an update on recent developments of the theory of **int**erfaces of **i**mmiscible **e**lectrolytic **s**olutions and their comparison with experiments. The topics to be covered are:

▪ Potential distribution across the the interface: 2006.

▪ Interface fluctuations: new effects induced by ion transfer and ionic current across the interface.

▪ Three phase system: new electrowetting problem.

▪ Localization of nanoparticles at the interface: the interplay of electrical and cappilary forces.

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Symposium 6 - Oral

Liquid-liquid Electrochemistry

Electrochemistry of DAB-AM-n and PAMAM Dendrimers at the ITIES

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The *i*nterface between *t*wo *i*mmiscible *e*lectrolyte *s*olutions (ITIES), also known as liquid-liquid electrochemistry, is proposed as a simple method to detect a series of dendrimers with no need of labelling with electroactive functionalities to enable the detection, in contrast with classical investigations with dendrimers using solid-state electrochemistry. Different generations of poly(propylenimine), (DAB-AM-*n*) and poly(amidoamine) (PAMAM) dendrimers where studied. The detection was based on the transfer across the ITIES of low concentrations of dendrimers presenting a net charge in solution. The electrochemical behaviour of the dendrimers was observed to be quite different depending on the dendrimer family (DAB-AM-*n* and PAMAM) and the generation number, as well as being a function of the experimental pH. The electrochemical detection of the lower dendrimer generations presented similar behaviour to that observed from traditional ion transfer of simple ionic species. However, the increase of the generation number resulted in very distorted voltammograms. Electrochemical properties such as the diffusion coefficients, the formal potential transfer and the Gibbs free energies of transfer were determined using cyclic voltammetry.

Symposium 6 - Oral

Liquid-liquid Electrochemistry

Probing the organization of molecular aggregates in liquids by hyper rayleigh scattering

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Considerable interest has been devoted in the past to the use of optical techniques to investigate the organization of molecular systems at the nanometre scale. Among these techniques, nonlinear optical techniques, and especially second harmonic generation (SHG), have proven very useful in the sense that the coherent nature of the signal allows to get an insight into the short-range correlation of molecules.

This property of the SH process has been used to investigate the organization of molecular aggregates in water-methanol liquid mixtures. The method entails the recording of the SH intensity scattered at right angle from the excitation direction defined by the fundamental wave with a well defined polarization state. These measurements were performed for an amphiphilic dye molecule with a large quadratic hyperpolarizability and an axial symmetry. The plots of the HRS intensity as a function of the incoming fundamental wave polarization angle display characteristic patterns the analysis of which leads to an insight into the organization of the dye molecule into the aggregate.

In absence of a co-surfactant, the dye aggregates present a strong non centrosymmetrical organization. However, with an increasing concentration of a co-surfactant, the organization evolves towards a more centrosymmetrical structure. A quantitative analysis of the data indicates that, among the different possible structures, the latter organization is compatible with a micelle-like structure where the charged head groups of the dye are in contact with the solvent. It is therefore demonstrated that this non invasive non linear optical technique allows one to get an insight into the organization of heterogeneous liquids and liquid interfaces at the nanometre scale.

Metal Deposition at the Liquid/Liquid Interface

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Metal deposition at the liquid/liquid interface represents an interesting intermediate case between deposition from purely homogeneous solution and (electro)deposition on solid substrates. We have been exploring the parameters that control the deposition process, aiming specifically to understand which factors control particle formation and assembly geometry [1-5]. One key restriction is the difficulty in applying many of the conventional characterisation techniques (probe and electron microscopy) to deposits formed at the liquid/liquid interface. Interesting analogues with recent work describing the assembly of (pre-formed) particles at liquid/liquid interfaces can be drawn: such factors will be discussed.

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Symposium 6 - Oral

Liquid-liquid Electrochemistry

Symposium 6 - Oral

Liquid-liquid Electrochemistry

Electrodeposition of nanomaterials in air and water stable ionic liquids

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Ionic liquids, especially air and water stable, have attracted considerable attention since they have extraordinary physical properties superior to those of water or organic solvents. They have extremely large electrochemical windows, more than five volts, and hence they give access to elements which cannot be electrodeposited from aqueous solutions such as, e.g., Al, Mg, Ta, Ge and Si. Moreover, the problems associated with hydrogen ions in conventional protic solvents can be eliminated in ionic liquids because ionic liquids are normally aprotic. In this paper, we report on the electrodeposition of tantalum on different substrates such as, single crystalline gold Au(111), polycrystalline platinum, NiTi alloy and stainless steel in the water and air stable ionic liquid 1-butyl-1-methyl-pyrrolidinium bis (tri-fluoromethylsulfonyl) imide ([BMP]Tf_2N) containing TaF_5 as a source of tantalum. The results show that, in addition to the formation of insoluble compounds, Ta can be electrodeposited in the ionic liquid ([BMP]Tf_2N) containing 0.5 M TaF_5 at 200 ^{o}C. The XRD patterns of the electrodeposit show the characteristic patterns of crystalline tantalum. Moreover, it was found that the deposition of an only 500 nm thick film of Ta on NiTi alloy improves its corrosion resistance which, in turn, enhances its biocompatibility. We report also the first results of the electrodeposition of nano- and microcrystalline aluminium in some water and air stable ionic liquids namely, 1-butyl-1-methylpyrrolidinium bis(tr ifluoromethylsulfonyl) imide [BMP]Tf_2N, 1-ethyl-3-methylimidazolium bis(trifluoro methylsulfonyl) imide [EMIm] Tf_2N and trihexyl-tetradecyl phosphonium bis(trifluo romethylsulfonyl) imide ($P_{14,6,6,6}$ Tf_2N).

Nanoparticles at immiscible liquid interfaces.

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The synthesis of nanoparticles has been the focus of numerous publications in recent years, and whilst many solution based synthesis have been described, the ability to control, study, and understand the reactions taking place can be a challenge. One such novel route to the fabrication of nanoparticles is the interface between two immiscible solutions, where the reactions are driven either by simple redox chemistry or by application of a potential difference across the interface[1,2]. The use of a potentiostat in fabrication allows either the rate of the reaction to be controlled, or insitu fabrication of reactants at an electrode.

We present our recent work utilising microfuidic devices as a reaction vessels for the fabrication of particles[3]. Channels where fabricated using photolithography techniques, producing channels with typical features as small as 500 μm. Our initial studies are with Palladium and presented will be our novel work on other metals and semiconductors. Performing the reactions in these devices allows a greater control over the reaction parameters, such as the cell geometry, high through put of materials, the ability to study the reaction under steady state, and well defined conditions[4].
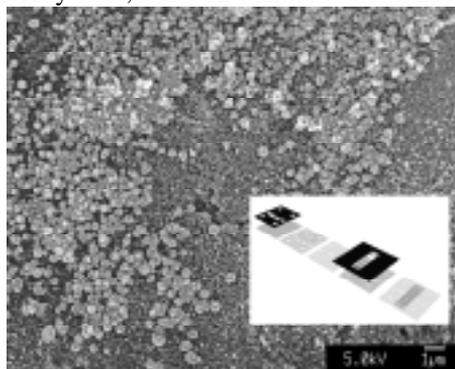
Fig 1. SEM of Palladium particles captured after being produced in a microfluidic channel, Insert shows a schematic of the fabrication process.

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Symposium 6 - Oral

Liquid-liquid Electrochemistry

Lutetium bisphthalocyanines, Lu(III)[Pc']$_2$, as redox probes for charge and electron transfer studies across liquid-liquid interfaces between water and solvents or ionic liquids: thin-film and three-phase electrodes.

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Solid electrodes covered with droplets or layers of organic solvents or ionic liquids containing redox compounds, in contact with an immiscible aqueous solution, constitute thin-film or three-phase electrodes. Oxidation, or reduction, of the solute in the organic phase requires that an ion is exchanged with the aqueous phase. The overall electrode reaction is a very convenient way to study charge transfer processes across liquid|liquid interfaces, giving very reliable results.

Ferrocenes, particularly the highly lipophilic derivative, decamethylferrocene, are frequently used. For the present studies, lutetium bisphthalocyanines [LuPc'$_2$] have been preferred. These are also molecular sandwich complexes, lipophilic, but much more stable than ferrocene and particularly its oxidized form. Moreover, LuPc'$_2$ can be reduced as well as oxidized by reversible, one-electron steps. This opens the way, not only to the study of anion transfers but also to that of cation exchanges with the aqueous phase.

Gibbs energies have been measured for the transfer from water to nitrobenzene and dichloroethane of a very large series of anions ($B(C_6H_6)_4^-$, Cl^-, PF_6^- …) and cations (Bu_4N^+, Na^+ …). The three-phase electrode is particularly suited for the study of highly lipophilic anions and cations (H^+, OH^-, $H_2PO_4^-$ …) which cannot be examined by voltammetry at ITIES, because of the more easy transfer of the supporting electrolytes. The same technique was also used for tranfer studies between aqueous solutions and tetraoctylphosphonium bromide, an ionic liquid.
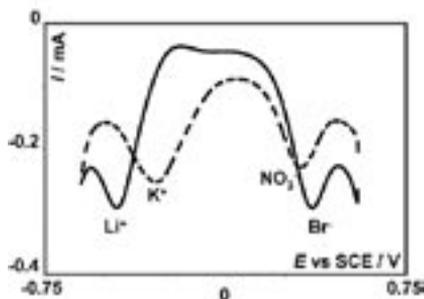
SWV at a LuPc'$_2$ three-phase electrode : transfer of ions from water to nitrobenzene.

The electron exchange between a species in the organic phase and a redox compound in water is equivalent to electrocatalysis mediated by the modified electrode. The interfacial potential, which can be tuned by the choice of electrolytes, has a spectacular influence on the behaviour of the modified electrode.

Chemiluminescence Accompanied by Ion Transfer at the Aqueous-Organic Solution Interface

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The chemiluminescence (CL) accompanied by the transfer of N,N'-dimethyl-9,9'-biacridinium ion (lucigenin ion, Luc^{2+}) across the interface from an organic solution (O) to an aqueous solution (W) containing NaOH and hydrogen peroxide was investigated. The interfacial transfer of Luc^{2+} was realized at a flat W | O interface of 3 mm diameter by the potential-step electrolysis with a three-electrode system, and the CL was detected from the W side of the interface by a photomultiplier through an optical fibre and a monochromator. It had been confirmed by the voltammetric measurement that the transfer of Luc^{2+} across a W | O interface was electrochemically reversible. Nitrobenzene (NB), 1,2-dichloroethane (DCE) or chloroform (CF) was employed as an organic solvent.

It is well-known that Luc^{2+} reacts with hydrogen peroxide in an alkaline solution to split into N-methylacridone (MA) and excited MA (MA*). When the concentration of Luc^{2+} in DCE was as low as 10^{-5} mol dm^{-3}, the CL spectrum at a W | DCE interface coincided with the fluorescence spectrum of MA measured in DCE. When the concentration of Luc^{2+} was as high as 10^{-3} mol dm^{-3}, the CL spectrum was composed of a new spectrum component around 470 nm in addition to MA* emission around 420 nm (Fig. 1a). The new component around 470 nm might be explained by the energy transfer from MA* to an excess of Luc^{2+}, followed by the emission of excited Luc^{2+} (Luc*) [1]. It is noted, however, that the new component agreed with neither fluorescence spectrum of Luc^{2+} in W nor that in DCE, both of which had a maximum around 500 nm. The conventional CL spectrum in W also was measured, which did not show an emission around 420 nm and had an emission maximum around 500 nm (Fig. 1b). When NB was used as O, the emission component around 420 nm was weak because of the MA* quenching by NB. In case of CF, the spectrum of MA* emission only was observed.

The above results can be explained as follows. When Luc^{2+} is transferred from O to W, it reacts with NaOH and hydrogen peroxide to generate MA*. Since MA* is neutral and hydrophobic, MA* generated in W is easily distributed to O and emitted in O. When DCE or NB is used as O, the energy transfer from MA* to Luc^{2+} occurs in the mixed solvent region between W and O during the distribution of MA*, and hence the resulting Luc* emission shows a spectrum specific to the W | O interface. The energy transfer is hard to occur at a W | CF interface.

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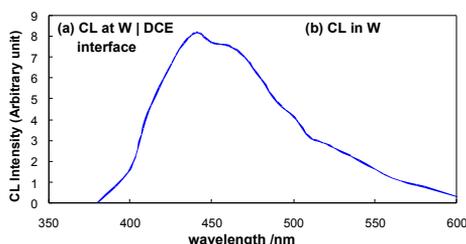
Fig. 1 CL spectra Luc^{2+} at W | DCE interface and in W

Symposium 6 - Oral

Liquid-liquid Electrochemistry

Scanning Electrochemical Microscopy (SECM) as a Probe of Metal Particle Nucleation at Liquid/Liquid Interfaces

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The electrodeposition of metals on solid surfaces has been studied extensively [1], but the mechanistic interpretation of nucleation and growth from electrochemical data has proved to be complex and has been the subject of considerable debate [2]. Liquid/liquid interfaces are free from defects, which usually serve as permanent preferential nucleation sites on solids, making liquid interfaces attractive for the investigation of interfacial nucleation phenomena. Previous studies of metal deposition at the interface between two immiscible electrolyte solutions (ITIES) have focused primarily on the macroscopic scale, and under these conditions it has been difficult to eliminate spontaneous nucleation and to follow short time-scale events.

In this paper we demonstrate how SECM can be used to both initiate and follow the deposition of metals at liquid/liquid interfaces. The concept is to use an ultramicroelectrode (UME; solid metal or micropipette) in one liquid phase to inject a flux of metal ions towards an interface with a second immiscible phase containing a reductant. This approach has several advantages, including: the ability to trigger the electrogeneration of metal ions in one phase thereby minimising extraneous nucleation; the possibility of making measurements on small length scales; the ability to follow short-time events. The current-time behaviour of the probe UME [3] is shown to be highly sensitive to the metal nucleation process. We present studies on the electrodeposition of Ag at the water/1,2-dichloroethane interface (with decamethylferrocene serving as a reductant), which clearly show how the Ag^+ flux and the potential across the liquid/liquid interface influence nucleation kinetics. The use of SECM for the study of other metal deposition processes will be discussed.

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Understanding the Capacitance of ITIES

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Much research in the last decade has explored **i**nterfaces between **t**wo **i**mmiscible **e**lectrolytic **s**olutions (ITIES). Several questions regarding fundamental physical phenomena at ITIES have been raised by both theorists and experimentalists. Does a mixed-solvent compact layer form between the two phases? How are the potential and ionic concentrations distributed near the interface? Do ions penetrate the ITIES over a short range, even when the ionic free energies of transfer are large? Can pairing interactions between ions from different phases play a significant role? Here, a simple theory [C. W. Monroe et al., *J. Electroanal. Chem.* **582** (2005) 28-40] explains how each question can be answered by the potential dependence of the capacitance, which is the simplest tool with which to study the interface.

The presented theory (the MUK theory) employs a three-phase model of the ITIES, which treats the interface as a mixed-solvent region that can be penetrated by ions. On either side of this inner layer, nonlinear Poisson-Boltzmann analysis yields distributions of the concentrations and potential. The relative frequencies of penetration events are determined without any extra assumptions through the ionic free energies of transfer, which are experimentally known. Inner-layer ion pairing is also included in the model. This description is significantly more detailed than the standard Verwey-Niessen (VN) theory, which treats the interface as an impenetrable plane. However, the MUK theory remains analytically simple and readily allows fitting of experimental data.

Fig. 1. Comparison of MUK theory (solid line) and VN theory (dashed line) with data for a nitrobenzene/water ITIES with high free energies of transfer.

Fig. 1 compares experimental results with the MUK and VN models. Our theory explains the shift of the minimum away from zero potential and the asymmetry of the curve. Both of these commonly observed features are caused by ion penetration and owe to differences among the ionic free energies of transfer.

This work provides the first theory that both incorporates ion penetration and allows direct fits of measurements with a single, easily estimated free parameter. It also shows that ion pairing does not play a significant role in typical systems.

Symposium 6 - Oral

Liquid-liquid Electrochemistry

Electrochemical processes of redox liquid deposited on nanoparticles- or nanofibers-silicate composite film electrodes

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Liquid | liquid ion transfer processes can be observed and applied using electrodes with an immobilised liquid phase [1,2]. Therefore the development of suitable electrode support is desirable. The close proximity of the electrode surface and both liquid phases (at the three phase junction) has been shown to be a condition for efficient electrode process for unsupported organic liquids, where no electrolyte salt has been intentionally added into the organic phase. This aspect is less important for supported redox liquid deposit when large surface area is desirable Heterogeneously structured bulk modified carbon ceramic electrodes with electronically conductive graphite particles [3] or carbon nanofibers (CNF) [4] already proved provides favourable conditions for this process.

Following this strategy thin film electrodes were prepared. The electrode surface modification based on conducting ITO nanoparticles or CNF embedded in a hydrophobic silicate film will presented. AFM and FEGSEM images demonstrate the presence of porous ITO nanoparticle or CNF films.

These highly conducting films are employed as matrix for redox liquid immobilisation. After modification of these electrodes with liquid redox probe - t-butylferrocene or its solution in unsupported or supported 2-nitrophenyloctylether their electrochemical behaviour was studied by cyclic voltammetry and differential pulse voltammetry in aqueous solution. The presence of conducting nanoobjects embedded in the mesoporous matrix substantially increases the efficiency of the electrode process and stability under voltammetric conditions. Also well defined response for diluted redox liquids is obtained. From measurements in a range of different aqueous electrolyte media a gradual transition from anion transfer dominated to cation transfer dominated processes is inferred depending on the hydrophilicity of the transferring anion or cation. This behaviour is similar to analogous CNF-silicate film electrodes modified with room temperature ionic liquid [5].

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Electroassisted two-dimensional phase formation at a liquid/liquid interface

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The formation of two-dimensional structures based on di-alkyl viologen derivatives at a liquid-liquid interface is discussed. Bipyridyl derivatives have received recently considerable attention as molecular wires. Their electrochemical properties at interfaces in the absence of metallic contact are of interest as an example of how to relate properties of adsorbates in contact with molecular liquids. The molecules investigated are shown in Scheme I. Some cyclic voltammetry results at different sweep rates for the C_{16} compound are shown in Figure 1. At applied potentials < 0.07 V the formation of an adsorbed monolayer is observed. At more negative potentials the interfacial formation of a new multilayer phase is clearly observed.
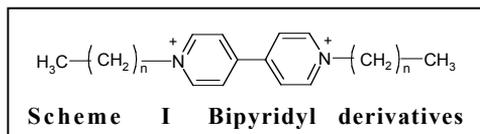
$$H_3C{-}(CH_2)_n{-}N^+{=}\langle\text{bipyridyl}\rangle{-}N^+{-}(CH_2)_n{-}CH_3$$

Scheme I Bipyridyl derivatives

Adsorption at these interfaces was investigated by AC impedance spectroscopy and square pulse voltammetry. The monolayer charge calculated from these results was (1.5 ± 0.2) nm^2 considering the adsorption of a divalent cation. An approximately value of the area of this molecule is 2 nm^2 indicating adsorption of the viologen cation parallel to the interface. The multilayer formed at the interface is related to the presence of the citrate anion since this is absent when the aqueous electrolyte contained Cl^- or F^- anions. In addition, investigation of the adsorption properties of the reduced viologen radical showed that the formation of these multilayer films is related to electrostatic interaction between the citrate anion and the viologen dication.
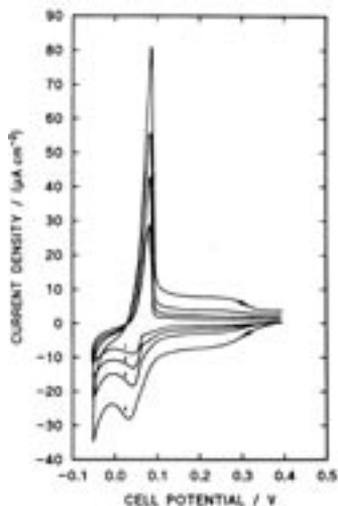
Fig 1 CV of the $C_{16}VC_{16}$ viologen in 1,2-DCE in contact with 1 M aqueous Na citrate

Electron transfer between the viologen compounds synthesized and several aqueous redox couples was investigated and the dependence of the electron transfer between the bipyridyl group and the aqueous redox couples for different chain lengths will be discussed.

Symposium 6 - Oral

Liquid-liquid Electrochemistry

Double-barrel micropipet and its applications

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In this presentation, we will briefly introduce the work, which has been done in our group about the applications of double-barrel micropipets in the investigations of charge transfer reactions (CTRs) at liquid/liquid interfaces.

Double-barrel (or dual or θ) micropipet was first introduced by Shao and Mirkin in 1998 as a novel electrochemical generation/collection (G/C) technique to study the ionic reactions occurring at a liquid/liquid interface that involve no oxidation/reduction steps [1]. This technique can be used to study the concurrent ion transfer (IT) reactions occurring at a liquid/liquid interface and to probe the kinetics of homogeneous reactions involving ionic species [2-4]. However, in view of large amount of studies made on investigation of complicated mechanisms and probing charge/mass transport in various media employing other conventional steady-state G/C techniques focused on the ET reactions, such an ionic G/C technique has not been widely utilized in the electrochemical studies. One of the reasons is that this G/C device usually has more complicated geometry compared with other G/C techniques. It is challenging to simulate mass transport in such a system with an irregular shape, and there has not been a theory available for double-barrel micropipets until now.

Here, we report the simulation and experimental verification of the collection efficiency of double-barrel micropipets as G/C devices in the studies of CTRs at liquid/liquid interfaces. The influence of the shape of a double-barrel micropipet on the collection efficiency, such as curvature and symmetry of the pipet, as well as the thickness of glassy band between generator and collector, is presented and discussed specifically. Also, we will briefly present some work related to nano-double-barrel micropipets.

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Electrochemistry with cylindrical microelectrode in contact with two immiscible liquids

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Investigation of the phenomena occurring at the electrode in contact with two immiscible liquids significantly extends the field of application of electrochemical methods [1]. Particularly interesting is investigation of ion transfer across the phase boundary and of the reactions that require the transfer of ions [2]. Three-phase electrochemistry gains in importance also due to its usefulness in mimicking various biophysical phenomena. The key idea of the approach presented in this paper is that the electrode (microwire) crosses perpendicularly the liquid-liquid phase boundary. The result is that one part of the microcylinder is located in one liquid while the second part stays in the second liquid [3]. The organic liquid contains a hydrophobic depolarizer and, importantly, no supporting electrolyte. The aqueous phase contains appropriately selected salts that provide counterions to the electrode reaction product. Formally this setup can be reversed. Configurations involving organic-liquid drops and microcylinders were examined also.

In terms of the determination of the standard potential of transfer of the anions from water to the organic phase, the microcylindrical method is more precise than the other methods, since the three-phase boundary formed with a metallic wire is better defined and better reproduced. The new method appears also to be applicable to a larger set of organic liquids.

The examination of the reaction layer and the penetration of anions into organic phase was made possible after placing some monomers into the organic phase. Under the experimental conditions the polymerization process was controlled by the availability of the counterions. Poly(N-vinylcarbazole) could be deposited exactly at the nitrobenzene/water/platinum three-phase boundary when the counterions could not penetrate the organic phase easily. The ions penetrating the organic phase allowed the polymer layer to extend into the organic phase. Interestingly the structure of the polymer layer changed substantially with the distance from the three-phase boundary. The polymer structures included, among others, sets of perfectly arranged deep and oval channels and sets of microcrystals.

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Symposium 6 - Oral

Liquid-liquid Electrochemistry

Voltammetric study of the interfacial electron transfer between ferrocene in organic solvent and hexacyanoferrate in water

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Theory of the voltammetric current of electron transfer (ET) reaction at organic solvent(O)/water(W) interface between a redox couple of A species, A_{RED} and A_{OX}, in O phase and another redox couple of B species, B_{OX} and B_{RED}, in W phase has been discussed. A_{RED} is supposed to be a neutral molecule and A_{OX} a cation, whereas both B_{RED} and B_{OX} are supposed to be highly hydrophilic. Two kinds of the reaction mechanism, that is, (1) the heterogeneous ET reaction: $A_{RED}(O) + B_{OX}(W) = A_{OX}(O) + B_{RED}(W)$ at the O/W interface producing the voltammetric current, and (2) the transfer of $A_{RED}(O)$ molecule from O to W phase across the interface, then the homogeneous ET reaction: $A_{RED}(W) + B_{OX}(W) = A_{OX}(W) + B_{RED}(W)$ in W phase, followed by the transfer of $A_{OX}(W)$ cation from W to O phase producing the voltammetric current, called the ion transfer (IT)-mechanism, are considered. Theoretical equations of normal-pulse and cyclic voltammetric currents are derived under the assumptions (i) that the ET reaction is pseudo-monomolecular with respect to A species, (ii) that the partition of A_{RED} molecule between O and W phases is highly biased to O phase, and (iii) that the rate constants of homogeneous ET reaction in W phase are sufficiently large.

The theoretical equations were applied to investigate the mechanism of the ET reaction between ferrocene ($[Fe^{II}(C_5H_5)_2]$) in 1,2-dichloroethane (1,2-DCE) and in nitrobenzene (NB) and hexacyanoferrate redox couple ($[Fe^{II/III}(CN)_6]^{4-/3-}$) in water (W). The voltammetric results indicate that the ET reaction takes place not by way of the heterogeneous-ET-at-O/W-interface-mechanism but by the IT-mechanism. From the limiting currents of the normal-pulse voltammograms, the forward rate constants of the homogeneous ET reaction: $[Fe(C_5H_5)_2] + [Fe(CN)_6]^{3-} = [Fe(C_5H_5)_2]^+ + [Fe(CN)_6]^{4-}$ in W phase, k_f^{IT}, were determined to be $(3.2\pm2.0) \times 10^{10}$ M^{-1} s^{-1} and $(2.0\pm1.3) \times 10^{10}$ M^{-1} s^{-1} with the 1,2-DCE/W(1.5 M Li_2SO_4) and NB/W(1.5 M Li_2SO_4) interfaces, respectively. These values are in the order of the rate constant of diffusion-controlled bimolecular reaction in solution. Also, the formal (standard) potentials of the transfer of $[Fe(C_5H_5)_2]^+$ ion at the interface, $\Delta_O^W\phi_{Fc+}^0$, were determined to be -0.015 ± 0.014 V and -0.087 ± 0.015 V with the 1,2-DCE/W(1.5 M Li_2SO_4) and NB/W(1.5 M Li_2SO_4) interfaces, respectively.

The ET reaction between dibutylferrocene ($[Fe^{II}(C_5H_4Bu)_2]$) in 1,2-DCE and $[Fe^{II/III}(CN)_6]^{4-/3-}$ in W has also been studied and shown to take place by the IT-mechanism.

Determination of standard Gibbs energies of transfer of anions across 2-heptanone/water and acetophenone/water interfaces using the three-phase electrode approach

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Methyl n-pentyl ketone (2-heptanone) and methyl phenyl ketone (acetophenone) have been used as organic solvents in electrochemical studies of the water/organic solvent interfaces. The transfer of more than thirty anions that were ionized from inorganic salts, organic acids and phenols was studied across the water/organic liquid interfaces and the standard Gibbs energies of ion transfer were determined. The ion transfer was achieved by the oxidation of decamethylferrocene that was dissolved in the organic phase and attached as a droplet to the graphite electrode immersed in the aqueous electrolyte phase containing the anions. Square wave voltammetry was used to determine the formal potential of decamethylferrocene/decamethylferrocenium (dmfc/dmfc$^+$) redox couple. The electrode reaction is described by the equation:

dmfc (o) + X$^-$ (w) $\rightarrow$ dmfc$^+$ (o) + X$^-$ (o) + e$^-$, where X$^-$ is the transferred anion. Standard Gibbs energies of ion transfer from water to the organic solvents were calculated based on Abraham's model and a comparison was made between theoretical and experimental results.

Symposium 6 - Poster

Liquid-liquid Electrochemistry

Symposium 6 - Poster

Liquid-liquid Electrochemistry

Novel Room Temperature Ionic Liquids for the development of Highly Poliarisable Ionic Liquid/Water Interfaces

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Ionic Liquids have become highly topical in a number of different areas of chemical research. They are of interest as replacements for common organic solvents due to their negligible vapour pressure, thereby reducing the effect on the environment due to their easy containment[1]. The electrochemical properties of air stable, room temperature ionic liquids (RTILs) have also been studied extensively[2]. Very recent work has extended to the ITIES (Interface between Two Immiscible Electrolyte Solutions)[3], including some work where the aqueous/RTIL interface has been polarised[4]. However, studies have been limited by the difficulty in producing suitable ionic liquids that can exhibit potential windows comparable with those commonly found at aqueous/organic interfaces (ca. 1 V).

The research reported here describes a number of new highly polarisable RTILs based around tetraalkylammonium cations coupled with a number of different anions such as the bisperfluoroalkylsulfonylamides and the tetraarylborates. A discussion of their physical and electrochemical properties at the ITIES formed with aqueous solutions will be presented.

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Symposium 6 - Poster

Liquid-liquid Electrochemistry

Symposium 6 - Poster

Liquid-liquid Electrochemistry

Visualising Dynamic Processes at Polarised Liquid/ Liquid Interfaces

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This work is concerned with two aspects of dynamic processes at liquid/liquid interfaces: first, investigating variations in interfacial area as the potential across a polarised interface is changed and second, the use of electrochemistry to follow phase formation (polymer film) at liquid/liquid interfaces.

The externally-polarised interface between two immiscible electrolyte solutions (ITIES) has been visualised using laser scanning confocal microscopy (LSCM). A water|1,2-dichloroethane interface was formed using a micropipette [1], which was inverted so that the liquid/liquid interface at the tip could be imaged. The organic phase, inside the pipette, contained Nile Red, a fluorophore which did not transfer across the interface in the potential range of the supporting electrolytes. While varying the potential across the liquid/liquid interface, LSCM was employed to visualise movements in the interface. The dynamic changes in the morphology of the interface were found to be most significant when a lipid (L-a-phosphatidylcholine, disteroyl (C18:0)) was introduced into the organic phase, so as to change the surface tension by adsorption.

A polymeric membrane (poly(urea)), was formed at the liquid/liquid interface at the tip of a micropipette, and the kinetics of formation were monitored using electrochemistry. The decrease in the peak current for the transfer of tetraethyl ammonium cation from the water phase to the 1,2-dichloroethane phase was used as a non-optical means of following the formation of the membrane in real time.

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Symposium 6 - Poster

Liquid-liquid Electrochemistry

Fabrication and characterization of nanostructured electrochromic films

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Iridium oxide is known to have excellent electrochromic[1] and pH sensing properties.[2,3] Films of iridium oxide were deposited anodically according to Yamanaka's recipe[4] and characterized by voltammetry in the growth solution and subsequently in acid and base electrolytes. SEM was used to assess the morphology and texture of the films. Attempts were made to create a nanostructure by depositing the films within a molecular template formed by the self-assembly of liquid crystal molecules according to the method developed in Southampton.[5] An alternative approach attempted to decorate a nanostructured Pt film with iridium oxide. Macroporous iridium oxide films with varying thicknesses were successfully fabricated by deposition within a template made with self-assembled polystyrene spheres (typically 600 nm $\varnothing$) as described by Bartlett et al.[6] Dissolution of the template reveals smooth films with ordered arrays of hollow cups hexagonaly distributed, see Fig. 1. Films were also formed by decorating macroporous Au films. Films with graded thicknesses were obtained. The effect of the structure on the electrochromic properties was investigated. Preliminary results for the fabrication and characterization of this novel nanostructured iridium oxide films will be presented.

Fig. 1 Macroporous iridium oxide films grown with 30 (left) and 100 (right) sweeps between -0.8 and +0.7 V vs. SCE at 100 mV s^{-1}. Template: polystyrene spheres 600 nm $\varnothing$.

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Multilayer assmblies for light energy conversion

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In recent years, the fabrication of novel ultrathin film systems featuring multi-functionalities has been extensively studied because of their potential applications in electronics, photonics, sensors and photoelectrochemical cells. The goal of the present work was to develop film-modified electrodes for light energy conversion applications. Ultrathin polypeptide multilayer films are assembled by the electrostatic adsorption of alternating monolayer of poly-L-lysine and poly-L-glutamic acid onto carboxylic acid terminated alkanethiol-modified gold surfaces. These polypeptide multilayer films are hydrophilic, can bind electroactive anions such as ferri/ferrocyanide, and are stable when immersed in organic solvents such as 1,2-dichloroethane. Cadmium selenide (CdSe) quantum dots stabilised by citrate groups have been synthesised and characterized by UV-Vis spectroscopy and transmission electron microscopy. The CdSe QDs were electrostatically attached to the multilayer film assembly and used photoactive species. Photocurrent responses originating from the CdSe sensitised ultrathin multilayer film were investigated as a function of the applied potential, the thickness of the film and the presence of a quencher in the organic phase. A theoretical model and simulations are proposed in order to rationalise the kinetics of the electron transfer and the photocurrent responses.

Symposium 6 - Poster

Liquid-liquid Electrochemistry

Symposium 6 - Poster

Liquid-liquid Electrochemistry

Voltammetry of picrates at a micro ITIES without supporting electrolytes.

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A micro liquid|liquid interface is established between water and a solvent, nitrobenzene (NB) or dichloroethane (DCE), at the end of a channel drilled through a polyimide film ; the interface is circular (diam. = 50 μm). At low scan rates, *e.g.* 5 mV s^{-1}, waves with well defined plateaus are observed, typical of a radial diffusion state. As intensities are low (~nA), ohmic drop is reduced [1]. Voltammetry of tetraalkylammonium picrates at the interface between water and NB or DCE has been previously studied in the presence of supporting electrolytes in both phases [2]. The same series of salt was examined when no other electrolyte has been introduced in the aqueous and organic phases. For these experiments, the reference electrodes must be replaced by silver or platinum wires, to prevent contamination from the electrolytes.

The influence of the supporting electrolytes on voltammetry is important. When there is no electrolyte in both phases, effect of iR drop on the voltammograms is apparent. For a picrate staying in the organic phase because of its highly hydrophobic cation, the addition of a supporting electrolyte in water reduces the distorsion of the voltammograms but does not change much the intensity of the plateau currents. On the contrary, the addition of another electrolyte in the organic phase where the picrate is dissolved, lowers importantly the current, by a factor of two. The limiting currents are much higher in the absence of supporting electrolytes because of the common influence of diffusion and migration on mass transport. As expected, from experiments at solid ultramicroelectrodes, addition of traces of the electrolyte reduces importantly the plateau current which almost reaches the diffusion level when the supporting electrolyte concentration is two times that of the picrate.

It could be argued that the interest of working without added electrolyte is limited because of the more complex phenomena involved; however, the advantage is obvious. Voltammetry of some picrates, *e.g.* Me$_4$NPi, which partition between water and NB illustrates the very important influence of electrolytes on the repartition of the salts. Half-wave potentials for ion transfers, consequently Gibbs energies measured by voltammetry, are conditional values which depend on the supporting electrolyte used for the experiment.

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Symposium 6 - Poster

Liquid-liquid Electrochemistry

Electrochemical Investigation of Bimolecular Reaction at Liquid/ Liquid interfaces

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The bimolecular reaction at the liquid/liquid interface was driven by the difference in the formal redox potentials of the two reactants confined to the two adjoining, immiscible phases, respectively, and presented interfacial electron-transfer process. Rate constant of the interfacial reaction was obtained by both thin-layer cyclic voltammetry (TLCV) method and scanning electrochemical microscopy (SECM) technology. The studying of electron-transfer reaction between ascorbic acid (AA) and Zinc mono-hydroxyl-tetraphenyl Porphyrin (ZnTPP(OH)) verified the antioxidant activity of AA in life system. Thin-layer and SECM methodology were applied as investigating means to evaluate rate constant of electron transfer at ITIES achieved and expressed concerns about the simplicity and reliability.

Porphyrin derivatives play a key role in essential biological processes such as photosynthesis, dioxygen transport and storage. Such complexes have been used in a variety of applications as models for biological electron transport in biomembranes is well known. In the report, electron transfer between Zinc porphyrin of different substitutes and K4Fe(CN)6 was detected by SECM and different substitutes presented different electrochemical activity at ITIES. Such behaviors were also verified that substitutes with different electron affinities could make the ligand body behave different properties and result in some influence to kinetics reactions of heterogeneous of ET.

Structure of the interface between two immiscible liquids and interfacial tension

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Adsorption of hydrophobic, hydrophilic, and amphiphilic ions at the interface between two immiscible liquids was investigated. The results were analyzed in three different models: (i) the Gouy-Chapman model, (ii) ions as hard spheres, (iii) ion pair formation at the interface. In the Gouy-Chapman model, an analytical expression for the interfacial tension was obtained. It predicts that interfacial tension should be proportional to the square root of the electrolyte concentration. This prediction does not agree with experimental data. Modeling ions as hard spheres slightly improves the agreement between the theoretical and experimental results. The third model of interfacial ion pairing as the main origin of adsorption was analyzed using the amphiphilic isotherm (MV isotherm) [Markin, V. S.; Volkov, A.G. In Encyclopedia of Electrochemistry; Bard, A. J., Stratmann, M., Gileadi, E., Urbakh, M., Eds.; Wiley-VCH, Weinheim, 2002; Vol. 1, pp. 162-187]. A good agreement between ion pairing theory and experimental values was achieved. The MV isotherm takes into account the limited number of adsorption sites, finite size of molecules, complex formation at the interface and interaction between adsorbed particles. The analysis revealed repulsion between adsorbed tetraalkylammonium ions at the nitrobenzene/water interface and demonstrated linear dependence between adsorption site area and the size of a molecule. Classical isotherms of adsorption (Frumkin, Langmuir, Henry) were based on the model of non-penetrable interface, where an adsorbate can substitute only molecules of one solvent. At the interface between two immiscible electrolytes, nonpolar oil/water interfaces, and liquid membranes amphiphilic molecules can substitute molecules of both solvent and classical isotherms cannot be used. The generalization of Frumkin isotherm for permeable and non-permeable interfaces, known as the Markin-Volkov isotherm, gives the possibility to analyze adsorption in a general case. The adsorption isotherms of pentafluorobenzoic acid (PFBA) at the octane/water interface at the different pHs were measured by the drop-weight method. From the measurements of PFBA adsorption, the structure of the octane/water interface was determined. Adsorbed octane molecules have a lateral orientation with respect to the interface. Gibbs free energy of adsorption equilibrium and thermodynamic parameters of PFBA adsorption show that the adsorption of PFBA at the octane/water interface is accompanied by a reduction in the attraction between adsorbed PFBA molecules as the pH decreases to the acidic region.

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Liquid-liquid Electrochemistry

Direct spectroelectrochemical measurement of rhodamine dyes at the polarized liquid/liquid interface

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Ion transfer processes across polarized liquid/liquid interfaces can be described in terms of a series of elementary steps involving transport phenomena and specific adsorption at the interfacial region. The potential modulated fluorescence (PMF) spectroscopy allows evaluating the interfacial process of the fluorescent ion without controversial contributions from base electrolyte transfer, capacitive current and so on [1]. By analyzing the ac-perturbation of fluorescence signal forced by potential modulation, the ion transfer and adsorption processes can be investigated separately from the contribution of bulk phases. The dependence of the amplitude and phase shift of the optical signal contains information on the nature of the charge transfer and adsorption process [2, 3]. In this work, the ion transfer mechanism of amphoteric rhodamine dyes, rhodamine B (RB) and rhodamine 19 (R19), at the water/1,2-dichloroethane interface were investigated by means of the PMF spectroscopy.

The interfacial behavior of RB and R19 significantly depends on the pH condition since the charge of the molecule is affected by the dissociation equilibrium of carboxyl group. At pH 3.0, the PMF response for both rhodamine systems indicated the presence of adsorption process at the potentials more positive than the formal ion transfer potential. The frequency response and phase shift of PMF signals indicate the adsorption process of the cationic rhodamines in the organic side of the interface. The dependence of the PMF intensity on the emission wavelength was analyzed at the adsorption potential and the emission spectrum of the interfacial species could be successfully observed. The interfacial spectrum roughly coincides with the bulk organic spectrum suggesting that the solvation structure of the xanthene moiety is similar to the bulk organic species.

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Electrochemical extraction of proteins by reverse micelle formation

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The transfer of proteins by the anionic surfactant bis(2-ethylhexyl) sulfosuccinate (AOT) at a polarized 1,2-dichloroethane/water (DCE/W) interface was investigated by means of ion-transfer voltammetry. When the tetrapentylammonium salt of AOT was added to the DCE phase, the facilitated transfer of certain proteins, including cytochrome c (Cyt c), ribonuclease A and protamine, could be controlled electrochemically, and a well-defined anodic wave for the transfer was obtained. At low pH values (e.g., pH 3.4), the anodic wave was usually well separated from the wave for the formation of protein-free (i.e., unfilled) reverse micelles (Fig. 1a). The anodic wave for the protein transfer (Fig. 1b) was analyzed by applying the conventional theory for facilitated transfer of metal ions by neutral ligands, and then supplying information regarding the number (n) of AOT anions reacting with one protein molecule and the total charge (z) carried by the protein transfer. The observed dependence of n on the nature of the aqueous supporting electrolyte suggested that the protein-AOT complexes may present *primitive* reverse micelles containing a minute fraction of the W phase. Controlled-potential electrolyses performed for the transfer of Cyt c, which is red, revealed that the primitive reverse micelles were unstable in DCE when the pH of the W phase was 3.4. However, at pH 7.0 when formation of unfilled reverse micelles occurred simultaneously, the primitive reverse micelles containing proteins were able to grow into stable reverse micelles, probably via fusion with unfilled reverse micelles.
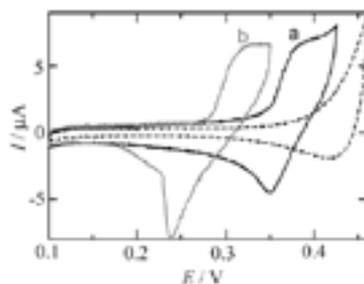
Fig. 1. Cyclic voltammograms obtained at the DCE/W interface in the presence of 0.5 mM AOT in DCE with (a) 0 mM or (b) 0.1 mM Cyt c in W (pH 3.4). The dashed line represents the background current in the absence of both AOT and Cyt c. Scan rate: 100 mV s^{-1}.

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Liquid-liquid Electrochemistry

Adsorption of phosphatidylcolines at oil/water interfaces

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The properties of assemblies of phospholipids are of considerable importance in the life science, being the objective of many studies. Among those studies are those using as simplified models for biological interfaces such as ITIES-interfaces between two immiscible electrolyte solutions.

The adsorption of a series of phosphatidylcolines with saturated carbon chains of different length (C12, C16, C18, C20 and C22) and the effect of experimental parameters on the adsorption process were studied at the electrified 1,2-DCE/water and NPOE/water interfaces. Electrochemical impedance spectroscopy was used to determine the interfacial capacitance at the polarized interface which allowed to follow the adsorption phenomena of lipids at the ITIES.

A theoretical model based on the solution of the Poisson-Boltzmann equation for the interfacial system coupled to the bulk phases was developed. The model provides successful explanation of all experimental trends observed for the dependence of phospholipid adsorption at the interface on the applied potential, lipid concentration and chain length.

S6·P-13

Random nucleation and growth of pt nanoparticles at the polarised interface between two immiscible electrolyte solutions

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Metal deposition at the polarised interface between two immiscible electrolyte solutions is a relatively new electrochemical phenomenon. In the present study, cyclic voltammetry and potential-step chronoamperometry are used to investigate the Pt deposition at the polarised water|1,2-dichloroethane (DCE) interface through reduction of a Pt(II) chloro-complex in water by 1,1'-dimethylferrocene in DCE. Thermodynamic analysis suggests that the deposition is controlled by the interfacial kinetics, and that the activity of the metal particle at ITIES does not differ much from that of the bulk metal phase. It is shown that the shape of the experimental potential-step current transients could be described with the help of the available theory of nucleation and growth of a metal particle at a liquid-liquid interface. However, the repeated potential-step experiments on the bare interface reveal that the initial rate of the Pt deposition can attain a broad range of values that spans over two orders of magnitude. It is proposed that this surprising feature is related to the random rate of the formation of nuclei with a critical size that is necessary for a stable growth to occur. Explanation is supported by computer simulation for a model assuming that the interfacial metal particle can either grow or decline by one atom, or remain inactive with a comparable probability.

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Liquid-liquid Electrochemistry

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Liquid-liquid Electrochemistry

Electroanalytical application of zeolite modified electrode: heavy metal ions sensing assisted by ligands at liquid-liquid interface

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During the last decade, Zeolite Modified Electrodes (ZME) have received great interest from electrochemists for their various applications. Zeolites offer the most complete range of interesting properties required at the electrochemical interface, including shape, size and charge selectivity, physical and chemical stabilities, high ion exchange capacity in a microstructured environment and hydrophilic character.

Studies on electrochemical reactions at the liquid-liquid interface have attracted much attention due to the wide range of application in chemistry and biology. Koryta and co-workers pioneered the electro-assisted transfer of metal ions at the liquid-liquid interface using ligands and this approach has been followed by electrochemical studies on the sensing of metal ions.

The aim of the present study is the use of the ZME for sensing of Cadmium and Lead ions by voltammetry at the liquid-liquid interface. Basically, zeolite molecular sieves selectively exchange cations, but there is no specificity. In order to get the specificity, ligands are used for the metal ions sensing. The possibility of interference effect in the heavy metal ions sensing is less in this method. Zeolite-Y type pressed disk membranes are used for the sensing of metal ions and the ligands used for this work are hexathiacyclooctane (HTCO) and tetrathiacyclononane (TTCN). The metal ion and ligand are initially present in the aqueous and organic (1,2-dichloroethane) phases. Electrochemical experiments are carried out using a four-electrode potentiostat with iR drop compensation. Further experiment involves the detection of Cadmium and Lead ions at various concentrations with and without the zeolite membrane.

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Preparation of nanostructures composed of dextran sulfate/ruthenium nanoparticles and their interaction with phospholipid monolayers at a liquid–liquid interface

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The interactions between phospholipids and glycosaminoglycans (GAGs, which are polysaccharides highly sulfated and negatively charged, and can be found in the extracellular matrixes of many tissues as well as inside and on the surface of cells)[1] are of great biological importance and are fundamental to understand both their physiochemical behaviour and their pharmacological properties. In previous studies we have shown how dextran sulfate (DS, used here as model for GAGs due to their structural similarity) interacts with phospholipid monolayers at air–liquid and liquid–liquid interfaces,[2] and how polyelectrolyte (PE)–gold nanoparticles (NPs) self-assembled multilayers deposited on a lipid-DS monolayer can be used to fabricate nanocomposites and nanopartterning materials fundamental for delivery devices.[3] Continuing this work on the interactions between lipid monolayers and water-dispersible metal NP systems that could be used in pharmacology, our current interest is the self-assembly of ruthenium (Ru) NPs using biomolecules (such as DS) as templates. Ru NPs are considered because of the well-known catalytic activity of Ru, and because positively charged

Fig. 1. TEM image of the composite nanoclusters (DS-modified Ru NPs).

Ru NPs can be prepared in aqueous medium, providing new opportunities for the surface functionalisation with biological ligands such as PEs, DNA, and oligonucleotides. In the present study, novel interfacial nanostructures composed of DS/Ru NPs adsorbed on phospholipid monolayers at the ITIES were prepared and characterized electrochemically in relation to their potential use in drug delivery systems. TEM pictures (Fig. 1) shown well-defined and organized structures. The interaction of lipid/DS-modified Ru NPs analysed with capacitance curves and interpreted with a theoretical model shown a lower relative permittivity of the hydrocarbon region and an increase in the surface charge density with increasing of the surface pressure. Using cyclic voltammetry was also demonstrated that the lipid layer retards the rate of drug transfer by a factor of 2/3 and 1/2 in the case of aminacrine and tacrine, respectively. In drug

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Liquid-liquid Electrochemistry

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Liquid-liquid Electrochemistry

Quantum-chemical study of electro-chemical reduction of some γ-piperidones

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The electronic structure of molecules 2,5-dimethylpiperidone (DMP), 1,2,5-trimethylpiperidone (TMP) and possible intermediate compounds at their electrochemical reduction to secondary alcohols – anions, dianions, complexes of a radical type including protonated ones has been calculated by semi-empirical quantum-chemical method MINDO/3. The analysis of energy of formation of anion-radicals and dianions of mentioned molecules also energy and structures of their lower unoccupied molecular orbital (LUMO) of the calculated compounds shows that TMP is reduced easier than DMP.

According to polarography data half-wave potential of reduction is equal 2,625V for DMP and 1,155V for TMP that confirms the results of quantum-chemical calculation. Protonation of initial molecules both on oxygen and on nitrogen atoms results in decrease of energy level of LUMO. It indicates the lightening of electrochemical reduction of protonated complexes in comparison with initial compounds. This fact agrees with the results of polarography study on reduction of carbonyl compounds.

Lower unoccupied molecular orbital of protonated complexes on oxygen has π-antibonding character for carbonyl group. Atomic orbital of C4 atom endows primary contribution to it. Hence, when filling this molecular orbital one or two electrons are mostly located at atom C4. It should be noted that the formation of the centre can take place and this centre can join proton. It results in formation of secondary alcohols. Hence carbon atom of carbonyl group serves as the reactionary centre being sensitive to structure of LUMO.

The formed secondary alcohols with equatorial and axial orientations of hydroxyl groups have been calculated. It is shown that piperidol with equatorially oriented hydroxyl group are more stable than molecule with axial orientation of this group.

Thus on the basis of calculations and analysis of structures and properties of intermediate compounds it is offered the most acceptable way of realization of electrochemical reduction of studied γ-piperidones to secondary alcohols in protogenic media under the following scheme:

$$R + H+ \ \square \ RH+;$$
$$R + H+ + 2e \ \square \ RH- ;$$
$$RH- + H+ \ \square \ RH2$$
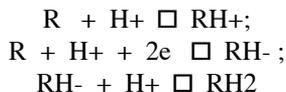
Electroless Deposition of Transparent Conducting and (0001)-oriented ZnO Films from Aqueous Solutions

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Transparent conductive oxides (TCOs) such as ITO, F:SnO_2, and Al:ZnO are an indispensable material as transparent electrodes applied to liquid crystal displays and solar cells [1]. ZnO is a realistic candidate for the hostmaterial of TCO due to the high Clarke number and low material cost. Also, electroless deposition using chemical reactions in a solvent is a key process to fabricate smart thin films on various substrates from the viewpoint of making economical use of energy and manufacturing costs.

Here, we report transparent conducting and ⟨0001⟩-oriented ZnO films prepared on glass substrates by electroless deposition at 343 K from a solution containing zinc nitrate and dimethylamine borane (DMAB) and following heat treatment in H_2/Ar atmosphere. The reductive reaction of NO_3^- to NO_2^- by oxidizing DMAB has an important role in the ZnO deposition [2-3]. Also, dissolved oxygen (D.O.) in the chemical bath will strongly affect the deposition due to its reductive reaction. The ⟨0001⟩-oriented ZnO film with electrical resistivity as low as 4×10^{-3} (Ω cm) has been obtained from the chemical bath not containing D.O. as shown in Fig. 1. Since the initial stage of the growth determines the structure of the resultant film, controlling the competitive reductions of NO_3^- and D.O. is needed to optimize the nucleation step.
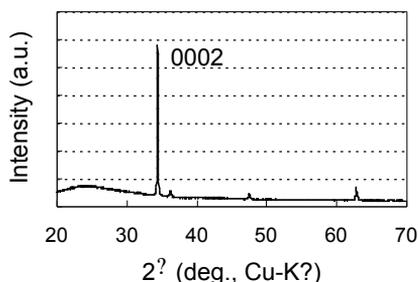
Figure 1. XRD pattern for the ZnO film deposited on a glass substrate from the chiemical bath not containing D.O.

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Liquid-liquid Electrochemistry

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Liquid-liquid Electrochemistry

Ion transfer across ionic liquid / aqueous electrolyte interface supported by carbon paste electrode

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The liquid / liquid ion transfer is an important phenomenon in systems involving an interface between two immiscible liquids. It occurs at electrodes where three phases solid conductor / organic phase / aqueous phase are in close contact [1, 2]. The electrogeneration of charged species in the organic phase forces the ion transfer across liquid / liquid interface in order to maintain electroneutrality of both liquid phases. Two processes are possible: the expulsion of electrogenerated charge species to the aqueous phase or/and insertion of counterion from aqueous phase.

We will present new electrode, where such process can be observed, elecroactive carbon paste electrode, CPE, with ionically conducting binder (room temperature ionic liquid, RTIL). It exhibits electrochemical signal connected with electrode reaction of the redox probe (tert-butylferrocene) dissolved in RTIL. The efficiency of the electrode process is much larger than that of similar CPE modified with the redox probe solution in less viscous organic polar solvent [3]. This can be connected with the presence of conducting liquid phase, and as a consequence with the enlargement of electron transfer zone from the three-phase junction to two-phase junction: graphite particle / RTIL. Moreover, the midpeak potential depends on the hydrophobicity of the anion present in the aqueous solution indicating significant contribution of anion injection into the ionic liquid following the electron transfer. In addition, this electrode exhibits sensitivity (both current and midpeak potential) towards the concentration of anion in the aqueous phase. These results will be compared with that obtained with composite ceramic carbon electrode modified with tert-butylferrocene solution in RTIL [4].

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Simultaneous solvent extraction and electrowinning of silver from silver-calixarene complexes

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Calixarenes are a class of oligo-molecules that are able to complex heavy- and precious metals but also some alkali and alkali-earth metals from water solutions [1]. Beside this, calixarenes are studied to be used for direct electrochemical detection of metal ions [2].

This article presents a study about the electrochemical behaviour of silver-calixarene complexes, formed in the solvent extraction step.

Solvent extraction of silver nitrate from nitric acid solution was used as a model-system in the experiments. Dichloromethane solutions of calix[4]arene tetramide and calix[4]arene thiotetramide were used as extractants. The experiments were carried out by using cyclic voltammetry, chronoamperometry, as well as the electrowinning of silver from loaded organic phase. To prevent the anodic oxidation of calixarenes at the electrowinning experiments the organic phase is used as a catholyte, while the aqueous phase served as an anolyte.

Experimental results have shown a very high extraction degree of targeted ion from the aqueous phase as well as high electrowinning degree of complexed metal during two-phase electrolysis of silver. High current efficiency and reasonably low specific energy consumption were achieved, as well. The most important fact is the possibility to deposit metal without damaging the extractant, making it able to be recycled in the extraction step.

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Liquid-liquid Electrochemistry

Controlling the surface properties of electrodes by means of hydrophobic magnetic particles or redox reactions

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Magnetic nanoparticles (NPs) (5 nm) capped with a hydrophobic monolayer are employed to control electron transfer at electrode surfaces. The NPs were solubilized in a toluene phase, and an aqueous electrolyte/magnetic NP-toluene biphase system was employed to reversibly control the electrochemistry at the electrode-solution surface.[1] (i) The magnetic attraction of the hydrophobic magnetic particles to the electrode induced the blocking of electron transfer to the electrolyte-soluble redox species, resulting in the selective operation of surface-confined electrochemistry.[2] (ii) The magnetic attraction of the hydrophobic magnetic particles facilitated selective bioelectrocatalysis.[3] (iii) The magnetic attraction of the NPs to an electrode modified with CdS NPs enabled the directional and switchable generation of anodic or cathodic photocurrents.[4] (iv) The low dielectric constant of the hydrophobic magnetic NPs yields, upon attraction to a Au NP (1.4 nm)-functionalized electrode, a low capacitance microenvironment. This facilitates the single electron (or hole) charging of the Au NPs.[5]

The binding of metal ions, e.g., Ag^+ or Hg^{2+} to a thiolated monolayer yields an electroswitchable hydrophilic/hydrophobic electrode surface.[6] The kinetics of metal nanoclustering on the monolayer and the electrochemical dissolution of the nanoclusters was followed by electrochemical methods, SPR and SEM. The hydrophobic/hydrophilic functions of the electrode are regulated by the metallic nanoclusters.[6]

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Novel Room Temperature Ionic Liquids for the development of Highly Poliarisable Ionic Liquid/Water Interfaces

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Ionic Liquids have become highly topical in a number of different areas of chemical research. They are of interest as replacements for common organic solvents due to their negligible vapour pressure, thereby reducing the effect on the environment due to their easy containment[1]. The electrochemical properties of air stable, room temperature ionic liquids (RTILs) have also been studied extensively[2]. Very recent work has extended to the ITIES (Interface between Two Immiscible Electrolyte Solutions)[3], including some work where the aqueous/RTIL interface has been polarised[4]. However, studies have been limited by the difficulty in producing suitable ionic liquids that can exhibit potential windows comparable with those commonly found at aqueous/organic interfaces (ca. 1 V).

The research reported here describes a number of new highly polarisable RTILs based around tetraalkylammonium cations coupled with a number of different anions such as the bisperfluoroalkylsulfonylamides and the tetraarylborates. A discussion of their physical and electrochemical properties at the ITIES formed with aqueous solutions will be presented.

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Liquid-liquid Electrochemistry

Electrochemical reaction at oil|water|electrode boundary

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A limited current was obtained through the oil|water|electrode three-phase boundary that is the thin annular part on the electrode to which the water and the oil phase merge (Fig.1). The width of the boundary can be controlled to be smaller than 10
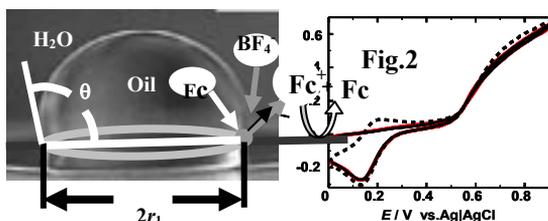
μm, evaluated from the limiting current on the basis of the micro-band model. This kind of three-phase boundary may be generated when a sensor electrode is inserted in living tissues, piercing oil|water interfaces. The electrochemical measurement presented here is the oxidation of ferrocene in the hemispherical droplet of nitrobenzene (NB) at the ring shape of the oil|water|electrode interface. The NB phase contained neutral electroactive species ferrocene without deliberately adding supporting electrolyte, whereas the aqueous phase contained electrolyte without electroactive species. The steady-state current potential curve was obtained at $E > 0.5$ V (Fig.2). The proportionality of the limiting current to the radii of the droplet indicates that ferrocene should be oxidized at the three phase boundary of oil|water|electrode. It is only at the three phase boundary that both the electroactive species and the double layer are present. The ring width of the three-phase boundary was changed with the interfacial tension which was changed by the different concentration of surfactant (Fig.3). It was much larger than a molecular length or thickness of a diffuse double layer predicted geometrically from intersection of two plains even used of a surfactant to stabilized oil|water interface. The large values of width suggest participation in fluctuation of the three-phase boundary. The fluctuation was observed by a movie of the droplet that was taken through an optical microscope during the potential application. The contacting angle between two phases has the charm of variety. They were plotted with the concentration of SDS, as shown in Fig.4, before (Fig.4•) and after (Fig.4Δ) applied potential.
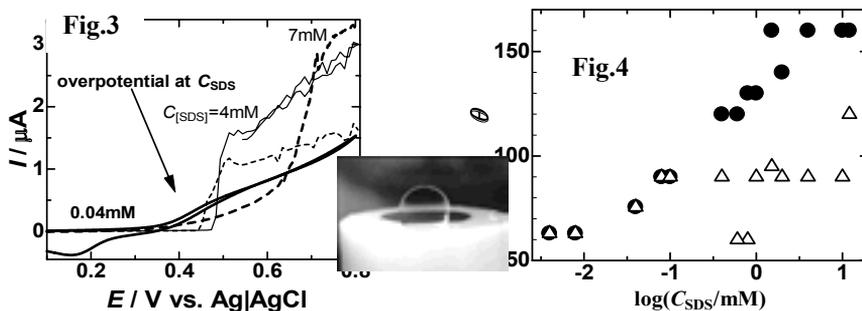
Oscillatory growths of dendrites in metal electrodepositions at liquid|liquid interfaces

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Electrodepositions of metals under diffusion-limited conditions give rise to formations of dendritic crystals. We reported that the electrodeposition of metals under a diffusion-limited condition sometimes shows spontaneous potential oscillations accompanied with the self-organized formation of ordered periodic microstructures.[1,2] On the other hand, it was reported that the electrodeposition of metals at liquid|liquid interface, in which the crystallization proceeds two dimensionally at the interfaces, also show potential oscillations together with the formation of dendrites, though the mechanism was not clarified yet.[3] In the present paper, we report the mechanism of the oscillatory growth of dendrites at liquid|liquid interfaces, which can be explained in the same mechanism as our previously proposed model.
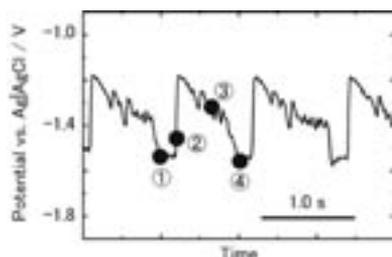
Figure 1   A potential oscillation observed in electrodeposition of Zn at butylacetate|$ZnSO_4$ solution interface.

Figure 1 shows a potential oscillation observed in electrodeposition of zinc at butylacetate|$ZnSO_4$ solution interface under current-controlled condition. In-situ optical microscopic inspection revealed that the growth rate of the dendrite oscillated in synchronization with the potential oscillation as shown in Figure 2. The similar oscillations were also observed in electrodepositions of silver and gold, indicating common mechanism can work in metal electrodeposition generally.

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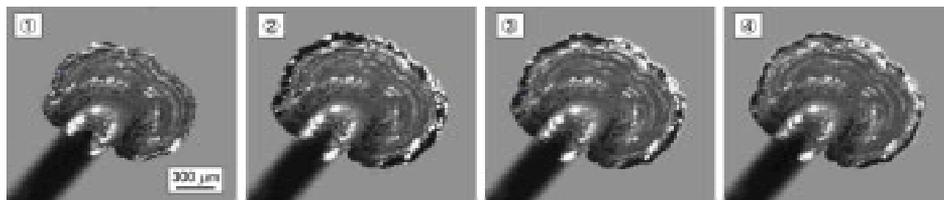
Figure 2   Optical microscopic images of oscillatory growth of dendrite in the electrodeposition of Zn at butylacetate|$ZnSO_4$ solution interface. The numbers in the figures are corresponding to the stages marked in the same numbers in Figure 1.

Symposium 6 - Poster

Liquid-liquid Electrochemistry

Sensing of biomolecules at the polarised liquid|liquid interface

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Electrochemistry at the liquid | liquid interface, or at the interface between two immiscible electrolyte solutions (ITIES), is frequently offered as a simple model of the biological cell membrane: it provides a means for study of biomembrane-related charge transfer processes as well as development of biomimetic analytical tools. Recent studies have demonstrated the electroanalytical properties of the ITIES for direct sensing of dopamine, a neurotransmitter [1-2]. The selective transfer of dopamine eliminated the problems associated with its detection at solid electrodes, such as surface fouling and interference by ascorbic acid.

The work presented here focuses on the detection of amino acids and peptides of biological importance, using the ITIES as a means of transduction. Electrochemical characterisation of the transfer of a range of amino acids and peptides was investigated. The analytes were selected for their different parameters such as hydrophobicity, side chains and charge number. The influence of these different characteristics as well as the experimental conditions on the transfer of the analytes was investigated. The voltammetry of insulin, a small protein, was also investigated at the ITIES revealing a linear correlation between the transfer current and the concentration of bovine insulin over a range from 0.01 – 0.05 mM. In this case, the ITIES provided an alternative technique for the direct electrochemical detection of insulin, eliminating problems such as surface fouling and use of mediators associated with insulin detection at solid electrodes.

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Metalloporphyrin Electrochemistry at Solid | Liquid | Liquid Triple Phase Boundaries

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Processes at electrode surfaces strongly depend on the nature of the solid | liquid (electrolyte) interaction. This is the case in particular for processes at solid | liquid | liquid line interfaces and demonstrated here for the case of electrochemical processes at electrode | organic liquid | aqueous electrolyte triple phase boundaries.
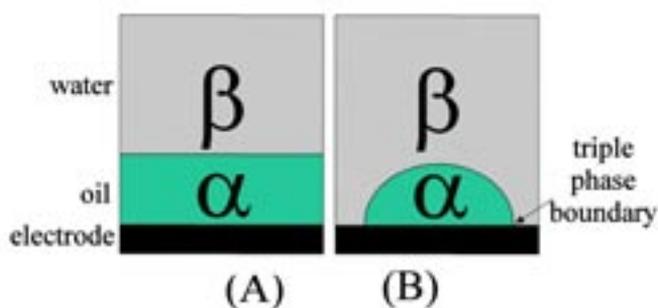
Experimental data are obtained at metal, carbon, and ceramic electrodes and for porphyrinato metal complexes immobilised in water-immiscible organic liquids and in contact with an aqueous electrolyte [1,2,3]. Voltammetric data are discussed and the porosity of surfaces identified as a key parameter for optimising electrochemically driven ion transfer processes at triple phase boundaries. Both the transfer of inert ions and facilitated ion transfer are considered.

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Symposium 6 - Poster

Liquid-liquid Electrochemistry

Structure of the interface between two immiscible liquids and interfacial tension

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Adsorption of hydrophobic, hydrophilic, and amphiphilic ions at the interface between two immiscible liquids was investigated. The results were analyzed in three different models: (i) the Gouy-Chapman model, (ii) ions as hard spheres, (iii) ion pair formation at the interface. In the Gouy-Chapman model, an analytical expression for the interfacial tension was obtained. It predicts that interfacial tension should be proportional to the square root of the electrolyte concentration. This prediction does not agree with experimental data. Modeling ions as hard spheres slightly improves the agreement between the theoretical and experimental results. The third model of interfacial ion pairing as the main origin of adsorption was analyzed using the amphiphilic isotherm (MV isotherm) [Markin, V. S.; Volkov, A.G. In Encyclopedia of Electrochemistry; Bard, A. J., Stratmann, M., Gileadi, E., Urbakh, M., Eds.; Wiley-VCH, Weinheim, 2002; Vol. 1, pp. 162-187]. A good agreement between ion pairing theory and experimental values was achieved. The MV isotherm takes into account the limited number of adsorption sites, finite size of molecules, complex formation at the interface and interaction between adsorbed particles. The analysis revealed repulsion between adsorbed tetraalkylammonium ions at the nitrobenzene/water interface and demonstrated linear dependence between adsorption site area and the size of a molecule. Classical isotherms of adsorption (Frumkin, Langmuir, Henry) were based on the model of non-penetrable interface, where an adsorbate can substitute only molecules of one solvent. At the interface between two immiscible electrolytes, nonpolar oil/water interfaces, and liquid membranes amphiphilic molecules can substitute molecules of both solvent and classical isotherms cannot be used. The generalization of Frumkin isotherm for permeable and non-permeable interfaces, known as the Markin-Volkov isotherm, gives the possibility to analyze adsorption in a general case. The adsorption isotherms of pentafluorobenzoic acid (PFBA) at the octane/water interface at the different pHs were measured by the drop-weight method. From the measurements of PFBA adsorption, the structure of the octane/water interface was determined. Adsorbed octane molecules have a lateral orientation with respect to the interface. Gibbs free energy of adsorption equilibrium and thermodynamic parameters of PFBA adsorption show that the adsorption of PFBA at the octane/water interface is accompanied by a reduction in the attraction between adsorbed PFBA molecules as the pH decreases to the acidic region.

Ion Transfer Across Supported o-Nitrophenyloctylether | Aqueous Electrolyte Solution Interface Coupled to Electrochemical Redox Reaction

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Recently ion transfer across two immiscible liquids generated by electrochemical redox reaction attracted a lot of interest [1,2]. Typically in these studies aqueous phase contained dissolved salt whereas organic phase is unsupported namely it consists exclusively redox active molecules or redox active molecule solution in hydrophobic polar solvent. In literature there are only few examples of similar studies involving supported organic phase [3,4]. Biphasic systems with room temperature ionic liquid phase also belong to this group [5].

In this communication the electrochemical behaviour of redox probe: t-butylferrocene or decamethyloferrocene, dissolved in drop of 2-nitrophenyloctylether based tetraalkylammonium salt solution, deposited on gold disc or used as a binder of carbon paste electrode [6], was studied in aqueous solution by cyclic voltammetry and differential pulse voltammetry. The electrochemical generation of cation is followed by ion transfer across liquid|liquid interface: anion insertion into or cation ejection from organic phase, in order to keep neutrality in organic or aqueous phase. It has been shown that apart from hydrophobic-hydrophilic properties of anion present in aqueous phase the direction of ion transfer can be driven by the type of cation present in the organic phase or the geometry of the electrode. The presence of more hydrophobic cation in organic phase or larger distance between electrode|liquid and liquid|liquid interface promote anion insertion into organic phase. Also the addition of salt to organic phase increases the efficiency of the electrode process at carbon paste electrode indicating that reaction place is not restricted to three phase junction: graphite particle|organic phase|aqueous phase.

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Symposium 6 - Poster

Liquid-liquid Electrochemistry

Electrochemical motion of an air bubble at oil|water interface

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An air bubble at the interface between a nitrobenzene (NB) droplet and a water phase moved up and down, responding to electrochemical potential, when the oil phase contained electrolyte and the aqueous phase contained electrolyte without electroactive species. The potential was applied between the aqueous phase through a reference electrode and the oil phase through a glassy carbon electrode (Fig.1). The steady-state current potential curve was obtained at $E > 0.5$V (Fig.1). The proportionality of the limiting current to the radii of the droplet indicates that ferrocene should be oxidized at the three phase boundary of oil|water|electrode [1]. It is only at the three phase boundary that both the electroactive species and the double layer are present. The distance, x, from the top of the bubble to the interface (Fig.1) varied with the potential, associated with hysteresis (Fig.2). On the assumption that the buoyancy on the bubble is balance with the summation of the surface tensions at oil|water, water|air and air|oil, we derived $f_s + f_b = 0$,
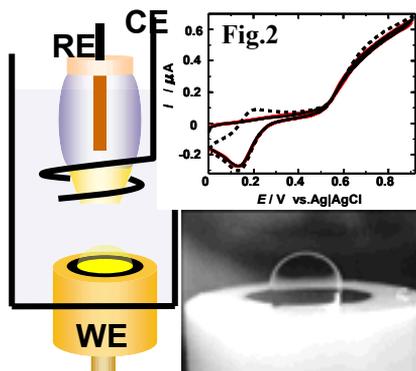
$$\frac{a^2 g d_o}{6}[4 - \frac{x^2}{a^2}(3 - \frac{x}{a})(1 - d_w/d_o) - \gamma_w - \gamma_o - \gamma_{wo}(1 - x/a)$$, as illustrated in Fig.3.

This equation allowed us to evaluate surface energies. In order to observe a behavior of the fluctuation of the bubble, a movie of the droplet was taken through an optical microscope during the potential application. The distance, x, with various applied potential was plotted in Fig.4.

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Liquid-liquid Electrochemistry
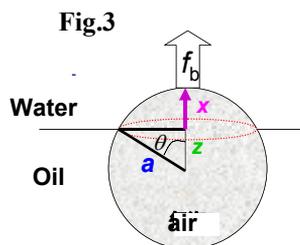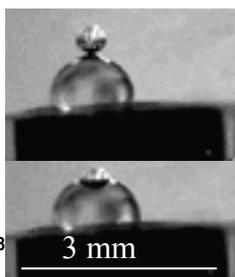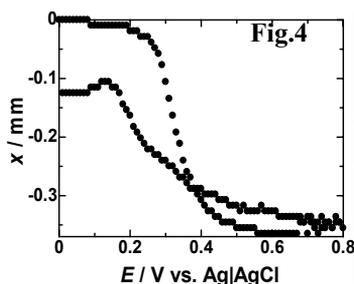
Biomolecules detection by means of liquid‖liquid electrochemistry

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Some proteins are known to be precursors of certain pathologies, regulators of physiological activity, toxins for human or animals, markers for dangerous viruses etc. The common methods of analysis based on immunology either requires poisoning of animals or involve complicated and expensive hybridome techniques.

The analysis of gene sequences plays a fundamental role in rapid detections of genetic mutations. Pathogens also can be determined by their specific sequences. Direct or label-free electrochemical detection of specific hybridization is useful because it eliminates indicator addition/association/detection step. The reagentless manner offers an instantaneous detection of affinity complex formation. Thus the elaboration and development of new method of analysis for specific DNA sequences is an important fundamental assignment.

Since water-soluble proteins and DNA molecules contain ionogenic groups, and can even be considered as polyelectrolytes, it might be possible to detect them by means of electrochemistry at liquid‖liquid interface by their transfer from water to organic phase or by bioaffinity interactions at interface affecting counter-ion flow.

Recently the novel system based on a electrode shielded with the thin liquid film of solution of water-insoluble redox polymer in water-immiscible organic solvent was elaborated and applied for investigation of thermodynamics of ion transfer across liquid‖liquid interface [1]. The electroactivity of redox-inactive proteins was observed by cyclic voltammetry in presence of surfactant in organic phase [2]. Unlike the pure buffer the incubation in protein solution lead to the sufficient increase of currents of redox-activity of polymer, which in certain cases exceeds two orders of magnitude. Our studies gave strong evidence, that the raise in current at liquid‖liquid interface is generated by the proteins. The peak current of electroactivity is linearly dependent on the protein content in a wide concentration range, which gives promise for analytical applications of the system. The certain selectivity was achieved by electrochemical impedance spectroscopy.

It was proposed to use common screen-printed graphite electrodes as a support for liquid layer. NPOE was used as a water-immiscible polar organic solvent and as a plasticizer for PVC. It was suggested to use adsorptive immobilization onto supported ITIES of three oligonucleotides modified by hydrophobic alkyl linkers as probes for hybridization with DNA targets with sequence from *Salmonella* genome. The differences in electrochemical impedance spectra at high-frequency domain of spectra have been obtained for all pairs after hybridization.

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Symposium 6 - Poster

Liquid-liquid Electrochemistry

Electrochemical Detection of Protein Transfer through Liquid | Liquid Interface

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The electrochemistry of interface between two immiscible liquids became an important tool of modern analytical chemistry. The transfer of redox-inactive ions through the interface gives the amperometric response similar to the Faradaic processes at metal-solution interface.

To observe protein transfer across liquid|liquid interface it is necessary to form water-in-oil microemulsion with solubilized protein stabilized with surfactant molecules. Generally micelles, which are able to solubilize proteins, can be formed exclusively in non-polar organic solvents. Therefore we developed an improved electrochemical setup based on the solid electrode shielded with thin layer of redox polymer solution in organic solvent [1]. In contrast to the traditional four-electrode setup our system allows operating with non-polar organic solvents and as a result to observe electrochemistry of protein transfer through liquid|liquid interface.

The dramatically increase of current which exceed two orders of magnitude has been obtained by cyclic voltammetry after incubation of electrode in buffer solution of redox-inactive protein. At the same time the incubation of electrode in protein free solution with similar salt content causes only minor changes in cyclic voltammograms. Background voltammograms recorded in the absence of surfactant in organic phase did not display any raise in electroactivity indicating no solubilization of protein by redox polymer. Also, no increase of current was observed with polar organic solvent dichloroethane. This result is in agreement with evidence that the water-in-oil microemulsion droplet dimension is under control by the dielectric permittivity of organic solvent [2]. The additional proof of protein transfer in the developed electrochemical system was obtained by the kinetic measurements of enzymatic activity in organic phase.

Varying the protein nature and concentration we gave the significant results. For some protein the peak current of electroactivity is linearly dependent on the protein content in a wide concentration range, which gives promise for analytical applications of the system [3]. In addition, the opposite charge of protein and surfactant led to stronger current increase and only minor current increase was observed in the contrary case. This result shows important role of protein-surfactant interaction. We suppose that using specific surfactants like alkyl boronic acid [4] a selectivity of protein determination may be achieved.

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Preparation of a silicate membrane at a liquid|liquid interface and its doping with a platinum ion

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Silicate films have been reproducibly formed at the interface of two immiscible liquids (water/1,2-dichloroethane) [1] by using a modified sol-gel process in which the template (trimethyloctadecylammonium ion, $TODA^+$), present in the organic phase, is transferred to the interface where it associates with the precursor silicate ions present in the aqueous phase. The process and, consequently, the properties of the film formed are finely controlled by the potential difference across the interface. The present contribution deals with chemical modification of the silicate film formed at the interface, through addition of another polyvalent anion to the silicate in the aqueous phase. This makes it possible to dope the silicate film formed with various ions, such as platinum in the present case. This approach to preparation of variously modified silicate films, that can also be formed on a solid porous support, bears promise for use in catalysis and for application to analytical chemistry, e.g., for treatment of the capillary walls in capillary chromatographic and electromigration separations, or for surface modification of chemical sensors. The process mechanism has been experimentally studied in some detail, using surface tension measurement, cyclic voltammetry and ESCA..
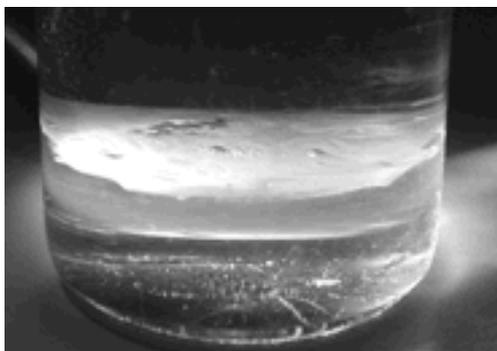
Fig. 1. A silicate layer formed at the interface between 1 mM $(NH_4)_2PtCl_4$, 10 mM SiO_2 and 2 mM TBACl in water; and 5 mM TODATPB, 10 mM TBATPB in 1,2-DCE, in a glass beaker with the organic phase placed in the lower part. The potential difference across the interface, which is essential for the layer formation, is created by the distribution of tetrabutylammonium (TBA^+) ion in the two phases in contact. The ratio of Pt/Si in the layer is 0.003, as determined by ESCA method.

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Dynamic Phenomena in Gibbs Monolayer Films at the Air-Water Interface

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Mobility of amphiphilic molecules diffusing along the water surface is affected, to a large extent, by the immersion depth of their polar fragment. The magnitude of the immersion depth of non-ionic functional groups often does not exceed 3-4 Å. This value coincides with the width of the aqueous liquid-vapor interfacial region. Therefore, measurements of lateral mobility of amphiphiles at the air-water interface could lead to the determination of the viscoelastic properties of the interfacial region of water. With this goal in mind, we have considered electrochemically active TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy).

2D-voltammetry was used to measure the lateral diffusion constant (D) of TEMPO at the air/water interface. When a line micro-electrode is positioned at the air/water interface, the recorded current consists of a linear diffusion component due to the TEMPO surface population and a cylindrical diffusion component due to the bulk population of the surfactant. The fact that the two diffusion constants of TEMPO are different induces additional fluxes with a component perpendicular to the air/water interface. Full interpretation of the electrochemical data requires FEMLAB modeling. Lateral mobility of TEMPO along the air/water interface was found to correspond to $D = 2 \times 10^{-4}$ cm^2/s. This result reflects the fact that TEMPO diffuses unimmersed and that its interactions with water are limited to hydrogen bonding with one or two water molecules in the interfacial region.

Symposium 7

Soft Materials
in Electrochemistry

Ion Transport Across Biomimetic Membranes

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The transport of ions across biological membranes may be passive (ion channels) or active (ion pumps, sinporters, antiporters). Biomimetic membranes are experimental models of biomembranes that may incorporate membrane proteins in a functionally active state.

A biomimetic membrane that can be conveniently employed for the study of ion channels is obtained by tethering a *thiolipid* monolayer to the surface of a mercury electrode. A thiolipid consists of a hydrophilic polyethyleneoxy or oligopeptide chain, terminating at one end with a sulfhydryl or disulfide group for anchoring to the metal surface, and covalently linked at the other end to the polar head of a phospholipid. Mercury provides a defect free and fluid surface to the thiolipid monolayer. Self-assembling a phospholipid monolayer on top of the thiolipid monolayer yields a lipid bilayer interposed between the hydrophilic *spacer* and the aqueous medium, which allows the incorporation of ionophores (e.g., valinomycin [1]), channel-forming peptides (e.g., melittin) and membrane proteins (e.g., OmpF porin [2], sarcolipin). Some channel-forming peptides form clusters within the lipid bilayer by a nucleation-and-growth mechanism, which can be revealed by potential-step chronocoulometry. Electrochemical impedance spectroscopy may allow a separation of the contributions from the different substructural elements composing this biomimetic membrane.

A metal-supported biomimetic membrane particularly convenient for the study of ion pumps is obtained by tethering a long-chain alkanethiol monolayer to a gold electrode and by self-assembling a phospholipid monolayer on top of it. Membrane fragments incorporating ion pumps or proteoliposomes are easily adsorbed on this mixed bilayer. The ion pumps are activated by rapidly injecting a solution of a suitable substrate into the microcell containing the electrode so prepared. ATP, translocating ions and drugs modulating the pump function can be used as substrates for these concentration jumps. At constant applied potential, concentration jumps generate current transients due to capacitive coupling between the proteoliposomes and the mixed alkanethiol/phospholipid bilayer. The capacitive current transients are analyzed, together with the charge under the transients, on the basis of an equivalent circuit. Ca-ATPase of the sarcoplasmic reticulum is studied by this procedure, thus determining the effect of pH, potassium ions [3] and a few drugs [4] on the function of this pump.

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Symposium 7 - Keynote

Soft Materials in Electrochemistry

Electron transfer and CO binding to immobilized cytochrome c' on thiol modified gold surfaces

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Monolayers of immobilized proteins on electrodes have proven to be valuable in the study of protein electron transfer mechanisms. The most commonly employed electrode materials employed are gold with an adsorbed thiol layer and edge plane pyrolitic graphite. Gold has the advantage that it enables a combination of electrochemical and spectroscopic techniques. Many papers have been published on gold with immobilized cytochrome c, a simple electron transfer protein. Papers on other proteins are scarce.

We have successfully immobilized *Allochromatium vinosum* cytochrome c' on gold modified with carboxylic acid-terminated carboxyl thiols of different length. Contrary to cytochrome c, cytochrome c' has an empty coordination site on its heme, where it can bind ligands such as CO and NO. Binding of these ligands results in monomerization of the protein. These properties make cytochrome c' an interesting protein to investigate in protein film voltammetry.

Immobilization of cytochrome c' could only be achieved for pHs below 5.5, since the protein has a pI of 4.9 and therefore only binds to the negatively carboxyl thiols at low pHs. The electron transfer rate between the hemes of the protein and the electrode depends on the thiol length in a similar way as for cytochrome c. However, the electron transfer rate to immobilized cytochrome c' is significantly slower, which suggests that the heme in the protein is located further from the gold surface. Upon saturation of the solution with CO a shift in the anodic peak potential by 250 mV is observed. This reflects the binding of CO to the empty sixth coordination site of the heme. The observed CO binding rate of 15 s^{-1} is significantly slower than the rate of 140 s^{-1} observed for cytochrome c' in solution. A reason for this decreased rate could be that the monomerization process is impeded by steric hindrance in the monolayer.
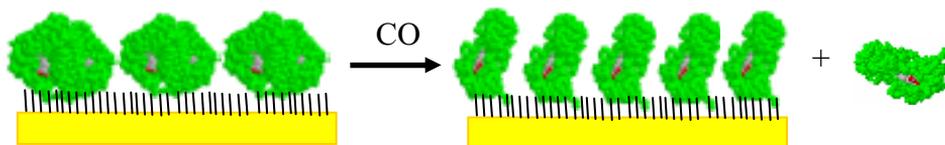
Figure 1. CO binding results in monomerization of the protein

S7·KN-3

The Effect of Potential Field and pH on Protein Immobilization on Gold using the Electrochemical Quartz Crystal Nanobalance, AFM and STM Imaging

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The role of potential field on the adsorption properties of proteins is important in understanding their interfacial behaviour for many applications such as biosensors, medical implants, and the fouling of surfaces in industrial situations. We present results obtained from the use of the electrochemical quartz crystal nanobalance (EQCN) to quantify the potential field adsorption behaviour of proteins at a gold electrode. These results are compared with STM images of the proteins on gold obtained *in situ* under electrochemical control. The self assembly behaviour of the proteins directly from solutions of various pH in the absence of potential field was imaged by AFM.

EQCN measurements of the adsorption behaviour of the globular proteins, β-lactoglobulin (β-LG) and α-lactalbumin (α-LA), were examined from phosphate buffer solutions prepared with a range of pH values (i.e., 2, 7.4, 11). These proteins undergo interesting conformational changes as a result of variation in the pH of the solution. The EQCN results showed very different adsorption behaviour of these proteins onto a gold substrate which was attributed to the charge on the protein and the potential field induced solvent effects at the electrode surface. AFM images of the self assembled arrays of these proteins on a gold surface, adsorbed directly from solutions of different pH values in the absence of potential field, were measured after the substrate was rinsed and allowed to dry. The self assembled arrays of protein differed substantially for adsorption from solutions of different pH, characteristic of their differing conformational behaviour in solution.

To study the effect of the potential field, STM images were made of protein adsorption onto a gold substrate *in situ* from a pH 7.4 phosphate buffer solution under electrochemical potential control. Normally, using gold as the substrate, protein molecules are not adsorbed firmly and cannot be imaged properly in the protein containing electrolyte solution. However, with potential control of +0.4 V relative to the open circuit potential, single β-LG molecules are fixed onto gold because of electrostatic interaction between the negatively charged protein (pI, 5.4) at this pH and the positively charged surface, allowing images of adsorbed protein to be captured. The images show the protein molecules with an apparent diameter of 7.0 nm, which is larger than the diameter when imaged in dry state (~3.4 nm), likely due to the formation of dimers, which occurs naturally in buffer solution at this pH. When the potential is decreased, the immobilized molecules disappear. The process is reversible. At potentials greater than +0.6 V, the imaged β-LG molecules appear to be denatured on the substrate. Thus, these three techniques provide complementary information.

Symposium 7 - Keynote

Soft Materials in Electrochemistry

Dynamic neutron reflectivity studies providing temporally and spatially resolved composition of electroactive films

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Structural characterization of electroactive films is crucial to understanding their mechanism of operation, optimising their performance and designing next generation materials. Recently, spectroscopic and imaging methods have been used to provide information from the level of local environment and electronic structure through to topological images at the nano- and meso-scopic levels. While these techniques have unquestionably advanced the understanding of electroactive films, they generally provide information averaged across or through the sample (transmission IR, UV/ visible spectroscopy, EXAFS) or localised at one interface (AFM, STM or XPS).

The missing feature, which we have provided using neutron reflectivity (NR) is spatially resolved information through the film. The penetrating nature of neutrons means that measurements can be made *in situ*. The great advantage over ellipsometry, its photon equivalent, is that NR responds to isotopic substitution, so one can selectively identify individual species, notably the solvent profile via deuteration[1]. To date, exploitation of this advantage has been at the expense of time resolution: the weak interaction of neutrons with matter that allows penetration of condensed phases frequently requires long measurement times, typically hours.

Here we report a new methodology for *in situ* NR measurements that decreases the effective measurement timescale by approximately three orders of magnitude, to a few seconds. We recently reported the concept of the method[2], but are now in a position to demonstrate the outcomes in terms of spatially and temporally resolved solvent profiles within electroactive films during potentiodynamically controlled redox switching. The capability of the method will be shown for PVF films, a model system for which we have spatially integrated time resolved solvation from EQCM data and spatially resolved temporally integrated data from static NR data. We then exploit this capability to probe transient solvation effects in PEDOT films undergoing redox switching.

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Electrochromic properties of disubstituted poly(propyle nedioxythiophene)s

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An electrochromic material is one where a reversible colour change takes place upon reduction (gain of electrons) or oxidation (loss of electrons), on passage of electrical current after the application of an appropriate electrode potential. Thin films of conjugated electroactive polymers are intensively studied for their electrochromic properties [1]. In the oxidised state, such conjugated polymers are charge balanced, 'doped', with counter anions ('p-doping') and have a delocalised π-electron band structure. Reduction of 'p-doped' conjugated polymers, with concurrent counter anion exit (or electrolyte cation incorporation) removes the electronic conjugation to give the 'undoped' (neutral) electrically insulating form. The energy gap (E_g, electronic bandgap) between the highest occupied π-electron band (the valence band) and the lowest unoccupied band (the conduction band) determines the intrinsic optical properties of these materials.

Of the numerous conjugated electroactive polymers that have been studied, alkylenedioxythiophene polymers have been shown to exhibit enhanced electrochromic properties over the parent thiophene polymers [2]. We here describe recent efforts at the University of Florida that have focussed on the development of solution processable alkyl- and alkoxy-substituted poly(3,4-propylenedioxythiophene)s (PProDOT-R$_2$) with fast switching speeds and higher optical contrasts. These polymers are soluble in common organic solvents and can be applied to various substrates using a spray-casting technique. As thin films on transparent substrates these disubstituted poly(3,4-propylenedioxythiophene)s exhibit electrochromic hysteresis. Furthermore, when incorporated into reflective electrochromic devices, the phenomenon of unsymmetrical switching occurs between the visible and NIR regions of the spectrum. Transmissive organic-inorganic hybrid electrochromic devices, incorporating these polymers and thin films of electrochromic Prussian blue, have been constructed and exhibit high luminance and transmission contrasts.

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Symposium 7 - Keynote

Soft Materials in Electrochemistry

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Soft Materials in Electrochemistry

Light-Emitting Electrochemical Cells: Direct Probing of Doping Progression and Emission

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We have performed a detailed spatial and temporal imaging study on the doping progression and the location of the emission zone in a number of different polymer light-emitting electrochemical cells (LECs) with an extremely large interelectrode gap of 1-3 mm. By systematically varying specific characteristics of the LECs (e.g., the size, type and mobility of the ions and the mobility anisotropy of the conjugated polymer), we have attempted to establish and understand their respective influence on important LEC properties, such as the desired formation of balanced, significant and reversible electrochemical doping and the positioning of the emission zone in the center of the interelectrode gap.

We find that the combined size and type of the cation is a critical factor: large alkaline cations, such as K^+ and Rb^+, allow for a significantly more balanced electrochemical doping of the conjugated polymer MEH-PPV than the smaller alkaline cation Li^+ or the molecular cation [tetrabutylammonium]$^+$ (TBA$^+$). Consequently, the emission zone in Au/(MEH-PPV + PEO + KTf)/Au devices is found to be significantly more centered than in LiTf- and TBATf-based devices [PEO = poly(ethylene oxide); Tf = CF_3SO_3].

We find that the doping progression behavior and the emission zone appearance varies significantly between different active materials: in (MEH-PPV + TBATf) the doping progression is characterized by a large number of discrete needle-like fronts that are highly diffuse at the edges, while it in (MEH-PPV + PEO + KTf) is characterized by one homogenous, albeit irregular, doping front with a sharp front edge. The emission zone in (MEH-PPV + TBATf)-based devices is discontinuous and interrupted by (10-50 μm thick) doping-induced micro shorts, while it in (MEH-PPV + PEO + KTf)-based devices appears to be continuous (see figure to the right).

We also demonstrate, quite remarkably, that it is possible to attain significant light emission from 1 mm-thick Au/(MEH-PPV + PEO + KTf)/Au devices operating at a temperature of 360 K and with a modest applied voltage of 5 V.
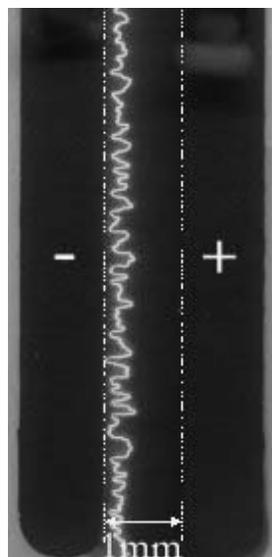
Electrochemical modification of carbon and metal surfaces

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The electrochemical functionalization of carbon and metal electrodes was achieved by reduction of *in-situ* generated diazonium cations. Several diazonium cations were used and selected examples will be given during this talk. The diazonium cations were synthesized by reaction of the corresponding amines with sodium nitrite in aqueous HCl. This functionalization method, which involves simple reagents and does not require the isolation and purification of the diazonium salt, enabled the grafting of covalently bounded layers which exhibited properties very similar to those of layers obtained by the classical derivatization method involving isolated diazonium salt dissolved in acetonitrile or aqueous acid solution. The modified electrodes were characterized by cyclic voltammetry and electrochemical impedance spectroscopy measurements. Such experiments were carried out in aqueous solutions containing electroactive redox probe molecules and were used to investigate the barrier properties of the deposited layers. The chemical composition of the grafted layers was also determined by X-Ray photoelectron and Infrared reflection-absorption (IRRAS) spectroscopies.

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Fabrication and High Resolution Characterisation of Charge Transport in Ultra-Thin Langmuir-Schaefer Nafion Films

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Ultra-thin films of Nafion have been prepared using a novel Langmuir-Schaefer (LS) technique. This technique allowed ordered ultra-thin (nanometer) scale films of Nafion to be produced. Two different approaches were developed to incorporate electroactive species such as a cationic ferrocene derivative, (FA^+), and $Ru(bpy)_3^{2+}$ within the films. The first (two step) method involved deposition of a pure Nafion LS film followed by loading of the electroactive species within the film [1-3]; the second (one step) method involved spreading a Langmuir film from solution containing both Nafion and an electroactive mediator. Apparent diffusion coefficients as well as surface coverages and other parameters, were extracted using cyclic voltammetry (CV). We have also developed a novel scanning electrochemical microscopy (SECM) method for determining the apparent diffusion coefficients within Nafion LS films. The results of the CV and SECM studies are compared and discussed. The Nafion LS films have been used to host palladium nanoparticles (2-5 nm diameter) produced by conventional methods and a novel methodology [4] that we shall report and the properties of the particles have been elucidated. In particular, SECM and CV were used to study hydrogen evolution catalysed by palladium nanoparticles.

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S7·O-3

Heterogeneous Doping Effects in Solid and Liquid Ionic Conducting Systems

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Heterogeneous doping[1] involving the introduction of a second phase oxide material (e.g. SiO_2, Al_2O_3) into a weak electrolyte e.g. AgCl, PbF_2 is a powerful technique to enhance ionic conductivity of weak electrolytes. The technique involves the internal adsorption of one ion sort at the oxide surface leading to high concentration of defects in the space charge layer at the interface of the conductor and insulator. Compared to conventional form of doping, heterogeneous doping introduces higher dimensional defects in the form of interfaces. Based on materials selection and optimization we present here the applicability of the technique to two different systems:

a) Dispersion of acidic oxide particles e.g. SiO_2, TiO_2 etc. in non-aqueous Li-salt solutions (e.g. $LiClO_4$ in MeOH, THF etc. or commercial solutions $LiPF_6$ in EC:DMC) resulted in a composite with high ionic conductivity and advantageous soft matter consistency (similar to "soggy sand")[2] making them highly suitable for application as electrolytes in electrochemical devices e.g. lithium battery. The enhancement is attributed to the formation of space charge layer in the vicinity of oxide particles resulting from adsorption of the anions on the oxides´ surface leading to dissociation of Li^+ out of ion pairs. The conductivity variation with oxide volume fraction showed a percolation type behavior. Initiation in ionic conductivity enhancement takes place at the oxide volume where an attractive particle network is formed.

b) Silver ionic conductivity[1] in AgX (X=Br,I) materials has already been demonstrated to be significantly enhanced by dispersion of solid micron or nanometer sized Al_2O_3 particles. The strategy of using smaller insulator particle sizes (i.e. higher surface area) might not always lead to predicted enhanced ionic conductivity due to several factors e.g. agglomeration of insulator particles, porosity effects etc and hence reduced percolation efficiency. However, with dispersion of mesoporous Al_2O_3 the conductivities of the above composites were extremely enhanced[3]. Conductivity enhancement is explained satisfactorily by the concept of Heterogeneous Doping with an additional contribution of stacking disorder to conductivity for $AgI-Al_2O_3$ composite.

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Bioelectrodes for catalytic reduction of oxygen

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Two ways of connecting laccases to the electrode surfaces will be discussed:
- covalent binding of the enzyme to thiol monolayers using 11-mercaptoundecanoic acid as the organic junction,
- immobilization in thin films of lyotropic liquid crystal - lipidic matrix with cubic symmetry.
Electrochemical, STM and Raman spectroscopy characteristics of fungal laccases *Trametes hirsuta* and *Cerrena unicolor* immobilized on electrode surfaces are described. Native laccases were studied and laccase modified with palmytic chains to turn it more hydrophobic.
Incorporation of laccase into lyotropic liquid crystal - lipidic matrix with cubic symmetry lead to efficient catalysis oxygen reduction.[1,2] The diamond type monoolein cubic phase prevents the enzymes from denaturation on the electrode surface and provides a flexible environment. Electronic contact of the enzyme with the electrode is maintained either directly or through the mediation of electroactive probes. The enzyme electroactivity and its catalytic activity parameters towards oxygen on both types of bioelectrodes will be discussed.

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LbL Self-Assembled redox multilayer films: Effect of acid-base equilibria on the ion exchange during redox switching

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The structure and fuctionalities in layer-by-layer self assembled molecular thin films can be designed by selection of polyelectrolytes, the order of alternate deposition, the ionic strength and the pH of the assembling electrolyte. In particular redox active poly-electrolyte multilayers (redox-PEM) are modified electrodes with control of properties in the nanoscale [1,2].

In the present stydy redox-PEM´s were built with poly(allylamine) derivatized with an osmium bipyridine pyridine chloro complex (PAH-Os) and polystyrene sulfonate (PVS).

The ellipsometric bilayer thickness determined after each electrostatic adsorption step increases the higher the pH of the PAH-Os adsorption solution. Similar results have been reported for PAH/PVS multilayer films [3]. In both cases the increase in film thickness has been attributed to conformational changes of poly-allylamine at different pH, with fully extended rod-like conformations in acid solutions due to the high linear charge density and coiled structures in alkaline solutions.

Infrared reflection-absorption spectroscopy by Fourier Transform (FTIR-RAS) shows the presence of NH_2 and NH_3^+ groups in films grown from PAH-Os solutions of pH 8.3 while at pH 3.5 only protonated amino groups have been observed.

The electrochemical behaviour of these LbL self-assembled multilayer films has been studied by cyclic voltammetry (CV), electrochemical quartz crystal microbalance (EQCM) and probe beam deflection (PBD). The integrated redox charge for a given number of bilayers increases with the assembling solution pH.

Films self-assembled at pH 8.3 have positive fixed charges and are predomintly exhange anions while those self assembled at pH 3.5 have negative fixed charges and are cation exchangers. Films with PAH-Os as the topmost layer carry a larger positive charge excess at the surface than those terminated in PVS. EQCM experiments reveal an exchange of +186 g/mol for films assembled at pH 8.3 and +18 g/mol for films assembled at pH 3.5. This shows that in the first case anions and solvent are exchanged during the oxidation while in the second case the egress of cations is masked by the ingress of water.

The pH of weak polyelectrolyte solutions determines the film thickness and the internal composition which result in either anion or cation exchange during the oxidation-reduction

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Symposium 7 - Oral

Soft Materials in Electrochemistry

Atomic force microscopy characterization of nucleic acids nanofilms adsorbed onto HOPG electrode surfaces

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Nucleic acids are very important biomolecules that play an essential role in the determination of hereditary characteristics, storing and replicating the genetic information of living organisms. In developing DNA electrochemical biosensors a important step consists in the immobilization and stabilization of the nucleic acid molecules on the electrode surface.

The mechanism of interaction of nucleic acids with carbon electrode surfaces was elucidated using magnetic AC mode atomic force microscopy (MAC Mode AFM) and different dsDNA, ssDNA, RNA and synthetic 10-mer homo and hetero-ODN molecules of known base sequences.

AFM images in air revealed different adsorption patterns and degree of HOPG surface coverage, and correlations between the pH of the solution and individual structure and base sequence of the molecules were observed. During free adsorption, the hydrophobic interactions of the molecules with the HOPG represent the main adsorption mechanism, although other effects such as electrostatic and Van der Waals interactions may contribute to the free adsorption process. The molecules interact differently with the HOPG surface, according to the nucleic acid sequence's hydrophobic characteristics, depending directly on the molecular mass, the hydrophobic character of the individual bases and the secondary structure of the molecule. The importance of the type of base existing at the chain extremities on the adsorption process was investigated with ODN sequences composed by the same group of bases in a different order.

When a positive potential is applied to HOPG, electrostatic interactions between the positively charged electrode surface and the negatively charged sugar-phosphate backbones of DNA molecules are predominant. The applied potential modified the DNA adsorption pattern on the surface significantly. The robustness and stability of the adsorbed molecules with respect to mechanical stress increased, due to electrostatic interaction.

S7·O-7

Electrochemical behavior of poly(aniline) and poly(phenylene sulfide) copolymer in ionic liquids

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Recently, the electrochemical behaviour of several conducting polymers have been studied in ionic liquids [1,2]. Poly(phenylene sulfide phenyleneamine) (PPSA) is an alternated copolymer of poly(aniline) (PANI) and poly(phenylene sulfide) (PPS) and due to its great solubility in several organic solvents and other interesting properties has attracted a lot of attention. Besides these advantages, this polymer is not electroactive in aqueous media; thereby the search for other alternative media, such as, ionic liquids is necessary. In this abstract, we have shown the electrochemical behavior of PPSA in 1,2-dimethyl-3-n-butylimidazolium bis(trifluoromethanesulfonyl)imide (BMMITFSI) using cyclic voltammetry and other spectroscopic techniques "in situ", such as, Raman and UV-Vis (Figure 1).
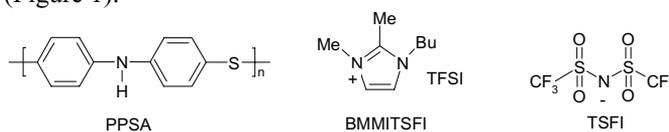
Figure 1

The copolymer was synthesized in our laboratory following procedure described in literature [3]. This compound was characterized by spectroscopic techniques and it has shown excellent solubility in organic solvents.

BMMITSFI was prepared by ion exchange reaction with LiTSFI using the respective imidazolium bromide. The electrochemical behavior of PPSA films studied by cyclic voltammetry has shown that up to 1.10 V this polymer is oxidized reversibly. Above 1.10 V the PPSA starts loosing electroactivity probably due to an irreversible chemical reaction.

The UV-Vis and Raman data have proved that the reversible electrochemical process occurring up to 1.1 V is attributed to the formation of polarons. We could also confirm that above 1.10 V the oxidized species, bipolarons, are instable and their reaction with aromatic rings is the main reason for the irreversibility observed in the cyclic voltammogram.

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Electrochemistry of glycopeptides in biomimetic membranes

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Florence laboratory has a notable expertise in the "Electrochemistry of peptides and proteins in supported lipid films". In this context, we have been investigating peptides using different biomimetic membranes, such as Hg-supported phospholipd monolayers [1] and tethered lipid bilayers supported by both Hg [2] and Au. Thus, we studied commercial gramicidin in a monolayer [3] and valinomycin in a tethered bilayer, both supported by Hg [4].

We have recently concentrated on the CSF114(Glc) glycopeptide, the first specific Multiple Sclerosis (MS) Antigenic Probe (developed in the Laboratory of Peptide & Protein Chemistry & Biology), which is capable of detecting autoantibodies as biomarkers of this disease. A simple ELISA test on sera of MS patients, based on CSF114(Glc) [5], was proposed to follow up disease activity, guiding customized therapeutic treatments [6]. Autoantibody recognition is strongly dependent on the presence of Asn(Glc) and on the conformational behavior of CSF114(Glc), both in solution and under the solid-phase conditions of the ELISA. We hypothesize that an aberrant N-glucosylation of myelin proteins may trigger a pathogenic autoantibody response in MS and that CSF114(Glc) may possibly mimic all aberrantly glucosylated myelin proteins [7].

This study aims at characterizing CSF114(Glc) in biomimetic membranes. Therefore, we investigated the behavior of CSF114(Glc) in our model systems (monolayers and tethered bilayers on Hg) using Electrochemical Impedance Spectroscopy (EIS), AC voltammetry, and other electrochemical techniques.

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Fabrication and characterization of nanostructured electrochromic films

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Iridium oxide is known to have excellent electrochromic[1] and pH sensing properties.[2, 3] Films of iridium oxide were deposited anodically according to Yamanaka's recipe[4] and characterized by voltammetry in the growth solution and subsequently in acid and base electrolytes. SEM was used to assess the morphology and texture of the films. Attempts were made to create a nanostructure by depositing the films within a molecular template formed by the self-assembly of liquid crystal molecules according to the method developed in Southampton.[5] An alternative approach attempted to decorate a nanostructured Pt film with iridium oxide. Macroporous iridium oxide films with varying thicknesses were successfully fabricated by deposition within a template made with self-assembled polystyrene spheres (typically 600 nm ∅) as described by Bartlett et al.[6] Dissolution of the template reveals smooth films with ordered arrays of hollow cups hexagonaly distributed, see Fig. 1. Films were also formed by decorating macroporous Au films. Films with graded thicknesses were obtained. The effect of the structure on the electrochromic properties was investigated. Preliminary results for the fabrication and characterization of this novel nanostructured iridium oxide films will be presented.

Fig. 1 Macroporous iridium oxide films grown with 30 (left) and 100 (right) sweeps between -0.8 and +0.7 V vs. SCE at 100 mV s^{-1}. Template: polystyrene spheres 600 nm ∅.

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Symposium 7 - Oral

Soft Materials in Electrochemistry

Redox-active ionic liquids

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Research over the last decade has shown that ionic liquids (ILs) have great potential as "green" replacement solvents for a variety of chemical transformations [1] including their use in organic electrochemistry [2-4]. Significantly, the use of ILs in molecular electrochemistry negates the usual requirement for molecular solvents (organic or water) and supporting electrolytes; both of which are often cited as the main barriers to the implementation of organic electrolytic processing.

Over recent years, "task specific" ILs have been introduced where the IL structure is deliberately design to perform specific function(s) beyond acting as mere solvents e.g. salts with the capacity to interact with dissolved substrates in specific ways [5]. From the electrochemical perspective, deliberately introducing reversible redox functionalities within the conventional IL structure introduces a new class of hydrophobic liquid electrochemical material where redox chemistry can be performed in the total absence *dissolved* redox species, or supporting solvents, such as water or organics. In principle, these materials can perform either simple electron-transfer reactions, or effect atom transfer processes; behaviour akin to normal redox reagents in molecular solvent systems. These materials have diverse applications e.g. from solvent-free redox chemical transformations to high-density electrical energy storage. This paper will describe approaches to bulk synthesising redox-active ionic liqids, their electrochemical characterisation, and their applications in chemical transformations.

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Molecularly flat films of os containing redox polymers on hopg electrodes

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Control over the thickness, roughness and electron transport properties of conducting and redox polymers deposited on electrode surfaces is an essential issue for the use of these materials in electronic devices and sensors. One of the most studied redox polymer exhibits the general structure $[Os(bpy)_2(PVP)_xCl]Cl$, where bpy is $2,2'$-bipyridyl, PVP is poly(4-vinylpyridine) and the subscript 'x' corresponds to the number of 4-vinylpyridine units in the chain. The electrochemical properties of these polymers can be determined by several processes including, (i) electron hopping between the Os centres, (ii) counter-ion transport and (iii) polymer movement. In the present contribution, we investigate the correlation between morphology and electrochemical behaviour of ultrathin films of $[Os(bpy)_2(PVP)_5Cl]Cl$ formed by spontaneous adsorption from aqueous solution on HOPG surfaces. Cyclic voltammetry, ac-impedance spectroscopy as well as Atomic Force and Scanning Tunnelling Microscopies indicate the development of distinctive growth regimes as a function of the adsorption time. As illustrated in figures 1 and 2, films several monolayers thick are characterised by a molecular scale roughness and narrow voltammetric features ($\Delta E_{1/2}$ < 90 mV). The remarkably flat topography of these films appears to be connected to polymer reorganisation induced by lateral attraction of the PVP chains. Fundamental issues concerning the dynamics of electron injection to the electrode vs. charge transport across the films will be discussed.
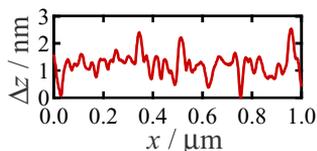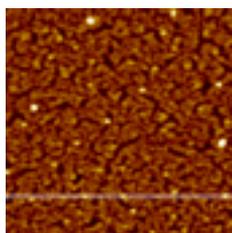
Fig. 1. Ex-situ 1μm×1μm AFM image of a $[Os(bpy)_2(PVP)_5Cl]Cl$ film obtained by adsorption on HOPG. Typical height fluctuations are of the order of the molecular dimension.
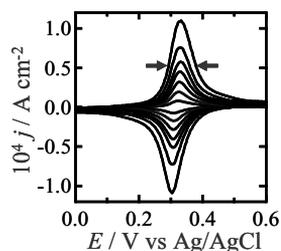
Figure 2. Cyclic voltammograms of the film imaged in figure 1 recorded at 10, 20, 30, 40, 50, 70 and 100 mV/s.

Symposium 7 - Oral

Soft Materials in Electrochemistry

X-Ray characterisation of structural and functional metal ions in polymeric salen based thin films

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Salen ligands are easily functionalized with receptor sites and their metal complexes exhibit molecular recognition properties in solution.[1] Recently, we began to explore the properties of poly[Ni(*salen*)] functionalized with receptor sites, namely crown ethers, as a starting point for the production of metal cation sensors.[2] In this work we used *in situ* X-ray spectroscopy and *ex-situ* XPS to study the structural origins of ion recognition by electrochemically addressable poly[Ni(*salen*)] thin films. XANES and EXAFS at the Ni K-edge and, after exposure to Ba^{2+} solution, at the Ba K-edge provided information on the local environment (nearest and next-nearest neighbours) around these atoms within the film. Since these were *in-situ* measurements, we were able to monitor the influence of electrochemical potential perturbations. XPS measurements were used to determine the composition, particularly Ni to Ba ratio and metal atom to donor ratio. Unlike the EXAFS and XANES, XPS is surface specific, which allows us to explore the penetration depth of Barium into the film.

Fitting of EXAFS and XANES spectra provides oxidation state and geometry around the Ni and Ba for poly[Ni(3-MeOsaltMe)], we find that Ni is covalently bound (to two N and two O donors) and square planar, irrespective of film redox state and the presence (or absence) of bound Ba^{2+}; Ba^{2+} is bound within pseudo crown pocket formed by four O donors, two from the methoxyl groups and two shared with Ni atom. We also report data for poly[Ni(3-Mesalophen-b15-c5)], in which a crown ether provides less flexible pocket for Ba. The Ba^{2+} signal from the relatively thick films (10 μm) used in these experiments is significantly below that anticipated from electrochemical on thin films (< 100 nm). We explain this by the fact that EXAFS and XANES responses average the signal over the entire film volume, but only the diffusionally accessible outer region contains Ba^{2+}; XPS data confirm this.

We conclude that the role of the Ni is purely structural. The dramatic changes in i-E response that accompany Ba^{2+} uptake are assigned to the delocalised poly(*salen*) polymer spine, through the barium-(pseudo)crown oxygen atoms. Combination of XAS and XPS data provides a route for optimising film thickness in terms of response times during exposure to barium in solution.

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Derivatives of Poly(3,4–ethylenedioxythiophene) for biosensing at microelectrodes

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Poly(3,4–ethylenedioxythiophene) (PEDOT) is a commercially-successful polythiophene derivative with a very low oxidation potential, favorable optical properties and extraordinary stability in its oxidised (p-doped) form. It therefore makes an idea platform for electrochemical (bio)sensing. We have synthesised EDOT derivatives bearing covalently-attached carboxylic acid, metal–tetraazamacrocycle complexes or biotin (*e.g.* **1**, **2**).

1

2
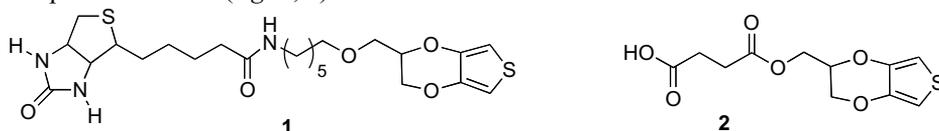
These have been electrochemically copolymerised with EDOT itself, to give conducting polymer-modified electrodes, which have been characterized by electrochemical and *in situ* spectroscopic methods. The biotinylated PEDOT, on 10 μm radius Pt disk microelectrodes, responds electrochemically to the binding of avidin at the 10^{-16} mole level. The PEDOT-**2** copolymer has been used for *in situ* grafting of aminoalkyl-terminated oligonucleotides, and the electrochemistry of these polymers undergoes marked and reproducible changes upon hybridisation with the complementary oligos.
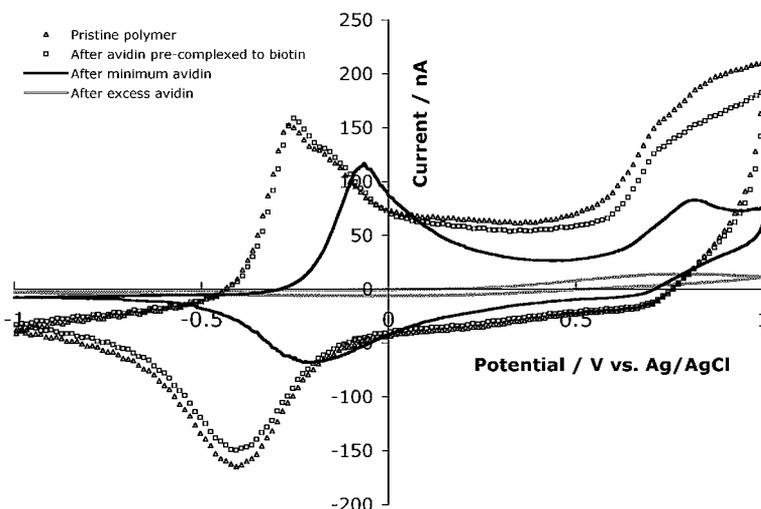
*Response of 10 μm Pt disk electrode coated with PEDOT :**1** copolymer to avidin, monitored in aqueous buffer. Redox wave shifts positive and diminishes on exposure to increasing [avidin].*

Symposium 7 - Oral

Soft Materials in Electrochemistry

Symposium 7 - Oral

Soft Materials in Electrochemistry

Viscoelastic investigations of polyaniline: correlation between film dynamics and composition

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The redox-driven transfers of ions and solvent between an electroactive polymer film and its bathing solution have been widely studied using the EQCM. It is also generally appreciated that highly solvated films are likely to show viscoelastically controlled EQCM responses, associated with polymer dynamics. However, these viscoelastic phenomena are only infrequently quantified (for example via shear moduli), their relationships to physical control parameters and to redox-driven solvation changes are poorly understood, and their inherent connections to molecular processes have barely been investigated. It would be valuable to understand these relationships, since they may influence performance of a range of electroactive film-based devices, for example through switching times associated with ion transfer through the viscous film medium or mechanical actuation associated with polymer stiffness.

In this presentation we describe crystal impedance studies of the electromechanical properties of potentiodynamically deposited conducting polyaniline films exposed to aqueous $HClO_4$. The admittance spectra yield polymer shear modulus data, $\mathbf{G} = G'$ + jG'' (where G' is the storage modulus and G'' is the loss modulus) as functions of applied potential (polymer redox state), timescale (via harmonics of the angular frequency, $\omega = 2\pi f$) and temperature (T). The potential was scanned between $-0.2 <$ E/V < 0.4. The frequency ranged from 10 MHz (the fundamental resonance) up to 110 MHz (11th harmonic). The temperature was varied over the range $5 <$ T/°C < 60.

The matrix of $\mathbf{G}(E,T,\omega)$ data was mapped onto a master relaxation curve using the principle of time-temperature correspondence. The effects of temperature and potential on $\mathbf{G}$ components were surprisingly small. However, the effect of experimental timescale (frequency) was dramatic, with G' and G'' varying by approximately three orders of magnitude. In a novel approach, we are able to correlate the polymer matrix dynamics (represented by shear moduli, acquired for acoustically thick films) with film composition (represented by solvation changes, acquired gravimetrically for acoustically thin films) in response to film redox switching. This is the first time, to our knowledge, that the relationship between film dynamics and composition has been determined for an electroactive polymer film.

Formation of Surface-Attached Responsive Gel Layers via Electrochemically Induced Free-Radical Polymerization

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We report on the formation of hydrogel layers on conducting substrates via a simple electrochemical route. A free radical polymerization is initiated by an electron transfer from the substrate to a redox-active initiator. Gels of the thermally responsive material poly-*N*- isopropylacrylamide (p-NIPAM) with a thickness between 25 and 250 nm were produced and characterized. Typical polymerization times are between a few seconds and a few minutes. The gels adhere well to the substrate. They show the characteristic swelling transition at 32 °C. While the films appear homogeneous in optical microscopy, AFM images reveal a slightly heterogeneous, globular structure. The gels are permeable to small ions as evidenced by electrochemical experiments with gel-covered electrodes. We also report on arrays of hydrogel-dots formed by electrochemical di-pen lithography.

[1] Langmuir 2006

Symposium 7 - Oral

Soft Materials in Electrochemistry

Electrochemical charging and reactivity of conducting polymer-linked polyoxometalate-modified carbon nanostructures

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The concept of fabrication of the phosphomolybdate-stabilized colloidal suspensions of metal particles is extended here to the formation of the analogous dispersions of carbon nanoparticles and multi-walled carbon nanotubes and utilized to the generation of network films of conducting polymer linked carbon nanostructures on electrode substrates [1,2]. Recently, a great deal of recent research has been centered on the preparation and investigation of carbon nanomaterials. Because of their unique properties, that include high surface area, good electrical conductivity, exceptional physicochemical stability and significant mechanical strength, the carbon nanotubes have been considered for such technological applications as fabrication of high density charge storage devices and supercapacitors. We demonstrate here that by repeated alternate treatments in the colloidal suspension of polyoxometallate-protected carbon nanotubes (or particles) and in the solution of monomer (e.g. anilinium) cations, the amount of the material can be increased systematically (layer-by-layer) to form stable three-dimensional organic-inorganic assemblies on electrode surfaces. In the resulting films, the layers of negatively charged polyoxometallate-stabilized carbon nanostructures are linked or electrostatically attracted by ultra-thin layers of such positively charged conducting polymers as polyaniline or PEDOT. Consequently, the attractive mechanical and electrical characteristics of nanostructured carbon, unique properties of polymers and reactivity of polyoxometallates are combined. The formation, morphology, structural transformations and electrochemical properties of the carbon nanostructures containing three-dimensional network films are examined using cyclic voltammetry, potential step techniques, microgravimmetry, FTIR spectroscopy, STM and scanning electrochemical microscopy. The functionalization of carbon nanotubes or carbon submicroparticles with heteropolyanions constitutes an effective route to their homogeneous dispersion in polymer matrices. Our new hybrid three-component materials are characterized by fast dynamics of charge propagation. The research is of potential importance to the construction of effectively operating charge storage devices (capacitors), charge mediators (relays), molecular electronic, chemical and biochemical sensing devices, as well as electrocatalytic systems.

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Control of Electron Transfer in Self-Assembled Monolayers

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Electron transfer through nanometer-thick organic films is of fundamental importance to the development of nanometer-scale electronics and chemical sensors. Knowledge of how chemical compositions and chemical structures affect the electron transfer between a solid substrate and a redox-active molecule is central in the study of molecular-level electron transfer. In particular, concepts of "molecular switching" and "molecular rectifier" are of relevance to the design and development of new electronic nano devices. Herein we report the molecular switching by anion adsorption and the molecular rectifier by the asymmetric electrostatic interactions in self-assembled monolayers (SAMs).

First, the anion-directed Ru^{3+}/Ru^{2+} redox-switchable SAM surfaces will be presented. The gold surfaces were coated with imidazolium salts, 1-(12-mercaptododecyl)-3-methylimidazolium salts. The electron transfer on this SAM occurs in the presence of $Fe(CN)_6^{3-}$ (anionic redox-probe molecule) but did not occur in the presence of $Ru(NH_3)_6^{3+}$ (cationic redox-probe molecule). The SAM having $Fe(CN)_6^{3-}$ as an anion showed the electron-transfer toward $Ru(NH_3)_6^{3+}$, and the $Ru^{3+/2+}$ redox-switchable SAM was generated by reversible anion exchange between $Fe(CN)_6^{3-}$ and SCN^-.

Second, the pH-dependent rectification in SAMs based on asymmetric electrostatic repulsion was accomplished in the SAM of 1-(12-mercaptododecyl)imidazole. Imidazole group acts as surface-charge and affects the electron transfer kinetics of the ferrocenemethanol $FcOH/FcOH^+$ redox couple asymmetrically. When the basic imidazole group on the top of the SAM is deprotonated at high pH, access of both FcOH and $FcOH^+$ to the electrode is allowed, resulting in bidirectional electron transfer. At low pH, however, the protonated imidazole group repulses the positively charged $FcOH^+$ and does not exert any force on the neutral FcOH. These asymmetric electrostatic interactions influence the electron-transfer kinetics of oxidation and reduction asymmetrically leading to the rectifying function. The reversible protonation/deprotonation of the imidazole group enables the selection between unidirectional and bidirectional electron transfer by adjusting pH.

Ion exchange properties and selectivity of PPy/PSS composites

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A composite of polypyrrole (PPy) and polystyrenesulfonate (PSS) exchanges cations controlled by the degree of oxidation of PPy. This composite is a promising material for the technical application of water softening [1].

In this presentation the ion exchange properties of electrochemically prepared PPy(PSS) are studied by investigating the polymer using a electrochemical quartz crystal microbalance (EQCM) [2] and by analyzing the solution surrounding the polymer by atomic absorption spectroscopy (AAS) [3].

The exchange of cations by PPy(PSS) is found to be caused by three driving forces: (i) electrochemical oxidation/reduction of PPy; (ii) chemical oxidation of PPy by dissolved oxygen; (iii) gradients of cation concentration between polymer and solution. The ion selectivity of PPy(PSS) is investigated and ion exchange isotherms for the binary systems Ca^{2+}/Na^+ (Fig. 1) and Ca^{2+}/Mg^{2+} are determined.
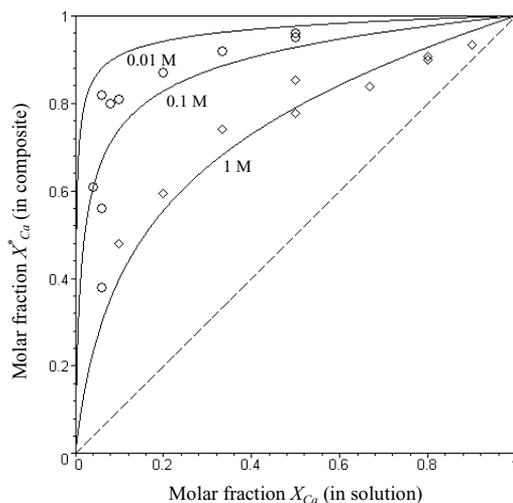
Fig. 1: Ion exchange isotherms of the system: PPy(PSS) / x M $CaCl_2$ + y M NaCl at E = -0.7 V with (x + y) = C: 1 M (   ) and 0.005 M (o); curves (——) calculated by eq. 8 with K_{Na}^{Ca} = 9, C* = 1 M; and C = 1 M, 0.1 M, 0.01 M.

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Cations of Fullerene and their Reactivity in Solution

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The facile reduction of fullerenes, exemplified by the electrochemical stepwise reversible addition of up to six electrons to C_{60},[1] contrasts with its difficult oxidation.[2] As observed in the early electrochemical experiments, fullerenium radical cations react immediately with any nucleophile present in solution leading to decomposition.[2] This is responsible for the generation of multielectron voltammetric oxidation peaks, as the decomposition products undergo further oxidation.

In 1993 the observation of electrochemical reversible one-electron oxidation of C_{60} in tetrachloethane at $E_{1/2} = 1.26$ V (vs. Fc$^+$/Fc) was reported for the first time by Echegoyen.[3] Finally, in 2003, we reported on the cyclic voltammetric reversible generation of C_{60}^{2+} and C_{60}^{3+} with $E_{1/2} = 1.71$ and 2.14 V respectively.[4] This was allowed by the adoption of suitable experimental conditions based on ultra-dry solvents and electrolytes with very high oxidation resistance and low nucleophilicity.[5]

The present work adds valuable information on the still relatively unknown physical-chemical properties of this important *all-carbon* carbocations and reports some aspects of their unexpected reactivity, in particular, on the formation of an electroactive film onto the electrode surface, attributed to a C_{60}-polymer.

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Symposium 7 - Oral

Soft Materials in Electrochemistry

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Soft Materials in Electrochemistry

Preparation of PEDOT/Fe(CN)$_6^{3-}$ films and their electrocatalytic activity towards the Vitamin C oxidation

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The preparation of modified polymer film-coated electrodes with inorganic redox species has been performed with the aim to enhance some desired properties or to induce new features to the organic conducting polymers [1-4]. One of the most often used material, polypyrrole, has been modified with cobalt and nickel phthalocyanines in order to increase the electrochemical stability of the polymer film [1] or to electrocatalyse the oxidation of some alimentary antioxidants [2]; Fe(CN)$_6^{-3}$ has also been immobilized in this polymeric layer with the purpose to built a D-lactate biosensor [3] and to electrocatalyse the ascorbic acid oxidation [4]. The modification of other polymers, namely poly (3,4-ethilenedioxythiophene) (PEDOT) [5] and polyaniline [6] with Prussian blue as also been reported in the literature.

In this work, the preparation of modified electrodes by PEDOT/Fe(CN)$_6^{3-}$ was made in a two-step method. Firstly, the PEDOT film was potentiodinamically deposited on a platinum electrode from an acetonitrile solution with 50 mM EDOT and 0.1 M TBAPF$_6$. In the second stage, the incorporation of the redox mediator Fe(CN)$_6^{3-}$ on the PEDOT layer was achieved by the application of a constant potential to the working electrode, in an aqueous solution containing K$_4$Fe(CN)$_6$ in 0.1 M KCl. The presence of Fe(CN)$_6^{3-}$ in the modified electrodes is analysed by XPS. The influence of the PEDOT film thickness, the K$_4$Fe(CN)$_6$ concentration and the ferricyanate deposition potential on the amount of Fe(CN)$_6^{3-}$ inserted in the films were evaluated by potential scanning of the modified electrodes in 0.1 M TBAPF$_6$ in a mixed solvent system of acetonitrile/water. The catalytic activity of the film incorporating the redox mediator towards the Vitamin C oxidation was studied by cyclic voltammetry in the mixed media containing 5 mM of ascorbic acid, and its response was contrasted with that of a simple PEDOT film, and a bare Pt electrode. The results show that the PEDOT/Fe(CN)$_6^{3-}$ film presents a lower oxidation potential and a higher oxidation current for the ascorbic acid oxidation and, consequently, a better electrocatalytic activity, comparatively to the simple PEDOT film.

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Electrochemical analysis of a phospholipid phase transition

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A phospholipid monolayer undergoes three consecutive phase transitions in response to the application of electric field. This study involves an examination of the intermediate phase transition which follows the entry of electrolyte into the monolayer and precedes the desorption of the phospholipid. To examine the phase transition both chronoamperometry and impedance methods were used. The chronamperometric results showed as before that the phase transition proceeded by a nucleation and growth mechanism in response to voltage pulses in the cathodic direction but not nucleation and growth in response to potential pulses in the anodic direction. The charge on the electrode changed by about 0.85 μC cm^{-2} over a ~0.015V window and each potential in between was therefore characterised by a definite charge value. The impedance results with applied sine wave ΔV of 0.002V showed that at potentials corresponding to the change in the charge structure, the data exhibited an extra Debye element in addition to RC with a characteristic time constant. At higher ΔV (=0.005V) of the applied *ac* sine wave, the extra Debye element deviated from ideal behaviour and the relaxation time constant was shorter. The logarithm of the half life of the nucleation and growth transient showed at high overpotentials a linear relationship with the reciprocal of the overpotential tending to a decrease in slope at lower overpotentials. This plot indicated that at high overpotentials, nucleation and growth is the prevalent mechanism but at lower overpotentials the growth mechanism becomes more significant. In the impedance experiments, where the applied sine wave has a ΔV of 0.002V, the Debye element represents the growth only of the new phase.

The results point to the phase change as representing the break up of a surface emulsion into electrolyte and phospholipid patches. The nucleation therefore corresponds to the nucleation of clusters of phospholipid and the growth corrresponds to the surface diffusion of phospholipid. The charge associated with the transition corresponds to the increased density of phospholipid head groups on the electrode.

Soft, wet, swelling and shrinking three-dimensional electrodes at molecular level: theoretical treatment

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Films of conducting polymers, when used as polymeric electrodes in electrolytes oxidize and reduced following electrochemical models, but as organic polymers, they must follow the Polymer Science. During those processes either, polymer/polymer, polymer/solvent, polymer/cations and polymer anions interactions change. As a result of the electrochemical reaction, ions and solvent are interchanged between the electrode and the solution: the electrode swells or shrinks.

The construction of artificial muscles and smart membranes are practical demonstration of either the changes of volume taking place in those materials under electrochemical reactions and of the conformational movements stimulated and controlled on the polymeric chains by those reactions. During the oxidation of **basic polymers**, interchange of balancing anions with the solution takes place: entrance (and volume increase) by oxidation, and expulsion (volume decrease) by reduction. Conducting polymers generated in presence of large counterions (polyelectrolytes or large organic or inorganic anions) suffer prevalent interchange cations: expulsion during oxidation (decrease of volume) and insertion during oxidation (increase of volume). Conformational movements of the polymeric chains and changes on intermolecular and coulombic interactions, promote the generation or destruction of interchain free volume.

From a theoretical point of view the stated task is how to overlap the electrochemical models (macroscopic) with the Polymer Science (microscopic) that those processes must follow. Among the different approaches our group has developed a relaxation model. All the relaxation models (magnetic, mechanic or polarization currents) are controlled by a relaxation time τ that is a function of the variation of a molar enthalpy, H. Under limiting conditions, polarization at high overpotentials, the electrochemical reaction allows to close and compact the polymeric structure. We assume that the structure is closed when the dimensions of the pores between polymeric chains is lower that the counterion diameter. In our systems the molar enthalpy, H, includes all the energy related to the system in absence of any electrochemical polarization, H^* being ther implicit all the Polymer Science. Also includes the electrochemical energy): $z_c\eta_c$, related to consecutive shrinking and compaction of the polymeric structures by cathodic polatization, η_c, (for the basic polymers) or by the anodic polarization (for the CP/macroanion blend). Moreover, H contains the electrochemical energy required to relax and swell the polymer: $z_r\eta$ by oxidation at an anodic overpotential, η.. The subsequent oxidation, or reduction, of a compacted structure occurs under relaxation/ nucleation kinetic control of the conformational movements required for the penetration of the counterions. Under geometrical consideration and applying electrochemical laws, the model allows, without any adjustable parameter, a good description of the experimental chronoamperograms, voltammograms or chronocoulograms, obtained for different values of physical or chemical variables, in particular of those named anomalous electrochemical results. The model includes, moreover the classic Electrochemistry, structural shrinking, closing, swelling and nucleation electrodic processes.
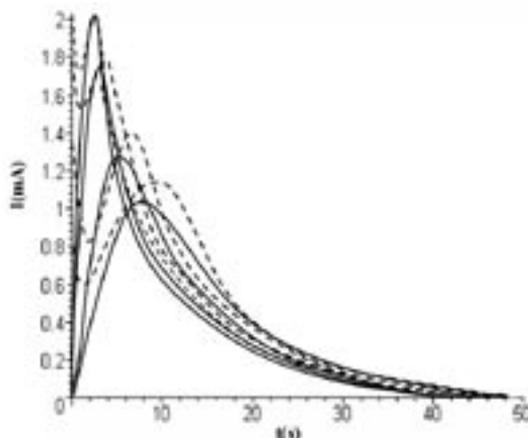
In situ esr spectroscopic detection of an electrochemically generated superoxide radical, $o_2^{\bullet-}$, by spin trapping

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The superoxide radical, $O_2^{\bullet-}$, formed in electrochemical reactions of oxygen was never detected by ESR spectroscopy. Here we use a combination of *in situ* ESR spectroelectrochemistry and spin trapping to prove the existence of this radical for the first time. The $O_2^{\bullet-}$ radical was electrochemically generated and, then, detected by electron spin resonance (ESR) spectroscopy in the presence of the 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a spin trapping agent. $O_2^{\bullet-}$ was generated at room temperature by electroreduction of oxygen in an air-saturated 0.1 M (TBA)ClO$_4$ DMSO solution. Under these conditions, DMPO forms with the $O_2^{\bullet-}$ or $HO_2^{\bullet-}$ a stable paramagnetic adduct, DMPO-HO$_2^{\bullet-}$, of a half-life time sufficiently long ($\tau_{1/2} \approx 8$ min) for its detection by ESR spectroscopy. The ESR hyperfine splitting constants of DMPO-HO$_2^{\bullet-}$ in several solvents are described [1]. The method is very useful for examining electrochemical reaction mechanisms involving $O_2^{\bullet-}$.

ESR spectroelectrochemical measurements were performed in a typical flat cell. A laminated platinum-mesh electrode, silver wire and platinum wire, served as the working electrode, pseudo reference electrode and counter electrode, respectively. As soon as the potential of the oxygen electroreduction was reached, an ESR signal appeared (Fig. 1). The obtained experimental spectrum was simulated and the hyperfine splitting constants for DMPO-HO$_2^{\bullet-}$ were determined to be $a_N = 1.285$ mT, $a_H = 1.042$ mT and $a_H = 0.142$ mT. These constants correspond well to those of the literature structure of the DMPO-HO$_2^{\bullet-}$ adduct.
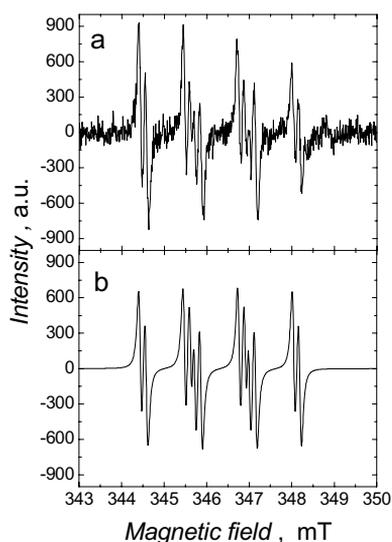
Fig. 1. (a) Experimental and (b) simulated ESR spectrum of the adduct of a DMPO spin trap and electrochemically generated $O_2^{\bullet-}$ in DMSO. Instrumental settings: microwave power 2 mW, modulation amplitude 0.04 mT, gain 5.64×10^4, sweep width 7 mT, time conversation 20.48 ms, scan time 41.94 s.

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Immobilization of laccase on gold, silver and indium tin oxide by zirconium-phosphonate-carboxylate coordination chemistry

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Controlling the molecular structure and organization of the interfacial region between a solid surface and an electrolyte solution has become a matter of routine using several different chemical methods. Among areas that have benefited from the tailoring of surface properties are bioelectrochemistry, bioelectronics, chemical and biological sensing, and bioenergetics. The major issue and challenge in such studies is the electrical coupling of redox enzymes with electrodes, because of their possible applications as enzyme-based bioelectronic devices, e.g., biosensors or biofuel cell elements, also in nanoscale applications. Laccases (benzenediol:oxygen oxidoreductases; E.C. 1.10.3.2) are copper-containing redox enzymes that catalyze the oxidation of broad range of polyphenols and aromatic surfaces. In contrast to widely-used peroxidases, laccases are more stable, versatile and dependent only on atmospheric oxygen. Since laccase oxidation is coupled with the reduction of dioxygen, these enzymes were employed as part as cathode "active" material in biofuel cells. The effective use of an enzyme can be enhanced by its immobilization on a solid support. The surface-attachment chemistry should provide the proper orientation of an enzyme to establish efficient electronic contact between such an enzyme and the electrode surface. We present here a simple method allowing for stable laccase immobilization on various conducting surfaces that retains the activity of the enzyme. The strategy for laccase immobilization presented in this paper relies on ionic coordination chemistry involving –COO$^-$ terminal groups present on the protein. In our previous work we have used zirconium phosphate/phosphonate (ZP) chemistry, pioneered by the Mallouk, Thompson and Katz groups, to attach molecules to boron-doped diamond (BDD). As shown previously, Zr^{4+} ions coordinated to phosphonate and phosphate groups can bind carboxylic and sulfonate functionalities. This chemistry allows immobilization of carboxylic (ZPC) and sulfonate acids to zirconated phosponate/phosphate monolayers. It has been also demonstrated that Hf^{4+} cations can also be used to bind –COO$^-$ and –SO$_3^-$ groups to phosphonate containing monolayers on the surface. Therefore, this chemistry appears to be sufficiently versatile to be used for the surface modification of a variety of surfaces with redox enzymes via their terminal carboxylate groups in a way that provides sufficient flexibility of the surface binding functionality to retain the requisite bio-activity. Using a host of techniques, including surface plasmon resonance (SPR), quartz crystal microbalance (QCM) gravimetry, atomic force microscopy (AFM), surface enhanced Raman scattering (SERS), resonance Raman scattering (RR) and electrochemical techniques, we show that laccase bound to a surface coordinatively through zirconium phosphonate/carboxylate (ZPC) functionalities forms a stable enzymatic layer with the enzyme retaining its activity to a significant extent.

Correlation Between Morphology, Local Conductivity And Doping Charge Distribution In Conducting Polymer Films

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Earlier [1], we have found using Kelvin probe force microscopy (KFM) that the doping charge distribution in conducting polymers of the polythiophene series directly correlated to their morphology: the grains of as-grown polymers constantly differed in the local work function and in the local doping level from the grain peripheral regions. Later these findings were confirmed by other groups and for other polymer systems [2;3]. However, there have been some criticism that such a correlation could be at least partially due to cross-talk between morphology and electric forces as measured in the KFM technique, even despite implementation of its recent refinements such as the lift mode. Therefore, there has been a need to prove beyond any doubt that such correlation does exist and that it is not due to some deficiencies of the measurement technique.

Since variations in the doping level of conducting polymers should translate into corresponding changes in their conductivity, the technique of choice to prove or disapprove this correlation would be to measure the local conductivity of a polymer sample and find out whether or not it is related to the surface morphology. The technique that allows such local conductivity measurements is called conducting or current-sensing AFM (C-AFM). There have been a few reports on C-AFM studies of conducting polymers [4;5]; however, no convincing evidence has been obtained of the presence or absence of the correlation of local conductivity and the surface morphology. In this work, we have used both KFM and C-AFM to characterize the morphology, local conductivity and doping level distribution for the same polymer samples. The results unambiguously show that indeed there is a direct correlation between local dopant distribution, conductivity and morphology in conducting polymers. This behaviour is explained by a higher molecular weight of polymer molecules that form primary nuclei. Importantly, this conclusion should hold for any type of nucleation and therefore should be applicable not only to electrochemically deposited but also to solution-processed polymer films.

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Electrochemically Induced Formation of Fatty Acid Monolayers as Molecular Glue for Electrodeposited Polypyrrole Films

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The increase interest in drug eluting implants based on polymer films has raised the need of adherent, uniform and thin biocompatible coatings (1-2 µm) on stainless steel (SS) medical devices. A polymeric carrier that meets these criteria provides a key component for a successful drug eluting stent technology. We have shown that electropolymerization of conducting polymers (pyrrole and its derivatives) on metal surfaces provides stable and homogeneous films, whose thickness can be controlled[1]. The organic coating can be grafted with various functional groups, which improve biocompatibility and modify its mechanical and chemical properties. In addition, complex shapes of SS surfaces, such as grids and coils, were coated uniformly where the electrodeposited polymer film acquired the surface morphology.

However, the adhesion between hydrophobic organic films and hydrophilic metal surfaces is insufficient for applications, such as coating of implantable medical devices. Motivated by a need for adhesion improvement, we aimed at the development of "molecular glue" that improves the linkage between the SS substrate and the organic coating. Recently, we reported on the electrochemically-induced formation of a self-assembled monolayer (SAM) based on fatty acids as an intermediate layer prior to pyrrole electropolymerization[2]. We found that a dense SAM of *n*-alkanoic acid can be formed on 316L SS by sweeping the potential anodically in aprotic solvents. Besides activating the SS towards attachment of the fatty acids, electrochemistry reduces drastically the time of self-assembly. While decanoic acid formed a disorganized monolayer, longer acids, e.g., myristic and palmitic acids, form highly ordered closed-packed monolayers. The SAMs were characterized by numerous surface techniques such as FTIR, XPS, electrochemistry and contact angle measurements.

The monolayer had a remarkable effect on the adhesion of polypyrrole onto SS acting as molecular glue[3]. Moreover, chronoamperometry, which was used for studying the initial stages of growth and nucleation, revealed that the SAM dictated the electrodeposition mechanism of polypyrrole. AFM images were in excellent agreement with the deposition mechanism derived from chronoamperometry.

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Dynamics of sds structures formation at gold electrodes

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There is a growing interest in studying surfactant aggregates due to their potential applications in industrial processes and in biology [1, 2]. The adsorption of surfactants on solid surfaces allows the simulation of a membrane-like structure formation which can be used in diverse biological/industrial processes as protein immobilization, charge and mass transfer, solubilization of the membrane, etc [2, 3]. In this work we report on the dynamics of formation of self-assembled molecular layers of Sodium Dodecyl Sulfate (SDS) on gold surfaces. Resonant frequency changes of the quartz crystal microbalance (QCM) immersed in water were registered before and during the addition of SDS. Changes of the open circuit potential value U (vs. Ag/AgCl) of the $0.28\ cm^2$ area gold coated electrode of the QCM were also registered, Fig. 1. After the first SDS addition (final concentration 1mM), the resonant frequency decreased initially linearly and then in an exponential like form. Simultaneously, the potential curve increased to a peak value and decreased continuously. At the 2nd SDS addition (final concentration 2mM), a similar linear-

Figure 1

exponential frequency decrease was observed. The *U* versus *t* curve increased again to the peak value and then decreased continuously as before. The potential peaks were time coincident with the frequency transition from linear to exponential-like form for the two SDS additions. Next additions of SDS resulted in the same pattern (not shown here). From these measurements we were able to propose a model for the dynamics of the adsorption process of SDS on the bare gold surface. Properties like density, form and structure of compact-monolayers as well as of bilayers could also be inferred.
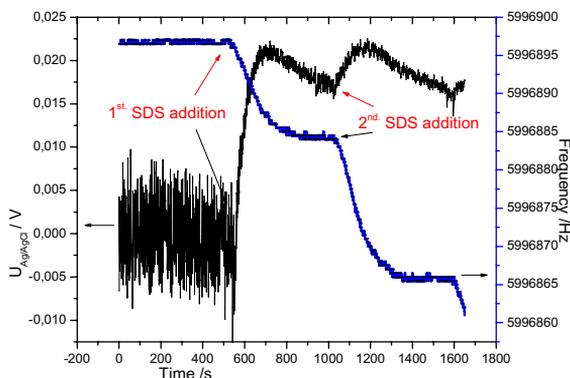
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Redox-active Covalent Modifications on Spherical Non-porous Silica Nanometric Particles

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Non-porous, spherical silica nanoparticles ($d \approx 100 - 800$ nm) with high monodispersity resulting from a controlled Stöber process are covalently surface-modified with redox-active molecules. Ferrocene, a ruthenium(II) complex with an $N_2P_2Cl_2$ ligand set, and a sterically hindered biphenylamine are used as modifiers. The resulting materials are characterized by physical (BET measurements, scanning electron microscopy, dynamic light scattering), spectroscopic (UV/Vis, ^{1}H-, ^{13}C- and ^{31}P-solid-state and suspension NMR, AAS), electrochemical (CV, EQCN), and chemical methods. The surface concentration of the modifiers is determined. The particles adsorb spontaneously on a Pt electrode surface. The shape and peak currents of cyclic voltammograms recorded at various scan rates indicate, besides the adsorption feature, a kinetic component similar to that observed for dendrimers by Amatore et al. [1]. This is interpreted as an electron-hopping process along the three-dimensional spherical surface. The ruthenium(II) complex retains its catalytic hydrogenation activity (substrate: acetophenone) upon immobilization on the silica particles.

These materials present examples of geometrically, physically, and chemically defined three-dimensional inorganic-organ(ometall)ic hybrid structures with a hard core and a soft molecular shell and provide a unique environment for the immobilized molecules. In particular, they can be applied for the heterogenization of homogeneous catalysts ("chemistry in interphases" [2]).

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Synthesis and characterisation of composite materials based on polythiophenes including metal nanoparticles

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Conducting polymers (CPs) are widely employed as electrode coatings, aiming at improving the electrocatalytic capability and at inducing antifouling effects. A step forward consists in the preparation of composites including metal functionalities inside the polymeric matrix, in order to further increase the electrocatalytic performance. In particular, inclusion of noble metal nanoparticles, whose catalytic properties are well known and that are widely exploited in a variety of applications, constitute one of the most interesting possibilities. As an example, metal nanoparticles have been included into carbon black or supported by self assembled structures; CPs based on polypyrrole and polyaniline have been also employed as a support, although structure and properties of the resulting composites are far from being exhaustively investigated. Even less widely studied are composite materials based on polythiophenes (PTs).

Our recent and present research activity is carried out along such lines. In particular, we realised Au and Pt nanoparticles with size ranging from 2 to 10 nm, encapsulated by citrate, tannic acid, 3,4-ethylenedioxythiophene (EDOT) and different tetraalkylammonium salts bearing neutral and charged moieties. The resulting nanoparticle systems have been characterised by the most suitable spectroscopic and microscopic techniques, such as XRD, TEM-EDS, NMR, IR, UV. Au and Pt nanoparticles differently encapsulated have been successfully included into electrogenerated PEDOT, carrying out the electropolymerisation of EDOT in aqueous medium dissolving the nanoparticles; suitably planned experimental conditions have been proven to lead to composite coatings with tuned electrochemical properties. The composites formed on the electrode have been characterised by TEM-EDS, AFM, SEM, electrochemical and spectroelectrochemical tecniques. In view of the applications in amperometric sensors, the electrochemical behaviour with respect to benchmark depolarisers like ascorbic acid and dopamine has been tested by voltammetric techniques, comparing the results obtained, in terms of sensitivity and resolution of the responses, with those of simple PEDOT coating, in the absence of metal nanoparticles. Quite interestingly, the nature of the encapsulating agent has shown to induce selectivity to the electrochemical device. Encapsulating species suitably functionalised with ionic moieties activate a sort electrostatic shield: the access of charged depolarisers to the redox active centres on the electrode can be modulated by changing the charged residues on the nanoparticle encapsulating agent.

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Polypyrrole/vitamin B12 composite, a new redox mediator system

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One of the most promising properties of electronically conducting polymers is their ability to incorporate biologically or physiologically important materials. These composites, in which the activity of the immobilized substance is not only preserved but the redox process is electronically wired to the metallic electrode, are of prime importance *e.g.* in biosensors. In this contribution the successful realisation of the polypyrrole/vitamin B12 composite (PPy/B12) is reported – to the best of our knowledge – for the first time, meaning that the electroactive pattern of the polymer is undisturbed [1].

First, the reduction of vitamin B12 – in form of cyanocobalamin – has been studied following its adsorption on the surface of the conducting polymer layer of PPy/piperazine-1,4-bis(ethane sulfonate), called PIPES. Vitamin B12 exhibited sustained electroactivity at this polymer electrode. The reduction process could be described by a Roginskiy – Zeldovich mechanism, which involves a Temkin – Frumkin-type adsorption followed by the charge transfer step.

B12 could also be incorporated into the PPy film during its electrochemical polymerisation in the presence of this widely used biological buffer solution, and B12 has preserved its electroactivity in its immobilized state in the films, as well (Fig. 1). The cobalt redox centre of the molecule – which can be transformed into the Co(I) superreduced state [2] – remained reducible in the composite layer. The electrochemical properties of the composite prove that the redox transformation of the cobalt centre takes place at potentials less negative than the complete reduction of the film occurs, i.e. before it loses its conductivity.

The sustained redox activity of B12 immobilized in this conducting polymer composite electrode may give the opportunity to exploit the high reactivity of cobalt(I) in mediated reactions. The results are the starting point to conducting polymer electrode based mediated reduction processes in bio-electrochemical systems.
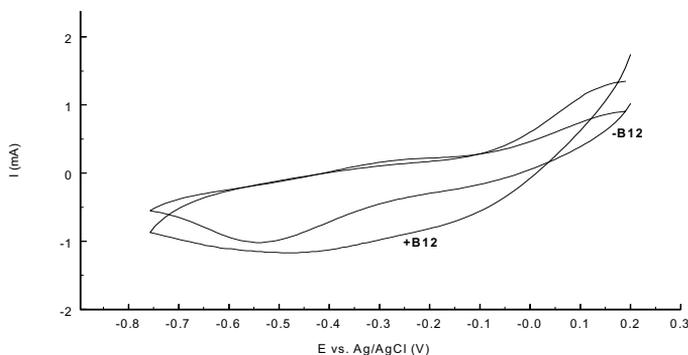
Fig. 1. Comparison of the behaviour of PPy/PIPES films with and without incorporated B12.

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Electrochromic systems based on self -assembled monolayers of phosphonated viologens anchored on high surface area titanium dioxide

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Viologen (V^{2+}) molecules containing phosphonic acid groups on nanostructured titanium dioxide layers have been demonstrated to possess interesting electrochromic properties. Such substrates, with a surface roughness factor in the range 100-1000, have recently attracted a considerable interest for a number of applications, including solar cells, batteries and electrochemical biosensors. Colorless V^{2+}, with a surface concentration in the order of 10^{-7} mol/cm^2, is reversibly reduced to the coloured cation radical species $V^{+\bullet}$, which also remains chemisorbed.. Both V^{2+} and $V^{+\bullet}$ remain attached to the electrode upon multiple cycling.

The above results suggest the successful use of viologen dyes to electrochromic cells. A display-type variant has been constructed with a viologen/TiO_2/ITO glass negative electrode, a porous Sb-doped tin oxide positive electrode, whose operation is based on pseudocapacitive charging-discharging, and an aprotic electrolyte. Spectrochemical and electrochemical data related to the individual electrodes and to the 2-electrode device will be presented and the related processes analyzed.

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Spectroelectrochemistry of reduction of titanocene dichloride complex in solution and inside a conducting-polymer film

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Titanocene dichloride (Cp_2TiCl_2, $Cp=C_5H_5^-$, cyclopentadienyl ligand) in its free form is used (after its reduction) as an active catalyst for polymerisation of olefins and various organic reactions. Recently, this complex was incorporated into electron-conducting polymer films with a polypyrrole (pTc3Py) or PEDOT matrices for the applications in the supported catalysis.

The mechanism of the reduction process of the complex both in a free and immobilised state depends on the solvent. In THF the generated anion radical, $Cp_2TiCl_2^-$, is the principal product, with relatively small fractions of dissociated forms, "monochloride" Cp_2TiCl and its dimer, $(Cp_2TiCl)_2$. On the contrary, monochloride represents the principal product in AN (CH_3CN) and DMF.

Spectroelectrochemistry in UV-visible range provides information on the evolution of the electronic spectrum in the course of the complex reduction and its reoxidation. All experiments were performed under dry Ar atmosphere, with the use of schlenk technique, in view of an extreme sensitivity of the reduced forms to oxygen.

The first series of spectra measurements was performed in a hermetic cell with a thin-layer of solution between the quartz wall and the reflecting Pt electrode (in Freiburg). The layer thickness varied from 100 μm up to about 300-400 μm. The current and the spectrum of the Cp_2TiCl_2 solution (of various concentrations) in AN or THF were registered in the course of a slow scan rate voltammetry or with a double (reduction-reoxidation) potential step.

The second group of experiments (in Dijon) included the reductive electrolysis of Cp_2TiCl_2 solutions in AN or THF, with a periodical control of the solution content variation with the use of the microelectrode. The reduced solution was transferred to a quartz cell for spectra measurements. For the sake of comparison we have also performed measurements with the use of optical fibres delivering the light to quartz sondes immersed into the solution.

The third approach was based on the preparation of the reduced titanocene complex by chemical reduction of Cp_2TiCl_2 by metallic Al. Thus obtained product was transferred to AN or THF solution for electrochemical and spectroscopic studies, in a quartz cell or with the use of immersed sondes.

Spectra of immobilised Cp_2TiCl_2 centers attached to PPy matrix (for films deposited at ITO electrode surfaces) have also been studied in contact with AN or THF solution, for various potential values, both within the redox activity range of the matrix and of centers (their reduction and reoxidation).

The comparison of spectra changes for solute and immobilised complexes allowed us to trace the changes of the redox state of titanocene complexes inside conducting polymer films.

Nafion[Ru(bpy)$_3$$^{2+}$] as the Solid Organic Charge Transport Material for the Solid-State Photovoltaic Cell

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The studies of organic photovoltaic cells or nano inorganic-organic hybrid solid-state photovoltaic cells and light emitting diodes are attracting attention for future electronic and photonic devices as well as for photoenergy conversion devices. Many researches focused on searching for appropriate solid charge solar energy transport materials, which plays a key role in fabrication of photovoltaic cells and light emitting devices .

In this work, the Nafion-based redox polymer(Nafion[Ru(bpy)$_3$$^{2+}$]) was developed into a kind of solid organic charge transport materials which can act as a kind of hole transport material when redox centers are located in the reductive states initially(as shown in fig.1). The charge transport performance of this solid redox polymer has been investigated by electrochemical methods. The results of charge transport performance showed that D_{ct} of the ITO / Nafion[Ru(bpy)$_3$$^{2+}$]/Au solid cells is about 10^{-7}~10^{-8} cm^2·s^{-1} and μ is about 10^{-6} cm^2·V^{-1}·s^{-1}. PEG was also added to improve the charge transport performance in dry state Nafion. Finally we employed the Nafion-based redox polymer as the hole transport material for the solid-state photovoltaic cell using narrow band gap nano-semiconductor CdS as active photoelectrode. So far, its IPCE is about 15% and η_e about 3.2% for 395nm light. The IPCE for 350nm light is about 23%. The future of this novel photovoltaic cell is promising along with the potential enhancement of the charge transport performance of the redox polymers.

Fig. 1 The scheme of construction(upper) and operating process(lower) of the solid-state photovoltaic cell. M is for Ru, Red for reduced state of Ru complex.

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Role of protonation in the reduction of hydrazones and oximes

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Both hydrazones and oximes derived from benzaldehydes and acetophenones are reduced at pH > 3 in a single four-electron wave. At pH about 5 to 8 the reduction involves a diprotonated species, which is formed by protonation of the adsorbed unchanged azomethine derivative. The transfer of two protons prior to the first electron uptake was confirmed by the shape of the i = f(pH) plots and by comparison with reduction of ω,ω,ω-trialkyl derivatives of hydrazones and with nitrones, where the pH-dependence of $E_{1/2}$ indicates reduction of species bearing positive charges on two adjacent heteroatoms. This is the first reported experimental evidence of such diprotonated species. Our investigations also indicate that such diprotonated forms are the reactive species in acid catalyzed hydrolysis of oximes. At pH lower than about 4 a change in mechanism takes place. The predominating monoprotonated form is not adsorbed and is reduced. This is confirmed by the agreement of the pK_a of the monoprotonated form obtained form UV-spectra and from shifts of $E_{1/2}$ of the oxime reduction. The reductions of both di- and monoprotonated forms are initiated by a cleavage of the $N-NR_3^+$ or $N-OH_2^+$ bond facilitated by the structure of the good leaving group. Initial cleavage of the N-N or N-O bond is further supported by the presence of two two-electron waves of some hydrazones and oximes at pH < 2, where the more negative wave corresponds to a reduction of the imine. The separation of these two waves is due to a difference in pK_a-values of oximes and imines, as pK_a of the oxime is always much lower than that of the imine. For benzophenone and fluorenone hydrazones the imine formation was confirmed by comparison of potentials with these of corresponding imines, which for these compounds are stable between pH 5 and 10. For corresponding oximes such comparison was not possible, as the reduction of the imine is in all cases more positive than that of the oxime. -The typical behavior of some oximes bearing CF_3 and CN groups as well as monoximes derived from asymmetrical 1,2-diketones will be mentioned.

Effect of MWCNT on Electropolymerization of Pyrrole

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Polypyrrole is one of the most important conducting polymers and became a very interesting candidate for a number of applications which have been reported in some review papers [1,2]. In the present work, we attempt to inspect the effect of multi-walled carbon nanotubes (MWCNT) on the electropolymerization of pyrrole under the galvanostatic, potentiostatic and potentiodynamic conditions. For this purpose, CNTs were dispersed within the electrolyte solution. A typical chronopotentiogram of the pyrrole electropolymerization (performed with an applied current of 3.3 mA cm^{2-}) shows that in the presence of CNT, electropolymerization reaction starts at relatively high potential (0.75 V), which is accompanied by a more effective polymerization. In potentiostatic technique as can be seen in the typical chronoamperogram (perfomred with a potential of 0.7 V vs. Ag/AgCl), a current spike followed by a decrease to a minimum, pursued by a current increase with time, which corresponds to a nucleation and growth mechanism [3]. In the presence of CNT, the charge transfer is very fast and chain growth occurs at higher current. The higher amount of the consumed charge was measured from the chronoamperometric curve when the solution contais CNT. Due to fast charge transfer of CNT, we are able to electropolymerize the pyrrole with higher efficiency in the presence of CNT.
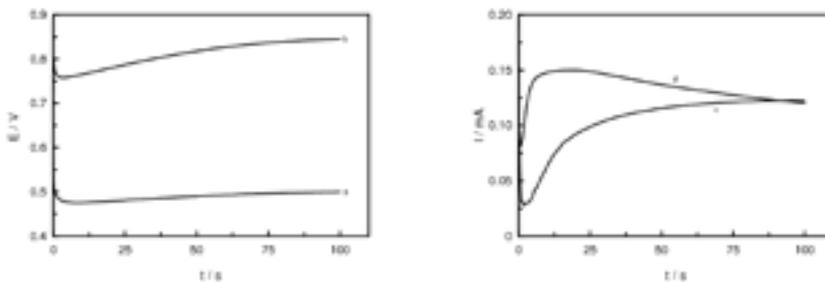
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Palladium electrodeposition on polyaniline films

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Conducting polymers can be used as proper hosting matrixes to obtain highly dispersed metallic particles and have been subject of great scientific interest [1,2]. In particular, Pt or Pd microparticles dispersed in polyaniline films are recognized to enhance the electrocatalytic activity as compared with the bulk-form metal electrodes [2-5]. For catalysis purposes, the synthesis of well-defined highly dispersed metal micro- nanoparticles and control over the nucleation and growth process is essential. In this sense, composite electrodes were prepared by Pd electrodeposition from a Pd (II) solution into electropolymerised polyaniline (PAni) films [5] of variable thickness formed at different potentiodynamic polymerisation conditions, although with similar electroactivity. A combined investigation of composite polyaniline/Pd electrodes by electrochemical techniques, and AFM measurements was performed.

The AFM images of PAni films showed a strong influence of the potential sweep rate during polymerisation on the sub-micrometer scale surface morphology of the film. The analysis of the cathodic currents obtained in the initial moments of the Pd nuclei growing on the polymer, point out to an instantaneous nucleation with the 3D growth mechanism limited by diffusion of the Pd ions when the deposition takes place on the PAny film grown at 60 mVs^{-1}, confirmed by AFM-Phase measurements. The differences on the loading level, size and dispersion of Pd clusters obtained after different deposition times are also discussed in this contribution, and related with the homogeneity of the PAni matrix. The electrocatalytic properties of the distinct polyaniline films containing dispersions of Pd particles with respect to the hydrogenation of nitrobenzaldehyde were also evaluated. The results allowed to correlate the polymer topography and the optimal size and spatial distribution of the catalytic particles.

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Chemically – modified carbon fiber as electrode material used for deep brain stimulation of the subthalamic nucleus in rats

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Deep brain stimulation, the electric stimulation of basal ganglia nuclei, is a powerful therapeutic tool for the treatment of various movement disorders in patients associated with Parkinson's disease. However, the pathophysiological mechanisms of such therapeutic approach on basal ganglia network function are still largely unknown. Hitherto, experimental studies have focused on short – term stimulation. Since patients underwent such treatment for many years, animal studies which reproduce the conditions of long term stimulation will be necessary to accurately investigate the effects of DBS. However, stimulation parameters of acute DBS cannot be easily transferred to long term conditions. Accordingly, for this purpose, we studied the influence of different charge densities (0, 3, 6, 13 and 26 $\mu C/cm^2$/phase) and duration (6 h or 4 days) of subthalamic nucleus (STN) using chemicall-modified carbon fiber electrodes on neuronal tissue damage in rats. A redox mediator, poly(Fe(III)–4VP), was electropolymerized onto the carbon fiber at +0.40 V vs Ag/AgCl. Our data demonstrate the advantage of chemically – modified carbon fiber over stainless – steel electrodes when used in short term high frequency stimulation (HFS) (frequency 130 Hz, pulse width 60 μs) and indicate that HFS using chemically – modified carbon fiber electrodes pulsed with 3 $\mu C/cm^2$/phase over 3 days did not produce any relevant tissue damage in STN. In addition, the neurotoxicity of iron, produced from the corrosion of electrodes, proved that avoiding stainless steel electrode imperative. Future developments of employing carbon fiber as electrode material for deep brain stimulation should include possible mechanisms of action and real time clinical application as carbon fiber looks promising to replace stainless steel as the electro – active materials.

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Development and application of hydrophobic polypyrrole films for the sensing of alcohols

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There are several reports in the recent literature to suggest that conducting polymers, particularly polypyrrole, can be formed to give hydrophobic surfaces [1,2]. These conducting polymer films with low energy hydrophobic characteristics have many applications including corrosion protection, conductive textiles and antistatic coatings. In this paper, the development and possible application of hydrophobic polypyrrole films for the electrochemical sensing of organic compounds, for example alcohols, are presented and discussed. Hydrophobic polypyrrole films were deposited using various electrochemical methods such as cyclic voltammetry, constant potential and constant current techniques. The hydrophobicity of the polypyrrole films was altered by employing different dopants such as, sodium dodecylsulfate, *p*-toluene sulfonic acid and tetrabutylammonium hexafluorophosphate, during electropolymerization. Contact angles were obtained to determine the hydrophobicity of the polymer. Various methods were employed to characterize the films including infrared spectroscopy, UV-vis spectroscopy and differential scanning calorimetry. Once this characterization was complete the polymer films were utilized as sensors to detect between a range of alcohols i.e. methanol, butanol, hexanol and heptanol. It was found that the degree of hydrophobicity of the polymer plays a very important role in allowing the alcohol molecules to pass through the polypyrrole film and react at the platinum substrate, with the more hydrophobic polymers favouring the more organic alcohol.

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Study of the Electropolymerization of Tetrakis (3-aminophenyl) Porphyrin Fe(III) Chloride on Au Electrodes by Cyclic Voltammetry and STM

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Conducting Tetrakis (3-aminophenyl) porphyrin Fe(III) chloride films are prepared by electropolymerization on Au(111) electrodes in DMF + TBAP solutions by cycling the potential between -1.6 V to 1.5 V vs SCE at 0.2 Vs^{-1}. The film thickness is controlled through the number of cycles and the voltammetric response of the modified electrode is stable and reproducible. STM images show that during the first 20 cycles only 2D islands 0.35 nm high and up to 50 nm long are formed. These islands grow laterally by the incorporation of new oligomers on their borders. When the electrode surface is almost fully covered a transition from 2D to 3D growth is observed. This transition in the growth mode can be followed through the anodic charge of the cyclic voltammograms.

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Electrografting of Poly(3-Alkylthiophenes) And Thiophene Random Copolymer Onto Carbon Fiber Microelectrode

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Since their first appearance in 1986, [1-4] poly(3-alkylthiophenes) (PATs) have attracted increasing interest due to the significant improvement in solubility besides good environmental stability. Therefore these compounds are extensively studied. On the other hand carbon fiber offers unique properties such as high strength, high modulus and low density. It is expected to increase surface characteristics of the carbon fibers by electrografting of 3-alkylthiophenes and thiophene random copolymer.

In this study, we investigated the electropolymerization conditions of 3-methylthiophene, 3-hexylthiophene and thiophene random copolymers of these monomers. The effect of feed ratios, concentration effect, and solvent effect, electrolyte effect on the electrografting of copolymer of 3-Methylthiophene, 3-hexylthiophene and thiophene was studied in detail. The copolymerization of corresponding monomers carried out under suitably chosen electrochemical conditions (i.e. supporting electrolyte, current density and charge density, etc.) were fallowed by FTIR-ATR. Correlation between the feed ratio of the comonomers and morphological studies of the same electrografted copolymers was examined by scanning electron microscopy.

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Incorporation of Sarcolipin in a Hg-supported Biomimetic Membrane

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Sarcolipin is a 31 aminoacid integral membrane protein that regulates the sarco(endo)plasmic reticulum Ca-ATPase (SERCA) in skeletal muscle. It is known to span lipid bilayers by adopting a highly defined α-helical structure, and to orient perpendicularly to the plane of membrane bilayers [1]. Sarcolipin inhibits SERCA at low Ca^{2+} concentrations and activates it at high Ca^{2+} concentrations, via intramembranous interactions. Chemical cross-linking showed that sarcolipin has the ability to self-associate to oligomers in liposomes [2], although its helical content is a basic feature of the monomer rather than a consequence of oligomeric interactions.

To verify whether the presence of of sarcolipin in a lipid bilayer may give rise to the formation of ion-conducting pores, attempts were made to incorporate it in a biomimetic membrane from 0.1 M KCl aqueous solutions containing 1.3×10^{-7} to 1.3×10^{-6} M sarcolipin. The biomimetic membrane was obtained by tethering to a hanging mercury drop electrode a "thiolipid" consisting of a tetraethyleneoxy hydrophilic chain terminated at one end with a disulfide group, for anchoring to the mercury surface, and covalently linked at the other end to two diphytanyl chains mimicking the hydrocarbon tails of a phospholipid. By self-assembling a lipid monolayer, of composition phosphatidylcholine:sphyngomyelin:cholesterol (59:15:26), on top of the thiolipid monolayer, a lipid bilayer was obtained, which was interposed between the tetraethyleneoxy hydrophilic "spacer" and the 0.1M KCl aqueous electrolyte. The conductance of the resulting biomimetic membrane induced by melittin was monitored as a function of the applied potential by using electrochemical impedance spectroscopy.

Sarcolipin incorporates in this biomimetic membrane very slowly, yielding a maximum conductance only after several hours. The conductance shows a peak at about –600 mV/SCE, with a relaxation time of about 1 s, and a further peak at about –800 mV/SCE, with a relaxation time of 30 ms.

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Electrochemical Study of the Redox Properties of Polyaniline Modified Electrode in Ammonium Salts Solutions

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Electrochemical redox properties of polyaniline and sulfonated polyaniline modified platinum electrode have been studied in solutions of ammonium salts in 0.5 M sulfuric acid or distilled water. The platinum electrode plated with electrochemically synthesized polyaniline was directly chemically sulphonated with an excess of 1,3-propanesultone solution in dioxane (0.1 g/ml). The chemical reaction of electrochemically synthesized PANI with the excess of 1,3-propanesultone was carried out at 90 ^{0}C (t = 50 min).

The electrochemical measurements using cyclic voltammetry were performed in a three-electrode system containing a platinum counter electrode and a saturated calomel electrode as reference. Polyaniline films were synthesized on the platinum electrode with a diameter of 4 mm between -0.1 and 1.1 V in aqueous 0.5 M H_2SO_4 baths containing 0.1 M aniline at a scan rate of 50 mVs^{-1}. The influence of the nature of the anions (HSO_4^-/SO_4^{2-}, PO_4^{3-}, VO^{3-}, Cl^-) on the electrochemical behavior (anodic and cathodic peak height and position on the potencial scale) and the charge, Q_{cath}, was examined at 20 mVs^{-1}. The electrode covered with polyaniline was equilibrated in the ammonium salt solution and the charge Q_{cath} was calculated from the voltammogram.

Sulfonated polyaniline films show suppressed redoks properties compared to those of polyaniline. The film redox activity in acidic and less acidic solutions strongly depends on the anions present in the electrolyte.

Interactions of Electroactive Chromophores with Biomimetic Lipid Layers

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We have synthesized and characterized a family of self-assembled monolayers containing pyrene derivatives on gold, indium tin oxide (ITO) and silica substrates. The covalently bound pyrene functionalities serve as either spectroscopic or electrochemical probes of their immediate environment, and we explore both of these responses. When these compounds are the only constituents bound to the interfaces, the molecules enjoy significant structural freedom. The addition of aliphatic adsorbates to the interfaces serves to place the pyrene derivatives in a more restricted environment. Cyclic voltammetry shows that the organization of a monolayer with pyrene derivatives, and the position of terminal pyrene ring within such a monolayer, depend sensitively on the length of the pyrene tether and the presence or absence of aliphatic interfacial species, as well as the identity of the substrate.

We have studied the steady state and time-resolved emission spectroscopy of the pyrene-containing monolayers reported in the previous article, where in this work we have bound the monolayers to SiO_x. We find that these monolayer structures are sensitive to the identity of the solvent overlayer, with the solvent playing a significant role in the organization of the surface-bound monolayers. We discuss our findings in the context of the known polarity-dependence of the pyrene emission spectrum and find that the motional freedom of the chromophores varies with both the monolayer composition and the identity of the solvent overlayer. Our data point to the importance of neighbor-neighbor interactions within the monolayer structures in mediating the motional freedom of the tethered pyrene chromophores.

The deposition of phospholipid layers on top of the surface-bound monolayers indicates that under most circumstances, the pyrene moiety does not penetrate the phospholipid layer, but lies at the interface between the monolayer and the phospholipid.

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Electropolymerization and characterization of poly(N-methylaniline) and poly(N-butylaniline) in mixtures of aqueous and organic solvents

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Electropolymerization of *N*-methylaniline (NMA) and *N*-butylaniline (NBA) was studied on glassy carbon and optically transparent tin oxide electrodes in mixtures of aqueous and organic solvents [1]. Five different organic solvents, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), propylene carbonate (PC) and acetonitrile (ACN) were mixed with aqueous 1.0 M $HClO_4$ solutions. The results show that NMA and NBA can be electropolymerized in aqueous-organic solvent mixtures with max. 30 % (v/v) and 50 % (v/v) organic solvents, respectively. The choice of organic solvent strongly influences the film formation. With addition of 10-20 % THF, ACN and PC to the aqueous polymerization solution, the film formation was highly improved. The poly(*N*-methylaniline) and poly(*N*-butylaniline) films were characterized with cyclic voltammetry, in situ UV-vis spectroscopy, size exclusion chromatography and with electrical conductivity measurements.

The UV-vis measurements confirm that all PNMA and PNBA films have three oxidation states; leucoemeraldine, emeraldine and pernigraniline.

The results of the conductivity measurements indicate that PNMA and PNBA films with higher electrical conductivities can be obtained when polymerizing in aqueous-organic solvent mixtures containing 10 % ACN, 10 % PC or 10 % THF.

SEC measurements indicate that a narrower and more even MW distribution is obtained in ACN, PC and THF resulting in higher electrical conductivities. The PNMA film prepared with 10 % ACN have a MW distribution between □600-30000 Dalton (DP□6-285; peak at DP□12), whereas the MW distribution of the PNBA films polymerized in 10 % THF is □4500-45000 (DP□31-306; peak at DP□65). The polymerization process favours, however, in both cases the formation of lower MW fractions.

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A strategy toward self-doped polyaniline: conversion of luminol into aminophthalate

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Among other conducting polymers, polyaniline (PANI) has found numerous applications as a result of its straightforward polymerization, chemical stability and relatively high conductivity. However, PANI is electroactive only in acidic conditions, normally pH < 4, which greatly confine its operation at near pH neutral or slightly acidic solutions [1].

In order to overcome this problem an ionisable, negatively charged functional group, which acts as an inner dopant anion, can be bound to the polymer backbone. Self-doped polyaniline films revealed an extended redox activity and conductivity over a wider pH range [1].

Recently, luminol has been regarded as an aniline monomer derivative, which means that electropolymerization can be used as useful method for polyluminol films deposition at solid electrode surfaces [3-4].

This work describes a new strategy to obtain self-doped polyaniline films through the electrochemical polymerisation of luminol in the presence of aniline and subsequent conversion of the incorporated luminol into aminophthalate.

Luminol conversion is performed on the basis on the well-known electrochemiluminescence reaction with hydrogen peroxide [5]. The degree of aminophthalate production can be established throughout the control of the polarisation time and applied potential. The so formed films revealed good electrochemical redox activity in acidic, slightly acidic, and pH neutral solutions.

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Preparation and Electrocatalytic Properties of the FAD Hybrid Film Modified Electrodes

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The flavin adenine dinucleotide (FAD) modified zinc oxide films have been prepared using repeated cyclic voltammetry to investigate both the deposition process and the films' electrocatalytic properties. The cyclic voltammograms recorded the direct deposition of the FAD/zinc oxide films over different scanning potential ranges from the mixed aqueous Zn^{2+} ions and FAD. In addition to the cyclic voltammetry, an electrochemical quartz crystal microbalance, UV-visible absorption spectroscopy, and the stopped-flow method were used to study the growth mechanism and their properties of the FAD/zinc oxide films. The FAD/zinc oxide films exhibited a single redox couple that included both the electron and proton transfer, with a formal potential that demonstrated a proton effect in acidic and basic solutions. The electrocatalytic reduction of $S_4O_6^{2-}$, SO_5^{2-}, $S_2O_8^{2-}$, ClO_3^-, BrO_3^-, and IO_3^- ions using a FAD/zinc oxide film occurred in neutral aqueous solutions. The electrochemical reaction of the hemoglobin with the FAD/ZnO self-assembly film-modified electrodes and their electrocatalytic properties were investigated. The electrocatalytic properties of the O_2, H_2O_2, trichloroacetic acid and SO_3^{2-} were studied by the FAD/zinc oxide films in the absence or in the presence of hemoglobin. The electrocatalytic reduction current had been developed from the cathodic peak of the FAD/zinc oxide redox couple. The electrocatalytic process involved an interaction of hemoglobin and FAD/GC film-modified electrode to increase the electrocatalytic reduction current. The electrocatalytic reduction of O_2 using the FAD/zinc oxide films was investigated by cyclic voltammetry, and rotating ring-disk electrode methods. Hybrid films composed of **electropolymerized acriflavine-**flavin adenine dinucleotide (AF/**FAD**) film modified electrodes have been prepared in neutral aqueous solution. The hybrid poly(acriflavine)/FAD film showed two redox couples. The electrochemical quartz crystal microbalance and cyclic voltammetry were used to study the *in situ* growth of hybrid poly(acriflavine)/FAD films. The electrocatalytic oxidation and reduction of NADH and NAD^+ by a poly(acriflavine)/FAD hybrid film in aqueous solution were carried out. The poly(acriflavine)/FAD hybrid film were found active for both electrocatalytic oxidation as well as **reduction reaction of NADH.** The electrocatalytic reduction of L-cystine, $S_4O_6^{2-}$, SO_5^{2-}, $S_2O_8^{2-}$, NO_2^- and H_2O_2 by a poly(acriflavine)/FAD hybrid film in a neutral aqueous solution found to be an electrocatalytic reduction activity.

Sonochemically synthesized mixed Ni(OH)$_2$ / Co(OH)$_2$ nanoparticles and their application in high efficient electrochromic electrodes.

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The present work describes the behavior of nanosized nickel hydroxide doped by different amounts of Co(OH)$_2$, synthesized by a sonochemical method, deposited onto ITO transparent electrodes by using the electrostatic deposition layer-by-layer technique, using poly(diallydimetilammonium, PDDA) as polycation. Particles of about 5 nm diameter were obtained and characterized by High Resolution Transmission Electron Microscopy, figure 1. The electrostatic self-assembly provides very thin electrochromic electrodes more homogeneous than those obtained by the ordinary electrodeposition method.
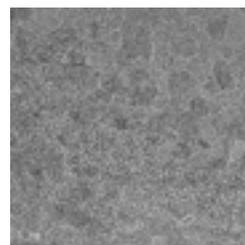
Figure 1
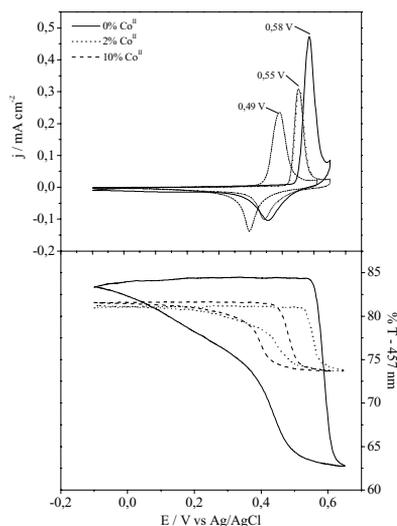
Figure 2

The amount of Cobalt incorporated in each mixed nanoparticle was varied as a function of the proportions in the synthesis solution. The final proportion of Co/Ni was determined by ICP-OES of dissolved films. The change in the amount of cobalt is also denoted in the voltammetric experiemnts as shown in Figure 2. When the amount of Co increases in the nanoparticles, the anodic peak is shifted to less positive potentials , far from the oxygen evolution reaction. Also, as the amount of Co increases, the electric charge diminishes indicating that less mixed material was imobilized. This is in agreement with the fact that the mixed nanoarticles are smaller than the Ni(OH)$_2$ or Co(OH)$_2$ ones[1].

The electrochromic efficiency obtained with mixed nanoparticles is higher than electrodeposited films (normalized by the amount of material measured by ICP-OES). The performance of theses electrode was found to better showing a shorter response time (in the order of ms) and higher durability.

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Soft Materials in Electrochemistry

SYNTHESIS AND CHARACTERIZATION OF BOTRYOSPHAERAN-POLYPYRROLE MEMBRANE

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New tissue engineering technologies will rely on biomaterials that physically support tissue growth and stimulate specific cell functions. The goal of this study was to create a biomaterial that combines inherent biological properties which can specifically trigger desired cellular responses (e.g., angiogenesis) with electrical properties which have been shown to improve the regeneration of several tissues including bone and nerve. To this end, composites of the biologically active polysaccharide botryosphaeran (EPS, secreted by the ascomyceteous fungus *Botryosphaeria rhodina*) and the electrically conducting polymer polypyrrole (PPY) were synthesized and characterized.

The polypyrrole films were electropolymerized on the surface of ITO. From two solutions: (i) pyrrole 0.025 M and KCl 0.1 M; (ii) pyrrole 0,025 M and botriospherana 0,5 mg mL^{-1}, applying a potential of + 0.7 V, the polymeric film was deposited until reach a relative thickness of 20 μC cm^{-2}. The electrochemical experiments were carried out in a potenciostat (MQPG01 Microquimica). The electrode of reference utilized was Ag/AgCl (1.0 M) and as counter electrode a Pt foil.

The comparison of the cyclic voltammograms, in KCl 1.0 M solution, for the polypyrrole films electropolymerized in a solution with KCl (PPy/Cl) and another in a solution containing the botryosphaeran (PPY/EPS) observes a significant change in the profile, indicating that the botryosphaeran has a significant influence in the electrochemistry behavior of the polypyrrole film.

The FTIR results, for both polypyrrole films, were awfully similar. In the spectra is observed a band more pronounced in 1619 cm^{-1}, characteristic of the angular vibration N-H, in 1373 cm^{-1} presents a band characteristic of the C-N stretching from the amine, and the band between 3200 to 3500 cm^{-1} is characteristic of the OH. For the film of PPy/EPS two bands, an in 1384 cm^{-1} and another one in 1163 cm^{-1}, characteristic of C-O from the phenol group, were attributed the incorporation of the polysaccharide to the polymeric matrix.

Furthermore to the oxi-reduction process in the polymer films was observed the electrochromic effect, by the promotion of a change in the coloring of the film from the blue dark (oxided) to yellow (reduced). This color change was accompanied by the transmittance variation in 420 nm. The results presented change of approximately 30% in transmittance value. Moreover, an analysis of the transmittance as a function of time, shows that not all the current densities involved in the redox process, was utilized for the color change in the polymeric film.

Sol-gel synthesis and magnetic properties of Nd^{3+}-doped Co$_2$SiO$_4$:X$_y$ [X= Nd^{3+};0.05≤ y ≤ 0.60]

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Synthesis of Nd^{3+}-doped Co$_2$SiO$_4$:X$_y$[X=Nd^{3+}; S1(y=0.02), S2(y=0.15), S3(y=0.3), S4(y=0.45), S5(y=0.60)] is performed via sol-gel route followed by sintering the samples at 850 °C for 4 h. The powder x-ray diffraction patterns of the samples show broad peak which vanishes at higher diffraction angles characteristics of amorphous materials. However, low intensity diffraction peaks are found to be superimposed on the amorphous patterns. The average crystallite sizes of the dispersed polycrystalline phase in the samples S1-S5 calculated by using the Scherrer formula are found to be in the ranges 25.39-204.85 Å, 12.71-201.95 Å, 12.81-206.98 Å, 10.89-184.75 Å and 16.63-204.74 Å, respectively. The observed values of the densities and the concentrations of the Co^{2+} ions in S1-S5 are found to be 2.26, 2.29, 2.37, 3.44, 2.49 g/cm^3, and $\sim 10^{20}$ ions/g, respectively. The DTA and TG traces in the range 27-700 °C do not show any significant thermal events in the samples. The room temperature IR results show peak in the range 412-424 cm^{-1} due to the octahedral [NdO$_{6/2}$]$^{3-}$ unit, peak ~ 670 cm^{-1} due to the tetrahedral [CoO$_{4/2}$]$^{2-}$ unit and the peak ~ 800 cm^{-1} is due to the tetrahedral [SiO$_{4/2}$]$^{4-}$ unit in all the samples. The Room temperature Raman spectra of S1-S5 also indicates the presence of the tetrahedral [CoO$_{4/2}$]$^{2-}$ and [SiO$_{4/2}$]$^{4-}$ units. Studies of magnetic moments in the cyclic range -10 kG to +10 kG do not show the hysteresis behaviour in the samples showing the absence of ferromagnetic neture of the samples. The calculated values of the magnetic susceptibility from the observed magnetic moments of the samples at 300 K are found to be $\sim 10^{-6}$ emu/gG with abrupt increase from S1 to S2 which then remains fairly the same in the samples S2-S5. These values further show that there is significant concentration of the paramagnetic sites in the samples. The EPR lineshapes of the samples S1-S5 at 6 K 50 K, 77 K and at 300 K show g-values at ~ 2.3 and ~ 2.0. The g-value ~ 2.3 is attributed to the tetrahedral [CoO$_{4/2}$]$^{2-}$ coordination of Co^{2+}(3d^7, S=3/2) in intermediate ligand field. The g-values ~ 2.0 are assigned to the ochahedral coordination of the Nd^{3+}(4f^3, S=3/2) sites. However, the octahedral coordination of Co^{2+} ion which corresponds to g ~ 2.1 is found to be absent in the matrices.

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Remediation of chromium(vi) in acidic conditions with polypyrrole coated titanium

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To date, the application of polypyrrole and polyaniline-coated substrates in Cr(VI) remediation has received much attention[1,2,3]. In this paper we present polypyrrole-coated titanium as a new material for the reduction of Cr(VI) to the less toxic trivalent state, Cr(III). Prior to the electrodeposition of polypyrrole, the titanium substrates were modified using an alkaline-peroxide etch, ensuring adherent and durable coatings, which were resistant to strong acid solutions and physical abrasion/detachment. The durability of the materials on exposure to the Cr(VI) test solutions made them suitable for repeated remediation experiments. After several applications, the cleanup efficiencies of the material were found to decrease somewhat, however increasing the exposure/experiment time resulted in further reduction of the Cr(VI) to Cr(III). Other experimental parameters such as the thickness of the polypyrrole coating, the potential used to reduce the polypyrrole prior to the remediation step and the degree of solution agitation were investigated in order obtain some degree of optimisation of the remediation process. It was concluded that the best performance was obtained with thicker coatings, more negative reduction potentials and vigorous agitation of the test solution.

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Spectroelectrochemical characterization of poly[Pd(salen)] films

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We have been interested in the preparation and characterisation of M(*salen*) based polymers (M=Ni, Cu) that are novel soft materials with relevant properties, dictated by the presence of localised redox centres (M centres) and delocalised redox centres (the extended conjugated p system of the polymeric ligand).[1,2] Now we intend to exploit the properties of *salen* based polymeric films containing metal centres with different optical properties, such as 2nd and 3d transition metals (Pd and Pt), in order to study their influence in the overall optical properties of the *salen* films. In this work we have studied the polymerization of Pd(II) complexes with *salen* ligands, generally denoted as [Pd(*salen*)], and have characterised the respective polymeric films by cyclic voltammetry and *in situ* UV-vis spectroscopy.

The [Pd(*salen*)] complexes were prepared by reaction between acetonitrile solutions of $Pd(CH_3COO)$ and the ligands. The respective films were prepared by potential cycling, between -0.1 and 1.2 V, of acetonitrile solutions containing the monomers ≈ 1 mmol.dm^{-3} and 0.1 mmol.dm^{-3} TBAP, using a standard three electrode cell with Pt disk working electrode, Pt counter electrode and an Ag/AgCl (1mol dm^{-3} NaCl) reference electrode. The polymerisation was performed with scan rates of 0.02 V s^{-1} and 0.1 V s^{-1}. Films with different thickness were prepared by using 1-100 potential cycles. The redox switching of the films were made in monomer free electrolyte solution using scan rates from 0.01 to 1 V s^{-1}. The transmission *in situ* UV-vis spectra, in the region $\lambda = 300$ to 1100 nm, were obtained in a cell with a Pt gauze counter electrode, an ITO working electrode and an Ag/AgCl (3 mol dm^{-3} NaCl) reference electrode; the films were prepared with 5 cycles at 0.02 V s^{-1}. All the films (with different thickness) show high electrochemical and chemical stability within the potential range used. Their cyclic voltammograms show two reversible oxidation processes: one at ≈ 0.40 V and a less intense at ≈ 0.75V. The similarity between the electronic spectra of the monomers and the films (reduced state), indicate that the coordination sphere of the metal centre have been kept in the film. During the redox switching of the films new electronic bands were formed at $\lambda \approx 320$, 395 and 800 nm that were assigned to charge carriers.

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Soft Materials in Electrochemistry

Investigation of the insertion of ions in Prussian Blue by a combined electrical and mass transfer function approach.

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The insertion/deinsertion of ions in the host material occurring during the charge compensation related to a redox process imposed to Prussian Blue in KCl medium was investigated by a combined electrical and mass-potential transfer function technique (1). This technique consists in measuring simultaneously the electrochemical impedance and the mass-transfer function obtained by means of a fast quartz microbalance. It was shown that K^+, H^+, and H_3O^+ are exchanged depending on the potential. The change of the concentrations of these species was determined with respect to the potential.

This approach leads to hypotheses concerning the structure of the Prussian Blue related to the insertion sites of the various ions (2).

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Peculiarities of Adsorption of Amino Acids on Copper Cathode in the Presence of Oxygen

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An investigation of adsorption of amino acids (AA) and oligopeptides on solid electrodes is of great importance for understanding their behaviour in various processes at charged surfaces including self assembled chiral structures formation and participation of AA in electron transfer reactions on bio membrane surfaces [1, 2].

Adsorption of several proteinogenous L-AA namely glicine (Gly), α-, β-alanines (Ala), asparagine (Asn), glutamine (Gln), aspartic acid (Asp), and glutamic acid (Glu) on a copper cathode have been investigated by electrochemical impedance spectroscopy technique both in the presence of oxygen dissolved and in deaerated 0.1 M NaCl supporting solution. The measurements have been carried out over potential range from -300 mV to -1200 mV vs. SCE where dissolution of copper electrode as a result of complexation with copper is not observed.

It is found that neutral AA Gly, α-Ala, β-Ala, Asn, Gln decrease a double layer capacity C_{dl} over whole investigated potential range both in deaerated supporting solution and in the presence of oxygen dissolved. Maximum C_{dl} lowering 6.2 mkF·cm^2 have been observed in the case of Gly. An adsorption isotherm calculated for Gly has the simplest shape and it may be closely approximated by Langmuir isotherm. Analysis of calculated adsorption isotherms for α-Ala, β-Ala, Asn, Gln allowed us to suggest occurring reorientation of these molecules depending on their concentration in the bulk during the adsorption process.

Dicarboxylic amino acids Asp and Glu are shown to increase C_{dl} of copper electrode in potential range -300 – -800 mV in the case of deaerated electrolyte solution that is the evidence of their adsorption in anionic form under such conditions. In the presence of oxygen these AA decrease C_{dl} over whole investigated potential range at AA concentrations less then concentration of oxygen dissolved or comparable with it. It indicates that in the presence of oxygen Asp and Glu are adsorbed as neutral species. The supposition is made that the species adsorbed at the surface of copper cathode from dicarboxylic AA solution containing O_2 are the complexes of these AA with oxygen. This supposition is confirmed with a shift of potential of oxygen reduction peak to anodic region that have been observed in the presence of Asp or Glu. Besides, it is found that Asp and Glu adsorbed at a copper cathode interact with active intermediate products of oxygen reduction.

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Multilayer polypyrrole electrodes – electrodeposition and ion transport

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Electrodeposition of thin polypyrrole layers was done under potentiostatic regime using pyrrole in aqueous sodium hexafluoroaluminate or sodium chloride. The substrate electrodes were polycrystalline gold, gold deposited on quartz and polypyrrole deposited on the both types of gold electrodes. Current – time curves for layer-by-layer electrodeposition from the same solution were analysed in order to determined differences in the mechanisms of formation of the consecutive layers. Cyclic voltammetry, electrochemical quartz crystal microbalance, electrochemical impedance spectroscopy were used to examine characteristics of the polypyrrole films in a course of the redox switching of the polymer. Polypyrrole electrodes of sub-micrometer total thickness were studied mostly.

It was shown that the multilayer structure of the polypyrrole electrode results in a hindrance of charge and mass transport between the sublayers of polypyrrole prepared from a solution of the same composition. The resistance to ion transport across the polymer/polymer interface causes slower ion diffusion in the multilayer polypyrrole electrode as compared to the corresponding single–layer polypyrrole electrode. The redox capacitances of the both structures are similar. Furthermore, current traces of potentiostatic deposition differ significantly for nucleation and growth of polypyrrole on polypyrrole electrodes as compared to growth of polypyrrole on gold electrodes.

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Conformational change in polyaniline films studied by *in-situ* reflection measurements

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Conformational changes in polyaniline (PANI), poly(methylaniline), and poly(methoxyaniline) are studied by means of an *in-situ* laser reflection technique [1], which is based on measurements of intensity of a laser light reflected at a polymer film as shown schematically in Fig. 1. The light intensity reflected from the PANI film varied with the applied potential and the changes were explained as follows: In the reduced state of the PANI film where polymer chains have a coiled structure, a diffuse reflection takes place in the polymer layer and thus a negligible intensity of light reaches the photodetector placed at a right position of

Fig. 1. Illustration of an experimental setup for *in-situ* measurements of specular reflection from a polyaniline film.

specular reflection. By increasing the potential, polymer chains stretch and the coiled structure comes loose. Consequently, Mie scattering is reduced in the polymer film and the incident light can go deep into the polymer layer to reach a highly reflective Pt surface. Then, a specular reflection at the Pt surface can be enhanced and the reflected light gains its intensity. When the potential is raised further, the PANI film turns a blue-black color and starts to absorb the incident 633-nm light.

Thus, polymer chain conformation can be *in-situ* monitored by measuring the intensity of reflected light. It is found that the conformational change is well correlated with a drastic increase of carrier mobilities reported earlier for PANI and its family [2,3]. The concomitant change in mobility and chain conformation with doping level provides a further support for the formation of polaron lattice being responsible for the enhanced mobilities at increased doping levels. Kinetics of conformational change is also studied by using the reflection technique. When the constant oxidation current is applied to the polymer film, the change of the reflected light intensity is found to be delayed. The delay is enhanced for higher currents. By analyzing the delay time as a function of the applied current, rates of a conformational change are evaluated as 1-10 s^{-1}, depending on the sort of polymers, film thickness, preparation rate, and pH of the solution.

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EIS OF POLYANILINE AND POLY (o-ETHOXYANILINE) FILMS BETWEEN INSULATING AND CONDUCTING STATES

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Electrochemical Impedance Spectroscopy, EIS, was applied to polyaniline, PANI, and poly(o-ethoxyaniline), POEA, thin (~300-500 nm) films prepared by potential cycling between -0.20 V and +1.0 V *vs.* SCE at Pt substrate electrodes/0.5 M monomer + 3 M H_3PO_4 solution. Quasy-stationary Bode plots measured in a range of transition potentials (-0.20 V and +0.35 V *vs.* SCE) between insulating, LE, and conducting, EM, forms in pure 3 M H_3PO_4 electrolyte solution (*cf.* Figure) showed well developed spectra between almost (interfacial) capacitive impedance spectra, IS, characteristic for LE form and almost solid ion diffusion limited capacitive IS characteristic for EM forms of polymer films. The features of IS at transition potentials pointed to contributions of: 1) two partly overlapped RC impedances at higher frequencies, 2) FWO solid diffusion element[1] at medium frequencies, approaching at higher potentials to semi-infinite Warburg for POEA or to pure capacitance for PANI films and 3) another FWO element at lower frequencies, approaching at higher potentials to pure capacitance for both films. Common modelling of all IS was performed using the model shown in the inset of Figure, where impedances due to high-frequency experimental artefacts influencing measurements of EM form of both films[2] are denoted by asterisks. The results of fitting procedure (full lines in Figure) showed that serial combination of two FWO elements with different diffusion times and effective chemical diffusion coefficient determined by higher impedance was able to explain specific features of IS of PANI and POEA thin films at transition potentials and potentials of conducting region.
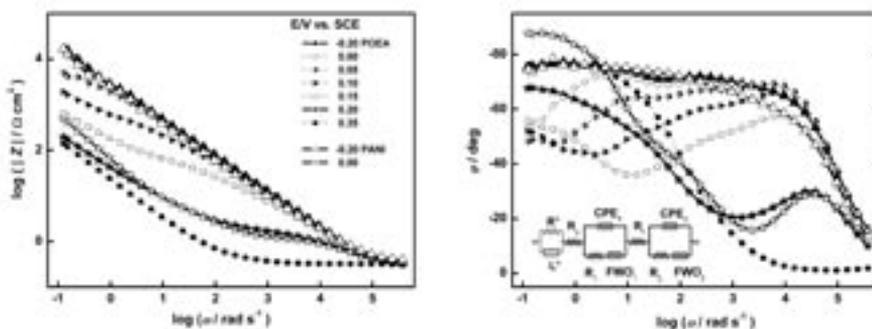
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Evaluation of Parameters Affecting Reduction and Oxidation of M(0)-aminocarbene Complexes (M=Cr,W,Fe)

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Fischer carbene complexes are powerful synthetic precursors. Understanding their redox properties gives us a deeper insight into their reaction possibilities. Two general types of compounds, non-chelated **A** and chelated **B** ones, were prepared and studied electrochemically. For the data interpretation a linear free energy relationship (LFER) approach was used. Complexes of the three metals exhibit almost identical trends with respect to the intramolecular interactions of *p*-substituents on the ligand phenyl ring with the reduction and oxidation centres of the molecules [1].

The **reduction center** is located on the ligand and the reduction potential depends substantially on its substitution ($E_{1/2}$(red) varies within approx 300mV range). The slope ρ (reaction constant) of $E_{1/2} = \rho \cdot \sigma_p$ is the same for **A** of Cr and Fe; Fe compounds are reduced by 0.11V more positively. The **A** and **B** type complexes of the same metal are reduced at the same potential, but the reaction constant of **B** is always about 1/3 smaller. The decrease of its value reflects a lower electronic communication between the substituent and the reduction centre. This fact is in agreement with higher rotation barrier of the phenyl group in chelated (**B**) complexes confirmed by NMR data [2].

The **oxidation** was found to be metal-centered and practically independent on the phenyl substitution for both **A** and **B**. When the central metal is replaced with another one, the oxidation potential is shifted by hundreds mV. With the same central metal atom, the oxidation potential of **A** and **B** differs considerably, **A** are oxidized about 0.3V more positively. This observation shows an important impact of the number of CO ligands (strong π-acceptors) on the electron density of the metal atom. These results are in accordance with IR frequencies of ν(CO).
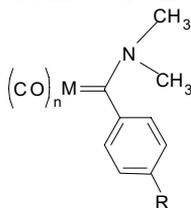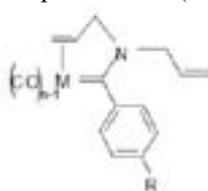
n = 5 for Cr, W
n = 4 for Fe
R = OCH$_3$, CH$_3$, H, Cl, COOCH$_3$, CF$_3$

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Soft Materials in Electrochemistry

Development of low-emission electrochemical etching process using ion-conducting polymer

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Electrochemical machining enables processing without deteriorating the physical properties of the workpiece. Moreover, a material can be electrochemically machined irrespective of its hardness, and without being subjected to any undue stresses. Thus, the method is used in various applications, such as the machining of hard material and the mirror polishing of the inside of vacuum equipment.

However, electrochemical machining has not been used for processing semiconductor materials, such as in the manufacture of electronic devices due to contamination of the workpiece surface by metal ions in the electrolytes. In addition, machining requires chemicals and necessitates cleaning of the machined surface. Thus, electrochemical machining is harmful to the environment.

Against this background, we have developed the following etching method. Ion-conducting polymer-particles are dispersed in ultrapure water. For the ion-conducting polymer either strong-acid cation exchange groups-poly styrene sulfonic acid(PSS), which bind H^+ ions, or strong-basic anion exchange group-poly ethyrene poly amine(PA), which bind OH^- ions, can be used to produce an acidic or alkaline dispersion. In this method, impurity ions can be easily removed using filtration or dialysis. Hence, etching or electrochemical etching can be conducted in the absence of impurity ions. Thus, this method can be applied to the manufacture of semiconductor devices and to nanostructure fabrication processes. In addition, three-dimensional transcription, which cannot be achieved by the mask-etching technique, is possible with electrochemical etching. Furthermore, the etching waste can be reused by removing impurity ions with a dialysis membrane, and consequently the method has a small environmental burden.

In the present study, ultrafine particles of Poly-styrene-sulfonic acid (PSS; molecular weight: 1,000,000) and polyethylene-polyamine (PA; molecular weight: 250,000) were used. PSS particles and PA particles have bound sulfonic acid group, which are cation exchange group, and quaternary ammonium groups, which are anion exchange groups, respectively. We first pre-prepared an acidic and alkaline dispersion by dispersing the respective ultrafine particles in ultrapure water, next prepared pH controlled dispersion by mixture the each dispersion for an arbitrarily-shaped aluminum etching and preventing from corrosion of processing equipment. Then we measured the concentration of impurity ions in the prepared dispersion, and conducted an electrolysis experiment. In addition, electrochemical etching was demonstrated using aluminum film on silicon wafer. The dispersion of ion-conductive particles gave a current increase of about 19,600 times that obtained for ultrapure water over the same voltage range. The etching rate of aluminum was 0.62nm/s. Based on these results; we discuss the applicability of the proposed etching method.

A Template-Guided Electropolymerization of Aniline Using an Anionic Surfactant

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As well as hard templates, surfactants as soft templates can be used for the preparation of nanostructured materials. Among these materials, sodium dodecyl sulfate (SDS) is a famous anionic surfactant, which has been widely used for the synthesis of nanomaterials including nanostructured polymers. This soft template is usually utilized in chemical synthesis of conductive polymers, but in the present work, we aim to use this soft template for the preparation of nanostructured films of conductive polymers in the course of electropolymerization. Here, we demonstrate a facile and general strategy, namely *in situ* electropolymerization by using the anionic surfactant, SDS, dispersed within an acidic medium of aniline. To determine the mechanism by which the film formed, we examined the role of the specific surfactant in the above procedure. The surfactant was first examined by electrodeposition of SDS on Pt in an acidic medium. The surface morphology helps one to have a visual imagination of what we call a template for subsequent polymerization proceeding on it. However, in the presence of aniline and keeping other experimental parameters constant, the three characteristic redox couples of aniline are exhibited, and this is indicative of polyaniline deposition at template surface. As it is obviously recognized, the shape of the cyclic voltammogram has been affected by the presence of SDS, meanwhile the strong oxidation peak at the first cycles sounds odd. On the other hand, we aim to control the synthesis conditions in electrochemical synthesis as well as chemical methods. Moreover, the potential incorporation of the surfactant into the films may modify the properties of the coatings hopefully in a desired manner and thus increases the versatility of their application in the surface modification of various substrates.

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Soft Materials in Electrochemistry

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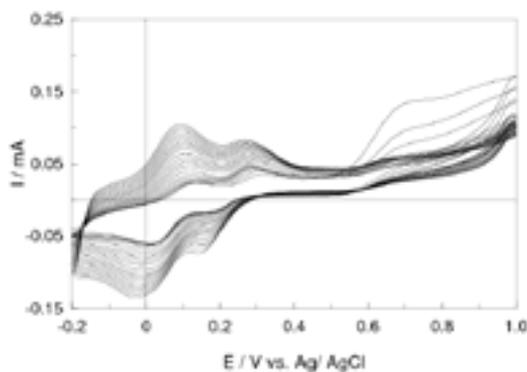
Electrochemistry of centropolyindanes. Reduction of chloro-10-methyltribenzotriquinacenes

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Centropolyindanes belong to a new group of polycyclic aromatic hydrocarbons which are promising building blocks for molecular architecture. Synthetic routes leading to a variety of their derivatives are well recognized but their physicochemical properties not yet. Their electrochemical investigation was started by us in 2004 in a cooperation with D. Kuck (Bielefeld, Germany). It was found that hydrocarbons (centrohexaindane, tribenzotriquinacenes) are not electroactive, as expected for non-planar molecules with no π-electronic interactions between benzene rings. However, carbonyl groups in triptindanones as well as C-Cl bonds in chloro-substituted derivatives of tribenzotriquinacenes can be easily reduced at electrodes. In acetonitrile (ACN) and dimethylformamide one, two and two C-Cl bonds are irreversibly reduced in 1-chloro- (RH_2Cl), 1,4-dichloro- ($RHCl_2$) and 1,4,7-trichloro- (RCl_3) 10-methyltri benzotriquinacenes, respectively. The third C-Cl bond in RCl_3 is not reduced because of its spatial orientation: when two C-Cl bonds are directed into the electrode surface, the third one is on the opposite side of the molecule top. The detailed mechanism for RH_2Cl was investigated. At a gassy carbon electrode in benzonitrile the reduction is a two-electron irreversible process with CV characteristics ($\partial E_p/\partial \log v$ = -29 mV/decade, $E_{p/2} - E_p$ = 55 mV) indicated ECE or DISP1 mechanism with the kinetic control by the C-Cl bond cleavage. On the other hand, in ACN the process is a one-electron irreversible reduction, giving $\partial E_p/\partial \log v$ = -108 mV/decade and $E_{p/2} - E_p$ increasing from 63 to 79 mV with the scan rate increase from 0.04 to 1.00 V/s. This indicates an EC mechanism with the mixed control of the kinetics by the bond cleavage and the electron transfer step, which becomes more significant as the scan rate is increased. The above change of the mechanism with the solvent change can be explained by a slower electron transfer in ACN because of a bigger solvent reorganization energy due to a higher Pekar factor and by an acceleration of the cleavage because its rate constant is larger in ACN due to a higher solvent Lewis acidity. The homolytic dissociation energy of C-Cl bond in RH_2Cl was estimated to be equal to 2.9 eV. After the controlled potential electrolysis of RH_2Cl in ACN at a mercury electrode only one product was found by chromatography and identified with a parent hydrocarbon. This indicates H atom abstraction from the solvent by a neutral radical formed in the bond cleavage. Moreover, two C-Cl bonds in $RHCl_2$ are reduced successively and the radical $RHCl^{\cdot}$ formed after the first cleavage undergoes competitive reactions of the further reduction at the electrode and the H atom abstraction.

Bidimensional Spectroelectrochemistry study of electrochemically controlled release of Hexacyanoferrate from Polypyrrole films

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Conducting polymers are used in very different applications. Understanding the properties of this kind of materials is a key point to use them correctly. One interesting application of conducting polymers consists of the controlled local release of drugs at desired points in time for the treatment of some diseases [1]. Knowledge about the mechanism of ion release from the polymer film is very important in order to use this kind of material as a local pump. Until now, a number of studies about the role of counterions during doping and dedoping of polymers have been done using very different analytical techniques. In this work we present Bidimensional Spectroelectrochemistry [2] as a hyphenated technique to study the release of an absorbent anion, hexacyanoferrate(III), from polypyrrole films during the polymer discharge. Bidimensional Spectroelectrochemistry provides simultaneously one electrochemical and two different spectroscopic signals about the process under study in a single spectroelectrochemical experiment. Taking the plane of the electrode surface as spatial reference, the spectra are recorded in two different arrangements: i) normal configuration, in which the light beam samples perpendicularly the electrode surface, and ii) parallel configuration, in which the electromagnetic beam follows a direction parallel to the electrode surface, sampling the solution adjacent to the electrode. The information supplied by each kind of measurements is different because the normal configuration signal accounts for the electrochromic changes of the polymer film adsorbed on the electrode surface, while the parallel configuration response obtains information about the compounds released from the film to solution.

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Studies of azobenzene-containing self-assembled monolayers on Au

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Azobenzene can undergo a reversible trans-cis isomerization via photochemical or electrochemical processes [1]. Specifically, it can be switched from trans to cis isomer by UV irradiation at ~ 365 nm and back from cis to trans isomer by visible light irradiation at ~ 435 nm and electrochemically reduced to hydrazobenzene, which is oxidized exclusively to trans azobenzene in the reverse reaction.

In this work self-assembled monolayers of different alkyl thiols containing azobenzene moieties were fabricated on polycrystalline gold or Au(111) surfaces via direct adsorption or surface synthesis [2]. Furthermore, mixed monolayers of these azobenzene containing thiols and n-alkyl thiols were prepared.

The systems were characterized by cyclic voltammetric measurements, using a spectroelectrochemical cell, which allowed UV irradiation of the sample during the electrochemical measurements.

A pair of waves corresponding to the reduction of the azobenzene moiety to hydrazobenzene and the oxidation of hydrazobenzene to trans azobenzene, respectively, was observed for all examined systems. These features of the cyclic voltammogramms were not altered by irradiation with UV light.

The peak separation for anodic and cathodic peak ranges from -60 mV to ~ 600 mV depending on the examined system. The area per molecule in the SAM is 25-35 Å², indicating, that dense-packed monolayer films were formed. For mixed monolayer of azobenzene-containing alkylthiols and n-alkyl thiols, again no photoswitching could be observed, although the average area per molecule exceeded 50 Å², suggesting, that surface seggregation into azobenzene-containing thiol and n-alkyl thiol domains occurred.

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Adsorption behaviors of 6-octylthio-1,3,5-triazine-2,4-dithiol monosodium sam on au(111) investigated by electrochemical stm

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In order to understand the self-organization of various materials on the surface of a solid with atomic and molecular levels, scanning tunneling microscopy (STM) techniques are now well recognized as powerful and direct measurements. The triazinedithiol derivatives (TADs), which are well known as very excellent corrosion inhibitors for copper,[1] are widely used in industrial technologies such as anti-corrosion, water-repellent, and adhesives between metals and polymers.

However, the adsorption behaviors of such TADs have been rarely reported. In this study, we first report the adlayer structure and adsorption behavior of 6-octylthio-1,3,5-triazine-2,4-dithiol monosodium (OTDS; Fig. 1) on Au(111) in $HClO_4$ using electrochemical STM.

Fig. 2 shows the STM image of the OTDS adlayer. We previously reported that the diameter of

an OTDS molecule estimated from the results of CV measurements in KOH is ca. 0.62 nm and almost the same as the theoretical molecular size of OTDS.[2] This result was confirmed by the fact that the average distance between the developing molecular rows is ca. 0.62 nm as shown in Fig. 2, suggesting that each OTDS molecule forms the dimer-like structures in a shape such that the triazine rings are opposite each other.

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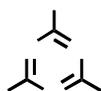
Fig. 1 Structural formula of 6 - octylthio-1,3,5-triazine-2,4-dithiol monosodium salt (OTDS)

5 nm
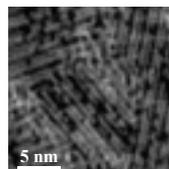
Fig. 2 STM image of OTDS   adlayer formed on Au(111) in 0.05 M HClO₄.

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Electroinduced oxidative copolymerization of polyacrylonitrile with polydimethyl siloxane

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Polydimethyl siloxane(PDMS) copolymers have been recently studied for their potential technological importance as thermoplastic elastomers and for their unusual properties[1]. Di-, tri-, and multiblock siloxane containing copolymers have been prepared by different synthetic methods. Recently polymerization of acrylonitrile (AN) have reported in the presence of catalytic amounts of a ceric salt an oxidant during the electrochemical cell [2]. This method has been providing advantages for the production of copolymers using catalytic amounts of cerium (IV).

In this study, copolymerization of AN and PDMS initiated by Ce(IV) was performed in an divided electrolytic cell. The precipitated copolymer was formed in the catholic compartment, and the reduced initiator was reoxidized in the anode. Thus allowing for the continuation of the process. The effects of concentrations of the AN, PDMS, ceric salt and sulfuric acid (the electrolyte) were investigated as well as the potential and the temperature. The copolymers were characterized by FTIR, NMR, DSC and its molecular weight was determined by viscometric methods. A possible structure of copolymer is suggested.

PDMS

X: -OH   Tegomer H-Si 2111
X: -NH$_2$ Tegomer N-Si 2120

Regeneration
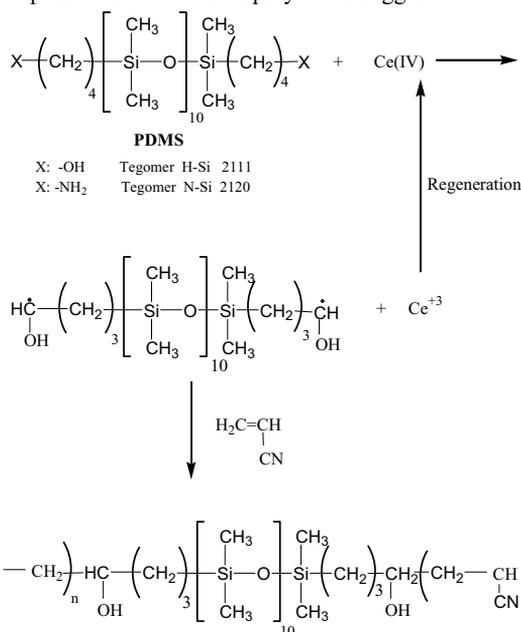
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Anticorrosive property of electropolymerized films of aniline derivative having triazine-dithiol unit (part II)

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INTRODUCTION: The advantage of conducting polymer coatings to other corrosion protection methods are seen to be the protection provided over pinholes and scratches, since their anticorrosive action is based on the electrochemical process. Although polyaniline is a promising conducting polymer for this purpose, the development of polyaniline derivatives having higher anticorrosive functions is needed. We have shown that the electropolymerized films of aniline derivatives having triazine-dithiol unit are quite promising for the corrosion protection of iron [1]. In this paper, we would like to report the further progress of this research.

EXPERIMENTAL: 2-Phenylamino-1,3,5-triazine-4,6-dithiol monosodium (AP) was used as a monomer. At first, AP was polymerized electrochemically either with potential sweep or potentiostatic method onto iron electrode in sodium carbonate solutions. Polyaniline was then formed with potentiostatic electropolymerization in neutral phosphate buffer solutions containing aniline. Anticorrosive functions of polymers were evaluated with the measurement of steady current (Tafel method).

RESULTS: Although poly-AP itself is electroinactive in aqueous solutions, the modified electrode became electroactive in acidic solutions after further electrochemical treatment in 0.1 M aniline solution suggesting the formation of polyaniline unit. The anodic dissolution current of iron became smaller after the formation of poly-AP film and drastically suppressed by the deposition of polyaniline.

The anticorrosive property was evaluated in sulfuric acid solutions with using Tafel method. The corrosion current decreased to 8 % of its original value after the deposition of both poly-AP and polyaniline films. The anticorrosive property was also measured in neutral solutions. The results are summarized in Table 1, where values in parenthesis show the electricity during polymerization. It was clearly shown that further deposition of polyaniline onto poly-AP film is quite effective for corrosion protection. The corrosion currents do not depend on the thickness of poly-AP films.

Table 1 Corrosion potential and current of polymer coated electrodes in neutral media.

Polymer (Q/mC)	Corrosion potential / mV	Corrosion current / mA
Poly-AP (0.5)	-414	0.024
Poly-AP (0.5) + Polyaniline (0.2)	-367	0.004

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Polypyrrole: Magnetic field influences on the electropolymerization and its redox behavior

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This paper deals with the influence of static magnetic fields (up to ca. 1T) on the anodic deposition of polypyrrole (PPy). It is well known that the properties of such layers depend strongly on the electrochemical preparation conditions. Using the Electrochemical Quartz Crystal Microbalance (EQCM) technique we investigated the electropolymerization of pyrrole from aqueous solutions containing several supporting electrolytes. Using the network analysis technique the shift of resonance frequency and change of peak width at half-height (damping) of a quartz crystal can be recorded together with the electrochemical data. After the deposition the redox properties of the PPy layers were investigated by cyclovoltammetry (CV) in monomer free solutions of the corresponding supporting electrolyte. While rough layers are formed in perchlorate solutions combined with a strong shift of damping, smooth layers were obtained in the presence of aromatic and polymeric anions (template effect) associated with a small damping shift. In the presence of a magnetic field an increase of the limiting current density was observed for PPy|ClO_4^-, which can be attributed to magnetohydrodynamic stirring. An estimation of the forces shows that the Lorentz force is dominating. From comparison with measurements on a rotating disc electrode (RDE) [1] the stirring effect could be estimated to correspond to ca. 100 rpm. In the case of aromatic and polymeric anions no similar effect was found. However, there are hints from the EQCM data [2] indicating that the magneto-deposited layers were mechanically more rigid. Calculations using the model of Kimura [3] show that an alignment of polypyrrole structure in a magnetic field of 0.7T within the timescale of the deposition is possible. Furthermore, a suppression of the ion exchange during the oxidation and reduction of PPy|TsO and PPy|DBS was found. These results are in agreement with literature data obtained for similar systems [4,5]. For the system PPy|PSS an irreversible change of surface morphology was observed during the reduction in the first cycle of the CV. After this no differences between the films synthesized at 0T and 0.7T were obvious. To distinguish between aging and magnetic field effects on the semi conducting properties and the ion exchange behavior results from Electrochemical Impedance Spectroscopy (EIS) measurements shall be discussed.

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Synthesis of hydrophilic and electro-conductive polymer including viologen derivatives

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The potential range of hydrophilic and electro-conductive osmium polymers for enzyme immobilization are known to be +500 ~ -200 mV *vs*. Ag/AgCl depending on ligands of its metal complex.[1,2] Here we report synthesis and characterization of water soluble polymers with more negative redox potential than those of osmium polymers.

The polymers are aimed to be used in CO_2 activation by carbon monoxide dehydrogenase (CODH). The new moiety of polymer is a propylamine viologen (1, 1'-Dipropylamine-4, 4'-bipyridydinium dibromide) derivative which has four or two methyl groups on its aromatic ring. The introduction of methyl group on aromatic ring of viologen derivative caused negative shift of electrode potential by approximately 300 mV per addition of two-methyl groups. The viologen derivatives showed two-step reversible reduction- oxidation behaviors. The propylamine viologen derivatives were polymerized with PEGDGE (Poly(ethylene glycol)(n)diglycidyl ether). The polymers that cross-linked by viologen moiety showed very negative standard electrode potential and good reversibility in physiological buffer solution.

PEGDGE(Poly(ethelene glycol)(n)diglycidyl ether)

n = 200, 400, 600

1-(c) $R_1, R_1' = R_2, R_2' = H$
2-(c) $R_1, R_1' = CH_3, R_2, R_2' = H$
3-(c) $R_1, R_1' = R_2, R_2' = CH_3$

NaOH
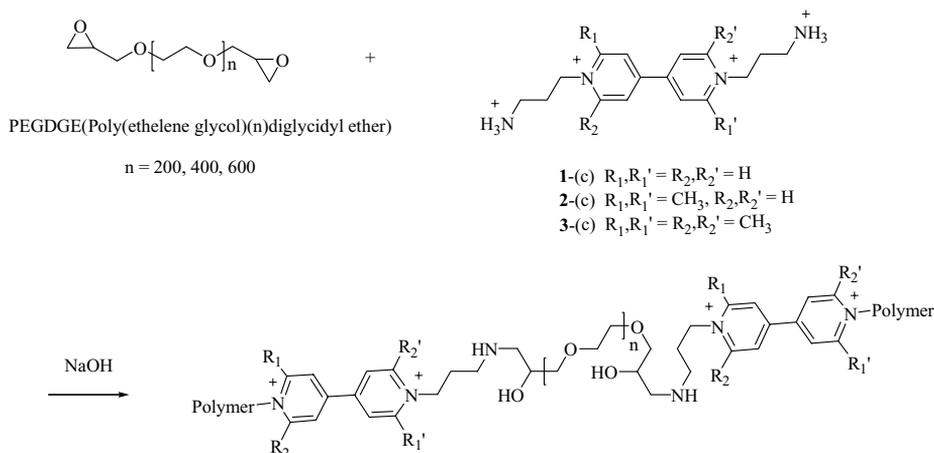
Scheme 1. Synthesis of viologen polymer

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Electrochemical analysis of ZnSe electrodeposition

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Semiconductors of transition-metal selenides are considered as the very important materials because of their potential applications in optoelectronic devices. Usually, thin films of these materials are prepared by high temperature and vacuum techniques. However, electrodeposition has been found to be a very efficient and low-cost method to fabricate thin polycrystalline films of these compounds.

In this work electrodeposition mechanism of pure Se, Zn and ZnSe phase on copper substrate was studied by an electrochemical method. Chronoamperometry and cyclic voltammetry techniques were combined with electrochemical quartz crystal microbalance to analyze this process in details.

Cyclic voltammogram for copper as a working electrode, in the electrolyte containing Zn_{2+} and $H2SeO_3$ species, showed a reduction wave at potential -0,1 V vs. Saturated Calomel Electrode (SCE). According to M/z value this process was identified as selenium deposition. Second wave appeared at -0,6 V vs. SCE and it is connected with formation of ZnSe. This process is interrupted at -0,7 V vs. SCE, which suggests that initially deposited selenium is covered by zinc, and additionally reduction of hydrogen occurs. Bulk deposition of zinc starts at -1,1 V vs. SCE.

The anodic peaks represent successively an oxidation of deposited elemental Zn from -1,1 to -0,9V and decomposition of ZnSe from -0,5 to -0,3V during reversal scan.

Chronoamperometric measurements and the registered $\Delta f/\Delta t$ transient showed strong dependence of the applied potential on the deposition process. These results confirm the deposition of selenium up to -0,5 V vs. SCE and formation of ZnSe film at potential -0,6. The hydrogen evolution starts at -0,7 V vs. SCE, which makes the interpretation of the obtained results very difficult.

Electochemical activation for selective attachment of DNA on a microelectrode array

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Simultaneous analysis of a large number of bioanalytes has been important issue in a biochip technology. For this reason, the patterning of many kinds of biomolecules as probes on the same solid surface is essentially required. Therefore, many research efforts have been focused on the thin film technology including self-assembly method. Most popular method to attach the various biomolecules on surfaces is to form the activating ester by 1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimide (EDC) / N-hydroxysuccinimide (NHS) coupling reaction with carboxylic acid terminated surfaces. However, this method is time-consuming and has drawbacks in selective patterning on surfaces.

We have developed a new electrochemical method to pattern many biomolecules. This is based on eletrochemically-induced and site-selective NHS patterning on self-assembled monolayer for subsequent covalent binding of biomolecules. We have studied potential-induced binding of different sequence DNA on microarrayed electrodes and characterized the modified surface with surface plasmon resonance spectroscopy(SPR), grazing angle FT-IR spectroscopy, and X-ray photoelectron spectroscopy(XPS) experiments.

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Soft Materials in Electrochemistry

Effect of ultrasonic wave on the electropolymerization and the degradation of conducting polymer films

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Symposium 7: Soft Materials in Electrochemistry

Recently, conducting polymer films have received a lot of interest from chemists and physicists concerning both fundamental and practical aspects, due to their electroconducting properties as well as their chemical and biological ones. Moreover, it is possible to control the thickness of the film by electroorganic processes. Many of the studies have been made towards an understanding of the electronic and transport phenomena in the conjugated polymers such as polyacetylene, polyaniline, polythiophene and polypyrrole. In these types of polymers, the polypyrrole electrochemically prepared stand out as an excellent class of materials, because of its high electronic conductivity and their good ability to form strong and coherent films. To elaborate these conducting polymer films, water constitutes an ideal solvent for industrial applications due to its lack of toxicity, its low cost and its reduced environmental impact. However, several difficulties appears including a weak solubility from pyrroles and thiophenes in this medium. A new polymerization of an immiscible monomer in aqueous electrolytes, such as the polythiophene (EDOT), has been developed by using acoustic emulsification. This original methodology has many practical advantages and shows typical characteristics as the formation of stable monomer droplets in aqueous electrolytes without the help of added surfactants [1]. In the same time period, many recent works reported a variety of low frequency ultrasound effects upon electrochemical processes. Particularly, the effects on electroorganic reactions seem to be significant as demonstrated by Atobe et al [2]. They observed a preferential polymerization of the thiophene thanks to an ultrasonic low frequency irradiation (20 kHz). The present work is dedicated to the elaboration of a conducting polymer film in the presence of higher ultrasound frequencies (500 kHz). The reduction of the wavelength leads to a completely different behaviour, with strong chemical effects and low mechanical shocks. Therefore, the expected modifications by ultrasonic irradiation on electropolymerized polymer films concern physical properties and morphology. Moreover, keeping in mind the several ultrasound applications described in the recent literature, the possibility of induced mechano-chemical alterations in polymeric materials appears to be useful [3]. A secondary objective will be also to allow local modification of the conducting polymer films by using focused high frequency focused transducers after electropolymerization, even those last one is carried out in silent or ultrasonic conditions.

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Electrochemical Synthesis of Polymer Films Trapping Copper Ions by Complexation

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Electroactive species often exhibit new optical absorption bands in accompaniment with an electron transfer or redox reaction. Such coloration was first termed electrochromism by Platt [1]. Generally, apart from the conductive electrode, electrochromic species can be a liquid (e.g. the ferro-ferricyanide system), an inorganic solid (WO_3), an organic one (polyaniline), or it can undergo liquid-to-solid conversion following oxidation or reduction (as in bipyridilium systems). Practical application of electrochromic device includes the smart window, information display, rear-view mirror in the automobile or protection glassware.

We examined here a FTO anode coated with a thin polymer film, that could trap Cu^{2+} ions [2]. Recently we showed that copper (+I) salt-based electrolytes can be used for building electrochromic devices [3]. At the anode Cu^{2+} ions can be formed under anodic bias. Although one can prevent the diffusion of these Cu^{2+} ions towards the cathode by increasing or tuning the viscosity value of the liquid electrolyte, to avoid the reaction: $Cu^{2+} + Cu(s) \square 2\ Cu^{+}$. It is interesting to trap these ions by a polymer containing amino groups such as polyethyleneimine, polypropyleneimine or poly-p-(phenylenediamine) since these polymers can be easily coated from oxidation aliphatic or aromatic di- or triamines. So, as an exploratory work to electrochromic properties of these systems, we studied the electrochemical properties of copper ion complexed polymers to determine whether Cu^{2+} can be trapped into these polymer films using their chelating properties. This was made by means of electrochemical quartz crystal microbalance experiments.

As expecting, the complexing properties of FTO coated with polymer films towards Cu^{2+} ions are strong. Thus FTO coated with polymer films could be used for building electrochromic devices. The terminal $-NH_2$ groups on the polymer surface allow the trapping of copper (+II) ions issued from the bias of copper (+I) salt-based electrolytes, and the formation of colored complexes close to the anode. Copper (+I) salt-based electrolytes are good candidates for electrochromism in non aqueous solvents. 1,3-DAP leading to polypropyleneimine appeared to be the best coating.

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In situ atomic force microscopy in the study of electrogeneration of polymers

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Electrosynthesized conducting polymers are particularly interesting materials for a number of applications, ranging from batteries to molecular electronic devices. Indeed, polymer films can be easily set either in the insulating or in the conductive state, exhibiting correspondingly different electrical, optical, and chemical properties. In comparison with the impressive amount of work carried out on the synthesis of these materials, not so much is known about their electronic and molecular structure, as well as about the morphological modifications they undergo when switching from insulating to conductive state and vice versa: these changes are reasonably fairly important in order to give a rationale to the factors affecting the switch itself and the related conducting properties. The characterization and the performances of these polymers, in fact, are critically linked to the surface status, due to the interfacial character of the electrode processes. Furthermore, a number of efforts have been directed towards the development of suitable and 'ordered' structures, because of the possible improvement in the conductivity achieved by growing films with controlled morphology. The need for a deeper understanding of these systems requires the use of ultra-high resolution techniques, such as Scanning Probe Microscopies (SPM). Among the various SPM techniques, Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) have been extraordinarily useful for obtaining images of the electrode surface directly, also under a controlled polarisation potential. In particular, AFM has been extensively used in the study of the polymer deposition process at varying the polymerisation conditions, such as type of substrate, solvent, supporting electrolyte, temperature, etc., as well as in the investigation of the polymerisation procedure. In this paper, we present the results of an in situ investigation of the early stages of electrochemical generation-deposition on the Pt electrode of polypyrrole. Thus, we will show the evolution of the morphology and of the thickness of polypyrrole films electrosynthesized on different substrates.

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Soft Materials in Electrochemistry

Analysis of the impedance spectra of Au poly(3,4-ethylenedioxythiophene) electrodes in aqueous solutions

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Since its development in the late 1980s, poly(3,4-ethylenedioxythiophene) (PEDOT) has received considerable attention because of its many possible technical applications. PEDOT and its derivatives appear to be among the most stable organic conducting polymers currently available. Previous studies have shown PEDOT is electroactive in aqueous solutions, and ion diffusion in PEDOT contacted by a polymer electrolyte was several orders of magnitude faster than for other conjugated polymers. On the basis of these results studies have been performed to investigate the electrochemistry of PEDOT in more detail by using electrochemical impedance spectroscopy (EIS) which is a useful technique to study the mechanism of charge transfer and ion diffusion in conducting polymers, and several impedance models have been proposed to describe the electrochemical properties of the electrodes, especially in organic solutions.

Hovewer, despite the spectacular advancement in the field of electrochemical impedance spectroscopy of polymer modified electrodes, due to the high complexity and diversity of the systems studied deviations of the impedance response predicted by the theories have been observed in many cases. One of the crucial points is in connection with the structure and morphology of the surface polymer layer. Therefore, a structural model has been proposed in which short and long polymer chains forming bundles attached to the metal surface. In this so called "brush" model it is assumed that the bundles contain "micropores" and "nanopores", and between bundles there are pores which are filled by the solution of supporting electrolyte [1,2].

In the present work, cyclic voltammetry and EIS was used to study the electrochemical properties of PEDOT films doped with small anions or large polyanions in contact with different aqueous solutions. Impedance measurements at different potentials were carried out, the spectra were taken at different potentials using polymer films of different thickness. Complex nonlinear least squares (CNLS) fitting program based on Gauss-Newton-Jacobi-Marquardt method was applied for the parameter estimation. The results of the electrochemical impedance measurements in accordance with the cyclic voltammetry on Au/PEDOT confirm that the brush model gives a realistic description of the surface film structure.

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Surface states and field effects at $(nh_4)_2s$-modified gaas(100) electrode

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The passivation effects of $(NH_4)_2S$ treatment on GaAs(100) surface were explored by electrochemical impedance spectroscopy, spectroellipsometry and second harmonic generation investigations. The analysis of the spectroelliposmetric data led to the conclusion that ammonium sulfide treatment reduces the content of oxygenated species in the interface region and replaces the As excess present on the bare surface by a Ga surface excess, in good agreement with results of the ex-situ XPS measurements [1]. The influence of the applied potential on the isotropic amplitude of the of SH-signal closely reflects the change in the field effects operating in the space charge region as revealed by the slope changes of the Mott-Schottky plots for bare and sulfide-treated electrodes. It is worth mentioning that the best fit of the impedance spectra was given by a model circuit considering both the surface state contribution (consisting in a series of resistance and capacitance [2]) and recombination impedance in parallel to capacitance of the depletion layer of the semiconductor [3]. The ammonium sulfide treatment was found to bring about a decrease in the population of both the midgap donor states (responsible for the Fermi level pinning) and the acceptor states located near the valence-band maximum, along with a significant decrease in the recombination capacitance. Similar effects observed in the gas phase studies were explained by Spindt and Spicer [4] by a mutual compensation mechanism of the two types of surface/interface states.

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Surface pasivation of p-Si(111) by thiols

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Treatment of hydrogen-terminated p-Si(111) surfaces with 4,4'-bis-benzenethiol solution results in a passivation layer which prevents the further oxidation both in air and in aqueous electrolytes. A comparison of the X-ray photoelectron spectra for a p-Si(111) substrate with native oxide, an oxide stripped- and the thiol-modified surfaces stored in air for several days (Fig. 1) shows that the organic layer brings significant stability toward the Si oxidation as evidenced by the major drop in the intensity of the Si-2p (103.2 eV) associated with SiO_2 on the thiol-treated samples. In electrolytes, the stability of the thiol-coated surface was monitored by cyclic voltammetry and impedance spectroscopy. Cyclic voltammograms revealed a drastic suppression of both oxidation and reduction processes at the thiol-modified Si electrode/solution interface while impedance spectra taken under different bias potentials validated the remarkable increase in the interface resistance (Fig. 2).
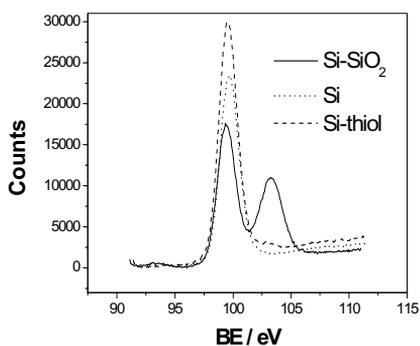
Fig. 1 XPS spectra of native oxide-covered (—), oxide-stripped-(···) and thiol-coated (—·—) p-Si(111) surface, in the Si-2p region
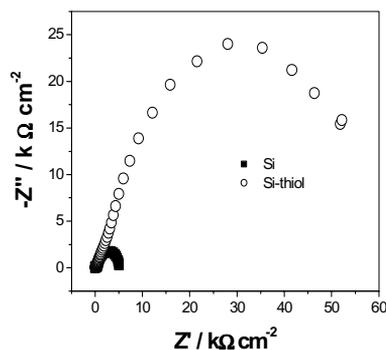
Fig. 2 Impedance spectra of bare (■) and thiol covered p-Si(111) surface (○) taken at -0.6 V vs. SCE in 0.1N H_2SO_4

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Soft Materials in Electrochemistry

On the reasons for charge reversal upon polyelectrolyte adsorption on a charged surface

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Polielectrolytes (PE´s) are linear chains of polymers that in aqueous solutions may acquire a net electric charge at their monomers. These PE´s solutions may show remarkable physicochemical properties. One of these is the adsorption on a surface with opposite charge. In principle, this adsorption seems to be driven by electrostatic interactions. The experimental observation is that under certain conditions, the amount of PE adsorbed is larger than that necessary to achieve charge neutralization (charge overcompensation), so that the surface presents a net surface charge density opposite to that of the initial surface (charge reversal). This phenomenon plays a fundamental role in the sequential adsorption of PE's. (PE multilayer).

 In the present work we make an extensive study of PE adsorption on a charged surface by means of computer simulations. This is made using a primitive model for PE and ions, taking into account all ions explicitly. A Grand Canonical Monte Carlo procedure is implemented for the ions, where the ionic strength is explicitly varied. With this methodology, we find charge reversal on a surface caused by PE adsorption, taking into account only electrostatic interactions between the particles of the system. The free energy changes involved in the adsorption process are calculated, taking into account the entropic gain due to ion release, the conformational changes undergone by the polyelectrolyte and the electrostatic interaction energy. From these magnitudes we can assess that the driving force for charge overcompensation is the increase of translational entropy of ions upon PE adsorption.

Cyclic voltammetric studies on electroreduction of substituted chromones

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Chromones are important bioactive components in different natural products. Further research in the field could lead to discovery of new therapeutic agents with bioassay direct isolation [1-4].

It has been proved that electrochemical methods are very useful to obtain new data regarding physico-chemical properties of chromones [5]. By using cyclic voltammetry it has been established that electrochemical reduction of 1 mM chromone in DMF containing 0.15 M $LiClO_4$ take place in five steps in the potential range between -3.5 and + 0.1 V vs SCE. The first step is monoelectronic and quasi-reversible. All the other steps are irreversible with involving the transfer of more than one electron.

The influence of   OH, NO_2, CH_3 and Cl fuctional groups on the electroreduction processes have been studied. By comparing the electrochemical behaviour of meta – and ortho- hexyl substituted chromones we may conclude that any substituent in metaposition leads to more stable structures.

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Soft Materials in Electrochemistry

New modified electrodes by electrodeposition of polymeric films based on azulene derivatives

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Due to theirs special electronic properties such as an appreciable dipole moment, high electron affinity, low ionisation energy, and a tendency to form stabilized radical cation as well as anions, azulene compounds are interesting new materials for the modification of the electrode surfaces for the catalytic, analytical and biothenological applications.

In the last years electrically conducting polymers such as polyaniline1 2 polythiophene3 4, polyazulene5 6 and polypyrrole7 8 9 have gained a special interest in modern technologies due to their optical and electrochemical properties.

The polymeric films were electrodeposited on a platinum electrode by potentiodynamic and potentiostatic methods from solutions containing 1 mM monomer 3-methylazulene-1-azobenzene, 4,6,8,4' tetramethylazulene-1azobenzene, azulene-1-azo-(4'chlorobenzene) and 0.1 M tetrabutylammonium perchlorate (TBAP). The polymers obtained by electrochemical oxidation of derivatives of azulene have been studied by mean of cyclic voltammetry method. In the first step of anodic coupling the neutral monomer is oxidized to radical cations with reacts with other radical cations in the electrolite solution. The cyclic voltammetric behaviour of the modified electrode sugest that these conducting polymers could have a potential application as biosensors.

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Soft Materials in Electrochemistry

Copolymerization of aniline and propylene oxide in 1-butyl-3-methylimidazolium hydrogen sulfate

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With high stability and wide electrochemical potential window, ionic liquids are expected to be promising media for electropolymerizations[1]. In our group, PAN has been synthesized in 1-ethylimidazolium trifluoroacetate ionic liquid and exhibits high stable electrochemical activity[2]. While electropolymerization of aniline in pure 1-butyl-3-methylimidazolium hydrogen sulfate(BMIHSO$_4$) is quite difficult. Propylene oxide is often added to the electrolyte as one of the monomers during electropolymerization to improve some properties of polymers[3]. In this paper, copolymerization of aniline and propylene oxide is carried out in BMIHSO$_4$.

Electrocopolymerization of aniline and propylene oxide is carried out in pure BMIHSO$_4$ by cyclic voltammetry between -0.5 V and 1.5 V. FTIR spectrum peaks appearing at 2929 and 2852 cm^{-1} are assignable to C-H stretching vibrations of poly(propylene oxide) [3].

Fig.1 shows the cyclic voltammograms of the copolymer polyaniline-poly (propylene oxide) (PAN-PPO) in 0.5 mol/l sulfuric acid for 30 cycles between -0.2 V and 1.0 V at a scan rate 50 mV/s. There are two pairs of reversible redox current peaks on every cycle, which show that reversibility of

Fig. 1. Cyclic voltammograms of PAN-PPO in 0.5 mol/l sulfuric acid between -0.2 V and 1.0 V at 50 mV/s; cycles 1, 10, 20 and 30 shown .

PAN-PPO in sulfuric acid is quite perfect. After 30 cycles, the peak currents and the reversibility of PAN-PPO in 0.5 mol/L sulfuric acid have not obviously decreased, and no detachment of PAN-PPO from the Pt matrix is observed. So it can be stated that PAN-PPO prepared in BMIHSO$_4$ is quite reversible and stable.

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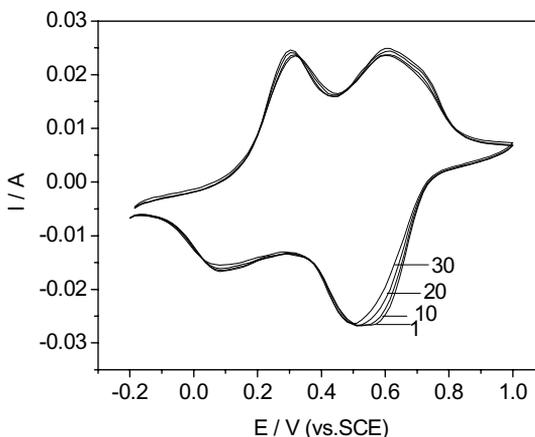[3]   C.J. Shi, H.G. Xue, Z.Q. Shen, Y.F. Li, C.H. Yang, J. Appl. Polym. Sci. 89 (2003) 2624.

Incorporation of Niclosamide into Poly(pyrrole)

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Niclosamide (NA), 2',5-dichloro-4'-nitrosalicylanilide, is widely used as a molluscicide to control populations of aquatic snails that cause schistosomiasis [1]. This disease, also known as Bilharzia after Theodor Bilharz who first identified the parasite in Egypt in 1851, is endemic in 74 developing countries, affecting millions, with more than 80% of infected people living in sub-Saharan Africa, South America and some Asian countries [2]. NA is a relatively expensive and toxic for aquatic plants, birds, fish and mammals, presenting economic and environmental limitations to its widespread use.

Controlled release strategies have been devised for leaching NA from ethylene-vinyl acetate copolymer [3] and calcium alginate beads entrapped in glycidyl methacrylate [4]. Controlled release of copper sulphate as a molluscicide for schistosomiasis [5,6] has also been reported.

We have used poly(pyrrole), a conducting polymer, as a matrix to entrap NA. A simultaneous production and incorporation of NA onto surfaces such as Pt, ITO and stainless steel has been carried out. Drug release rates have been assessed by UV spectroscopic methods and toxicological assays. The ability to control the release of this drug from a polymeric system offers significant opportunity for ???? treatments for the eradication of snail parasites.

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Synthesis and electrocopolymerization of pyrrole with ferrocene pending group and electrochemical characterization of the polymer films

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The new type of monomer – pyrrole containing ferrocene group was synthesized, (Fig.1.) As a result of the electro copolymerization of monomer and pyrrole the platinum electrode surface can be easily coated by stable and electroactive films (Fig. 2). Oxidative electrocopolymerization has been examined during repeated cycling and controlled potential conditions.

The stability and electrochemical properties of the copolymer have been examined. Electric capacitance, electrode redox potential as well as electroactive properties of monomer have been established. Diffusion coefficient of the monomer in acetonitrile electrolyte and kinetic rate constant of the monomer electrode reaction were calculated.

Polymerization of monomer was not successful in the absence of pyrrole. New polymer was tested as a material for electrochemical capacitor in non-aqueous media.

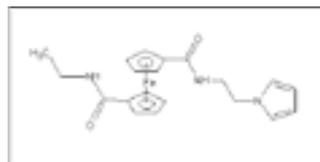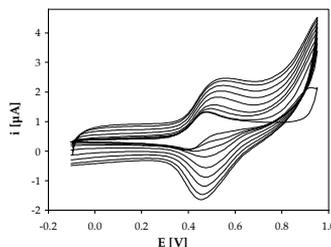Fig. 1. Monomer N-ethyl-N'-[(pyrrole-1-yl)ethyl]ferrocene-1,1'-dicarboxamide.

Fig. 2. Electrocopolymerization upon repeated cycling of N-ethyl-N'-[(pyrrole-1-yl)ethyl]-ferro-cene-1,1'-dicarboxamide – 2 mM and 84 μM pyrrole in 0.1 M TEAP/CH$_3$CN on a Pt electrode; v=0.1 V/s; only few from 25 scans are shown; (vs. Ag+/Ag (0.01M AgNO$_3$) 0.1M TEAP/ CH$_3$CN.

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Soft Materials in Electrochemistry

Electrocodeposition of Polyaniline and Molybdenum Oxide in Aqueous Media

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Polyaniline (PANI) is easily obtained through oxidative electropolymerization of aniline in low pH aqueous solutions, which is incompatible with electrodeposition conditions for most oxides. Reports about electrodeposition of organic-inorganic composites based on PANI and oxides are very limited. PANI and molybdenum oxide (MoO_x) were tried to electrocodeposite for the first time from aniline and $(NH_4)_6Mo_7O_{24}$ in slightly acidic to neutral solutions through comparatively large-scale potential cycling between – 0.6 and 0.9 V *vs*. SCE. Cyclic voltammogram of the resulting composite film in monomer-free acidic solution showed redox couples for PANI and MoO_x, respectively.

Electroreduction of oxoanions, such as chlorate and bromate on the composite film occurred at about 0.4 V more positive than that on similarly prepared MoO_x due to the presence of hydrogen molybdenum bronzes as the result of composition with PANI. Results of cyclic voltammetry and chronopotentiometry measurement in 1.0 mol□dm^{-3} $NaNO_3$ showed that the potential window for the composite film to display pesudocapacitive properties was – 0.6 □ 0.6 V. This is the most negative potential limit for PANI based materials to display pesudocapacitive properties, to the best of our knowledge, with at least 0.4 V more negative than PANI. The specific capacitance of the composite film measured by charging-discharging at 1.5 mA·cm^{-2} was 363.6 F□g^{-1}, while similarly prepared PANI displayed a capacitance of 146.4 F·g^{-1} for this potential window. When the potential window of charge and discharge test is limited to 0 ~ 0.6 V, the specific capacitance of PANI was 196.1 F·g^{-1}. The composition of PANI with MoO_x displayed synergistic effect. The existence of PANI and MoO_x in the film was indicated by FT-IR, XRD and XPS observations.

Multiresponse techniques in the study of poly(3,4-ethylenedioxythiophene) films.

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Mass changes occurring during the electrochemical characterization of poly(3,4-ethylenedioxythiophene) films (PEDOT) are not yet fully understood despite the number of studies carried out in the last years.

Multiresponse techniques have been successfully applied to understand complex mechanisms. We present here two multiresponse techniques: Bidimensional Spectroelectrochemistry (BSEC) [1] and Spectroelectrochemical Quartz Crystal Microbalance (SEQCM) [2], to study the behaviour of PEDOT films in aqueous solution.

SEQCM technique consists of acquiring simultaneously electrical, gravimetric and reflectance signals. SEQCM measurements have shown mass changes during the doping-dedoping of the polymer film that cannot be only accounted for by ion exchange with solution. The spectroscopic signal, in its turn, changes due to oxidation and neutralization of PEDOT films.

BSEC is based on the separate and simultaneous acquisition of spectra corresponding to the compounds adsorbed on the electrode surface and to the solution adjacent to it, together with the electrical signal. Using BSEC measurements to study the doping-dedoping of PEDOT films, complementary information from the two spectroscopic signals is obtained. Absorbance in normal configuration provides information related only to the spectral changes of the film during this process. Simultaneously, many soluble compounds arising from the polymer film are detected in parallel configuration during oxidation-neutralization of PEDOT films.

The joint information supplied by multiresponse techniques (electrical, gravimetric and spectroscopic signals) helps to shed light on the phenomena occurring during PEDOT film characterization.

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Ruthenium and copper complexes with biquinolyl –containing polymer ligands as a new redox active materials

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Transition metal complexes have been extensively investigated because of their ability to act as catalysts for the oxidation of a wide variety of substrates. The polymers with biquinolyl fragments in the main chain capable of coordination to transition metal containing moieties provide a route to new materials, which combine useful properties of polymer backbone with the catalytic activity of metal centers.

New metal –containing polyamic acids were synthesized and their redox properties in solution and in the immobilized form at the graphite electrode were investigated.
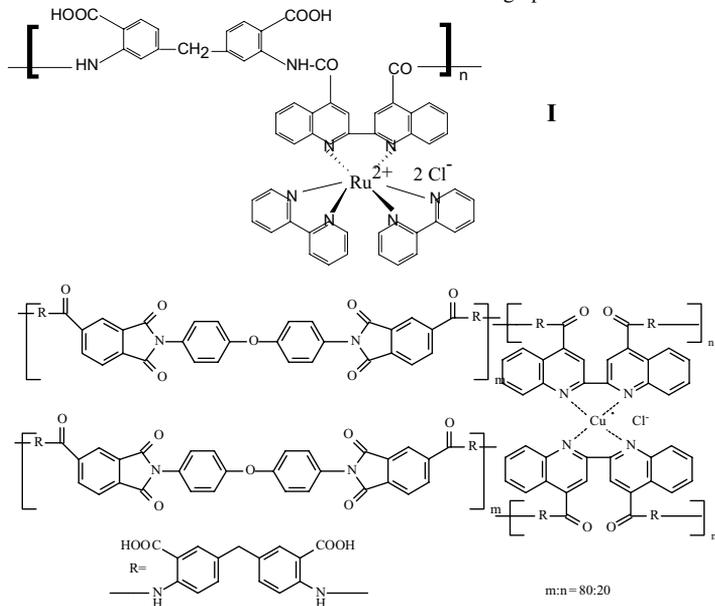
There is a considerable negative shift for Ru(II)/Ru(III) oxidation potential compared to that for $[Ru(biQ)(biPy)_2](ClO_4)_2$, which show ability of polymer N,N-containing ligand to stabilize the higher oxidation states of Ru. The computation data revealed that the basicity of the ligand is sensitive to the polymerization degree: the more is a polymerization degree, the shorter is the distance between Ru and N atoms of biquinolyl fragment. The significant cathodic shift in the Ru^{2+} oxidation potential, characteristic for the synthesized polymer, makes it very attractive for utilization in electrocatalysis, due to an active form of the catalyst can be obtained at the small anodic potentials.

Electrochemical approach to Cu-containing polymer (II) using sacrificial Cu anode have been elaborated.

New data on the application of the metal-containing polyamic acids as redox catalysts will be presented.

Ni / WC composite coatings as an active cathode material for hydrogen evolution

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This work is dedicated to memory of Prof. Aleksandar Despić

The catalytic activity for the hydrogen evolution reaction (HER) of Ni/WC composites obtained by electrochemical deposition of nickel from a conventional Watt's bath, using two different ways of depositing the WC particles, was investigated. All the composite coatings exhibited electrocatalytic activity for the HER larger than that of pure Ni in both alkaline and acid solution. The activity increased with increasing content of WC in the coating and, in the pulsed current regime, with increasing frequency of pulsation. In addition, coatings with smaller particles incorporated exhibited higher activity than those with larger particles. At a constant potential, an order of magnitude higher current densities were obtained in some cases.
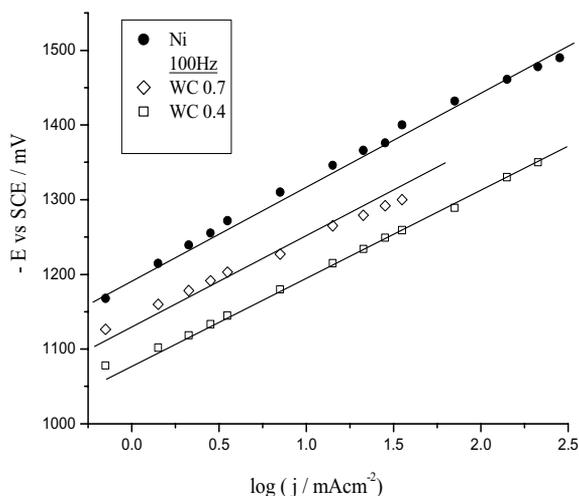
Tafel plots obtained in 1M NaOH for electrodes of pure Ni and of Ni/WC composites with 0.4 and 0.7 μm WC particles, deposited using a current pulsating at a frequency of 100 Hz (at j_{av}=2.5 mA cm^{-2}, p=1, rpm 3000),.

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Soft Materials in Electrochemistry

Mechanistic Study on Electrochemical and Nitrite Ion-catalyzed Oxiations of Adamantane

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Oxidation of adamantane **1** has been attracting much interest because of an multiple application of the products, one of which is 1-adamantanol **2**. Among a variety of methods for the transformation of **1** to **2**, the electrochemical oxidation of **1** is important from a view point of green chemistry. Similarly, the oxidation using oxygen as an oxidant is inretesting from both economical and mechanistic viewpoints, while there have been few efficient oxdiation methods using oxygen. We recently exploited an efficient oxidation of **1** to **2** by oxygen in the presence of cat. $NaNO_2$, and proposed the reaction mechanism by comparing the oxdiation with the electrochemical oxidation as described below (three ways). We report herein the detail of the results.

1) Effect of TEMPO;

TEMPO (equiv)	ratio of 1/2	
	Electrochemical Oxid. 1F/mol	$O_2/NaNO_2$
0	51 : 49	1< : >99
1.0	52 : 48	>99 : <1
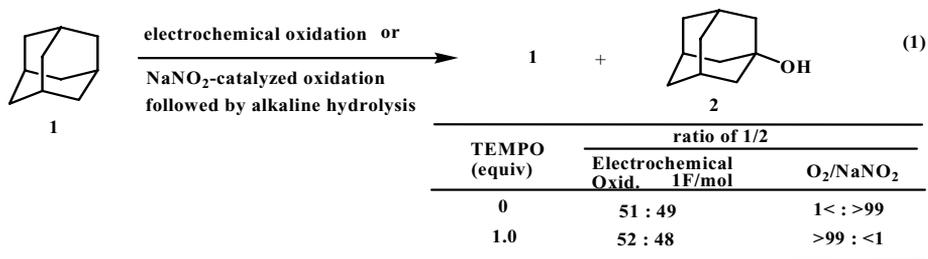
2) Intramolecular Isotope Effect; k_H/k_D 1.83 for electrochemical oxidation

k_H/k_D 2.23 for $NaNO_2$-catalyzed oxidation

3) Competitive Oxdiation; oxidation between **1**, methyladamantane, and 1,3-dimethyl-adamantane for both mthods was carried out.

S7·P-53

Interfacial signature of the polymer-to-metal bonding

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Cathodic electropolymerization has already proven its ability to produce robust and conformal organic films chemically grafted on metallic and semiconducting surfaces used in various domains such as microelectronics, biomedical applications, soldering, chemical waste treatment or corrosion protection. (1) Contrary to the electrodeposition of semi-conducting polymers like polypyrrole or polyaniline, strong covalent bonds between the cathode and the polymer film area created during the process, as indirectly proved by numerous studies including chemical post-treatments, electrografting on rotating electrodes or mechanical measurements (1). A direct evidence can however be obtained from XPS.

Probing the chemical interface between a polymer film and a metallic substrate is very difficult. Indeed, the interface is "buried" under the polymer film and thus difficult to reach. For instance, XPS cannot probe more deeply than ca. 15 nm below the outmost surface. It is thus necessary to limit the growth of the polymeric film to be able to probe the interfacial signature.

This was done by using a redox active molecule that cannot polymerize. Indeed, with classical vinylic monomers such as acrylonitrile or methyl methacrylate, the grafting step that immediately follows the electron transfer from the cathode, gives a very unstable species bearing a negative charge very close to a negatively charged electrode. The instability is classically relaxed by the polymerization that moves away the charged species from the electrode (1).

With crotononitrile, another relaxation route is possible through a proton transfer that heals the carbanion before polymerization occurs. Hence, ultrathin grafted films are obtained. XPS analysis of the resulting films allows the direct observation of the carbon-metal bond that is buried under the grafted film and contributes greatly to its robustness. A clear and distinct peak at 283.5 eV is observed which is attributed to C-Ni bonding. (2) Its full width at mid-height is only 0.8 eV, which indicates that the bonding is probably perpendicular to the surface.
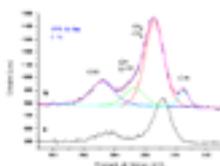
XPS spectra (C1s area) of the Nickel surface before (a) and after (b) electrografting of crotononitrile.
Spectrum (a) shows classical carbon contamination of the crude Nickel surface

(1) Palacin, S.; Bureau, C.; Charlier, J.; Deniau, G.; Mouanda, B.; Viel, P.; Electrografting: "Covalent bonding at Metals and Semiconductors" *ChemPhysChem* , 2004, **10**, 1469-1481

(2) Bureau, C., Defranceschi, M., Delhalle, J., Deniau, G., Tanguy, J. and Lécayon, G.; "Theoretical monomer cluster model of a polymer-metal interface- Poly(methacrylonitrile) on a Nickel Surface". *Surf. Sci.* 1994. **311**, 349-359

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Soft Materials in Electrochemistry

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Soft Materials in Electrochemistry

Microstructuring of polyaniline electrode films using silica nanoparticles

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Micro- and nanostructured electrode interfaces have the potential to exhibit improved performance characteristics. Here, we illustrate the interaction of an electropolymerised polyaniline film with silica micro-particles on glassy carbon electrodes. It was found that the polyaniline grew preferentially around the silica particles rather than on the underlying electrode. This was found to be due to the adsorption of aniline monomer to the silica surface, followed by in-situ electropolymerisation. The thickness of the PANI layer could be controlled through the adjustment of polymerisation time from several to many tens of nanometres.

In conjunction with immobilisation of the enzyme, horseradish peroxidase (HRP), the electrocatalytic reduction of hydrogen peroxide was found to be enhanced under certain conditions over polymer films grown in the absence of silica particles. It is believed that this may be due to increases in active electrode surface area and/or possible improvements in diffusion limitation.

Electrochemical impedance spectroscopy of functionalised Ni-salen films

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A variety of Schiff base metal complexes have been electrochemically polymerized to form polymeric films on electrode surfaces[1-3]. The prepared modified electrodes with electroactive polymers are promising electrode materials for many potential applications; nevertheless the use of these novel [M(*salen*)] based modified electrodes in the different areas of technology is markedly influenced by their intrinsic structural, electronic and kinetic properties. In this work we report the study of poly[Ni(3-Mesalophen-4,5-Cl$_2$)] by cyclic voltammetry and electrochemical impedance spectroscopy: we endeavour the full characterisation of charge transfer and transport processes within this film prepared with a [Ni(*salen*)] monomer with substituents in the aldehyde moiety and imine bridge.

The polymeric films were deposited on Pt electrode by cycling the potential between 0.0 and 1.3 at 0.1 Vs^{-1}, immersed in a CH$_2$Cl$_2$ solution containing 1 mmol dm^{-3} [Ni(3-Mesalophen-4,5-Cl$_2$)] monomer and 0.1 mol dm^{-3} TBAP. Films of different thickness were prepared by using different numbers of potential cycles (up to 160 cycles, which corresponds to $\Gamma \approx 100$ nmol cm^{-2}). The redox switching of the films were made in monomer free electrolyte solution using scan rates from 0.01 to 1 V s^{-1}.

To describe the charge transport through the film and the charge transfer at metal‖polymer and polymer‖solution interfaces, we explored the impedance responses over a wide frequency range (100 kHz-0.01 Hz) as a function of experimental variables such electrode potential (from 0-1.3 V, in 0.1 V intervals) and film thickness (films with Γ up to 40 nmol cm^{-2}). The main bulk parameters for diffusion and charge accumulation during doping were determined by fitting the impedance responses.

1 M. Vilas-Boas, C. Freire, B. de Castro, A. R. Hillman. *J. Phys. Chem.* B **1998**, *102*, 8533-8540.

2 M. Vilas Boas, I. C. Santos, M. J. Henderson, C. Freire, A. R. Hillman, Eric Vieil. *Langmuir* **2003**, *19*, 7460-7468.

3 M. Martins, M. Vilas Boas, C. Freire, A. R. Hillman. *Electrochimica Acta,* **2005**, 51, 304-314.

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Soft Materials in Electrochemistry

Immobilization of Ferrocene Derivatives on (111) Surface of n-Type Silicon

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Redox-active molecules have an ability to store and release electric charges reversibly. Self-assembled monolayers (SAMs) consist of such redox-active molecules attached to silicon surface are, thus, expected to be applied to solid-state memory devices. Ferrocene has favorable properties, such as redox activity, reversibility in redox reactions and durability in repetition of the reactions. The main aim of this work is to immobilize ferrocenecarboxaldehyde (FCA) and vinylferrocene (VFC) molecules by a thermal reaction on a Si(111) surface through Si-O-C and Si-C bonds, respectively, and to compare the growth behavior and electrochemical properties of the monolayers.

The FCA and VFC monolayers were formed by immersing hydrogen-terminated Si(111) substrates to baths of 10 mmol dm^{-3} FCA and VFC, respectively, dissolved in deaerated mesitylene at an elevated temperature, 150 ˚C. The resulting monolayers were characterized by contact angle measurements, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry.

Cyclic voltammograms (CVs) for the two monolayers (Fig. 1) gave a couple of redox waves at *ca.* +0.45 V (anodic) and +0.29 V (cathodic), indicating that the ferrocenyl molecules immobilized on the Si substrate are still electrochemically active. Similar CVs can be measured under both dark and illuminated conditions, since the Si substrates employed were heavily doped with resistivity of 1–4 mΩ cm. Growth curves for the monolayers obtained from the cathodic wave revealed that, in each case, the reaction was terminated within 5 h; the behavior was confirmed by the Fe 2p spectra of XPS. The XPS indicated that some part of ferrocenyl groups are in a ferricinium state with Fe^{III} ion. The final surface densities of the ferrocenyl molecules were estimated to be 0.75 nmol cm^{-2} (VFC) and 0.21 nmol cm^{-2} (FCA), which correspond to the adsorption ratios, or the numbers of molecules per surface Si atom, of 57% and 16%, respectively. The lower coverage for FCA molecules may well be attributed to a repulsive interaction of electronegative oxygen atoms anchoring ferrocenyl moieties to the substrate.

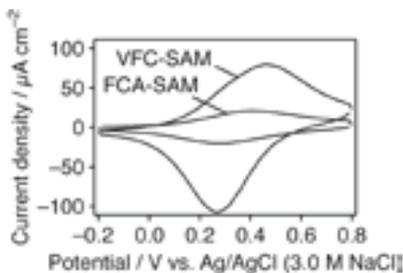Fig. 1   CVs in 0.1 M HClO$_4$ aqueous solution for n-Si(111) substrates functionalized with VFC and FCA molecules (scan rate: 0.5 V s^{-1})
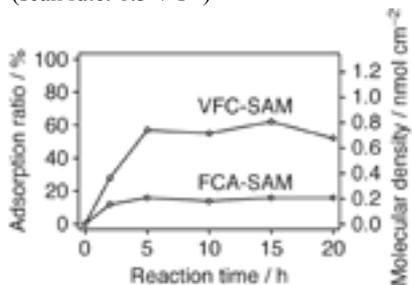

Fig. 2   Growth curve for the monolayers of VFC and FCA calculated from the areas of cathode waves of CVs.

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Soft Materials in Electrochemistry

Electrochemical activity of 2-(2',5-bithiophene)-branched oligothiophenes

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From its beginnning in the sixties, the extensive search in the chemistry and physics of 2,5-interconnected linear oligothiophenes has inspired the decoration of such simple linear substrates with an incredible variety of more or less exotic substituents, designed to confer new properties to the conjugated system or tailored to modulate some specific attribute in view of a precise application. It is impossible to enumerate all the substitution typologies applied to oligothiophenes, which range from highly electron-donating to extremely electron-withdrawing pendants in their all possible combinations, from alkyl to aryl groups, including fullerenes, from basic to strongly acidic functions etc. The substituents are generally located in some selected positions of the backbone, where the backbone-substituent communication is maximized.

In our current research project we are preparing, structurally characterising and investigating the electrochemical properties of a new class of branched oligothiophenes. The present communication deals with an exhaustive electrochemical characterization of the first two terms of this innovative series, designated as $T5_2$ and $T6_4$, being characterized by an outer shell of two and four 2-(5,2'-bithienyl) units surrounding an inner penta- and sexy-thiophene core, respectively. After preliminary CV investigation of the redox properties of the starting oligothiophenes, conducting films have been prepared from both of them, on different substrates including GC, Pt, Au (electrochemical quartz crystal micro-balance for *in-situ* monitoring of the film growth) and ITO, by repeated cycling around the first oxidation potential. Such films, being stable and reproducible, have been characterized (a) from the structural point of view, by MALDI mass spectroscopy, revealing a mixture of oligomers of the starting molecules (to be considered border-line between oligo- and polythiophenes on account of the high number of conjugated thiophene units even in dimer and tetramers) while experiments on deuterated molecules pointed to a highly regio-selective process; (b) from the electrochemical point of view, by *in-situ* conductivity measurements and CV investigation, revealing promising redox properties.

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Soft Materials in Electrochemistry
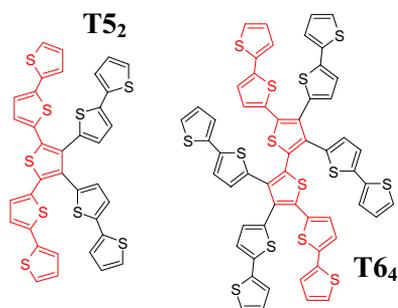
Electrochemical activity in aqueous electrolytes of pedot films modified by prussian blue network

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Electrode material consisting of poly(3,4-ethylenedioxythiophene) matrix penetrated by solid red-ox system of ferrous hexacyanoferrate was prepared by electrochemical synthesis on Pt and Glassy Carbon substrate electrodes. Direct chemical interaction between organic and inorganic counterparts was detected by XPS method as chemical Fe-S bonds. These Fe-S bonds are supposed to be responsible for electroactivity of the material. Films show two red-ox couples analogical to the Prussian Blue activity: one at about +0.1 V/ Ag/AgCl and the second, originated from BP network, at about +0.6 V versus Ag/AgCl which overlaps with water molecules oxidation current. Third red-ox couple, which is not observed for pEDOT and PB separately, appears at about -0.7 V / Ag/AgCl. Presence of the red-ox couples in the vicinity of hydrogen adsorption and in the vicinity of oxygen adsorption may contribute to catalytic properties of pEDOT-PB films towards both types of reactions: oxidation and reduction as it is desired *e.g.* in so called unitized regenerative fuel cells.

The aim of this work is to characterise structure of the material and electrode activity of the polymer modified by Prussian Blue red-ox solid in contact with aqueous electrolytes. The X-ray diffraction pattern obtained for thin film of PB covering Pt substrate electrode shows strong similarity with XRD pattern obtained for studied material. Both results differ clearly from literature data of the bulk Prussian Blue solid.

Electrochemical studies were performed using cyclic voltammetry, chronopotentiometry, Impedance Spectroscopy and RDE (for O_2 reduction). Stability and reproducibility of redox reactions (at +0.1, +0.6, -0.7) depends on the composition of outer electrolyte and is related to both type of ions. The activity of red-ox centres at about +0.6 V is dependent on anions' contribution where activity at +0.1 V is dependent on cationic exchange. Electroreduction of oxygen in neutral electrolytes was observed at about -0.38V ¸ -0.45 V/Ag/AgCl as clearly defined voltammetric peak with linear dependence of current maximum with sweep rate (at slow and moderate sweep rate values).

Synthesis, characterization and electrochemistry study of V$_2$O$_5$/poly(ethylene oxide) utilizing different molecular weight of polymer species

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Recently, there has been considerable interest in the synthesis of polymer/inorganic nanocomposites. The combination of organic and inorganic materials can lead to unusual electrical, optical, and mechanical properties, which might not be achieved with each component separately. In this work, it was realized the synthesis of V$_2$O$_5$/PEO nanocomposites by direct reaction between V$_2$O$_5$ hydrogel with poly(ethylene) oxide (PEO) (100,000 g.mol^{-1} and 600,000 g.mol^{-1}). In addition, we studied the influence of the different amounts of PEO as well as varying the average molecular weight into V$_2$O$_5$ interlayer domain on the reversibility of insertion/desinsertion of Li$^+$ ion in V$_2$O$_5$ xerogel films as well as their stability during charge-discharge cycling.

Cyclic voltammograms of the nanocomposites with different molecular weight are similar exhibiting reversible peaks in the potential range from -0.60 to +1.00 V (SCE), in acetonitrile solutions containing 0.1 M LiClO$_4$. It was observed, when increased the polymer content, a decrease of total charge value due to the higher difficulty of lithium ions reach the active sites in the internal area of the composite material. Impedance spectra (figure 1) show an increase of resistance during Li$^+$ intercalation for materials with higher content of organic polymer. The absence of a depressed arc in the high-frequency range can be related to charge transfer of V^{IV}/V^{V} in the electrode interface suggesting that this process does not contribute significantly for the impedance. Inclination values inferior to 90º can be related to the non-homogeneous electroactive surface. Therefore, the results showed a decrease in the diffusion of lithium ions through the matrix and a improvement in the resistivities of the film after polymer introduction since this resistance decrease according the content and molecular weight of the PEO are increased.
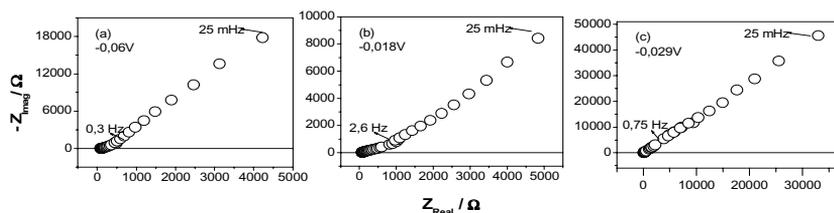
Figure 1 - Complex-plane plots of the V$_2$O$_5$/PEO in different contents and in 100,000 g. mol^{-1} of polymer specie.

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Soft Materials in Electrochemistry

Rest potential and dynamic light scattering study on the dissolution behavior of O_2 – filled nanobubbles : Ar bubbling effect

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The accelerated interest in various, practical applications of nanobubbles to water environments on the small - and large - scale has been generated by the recent activity in the development of bubble production in civil and mechanical engineering . The hydrodynamic bubble generation can provide a lot of a solution containing micro- and nano-bubbles [1].Despite many reports on practical applications, little is known about the formation, stabilization and dynamic behaviors of the hydrodynamically generated bubbles in the bulk solution. Understanding of how the stabilized nanobubbles respond to environmental changes is very important in a practical application such as the use as oxygen carriers. We have investigated the effect of Ar purging on an O_2-filled nanobubbles containing NaCl solution by dynamic light scattering (DLS) and rest potential (RP) in order to gain insights into the dissolution behavior of the nanobubbles. An O_2 bubble containing 0.5M NaCl aqueous solution was stored in a sealed polyethylene bottle for more than 3 months at room temperature. This preteatment can produce stabilized bubbles. The treatment of Ar bubbling was carried out by passing pure Ar gas (> 99.9999 %) through a fritted glass for 4 h. All preparations and measurements were performed in usual laboratory atmosphere at room temperature. The dimensions of the stabilized nanobubble was around 350 nm in diameter (d), which is similar to those of nanobubbles generated by compression and expansion (d=300 nm) [3]. Comparison of DLS measured size distributions for the bubble containing solution before and after the Ar purging indicates that a peak observed in the nanometer-ranged distribution shifted from 350 nm to 430 nm, and that the number of smaller bubbles with the diameter less than 430 nm decreased. This implies that the Ar bubbling causes the dissolution and ripening of the smaller nanobubbles via the depletion of oxygen molecules outside of the bubbles in solution. RP measurements is complementary to DLS for the exploration of the dissolution of the nanobubbles, because scattering particles can be both nanobubbles and impurities. The rest potential for a glassy carbon electrode in the nanobubble containing solution may directly reflect a response of dissolved molecular oxygen concentration in the outside the bubbles, and was measured with a closed cell that can prevent atmospheric oxygen molecules from penetrating. A RP – immersion time response obtained after the Ar bubbling clearly shows that the initial value(+0.102 V vs SCE) drifted back to a constant potential of + 0.135 V 140 min later, which is identical to that of RP before the Ar bubbling. These DLS and RP behaviors imply that the O_2-filled nanobubbles in the bulk solution can play a role of the source of molecular oxygen slowly permeating from the inside of the bubbles, although the dissolution of microbubbles partly contribute to the RP.

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Soft Materials in Electrochemistry

Microgravimetric studies at poly(3,4-ethylene-dioxythiophene) films with regard to anion sensing

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"Synthetic metals" like poly(3,4-ethylenedioxythiophene) (PEDOT) have of a broad range of possible applications.[1] PEDOT gained attention because of its high electric conductivity and good stability especially in the oxidized form.[2] The latter property makes it a promising candidate for technical applications.

One fundamental property of conducting polymers is their redox-activity. Oxidizing PEDOT will force anions to move into the polymer film in order to maintain electroneutrality. During reduction these anions will be expelled. This feature is the basis for regenerative sensors.

In this work PEDOT films were electropolymerized on an electrode of a quartz crystal microbalance (EQCM) which allows in-situ monitoring of the polymer's mass. The mass changes during oxidation and reduction are caused by ion transfer into or out of the polymer film, respectively. PEDOT films were subjected to potential cycling and potential step experiments in aqueous solutions of multivalent anions like sulphate and phosphate as well as perchlorate as monovalent equivalent of similar molar mass. By combining electrochemical and gravimetric information it should be possible to identify the ion and its concentration. In Fig. 1 is shown that the time constants and also the total amount of mass for ion incorporation are different for the investigated anions.
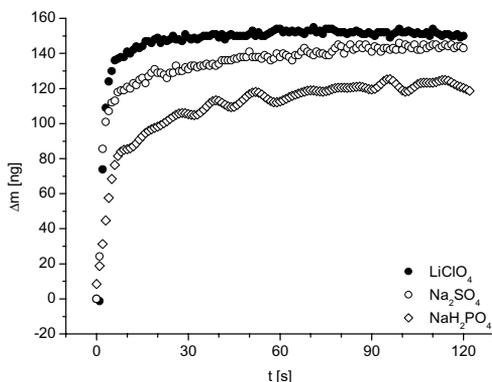
Fig. 1 Mass response of a sulphate-doped PEDOT film after a potential step from -400 mV vs. Ag/AgCl (60 s polarization) to +600 mV in different 10 mM electrolytes

[1] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J.R. Reynolds; *Adv. Mat.*, 2000, **12** (7), 481-494
[2] M. Dietrich, J. Heinze, G. Heywang and F. Jonas; J. Electroanal. Chem., 1994, 369 (1-2), 87-92

Electrochemistry and Luminescence Properties of Surface-Active Thiolated Ruthenium and Osmium Polypyridyl Complexes

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The adsorption, electrochemistry and luminescence properties of thiolated ruthenium and osmium polypyridyl complexes are reported. Different thiolated ruthenium and osmium complexes have been synthesized and characterized using cyclic voltammetry. Using cyclic voltammetry key parameters such as surface coverages and diffusion coefficients have been evaluated. The apparent diffusion coefficients in solution were of the order of 10^{-6} cm^2 s^{-1} and the surface coverage on Pt electrodes was around 10^{-11} mol cm^2. Analysis of surface coverage vs complex solution concentration indicated that the surface coverage was independent of the solution concentration, suggesting the irreversible adsorption of the complexes to form self-assembled monolayers (SAMs) on the Pt surface. Luminescence studies have shown that SAMs of Ru(II) bipyridyl [1] and Os(II) terpyridyl complexes emit at characteristic wavelengths from their ^{3}MLCT states when adsorbed on the Pt surface. Preliminary studies of these compounds for the construction of electro-active wires are also reported.

[1] P. Bertoncello, E.T. Kefalas, Z. Pikramenou, P.R. Unwin, R.J. Forster, J. Phys. Chem. B **2006**, accepted.

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Soft Materials in Electrochemistry

Diffusion towards partially blocked electrodes: The reduction of Tl(I) ions on dyoleoylphosphatidylcholine coated mercury electrodes through defects and trough gramicidin channels

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Mercury electrodes covered with self-assembled monolayer of phospholipids are being used as a model system that mimics biological membranes, [1]. Dyoleoylph osphatidylcholine (DOPC) forms monolayers on mercury that at electrode potential values higher than c.a. -0.75 V vs SCE are well organised and exhibit impermeability to electroactive cations like Tl(I) that could, in case of permeability of the monolayer, undergo the reduction on the electrode.

However, in the presence of gramicidin the DOPC monolayer becomes permeable to monovalent cations, so the reduction of Tl(I) can be observed on these gramicidin modified electrodes. This reaction has been widely studied by means of electrochemical dc, [2], and electrochemical impedance measurements, [3]. The results obtained cannot be explained according to a single electron transfer process, as in the reduction of Tl(I) ions on unmodified mercury electrodes. Different reaction schemes have been proposed to explain the results, including preceding and following chemical reactions, but the physical meaning of these chemical steps is still unclear.

Previous studies have not considered the axial diffusion model towards a partially blocked electrode, in which the gramicidin channels act as electroactive pinholes, [4]. In this work, the data obtained by Electrochemical Impedance Spectroscopy measurements of Tl(I) reduction on a Hg-DOPC electrode in the presence of gramicidin over an extended frequency range are presented and analysed according to a diffusion model towards a partially blocked electrode. The results are compared with those obtained in the absence of gramicidin at potentials on the electrode at which the monolayer becomes permeable to ionic species as a result of defects formation.

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Soft Materials in Electrochemistry

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Oxidant and acid effects revisited for chemical and electrochemical aniline polymerization in polymer dispersion media

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Oxidant and acid nature as well as their concentration are well known factors affecting chemical aniline polymerization kinetics and quality of forming polyaniline (PANI) [1, 2]. However, to our knowledge there are no systematic studies of their effects on running this process in different common polymer powder dispersion water media. We have found that in this case these effects can be more complicated both due to specific interactions of the reagents with the polymer particles and to a posterior distribution of the formed PANI-acid complex in a final composite material.

As an alternative way to change these interactions we used electrochemical polymerization of aniline at Pt mesh electrode in the range of E=0.7-0.8 V in the acidified polymer powder dispersions in absence and presence of hydrogen peroxide when strong stirring. Comparing to the chemical way this allowed avoiding leavings of inorganic by-products from typical salt oxidants in the final material.

In order to evaluate a specificity of each of chemical or electrochemical systems the simultaneous pH, redox-potential and temperature monitoring of the reaction mixtures was applied. Additionally, in the electrochemical polymerization a simultaneous chronoamperogram of the process was measured. As in known cases [1,3], in comparison with polymerization of aniline in an absence of dispersion phase this process in the polymer powder dispersion run faster and its rate depended on a size of polymer particles. This can be probably explained not only by a catalytic effect of the surface of the polymer particles but also by running the polymerization process in an aniline adsorption layer formed at this surface where concentration of aniline is higher comparing to the solution bulk.

The obtained pH, redox-potential and temperature kinetic dependences for the chemical and electrochemical cases differed by shape. Specifically, we did not observe sharp changes of any monitored parameter in the electrochemical polymerization unlike the chemical polymerization case. In turn, in the latter case a position of characteristic points of change of pH, redox-potential and temperature at the obtained kinetic profiles strongly depended on oxidant, acid, temperature of the reaction mixture and some other factors.

Conductivity, thermal stability and mechanical properties of obtained polymer/PANI composites have been investigated.

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Morphology data of platinum/HOPG electrodes and their electrocatytic properties

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The electrocatalytic reactivity of metal electrodes, such as Pt and Pt alloys utilized in different electrochemical conversion devices, exhibit a scale-dependent the surface morphology and a relative distribution of crystal faces at metal clusters and aggregates that depend on the preparation procedure.

This work reports the influence of electrical perturbations on the surface properties of electrochemically prepared platinum/highly oriented pyrolitic graphite electrodes. Data from atomic force and scanning tunneling microscopy imaging offers the possibility to establish a correlation among surface properties of these electrodes, size distribution functions, aspect ratio of aggregates, fractal dimension, energy distribution of surface sites, and their electrocatalytic behaviour for three test electrochemical processes, namely, H-atom electrosorption processes; molecular oxygen electroreduction; methanol electrooxidation.

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A comparative investigation of reference redox couples for intersolvental comparison of electrode potential scales

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Our research group is concerned with the problem of intersolvental comparison of fundamental electrochemical quantities, in particular (a) pH, since we are currently extending to aqueous/organic and nonaqueous solvents the 2002 IUPAC protocol for primary pH standardization in water; and (b) electrode potentials, since we are currently studying the solvent effect on the mechanism of model electrocatalytic organic processes. Now, while intersolvental comparison of pH scales is based on the evaluation of the primary medium effect on the H^+ ion, voltammetric studies in non-aqueous solvents are currently referred to the ferricinium|ferrocene reference couple, following the 1986 IUPAC document [1], assuming the above redox process to take place at an invariant potential in all solvents. However, the data on the behaviour of the Fc^+|Fc redox couple in different (solvent+supporting electrolyte) combinations available in the literature are not exhaustive and often lack consistency. Moreover, the above assumption of intersolvental invariancy of the Fc^+|Fc redox potential has been recently questioned by authoritative papers [2, 3], suggesting that only permethylated ferrocene derivatives ("electron-reservoir sandwich complexes") could be considered unaffected by solvent coordination and therefore reliable intersolvental references.

In this context, we have carried out along a careful protocol an exhaustive voltammetric reactivity study on ferrocene, either as such or functionalized on the cyclopentadienyl rings, together with several other reversible redox couples, on both stationary and rotating electrodes, in a series of model organic solvents with constant supporting electrolyte. Our study now provides: (a) an exhaustive and consistent data set of redox potentials for the investigated couples in the model solvents, at constant supporting electrolyte and operating reference electrode; (b) a verification of the reversibility constancy for each redox couple in the model solvents; (c) new evidence supporting the above statements [2, 3] about the appropriateness of decamethyl-ferrocene as intersolvental redox potential standard; (d) the first application of the above concepts for the study of the solvent effect in a model organic electrocatalytic process.

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Electrochemical activity of novel amphoteric polyamidoamines responsive to redox stimuli

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Considerable interest is being focused on soluble synthetic polymers containing in the main chain chemical bonds stable in the bloodstream, but degradable after internalization in cells. Typical examples are biocompatibile polymers bearing disulfide linkages in their main chain, which can be regarded as stimuli-responsive release systems, with the disulfide reduction triggering conformational expansion and the release of the active substance. These systems are susceptible to be specifically designed for intracellular delivery thanks to the stronger reducing environment within cells than in extra-cellular fluids.

In this context, polyamidoamines (PAA), synthetic polymers based on regular sequences of amide and tertiary amine groups, are very attractive substrates. In particular, amphoteric PAAs are very promising as soluble carriers of antitumoral drugs. In fact, they are biocompatible and hydrosoluble, and remain unperceived by the immunitary system ("stealth") while tending to be accumulated in tumour tissues ("Enhanced Permeability and Retention (EPR) effect"). According to their structure, they can act as good chelating agents for heavy metal ions, an interesting feature especially with such cations as Co^{2+} (for cobalt therapy purposes) and Cu^{2+} (for purposes of cellular growth promotion). Also very interesting for biomedical applications are the recently appeared reticulated PAAs, especially hydrogels (being able to swell without dissolving when immersed in water) which can be used as polymeric scaffolds for tissue regeneration.

The Authors will present an investigation on the electrochemical activity on HDME electrode of two novel amphoteric PAAs carrying disulphide linkages in their main chain, with the support of their acid-base characterisation for both speciation assessment and mechanistic interpretative purposes. The behaviour of the new polymers will be discussed with respect to the well-known case of their parent compound cystine, which has been also electrochemically characterised as a suitable model in the same operating conditions.

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Soft Materials in Electrochemistry

Biomedical Applications of Conducting Polymers

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All bioelectrodes and pacemaker electrodes contain an electrode|bioliquid interface where the ionic conductor meets the electronic conductor, and since uncompensated charge exists only at the surface in steady-state for conductors (metals and ionic conductor which is the bioliquid), a capacitive impedance exists as an element of the equivalent circuit. Stimulation and sensing, the two functions of the bioelectrode, are affected differently by this reactive element. The effect on stimulation can be overcome by supplying redundant current based on monitoring of biologic response; in this sense it can be dealt with in hardware. Sensing is detrimentally affected, as the reactive impedance creates a filter: it introduces an obligatory non-linear ill-behaved high-pass filter section. For this reason, the achievement of an Ohmic interface would be highly desirable. We have investigated a number of different conductive polymer surface coatings, and have found that the effectiveness of the coating depend on polymer film thickness and porosity, identity, and homogeneity of structure. The elimination of the high pass filtering interface which has been accomplished with some of these electrodes constitutes a major advance in bioelectrode materials design. Results will be reported for the optimization of conditions for reproducible production of electrodes with behavior that appears ohmic over a broad frequency range has been carried out for poly-(3,4-ethylenedioxythiophene). Our findings are in sharp contrast to those reported by a number of groups regarding the stability and in vitro stability of PEDOT. These difference appear to be a result of the result of the nature of the films themselves as well as the conditions for acquisition of the impedance spectroscopy data. Implication of these results for bioelectrode design and results for their in vivo applications will be discussed.

Reactions of orthophthaladehyde with water and hydroxide ions- effects on reduction and oxidation

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Orthophthaladehyde (1,2-benzenedicarboxaldehyde) (OPA) and more recently 2,3-naphthalinedicarboxaldehyde (NDA) react in the presence of nucleophiles (like RS^- or CN^-) with amino acid to yield isoindole derivatives. Fluorescence of this product is used for determination of amino acids. As the mechanism of the formation of the isoindole derivative is not known, reported analytical methods had to be developed empirically. Electroanalytical techniques together with UV and NMR spectra reported here for OPA contributed to the understanding of processes involved.

Polarographic studies indicated presence of three forms in aqueous solutions of OPA: the unhydrated one (I) reduced in wave i_1, the monohydrated acyclic form (II) reduced in wave i_2 and the electroinactive form (III):
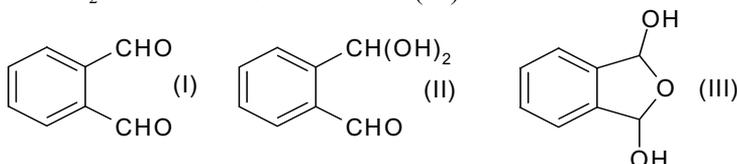
Between pH 3 and 8 the limiting currents of wave i_1 and between pH 1 and 4.5 those of wave i_2 remain pH-independent and controlled by diffusion. This indicates that in this pH-range the equilibria between forms I and II and those between II and III are established relatively slowly, relative to the time-window of the experiment. Comparison of limiting currents i_1 and i_2 with the limiting current of the unhydrated 1.3-isomer (isophthalaldehyde) indicated that about 10% of OPA is present in form I, 20% in form II and about 70% in form III. Proton NMR and ^{13}C NMR spectra and their dependence on temperature confirmed presence of 3 forms. ^{13}C spectra in mixtures of CH_3CN and H_2O confirmed the distribution of forms I-III given above. – Variation of i_1 with pH demonstrated acid and base catalyzed conversion of II into I. Conversion of III into II is only base catalyzed. Decrease of currents i_1 and i_2 at pH > 10 is attributed to the formation of a geminal diol anion $[-CH(OH)O^-]$ by dissociation of the hydrated form or by addition of OH^- to the unhydrated form I. This attribution is supported by anodic waves of oxidation of $CH(OH)O^-$ into COO^-, increasing with increasing pH. The pH-dependence of anodic waves enables calculation of the rate of formation of the geminal diol anion. The rate constant is of the order of 10^4 $Lmol^{-1}s^{-1}$, indicating that addition of OH^- ions to $CH=O$ is the main chemical reaction preceding the electron transfer.

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Controlled Intensity Modulated Photo- and Impedance Spectroscopy on conductuing polymers

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Unlike the situation at a simple pn-junction in silicon, the photoactive layers of a semiconducting polymer in an electrolyte are embedded within a complex arrangement of several additional phases.

For a successful analysis of such systems it is necessary to combine different dynamic photo - and electrical techniques. In the present work , polythiophenes on different substrates were examined. A novel approach was used which allowed to perform EIS, intensity modulated photovoltage - and intensity modulated photocurrent spectroscopy on the test objects held in the same system state.

Controlled Intensity Photo Spectroscopy offered the necessary precision and long term stability of the photo intensity and modulation for such measurements.

The results of the photovoltage spectra at constant current, the corresponding photocurrent spectra at constant voltage and the EIS could be explained and successfully fitted by a common equivalent circuit model in which the photoactive layer could be assigned.

Electrochemical Investigation of the Mechanism of Glutathione Redox Reaction

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Electrochemical studying of redox reactions of glutathione attracts a particular interest as a way to obtain new notion about fine mechanisms of vitally important processes involving electron transfer in biosystems. Due to the presence of a sulfhydryl group, glutathione is readily oxidizable under an action of various factors with a disulfide formation. This process underlies the effect of this tri-peptide as a powerful endogenous antioxidant. In this work we investigated the mechanism of electrochemical reduction of oxidized glutathione (GSSG) and of its reduced form (GSH) under conditions of simultaneous generating an active oxygen species. Voltammetric investigations have been carried out at bare solid electrodes made of platinum, iron, and copper both in the presence of oxygen dissolved in the supporting 0.1 M NaCl and in the deaerated supporting solution. In the latter case the peak corresponding to a two-electron reduction of GSSG has been observed:

$$GSSG + 2e + H^+ \rightarrow 2GSH.$$
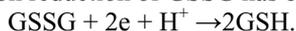
When oxygen presents in the supporting solution we have observed a reduction peak not only for GSSG but for GSH as well. It has been supposed that in the latter case GSH was pre-oxidized by the products of oxygen reduction. This assumption is supported with decreasing a peak current of oxygen reduction in the presence of GSH at platinum and iron electrodes. Apparently, the pre-oxidation occurs due to interaction of GSH by the following reaction with hydrogen peroxide generated in the concurrent process of oxygen reduction.

$$GSH + H_2O_2 \rightarrow GS^{\bullet} + HO_2^{\bullet} + H_2$$

Besides, hydroxyl radicals are shown to be generated along with hydrogen peroxide at a copper cathode. Decreasing the peak currents of hydrogen peroxide and of hydroxyl radical, with simultaneous increasing the peak current of oxygen reduction in the presence of GSH, indicates that GSH reacts with all oxygen intermediate species generated. In particular, its reaction with hydroxyl radical may occur with the following recombination of formed glutathione radical resulting in the formation of disulfide oxidized form of glutathione:

$$GSH + {}^{\bullet}OH \rightarrow GS^{\bullet} + H_2O,$$
$$GS\cdot + GS\cdot \rightarrow GSSG.$$
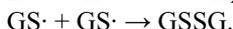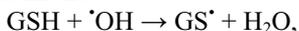
Recombination of two peroxyl radicals leads to the formation of hydrogen peroxide and oxygen; both of the products may be involved in the reaction with GSH over again.

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$
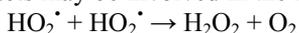
It is the cause of the increase of oxygen reduction peak current observed in the presence of GSH. Besides, formation of complexes GSH-oxygen at the electrode surface is possible that facilitates a process of oxygen electrochemical reduction.

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Soft Materials in Electrochemistry

Application of density functional theory calculations in the electrosynthesis of conducting polymers

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Density Functional Theory (DFT) is a computational technique that is gaining increasing interest owing to its comparable accuracy with Hartree-Fock (H-F) methods coupled with the significantly reduced computational resources such *ab initio* calculations. For example, computational time and memory scale with N^3 for DFT calculations compared with N^4 for H-F methods, where N is the number of atoms or electrons. DFT only considers the electron density, rather than the many-body wave-function in H-F theory.

DFT calculations have been used to determine the locations of highest unpaired electron spin density in monomeric radical cations of heterocyclic compounds, such as pyrrole and thiophene derivatives, used to produce conducting polymers. The locations of highest spin density determine the coupling positions in the resulting polymers. In the case of pyrrole, for example, the highest spin density is found at the 2- and 5- (α-) positions and thus α,α'-linkages, necessary for high conductivity, predominate.

The band-gap of electroactive polymers and monomer ionisation potentials can also be determined using DFT methods, further enabling a rational screening method for selecting novel heterocyclic compounds as monomers for producing new conducting polymers.

In the first part of this paper, we consider positions of highest spin density in the growing oligomeric radical cations and their subsequent coupling reactions. Interestingly, the ratio of spin densities at the α- to terminal β-positions increases with chain length. However, the ratio of α- to β-positions midway along the growing oligomer rapidly decreases, with the later positions soon becoming the locations of highest spin density. These results are discussed with reference to polymer conjugation lengths.

The electropolymerisation of some novel acrylonitriles containing pyrrole, thiophene and furan rings are described in the second part of the paper. The electro-oxidation reaction and the polymer thus produced is discussed in terms of the spin density distributions in the resultant monomers and oligomers together with the significance of oligomer/monomer coupling ratios.

Electrical wave transient generated by fast sds agreggate formation on gold substract

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In aqueous media, the adsorption of surfactants on solid surfaces allows the formation of aggregates in a membrane-like structure [1]. The structural and dynamic properties of the adsorbed surfactant molecular films are of both fundamental and applied biological interest [1,2]. We studied the fast adsorption of Sodium Dodecyl Sulfate (SDS) on gold surfaces at concentrations below the critical micellar concentration, *cmc*, (8mM). Resonant frequency changes of the quartz crystal microbalance (QCM) immersed in water and the changes of the open circuit potential value U (vs. Ag/AgCl) of the gold coated electrode (0.28 cm^2) of the QCM were registered before, during, and after the addition of SDS solutions to water. Frequency changes were correlated to mass changes (the sensitivity of the QCM, was: $S=3.584x10^{-9}g/Hz$). The SDS addition with a final concentration of 1mM caused a smooth frequency decay curve and a potential curve increase without transients. In contrast, the SDS addition with a final

Fig. 1

concentration of 2mM produced the frequency and potential transient waves shown in Fig.1. The frequency wave can be explained by considering that the dodecyl sulfate anions adsorbed on the electrode diffused to the activated nucleation centers (the number of these centers being determined by the bulk SDS concentration) to form compact regions which eventually coalesced into a monolayer [3]. On the other hand, the concurrent growing electrical flux at the electrode surface induced an ionic current which caused the potential transient at 1500 s. In conclusion, the experiment showed that electrical waves can be produced in the vicinity of the electrode when a compact-monolayer rapidly builds up on the gold electrode surface. This result has interesting consequences for the micelles formation in the bulk of electrolytes in biological systems.

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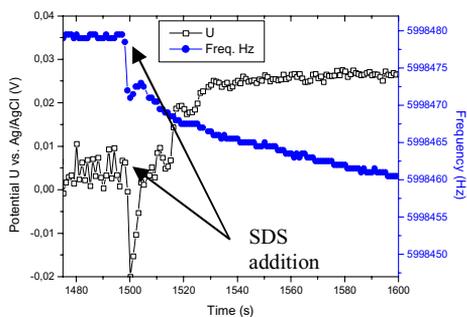
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Adsorbed Sodium Dodecyl Sulfate Molecular Films on Silicon: an AFM study

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Clearly, how an adsorbed surfactant molecule modifies the surface properties of a substrate is a subject of great importance for modeling industrial processes that use surfactants on a large scale, such as detergency, water purification, oil recovery, and ore refinement by flotation. We investigated the adsorption properties of the anionic surfactant SDS on silicon surfaces using atomic force microscopy (AFM). The force between the surface and the AFM tip was measured as a function of the separation between the surface and the tip (Si_3N_4). The SDS solution was injected into a liquid cell at room temperature of 25^oC. After about 2h (equilibration time) the force-distance data were collected from different locations of the substrate. Typical force vs separation curves for different SDS solutions are shown in Fig. 1 (curves a, c) for Si substrates and (curve b) for mica. In curve *a* for 10^{-4}M SDS the repulsion force is displaced by the 2nm surfactant layer thickness (the length of the fully extended molecule being about 1.3 nm plus the sodium hydrated layer being about

Fig 1

0.7nm). Due to the hydrophobic Si surface, it is assumed that the negative surfactant heads point to the solution. In curve *b*, for 10_3 M SDS the observed electrostatic force followed by a step in the force, corresponded to the interaction between the negative charged mica and a charged surfactant monolayer (2nm) adsorbed on the tip surface (not detected in 10^{-4} SDS concentration). In (curve c) for a 10_3 M SDS, an electrostatic repulsion force is again observed as the tip approaches the substrate, similar to the one measured for mica. Two other repulsive force components at 2.0 nm and at 4.5 nm from the silicon surface indicate that a monolayer is adsorbed on the tip surface and another monolayer adsorbed on the silicon surface. The results are in accordance with the SDS adsorption on gold substrates, measured with the Quartz Crystal microbalance[1].
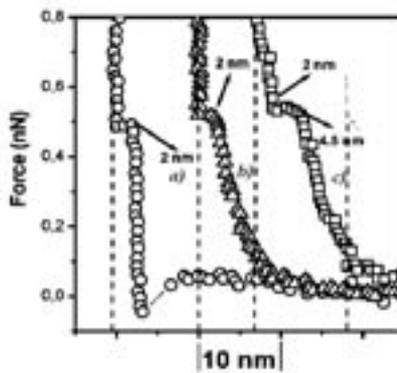
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Gold Nanoparticles on Electrodes as Effective Charge Transporting Units

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The objective of the work was to prepare and investigate the properties of self – assembled systems containing organothiol monolayers with anchored monolayer protected gold clusters (MPCs).

Recently we described the preparation of different gold nanostructures using gold electrodes modified with azocrown ethers. This compound immobilized by thiophene group on the electrode surface, can be used as specific chemical „generator" of gold clusters [1].

Well ordered assemblies of gold clusters, immobilized on the electrode through covalent or noncovalent bonds were obtained using organothiol compounds [2-4]. The best linker was proved to be 1,9-nonanedithiol and not simple alkanethiol. Gold clusters in this system are more uniformly distributed on the monolayer and firmly attached to the electrode by means of the Au-S bond. Most impressive result was that the gold clusters are able to accumulate charge and to effectively transport it between the electrode and compounds present in the solution. Gold clusters transfer charge to the electrode not only across the isolating monolayer, but they also exchange it laterally with neighbouring nanoparticles. The good charge transport properties of the investigated Au cluster – monolayer system were exploited in the process of ascorbic acid and 3,4-dihydroxyphenylalanine catalytic oxidation. Catalytic reduction of oxygen will be also shown. In both cases the peak current was higher and overpotentials were smaller, indicating electrocatalysis. Applications include electrochemical sensors and microbiofuel cells.

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Spectroelectrochemical study of electropolymerization of aniline on polyaniline films

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Polyaniline (PANI) is a conducting polymer widely used as base material in the developing of pH-sensors, biosensors, rechargeable batteries, selectively permeable membranes or corrosion-protecting coatings. Although many studies deal with the electrosynthesis of PANI films, the mechanism is not fully understood yet. One of the main drawbacks in PANI film electrogeneration is the difficulty of obtaining polymer films with similar electronic, optical or resistance properties.

We have demonstrated previously the influence of the flow rate in the potentiostatic electropolymerization of aniline in acidic medium [1]. Conducting polymers with different thickness and electrochromic properties were obtained.

In this work we present the spectroelectrochemical results obtained during the potentiodynamic electrosynthesis of PANI films in three steps: i) electropolymerization of aniline in acidic medium on a gold electrode surface; ii) potential cycling in acidic medium free of aniline; and, iii) re-polymerization of aniline in acidic medium on the PANI film electrode initially obtained. The influence of the flow rate in the last stage of electropolymerization has been assessed in several experiments carried out using a spectroelectrochemical flow cell [1] that operates in near normal incidence reflection mode.

We prove that electropolymerization of aniline on a PANI electrode is not influenced by the flow rate, achieving polymer films with similar electrochromic properties.

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S7·P-77

Some interesting aspects of aromatic dopant anions in polypyrrole

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Polypyrrole and other heterocyclic conducting polymers have already moved from 'scientifically interesting' to 'industrially manufactured' status. Even with these conductive polymers being produced and used more and more commonly, the understanding of many fundamental aspects of such materials is still quite far from being complete. Thus, both experiments and theoretical studies are still needed to gain further insight into the structure and properties of conducting polymers. The latter is especially true for polymer systems with slightly less common dopant anions, resulting in a variety of interesting and even unexpected properties of such films.

Polypyrrole is synthesized and used mostly in the conductive oxidized form where the positively charged chains are in strong interaction with counter-anions. The anions used in the synthesis bath also determine the future structure and behavior of the polymer film. In the present study accurate cyclic voltammetry (CV) measurements together with quantum chemical calculations were applied to study the behavior of the relatively small aromatic benzenesulfonate anions in polypyrrole films. The redox charge, influence of the sweep rate, the memory effect, the exchange rate and mobility of the anions in the polypyrrole films during redox cycling were studied using CV. The π - π interactions in the complexes of cationic pyrrole oligomers and benzenesulfonate anions were studied using a variety of quantum chemical methods ranging from density functional theory (DFT) to post Hartree-Fock *ab initio* calculations. The energetically optimal structures of the stacked polymer chains and anions were studied. High level calculations are necessary, as low level Hartree-Fock methods and most DFT functional fail to reasonably describe the stacking.

It was established from the CV measurements, that although relatively large and of low mobility, the benzenesulfonate anions can be easily replaced in the polymer film by small inorganic anions (nitrate, perchlorate) by both redox cycling and also by just soaking in a solutions of these anions. The high doping levels obtained by this kind of replacement suggests that the structure of the benzenesulfonate doped film is rather well organised, and also remains largely intact during the replacement. Therefore, higher doping levels can be obtained by replacing benzenesulfonate anions by small inorganic ones compared to films synthesised from the solutions of these small anions under similar conditions.

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Soft Materials in Electrochemistry

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Soft Materials in Electrochemistry

Electrochemical Characterization of Polycrystalline Gold Surfaces modified by Self Assembled Monolayers of Mixed Thiols in the Presence of Cytochrome-C

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CME's have been intensively studied in the last 20 years thanks to their wide possibilities of applications ranging from surface chemistry to biochemistry, from electroanalytical chemistry to ionic and electronic transport phenomena=. CME's formed by self assembling of organic monolayer, SAM, adsorbed on metallic surface have been deeply investigated. The most popular SAM's are those formed by alkanethiol molecules adsorbed on gold, which exhibit physico-chemical properties modulated by the organic chain length, the alkanethiol terminal groups, the molecule package density, the status of the metallic surface [1].

In particular, terminal groups can impart to the SAM's the sought chemical properties, as in the case of ω terminated COOH thiols which offer the appropriate electrostatic interaction site to immobilize Cytochrome C (CytC) protein, as well as other cationic biomolecules, as first step of fabrication of specific biosensors.

In addition to the thiol/protein interactions, the stability of the layer is crucial in determining the electrode performance and service-life. Since this property is mostly chained to the morphology of the gold surface, a large number of investigations is devoted to analyse the behaviour of monocrystalline surfaces.

,=[12]In this work we report the performances of SAM-Au electrodes based on electrodeposited polycrystalline gold surface of controlled roughness in comparison with (210) Au single crystal face, for both single and mixed thiol layers.

The studies on polycrystalline SAM-Au surfaces are then extended to the characterization of CytC/electrode interactions, in terms of kinetics of protein adsorption process and of electron transfer rates of the metallic centres.

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Symposium 7 - Poster

Soft Materials in Electrochemistry

AN Electrochemical and spm investigation of Laccase Biosensor Interfaces

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When preparing electrochemical enzymatic biosensors, there are a number of challenging aspects that must be carefully addressed, namely, the amount and orientation of the biomolecules on the surface, the correct choice of redox active mediators, the stability of the interface under the applied potential and over time. Numerous strategies have been employed to build such biosensor interfaces, including covalent attachment onto self-assembled monolayers (SAMs) [1]. This approach is advantageous to prepare reproducible interfaces, however, the drawback is the extremely low amount of enzyme that can be chemically linked to the electrode surface and consequently the low electrochemical responses (direct or indirect) achieved from the enzymatic performance. Therefore, in these systems a proper orientation of the enzyme must be the crucial factor.

In the present work, pure and mixed short chain SAMs of thiol/disulphides derivatives on gold have been investigated as platforms for the covalent immobilisation of commercial Laccase (EC 1.10.3.2). Special emphasis is given to the monolayers based on *N*-hydroxysuccinimide-ester functionalised disulphide [2,3] where no chemical activation of the underlying SAMs is required for the covalent attachment of Laccase to the surface. The bio-activity of the prepared enzymatic surfaces has been investigated towards ABTS.

The amount of adsorbed enzyme onto pure and mixed SAMs as well as the interface stability under the applied potential, required for the catalytic activity towards different substrates (e.g ABTS) is provided by EQCM.

A combination of Scanning Tunnelling Microscopy (STM) and Atomic Force Microscopy (AFM) is used to characterise the underlying SAMs and the Laccase distribution on the surface in order to establish a correlation between structure and biosensor performance.

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Electrochemical Characterization And Magnetic Properties of Electrodeposited CoPtW Thin Films

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In recent years particular interest is growing towards the electrodeposited CoPt alloys with perpendicular anisotropy, a very interesting material not only for perpendicular high-density magnetic recording media, but also as magnet for small electronic devices. By adding a third alloying element, W, the magnetic properties of the CoPt alloys at high thickness can be increased, and another advantage is the decreasing Pt content to less than half while maintaining high coercivity[1]. In the present study, the electrochemical essential for the electrodeposition of CoPtW thin films and magnetic properties are studied. As can be seen from the cyclic voltammetry that electrodeposition of ternary alloy began at a negative potential (-0.65V), simultaneously with the hydrogen evolution. A nucleation and growth process was involved in the electrodeposition of CoPtW alloy from the chronoamperometric analysis. It was also found that the critical time for nucleation decreased as the potential was made more negative (Fig.1). VSM measurement revealed that parallel and perpendicular coercivity of CoPtW was the function of W content at the early deposition times, and maintained invariable over 30min.
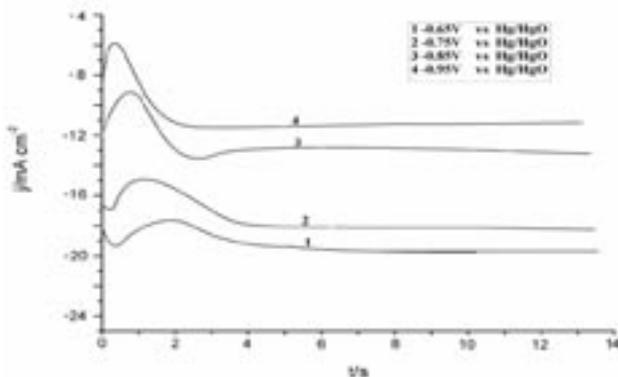
Fig.1 Potentiostatic I-t transient of 0.1M $Co(NH_2SO_3)_2$+ 0.01M$(NH_4)_2PtCl_4$+0.27M Na_2WO_4+0.2M $(NH_4)_2C_6H_6O_7$ solution, potential range from –650mV to 950mV vs Hg/HgO.

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Influnce of Bath Temperature on Magnetic Properties of Co-Pt-W(P) Thin Films

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Electrodeposition of Co-Pt-W(P) magnetic thin films, with reduced Pt content and improved magnetic properties at high deposit thickness has been studied in recent years[1]. In this paper, the effects of bath temperature on the magnetic properties of electrodeposited Co-Pt-W(P) films were investigated. As the temperature increased from 40℃ to 80℃, tungsten content in the deposit increased, while phosphorus content decreased. Moreover, the average grain size became smaller due to the increase of the nucleation number by chronopotential analysis. In Fig.1, these films when deposited from solution of T=40℃ exhibited soft magnetic properties, while from solution of T=70℃, hard magnetic deposits were obtained. The increase of tungsten content in the deposit due to temperature increase favoured the precipitation of tungsten or tungsten oxide at grain boundaries, which can explain the increase of the deposit coercivity. However, higher temperature can weaken hard magnetic properties, because grain size decreased in the higher temperature, a smaller grain size decreases the effective anisotropy of the crystallites and generally results in lower coercivities.
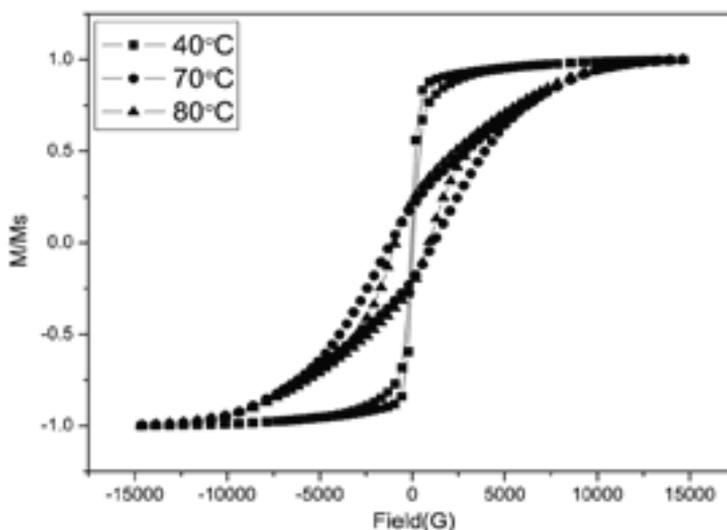
Fig.1 Hysteresis loops at the different temperature

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Soft Materials in Electrochemistry

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Development of conducting polymer layers on membranes to prevent biofouling and enhance biocide effects

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Biofouling on membranes causes damage and high costs in membrane processes.

The aim of our project is to prevent and reduce biofouling on membranes and to remove any biofilms that have already formed. To achieve this, membranes are coated with conducting polymers e.g. polypyrrole, polythiophene oder polyaniline and the polymer layer is polarised. This polarisation inhibits biofouling and enhances the effect of biocides.

The conducting polymer can be modified as cation- or anion-exchanger and its porosity can be controlled to avoid any impairment of the membrane by the polymer layer.

This new method of preventing biofouling offers economic and ecological benefits compared to conventional methods because it avoids or reduces the use of biocides and thus prolongs the operating time of the membranes.

A method and a cell for coating membranes have been developed and different membranes, such as cation- and anion-exchanger, ultrafiltration and reverse osmosis membranes, have been coated with polypyrrole (ppy). The coated membranes are investigated by scanning electron microscopy (SEM) and cyclic voltammetry. The ppy coatings can be depicted well by SEM (Fig.1A) and cyclic voltammograms (CV) show the electrochemical activity of the coated membrane (Fig.1B).
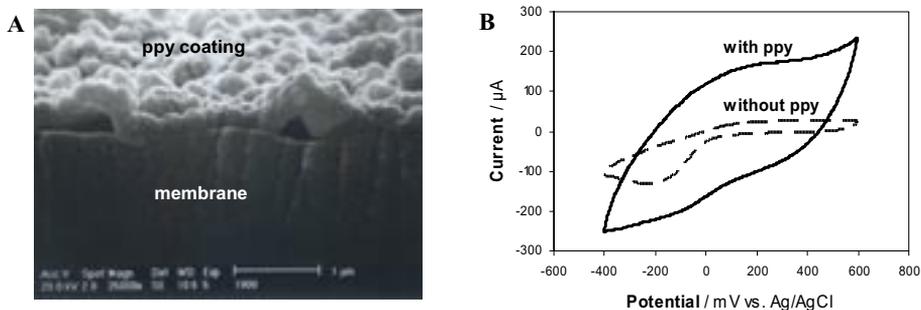
Fig.1: SEM picture of a ppy coated cation-exchanger membrane (**A**)
and CV of a reverse osmosis membrane without and with ppy coating (**B**).

Surface angle investigations show that the ppy coating increases the hydrophilicity of the membranes.

The adhesion of microorganisms is tested on stainless steel samples as well as ppy-coated membranes in dependence on different polarisation potentials.

This project is being carried out in cooperation with IWW in Mülheim / Ruhr.

Electrochemical Synthesis of Polyaniline/Graphite Oxide Nanocomposite

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Preparation of polyaniline-intercalated graphite oxide via chemical polymerization of aniline incorporated into exfoliated graphite oxide has been reported in the literature [1-3]. In the present work, we aim to prepare nanocomposites of polyaniline with graphite oxide during potantiodynamic electropolymerization method, as graphite oxide was dispersed into the polymerization bath. It was found that the electropolymerization process is significantly affected by the existence of graphite oxide. While the amount of graphite oxide was constant, the aniline concentration was varied to control the composite ratio. As a result, both the electrochemical behavior and morphology of the nanocomposite film were strongly changed. In addition, the electropolymerization was also performed in the presence of reduced form of graphite oxide. For this purpose, the reduced form of graphite oxide was prepared by dispersing the graphite oxide powder in a solution of 1.0 M $NaBH_4$ under hydrothermal treatment at 150 °C for 10 h. According to the SEM investigation, while electropolymerization in the presence of original graphite oxide during just 5 successive cycles, leads to the formation of a concrete polymer structure (left SEM), the reduced 'graphite oxide' results in the formation of a nanostructured film (right SEM). In fact, reduced 'graphite oxide' is significantly different from the initial graphite, which can lead the electropolymerization in a different manner resulting in the formation of nanostructured polymer with enhanced electrochemical properties.
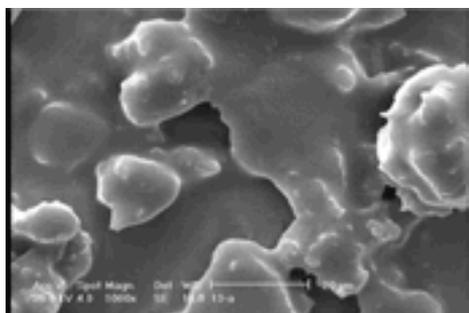
Graphite oxide/polyaniline nanocomposite.
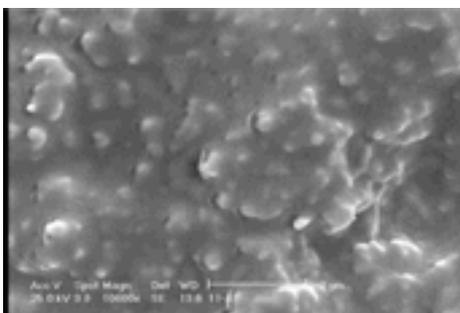
Graphite oxide/polyaniline nanocomposite made from reduced 'graphite oxide'.

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Soft Materials in Electrochemistry

Electroanalytical applications of novel hybrid materials consisting of polythiophene containing nanoparticles

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Polythiophene constitutes a very appealing class of materials thanks to properties such as electrical conductivity, electrochromism and electroluminescence. For this reason, they have been widely studied in the field of sensoristics, particularly for electrochemical sensors in which the polymer constitutes the coating of the electrode surface.

Among different conducting polymers, great attention has been recently devoted to poly(3,4-ethylenedioxithiophene) (PEDOT), which shows quite high conductivity and stability, and a particularly reduced band-gap, being both p- and n- doping well possible. Moreover, the presence of dioxyalkyl residues on the β-thiophene positions strongly reduces the potential at which p-doping occurs (-0.05 V), with respect to many other polythiophene derivatives. As an improvement to the physico-chemical properties of conducting polymer coatings, literature gives evidence of a great effort for inserting metals, both under metallic and ionic form. The presence of the metal is suppose to further increase the electrocatalytic performances of the pure organic material.

In the present work, the electrocatalytic properties of PEDOT have been studied in the detection of several analytes and compared with the performances of bare Pt electrode. The purely organic polymer actually exhibits interesting electrocatalytic properties, in terms of reduced overvoltage for oxidation, lower detection limit and increased sensitivity. The inclusion of Au and Pt nanoparticles during PEDOT electrogeneration from a solution containing both the nanoparticles and the EDOT monomer was also tested from an analytical point of view. To this aim, nanoparticles are synthesised and studied at changing the nature of encapsulating agent, i.e. decanethiol, 3,4-ethylendioxythiophene, neutral and charged tetralkylammonium salts, citric and tannic acid.

For all these composites, different analytes present in foods and pharmaceutical formulations are studied by cyclic and differential pulse voltammetry. Very interesting results in terms of increased sensitivity and peak resolution for the different analytes are observed, depending on nature and concentration of the metal nanoparticles and on the ionic charge of residues brought by the encapsulating agent. As a particularly appealing example, when nanoparticles capped with citric and tannic acid are included in the polymer, an electrostatic shield coating is obtained: no oxidation of negatively charged ascorbic acid is observed, while the signals due to differently charged analytes are enhanced and resolved. This effect is due to the presence of these particular nanoparticles, as PEDOT does not show the same effect. The same coating is also tested at different pH, where the analytes are differently charged, and, consequently, differently detected.

Nafion[Ru(bpy)$_3^{2+}$] as the Solid Organic Charge Transport Material for the Solid-State Photovoltaic Cell

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The studies of organic photovoltaic cells or nano inorganic-organic hybrid solid-state photovoltaic cells and light emitting diodes are attracting attention for future electronic and photonic devices as well as for photoenergy conversion devices. Many researches focused on searching for appropriate solid charge solar energy transport materials, which plays a key role in fabrication of photovoltaic cells and light emitting devices .

In this work, the Nafion-based redox polymer(Nafion[Ru(bpy)$_3^{2+}$]) was developed into a kind of solid organic charge transport materials which can act as a kind of hole transport material when redox centers are located in the reductive states initially(as shown in fig.1). The charge transport performance of this solid redox polymer has been investigated by electrochemical methods. The results of charge transport performance showed that D_{ct} of the ITO / Nafion[Ru(bpy)$_3^{2+}$]/Au solid cells is about $10^{-7} \sim 10^{-8}$ cm^2·s^{-1} and _ is about 10^{-6} cm^2·V^{-1}·s^{-1}. PEG was also added to improve the charge transport performance in dry state Nafion. Finally we employed the Nafion-based redox polymer as the hole transport material for the solid-state photovoltaic cell using narrow band gap nano-semiconductor CdS as active photoelectrode. So far, its IPCE is about 15% and _$_e$ about 3.2% for 395nm light. The IPCE for 350nm light is about 23%. The future of this novel photovoltaic cell is promising along with the potential enhancement of the charge transport performance of the redox polymers.

Fig. 1 The scheme of construction(upper) and operating process(lower) of the solid-state photovoltaic cell. M is for Ru, Red for reduced state of Ru complex.

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Soft Materials in Electrochemistry

Qualitative interpretations for the optimal composition of the bath used for the electrochemical deposition of the permalloy layers

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A lot of previous experiments have shown that   alloys exhibit magnetic properties which could be of interest in the industrial field, especially for data storage.

We have focused our attention on the electrolytic procedures in order to define simple technological methods of preparation; in most of previous experiments the electrolytical   procedures were running at temperature higher than the ambient temperature and implemented solutions whose concentration in metallic ions take higher values; the solutions were either basic or acid.

Starting from the previous experiments and the technological ways, which has been identified, it has been attempted to define optimal conditions for the reproducible electrolytical deposition of Ni-Fe alloys; an exhaustive analysis of the influence of the physical and chemical parameters has been examined for Ni-Fe layers whose atomic percentage in Fe is situated in the 10-50% range.

Preparation and Characterization of Copper-Doped Cobalt Oxide Electrodes (Ti/Cu$_x$Co$_{3-x}$O$_4$)

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Transition metallic oxides present a series of exceptional electronic, magnetic and catalytic properties. Cobalt oxides (Co$_3$O$_4$) or cobalt containing mixed oxides with spinel structure, (M$_x$Co$_{3-x}$O$_4$ with M = Cu, Ni, Mg, Zn, etc) have been extensively applied to the electrochemical treatment of wastewater [1,2]. We report the electrochemical characterization and a surface composition study of cobalt oxide (Co$_3$O$_4$) and copper-doped cobalt oxide (Cu$_x$Co$_{3-x}$O$_4$) electrodes, which have been prepared onto titanium support by the thermal decomposition method. The cyclic voltammograms of Ti/Co$_3$O$_4$ and Ti/Cu$_{0.5}$Co$_{2.5}$O$_4$ electrodes in 0.1M NaOH solution show the two characteristic redox couples of a typical Co$_3$O$_4$ electrode. As copper concentration grows, the first couple (Co^{II}/Co^{III}) vanishes. The shift of the second redox transition (Co^{III}/ Co^{IV}) and the OER to lower positive potentials, indicate a modification of the electrocatalytic features induced by Cu incorporation. When x exceeds 1.0, the characteristic features for Co$_3$O$_4$ electroactivity are lost.

The bulk and surface atomic composition were determined by EDX and XPS, respectively and are shown in Table 1. The Cu/Co ratio in the surface is rather close to the bulk ratio and to the nominal composition of the precursor solution. However, the copper over-saturated cobalt spinel (x > 1) exhibits a surface copper enrichment. Moreover, the similar bulk composition of the copper saturated (x = 1) and the copper over-saturated cobalt spinel (x > 1) suggests the existence of two well-defined phases in the latter oxide: a deeper copper cobaltite phase and a surface segregated CuO phase. This surface phase segregation is probably at the origin of the drastic change of the voltammetric profile at x>1.0.

Table 1

Bulk and surface composition of Ti / Cu$_x$Co$_{3-x}$O$_4$ electrode

Cu$_x$Co$_{3-x}$O$_4$ / Ti Electrode	Atomic Ratio		
	Nominal Cu/Co	$\left(\dfrac{Cu}{Co}\right)_{EDX}$	$\left(\dfrac{Cu}{Co}\right)_{XPS}$
Cu$_{0.2}$Co$_{2.8}$O$_4$	0.07	0.04	0.07
Cu$_{0.5}$Co$_{2.5}$O$_4$	0.20	0.19	0.23
Cu$_{0.8}$Co$_{2.2}$O$_4$	0.36	0.37	0.49
CuCo$_2$O$_4$	0.50	0.51	0.50
CuCo$_2$O$_4$ (+ Cu$_y$O)	1.00	0.56	4.55

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The Kinetics of Redox Mediation

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Redox mediation is a phenomenon by which a substance in contact with a metal on one side, and in contact with a solution that contains one or both component of a redox couple on the other, is capable of mediating electron transfer between the redox couple and the metal.

Redox mediators are substances containing redox centers that are electroactive, that is, when in contact with a metal and forming part of a suitable electrochemical cell, can be oxidized and reduced in a more or less reversible way. We will be interested in redox mediators in the solid state. An example of redox mediators are electroactive polymers. As examples of this kind of polymers we may mention Poly-*o*-aminophenol (POAP) and Os(II) bypyridil- poly-vynilpyridile (OsBPVP). In the first one the redox centers are the amino groups that are oxidized to imino ones. In the second is the coordinated Os(II), which is oxidized to Os(III).

Mediation involves electron transfer at the metal/ solution interface charge transport in the mediator, electron transfer at the mediator/ solution interface and mass transfer in the solution. One or more of these processes may control the kinetics of the global process. Except in part for the work of Laviron and of Ikeda *et al.*, until know, the criteria for analyzing the steady state current potential curves were mostly based on the analysis of the limiting currents. In this presentation we analyze the current potential curve in a rotating disk electrode at steady state and obtain some diagnostic criteria based on the shape of this curve. Particularly, this analysis allows explaining the observed phenomena of electrochemical rectification. The conditions for these phenomena to occur are discussed.

Symposium 8

Surface Chemistry and Dynamics

CO Adsorption/Oxidation Kinetics studied by combined ATR-FTIR Spectroscopy and Differential Electrochemical Mass Spectrometry under Continuous Flow Conditions

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In the recent years in-situ IR spectroscopic and on-line differential mass spectrometric studies have significantly contributed to the fundamental understanding of electrochemical reactions by providing information on the potential dependent appearance of absorbed surface species as well as detection and quantification of the volatile products evolved during these reactions. We have combined the advantages of both so far separately used techniques, allowing us to detect adsorbed species by using highly surface sensitive FTIR spectroscopy in an ATR-configuration, and to obtain information on the resulting products formed from these adsorbates by differential electrochemical mass spectrometry under fuel cell relevant continuous flow conditions.

Using this setup we performed CO adsorption transient experiments, at different constant potentials to investigate the CO adsorption/oxidation kinetics on CO_{ad} free and on partly CO_{ad} blocked surfaces. The CO consumption measured during CO adsorption at 0.06 V via DEMS can be used to calculate the actual surface coverage of CO_{ad} at any time, which then can be directly correlated to the in-situ measured IR-intensity resulting in a calibration curve IR-intensity (or wavenumber) against CO_{ad} surface coverage at different potentials. The data show i) a significant potential dependence of the ration between CO_L and CO_M for the same coverage and ii) in the regime of very low and very high CO_{ad} coverage there is no proportional relation between CO_{ad} coverage and CO_{ad} intensity. Furthermore, we can calculate the coverage and potential dependent CO sticking coefficient.

Performing CO adsorption transients at higher potentials, were CO_{ad} can already be oxidised to CO_2 allows to determine the CO_{ad} coverage dependent CO oxidation rates from the CO_2 production measured via DEMS, which is free from any effects due to re-adsorption of anions, prohibiting to use the faradaic currents for determining the CO_2 formation rates. We correlate the observed CO_{ad} oxidation rates with the CO_{ad} coverage measured in-situ with IR. The results show that for low CO_{ad} coverage i) the CO_{ad} oxidation rate increases with CO_{ad} coverage and ii) allow to distinguish between OH_{ad} formation and $CO_{ad}+ OH_{ad}$ reaction as the rate limiting step.

Symposium 8 - Keynote

Surface Chemistry and Dynamics

Adsorption/oxidation of CO On a highly dispersed Pt/C electrocatalyst Studied by combined electrochemical and ATR-FTIRAS

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ATR-FTIRAS measurements combined with linear potential sweep method were conducted to investigate nature of CO adsorbed on a highly dispersed Pt catalyst with average particle size of 2.6nm supported on carbon. A gold film chemically deposited on a Si prism window served as the substrate of the catalyst. ν(CO) bands free from the band anomalies were observed on the catalyst with loading of Pt ranging from 2.5 to 10 μg/cm^2. A new band was observed around 1950-2000cm^{-1} in 100% CO atmosphere in addition to the bands of linear and bridge bonded COs. The new band was not affected by prolonged N$_2$ purging at 0.05V while it almost disappeared at 0.4V. The Stark tuning rate of this band is 41cm^{-1}/V while it is 33 and 48 cm^{-1}/V for atop and bridge bonded COs, respectively. The tuning rate in-between at op and bridge led us to assign this band to asymmetric bridge CO adsorbed on (100) terr aces. Potential dependence of the ν(CO) band intensity of the linear, asymmetric and symmetric bridge COs almost coincide each other when normalized with respect to 0.05V. This is seen in the higher potential region as well where oxidation of the adsorbed C O takes place. This indicates equal reactivity of the three kinds of adsorbed COs under the linear potential sweep conditions at 5-50 mV/s. The ν(CO) frequency of the atop CO is lower than that on polycrystalline and single crystal Pt electrodes by 30-40 cm^{-1} at corresponding potentials. This implies a stronger electronic interactions between CO and Pt nano-particles as well as increasing terrace to edge sites coordination on the Pt nano-particle. However, ν(CO) frequency of the bridge bonded CO is not so different from those observed on the bulk platinum electrodes. Determination of the relative band intensities of the linear, asymmetric and symmetric bridge COs has led us to conclude higher bridge sites occupation on the Pt nano-particles than Pt polycrystalline electrode.
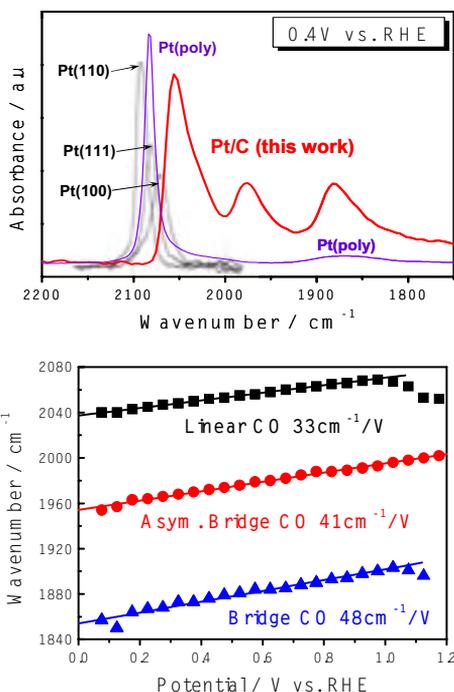
Sfg investigation of pt(hkl)/ethanol interface

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Infrared-visible sum frequency generation vibrational spectroscopy have been applied to study the Pt(110), Pt(100) and Pt(111)/ethanol interface in perchloric acid solution. The electrooxidation of ethanol is of considerable interest because of its application in the anodic part of a fuel cell. Adsorbed CO species are formed during the electrochemical oxidation of ethanol and these species constitute a poison of the Pt electrode surface. Thanks to the capability of SFG[1] to probe selectively and resonantly the interface between media with inversion symmetry.

We have investigated the effects of the electrode surface orientation, the electrode potential and the ethanol concentration on the structure of the interface . The structure of the CO/Pt interface depends strongly on the orientation of the electrode surface and the ethanol concentration. The Pt(110) surface is the most active surface for the ethanol oxidation but also the most poisoned surface by CO. Fig. 1 shows the potential dependence of the SFG spectra for Pt(110) electrode in contact with ($HClO_4$ 0.1 M + [CH_3CH_2OH] 0.1 M) solution [2]. Bands of different species indicating the evolution of the structure of the interface are observed between 1975 and 2050 cm^{-1} .

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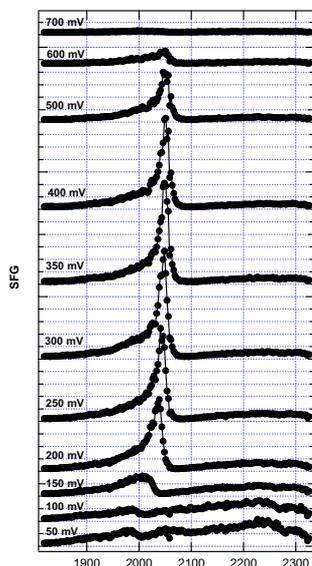
Potential evolved SFG spectra of Pt(110) in contact with 0.1M ethanol in 0.1 M $HClO_4$ solution.
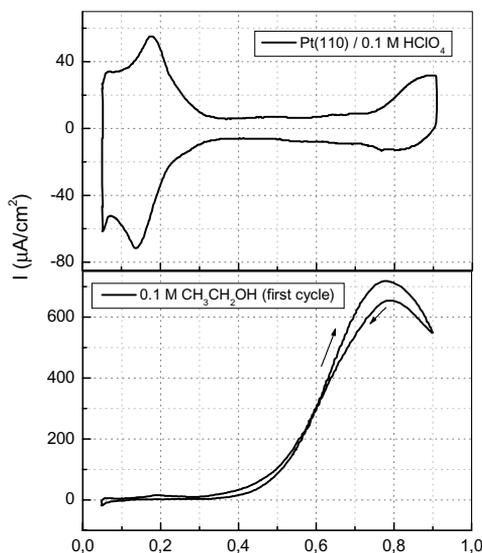
Voltammograms of Pt(110) in contact with 0.1 M $HClO_4$(50mVs^{-1}) and 0.1 M ethanol containing (10mVs^{-1})solution .

Symposium 8 - Keynote

Surface Chemistry and Dynamics

Symposium 8 - Keynote

Surface Chemistry and Dynamics

SERS Characterization of Surface Water and Hydrogen Using Core-shell Nanoparticles Modified Electrodes

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In the past three decades, the development of surface-enhanced Raman spectroscopy (SERS) into a powerful spectroscopic tool had been slower than expected. The major obstacle is the generality of SERS, *i.e.*, only three coinage metals (Au, Ag, and Cu) provide the huge enhancement. This fact severely limited the SERS application in other materials, including transition metals (group VIII B elements) that have a much wider application in electrochemistry and catalysis. Since the mid-1990s, we have developed several surface roughening procedures for electrodes of different metals and maximized the use of a high-sensitivity confocal Raman microscope, enabling us to obtain good-quality SER spectra on the electrode surfaces made from net Pt, Ni, Co, Fe, Pd, Rh and Ru that were traditionally considered to be non-SERS active [1]. These transition metals have been found to exhibit surface enhancement ranging from one to four orders of magnitude. Consequently, the investigation of diverse adsorbates at various transition metal electrodes can be realized. However, we were not able to study some surface species having very small Raman cross section but fundamental and practical importance, such as water molecules, on these weak-SERS-active substartes.

Recently, we utilized a strategy of "borrowing the SERS activity of a Au core" by chemically coating several layers of a transition metal on highly SERS-active Au nanoparticles. These core-shell nanoparticles have chemical properties of the shell but show the enhancement provided mainly by the core underneath. Therefore, their SERS signals can be enhanced as compared to those from bare transition metal substrates. We successfully obtained SERS of water on Pt and Pd surfaces that allows us to scrutinize the interfacial structure of water. The extent of the frequency shifts with potential (*i.e.*, electrochemical Stark effect) for the stretching mode of water on Pt is dramatically less than that of the Pd electrode, which is only about 15 cm^{-1}/V for Pt but about 65 cm^{-1}/V for Pd. Another progress is the simultaneous observation of Raman spectra of surface water and hydrogen for the first time. Based on the SERS results, we propose preliminary models of water adsorption for three representative metal surfaces (Pt, Pd and Au) with or without H adsorption. This development would stimulate and shed light on spectroscopic experimental and theoretical studies of complicated structures of interfacial water and surface hydrogen. The core-shell nanoparticles modified electrodes with its high SERS activity could be widely used. Further improvements of the generality of electrochemical SERS will be discussed.

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Symposium 8 - Keynote

Surface Chemistry and Dynamics

Picosecond Time-Resolved Surface-Enhanced Infrared Spectroscopy at the Electrochemical Interface: Monitoring of the Potential Jump Induced by Visible Laser Pulses

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Kinetic studies by conventional electrochemical methods are limited to reactions having rate constants less than 10^4 s^{-1} due to the time constant of the double-layer charging (typically 0.1-1 ms). A possible way to circumvent this limitation is the use of the so-called laser induced temperature jump method. Irradiation with a short pulse suddenly raises the temperatures of the electrode and the interface, which spontaneously change the rest potential of the electrode. In this presentation, we will report the first picosecond IR monitoring of the interface after visible laser irradiation. CO adsorbed on a Pt electrode was used as the model system to probe the laser-induced potential jump due to the large potential dependent shift of its vibrational frequency.

With the aid of surface-enhanced IR absorption (SEIRA), the CO vibrational mode was observed clearly in the picosecond time scale and a 6-cm^{-1} red-shfit of the C-O vibration was observed after the visible pump pulse irradiation with a delay about 200 ps as shown in Fig.1 (circles). The red-shift is ascribed to the heating of the in-plane frustrated translational mode of CO and the negative shift of potential. These two contributions can be separated with the aid of the transient of the background reflectivity of the electrode (triangles), which is a good measure of the surface temperature. The laser induced potential jump estimated from the Stark tuning shift of 30 cm^{-1} V^{-1} was about –150 mV. The heating of water layers near the surface is mainly responsible for the potential jump through the orientation change of water molecules. This method is promising as a tool to examine ultrafast electrode dynamics.
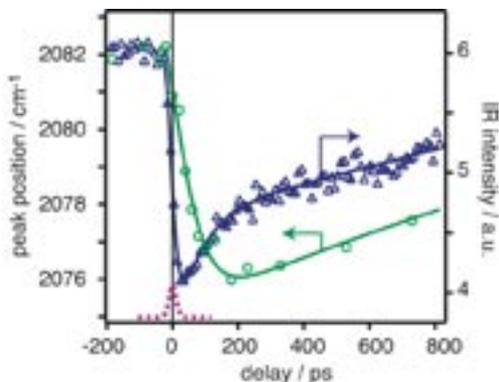
Fig. 1. Temporal profiles of the peak position of adsorbed CO (circle) and a reflected IR intensity measured at 2000 cm^{-1} (open) before and after the irradiation of a 532-nm pump pulse (35 ps, 3 mJ cm^{-2}).

Symposium 8 - Oral

Oxygen reduction on cobalt hydroxide and oxyhydroxide. Experiments and quantum chemical modelling

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Surface Chemistry and Dynamics

Hydrogen peroxide was observed as a by-product during electrochemical reduction of O_2 on electrodes consisting of Co supported oxide films[1] The surface oxides were found to be composed of $Co(OH)_2$ and $CoOOH$, depending on the applied potential. Experimental results show that O_2 reduction starts at a potential where the conduction properties of the $CoOOH$ overlayer changes. This change can be understood to result from the titration of surface sites with electrons, which fills up the electron holes. The experimental data strongly suggest the reaction with O_2 to be site specific. Quantum chemical calculations were employed to model the reduction process, assuming two complementary approaches for describing the site. These comprise hydrated mononuclear models and periodic slab models of a step edge site (see Figure 1).
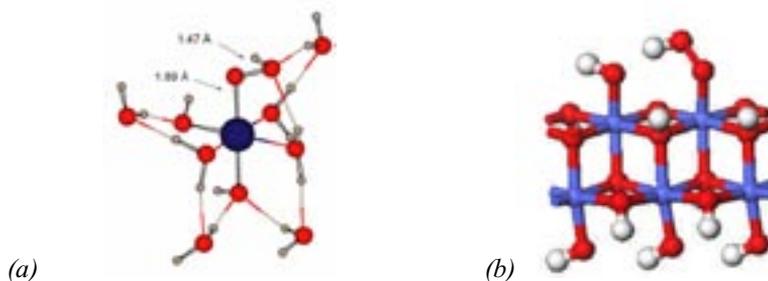
(a)   (b)

Fig. 1. Hydroperoxide formation on CoOOH: mononuclear Co cluster (a) and step edge model (b).

Both types of models were used for investigating the redox properties of Co(III). The results show that Co(II) sites can be formed on the surface at the potentials where O_2 is reduced. The square-planar coordination of the Co(II) site on the step edge invokes the low-spin doublet state. This coordination of the low-spin Co(II) state agrees with the structure of the mononuclear cluster. Both models predict small binding energies for O_2 on Co(II). The hydroperoxides in Fig. 1 are formed by adding a second electron and a proton from the solvent, oxidising the site to Co(III). Release of hydrogen peroxide is accompanied by the reduction of the site back to Co(II). The mechanism for the surface catalyzed H_2O_2 formation is summarized in the form of a redox cycle

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Symposium 8 - Oral

Surface Chemistry and Dynamics

Investigation of Surface Reaction Dynamics by Potentiodynamic Impedance Spectroscopy

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Potentiodynamic electrochemical impedance spectroscopy (PDEIS) acquires variable frequency response and potentiodynamic voltammogram in a single potential scan that can be either unilateral or bidirectional, by probing the interface with sequences of synchronised wavelets and real-time analysis of the response [1]. The 3D PDEIS spectra (Figure 1) present impedance spectra dependences on the potential in the frequency range sufficient for characterisation of the electrochemical interface by frequency analysis. Because of the dynamic nature of PDEIS, the frequency response is analysed just in two or three orders of frequency, but the additional variable (electrode potential) disambiguates the equivalent circuit fit. Due to the continuous dependence of the PDEIS spectra on the potential, equivalent circuit parameters are also continuous functions of the potential and this facilitates strongly the fitting. Equivalent circuit parameters in the narrow frequency ranges are more strictly independent on frequency than the parameters of stationary spectra that are usually recorded in wide frequency ranges; this favours fitting of the PDEIS equivalent circuit parameters to models of interfacial physicochemical processes. The opportunities provided by PDEIS to investigation of interfacial dynamics have been examined in various processes, including reversible and irreversible upd, electrochemically stimulated intercalation, electropolymerisation, diffusion, mutually correlated adsorption of cations and anions.
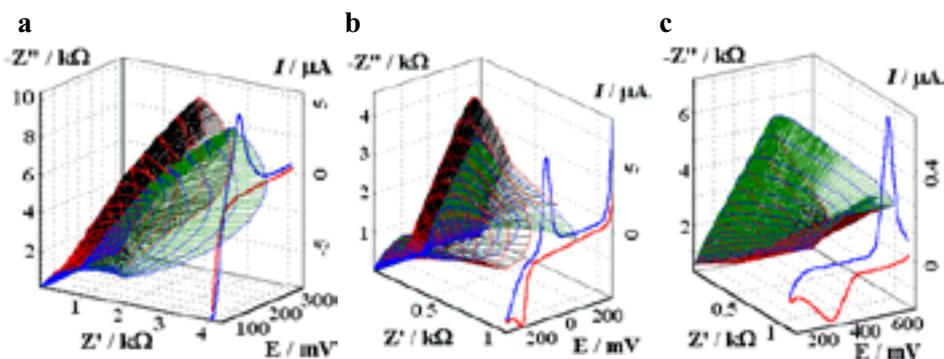
Figure 1. Examples of PDEIS spectra: (a) Cu upd on Te, (b) Pb upd on Te, (c) Te upd on Au.

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Symposium 8 - Oral

Surface Chemistry and Dynamics

Active Sites, Non-equilibrium Surface States and Electrocatalysis

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It is widely accepted that active sites play a vital role in surface catalysis and that such sites involve surface species in high energy, non-equilibrium, states. Well defined, atomically flat surfaces ideally contain no such states, and hence their use as model systems in electrocatalytic studies involving noble metal electrodes is debatable. The involvement of high energy surface in electrocatalysis is strongly indicated by the fact that many electrocatalytic processes (both oxidations and reductions) are triggered in the double layer region, i.e. in the potential range where the stable surface metal atoms are widely regarded as being faradaically inert, but where active surface atoms are assumed to undergo redox transitions.

Two types of interfacial species have been widely ignored in the electrochemistry of noble metals in aqueous media, non-equilibrium states of metals (M*) and the oxidized form of the latter, hydrous or β oxides, $M(OH)_x$. Noble metal surfaces exhibit two limiting types of electrochemistries, M/α oxide and $M*/\beta$ oxide responses. The importance of activated chemisorption in surface catalysis should not be ignored, but it cannot account for the remarkable catalytic behaviour of the Gp. 11 metals (Au, Ag and Cu). For such metals interfacial cyclic redox transitions, involving surface active site species, are assumed to be a dominant feature in electrocatalysis. Such behaviour, based on metal surface disorder or irregularities, also appears to be important in the case of platinum group metals; the evidence to support such a viewpoint will be surveyed.

Symposium 8 - Oral

Surface Chemistry and Dynamics

Cyclic thermammetry – Electrochemical reactions as a function of temperature

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The sensitivity of many electrochemical reactions to temperature has not been explored, with most electrochemical techniques relying on the electrode potential as a fundamental variable. This paper focuses on a new electrochemical technique, termed "cyclic thermammetry", in which the temperature of an electrode process is subject to a linear cyclic sweep whilst the reaction is held at constant electrpode ppotential. We have coined the word "thermammetry" to mean measurement (-metry) of current (-am-, from ampere) as a function of temperature (therm-). Many reactions show strong sensitivity to temperature, and the usual analysis for this is to perform an electrochemical experiment using [potential as the control variable, under thermostatic conditions, with several similar experiments made at different thermostatically controlled temperatures. The fact here is that such experiments show a degree of scatter normally associated with reproducing experiments. By setting the potential and scanning the temperature this irreproducibility is eliminated and continuous changes can be seen. This allows for example, a clear view of whether the anticipated Arrhenius plot expected from a temperature dependence is indeed followed, or whether there is a degree of curvature in the Arrhenius plot. Equally importantly however, is the fact that some electrochemical; reactions show a degree of thermal irreversibility, a feature which cannot be sensed by thermostatic experiments.

Effect of adatoms on the potential of maximum entropy of Pt(111) from pulsed laser experiments.

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It has been shown previously that pulsed laser illumination can be used to generate an ultra-short temperature jump on the surface of single crystal electrodes [1,2]. The coulostatic response to this temperature change allows the estimation of the sign and magnitude of the thermal coefficient of the potential drop at the interphase. The particular potential where this thermal coefficient becomes zero can be identified with the potential of maximum entropy of double layer formation (pme). In this communication we report on the effect of adatom deposition on the potential of maximum entropy. The surface of a Pt(111) single-crystal electrode has been modified with submonolayer coverages of Bi, As, Te, Se, Sn, Pb and S. Figure 1 summarises the dependence of the pme on the nature and coverage of the adatom. Two different behaviours can be distinguished from the plots of figure 1. The more electropositive adatoms (Bi and Pb) cause a marked decrease of the pme at high coverages, while the more electronegative As, Se and S cause a significant positive shift of this parameter. These trends follow the expected change of the potential of zero charge and are likely due to the appearance of surface dipoles between the adatom and the substrate. At low coverage, all adatoms exhibit similar behaviour, reflected in a small increase of the pme. The disruption of the water structure due to the presence of the adatom can account for this trend.
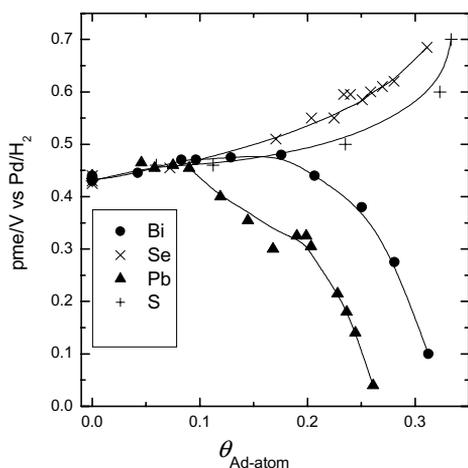
Figure 1: Selected plots of the pme as a function of adatom coverage for Bi, Se, Pb and S modified Pt(111) electrode in 0.1 M $KClO_4$ + 0.1 M $HClO_4$ solution.

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Symposium 8 - Oral

Surface Chemistry and Dynamics

Electrochemical and ftirs characterisation of no adlayers on cyanide-modified-Pt(111) electrodes: the mechanism of nitric oxide electroreduction on Pt

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We report a study, using cyclic voltammetry and FTIRS, of NO irreversibly adsorbed on a cyanide-modified Pt(111) electrode. NO adlayers were formed by immersion of the cyanide-modified Pt(111) electrode in an acidic solution of KNO_2. The behaviour of NO adsorbed on the cyanide-modified electrode is very similar to that of NO on the clean Pt(111) surface, suggesting that adsorbed cyanide (saturation coverage $\theta_{CN} = 0.5$) behaves simply as a third body, blocking some of the surface sites but leaving the free Pt sites unaffected. Comparison of the voltammetric profile for NO electroreduction on Pt(111) and on cyanide-modified Pt(111) electrodes has allowed us: (i) to confirm that the reduction of three-fold hollow NO and atop NO on Pt(111) electrodes occurs in two distinct reduction peaks, as previously proposed by Rosca et al. [1]; (ii) to suggest that the reduction of irreversibly adsorbed NO layers on Pt electrodes can proceed through two possible paths, one involving an EE mechanism in which the rate-determining step (rds) is an Eley-Rideal reaction, with a direct proton transfer from the solution to adsorbed NO, and the other involving an EC mechanism in which the rds is a Langmuir-Hinshelwood reaction of adsorbed NO with adsorbed H. The availability of adsorbed hydrogen determines which path is followed by the reaction; (iii) to identify the smallest atomic ensemble for the reduction of NO on Pt as being composed of two adjacent Pt atoms.

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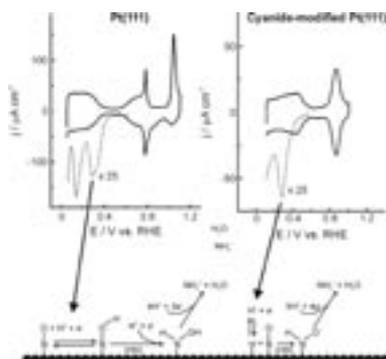
Symposium 8 - Oral

Surface Chemistry and Dynamics

Specific adsorption of halide anions from nonaqueous solutions on controlled-surface polycrystalline silver electrodes

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Specific adsorption studies play a determining role in the mechanistic elucidation of electrochemical processes, either non-catalytic (where adsorbed species not involved in the reaction act as a barrier for the electron transfer), and catalytic (in terms of specific adsorption competition with the species involved in the reaction). Furthermore, dealing with the electrocatalytic reduction of organic halides, the selected model process for our current mechanistic studies on electrocatalytic dissociative electron transfers [1-2], an incipient adsorbed halide anion is one of the three species involved in the three-centre intermediate of the process, promoting direct formation of the final reaction products in a concerted mechanism, with respect to a stepwise one including a stable radical anion intermediate; moreover, specifically adsorbed anions can be among the products of such reduction process, with significant implications on both the process thermodynamics and kinetics. However, unfortunately, halide specific adsorption has hitherto been exhaustively elucidated by authoritative schools only in the aqueous medium on single crystal electrodes, while data in organic solvents are still very few.

In this context, the Authors have performed a systematic investigation on the specific adsorption of bromide and iodide anions on controlled-surface polycrystalline silver cathodes, in different model organic solvents (ACN, PC, DMF, MeOH, AC, DMSO), combining differential capacity and impedance experiments with a recently proposed "indirect" voltammetric method based on the monitoring of the negative shift of the reduction peak potential of a "probe" organic halide molecule induced by progressive additions of halide anions, resulting in increasing adsorption competition. Notwithstanding the complexity of the target systems (organic solvents, polycrystalline surfaces), the three experimental methods provide consistent results. In particular, bromide and iodide anions are specifically adsorbed onto polycrystalline silver electrodes in the organic solvents studied. The adsorption process, which is slow and it is characterised by a partial charge transfer and by a slow diffusion step, is modulated by the different coordination abilities of the solvents for the species involved in the adsorption.

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Symposium 8 - Oral

Surface Chemistry and Dynamics

From reactions at steps to reactions at monoatomic rows: adsorption, hydrogenation and hydrogen evolution

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Step decoration of vicinally stepped platinum single crystals was achieved for many metals and can be easily monitored by cyclic voltammetry due to the suppression of the corresponding hydrogen adsorption at step sites. [1, 2] Step decoration for Pd at stepped Au surfaces is more difficult to prove. Au(111), Au(332) and Au(331) were used as the substrate for palladium deposition in the UPD-regime (cf. [3, 4]). Preparation and Pd deposition were checked by STM. Cyclic voltammetry shows two Pd-oxidation peaks, the first one being almost independent of coverage; it is therefore ascribed to Pd decorating steps. Hydrogen adsorption on the modified stepped surfaces, but not on Au(111)/Pd, takes place only when more than a critical amount of Pd has been deposited. A voltammetric peak at ca. 0.3 V vs. RHE is related to the adsorption of hydrogen at palladium terraces, at this potential the adsorption of hydrogen on steps is negligible.

Small amounts of Pd are extremely active for hydrogen evolution.[5] When normalizing the rate at stepped surfaces to the amount of Pd, the rate incrases at coverages below that corresponding to step decoration.

Using differential electrochemical mass spectrometry (DEMS), benzene adsorbing at step sites was distinguished from that adsorbing at terraces. Carbon monoxide at step sites is oxidized only at more positive potentials than that adsorbed at terrace sites, although the existence of steps is a prerequisite for the oxidation of CO from terraces at low potentials. Ethene forms an irrevesibly bound species on terraces; however, the adsorbate from steps - including monoatomic Pd rows – is easily hydrogenated at low potentials. All these species also adsorb at monoatomic rows of Pd.

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Influence of catalyst particle size on the CO_2 yield of ethanol oxidation on Pt/C electrodes: a DEMS study

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Cyclic voltametry and differential electrochemical mass spectrometry were used to evaluate the effect of particle size on the complete oxidation of ethanol over carbon-supported Pt catalysts. The ethanol concentrations studied were 0.1 M and 1 M. The sizes of the Pt catalysts ranged from 2 to 14 nm as the composition of the catalysts was varied from 10% to 80%. It was observed that the CO_2 yield is strongly dependent on the combination of catalyst particle size and alcohol concentration. For larger particle sizes (7 to 14 nm), the efficiency of CO_2 production decreases with increasing alcohol concentration. Namely, for an ethanol concentration of 0.1 M, the CO_2-related current varies from ~0% to 50% of the overall faradaic current observed in the potential from 0.6 to 0.9 V. For an ethanol concentration of 1 M, the CO_2-related current varies from ~0% to 20% of the overall faradaic current. For smaller particle sizes (2-3 nm), the reverse effect is observed: the efficiency for CO_2 production increases with increasing alcohol concentration. At low ethanol concentrations (0.1 M), the CO_2-related faradaic current in the potential range from 0.6 V to 0.9 V varies from ~0 % to 20% of the overall faradaic current. At high ethanol concentrations (1 M), the CO_2-related current is larger, ranging from ~0% to 40% of the overall faradaic current. Signficantly, at higher ethanol concentrations, the smaller particle size catalysts are two times more efficient towards the complete oxidation of ethanol than the larger particle size catalysts. It is suggested that the improved efficiency of smaller particles in concentrated solutions is due to an increase in turn over frequency of the platinum sites. This increased turnover may promote the adsorption of oxygenated species at lower potentials and thus favor earlier oxidation.

Symposium 8 - Oral

Surface Chemistry and Dynamics

Symposium 8 - Oral

Surface Chemistry and Dynamics

Nature and Strength of the Pt(111)-Ag$_{UPD}$ Surface Bond and the Ag$_{UPD}$ – Ag$_{UPD}$ Lateral Interactions

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The under-potential deposition (UPD) of hydrogen and metals has been a subject of extensive research for decades. Despite the existence of qualitative data for various cation-anion and substrate combinations, little is known about the nature of the surface forces acting between the substrate and the adsorbate. Our previous research on the thermodynamics of UPD H on Pt(111) based on temperature-dependent studies has allowed us to determine the Pt(111)-H$_{UPD}$ surface bond energy, $E_{Pt(111)-Hupd}$. This effort has been extended to the research on model atomic and molecular surface modifiers (S$_{ads}$, C$_6$H$_{6\,ads}$) and their influence of the thermodynamics of UPD H. In this contribution, we present temperature-dependent study on UPD Ag in aqueous H$_2$SO$_4$ + Ag$_2$SO$_4$ followed by a data analysis. We utilize cyclic-voltammetry (CV) and analyze qualitative and quantitative changes in CV transients brought about by T variation in the 273 – 333 K range. We observe two cathodic (Ag$_{UPD}$ deposition) and two anodic (Ag$_{UPD}$ stripping) CV peaks that shift toward lower potentials as the temperature is raised. Their individual charge-density values remain the same, thus indicating that the amount of deposited and stripped Ag is unaffected by the temperature variation. In addition, the total cathodic and anodic charge-density values balance, which proves that there is no formation of a surface alloy under the current experimental conditions. We utilize a general adsorption isotherm and determine the Gibbs energy of adsorption (ΔG°_{ads}) and desorption (ΔG°_{des}) for the 1st and 2nd monolayer (ML) of Ag$_{UPD}$ on Pt(111). Then, we determine the energy of lateral interactions (ω), entropy of adsorption (ΔS°_{ads}), and enthalpy of adsorption (ΔH°_{ads}) for the 1st and 2nd ML of Ag$_{UPD}$. Knowledge of ΔH°_{ads} the enthalpy of adsorption leads to the first-ever determination of the Pt(111)-Ag$_{UPD}$ surface bond energy. We observe that the Pt(111)-Ag surface bond energy is stronger for the 1st ML of Ag that for the 2nd ML. We also observe that the thermodynamic state functions of adsorption and desorption of the 1st and 2nd ML of Ag$_{UPD}$ assume different values, as expected, since the 1st ML of Ag$_{UPD}$ is bonded to Pt(111), while the 2nd to the Ag$_{UPD(1\,ML)}$-modified Pt(111).

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Surface Chemistry and Dynamics

CO electro-oxidation with Pt-deposits on Au(hkl) and quasi-single crystalline gold film electrodes

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The electro-oxidation of CO is an important reaction for fuel cell applications because of CO poisoning of the anode. Understanding of this reaction on platinum-type metals is crucial for the further development of CO tolerant fuel cell catalyst. Many papers were reported for the CO electro-oxidation reaction on Pt single-crystal electrodes as well as on electrode surfaces modified with Pt nanoparticles. The investigation of the relationship between the electrocatalytic behavior of Pt(hkl) electrodes and platinum particles deposited on "inert substrates" such as gold, has been explored because of fundamental aspects as well as of applied reasons to improve the performance of low temperature fuel cell catalysts.

The aim of the present study is to characterize Pt-particle modified Au(hkl) and quasi-single crystalline film electrodes, and to investigate the effect of the surface structures of the gold electrodes on the electro-oxidation of CO adsorbed on platinum particles by electrochemical and spectroscopic methods.

The preparation of platinum particles deposited on Au(hkl) and quasi-single crystalline film electrodes was carried out using two approaches. The first one involves the spontaneous deposition of tetrachloroplatinate from 100 μM acidic solution onto Au electrodes, contact time 1 ~ 10 min, and the subsequent electro-reduction in a separate electrochemical cell in K_2PtCl_4 - free electrolyte [1]. As a second method we applied the potential-controlled electrochemical deposition from 100 μM K_2PtCl_4 acidic electrolyte [2].

The CO electro-oxidation on the platinum modified Au(hkl) and quasi-single crystal-line film electrodes was studied by electrochemical methods and surface enhanced infrared spectroscopy (SEIRAS). Measured current – potential curves illustrated that this reaction depends on the structure of the gold substrates and on the coverage of the Pt - particles. Furthermore, the potential of zero total charge (PZTC) of the Pt-modified Au(hkl) and thin film electrodes was investigated by CO displacement measurements. The values of the PZTC for the Pt-particle modified Au(hkl) electrodes were consistent with results reported for Pt(hkl) electrodes [3]. These results imply that the structures of the Pt - particles are strongly affected by the substrate morphology. Our SEIRAS studies showed on-top adsorption of CO for sub-monolayer Pt deposited on quasi-single crystalline gold templates. Higher coverages of Pt up to one monolayer revealed CO adsorbed in on-top and bridge sites. These results suggest that the CO adsorption and subsequent electro-oxidation depend on size and morphology of the deposited Pt particles. The contribution will present a comprehensive discussion on this subject

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Single probe characterization of the surface of platinum nanoparticles

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Practical electrocatalyst are normally based on nanoparticles supported on an inert electrode material. Since most of the electrochemical reactions are surface sensitive, the surface structure of the nanoparticle has to be also characterized in order to optimize the electrocatalyst performance. The irreversible adsorption of Ge and Bi has been used to determine (100) and (111) terrace sites, respectively, on a given platinum sample [1-3]. In this work, irreversible adsorption of Te and Tl will be used to simultaneous determine the fraction of (111) and (100) sites. The results can be compared with those obtained with Bi and Ge.

The surface redox process of adsorbed tellurium on the Pt(111) electrode takes place at 0.82 V in a well defined peak. The behavior of this redox process on the Pt(111) vicinal surfaces indicates that the tellurium atoms involved in the redox process are only those deposited on the (111) terrace sites. Hence, this charge density can be used to measure the number of (111) terrace sites on any given sample. Structural information about tellurium adsorption is obtained from atomic resolution STM images for the Pt(111) and Pt(10,10,9) electrodes. On Pt(100) electrodes, the surface redox process of adsorbed tellurium takes place at 1.03 V in a well defined peak. STM images indicate that the adsorbed surface structure of the tellurium adlayer is ($\sqrt{2}x\sqrt{2}$) R45°, corroborating the coverage value measured from the voltammetry. However, the oxidation of the adsorbed tellurium on the (110) sites also takes place in the same potential range. For that reason this contribution at 1.03 V cannot be used to determine (100) sites. Nevertheless, it is possible obtain the fraction of step and edge sites on a platinum surface, by using the fraction of (100) sites determined from Ge probes.

A similar situation is found for irreversibly adsorbed Tl on (100) and (111) sites in perchloric acid solutions. In this case, the contribution of the redox process for adsorbed Tl on (100) and (111) ordered sites appear at different potentials without overlapping from other contributions. These contributions are only observed for terraces having more than 4 atoms. Adsorbed Tl can be used to determine simultaneously the fraction of sites on wide (100) and (111) ordered domains.

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Electrocatalytic properties of UHV-grown AuPt/Pt(111) model surfaces

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In a systematic study combining preparation and quantitative STM-investigation of model surfaces in ultrahigh vacuum (UHV) with their electrocatalytic characterization in a miniature flow cell, we have investigated structurally well-defined AuPt model surfaces, in particular, epitaxially growth Au thin layers (1-3 ML) and atomically dispersed Au_xPt_{1-x} surface alloys on Pt(111). The latter can be formed by annealing of Au layers on Pt(111) despite the bulk immiscibility of Au and Pt, and allow for an analysis of their atomic distribution by atomically resolved STM (see images below).

The microscopic structure (layer thickness of Au films, atomic distribution in the 2D Au_xPt_{1-x} alloys, density of step sites) of the respective surfaces is linked to their electrochemical adsorption and reaction properties as determined by base voltammetry and by technically relevant test reactions under flow cell conditions (hydrogen oxidation and evolution, oxidation of CO or methanol, oxygen reduction). The roles of electronic ligand, lattice strain, and ensemble size effects in the behavior of the distinct model systems are discussed.
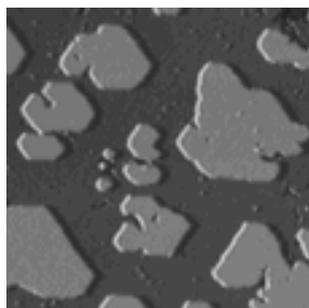
| 1.4 ML Au / Pt(111) thin film | $Au_{92}Pt_8$ / Pt(111) surface alloy | $Au_{44}Pt_{56}$ / Pt(111) surface alloy |
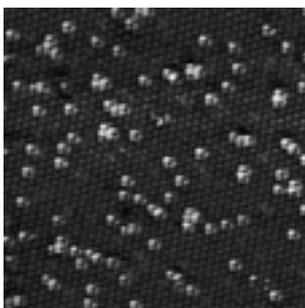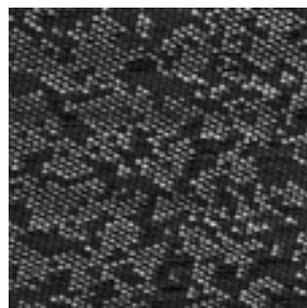
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Surface Chemistry and Dynamics

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Surface Chemistry and Dynamics

A First-Principles Analysis of the Electrooxidation of Methanol over Pt and Pt-based Alloys

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A novel ab initio approach for modeling electrochemical reactions at the metal-solution interface is developed and used to simulate the electrooxidation of methanol and CO over Pt and Pt-based alloys. The approach can be used to simulate overall reaction energies as well as activation barriers as a function of electrode potential, thus allowing for the prediction of electrode polarization curves. This method is applied to elucidate the key elementary steps that control the electrocatalytic oxidation of methanol over different model surfaces.

Recent evidence from both spectroscopic studies of the solution phase as well as surface intermediates have identified the presence of CO, HCO, H_2CO, and HCOO(H) intermediates. It is now commonly believed that methanol oxidation occurs via two parallel paths. The first path leads to the formation of CO, which is subsequently oxidized to CO_2. The second path leads to the formation of a CH_xO intermediate that can either desorb or subsequently oxidize to CO_2 without producing CO. Based on solution phase measurements of the products, Iwasita (Iwasita, 2002) suggested that the primary path passes through CO whereas a secondary path exists where methanol is dehydrogenated to formaldehyde which is seen in appreciable amounts in the solution phase. Osawa (Osawa 2003) also suggested a dual path but suggested that the secondary path proceeds through the formation of surface formate intermediates HCOO(H) which are seen via in-situ surface enhanced infrared experiments. Using combined chronoamperometry and fast cyclic voltametry Wieckowski et al. (Wieckowski 2000) were able to show that the dual path occurs on Pt(111) at potentials higher than 0.35 V. Despite these efforts the elementary steps which control the mechanism are not very well understood.

Previously we showed through the use of ab initio electrochemical calculations that the dehydrogenation of methanol can occur through both a primary path that results in adsorbed CO and a secondary path which leads to formaldehyde which is consistent with the results presented by Iwasita. In this talk we report on the oxidation pathways that result in formate as well as CO_2 production. We present a detailed analysis of the dependence of CO oxidation over different model Pt-Ru surface ensembles. The method is applied to illustrate the dual role of Ru in reducing the overpotential associated with CO oxidation at the anode. Both ligand as well as bifunctional effects act to reduce the overpotential down to 0.5 when Ru is added. The bifunctional effect, however appears to be the more predominant of the two thus enabling water to activate at much lower potentials. The activation barriers of elementary oxidation steps are reported over the pure Pt and different Pt/Ru alloy surfaces at varying potentials, and ab initio predicted CO oxidation rate constants are compared with data from chronoamperometry. In addition, a comprehensive set of simpler gas-phase/surface calculations were carried out in order to screen various different bimetallic systems for their ability to carry out specific reaction steps.

New Insight into The Electro-catalysis of Small Organic Molecules on Ru(0001) Electrode

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The structure, reactivity and surface catalytic processes of the well-defined Ru(0001) electrodes towards the adsorption and (electro-)oxidation of small organic fuel molecules in various electrolyte solutions have been studied by *ex-situ* (emersion) electron diffraction and Auger spectroscopy and *in-situ* (electrochemical) variable-temperature FTIR spectroscopy, and the new insight into the surface electro-catalysis has been obtained at molecular level.

It has been shown that the Ru(0001) electrode undergoes the potential-dependent formation of well-defined and ordered oxygen-containing adlayers of (2x2)-O(H) and (1 x 1)-O(H) and finally $RuO_2(100)$ oxide phases in perchloric acid solution. The adsorption and electro-oxidation of methanol, formic acid, formaldehyde and CO at the Ru(0001) electrode have been investigated as a function of temperature, potential and time using *in-situ* FTIR spectroscopy, and it was found that the oxide phases have a marked effect upon the reactivity of the surface towards the adsorption and (electro-)oxidation of such fuel molecules. Both linear (CO_L) and threefold-hollow (CO_H) binding CO adsorbates were observed on the Ru(0001) electrode from either the direct CO electrochemical adsorption or the chemisorption of formic acid and formaldehyde in 0.1 M $HClO_4$ at lower potentials where the (2x2)-O(H) layer was present. The (2x2)-O(H) phase was found to be inactive towards CO_{ads} (electro-)oxidation. The electro-oxidation of CO_{ads} took place *via* reaction with the active (1 x 1)-O(H) surface oxide/hydroxide phase. The remarked increase in the surface reactivity was observed on the novel $RuO_2(100)$ phase where bridging O atoms and co-ordinatively unsaturated Ru atoms acting as active sites.

To further discriminate between RuOH and RuO as the active surface species, novel experiments on the oxidation of CO_{ads} at open circuit conditions were performed, and the data obtained shows clearly that a significant fraction of the oxidation of adsorbed CO takes place *via* a non-Faradaic chemical process. The effect of thermal activation and the influence of anions and pH of the electrolytes were also evidenced.

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Surface Chemistry and Dynamics

Surface Chemistry and Dynamics

Electrocatalytic properties of metallic monolayers on foreign single crystal electrodes

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The potential of zero charge (pzc) of silver monolayers on different single crystal electrodes Au(111), Pt(111)[1,2], Pd(111), Ir(111) and Rh(111) has been determined in perchlorate solution by measuring capacitance-potential curves. The pzc of the Ag overlayers varies in the potential range between –0.8 V and –0.45 V, i.e., in a 0.35 V range. This variation in pzc is discussed in relation to available data for the electronic structure of the various systems.[3] While no dependence on the lattice constants of the substrates was found, a systematic change of the pzc with the location of the calculated d-band centre was observed (Fig. 1). The pzc of thick Ag deposits is always found to be identical to the pzc of Ag(111). In some cases – Au(111) and Pt(111) – already two monolayers of Ag reflect the properties of massive silver. Structural details about the Ag overlayers, e.g. taken from STM studies, add to the interpretation of electrochemical properties. The results are compared to a similar study with Pd monolayers.[5,6] Consequences of altered double-layer properties on electrocatalytic reactions will be addressed.

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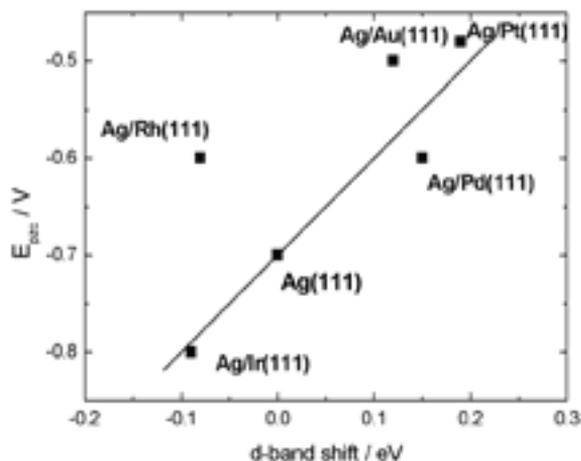
Fig. 1. Correlation of pzc for Ag monolayers with the d-band shift.

S8·O-17

Water-nafion interfacial interactions probed by infrared spectroscopy

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The application of infrared spectroscopy in the study of fuel cell polymer membrane materials is revealing information about interfacial interactions of water with different functional groups within pores of Nafion. Simple transmission measurements performed on freestanding Nafion 112 (50.8 μm thickness) and sub-micron cast films of Nafion exchanged with Na^+ or proton show the presence of water bound to channel walls, in addition to bulk-like water. In Na^+ exchanged films, interfacial water is detected as 1-2 sharp bands appearing in the spectral region between 3720 cm^{-1} and 3670 cm^{-1}. The lower energy feature has been observed in earlier studies and associated with water interacting with $-CF_2$ rich regions of the polymer. The higher energy band coincides with vibrational features of water at salt solution-air interfaces; hence, the band near 3700 cm^{-1} appearing in spectra of Na^+ exchanged Nafion is ascribed to water in regions rich in $-SO_3^-$ groups. In spectra of proton-exchanged Nafion 112, the lower energy feature of the pair can be detected. However, bands associated with hydronium ions tend to be more dominant. After dehydrating a proton-exchanged Nafion film at 90 °C under a few torr of vacuum, H_3O^+ bands are lost and those for protonated sulfonic acid ($-SO_3H$) groups become apparent. Least-squares modeling techniques are being applied to probe the kinetics of water uptake by Nafion 112 and to resolve features associated with the different environments for interfacial water. Measurements with sub-micron thick cast films of Nafion revealed polymer backbone and sidechain groups. A complex band structure in the region 1300 – 1200 cm^{-1} associated with overlapping modes of $-CF_2$ and $-SO_3$ groups was understood by performing Gaussian fits to spectra of dry films and films in different states of hydration.

Characterization of a Thiolipid SAM of DPTL - a Spacer in Model Membrane Systems

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The following paper presents the study of the archaea analogue amphiphilic thiolipid DPTL (2,3-di-phytanyl-sn-glycerol-1-tetraethylene glycol-DL-α-lipoic acid ester lipid) by electrochemistry and PM-IRRAS which finds application as a spacer molecule in tethered lipid bilayers. Tethered lipid bilayers are employed in the basic research of transmembrane proteins but also for biosensor applications. The molecules have a lipoic acid headgroup containing two thiol functions. The headgroup acts as a tether and gets chemically adsorbed on the Au surface. The middle part of the DPTL consists of an ethylene glycol spacer with four ethylene glycol units. This part of the molecule is supposed to form the hydrated subphase serving as water reservoir in the model membrane system. Its conformation is expected to be helical, as it has been discussed in the literature for polyethylene glycol chains [12-3]. The tail of the molecule is formed by two isoprenoid chains which carry four isoprene units each. These phytanyl chains are highly hydrophobic and very stable. Au(111) has been chosen as supporting substrate because it behaves as a capacitor over a broad range of applied potentials at the interface with an electrolyte solution. The single crystalline (111) face is the most stable gold plane and provides a very homogenous charge distribution across the electrode surface. Chronocoulometry measurements [4] on DPTL layers transferred in the Langmuir-Blodgett trough from the air-water interface have been employed to determine the charge per molecule. Infrared spectroscopy under electrochemically controlled conditions allows a close examination of the behaviour of DPTL at the Au(111) / electrolyte interface. PM-IRRAS studies give information about the conformation and orientation of the DPTL film. Thus, the influence of the electric field on the orientation and on the hydration of the polar regions of the molecule and on the packing and conformation of its phytanyl chains can be described. The hydration of the film has been studied with PM-IRRAS by looking at the C=O stretching region which provides information about the grade of hydration at different electrode potentials. With the help of electrochemical PM-IRRAS studies the conformation and hydration properties can be determined which is used for a complete characterization of the tether molecule DPTL.

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Surface Structure and Electrochemistry of Model Electrocatalysts

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Since the early days of modern surface science, a main goal in the electrochemical community has been to find correlations between the microscopic structures formed by surface atoms and adsorbates and the macroscopic kinetic rates of a particular electrochemical reaction. The establishment of such relationships, previously only developed for catalysts under ultrahigh vacuum (UHV) conditions, has been broadened to embrace electrochemical interfaces. In early work, determination of the surface structures in an electrochemical environment was derived from *ex situ* UHV analysis of emersed surfaces. Although such *ex-situ* tactics remain important, the relationship between the structure of the interface in electrolyte and that observed in UHV was always problematic and had to be carefully examined on a case-by-case basis. The application of *in situ* surface sensitive probes, most notably synchrotron based surface x-ray scattering (SXS) and scanning tunneling microscopy (STM) has overcome this "emersion gap" and provided information on potential-dependent surface structures at a level of sophistication that is on a par with (or, even, in advance of) that obtained for surfaces in UHV.

In this talk I will present recent results of *in situ* SXS and electrochemistry studies of both monometallic and bimetallic surfaces in which Pt is the active surface atom. Measurements of various potential-induced reactions on these surfaces, for example, the oxidation of carbon monoxide and the oxygen reduction reaction, and the effect of solution temperature on the reactions will be discussed. By varying the second metallic component in the alloy surfaces in the 3d series, it is possible to establish trends in catalytic activity across the periodic table. The results for single-crystal surfaces imply that nanoparticle materials for fuel cell catalysts can be designed from fundamental principles.

Viscosity effects in the interfacial ET reactions: interplay between the solvent dynamics and electronic structure of reactants

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Stochastic theories are employed to explore interfacial electron transfer reactions (one-step electrochemical reduction at a mercury electrode) proceeding in various liquid media. The solutions are described in terms of available experimental dielectric spectra. The reactants under consideration differ in their intramolecular reorganization: cobaltocene (small), $[Cr(EDTA)]^-$, $[Co(EDTA)]^-$ and Pt(II) aquachlorocomplexes (noticeable), peroxodisulphate and chloroantracene (bond break). The Agmon-Hopfield formalism (Sumi-Marcus model) [1] is used to calculate the rate constants as a function of the electrode overvoltage. The intramolecular reorganization is addressed in the framework of DFT calculations. Special attention is paid on aqueous sucrose and glucose solutions and pure non-aqueous solvents, which reveal the "non-Debye" nature. An approach is suggested to treat such media using an "effective" frequency factor [2,3] depending on the solution concentration. Changes in the Franck-Condon barrier induced by the reactant-electrode coupling are considered by using the Anderson-Newns model Hamiltonian [4]; quantum modes of the solvents are taken into account when calculating the rate constants. Several qualitative effects are predicted and explained in terms of the saddle point avoidance. Various types of the solvent effects are considered systematically in the context of experimental data treatment. Some ways are proposed to address the changes of the double layer structure, degree of ionic association in the solution bulk and the distance of closest approach (mixed with the true effects of relaxation time and permittivity). The original data on adsorption of carbohydrates are employed, in order to illustrate the principles of a correct choice of the viscous additive. The results of model calculations are discussed in the light of both original experimental data, and those known from literature.

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Surface Chemistry and Dynamics

Dynamics of adsorbed CO on a Pt electrode surface under irradiation of ps laser pulses

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【**Introduction**】The determination of time dependent structure of short-lived intermediates on surface is important in understanding surface chemical reactions. The observation of the species is, however, difficult by means of conventional surface vibrational techniques. Time-resolved vibrational spectroscopy using sum-frequency generation (SFG) process is one of the powerful tools to investigate the ultrafast surface reaction dynamics. In this study, transient site hopping behavior of CO adsorbed on Pt electrode surface was observed using time-resolved SFG spectroscopy (TR-SFG) initiated by picosecond laser pulse excitation.

【**Experimental**】TR-SFG experiments was carried out by ps Nd:YAG laser system.[1,2] Tunable picosecond infrared pulses for SFG were generated by a frequency conversion of 352 and 1064 nm pulses using an OPG/OPA/DFG processes. SFG measurements were performed in $HClO_4$ solution containing HCHO in a three-electrode spectroelectrochemical cell under potential control.

【**Result and Discussion**】At 0 mV, HCHO is known to adsorb dissociatively to form CO adlayer on a Pt electrode surface. SFG peak due to the stretching mode of the CO linearly bounded on top sites was observed at 2064 cm^{-1}. Upon the irradiation of intense 532 nm pump pulse (pump fluence: ca. 0.24 J/cm^2), the intensity of this peak was decreased and recovered to the initial value within ca. 16 ps. Transient SFG spectra (Fig. 1) show that this intensity decrease was accompanied with a peak broadening of the spectra and an appearance of new broad peak centered around ca. 1980 cm^{-1}. One of the plausible reasons for the SFG spectral change is the change of the CO adsorption site from the on-top to other multi-bound sites. Effects of potential and CO coverage on dynamics of adsorbed CO were also investigated.

Fig. 1 Transient SFG spectra of CO stretching region at the delay time of –80, 0, and 70 ps. Potential was kept at 0 mV.

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Surface Chemistry and Dynamics

Thermodynamic analysis of the temperature dependence of OH adsorption on Pt(111) and Pt(100) electrodes in acidic media in the absence of specific anion adsorption

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The effect of temperature on the voltammetric OH adsorption on Pt(111) and Pt(100) electrodes in perchloric acid media has been studied. From a thermodynamic analysis based on a generalized adsorption isotherm, ΔG^o, ΔH^o and ΔS^o values for the adsorption of OH have been determined. On Pt(111), the adsorption enthalpy varies between -265 and -235 kJ mol^{-1}, becoming less exothermic as the OH coverage increases. These values are in reasonable agreement with experimental data and calculated values for the same reaction in gas phase. The adsorption entropy for OH adsorption on Pt(111) ranges from -200 J mol^{-1}K^{-1} (low coverage) to -110 J mol^{-1}K^{-1} (high coverage). Figure 1 shows the calculated values of ΔG^o, lateral interaction parameter (ω), and ΔG^o in the limit of zero coverage for the process $OH + Pt(111) \rightleftharpoons Pt(111)\text{-}OH$. On the other hand, the enthalpy and entropy of hydroxyl adsorption on Pt(100) are less sensitive to coverage variations, with values ca. $\Delta H^0 = -280$ kJ mol^{-1} and $\Delta S^0 = -180$ J mol^{-1}K^{-1}. The different dependence of ΔS^0 with coverage on both electrode surfaces stresses the important effect of the substrate symmetry on the mobility of adsorbed OH species within the water network directly attached to the metal surface.
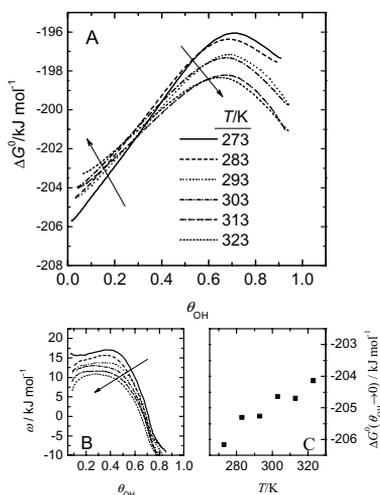
Figure 1. A) Plot of ΔG^0 for the process $OH + Pt(111) \rightleftharpoons Pt(111)\text{-}OH$ as a function of θ_{OH} for different temperatures. B) Plot of the lateral interaction parameter, $\omega(\theta_{OH})=(\partial \Delta G^0 /\partial \theta_{OH})_T$, as a function of θ_{OH}. C) Extrapolated values of ΔG^0 to zero coverage as a function of the temperature. Arrows in A and B indicate the increase of temperature.

Solutions of the Stefan problem applied to a solid phase growth on substrates of different geometries including the test of the theoretical equations

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The Stefan problem is related to transport phenomena contributions at moving interfaces. These mathematical problems are often called Stefan problems, irrespective of the driving force, and are found in a number of processes occurring in different areas of natural science an technology.

The Stefan problem appears under certain conditions in metal electrodeposition via a mass transport contribution in addition to diffusion, migration and convection. In this work the rate equations for the growth of a solid phase involving a moving front are obtained.

The paper refers to solutions of the Stefan problem in the 2D space for different geometries considering the boundary of a solid phase according to a known displacement law. The solutions for the growth of a solid phase on a plane, a spherical and a cylindrical substrate are given. In all cases, in the absence of convection and surface roughness effects, the phase growth kinetics is determined by diffusion and advection, the latter being due to the linear displacement of the growth front with time. The theory predicts two limiting kinetic situations, namely a diffusion control when the time and/or the radius of the substrate approach zero, and an advection control for the reverse conditions. For the spherical substrate, when its radius tends to infinity, the kinetics of the process approaches that found at the plane plate substrate. Theoretical current transients are tested utilizing growth pattern data for the formation of 2D silver dense branching electrodeposits on a plane plate cathode in a quasi-2D cell, and silver electrodeposits on spherical cathodes employing high viscosity plating solutions. Finally, the contribution of advection in a number of electrochemical processes is explored.

Symposium 8 - Oral

Surface Chemistry and Dynamics

Mechanistic aspects of electrocatalytic oxidation of ammonia on Pt(111) and Pt(100) surfaces

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This contribution describes the results of a detailed mechanistic study of ammonia electrooxidation on Pt(111) and Pt(100) surfaces, aiming particularly at understanding the initial stages of the reaction and explaining the differences in activity between these two surfaces. Taking the Gerischer-Mauerer mechanism [1] as starting hypothesis, we reconsider the mechanistic aspects of ammonia electrooxidation. The Pt(100) and Pt(111) surfaces were chosen as model electrocatalysts: the former is exceptionally active and the latter is inactive in ammonia oxidation to dinitrogen. On the basis of our experimental results, as well as relying on the available theoretical and ultra-high vacuum data, we propose a more detailed mechanistic picture of ammonia oxidation on the two surfaces and, importantly, identify factors controlling the activity of platinum electrocatalyst in dinitrogen production. [2]

The electrocatalytic oxidation of ammonia on Pt(111) and Pt(100) has been studied using voltammetry, chronoamperometry, and *in situ* infrared spectroscopy.

The oxidative adsorption of ammonia results in the formation of NH_x (x=0-2) adsorbates. On Pt(111), ammonia oxidation occurs in the double-layer region and results in the formation of NH and, possibly, N adsorbates. The experimental current transients show a hyperbolic decay (t^{-1}), which indicates strong lateral (repulsive) interactions between the (reacting) species. On Pt(100), the NH_2 adsorbed fragment is the stable intermediate of ammonia oxidation. Stabilization of NH and NH_2 fragments on Pt(111) and Pt(100), respectively, is in an interesting agreement with recent theoretical predictions. [2,3]

The Pt(111) surface shows extremely low activity in ammonia oxidation to dinitrogen, thus indicating that neither NH nor N (strongly) adsorbed species are active in dinitrogen production. Neither nitrous oxide nor nitric oxide is the product of ammonia oxidation on Pt(111) at potentials up to 0.9 V, as deduced from our *in situ* infrared spectroscopy measurements.

The Pt(100) surface is highly active in dinitrogen production. This process is characterized by a Tafel slope of 30 mV decade^{-1}, which is explained by a rate-determining dimerization of NH_2 fragments followed by a fast decay of the surface-bound hydrazine formed to dinitrogen. Therefore, the high activity of the Pt(100) surface in ammonia electrocatalytic oxidation to dinitrogen is likely to be related to its ability to stabilize the NH_2 adsorbate.

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Measurement of Changes in Surface Stress of Au Electrode during Underpotential Deposition of Cu

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The changes in surface stress of a gold electrode during underpotential deposition (UPD) of Cu in perchlorate-base solutions containing 10^{-3} M SO_4^{2-} or Cl^- were measured by a bending beam method for a better understanding of the roles of anions in UPD of Cu from the viewpoint of surface energetics. A gold film (111) with a thickness of 300 nm was evaporated on a thin glass plate and used as a specimen electrode. The principle of bending beam method was described elsewhere [1,2]. The cyclic voltammogram (CV) and surface stress change, Δg, vs. electrode potential, E, curve were measured simultaneously between 0.25 V and 0.80 V (SHE). The potential of cathodic limit, 0.25 V (SHE) corresponds to the equibrium potential of bulk deposition of Cu.

In the cathodic potential sweep from 0.80 V to 0.25 V, the surface stress changed to the tensile direction mainly due to desorption of SO_4^{2-} or Cl^-, passing through a maximum and then changed to the compressive direction as the UPD of copper proceeded. On the othr hand, in perchlorate-base solution without SO_4^{2-} or Cl^-, the surface stress did not change significantly between 0.25 V and 0.80 V and an overpotential of 0.15 V was needed for further changes in surface stress to the compressive direction and for the UPD monolayer formation of Cu.

Z. Shi *et al*. [3] revealed the coadsorption of copper atoms and SO_4^{2-} or Cl^- during UPD of Cu on Au (111) by chronocoulometry and surface thermodynamics. T. trimble *et al*. [4] have recently reported that a pseudomorphic Cu monolayer on Au (111) provides the changes in surface stress to the tensile direction, while the coadsorption of SO_4^{2-} induces the reversal changes in surface stress from tensile to compressive. A coadsorption of Cl^- as well as SO_4^{2-} may induce the reversal change in surface stress. The roles of anions in UPD of Cu on Au(111) will be discussed from the viewpoint of surface energetics.

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Symposium 8 - Oral

Surface Chemistry and Dynamics

The Liquid-Like Layer Between Metal and Frozen Aqueous Electrolytes. An Electrochemical Approach Employing the Quartz Crystal Microbalance

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The surface properties of any substance in the solid state differ from its bulk properties. This can give rise to the formation of a liquid-like layer (LLL) at the interface, at temperatures below the melting point. The phenomenon generated interest among both theoreticians and experimentalists for more than 150 years and was studied, employing different techniques. However, electrochemical techniques have not been implemented in studies of this phenomenon.

We used, for the first time, the Quartz-Crystal Microbalance (QCM) to study the LLL at the ice/gold and the frozen electrolyte/gold interfaces. It was shown that the QCM in contact with ice or with frozen electrolyte at temperatures well below the melting point shows detectable resonance. The parameters of the resonance depend strongly on temperature, composition of the frozen phase, adsorption taking place at the gold surface (including gold surfaces modified by different thiol-derivates) and, in the case of electrolyte, on the potential applied across the interface.

Corresponding theoretical models have been developed to understand the kind of information contained in the response of the QCM on the properties of the LLL. Independent data obtained with a device allowing direct optical measurement of the displacement show good agreement with the calculations of thickness of the LLL based on developed models.

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Electrochemical reduction of oxygen to hydrogen peroxide – an electron density functional theory study

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Hydrogen peroxide is a widely spread and powerful oxidizing and bleaching agent with many industrial and domestic applications. Methods for its production on a large industrial scale have been well established and exploited for more than a century. However, higher concentration solutions of hydrogen peroxide in water present various hazards, including risk of fire and explosion on contact with heat. New technologies are being developed which would allow for the production of the substance on a small scale at the site of its application and thus avoiding transportation.

Electrochemical reduction of oxygen to hydrogen peroxide is one of the best candidates for the on-site or in-situ production of the chemical. Experimentally it has been established that gold single crystal electrodes could be used for this purpose. It was also found that Au(111) are most active towards production of peroxide, while Au(100) in alkaline solutions results in the full four-electron reduction of molecular oxygen to water.

In this work we investigate this difference comparing computational models for the two surfaces and the reaction intermediates. Different reaction paths, including an active role of the solvating water molecules, are investigated providing a description of the (electro-)chemical processes and the reaction pathways on a molecular level.

Symposium 8 - Oral

Surface Chemistry and Dynamics

Spectroscopic and Reactivity Measurements of Catalytic Nanoparticles for Methanol and Formic Acid Oxidation: EC-NMR, XPS and Theoretical Studies

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The Direct Methanol Fuel Cell (DMFC) and the Direct Formic Acid Fuel Cell (DFAFC) are promising candidates for a wide variety of energy applications.[1] One of the limiting factors in both DMFC and DFAFC technology is unsatisfactory catalytic behavior of the cell anodes that usually consists of platinum intermixed (or alloyed) with other noble metal or/and oxides. Major effort has been made to improve the anode performance, especially in terms of alleviating the CO poisoning effect, by alloying Pt with Ru[2], and to advance understanding of the oxidation/poisoning processes on the Pt-Ru surfaces. The equivalent strategy for DFAFC is to intermix platinum with palladium, or use palladium-made-catalysts directly. Our work so far has employed a broad range of methods: EC-NMR,[3] XPS,[4] SFG[5] and electroanalytical methods, as well as used various Pt-Ru and Pd (Pt-Pd) surfaces: nanoparticles[3] and single crystal electrodes.[6] Evidence was presented concerning how these catalysts function in the CH_3OH and $HCOOH$ (acidic) environments. We have for instance found that the reactivity of interiors of thin films of Ru on Pt towards the CO is higher than that of the Pt/Ru edge, which shows the direction for further progress. More recently, we have identified the link between predictions from the general theory of heterogeneous catalysis (developed by Hammer, Norskov and Mavrikakis[7,8]) and the methanol and formic acid oxidation data. The studies that we will report are focused on XPS measurements of the electron core level binding energy (BE) for Pt-Ru and Pd nanoparticle catalysts.

Hammer, Norskov and Mavrikakis[7,8] propose that the change in a metal d-band center due to alloying (intermixing with other metals) is directly correlated to adsorption energies and activation barriers of molecules/intermediates involved in catalytic reactions on these metal/alloy substrates. In turn, the adsorption energies and/or activation barriers govern the rates in heterogeneous reactions, including the provision for the volcano relationship. Since the d-band center is correlated to BEs available from XPS experiments[9,10], electrocatalytic activities should display a clear relation to the BE change. Using Ru $3d_{5/2}$ transitions, we will show that here is no expected difference in the Ru $3d_{5/2}$ binding energy between pure Ru and Ru in Pt-Ru matrices, most likely due to a compensation between the charge transfer and the lattice strain effects[9]. However, there is a clear shift in BE of Pt $4f_{7/2}$ when the amounts of Ru in the Pt-Ru alloy matrices are changing. Details and discussion of these relationships will be provided.For formic acid electrooxidation on unsupported palladium nanoparticles, the particle size changed from 9 to 40 nm, and the most active catalyst is made of the smallest (9 nm) Pd nanoparticles. Besides the high reactivity, XPS data show that such smallest nanoparticles display the highest BE shift and the highest valence band (VB) center downshift with respect to the Fermi level. That is, we have found a correlation between the formic acid oxidation current and BE and VB center shifts, which, in turn, can be directly related to the electronic structure of palladium nanoparticles with different particle sizes. Our measurements demonstrate a particle size effect on the electronic nanostructure of palladium that yields different catalytic activity in the HCOOH oxidation reaction. This adds strength to the notion of predictive significance of the BE shifts in electrocatalysis, and highlights the significance of the theory that underscores our experimental efforts.

New method for the preparation of PtPd single crystal alloys

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Previous studies of bulk PtPd single crystal electrodes [1] and Pd overlayers on Pt single crystals [2-4] show quite different and distinct electrochemical behaviour. In this study we combine both approaches to generate well-defined PtPd single crystal alloys supported on Pt single crystals covering the whole range of alloy composition from 100% Pd to 100%Pt. These novel films are indistinguishable in their electrochemical response from bulk single crystal alloys of PtPd previously characterised using surface science probes. The method of preparation is quite general and works successfully for a number of other PtX alloy systems. In this paper we compare and contrast the voltammetry for our novel alloy films directly with analogous studies of Pd overlayers and bulk alloys. The oxidation of CO together with the formic acid oxidation reaction will be discussed and shown to provide interesting contrasts with Pd overlayers on Pt(hkl).
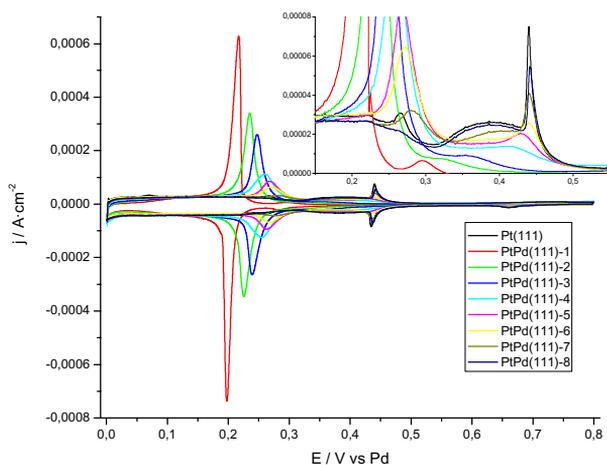
Figure 1. Voltammetric profiles of different PtPd(111) alloys. Test solution: 0.1 M H2SO4. Sweep rate: 50 mV·s⁻¹.

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Symposium 8 - Oral

Surface Chemistry and Dynamics

Formation of Stable Ag-Nanoparticle Aggregates Induced by Dithiol Cross-linking

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Aggregation of thiol stabilized silver nanoparticles induced by 1,6-hexane dithiol was studied in situ by dynamic light scattering. The aggregates were observed to reach a finite size in the 100-200 nm range. Growth kinetics were shown to be linked to the dynamics of the thiol-exchange reaction.

The parameters varied within experiments were temperature, dithiol to MPC ratio and total MPC concentration. The solution structure of the aggregates was analyzed by cryo-TEM and it was found to be quite densely packed and three-dimensional (Figure 1.).

A model for the aggregation process was developed based on a simple diffusion-kinetic approach assuming an elementary kinetic reaction at the surfaces and a spherical diffusion field surrounding the aggregates. The rate constant for the thiol exchange reaction was found to vary between $0.6 - 4.0 \times 10^{-4}$ s^{-1} and the activation energy was 46 ± 10 kJ mol^{-1}. The final size of the stable nanoparticle clusters was found to be practically independent of the total MPC concentration at the concentration range considered.

Figure 1. Cryo-TEM images of a Ag nanoparticle aggregate tilted at –50 (a), 0 (b) and 50 (c) degrees. The white line corresponds to the approximate center line of the aggregate at different tilt angles.

Symposium 8 - Poster

Surface Chemistry and Dynamics

Novel Chalcogenide Platinum Based Cathode Materials for ORR in Methanol in the Nanoscale Length

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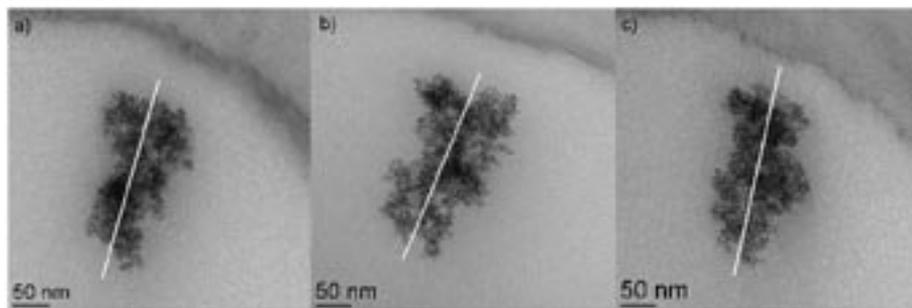[2]*Department of Chemical Materials on Catalytic Materials Nanostructured, Research Center on Advanced Materials, S. C ., Miguel de Cervantes 120, Complejo Industrial Chihuahua, 31109 Chihuahua, Chih., Mexico*
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It is well known that platinum, as cathode for the oxygen reduction reaction (ORR), has no inertness to crossover of methanol in a direct methanol fuel cell (DMFC). However, the tolerance to this phenomenon has been increased by alloying this noble metal with other non-noble transition metals, such as, e.g., Ni, Cr. Although the target, in the near future, is to develop materials based essentially on non-noble metals,[1] it was, however, illustrative to explore the advantage or disadvantage of chalcogenes, specifically the sulphur, to tailor novel platinum-based materials. Earlier works showed, indeed, that a full tolerance of methanol is obtained for the oxygen reduction reaction by means of ruthenium-chalcogenide.[2,3] This work focus on the development of electrocatalysts through a synthesis procedure with sulphur-platinum in combination with Mo and W.

The synthesis was performed by chemical reaction using thio-salts and metallic salts at room temperature. This chemical reaction produces chemical precursors which are thereafter supported in carbon Vulcan. After a thermal treatment ($300 – 400°C$) became catalysts in the nanoscale length: Pt_xS_y/C, $Pt_xMo_yS_z/C$, $Pt_xW_yS_z/C$. The loading of each catalyst was 20% wt. These materials were characterized by DTA-TGA, TEM and XRD.

The electrochemical kinetic study in sulphuric acid medium for ORR and the effect of methanol was performed on the whole set of materials. For the sake of comparison commercial 20 wt. % Pt/C (E-TEK) was employed. For the ORR on Pt/C, $Pt_xW_yS_z/C$, $Pt_xMo_yS_z/C$ and Pt_xS_y/C the electrode potentials in the activation region, at a current density of 0.1 mA cm^{-2}, were, respectively, 0.96; 0.95; 0.92 and 0.85V/RHE. In presence of 0.5M CH_3OH and at the same current density, we recorded 0.57; 0.81; 0.81; and 0.80V/RHE. The methanol tolerance is higher (ca. 90% in comparison to Pt/C) on Pt_xS_y/C. We arrive at the conclusion that surface sulphur atoms chemically modify platinum surface atoms as to avoid methanol interaction. Surface studies as well as structural ones are under way.

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Measurement of the Sticking Probability of n-Alkanethiol Adsorption on Gold Surfaces using Cyclic Voltammetry

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The sticking probability of self-assembled n-alkanethiols on polycrystalline Au and on Au(111) surfaces has been investigated using cyclic voltammetry. The change in the sticking probability with increasing the fractional coverage was followed and compared to the initial sticking probability for the following n-alkanethiols [$CH_3(CH_2)_{n-1}SH$]: propanethiol (n=3), dodecanethiol (n=12) and octadecanethiol (n=18). The method of copper under-potential deposition (Cu *upd*) electrochemical probing was used and the adsorption took place on a fixed surface area electrode with selected dipping times.

Langmuir-like adsorption kinetics was observed for the octadecanethiol adsorption on Au at high micromolar concentrations and became more precursor-like in the sub-micromolar region. At 0.5 μM, the adsorption isotherm revealed an additional feature which could be explained by the initial adsorption of the solvent, methanol, or its by-products and its subsequent removal by the formation of the stronger Au-S bond and/or by the formation of a "lying-down" phase.

The calculated average initial sticking probabilities were found to be 5×10^{-6} for octadecanethiol (C_{18}-SH), 3×10^{-6} for dodecanethiol (C_{12}-SH) and 2×10^{-6} for propanethiol (C_3-SH). A trend of increasing the sticking probability with chain length is obvious and this result is comparable to values obtained by the surface plasmon resonance technique.

The relative surface blocking time was studied by measuring the dipping time versus the average fractional coverage and the averaged normalised integrated area of the corresponding voltammetric peak. The results revealed that the ratio of experimental average block time to expected block time was 1.5 (average block times for C_{18}-SH at 5 μM was 12.2 seconds). Similarly, for the C_{12}-SH (2 μM), the ratio of experimental average block time to expected block time was found to be 1.2. Thus, while both alkanethiols exhibited small apparent depletion effects in weaker solutions, these effects appeared to be greater for the longer chained alkanethiol (*i.e.* C_{18}-SH solutions) which had a better ability to allow depletion at the surface at less dilute concentrations due to its lower diffusion coefficient.

Symposium 8 - Poster

Surface Chemistry and Dynamics

Symposium 8 - Poster

Surface Chemistry and Dynamics

Inhibition Efficiencies of Some Organic Compounds on the Corrosion of Zinc in Alkaline Media

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Work reported in the present paper investigated the inhibiting properties of six quaternary ammonium salts, three cationic surfactants and two non-ionic surfactants in 2M KOH. An attempt also was made to correlate some molecular parameters of these compounds with their corrosion inhibitor efficiency. The inhibition efficiencies of quaternary ammonium salts, cationic surfactants and non-ionic surfactants on the corrosion of zinc in 2M KOH solution were investigated by potentiodynamic polarisation, electrochemical impedance spectroscopy and linear polarisation methods. Inhibition efficiencies of quaternary ammonium salts were found to be due to physical absorption on the cathodic sides of zinc electrode and dependence of inhibition efficiencies on substituents were found. Physical adsorption of cationic surfactants on zinc electrode slow down both anodic and cathodic reactions; thus they were found as mixed type inhibitors. On the other hand inhibition behaviour of non-ionic was found to be due to adsorption on zinc via polar groups. It was found that non-ionic surfactants behave as mixed type inhibitors.

S8·P-5

Symposium 8 - Poster

Surface Chemistry and Dynamics

SERS study of absorption of some benzohydroxamic acids on silver sols

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Because of their metal chelating properties, hydroxamic acids have important applications in biology, medicine, and metal extraction technologies. Recent investigations have as well shown that certain classes of them, as for instance, some p-substituted derivatives of the benzohydroxamic acid (BHA), can be used as copper corrosion inhibitors [1,2]. Those studies proved that the nature of the derivative groups had an important influence on the protecting behavior when the copper corrosion in chloride solutions was concerned. This effect was ascribed to [3,4]: a) a different adsorption strength of the benzohydroxamic acids stemming from the unequal ability of the substituents to withdraw electrons from the hydroxamic group, and b) a possibility that some of the substituents can also react with the surface, and therefore, to represent a second adsorption center competing with the hydroxamic group. The complete characterization of the substituent's influence thus requires the confirmation of its adsorption geometry in-situ. In order to solve this problem, we have previously used a combination of a Surface Enhanced Raman Spectroscopy (SERS) and a quantum-chemical modeling for investigation of the adsorption geometry of BHA, p-choro BHA, p-methoxy BHA, and p-nitro BHA on a copper oxide [4]. Now we extend this work by studying the adsorption of those molecules on silver colloids. One motive to carry on this investigation is that the colloidal silver is a better defined SERS substrate than the oxidised copper plates. This allows for a more realistic modeling of the electric field distribution around the sol particles, and hence, for an improved understanding of some effects pertinent to SERS spectroscopy. In this sense, the use of computational approaches describing the electromagnetic field scattering on complexly shaped forms, and therefore, beyond the Mie approximation, seems especially interesting. The second reason for this study is to compare the adsorption interaction, including the adsorption geometry, of BHA's on copper plates and on silver colloids. The latter were prepared by adding diluted solutions of AgNO3 and KBH4. SERS measurements were done at 10^{-4} M concentrations. Raman spectra in solid state and in tetrachlormethane were also acquired so that to allow a comparison with the SERS ones. The peak assignment of the measured spectra was done by matching them with quantum-chemically calculated vibrational positions. The adsorption geometry of the benzohydroxamic molecules was derived by discussing the symmetry properties of some relevant peaks, and by comparing the Raman and SERS intensities of some specific vibrations with different orientations between their transitional polarizabilities and the electric field vector.

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Symposium 8 - Poster

Surface Chemistry and Dynamics

B3LYP study of the adsorption of water on (111) metal surfaces

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Water adsorption plays an important role in determining the interfacial behaviour of metallic electrodes. The adsorption of anions and neutral species must occur through displacement of adsorbed water. Besides, the water-adsorbate interactions in the layer in contact with the metal can influence the structure of the interface. In this work, the adsorption of water on the atop position has been studied on several close-packed transition and noble metal surfaces, using density functional theory (DFT). Specifically, adsorption has been examined on Pt(111), Rh(111), Ag(111), Au(111), Cu(111) and Pd(111). Geometry optimizations were performed using the Gaussian03 program at the B3LYP level of theory. We find three different behaviors. On Pt and Rh water lies nearly parallel to the surface, with the hydrogens pointing away the surface. The tilt angle between the molecular plane and the surface is 10º in both cases. On Ag and Au water lies also nearly parallel to the surface, but with the hydrogens pointing towards the surface. In this case, the tilt angle between the molecular plane and the surface is about 20º for the silver surface and 10º for gold. Finally, for the Pd and Cu surfaces the water molecule lies with the hydrogen atoms completely oriented towards the surface (O-up structure). Oxygen-surface distances vary from 2.2 Å for Rh to 3.2 Å for Ag. The internal geometry of the water molecule (O-H distances and HOH angle) deforms little upon adsorption.

Water binds weakly to all surfaces investigated, but the weakest interaction is found for Ag and the strongest for Pt. The adsorption energies range from -2.17 kcal mol^{-1} to -6.54 kcal mol^{-1} and are in the following sequence: Ag < Au < Cu < Pd < Rh < Pt. This energy range is comparable to the energy of the hydrogen bond between water molecules.

A comparative study of anion adsorption on poly and single crystal platinum by radioactive labelling and voltammetry

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Single crystals are in the centre of numerous electrochemical and surface analytical studies owing to their well-defined and relative great surface area. In these studies, polycrystalline surfaces are considered as reference specimens, which provide important information on the basic phenomena. Anion adsorption on single crystal electrodes of noble metals has a special importance in the understanding of the enhanced surface reactivity (if any) and may contribute to the comprehensive explanation of some processes in various fields of electrochemistry (e.g. electrocatalysis, metal deposition (especially underpotential deposition), fuel science and technology).

Many articles have been focused on the adsorption of sulfate/bisulfate and chloride ions on Pt(111) and polycrystalline electrode. Induced and/or enhanced adsorption of these anions on Pt(poly) and Pt(111) surfaces modified by either a chemically adsorbed chromate layers or metal adatoms has widely been investigated for two decades.

The updated version of the in-situ radiotracer 'electrode-lowering' ('thin-gap') technique used in our laboratory, combined with electrochemical methods is considered to be a powerful tool to investigate specific adsorption of anions (SO_4^{2-}/HSO_4^-, Cl^-) on noble metal surfaces. The present work is dealing with the comparative study of the adsorption of sulfate/bisulfate (labeled with ^{35}S) and chloride (labeled with ^{36}Cl) anions on Pt(poly) and Pt(111) surfaces in 0.1 mol dm^{-3} $HClO_4$ supporting electrolyte in the absence and presence of Cr(VI) species.

The main experimental findings are as follows:

1.) The surface excess values of adsorbed sulfate/bisulfate depend on the crystallographic orientation of Pt surfaces, and the maximum coverage does not exceed 0.2 ML.

2.) The electroreduction of Cr(VI) species presumably proceeds via a CE mechanism to yield Pt surfaces covered with intermediate surface adlayers containing Cr(VI) particles and added anions. The formation of intermediate complexes is indicated by the induced adsorption of SO_4^{2-}/HSO_4^- and Cl^- ions observed in the course of the Cr(VI) – Cr(III) reduction.

3.) The coverage of electrode surfaces by the intermediate complexes formed in the course of Cr(VI) electroreduction is independent of the crystallographic orientation of the Pt surface, but highly affected by the quality of the electrode material.

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Surface Chemistry and Dynamics

CO Island Formation at Submonolayer CO$_{ad}$ Coverage on a Pt Electrode in the H-upd Potential Region: IR Vibration Spectroscopic Evidence

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Electrochemical *in-situ* infrared spectroscopy has been widely used to study the nature of carbon monoxide binding to transition metal electrode surfaces, driven by the effort to improve the catalytic CO oxidation and to eliminate CO poisoning. The vibrational properties of CO$_{ad}$ molecules, especially the C-O stretching frequency, are found to be very sensitive to electrostatic as well as chemical and geometric environments. Hence the vibrational spectral features allow to derive structural information of the CO adlayer as well as its catalytic consequence.

In this contribution, we present vibrational features of adsorbed CO molecules at submonolayer coverages on a Pt film electrode in 0.5 M H$_2$SO$_4$ solution from electrochemical *in-situ* FTIR spectroscopic measurements in attenuated total reflection configuration (ATR-FTIRS). A concurrent increase in linearly bound CO band intensity and frequency with decrease in electrode potential from 0.25 to 0.1 V is observed at $\theta \leq 0.3$ ML, which is explained by H-induced CO islands formation with high local CO$_{ad}$ density due to the strong repulsive interaction between CO$_{ad}$ and H$_{ad}$ atoms. The kinetics of this process is followed by time resolved infrared spectroscopy. The impact of the CO$_{ad}$ structural change on the CO electro-oxidation kinetics will be discussed.

Sculpted surfaces for electrochemical SERS

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SERS substrates are usually prepared by roughening metals so as to create surfaces that have atomic-scale (< 10 nm) to nanometer-scale (10 to 100 nm) roughness features, often described as having a cauliflower like appearance. Whilst such surfaces have enabled the study of many electrochemical reactions, the electrode surfaces can not be described as well characterized, limiting the extent to which the results can be related to studies at flat electrode surfaces. We have developed a method to produce sculpted SERS-active substrates by assembling a closed packed monolayer of uniform polystyrene colloidal particles (diameter 350 to 800 nm) onto an evaporated gold surface and then electrodepositing gold through this template to produce films with controlled thicknesses, measured as fractions of the sphere diameter, d. The resulting surfaces consist of a regular hexagonal array of interconnected spherical cross-section dishes. The resulting surfaces have roughness factors of approximately 1.6. The surfaces show strong surface enhancements for Raman scattering from molecules adsorbed at the surface. The magnitude of this is enhancement is determined by the precise geometry of the surface and depends on the choice of void diameter and film thickness. The resulting SER active surfaces are stable, reusable, give reproducible surface enhancement and can be used for in situ electrochemical SERS studies. Electrochemical SERS investigations at a variety of sculpted metal surfaces will be presented, including Ag, Au, Cu, Pt, and Pd.

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Chemical and morphological heterogeneity at dissolving metal-electrolyte interfaces

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In spite of the intense effort devoted in the last years to the understanding of the complex dynamics of the different (electro-)chemical and physical mechanisms that take part in the metallic dissolution process, the influence of the dissolution mechanism on the surface dynamics is still an open question. We present the results obtained from simulations of a microscopic metal-electrolyte interface model. The model considers a single crystal metal that dissolves according to a reactive scheme with intermediate adsorbed species. Simulations show that roughness development induces a direct relationship between the spatial and temporal scales of the model. As a consequence of that, the time ordering of the chemical species, which is intrinsic to the dissolution mechanism, is projected spatially leading to an unexpected chemical ordering on the interface. We show how this self-organization depends on the overall reaction kinetics and that it can be modelled from the standard macroscopic approach. One of the main consequences of the chemical ordering is that dissolution is not longer random. The heterogeneous distribution of dissolution active sites gives rise to active dissolution domains on the surface, resulting in different degrees of roughness with respect to the random dissolution reference model. These morphological differences persist in all scales, so it can be observed in the macroscopic scales of our model. An important consequence of such complex behaviour is that surface morphology changes when applied potential is varied during driven electrochemical dissolution, as in polarization curves measurements. This is a remarkable result if we take into account that the proposed interface model evolves under very simple conditions, namely surface reaction kinetic control and reactivity not dependent on the local or global surface structure.

Voltammetry of palladium containing compounds

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Palladium is currently used in a wide range of fields, starting from electronics, water treatment and hydrogen purification, to medicine, in dentistry and medical devices. It is best known as a catalyst and playing a key role in fuel cell research. Recently, palladium complexes are reported in new promising applications in the treatment of cancer.

Palladium dichloride and tetrachloropalladates are useful synthetic starting materials for the preparation of complex palladium compounds. Due to their high sensitivity, voltammetric methods have been successfully employed for the detection and determination of different compounds. Moreover, studies of the behavior of their precursors by means of electrochemical techniques have the potential to provide valuable insights into the redox mechanisms of these molecules.

The electrochemical behavior of various palladium compounds has been studied at a glassy carbon electrode using cyclic, differential and square wave voltammetry. Palladium containing compounds undergo irreversible reduction at glassy carbon electrodes in a complex process transferring two electrons in a single step. The oxidation of palladium(II) is an irreversible process Palladium ions adsorb on the surface of the glassy carbon electrode. After transferring to a new supporting electrolyte solution consecutively recorded cyclic voltammograms in buffer only a continuous, but slow decrease of the palladium reduction peak. Impedance measurements corroborated the voltammetric results enabling the study of the adsorption of palladium on the surface of the glassy carbon electrode.

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An Electrochemical SERS Study on Coadsorption of Protonated DNA Bases with ClO_4^- on Au Electrodes

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Hydrogen bonding is an extremely important weak interaction in biological systems. The approaches for investigating the hydrogen bond between DNA bases include AFM, UV melting and osmotic pressure. For this purpose, it is advantageous to employ surface-enhanced Raman spectroscopy with its high spectral resolution and high surface sensitivity. Recently, we studied coadsorption of DNA bases with ClO_4^- on Au electrode surfaces and weak interactions between protonated DNA bases through hydrogen bonding by SERS.

As a commonly used electrolyte ion, ClO_4^-, does not chemically interact with metal electrodes. No SERS signal concerning this species can be observed in the solution containing only $NaClO_4$. However, after the addition of adenine into the solution with pH value less than 4, strong SERS signals from ClO_4^- at 933 cm^{-1} can be detected together with that of adenine (see Fig. 1). In the neutral solution, no ClO_4^- signal could be detected in the whole potential range. These results indicate that ClO_4^- is induced to adsorb on the electrode by the adsorbed protonated adenine (AH^+), which is called induced coadsorption. Of particular interest is that the frequency of coadsorbed ClO_4^- is identical to that of free ClO_4^- and independent of the electrode potential, which implies that this anion interacts indirectly with the surface. The decreasing intensity of ClO_4^- with negative shift of the potential is caused by the electrostatic repulsion of electrodes.

A direct detection of hydrogen bonds between DNA bases is still hard for SERS. However, monitoring SERS signal of the coadsorbed ClO_4^- with protonated bases in the presence of the other DNA base may provide an indirect way to probe the weak interaction between DNA bases. Fig. 2 shows that the intensity ratio of 933 cm^{-1} to 663 cm^{-1} (from guanine) increases with the addition of cytosine. This phenomenon may be a result of the interaction of GH^+ with CH^+ via at least one hydrogen bond and the coadsorption of CH^+ with ClO_4^- may bring more ClO_4^- close to the electrode. This result indicates that SERS is capable of probing the DNA pairing.
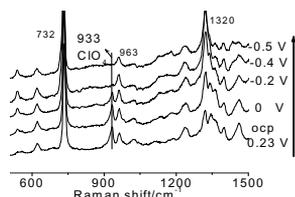
Fig. 1. Potential dependent SERS spectra of adenine on Au-nanosphere assembled Au electrode in 0.1 M $HClO_4$. Laser line: 632.8 nm
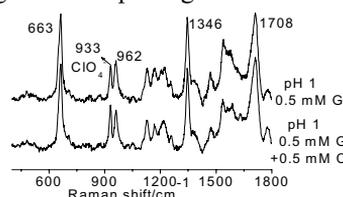
Fig. 2. SERS spectra of guanine in the solution containing 0.1 M $HClO_4$ (top) and 0.5 mM cytosine + 0.1 M $HClO_4$ (bottom).

RRDE Study of Underpotential Deposition and Nucleation of Copper on Platinum in the Presence of Acetonitrile

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Initial stages of copper electrocrystallization on polycrystalline platinum in solutions of 0.5 M H_2SO_4 + 10 мM $CuSO_4$ + 0-200 мM acetonitrile (AcN) have been studied by means of cyclic voltammetry and potentiostatic current transients on rotating ring-disk electrode. Adsorbed AcN molecules accelerate the UPD and bulk copper deposition due to local electrostatic effects on the charged interface. Increase in amount of the additive in solution leads to enlargement of contribution of Cu^+ producing in a total reaction of Cu^{2+} ions reduction as a result of complexes $Cu(AcN)_x^+$ formation (Figure), especially for [AcN] 4 мM, when the concentrations of acetonitrile and copper ions are comparable. In the presence of AcN, similar to the copper deposition in background solution of copper sulfate, the UPD proceeds according to the mechanism of two-dimensional growth of the islands of Cu(1x1) phase, nucleation loop is observed in underpotential region. Peculiarities of copper electrocrystallization on polycrystalline and single crystal [1,2] electrodes are discussed.
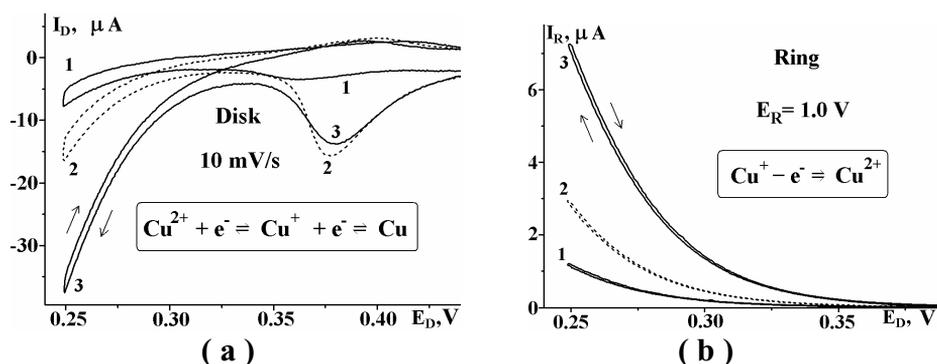
Figure.　Fragments of CVs of the disk (a) and ring (b) electrodes.
　　　　Concentration of AcN: (1) - 0; (2) - 4; (3) - 40 mM.

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Surface Chemistry and Dynamics

Optimizing supported Pd-nanoparticle catalysts for aqueous NO_3^- reduction: Effects of temperature, nitrate concentration and particle size

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The reaction of aqueous nitrate on carbon-supported palladium nanoparticles was studied as a function of nitrate concentration, temperature, and particle size using differential electrochemical mass spectrometry. Nitrate concentration was varied between 0.05 M and 0.5 M, temperature between 10º C and 55º C, and catalyst particle size between 9.32 nM and 14.91 nM. For all combinations of nitrate concentration, temperature, and catalyst particle size, the reaction of aqueous nitrate produces gas phase reduction products: N_2O and NO. As expected from kinetic arguments, increasing temperature leads to an increased yield of gas phase reduction products. Increasing nitrate concentration also leads to an increase in gas phase reduction products. Surprisingly, the larger particle size Pd catalysts produce greater yields of N_2O, indicating that the larger particle size catalyst more effectively fosters N-N coupling reactions.

ATR-SEIRAS Study of the Adsorption of Acetate Anions at Silver Thin Film Electrodes prepared by Sputtering and by Chemical Deposition

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The adsorption of acetate anions at silver thin film electrodes has been studied by in-situ infrared spectroscopy experiments with a Kretschmann internal reflection configuration. Stable silver thin films were chemically deposited on germanium substrates. Ex-situ STM images show mean grain sizes ranging from ca. 20 to 90 nm for deposition times between 2 and 20 min, respectively. The thickness of the silver film, measured by AFM, is typically around 10 nm for a deposition time of 10 min and increases up to 50 nm for a deposition time of 20 min.

Moreover, silver thin films were deposited on silicon substrates by argon sputtering in the vacuum chamber of a MED020 coating system. The thin film thickness and the deposition rate were controlled with a quartz crystal microbalance. Ex-situ STM images show mean grain sizes around 30 nm for a film growth rate of 0.05 nms^{-1} and 70 nm for a film growth rate of 0.005 nms^{-1}. The roughness factor obtained from the charge involved in lead underpotential deposition (UPD) is lower than that measured for the chemically deposited silver thin film.

A noticeable enhancement of the infrared absorption of adsorbed species (SEIRA effect) is observed when the silver films deposited either by sputtering or chemically are used as electrodes under internal total reflection conditions. Maximum intensities of the adsorbate bands were observed for a chemically deposited silver thin film with a deposition time of 10 min and an angle of incidence around 65°. Surface enhanced absorption is lower for the films deposited by sputtering and decreases when the film growth rate decreases. The potential-dependent infrared spectra of acetate and interfacial water are consistent with previously proposed models involving the existence of weakly hydrogen-bonded water molecules at potentials below the potential of zero charge and the reorientation of water molecules at potentials above the potential of zero charge. Results obtained in this work suggest a weak interaction between acetate and water molecules adsorbed at the silver thin film electrodes.

Figure 1. 3D plot of the infrared absorbance spectra obtained for a chemically deposited silver thin film electrode in a 0.01 M CH$_3$COONa + 0.1 M NaF solution.

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Surface Chemistry and Dynamics

DFT and in-situ Spectroscopic Study of the Bonding Mode and Infrared Behaviour of Adsorbed Acetate Anions on Silver Electrodes
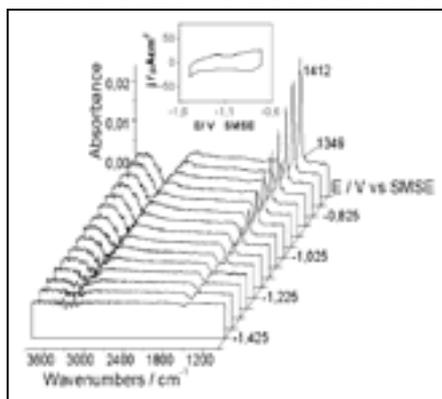
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The interpretation of spectra of adsorbed species on metal electrodes is frequently based in the comparison of the experimental frequencies with those reported from transmission experiments in solution, or with those (either experimental or calculated) characteristic of the species either in gas phase, or acting as a ligand in coordination complexes with metals. The theoretical calculation of the vibrational frequencies of adsorbed species allows for a better justification of the assignment of the experimental frequencies to vibrational modes and different adsorption geometries. In this work we address the theoretical analysis of the vibrational behaviour of adsorbed acetate on silver electrodes.

The adsorption of acetate anions on silver thin film electrodes has been studied by in-situ FTIR spectroscopy experiments. Stable silver thin films were deposited either chemically or by sputtering on Ge and Si substrates respectively. These stable silver thin films were used as electrodes under internal total reflection conditions (ATR-SEIRAS) using a Kretschmann internal reflection configuration. The ATR-SEIRAS experiment provides a better signal to noise ratio, that allows a more detailed study of the vibrational features of the adsorbed species, without the problem of the absorption by the solvent in the thin layer, typical of the external reflection configuration.

Optimized geometries and theoretical frequencies of adsorbed acetate on silver clusters modelizing electrode surfaces with Ag(111) and Ag(100) have been calculated using density functional theory, with the hybrid B3LYP functional. The effect of different basis sets on the calculated frequencies has been tested for different adsorption sites (on-top, bridge, hollow) and bonding modes (monodentate, bidentate). A good agreement is found between the experimental frequencies obtained in the ATR experiments and those calculated for bridge bidentate adsorption of acetate on Ag(111) and Ag(100) clusters. This confirms that bonding of acetate to the surface involves the oxygen atoms of the carboxylate group, with the O-C-O plane perpendicular to the metal surface. The calculated frequencies reveal that only a slight effect of the surface crystallographic orientation on the vibrational frequencies of adsorbed acetate is expected.

Self-organization and Oscillatory Electrodeposition of Ag-In alloy

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In the past two decades there has been enormous progress in the research on pattern formation in electrochemical systems. A wide variety of spatio-temporal structures were observed during electrodeposition of silver alloys such as Ag–In [1-2], Ag-Sb [3], Ag-Bi [4] and Ag-Sn [5]. In these cases it is possible to investigate the formation process of spatio-temporal patterns, like waves, spirals and targets (Fig.1) on the cathodic surface under defined and well-controlled electrochemical conditions.
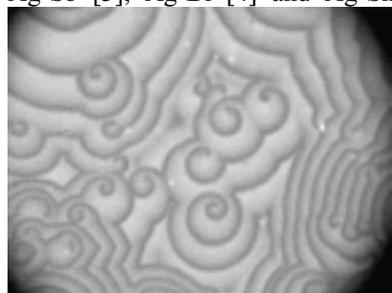
Fig.1. Optical image of electrodeposited Ag-In alloy

The appearance of these typical instabilities is characterized also by potential oscillations during the galvanostatic deposition of the Ag-In alloy (Fig.2). This pattern formation far from equilibrium is connected with an autocatalytic step in the electrochemical reaction, which is expressed by a region of the polarization curves with negative differential resistance (NDR).

Here we report about the relation between potential oscillations and formation of spatio-temporal structures on the basis of the observed cross-section structure and the corresponding surface morphology of the deposits.
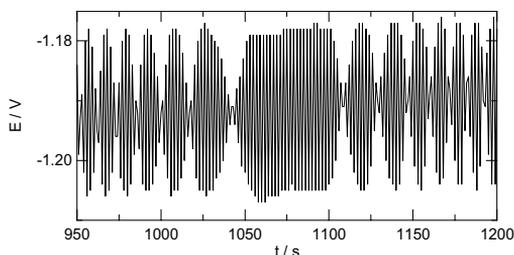
Fig.2. Potential oscillations; galvanostatic deposition

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Surface Chemistry and Dynamics

Interaction of Thymine and Copper adatoms during the Deposition on Au (111)

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Underpotential deposition (UPD) of Copper on Au(111) electrodes belongs to the most detailed investigated UPD systems. It is well accepted that specifically adsorbed anions promote the deposition process, whereas in presence of only perchlorate anions the Cu- UPD as well as the volume deposition (OPD) is inhibited. Our study demonstrates that it is possible to deposit Copper on Au(111) in absence of specifically adsorbed anions if only thymine molecules are physisorbed in a flat orientation with respect to the Au(111) surface. Thereby the thymine molecules act as catalyst for the Cu- UPD but as inhibitor for the Cu- OPD. This effect is independently on the lateral attractive interactions between thymine molecules on the surface. STM experiments reveal that thymine molecules are adsorbed on top of the Cu- monolayer in an upright position. This denotes a reorientation of thymine during the deposition. Detailed chronocoulometric as well as XPS- and UPS- studies with synchrotron radiation show that thymine molecules are chemisorbed on copper. Summarizing the experimental results we propose a mechanism for the different action of thymine molecules in the Cu deposition process: The potentials of zero charge (PZC) of Au(111) and Cu(111) in perchlorate solution differ by about 200 mV. In case that the first monolayer of copper is deposited during the process a recharging of the electrode surface from negative to positive values occurs. Because it is known that thymine molecules prefer to chemisorb positive of the PCZ it becomes directly evident that a reorientation of thymine molecules is favoured. The energetic reason for the promoted Cu-UPD process is the affecting of the PCZ of both metals due to adsorbed thymine molecules. Whereas the desorption of thymine molecules on Au(111) raises a PZC shift into negative potential regions, the chemisorption of thymine on top of copper leads to a positive PZC shift. As consequence both PZC's come closer together reducing the interface energy between the Au(111) substrate and the copper monolayer. In STM experiments could be recognized that a second copper layer is deposited negative of the Nernst potential. This would mean that the influence of the PZC shift is not restricted to the first monolayer deposition. If more than the second layer is deposited thymine molecules shield the surface against deposition in the common manner and three dimensional copper growths at kinks and sites is obtained.

It can be resumed that thymine acts for the same deposition system in a different manner depending on the changing attributes of substrate.

Kinetics of electrocatalytic reduction of CO₂ on Pt(210), Pt(320) and Pt(991) electrodes in sulfuric acid solutions

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Electrochemical reduction of CO_2 is of importance in fundamental research of electrocatalysis and environmental applications, and has received many attentions in recent years [1]. Well-defined single crystal electrodes can provide different models of surface atomic arrangement, and facilitate understanding the interaction of CO_2 with electrocatalyst at a microscopic level. We have studied CO_2 reduction on basal single crystal planes and stepped surfaces of structure [n(100)-(110)] [2]. In this paper, electrodes of Pt stepped surfaces Pt(210), Pt(320) and Pt(991) were prepared and employed to study the surface processes and kinetics of CO_2 reduction, by using both cyclic voltammetry and programmed potential step transient techniques.

As illustrated in Fig.1, the average rate $\bar{v}$ of CO_2 reduction on the 3 Pt electrodes cooled in air after flame annealing is varied with potential E_r, and that along with the decrease of (110) step density on the stepped surface, the electrocatalytic activity can be sorted by an order of Pt(991) > Pt(320) > Pt(210).

The results obtained in the current studies revealed the kinetics of CO_2 electrocatalytic reduction and the surface structural effects involved in the reaction.

Fig.1 Distribution of the average rate with E_r of CO_2 reduction on Pt electrodes.

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Why is the Experimental Transfer Coefficient for Simple Electron Transfer Reactions usually not equal to 0.5?

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Examination of the data in the literature reveals that the experimental transfer coefficient is often different from 0.5. In fact, values of this quantity greater than 1 have been observed. These observations are due to the effect of the double layer on the electrode reaction. An analysis of double layer effects is presented in this paper which explains the source of the observations. Examples discussed include reactions at Au single crystal electrodes and Hg electrodes.

Quartz microbalance investigation of electrochemical and electroless reactions for multilayers preparation

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The quartz crystal microbalance is a piezoelectric device often used to measure deposit thickness realized in vacuum systems. The measurement technique is based on the changes in the resonance frequency (Δf) of a quartz crystal as a function of a deposited mass variation (Δm) according to the Sauerbrey equation [1]

$\Delta f = k\Delta m$

where k is a calibration constant.

This device is used in many applications and its high precision is convenient for different domain like pollution, electronic noses …

It is also a relevant instrument in electrochemistry going from the classical faradic efficiency measurements to the mass/potential transfer functions measurements.

Here, few investigations realized with a quartz crystal microbalance exhibit the preparation of different multilayer deposits and the quantification of the electroless displacements are particularly presented

For multilayer preparations like Cu-Ni [2], the pulsed potential method gives a good concordance between the measurements of the mass evolutions and the currents corresponding respectively to the zones of copper and nickel reduction. So, it was relatively easy to realize multilayers with this system because the kinetics of the less noble metal (Ni) was very slow. But it was not the case for Cu-Co multilayer [3] because of the presence of a chemical displacement between copper and cobalt. The study of the mass evolution compared with the analysis of the composition deposit enables us to evaluate the importance of this phenomenon. Moreover, according to the pH value, we have show the formation of Cu_2O during the electroless reaction. This chemical displacement is also present for the preparation of Cu-Ag multilayers [4]. In this last case, we have shown the possibility to realize the multilayers applying an applied potential in the copper reduction zone following with a rest potential for the silver electroless process. The possibility to realize the Cu-Ag multilayers by pulsed potential was studied too.

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Symposium 8 - Poster

Surface Chemistry and Dynamics

Low frequency molecular oscillator

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Various authors describe impedance systems with negative differential resistance (NDR) [1-5]. These include anodic metal dissolution, cathodic metal deposition, oxidation of organic molecules, and reduction of H2O2. We reported on biological molecules with NDR [6]. Reverse impedance plots with NDR may extend into the 2d, 3d, and 4th quadrants. Microscopic views of dried materials from our NDR experiments show symmetric liquid crystals. But experiments have not expanded to show the materials function in larger circuits. Now we report studies in which a compound with NDR converts to impedance oscillation. Because of the novel plot geometry, assays were duplicated with two separate electro-analytic systems, with mercury and gold electrodes. The initial NDR sample was the palladium complex of lipoic acid (PLA) [6]. This complex was subsequently modified by bonding to an organified two-metal cluster battery complex (BC) (pat.appl.). The resulting compound (G3) exhibits oscillation impedance (Fig.1). DNA causes G3 oscillation to begin at higher frequencies, and show voltammetric oscillation (Fig.2).
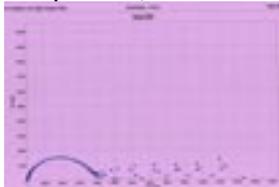
Fig.1

Fig.2

Fig.3

Fig.4

The DNA liquid crystal (Fig.3) is induced to wave form (Fig.4) by G3, a novel symmetry. Oscillation behavior of G3 may reside in two inductances : the paramagnetic spin of palladium and the self-inductance of BC. ESR measurements of PLA and G3 show a hyperfine shift, supporting interaction between PLA and BC. The G3 Bode plot shows oscillations in phase angle and capacitance, measures of a periodic potential – with implications of coherence.

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Surface Chemistry and Dynamics

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Symposium 8 - Poster

Silver electrocatalysis and dissociative electron transfer mechanisms

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Electron Transfer (ET) to organic molecules, bearing suitable leaving groups such as halides, is quite often accompanied by fragmentation of a σ-bond. There are two possible reaction mechanisms for such reductive cleavages. The stepwise one, with the intermediate formation of a radical anion (eqs 1 and 2) or the concerted way in which two fragments, a radical and an anion, are produced in a single step (eq 3).

$$RX + e \rightleftarrows RX^{\bullet-} \tag{1}$$
$$RX^{\bullet-} \longrightarrow R^{\bullet} + X^- \tag{2}$$
$$RX + e^- \longrightarrow R^{\bullet} + X^- \tag{3}$$

A large body of examples of both types of mechanisms has been reported for various classes of compounds [1].

Very recently, a series of papers dealing with the reduction of organic halides at silver cathodes has appeared [2]. The most important result emerging from such studies is that silver exhibits extraordinary electrocatalytic activities towards the reduction process. This important electrocatalytic activity has been successfully employed in the electrosynthesis of important antiinflammatory drugs [3].

In the reduction of halopyridines [4] we found that silver electrode shows a remarkable electrocatalytic effect for the reduction of the bromo derivative, whereas no effect was found for the chloro derivative.

To achieve a substantial refinement we investigated a series of organic halides to verify how electrocatalytic effects depend on the different reaction mechanisms. We compared the electrochemical reactivity of several bromides and the corresponding chlorides. The compounds were selected so as the major structural constituents were nearly the same but differently assembled to give benzyl halide, aryl halide, haloethylbenzene and halopyridine. This enables to compare active groups of widely different intrinsic reactivity, but having nearly the same chemical environment.

It appears that for the chloro derivatives the electrocatalytic activity of Ag is related to the concerted mechanism, whereas in the stepwise one there is no effect. In the case of bromo derivatives we found an electrocatalytic activity, at different extent, also for the stepwise mechanism.

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Surface Chemistry and Dynamics

First-Principles Molecular-Dynamics Simulations of Etching Processes in Ultrapure Water

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We proposed a new electrochemical etching and cleaning method of substrates using ultrapure water [1][2] which contains OH and/or H radicals, in order to develop an environmentally sound manufacturing processes especially for manufacturing of the electronic devices or MEMS (micro electro mechanical system).

In order to reveal the etching or cleaning process by OH and/or H radicals in ultrapure water, first-principles molecular-dynamics simulations of Si(001) ,Al(001) surface and organic molecule interacting with OH and/or H radicals were carried out on the basis of the Kohn-Sham local-density-functional formalism. Norm-conserving pseudopotential and plane-wave basis set were used, and the cut-off energy was 327eV(24Ry). In the simulations, the standard molecular-dynamics method for the optimization of the ionic system and the preconditioned conjugate-gradient (CG) method for the quenching procedure of the electronic degrees of freedom were adopted.

In case of Si(001) surface interacting with OH molecules, it was confirmed that the Si surface atom cannot be etched off as an $Si(OH)_4$ molecule and that two OH molecules react with each other producing an H_2O molecule and an oxygen atom. The oxygen atom bonds with two Si surface atoms at the surface bridge site or back-bond. However, in case of Si(001) surface interacting with H atoms and H_2O molecules, it was confirmed that an H atom reacts with H_2O molecules on the hydrogen-terminated Si(001) surface to produce an OH molecule, and chemisorption of two OH molecules to the hydrogen-terminated Si(001) surface atom breaks the back-bonds and the Si surface atom is etched off with forming an $SiH_2(OH)_2$ molecule. In the case of Al(001), the similar etching process of surface Al atom by H and OH radicals were observed.

In the electronic device manufacturing processes, it is required to remove organic masking materials for lithography and organic contaminations on the substrates. In the simulations of reaction between the organic molecule and OH radicals, polyethyene and benzene molecule were tested. It was confirmed that OH radicals pull out the H atom of the organic molecule and oxidize the C atom forming C-C double bond, and the neighbor C-C bond were dissociated.

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Symposium 8 - Poster

Surface Chemistry and Dynamics

Influence of the formation rate of a layer of CO adsorbed on polycrystalline Pt on the kinetics of its electrooxidation

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The electrooxidation of CO adsorbed on Pt has been studied since long ago, and especially since the development of fuel cells using either hydrogen from a reformer or methanol has become a main goal of energy strategy. The Pt-CO system is so unique that electrooxidation of bulk CO in acidic electrolyte can be made to proceed at only 0.5 V vs RHE, instead of at the usual potential of 0.90 V, by keeping the Pt electrode at a potential ≤ 0.1 V while CO is admitted in the cell, as serendipitously discovered by Kita et al. [1] in 1988. The CV in CO-saturated electrolyte then shows, besides a peak of dissolved CO at about 0.5 V, a peak of adsorbed CO at about 0.75 V [2]. We have reported [3] that increasing the rate at which CO was bubbled in the electrolyte, or increasing the time elapsed before starting the potential scan, shifted positively the peak of adsorbed CO up to about 0.90 V, the peak potential observed when CO is admitted at potentials ≥ 0.4 V. We attributed the influence of the bubbling rate, not to impurities in the solution, but simply to differences in the formation rate of the layer of adsorbed CO.

In order to confirm the above hypothesis, we have carried out experiments under conditions of extreme cleanliness. A polycrystalline Pt electrode was obtained by quenching in water a hanging drop of molten Pt (99.998%, Alfa-Johnson Matthey), the Pt polycrystal being then ground until reaching the maximum cross section and finally polished with alumina down to 0.05 μm. Ultrapure water (2-4 ppb TOC) was obtained from a MilliRO-MilliQ system. Nitrogen (N50) and carbon monoxide (N47, aluminium alloy cylinder) were from Air Liquide. Before each experiment the electrode was annealed in the flame of a Bunsen burner and transferred to the cell while protected by a droplet of ultrapure water. The hanging meniscus configuration was used. A Pt wire and a RHE were used as auxiliary and reference electrodes, respectively.

The same results reported in [3] were obtained: at low bubbling rates and short contact times, the peak of adsorbed CO appeared at 0.75 V, and at higher bubbling rates or longer contact times it was shifted to 0.90 V. Further experiments were carried out blowing the CO above the solution, instead of within it. This allows a very rapid saturation with CO, especially at high gas flow rates, at which the gas transfer rate to a thin surface layer of the electrolyte may be increased by several orders of magnitude. Again, the same results were obtained. It is concluded that the peak of adsorbed CO appears at 0.75 and 0.90 V when the CO layer is made up of a looser structure and of compact islands, respectively, formation of the latter being favoured at high bubbling rates, and that the diffusion of CO molecules on the Pt surface involved in the transition from the looser structure to one made up of compact islands is slow.
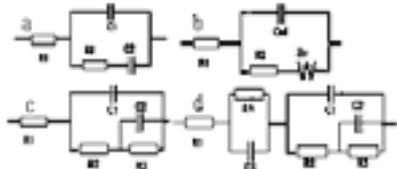
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Symposium 8 - Poster

Surface Chemistry and Dynamics

Impedance study of the electroreduction of hexaamminecobalt(III) cations at electrochemically polished Bi single crystal electrodes

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Electroreduction kinetics of the $[Co(NH_3)_6]^{3+}$ cation at Bi(hkl) planes from different surface inactive electrolyte solutions has been studied using impedance and rotating disk electrode methods. The data obtained using rotating disk electrode method indicate the small deviation of $Bi|[Co(NH3)_6]^{3+}$ + base electrolyte system from the classical Frumkin slow charge transfer theory [1]. The complex plane impedance $Z``,Z`$ (i.e., Nyquist) plots for the electrochemically polished Bi(111) and Bi(011$^-$) electrodes in $HClO_4$ (0.001…0.1M) with addition of the $[Co(NH_3)_6](ClO_4)_3$ (0.0001…0.0005M) have been measured using the Autolab PGSTAT 30 FRA 2 at ac frequency, f, (0.05 to 5000 Hz) within the region of the electrode potential $-0.85<E<-0.4$ V vs. Ag|AgCl|sat. KCl. Nyquist plots at different potentials where fitted using the various equivalent circuits, given in Fig 1. Equivalent circuits used for fitting the experimental Nyquist plots: R_1-high-frequency resistance, C_1-"true" double layer capacitance, R_2–charge transfer resistance, C_2-adsorption capacitance, R_3-adsorption resistance, Z_w–Warburg like diffusion impedance, R_4-medium frequency charge transfer resistance, and C_3-medium frequency adsorption capacitance. The shape of the Nyquist plots for the

electroreduction of $[Co(NH_3)_6]^{3+}$ depends on the base electrolyte and $[Co(NH_3)_6]^{3+}$ concentration, and total polarization resistance decreases with the rise of c_{HClO4} in solution. The shape of the Nyquist plots measured also depends noticeably on the electrode potential and crystallographic structure of Bi surface. The adsorption limited process at $E=-0.85V$ deviates toward

the mixed kinetics process at $E=-0.55V|Ag|AgCl|$ sat. KCl. The results of the nonlinear square root least minimization method of the experimental $Z``,Z`$-plots show that, to the first very rough approximation, the Randles (b) or Ershler (a) circuits can be used for fitting the experimental results. However a noticeably more exact fitting can be obtained if the equivalent circuit (c) has been used for analysis of the reaction mechanism.A better fit of the experimental results was observed when the equivalent circuit (d) was used.

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Symposium 8 - Poster

Metal-Porphyrin interactions with small molecules and its electrocatalytic activity towards CO_2 reduction

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Surface Chemistry and Dynamics

A water soluble metal-porphyrin was selected to be studied in the presence of small molecules (HCOOH, CO and HCHO), reported as being intermediates in the electroreduction of CO_2. On the basis of literature, we have assumed that water solubility of the electrocatalyst is necessary as water provides a cheap source of hydrogen if hydrocarbons are intended to be obtained from CO_2. On a previous work[1] it has been proposed that not only water but pH may play a fundamental role, as CO_2 entering into a neutral pH solution becomes mostly hydrogencarbonate species, which will be repeled by a negatively charged cathode. Even more, being the water discharge a competitive process, which produces relatively large amounts of OH^- species into the diffusion layer, the minute amount of dissolved CO_2 will be immediately converted to HCO_3^- and CO^{2-}. Into this context, we have characterized the behaviour of the metal-porphyrin in a buffered solution (pH 2) in order to maintain an acidic environment to prevent the "Carbonate Route" and to increase a higher effective concentration of CO_2 in the vicinity of the electrode surface. The metal-porphyrin itself may serve as a sequestration device keeping and even increasing CO_2 in solution and transporting it towards the electrode surface.

The metal-porphyrin was studied using cyclic voltammetry in presence and absence of the previously mentioned molecules. All molecules tested proved to interact with the metal porphyrin. In absence of the testing molecules, the metal porphyrin does not electrocatalyses the water discharge. In presence of the testing molecules the metal-porphyrin reduces the onset potential for the electroreduction of such molecules and current intensity increases in all experiments. Spectroelectrochemical and electrolytic experiments provide us with further evidences. All experiments were performed in single compartment cell. A glassy carbon disk served as working electrode and a platinum wire served as auxiliary. The reference electrode was at all times Ag/AgCl.

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Symposium 8 - Poster

Surface Chemistry and Dynamics

A Great Enhancement in the Oxidation Ability of Diluted Nitric Acid in the Nanoscale Water-Droplets of Reverse Micelle Systems

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In reverse micelle systems, a great enhancement of the oxidation ability of diluted nitric acid was discovered and its oxidation mechanism was explored. The Br^- ion of CTAB surfactant was oxidized into Br_2 (or Br_3^-) in $CHCl_3$/CTAB/H_2O reverse micelle system of W = 1.0 – 4.0 by diluted nitric acid of 0.25□2.5 mol dm^{-3} (in the 1.0 vol% H_2O portion) at 15 – 40 °C where CTAB stands for cetyltrimethylammonium bromide and the W value is the ratio of $[H_2O]$/[surfactant]. At the higher concentrations of nitric acid and temperatures, the faster reaction proceeded; otherwise long inductive periods were needed, e.g., 10 hours for 1.0 mol dm^{-3} HNO_3 at 25 °C. No effect of light or of ambient oxygen was apparently observed.

The ratio of produced Br_2 or (Br_3^-) to the initial HNO_3 amount indicated the following reaction scheme:

$2HNO_3 + 2Br^- \square Br_2 + NO_2^- + NO_3^- + H_2O$.
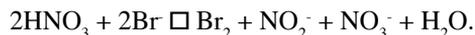
The nitroyl ion (or nitronium ion), NO_2^+, was suggested as the intermediate active species. The addition of $HClO_4$ as the proton supplier tended to cause the completion of the oxidation ability of N(V) as follows:

$NO_3^- + 6H^+ + 5e^- \square 1/2 N_2 + 3H_2O$.
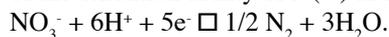
The hydrogen bonding structure of H_2O in the CTAB or CTAC (cetyltrimethylammonium chloride) micelle system was found to be distorted, compared with that in bulk water, by the ^1H NMR chemical shift of H_2O. The change of ^1H NMR chemical shift also demonstrated the consumption of protons during the oxidation of Br^- but not of Cl^- by diluted HNO_3.

Structural Effects on the Oxidation of Formic Acid on High Index Planes of Palladium

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Formic acid is oxidized on Pd electrodes without the formation of adsorbed CO [1]; the activity for the formic acid oxidation on Pd is higher than that on Pt. We have studied the oxidation of formic acid on high index planes of Pd for the elucidation of surface structures enhancing the rate of the oxidation. Four series of high index planes have been examined: $n(100)$-(111), $n(100)$-(110), $n(111)$-(100) and $n(111)$-(111).

Voltammograms of formic acid oxidation were measured in 0.1 M HClO$_4$ containing 0.1 M formic acid. The rate of formic acid oxidation was assessed using the peak current density j_P of formic acid oxidation in the first positive scan. Fig. 1 shows j_P plotted against the step atom density d_S. The series of $n(100)$-(111) have the highest rate for the formic acid oxidation in all the series, giving maximum of j_P on Pd(911) (=5(100)-(111)). The values of j_P on the surfaces with n 3 are as high as that on Pd(100), except Pd(911). These results show that (100) surfaces with more than three terrace atomic rows have high activity for formic acid oxidation in $n(100)$-(111) series. In $n(100)$-(110) series, however, the values of j_P do not give maximum, decreasing monotonously at n 4. Surfaces in $n(111)$-(100) series have maximum of j_P at $n = 5$, as is the case of $n(100)$-(111) series. The values of j_P decrease monotonously with the increase of step atom density on $n(111)$-(111) series. Pd(110) (=2(111)-(111)) has the lowest j_P in all the series. The structural effects will be discussed in detail according to the calculation using density functional theory.

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Acknowledgement:

Fig. 1 Peak current density of formic acid oxidation (j_P) plotted against the step atom deinsity of Pd electrodes(d_S)
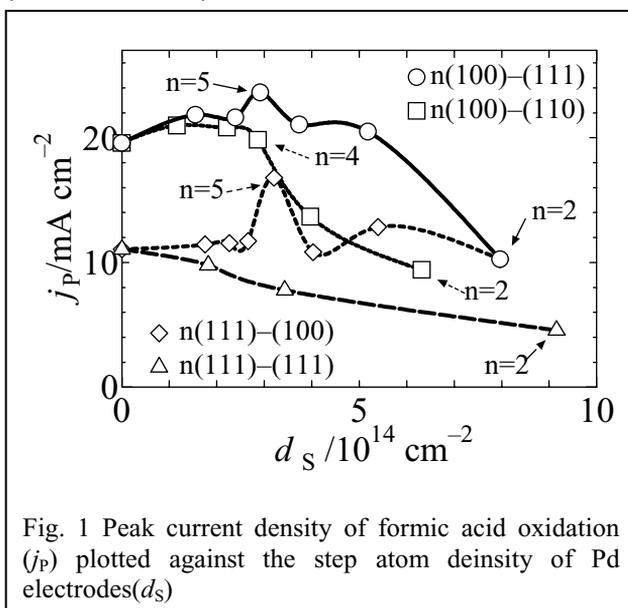
Ab-initio MO calculation for Zn cluster

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Cluster models have been applied to molecular orbital (MO) calculation to analyze various physico-chemical phenomena occurring on metal surface. In this study fundamental properties of zinc cluster were investigated by using ab-initio MO calculation. Zinc atom in bulk metal has nonlocalized metallic orbitals. Zinc atom orbital is, however, $4s^2$ closed-shell atomic configuration like He atom. Wang et al.[1] performed density functional calculations for Zn clusters and evaluated the binding energy and HOMO-LUMO gap. They also indicated that van der Walls binding- covalent bonding - metallic bonding transition occurs with increasing cluster size. To investigate this

Fig.1. Minimum distance between atoms, R_{min}, averaged binding energy, ΔE_b, and averaged population in 4p orbitals, P, calculated for Zn_n clusters as a function of cluster size, n.

transition in detail we performed density functional calculations for Zn_n clusters (n=1-32) as shown in Fig. 1. For example, minimum distance between two atoms, R_{min}, decreases dramatically at cluster size n=2-4, and shows stable value at larger cluster. Averaged binding energy, ΔE_b, shows rapid increase at n=3-4 corresponding to change in population in 4p orbital at n=3-4. In the presentation relationship between changes in these values and transition in binding form will be discussed.

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Influence of $C_6H_{6\,ads}$ on the Under-Potential Deposition of H and Anion Adsorption on Pt(111) in Aqueous $HClO_4$

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We analyze the adsorption of C_6H_6 on Pt (111) and subsequently the influence of $C_6H_{6\,ads}$ on the H_{UPD} and ClO_4^- adsorption on Pt(111) in 0.05 and 0.50 M aqueous $HClO_4$ using cyclic voltammetry (CV). CV profiles are recorded in the 0.02 – 0.80 V vs. RHE range. They reveal a sharp, symmetric cathodic peak (0.02 – 0.15 V) and a well-defined, asymmetric anodic one (0.04 – 0.20 V); there are no features in the potential range that corresponds to the anion adsorption. An increase of the C_6H_6 concentration from 1 to 20 mM leads to a peak shift toward less-positive potentials. The peak potential (E_{peak}) of the cathodic and anodic features is independent of the scan rate (for $s = 10 – 100$ mV s^{-1}), and the peak current density (i_{peak}) increases linearly with s. The cathodic and anodic charge-density (q) values agree and are 220 ± 3 μC cm^{-2}, thus slightly less that the charge density corresponding to the transfer of one electron per Pt surface atom (240 μC cm^{-2}). The results suggest that the CV features correspond to the adsorption and desorption of H_{UPD}. We analyze in detail the under-potential deposition of H (UPD H) on the C_6H_6-modified Pt(111) in C_6H_6-free aqueous $HClO_4$ by cycling the electrode in the 0.05 – 0.80 V range. The CV profiles evolve and the original well-defined cathodic and anodic peaks decrease in intensity (lower i_{peak} value); we observe that the repetitive cycling of the C_6H_6-modified Pt(111) results in a partial recovery of the CV features characteristic of a clean and well-defined Pt(111) electrode in aqueous $HClO_4$. We also analyze the impact of temperature (T) variation on the CV features. An increase of T from 274 to 318 K results in (i) a shift of the cathodic and anodic peaks toward more-positive potentials, and (ii) a gradual decrease of i_{peak}. The T-dependent studies and the comprehensive set of data allow us to examine the influence of $C_6H_{6\,ads}$ on the thermodynamic state functions for UPD H (ΔG°_{ads}, ΔS°_{ads}, ΔH°_{ads}), the Pt(111)-H_{UPD} surface bond energy ($E_{Pt(111)-Hupd}$), and the nature and strength of lateral interactions (ω) between the adsorbed species. We compare the present results with analogous data obtained in aqueous H_2SO_4 [1].

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Surface Chemistry and Dynamics

In-situ Transmission FTIR Spectroscopic Study on the Adsorption of Dodecyl Sulfate on Au Electrode

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The adsorption of molecules at interface is an important aspect in surface science. In situ transmission difference FTIR spectroscopy method has been developed as a convenient, relatively simple way to investigate the electrochemical process and to clarify the identity of species both adsorbed on the surface of electrode and dissolved in solution [1]. In this report it was used to probe the adsorption of sodium dodecyl sulfate (SDS) on Au electrode and the hydrolysis reaction mechanism of SDS in solution.

The working electrode was an optically transparent minigrid Au electrode with mesh of 500 lpi (Bucklee-Mears Com.). Its rough surface is benefit to the detection of adsorbed substances on electrode especially in the in-situ FTIR transmission differential spectroscopic study. Platinum wire and saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. The experiments were carried out using Nicolet 760 FTIR spectrometer. The differential transmission spectra of T_2/T_1 reflect the substance change in the cell, where T_1 and T_2 are the transmission spectra collected at reference and sample potential, respectively.

Fig.1 shows the in situ differential transmission FTIR spectra in C-H stretching (a), and S-O-H stretching (b) regions measured in 6mmol/L SDS solution at different sample potentials, while reference potential was 0.5V. The variation of spectra in Fig.1a suggests that SDS molecules start to desorb at potential near -0.2V and desorb entirely when the potential reaches –0.8V. This process was confirmed by electrochemical impedance measurements as shown in Fig.2.

Fig.1b was caused by hydrolysis process of SDS in solution. From the variation of spectra with time, the first-order reaction constant was measued as 6.00×10^{-4} s^{-1}.

Acknowledgement
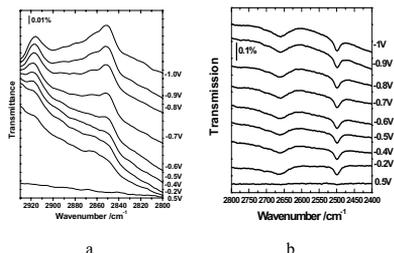
Fig.1 In situ differential transmission FTIR spectra of SDS   Fig.2 Electrochemical impedance of SDS
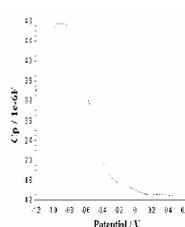
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Symposium 8 - Poster

Surface Chemistry and Dynamics

Differential capacity of Ag(111) in 0.01 M NaCl AND Ag(100) IN 0.01 M KBr

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It has been shown previously [1,2] that even single crystal electrodes cannot be treated as homogeneous surfaces and that instead of "ideal double layer capacity" a *CPE* should be used for fitting experimentally recorded C_{diff} vs. ω curves. In this communication more realistic equivalent circuit for presenting real single crystal surfaces was used including inhomogeneous and homogeneous charge distribution and corresponding capacities over such surfaces (R_{ad}^{ih}, CPE_{dl}^{ih}, R_{ad}^{h} and C_{ad}). Experimentally obtained C_{diff} vs. E curves were transformed into C_{diff} vs. ω dependences and fitted with the equation derived for such case

$$C_{diff} = C_{diff}^{ih} + C_{diff}^{h} = (C_{dl})^{\alpha}(\omega\, R_{ad}^{ih})^{\alpha-1}\sin(\frac{\alpha\pi}{2}) + \frac{C_{ad}}{1+\omega^2(C_{ad})^2(R_{ad}^{h})^2} \qquad (1)$$

Corresponding C_{dl}-E, C_{ad}-E, $(C_{dl}+C_{ad})$-E, R_{ad}^{ih}-E, R_{ad}^{h}-E, and α-E were plotted and discussed for both systems. In Fig. 1. are shown these dependences for the system Ag(100)/0.01 M KBr.
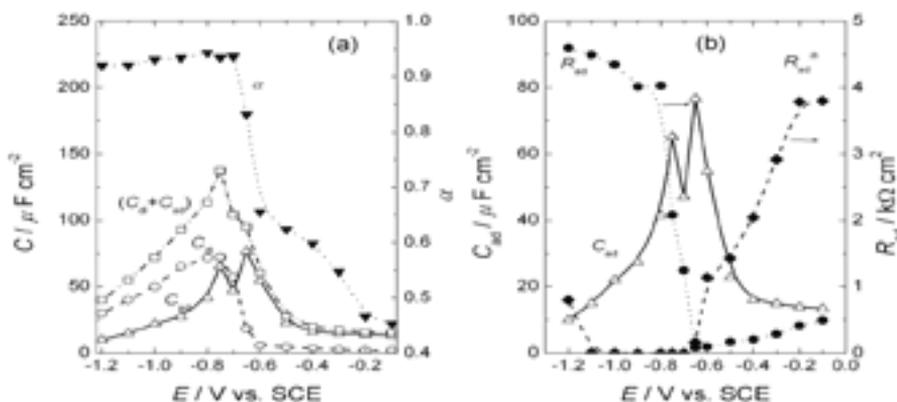
Fig. 1. (a) C_{dl}-E, C_{ad}-E, $(C_{dl}+C_{ad})$-E ,α-E and (b) C_{ad}-E, R_{ad}^{ih}-E, R_{ad}^{h}-E, dependences for the system Ag(100)/0.01M KBr

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Symposium 8 - Poster

Surface Chemistry and Dynamics

Adsorption of camphor and tiourea at Bi(111) electrode surface

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Two-dimensional (2D) phase transitions at solid surfaces have received much attention in recent years as this phenomenon is related to the very important aspects of surface and materials sciences. Kinetics of 2D condensation depends noticeably on the adsorption energy of solvent molecules, surface charge density and nature of anions and molecular organic compounds adsorbed. Our preliminary studies of the Bi(111) surface inactive electrolyte phase boundary [1] have demonstrated a very good stability of the atomic structure of the electrode surface within the wide region of potentials. The main aim of this work was to investigate the adsorption process of camphor and tiourea on the electrochemically polished Bi(111) plane by using the *in situ* STM method and for comparison cyclic voltammetry and impedance spectroscopy.

The *in situ* STM detectable adsorbed 2D camphor adlayer (Fig. 1. a) were formed at positive surface charge densities ($\sigma > 4$ μC cm^{-2}, $E > -0.45$ V) where the simultaneous contact co-adsorption of SO$_4^{2-}$ and camphor takes place with the noticeable partial charge transfer from the SO$_4^{2-}$ anions to the Bi(111) surface atoms. The adsorbed tiourea stacks (Fig. 1. b) were founded only in Bi(111) surface areas with low surface energy (sharp monoatomic steps and crystal defects).
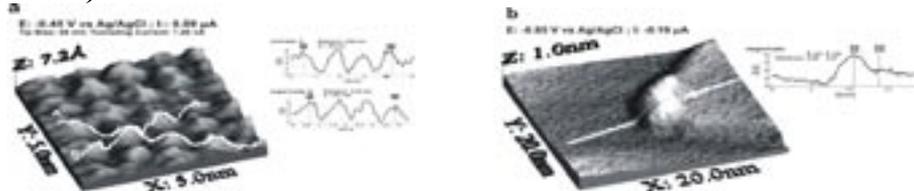
Fig. 1. *in situ* STM images and selected surface profiles of the camphor 2D layer (a) and tiourea stack (b) at Bi(111) electrode in 1×10^{-2} M camphor (a) and 1.7 M tiourea (b) + 5×10^{-2} M Na$_2$SO$_4$ + 2.5×10^{-5} M H$_2$SO$_4$ aqueous electrolyte.

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Adsorption of camphor on Bi(111) crystal electrode

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Two-dimensional (2D) phase transitions at solid surfaces or in the adsorption adlayers have received much attention in recent years as this phenomenon is related to the very important aspects of the surface and materials science and in nano- and molecular technology as well [1,2]. The important characteristics in 2D phase transition are related to the ordered adsorption, island nucleation and growth, oscillating of chemical and electrochemical reactions, surface reconstruction, selective corrosion and corrosion inhibition, chirality of the formed surfaces and electrodeposition mechanism.

Electrochemical behavior of camphor on the electrochemically polished Bi(111) single crystal planes in 0.05 M Na_2SO_4 and $2.5*10^{-5}$ M H_2SO_4 aqueous solution has been studied by impedance and cyclic voltammetry methods. Camphor forms a two –dimensional condensed phase on the Bi(111) crystal plane in the aqueous sulfate solution. The 2D condensed layer is stable in weakly acidic solutuion (pH= 4.4) in the wide pottential region ie from –1.2V to –0.5 V vs Ag|AgCl.

The differential capacitance vs electrode potential dependences has been measured and it can be seen that the cathodical adsorptison-desorption peak appears at the electrode potential –1.5 V. Differential capacitance decreases to 4.2 μFcm^{-2} at the region of zero charge potential and formes so called limiting adsorption plateau. At potential more positive than –0.5V the differential capacitance value increases indicating the desorption of the camphor molecules from Bi(111) surface.

The complex impedance plane (Z'', Z') and Bode phase angle vs log frequency plots at the peak and camphor two-dimensional condensation areas were measured. It can be seen that the adsorption kinetics of camphor on Bi(111) is mainly limited by the rate of the adsorption step.

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Surface Chemistry and Dynamics

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Surface Chemistry and Dynamics

EIS and CV measurements on noble metals and stainless steels up to 300 °C

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The electrochemistry of the noble metals and steels are well-known at room temperature, however, about the interfacial processes at high temperature a few knowledge exists. We have repeated the standard cyclic voltammetry and electrochemical impedance spectroscopy measurements on gold, platinum and three different stainless steel (AISI304, AISI316, 08H18N10T) samples in a static autoclave up to 300 °C. Surfaces of the samples were polished before installation into the autoclave. The platinum sample was annealed in gas flame. Samples were spotwelded to Teflon insulated zirconium wires; the electrical feedthrough was solved by Conax fittings. The electrolyte was 0.1M potassium hydroxide solution containing sulphuric acid (pH was between 3 and 7). The solution was bubbled with argon gas continuously except the time of the measurements. Three different reference electrodes were installed: external Ag/AgCl, internal yttrium stabilised zirconium-dioxide ceramic membrane (YSZ) filled with Ni/NiO and platinum hydrogen electrode. The stability of the reference electrodes was checked by long term monitoring between the measurements. Below 150 °C the Ag/AgCl, above 150 °C the YSZ was used for CV and EIS measurements. The counter electrode was the autoclave body.

The aim of our experiments was to gain detailed knowledge about the temperature dependence of well known and well described interfacial processes on well defined electrodes, and in the same time to abserve the same reactions on industrially important metals and alloys. The results were analysed by existing analytical double layer theories. We present the experiemtnal data together the shifting of redox peaks on the CVs and the changes the impedance parameters in the function of the temperature.

Galvanostatic oxidation of HCHO on Pt: Oscillations, bistability and bifurcations

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A variety of spatial and temporal patterns have been observed during the electrocatalytic oxidation of HCHO on Pt, such as bistability, periodic and chaotic oscillations, synchrony and intermittency [1]. A dual path mechanism has been proposed in order to interpret the potentiodynamic response and the galvanostatic oscillations. According to this mechanism, adsorbed HCHO molecules are oxidized to CO_2 via a direct and an indirect path [2].

In the present work an attempt is made to interpret the bifurcations taking place under galvanostatic conditions by considering the applied current as a bifurcation parameter. The oscillatory electrocatalytic oxidation of HCHO is studied experimentally and a bifurcation diagram is constructed, Fig 1(a). Subsequently, the dual path mechanism is modified by considering the desorption of adsorbed CO and the formation of higher valent oxides at high potentials. A mathematical model is constructed for this new mechanism by assuming Frumkin kinetics for the adsorbed species. The proposed model is studied numerically and a theoretical bifurcation diagram is obtained, Fig. 1(b), which reproduces the experimentally observed bifurcations, oscillations and bistability [3].
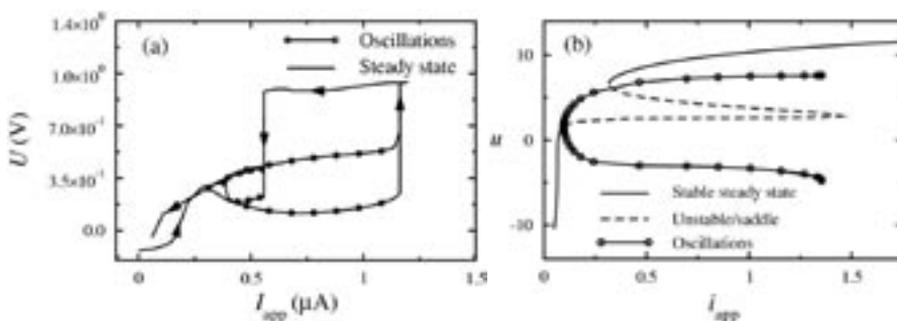
Figure 1: (a) Experimental and (b) theoretical bifurcation diagrams

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Symposium 8 - Poster

Surface Chemistry and Dynamics

Spatiotemporal oscillations in biological molecules: 3. Lysine and its electronic influence on gene expression

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L-lysine, a dibasic amino acid with a butyl ammonium side chain has pK_1(α-COOH), pK_2(α-NH_3^+), and pK_3(ϵ-NH_3^+) values of 2.16, 9.06 and 10.54 respectively so that it is positively charged at physiological pH. Elevated levels of lysine in blood and urine have been linked to mental and physical retardation. Histones have a large number of lysine residues and its positive charge promotes interaction with negatively charged phosphodiester linkages of DNA. Acetylation of lysine weakens this electrostatic interaction and loosens the chromatin structure allowing gene expression. Our impedance data with DNA-Lysine, characterized by spatiotemporal periodicities, suggest the electronic aspect of regulation of gene expression [1].

All living systems exhibit dynamical spatiotemporal periodicities [2]. We report here the data on lysine to complement our earlier data on DNA-Lysine. The reversible histone acetylation and deacetylation reactions control the activation and inactivation of gene expression. Our data suggest that we have to include the electronic properties of these molecules to complement the enzymatic process.

The Nyquist and Bode plots for 0.10 M L-lysine are shown in Figure 1. We attribute the impedance loci observed in four quadrants to the transition from the
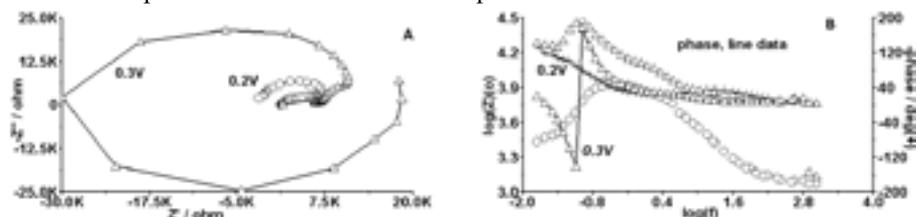
Figure 1. (A) Nyquist and (B) Bode plots for 0.10 M L-lysine, 0.021 M HCl, pH 9.59

nonminimum phase-type to the minimum phase-type and correspond to the Hopf bifurcation under current control [3]. The unique impedance behavior reflects periodicities and suggest global electronic coupling [4].

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Electrochemical and esr study of mechanism of electrocatalytical oxidation of organic compounds with partisipation of radical cations of pyrazine-di-n-oxyde and its derivatives as mediators.

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An important problem in chemistry and catalysis is to find an effective route of C-H bond activation for selective and mild oxidation of organic compounds. The main way of this activation is the interaction with an electrophilic oxygen-containing agent. The electrochemically generated radical cation of aromatic di-N-oxides carries active oxygen and is capable to activate C-H bond of substrates [1].

By the methods of cyclic voltammetry, quantum-chemical modeling, ESR at electrolysis at controlled potential and gas chromatography we have studied the mechanism of oxidation of organic substrates (cyclohexanol, methanol, diethylether, triethyl orthoformate and cyclohexane) in the presence of mediators, electrochemically generated radical cation of pyrazine-di-N-oxide (E_{ox} = 1.62 V) and its derivatives, 2,5-dimethyl-parazine-di-N-oxide (E_{ox} = 1.56 V), 2,3,5,6-tetramethyl-pyrazine-di-N-oxide (E_{ox} = 1.48 V), 2,3-dimethyl-5,6-cyclohexa-pyrazine-di-N-oxide (E_{ox} = 1.42 V) and 3-phenyl-5,6- cyclohexa-pyrazine-di-N-oxide (E_{ox} = 1.47 V). The study was carried out at glass carbon, Pt and Au electrodes in the presence of 0.1M $LiClO_4$ in acetonitrile, as well as in methanol and its deuterated derivatives (CH_3OD, CD_3OD) used as a solvent and a substrate simultaneously. The effect of temperature, acids, water, oxygen, the nature of substrate and solvent on the shape of CVs and the intensity of ESR signals has been studied. ESR spectra of radical cations and anions of pyrazine-di-N-oxide and its derivatives were revealed. The catalytic oxidation of investigated organic compounds were observed in the presence of mediators.

Quantum-chemical modeling of the reaction of radical cation of pyrazine-di-N-oxide with acetonitrile and methanol was carried out.

The obtained results were explained by the overall two-electron mechanism of electrochemical oxidation of substrate via formation of a complex of substrate with the radical cation of pyrazine-di-N-oxide . The rate constants of the C-H bond activation were determined by quantitative analysis of CVs on the basis of the proposed mechanism.

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Surface Chemistry and Dynamics

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Surface Chemistry and Dynamics

Enhancement of catalytic reactivity of Pt and RuSe nanoparticles towards oxygen reduction by assembling within metal oxide matrices

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An interesting alternative to activation of Pt nanoparticles towards oxygen reduction is their immobilization with large-surface-area inorganic oxide matrices that ensure mutual metal-support interactions, high dispersion of catalytic centers, unimpeded charge distribution and the overall good stability. Out of applicable systems, tungsten oxide has been demonstrated to promote oxygen reduction by interacting with Pt via hydrogen spillover and through the formation of highly conductive oxide bronzes that are reactive towards hydrogen peroxide intermediate. Regardless the actual reaction pathway, the optimum process (whether it occurs in one step proceeding directly to water or it consists of two steps with hydrogen peroxide as intermediate) would effectively require rapid transfer of total four stoichiometric electrons and protons.

Another solution for electrocatalysis originates from the possibility of self-assembling of polyoxometallate monolayers on Pt nanoparticles. We have considered Keggin type phosphododecamolybdate (PMo_{12}) or phosphododecatungstate (PW_{12}), the well-defined oxygen-bridged metal clusters related to the parent oxides of tungsten and molybdenum. By analogy to tungsten oxides, polytungstates are expected to enhance reactivity of Pt centers (via bifunctional mechanism) during reduction of oxygen. An important issue is the ability of an adsorbed polyoxometallate to shift potential of the interfacial Pt/PtO redox reaction towards more positive values. Thus the polyoxometallate stabilized Pt nanoparticles are characterized by a broader potential window where platinum metal is not covered by the inhibiting PtO. The structure of polyoxometallate adsorbate is spacious enough to permit O_2 molecule to reach and interact with metallic Pt. Both PMo_{12} and PW_{12} molecules are adsorbed on Pt only via corner oxygen atoms.

A serious drawback of platinum as the oxygen reduction electrocatalyst is its sensitivity to methanol that simultaneously undergoes oxidation while crossing-over from the anode space to the cathode area in a fuel cell. To overcome the problem, ruthenium-based selenium–containing ($RuSe_x$) catalysts have been recently considered. These catalysts have been demonstrated to be effective in promoting electroreduction of dioxygen almost directly to water but, in comparison to platinum, at more negative potentials. The overall oxygen reduction mechanism at $RuSe_x$ is complex and, realistically, it involves formation of smaller or larger amounts of hydrogen peroxide intermediate. Such situation is likely to occur when the low amounts of $RuSe_x$-catalyst are utilized for prolonged period of time under the enforced oxygen transport conditions. To activate $RuSe_x$ catalytic centers, their immobilization in tungsten oxide as an active matrix is proposed. Under rotating disk voltammetric conditions and at a fairly low loading (80 μg cm^{-2}) of the $RuSe_x$ catalyst, its modification with WO_3 results in the positive shift (ca. 150 mV) of the oxygen electroreduction potential and in the increase of the heterogeneous rate constant.

Voltammetry of citric acid at the solid electrodes

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Electrochemical behaviour of citric acid has been studied at the electrodes from Cu, Cd, Pt, Ta, Cu-Hg and alloys of Cd with Sn, Ni, Hg, In, Cu and Ag in aqueous solutions with various background electrolytes by the methods of voltammetry at the rotating disk electrodes and chronovoltammetry at the stationary electrodes. At all used electrodes in the neutral background solutions (0.1M) citric acid forms the well defined waves and chronovoltammetric peaks. The $E_{1/2}$ values are equal to –0.96V (Cu), –1.06V (Ta), –1.64V (Cu-Hg), –1.26V (Cd-Sn with 80% Sn), –1.44V (Cd-In with 1% In), –1.55V (Cd-Hg with 1-10% Hg). These values are close to the $E_{1/2}$ values of the hydrogen ions discharge process at the corresponding electrodes. The height of the waves of citric acid increases (without the appreciable change of the $E_{1/2}$ values) under the addition of the small amounts of H_2SO_4. The small additions of high-basic pyridine cause the sharp decrease of the height of the citric acid waves and shift of the $E_{1/2}$ values towards the negative direction. Moreover, a pronounced dependence of the $E_{1/2}$ values on the composition of the Cd alloys electrodes is observed. An increase of the Sn and Ni content in the Cd-Sn and Cd-Ni alloys causes the appreciable shift of the $E_{1/2}$ values towards the less negative direction. In case of the Cd-Hg and Cd-In electrodes an increase of the Hg and In content causes only small change of the $E_{1/2}$ values. All the described experimental facts testify that the above-mentioned waves of citric acid correspond to the hydrogen ions discharge process.

With the aid of suggested by us method the parameters of dissociation of citric acid in dilute ($10^{-4} - 10^{-3}$M) solutions (the degrees of dissociation for all dissociation steps, the equilibrium concentrations of mono-, di- and trianions and undissociated acid, pH values) have been calculated. For the millimolar solution of citric acid the values of α_1, α_2 and α_3 are equal to 0.568, 0.0164 and $1.112 \cdot 10^{-5}$ respectivly. These values show that tribasic citric acid from the aspect of formation of the hydrogen ions concentration can be considered as dibasic acid.

In our calculations the following equations were used:

$$K_1 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)(\alpha_1 - \alpha_2)c}{1 - \alpha_1} \qquad K_2 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)(\alpha_2 - \alpha_3)c}{\alpha_1 - \alpha_2}$$

$$K_3 = \frac{(\alpha_1 + \alpha_2 + \alpha_3)\alpha_3 c}{\alpha_2 - \alpha_3} \; ,$$

where K_1, K_2 and K_3 are the corresponding dissociation constants; c is the total (analytical) concentration of acid.

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Surface Chemistry and Dynamics

Palladium underpotential deposition on platinum single crystal with (111) orientation: a study of the low dimensional Pd-H system

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Insertion-desertion of hydrogen in metals, alloys and intermetallic compounds have been intensively studied, as they play a primordial role in the development of hydrogen storage materials, H_2 purification (gas permeation) or hydrogen sensors. Indeed technological applications could benefit from better understanding of the phenomena involved during hydride phase precipitation, that induce hysteresis during insertion-desertion cycles. In this scope, palladium [1-3] can be used as a model system because of its good mechanical properties and quite large hydrogen absorption capacity.

Particularly, the present study deals with a low-dimensional Pd-H system. It consists of Pd electrochemical deposits of atomic layer(s) on platinum single crystal substrate with (111) orientation, which are known to be epitaxial [4]. They are made through palladium underpotential deposition (UPD) in presence of chloride anions in order to allow 2D deposition of several quite complete monolayers [5]. Such samples provide nanostructured model systems that are known to reduce hysteresis while allow to bypass the problem of irreversible lattice expansion caused by hydrogen insertion.

We have achieved Pd deposition rates from submonolayer to multilayers. They have been electrochemically characterized in sulfuric and perchloric acid using hydrogen adsorption as a "probe". Beside the usual features specific to such deposits [4,5], under some experimental conditions an unexpected peak appears. Our attempts to get more insight into its origin (hydrogen adsorption, anions effect, etc.) using electrochemical methods seem to indicate the existence of surface alloy formation. Insertion phenomena have also been preliminary investigated in different Pd deposition, from one to several atomic layers: insertion isotherm and impedance spectroscopy have been undertaken.

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Computational study for the reaction of CO with OH· on the Pt(111) surface.

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Poisoning of Pt electrodes by CO is a critical obstacle for meeting the desired catalytic activity and is responsible for loss of power in fuel cells [1-3]. The often observed correlation between the potential of formation of OH(ads) on Pt anodes and the potential of CO(ads) removal supports the proposal that OH(ads) is the oxidant [2].

The present work is a computational density functional theory (DFT) study on the reaction of CO with the OH· radical, both species being adsorbed on a Pt(111) surface (reaction 1). Modelling of the metal surface was performed by means of slabs or clusters having different number of Pt atoms, and also employing periodic boundary conditions (PBC).

$$CO(ads) \quad + \quad OH^{·}(ads) \quad \rightarrow \quad COOH(ads) \qquad (1)$$
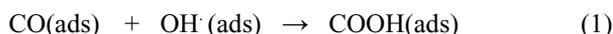
Reaction and activation energies for reaction 1 were calculated, and values obtained with different functionals, basis sets and the various metallic surface representations were compared. The program packages Gaussian 03 and SIESTA 1.1 were used.
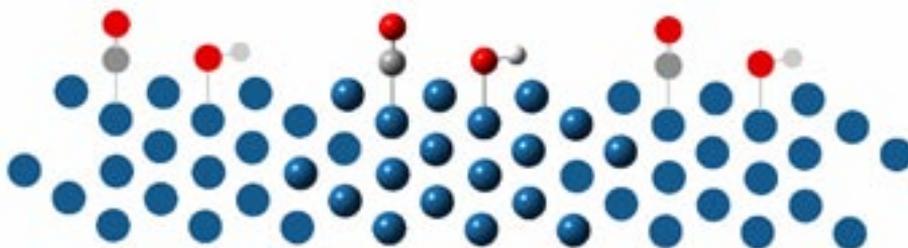
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Surface Chemistry and Dynamics

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Surface Chemistry and Dynamics

New oscillatory electrooxidation of iodide in alkaline solution

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Oscillations in current only during oxidation of iodide were first reported by Gokhshten on platinum in acid media [1]. Tributsch et al. studied current oscillations and simultaneous electrode reflectivity during iodide oxidation on illuminated n-type $MoSe_2$ semi-conductor electrodes [2]. Lately, Vitt and Ma investigated the current oscillations in nitric acid at a rotating gold-gold ring-disk electrode, and they attributed the oscillations to the film formation of iodine and its dissolution by forming I_3^- [3-4].

Oscillations both in potential and in current have been observed here for the first time during the anodic oxidation of iodide in alkaline solution on a static platinum electrode [5]. Phase transitions at the interface of electrode/solution are essential in this oscillatory system. The film formation of solid iodine acts as a negative nonlinear feedback slowing down the iodide oxidation due to its poor conductivity, and oxygen evolution as a positive nonlinear feedback by destroying the iodine film mechanically and by promoting its dissolution through convection mainly via a disproportional reaction. Based on the results of electrochemical experiments and in situ Raman spectroscopy, a tentative mechanism is given below concerning the interfacial phase transitions and the disproportional reaction.
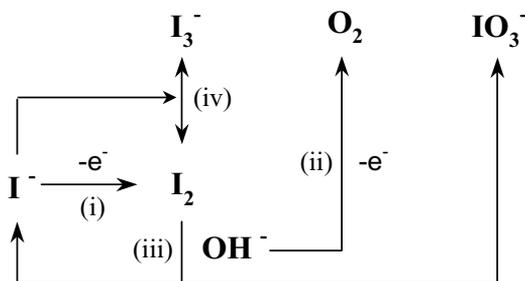
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Lyotropic Series in Redox Processes

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Alkaline cations form a well known lyotropic series in adsorption processes. Their different affinity with different surfaces affects the properties of these systems in physical and chemical processes.

In this work we present results on the influence that these cations exert on the charge transfer behaviour taking place on the lattice cations (Co^{2+}, Co^{3+}) of the mixed valence oxide Co_3O_4.

In cyclic voltammetry, the peak position and shape depend on the alkali cation present. Peaks are shifted more positive passing from Cs^+ to K^+ and Na^+, Li^+, so that the internal oxide charge transfer is easier in Cs^+ than in Li^+.

These results parallel previous ones concerning oxygen evolution from Mg-doped $LiCoO_2$ [1] where the reaction order with respect to OH^- was found to increase from 1 to about 3 from Li^+ to K^+ and Cs^+.

By mechanistic analysis the effect was reconciled with a variation in the rate determining step caused by interaction of the given cation with oxide surface sites.

Lyotropic interactions and hydrated cation size apparently have far reaching effects on the charge transfer behaviour of at least the at present considered cobalt-based oxides.

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Symposium 8 - Poster

Surface Chemistry and Dynamics

Symposium 8 - Poster

Surface Chemistry and Dynamics

Homogeneous Epoxidation of Ethene and Propene in the presence of hydrogen peroxide. A DFT study.

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The epoxidation reaction is technological important and both experimentally and theoretically challenging. In this study quantum chemical calculations were used to study the epoxidation of ethene and propene with hydrogen peroxide in gas phase and in aqueous media. Calculations for possible routes, including the alternative oxidation routes to the corresponding diol or aldehyde, and definition of the rate limiting steps and activated complexes were made, Scheme 1. The calculations were carried out at the B3LYP/6-311+G(d,p) level of theory and all stationary points have been characterised by full vibrational analysis. Microsolvation was accomplished by explicitly adding water molecules, thus allowing for hydrogen bonding. The effect of pH was studied by addition of a proton and a hydroxide ion, respectively.
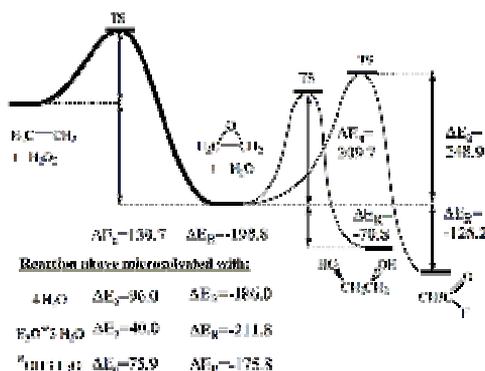
Scheme 1. Reaction path for oxidation of ethene with hydrogen peroxide. All energy differences are given in kJmol[-1] and include zero point energy corrections.

The results for the epoxidation step show that the activation barrier is very high in the absence of water and that proton transfer is rate limiting. By adding water molecules, the proton transfer is facilitated but the activation barrier is still high. In both acidic and alkaline solution the activation barrier is lowered and mainly attributed to rearrangement of hydrogen bonds. These results show that the homogeneous reaction will not take place in aqueous solution without a catalytic reaction site present. Calculations on the alternative oxidation paths to form aldehyde or diol clearly show that there is no direct path available, i.e. the epoxide is a reaction intermediate on the potential energy surface, Scheme 1. The possibilities for surface catalysed reactions will be discussed.

Symposium 8 - Poster

Surface Chemistry and Dynamics

Adsorption of tetraethylammonium and tetrabutylammonium ions on Bi sinlge crystal planes from solutions in ethanol and water

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Adsorption of tetraalkylammonium (TAA) cations has been of interest of electrochemists for a long time [1–3]. Alongside of theoretical studies, the TAA salts have important place in applied electrochemistry because of their use in nonaqueous electrical double layer supercapacitors. The theoretical description of TAA adsorption is complicated because its adsorption behaviour in aqueous solutions should be treated as that of ions as well as of organic compounds [1,2,4]. The main aim of the present study was to obtain the quantitative impedance data in the solutions of tetraethylammonium (TEA) and tetrabutylammonium (TBA) salts in ethanol and water. Adsorption of TEA and TBA ions on the Bi(hkl) planes has been investigated by using the Autolab PGSTAT 30 and FRA-2 system. The differential capacitance curves for aqueous solutions containing TBA ions and supporting electrolyte are like those containing neutral organic compounds (high adsorption–desorption peaks and depression of capacitance in the region of the potential of zero charge) and the experimental data for these systems can be treated similarly. In ethanol, however, the TEA ions behave more like ions because the sizes of TEA ions and solvent molecules are much closer than in water and ethanol is less structured than water. It was found that the ionic charge due to the specific adsorption of TEA ions in ethanol can be obtained using the classical calculation methods for simple ions. At the same time the adsorption of TBA ions in the region of maximal adsorption can be calculated by using the traditional Frumkin-Damaskin adsorption theory for neutral organic compounds. Only in the region of the adsorption-desorption peaks the ionic nature of TBA ions is clearly detectable. The experimental data for ethanolic solution were obtained in 0.02 M mixed-electrolyte solutions and the calculations performed with electrode potential as the independent electrical variable. The Gibbs energy of TEA adsorption has been calculated using the simple virial adsorption isotherm. It was found that TEA adsorption is weaker than the adsorption of halide anions. The electrosorption valency evaluated has a constant value in the potential region studied. It was concluded that the formed effective surface dipole is significantly screened by the solvent molecules and the metal electron gas.

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Adsorption kinetics of iodide ions on the electrochemically polished cd and bi single crystal electrodes

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The dependence of the differential capacitance on ac frequency for the real single crystal electrodes is a complicated problem and this effect has been explained by the atomic scale inhomogeneity rather than due to the macroscopic geometry (macroscopic roughness) aspects of the solid surface [1], as well as by the weak or strong specific adsorption of anions at the geometrically flat electrode surface [2]. The main aim of this work was to study the impedance characteristics of the electrochemically polished Bi(hkl) or Cd(0001 | x M KI + (1-x) M KF aqueous solution interface.

The complex impedance plane Z'',Z'-plots (so-called Nyquist plots, where Z'' and Z' are the imaginary and real parts of complex impedance, respectively) were measured using Autolab PGSTAT 30 FRA2 system in the region of ac frequencies f from 0.1 to 1×10^4 Hz and potentials from -0.5 to -1.6 V (vs. Ag|AgCl|sat. KCl) in the case of Bi(hkl) electrodes and from -0.95 to -1.6 V for Cd(0001) electrode. The surface structure of Bi(hkl) electrodes has been analysed by *in situ* STM [3] and it was found that the electrochemically polished Bi(111) surface has a very flat structure. The shape of the Nyquist plots measured at fixed E indicates that the limiting step, characteristic relaxation time of the complex adsorption process, and rate of adsorption depend noticeably on the electrode potential as well as on concentration of the iodide ions in solution. At $E >$ -1.3 V, the rate of adsorption of I$^-$ anions is limited mainly by the heterogeneous adsorption step as the phase angle δ values are lower than -83° at $f <$ 1×10^3 Hz and there is a linear dependence of complex impedance on log$f$. At $E <$ -1.3 V and at low frequencies ($f <$ 10 Hz) there is noticeable decrease of |δ| (δ ~ -5°) indicating the occurrence of the partial charge transfer of very slow cathodic faradaic reaction(s) at the Cd as well as Bi electrodes. The impedance data have been simulated using the Frumkin-Melik-Gaikazyan like circuit if $E \geq$ -1.3 V. At more negative potentials the more complicated equivalent circuits have to be used [3]. By fitting the experimental data to various equivalent circuits it was found that the Frumkin-Melik-Gaikazyan model yields to the best fit in the case of the base electrolyte as well as of solutions containing Br- as well as I$^-$ ions.

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Symposium 8 - Poster

Is Binding of Metal Ions by Self-Assembled Monolayers Different than in Homogeneous Solution?

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Surface Chemistry and Dynamics

Self-assembled monolayers (SAMs) have become one of the most popular approaches for modifying and architecturing metal surfaces. Applications of SAMs can be found in a wide variety of scientific fields, such as sensing and biosensing, corrosion inhibition, lubrication and catalysis. Since most of SAMs comprise the attachment of either aliphatic or aromatic organic molecules many of these can be used as ligands for metal ion binding. We have shown that a functionalized monolayer can exhibit extremely high sensitivity toward metal ions, e.g., Cd^{2+}, CrO_4^{2-} [1].

SAMs are basically 2D arrays, which exhibit substantially lower degree of freedom than found in 3D homogeneous matrix, such as in solution. Therefore, it is not trivial to assume that binding by functionalized SAM has the same rules as in homogeneous medium. Interestingly, only a few methods have been developed and applied for studying and determining the **heterogeneous** stability constants of metal ions by organic ligands.

We will present three different methods, which have been developed by us for the determination of the heterogeneous binding of metal ions by functionalized SAMs [2-4]. The first method is based on measuring the change of capacity upon binding of metal ions by the SAM. We have studied the heterogeneous binding of Cd^{2+} ions by ω-mercaptoalkanoic acid SAMs on Au. This was accomplished by adding metal ions at a constant pH and following the changes in the double layer capacity. A mathematical treatment based on calculating the electrochemical potential differences at the double layer–solution interface, has been developed. More recently we studied the difference in the heterogeneous binding of Mg^{2+}, Ca^{2+} and Sr^{2+} ions by 1-thioglycerol and 1,4-dithiothreitol monolayers on Au [3].

The second method involved ATR-FTIR and was based on measuring the changes in the vibration spectroscopy of the layer upon adding metal ions. Specifically, we studied [4] the binding of Cd^{2+} by SAMs of 4-heptadecylpyridine and 7-tridecyl-4-methyl-1,10-bipyridine supported on an octadecylsilane-modified Ge prism.

The third method utilized the scanning electrochemical microscopy (SECM) for determining the association of Cd^{2+} by a SAM of 8-mercaptoocatnoic acid. The feedback mode of the SECM, which is sensitive to the rate of electron transfer at the monolayer-solution interface, was affected by adding metal ions to the solution. Finally, we will present also recent results on the effect of functionalized monolayers at the liquid-air interface on metal ion binding.

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Symposium 8 - Poster

Surface Chemistry and Dynamics

Spectroelectrochemical study of benzylideneacetone onto silver whit and without Zn(II)

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This work investigated by means of Raman spectroscopy the structural behaviour of a common electroplating additive, benzylideneacetone, when adsorbed onto a silver electrode surface. We worked in two electrolytic media: first in 2.8M KCl, 0.32M H_3BO_3 pH5, to observe the behaviour of the organic molecule alone, and then in the same solution but with the addition of 0.6M $ZnCl_2$.

The spectroscopic results showed the influence of the electrode potential on the molecular surface behaviour. In both cases, with and without zinc, the spectroscopic response of the molecule surface interaction depended of the imposed potential. However the variation was stronger in the presence of zinc.

In the latter case the change to more negative potential enhanced the ring-breading bands. At E_{Ag} = -900mV (Ag/AgCl) this effect was strongest. The very strong adsorption band of $ZnCl_n^{(2-n)}$ complex is not changed by the addition of the organic molecule or by the imposed potential. In the absence of Zn(II) the strength of the ring-breading and the C=C bands diminished as the potential was swept to more negative values. Finally, the intensity of the absorption bands associated with the organic molecules diminished at E_{Ag} = -1000mV (Ag/AgCl), where reduction of benzylideneacetone occurs.

Effect of organic additives on the electrodeposition of Zn in an alkaline bath

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Addition of organic compounds is used to modify the characteristics of coatings. In alkaline zincate baths, quaternary ammonium compounds are used, especially heterocyclic derivatives and polyamines, which modify the morphology and improve the resistance against corrosion. However they have not been extensively studied.

In this work, cyclic and linear voltammetry, chronoamperometry, and electrochemical impedance spectroscopic studies were performed to examine Zn electrodeposition process in an alkaline gluconate complexing bath. The influence of additives on the electrochemical behavior and morphology was studied; the additives used were sodium nicotinate derivatives, N-benzyltrimethylamine, tetraethylammonium hydroxide, and two quaternary polyamines.

Cyclic voltammetry showed that the organic additives by increase the over potential for Zn reduction process. This effect is linked to adsorption of the additives on the electrode surface. Linear voltammetry showed changes in the kinetic parameters due to the presence of the additives. In addition, electrochemical impedance studies showed modifications in the inductive loop indicating that the mechanism involved during zinc reduction is modified with different surface intermediate species appearing compared to the situation without the additive. Chronoamperometric studies showed changes in the nucleation parameters, the polymeric additives being those that decrease the nucleation rate constant and the number of active sites.

Analysis of phase transformation in the two-phase domain of the PdH system

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It has been shown recently[1] that phase transformation mechanism in the two-phase domain of the Pd-H system should be analyzed using non-harmonic potential perturbations, after a careful measurement of the {potential; composition} isotherm of the system. The use of such non-harmonic perturbations is needed to avoid non-linear behaviors at measurement points located along irreversible thermodynamic paths. Potential steps are particularly well suited for analyzing hydrogen insertion mechanism in metals such as palladium where hysteresis is significantly large. The convoluted current responses obtained in the time domain, using appropriate sampling rates, are then numerically Fourier-transformed, yielding experimental impedance diagrams.

In this paper, impedance diagrams are obtained for the PdH system along hysteresis loops, using massive electrodes with planar symmetry, in 1M H_2SO_4 solutions. Diagrams of various shapes are obtained as a function of the mean H/Pd composition and in relation with the spatial distribution of the α (saturated solid solution) and β (non-stoichiometric PdH_{1-x} hydride) phases along the thickness of the membrane electrode. A review of the different model impedance equations in two-phase electrodes is given and their validity for the PdH system is discussed in relation with experimental results.

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Electrochemical noise study of the effect of electrode surface wetting on the evolution of electrolytic H$_2$ bubbles

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Ni and Ni-polytetrafluoroethylene (Ni-PTFE) composite electrodes were used as model systems for the study of the effect of electrode surface wetting on the evolution of electrolytic bubbles. The study of H$_2$ evolution was carried out by recording the fluctuations of both electrode potential and electrolyte resistance and was supported by video images of the electrode surface.

Ni-PTFE electrodes were prepared by a sediment codeposition method, i.e. by electrodepositing Ni while PTFE particles, initially suspended in the Ni^{2+} electrolyte, were forming a sediment on the electrode and becoming incorporated in the deposit. When the PTFE concentration in suspension was not very high (1.6 to 8.2%, based on mass) the concentration of PTFE particles in the deposits, estimated by EDX, was found to vary, in a roughly linear way, between 1.7 and 7.1%. SEM showed that the codeposition of PTFE induced an increase in the deposit roughness.

The analysis of the power spectral density of the fluctuations of the electrolyte resistance showed that the average radius of the H$_2$ bubbles detaching from the Ni-PTFE cathodes increased with the PTFE content, being mostly in the range 350-700 μm. This was attributed to the increase in the hydrophobicity of the composites with increasing PT FE concentration. Indeed, by increasing the PTFE concentration in suspension, composites with a PTFE concentration as large as 38 % were obtained, and on these PTFE-rich electrodes, bubble evolution occurred through the formation by coalescence of a single bubble with a size comparable with that of the electrode (2.5 mm in radius). The video images confirmed that the average size of the detaching gas bubbles determined from the electrochemical noise analysis was correct, and showed that coalescence phenomena were quite common and significantly contributed to the overall noise.

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Surface Chemistry and Dynamics

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Surface Chemistry and Dynamics

The solvent effect in the electrochemical reduction of organic bromides on silver

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Many aspects of the electrocatalytic reduction of organic halides, the selected model process for our current mechanistic studies on electrocatalytic dissociative electron transfers, have been elucidated in the last years. However, an investigation on the solvent effects was overdue, in spite of the importance of the subject, chiefly for the complexity of the task, requiring *inter alia* ancillary work on the key problems of (a) identifying a reliable standard for intersolvental normalisation of the electrode potentials and (b) determination of the potential range for the specific adsorption of the halide anions on the catalytic surface in the solvents considered.

Having complied with both of the above preliminary conditions, the present work provides a first, detailed overview, investigating the effects of six popular organic solvents of widely different properties (acetonitrile, dimethylformamide, dimethyl-sulfoxide, propylene carbonate, acetone and methanol) on the reduction of two model organic bromides (acetobromoglucose ABG and benzyl bromide $PhCH_2Br$), on glassy carbon GC (assumed as non-catalytic reference material) and silver (the best electrocatalytic material for organic halide reduction).

Our results show that the working solvent is much more influent in the electrocatalytic process than in the non electrocatalytic one. In particular, although silver maintains a high electrocatalytic activity for the target process in all solvents tested, such activity is significantly modulated by the solvent nature, the $(E_{p,Ag} - E_{p,GC})$ difference ranging no less than 0.85 to 1.25 V for ABG and 0.6 to 1 V for $PhCH_2Br$. We will discuss our observations in terms of both the thermodynamic and kinetic parameters affecting the process energy, in the frame of the Savéant theory for dissociative electron transfers. Actually, the solvent modulation appears to be chiefly connected with the solvation of the species having the highest charge density among those involved in the process, *i.e.* the product bromide anion Br^-. In fact, for both model compounds we observed a linear increase of the catalytic activity of the silver surface with decreasing primary medium effect on the bromide anion ($\Delta G^{\circ}_{Br^-, W \to S}$), *i.e.* with increasing solvent ability in bromide anion coordination, the protic and highly Br^--coordinating MeOH resulting in huge catalytic effects. This observation might be justified in terms of increasing solvent assistance in the turnover of the catalytic sites.

Variety of spatially inhomogeneous oscillations in H$_2$O$_2$ reduction at Pt-ring electrode induced via degenerate Hopf-instabilities

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Electrochemical systems with an negative differential resistance (NDR) show dynamic spatiotemporal reaction patterns at electrode surfaces. Various oscillatory waves, such as spatially uniform oscillation, traveling wave, and standing wave, have been reported so far in a lot of electrochemical reactions. We also have observed three types of oscillatory patterns experimentally in H$_2$O$_2$ reduction at a ring-shaped Pt electrode, depending on the geometry of the electrochemical cell and the applied potential (Figure 1). In the present work, we made a detailed bifurcation analysis of the previously proposed mathematical model in order to understand the origins of the oscillatory patterns.

The electrochemical system with an NDR was expressed in an approximate equation (1).

$$\begin{cases} \dfrac{\partial u}{\partial t} = p(-au^2 - bu^3 + v) + s\int_0^L \left(-\dfrac{a}{b} - u\right)dx + D_u\dfrac{\partial^2 u}{\partial x^2} \\ \dfrac{\partial v}{\partial t} = gu^2 - v - del + D_v\dfrac{\partial^2 v}{\partial x^2} \end{cases} \qquad (1)$$

where the variables *u* and *v* are the double-layer potential and the surface concentration of the electroactive species, respectively. The second term in $\partial u/\partial t$ expresses the negative global coupling (NGC)[1], in which *s* is a parameter to control the intensity of the NGC. Detailed bifurcation analysis of eq. (1) revealed that the degenerate Hopf-instability of Fourie modes 0 and ±1 occured depending on the value of the *s*. On the basis of the bifurcation diagram thus obtained (Figure 2), we explained the mechanisms of the three types of spatiotemporal patterns.
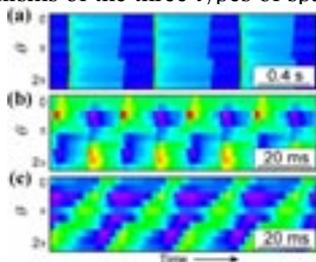
Fig. 1   Three types of spatiotemporal waves observed in H$_2$O$_2$ reduction at Pt-ring electrode. (a) Uniform Wave (UW), (b) Traveling Wave (TW), (c) Standing Wave (SW).
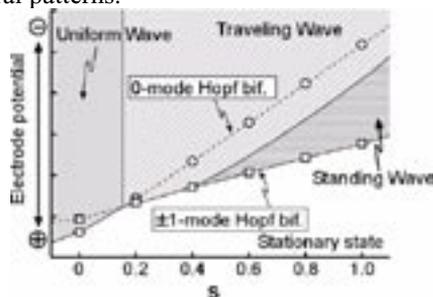
Fig. 2   Bifurcation diagram obtained from eq. (1).

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Symposium 8 - Poster

Surface Chemistry and Dynamics

Molecular modeling of the electrochemical discharge of a hydronium ion

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The mechanism of discharge of a hydronium ion at mercury and gallium electrodes is explored in the framework of a microscopic approach. The quantum mechanical aspects of the charge transfer are treated in the spirit of Dogonadze-Kuznetsov-Levich theory. The cluster model is employed to describe the electrode surface; the nearest solvent sheath of H_3O^+ is considered as well. The quantum chemical calculations were performed at the DFT level.

Molecular dynamics simulations for a hydronium ion at the mercury/water molecules interface show that the hydronium ion does not specifically adsorb. The Grotthus mechanism is assumed for the proton transport from the solution bulk to the reaction layer; its probability was estimated to be significantly higher as compared with the proton tunnelling from the hydronium ion to the metal surface. The electron transfer was found to proceed in a strong adiabatical regime. The proton tunneling terms were constructed for a set of the H_3O^+-metal distances. A model approach is proposed to address (within a self-consistent computational scheme) the non-equilibrium solvent effects, which allows equalizing with the quantum energy levels of the proton in a two-well potential. The proton tunneling probability is estimated by using a new effective computational method.

The origin of the Tafel plots on the model polarization curves is ascribed mostly to the interplay between partial contributions from the different proton energy levels. An attempt was made to predict the potential regions corresponding to the barrierless and activationless discharge. The kinetic isotope effect and the temperature dependence of transfer coefficient were also modelled and compared with experiment.

The effect of sodium and lithium cations on reduction of hexacyanoferrate(III) anions on cd(0001) electrode

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Electroreduction of the hexacyanoferrate(III) anions on the electrochemically polished Cd(0001) plane has been studied by the linear sweep and rotating disc electrode voltammetry methods. The lithium- and sodiumhexacyanoferrate salts were sythezised from potassiumhexacyanoferrate(III) using corresponding lithium- and sodium-perclorates. Lithium- and sodiumperclorate were used as base electrolytes.

The electroreduction rate of the $[Fe(CN)_6]^{3-}$ anions depend on the potential of the Cd(0001) electrode as well as on concentrations of the base electrolyte and $[Fe(CN)_6]^{3-}$ anion, i.e. on the diffuse layer thickness [1]. In the region of zero charge potential $E_{\sigma=0}$ the electroreduction of the $[Fe(CN)_6]^{3-}$ anion is mainly limited by the rate of diffusion of the $[Fe(CN)_6]^{3-}$ anions to the electrode surface. The values of the diffusion coefficient obtained from linear Levich plots were in a reasonable agreement with the literature data. In the region of small negative surface charge densities the inhibition of the $[Fe(CN)_6]^{3-}$ anion electroreduction takes place which has been explained mainly by the ψ_1-effect. At more negative surface charge densities the acceleration of the anion electroreduction has been explained by diminishing of the ψ_1-effect, as at $E << E_{\sigma=0}$, the derivative $d\psi_1 = dE \approx \text{const}$, as well as by weak specific adsorption of the cations on the electrochemically polished Cd(0001) surface. The minimum on the cyclic voltammograms disappears as the concentration of the base electrolyte increases. In the more concentrated solutions of the base electrolyte the limiting current densities are approximately same for $Li_3[Fe(CN)_6]$, $Na_3[Fe(CN)_6]$, and $K_3[Fe(CN)_6]$.

The apparent rate constant k_{het} has been calculated using the kinetic current densities obtained from linear Koutecký-Levich plots. The values of k_{het} depend on the base electrolyte concentration and the nature of the cation. The acceleration of the $[Fe(CN)_6]^{3-}$ anion electroreduction takes place in order of the cations $Li^+ < Na^+ < K^+$.

The corrected Tafel plots for the electroreduction of the $[Fe(CN)_6]^{3-}$ anion on electrochemically polished Cd(0001) electrode have been calculated using the classical diffuse layer potential values obtained according to the Gouy-Chapman theory. At higher cathodic polarizations the corrected Tafel plots are linear and coincident but there are deviations in the region of zero charge potential.

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Symposium 8 - Poster

Surface Chemistry and Dynamics

In situ nucleation-growth investigation of ZnO

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An experimental device allowed to investigate *in situ* electrodeposition on a transparent gold electrode [1, 2]. The observation of the electrode / solution interface was then possible through a microscope lens set behind the electrode. The CCD camera connected to the lens recorded versus time the surface evolution during the electrodeposition. This technique led the nucleation growth process to be identified simultaneously with the stationary or dynamic electrochemical measurements.

The electrodeposition of zinc oxide (ZnO) from a solution containing KNO_3 and $Zn(NO3)_2$ was investigated by using this set-up. A potential of -1.2V/SCE corresponding to the nitrate and dissolved oxygen reductions was applied, which promoted ZnO deposition via the increase of the interfacial pH. Figure 1 shows images recorded at two different crystallisation times. Nucleation-growth process of ZnO was studied for different deposition conditions (variation of bulk temperature, $Zn(NO_3)_2$ and KNO_3 concentrations, convection in the vicinity of the working electrode).
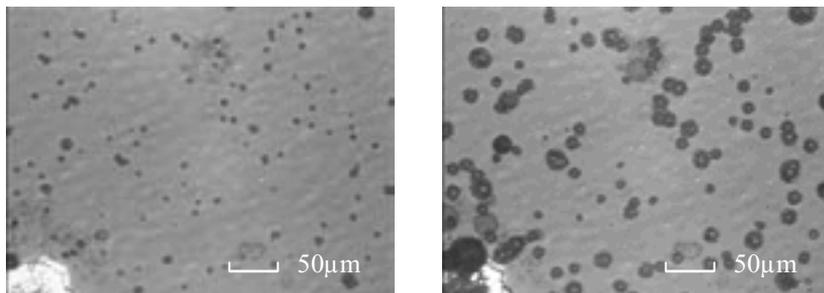
Figure 1: In situ images of ZnO crystals growing on the electrode surface for 33 min (left) and 50 min (right) of electrocrystallization.

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Formation and Behavior of Singlet Molecular Oxygen in TiO$_2$ Photocatalysis Studied by Detecting Near-Infrared Phosphorescence

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TiO$_2$ photocatalysis is becoming a popular technology to decompose and mineralize pollutants and/or undesirable compounds in our environments by using ambient light. For the better understanding, the photocatalytic mechanisms around the photo-irradiated TiO$_2$ surface are being studied intensively, and numerous reaction mechanisms in TiO$_2$ photocatalysis have been proposed so far. Singlet molecular oxygen (^{1}O$_2$) with a significant yield was detected from the TiO$_2$ photocatalyst powders irradiated with a laser pulse by monitoring the near-infrared phosphorescence at 1270 nm.[1] The lifetime measurements for the ^{1}O$_2$ produced at TiO$_2$(P25) in various environments such as in air and in suspensions of H$_2$O, D$_2$O and ethanol elucidated that quenching takes place mainly by TiO$_2$ surface in the absence of reactants. The quantum yields of the ^{1}O$_2$ generation were measured for ten commercial TiO$_2$ photocatalysts in air to range from 0.12 to 0.38, while the lifetimes were from 2.0 to 2.5 µs. Since the quenching by TiO$_2$ surface is too fast, the formation process of ^{1}O$_2$ has not been distinguished from the recombination of the photogenerated electron hole pairs. No contribution of ^{1}O$_2$ to the usual photocatalytic reaction is suggested. However, when the reactants were adsorbed on the TiO$_2$ surface and the reaction rate is faster than the quenching, photocatalytic reaction could be used as a source of ^{1}O$_2$ for specific organic reactions.

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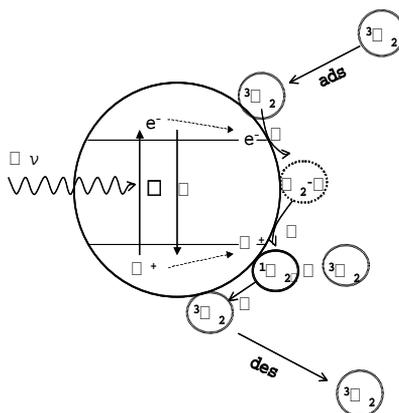
Figure 1. Photocatalytic processes of molecular oxygen on TiO$_2$ surface. 1, Excitation accompanied by the formations of valence band holes and conduction band electrons. 2, Possible recombination between electrons and holes. 3, Electron transfer to O$_2$ to form super oxide radical •O$_2^-$. 4, Oxidation of •O$_2^-$ to form partly singlet molecular oxygen ^{1}O$_2$. 5, Quenching of ^{1}O$_2$ at TiO$_2$ surface to back to the triplet molecular oxygen. ads, Adsorption. des, Desorption.

Symposium 8 - Poster

Surface Chemistry and Dynamics

Surface-enhanced study of electro-oxidation of formic acid on Pd electrodes in acidic solution

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Direct liquid fuel cells as the new generation power source are attracting much attention with their power density potentially higher than that of lithium secondary battery for portable applications. Recently, direct formic acid fuel cell (DFAFC) was successfully studied with Pd based nano-catalysts in Masel's group [1]. The DFAFC shows a higher power density than DMFC, and hence the reaction mechanism on Pd awaits clarification in relation to CO poisoning, which is a major issue for methanol oxidation on Pt.

In this work we report on in-situ IR spectroscopy of intermediates during FA oxidation on Pd. A SEIRA-active Pd thin-film electrode was chemically deposited on the plane of a hemicylindrical Si prism (Nippon Pastec Co., Ltd.). This was incorporated in a 3-electrode electrochemical cell in a Fourier transform infrared spectrometer (Digilab FTS 7000) equipped with a MCT detector and a homemade single reflection accessory. ATR-SEIRAS experiments are essentially same as those described in the literatures of Osawa et al [2]. The supporting electrolytes were prepared from $HClO_4$ (analytical grade, Kishida Chemical) and milli-Q-filtered water. The chemically deposited Pd surface was cleaned by a cycling potential between 0.25 and 1.2 V in electrolyte solution.

Fig. 3a shows a series of SEIRA spectra recorded during the potential sweep. Fig. 3b shows SEIRA spectra obtained with a CO-stripping voltammogram in N_2-saturated 0.1 M $HClO_4$ after CO was adsorbed at 0.21 V. During the HCOOH oxidation, a band is observed at 1730–1750 cm^{-1} assignable to multi-bound CO. The CO bands completely disappear around 0.9 V due to oxidative adsorption. Different from the HCOOC oxidation on Pt, the CO band intensities are very low. As compared with the CO intensity of Fig. 3b, the one resulted from the HCOOH oxidation is below 1/10 at the initial potential. Further, at $E >$ ca. 0.4 V, two bands appear at 1407–1422 and 1331–1340 cm^{-1}. These bands are ascribed to the carbonato (CO_3^{2-}) derived from the dissolved CO_2, the final product of HCOOH oxidation.

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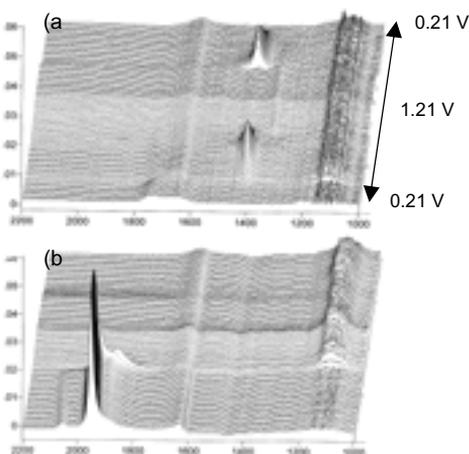
Fig. 1 (a) SEIRA spectra measured with the HCOOH voltammogram. (b) SEIRA spectra measured with a CO-stripping voltammogram between 0.21 and 1.21 V. The reference spectrum was collected at 0.21 V before adding HCOOH.

Symposium 8 - Poster

Surface Chemistry and Dynamics

Formaldehyde and formic acid potential oscillation related to coexisting oxygen

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In the potential oscillation observed during electrochemical oxidation of formaldehyde or formic acid on platinum under galvanostatic conditions, the adsorbed carbon monoxide plays a crucial role. Controlling the amount of the adsorbed carbon monoxide may, therefore, change the oscillation behaviour. We have investigated such behaviour by dissolving oxygen into the electrolytic solution to decrease the amount of the adsorbed carbon monoxide.

As to the potential oscillation produced during the formaldehyde oxidation, we have partly reported in the last meeting [1] that periodic and chaotic oscillation patterns persist to appear in spite of increasing the concentration of oxygen, although the oscillation amplitude becomes jagged.

We have found that the potential oscillation during the oxidation of formic acid appears after an induction time of several ten minutes in the presence of 1mM oxygen in the solution, as shown in Figure 1, while it does without an induction time in the absence of oxygen. Although the oscillation pattern is periodic, the oscillation amplitude and period becomes rather irregular with increasing the concentration of oxygen.

To gain insight into the cause of such behaviour, we have measured voltammograms with various potential profiles. Detailed inspection shows the effect of oxygen on the formation and oxidation of the adsorbed carbon monoxide. The results will be reported and discussed in the presentation.
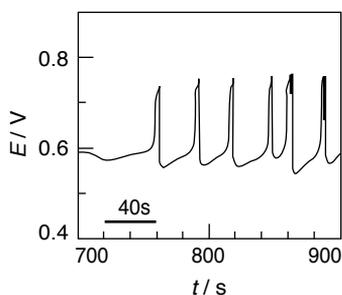
Figure 1 Potential oscillation pattern in the presence of oxygen at 315K (1 M formic acid, 1 mM oxygen).
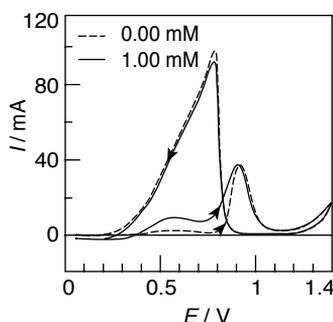
Figure 2 Voltammograms of 1 M formic acid related to the oxygen concentration (100 mV/s).

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Evidences of opened structures formatiom during the oxidation of conducting poly(o-aminophenol).

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Poly(o-aminophenol) films were deposited on gold electrode in a 0.1 mol dm^{-3} KCl solution at pH 1.2. The film is electrochemically active, reproducible and stable. The in situ FTIR analysis of the structural changes of the polymer during its redox process showed the existence of structures redox which involve the elimination and addition of protons coupled to an electronic transfer. Opened units are favored when the polymer is in its oxidized form and the closed units prevail in the polymer reduced. As the pH increases, the electrochemical activity from the polymer decreases; polymer becomes an insulator at about 5.0 pH units. This behavior can be observed in the FTIR spectra.

Electro-oxidation of D-galactose on MoCp$_2$(PAN)Cl$_2$ modified carbon Toray electrode

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The oxidation of monosaccharides on noble metals in alkaline medium is widely studied[1,2]. The easy oxidation of carbonyl group to the carboxylic acid in these conditions is well known. In this context, the use of mediators, considering their effect on product distribution, was investigated. The preparation of MoCp$_2$(PAN)Cl$_2$ (Cp = cyclopentadienyl, PAN = 2-pyridylazo-2-naphtol) is effectuated according to the literature[3]. The characterization of the complex was carried out using spectroscopic and electrochemical methods. The complex was deposited on carbon Toray surface using a Nafion/water solution.

Oxidation of D-galactose on MoCp$_2$(PAN)Cl$_2$ was studied by cylic voltammetry and Long-term electrolysis. Cyclic voltammetry allow to determine the voltammetric peaks due to the presence of redox couple on the electrode surface in 0.1 M NaOH medium. The important decrease of the current densities related to these peaks after the addition of D-galactose confirms a fast reaction between the complex and D-galactose. The kinetic parameters of the reactions and the stability of the electrodes were also investigated by cyclic voltammetry.

Long term electrolysis of D-galactose on MoCp$_2$(PAN)Cl$_2$ modified carbon Toray was carried out at 0.5 V *vs.* SCE in 0.1 M NaOH. The products of the electrolysis were analyzed by HPLC and GC using commercial reference compounds. The product distribution after 40 hours of electrolysis is given in Table 1.

Table 1. Chromatographic analysis of the solution of D-galactose electrolysed at a MoCp$_2$(PAN)Cl$_2$ modified carbon Toray electrode

Product	Chemical yield / %
D-galactose	42
Galactonic acid	9
Galactaric acid	2
Trihydroxypentanedioic acid	1
Tartaric acid	2.5
Tartronic acid	10
Glyceric acid	10
Glycolic acid	12
Oxalic acid	1
Formic acid	8.5

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Symposium 8 - Poster

Surface Chemistry and Dynamics

Electrooxidation of formic acid on PtBi alloy

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The activity of the PtBi alloy in the oxidation of formic acid has been studied and the results obtained compared to those on polycrystalline Pt (Fig.1). PtBi exhibits the significantly enhanced activity with respect to Pt in terms of the current density and the onset potential under both potentiodynamic (Fig. 1a) and steady-state conditions (Fig. 1b). The onset potential at PtBi alloy is shifted ~15o mV towards more negative potentials and the activity is more than two order of magnitude higher than on Pt at E = 50 mV.
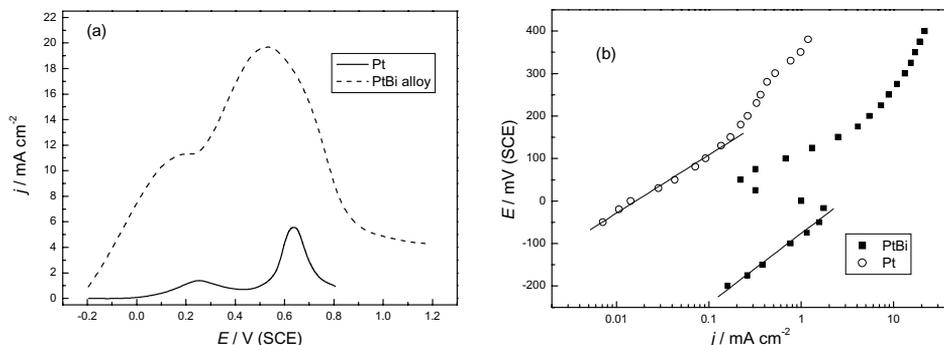
Fig. 1. *Cyclic voltammograms (first positive going sweeps) for the oxidation of 0.125 M HCOOH in 0.1 M H_2SO_4 on Pt and on PtBi alloy (a) and corresponding Tafel plots (b).*

Quite similar shapes of the voltammograms for Pt and PtBi however, indicate that the reaction proceeds on both electrodes most likely following the dual path mechanism:

$$HCOOH \quad \xrightarrow{\text{dehydrogenation}} CO_2 + 2H^+ + 2e^-$$
$$\xrightarrow{\text{dehydration}} CO_{ad} + H_2O \xrightarrow{k_{CO}} CO_2 + 2H^+ + 2e^-$$
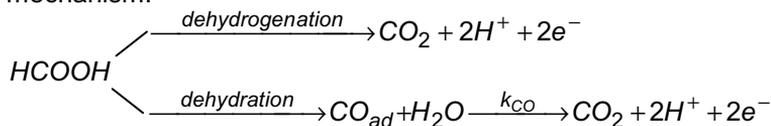
At low potentials the dominant path is dehydrogenation of HCOOH. At higher potentials the parallel path, i.e. oxidation of CO_{ad}, formed by dehydration of HCOOH, significantly contributes to the overall reaction indicating the poisoning effect on PtBi too.

Tafel slopes of ~120 mV dec^{-1} may imply that the transfer of first electron in the direct path, i.e. in dehydrogenation of HCOOH, could be the rate determining step.

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Surface Chemistry and Dynamics

Bistability in the anodic dissolution of metals in multicomponent electrolytes

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This communication presents a mathematical model of stationary diffusion-migration transport in anodic metal dissolution involving formation of a complex with anion of solution containing four sorts of ions with arbitrary charges and diffusion coefficients and examine the reasons of the appearance of bistability.

The outer Helmholtz plane (OHP) potential is the main variable for the description of dynamic instability and self-organization phenomena in an electrochemical system with nonlinear current-potential characteristics. A functional relation between the OHP potential and electrode potential has been established. It has been shown that at some values of parameters (ion charge, diffusion coefficients, transfer coefficients, etc.) in the case of controlling the rate of the mass transfer process in electrochemical systems with a number of components of ≥ 3, the OHP potential may take on two values at the same electrode potential value. Fig.1. shows the theoretical dependence of OHP potential on electrode potential for the case of anionic complex formation.
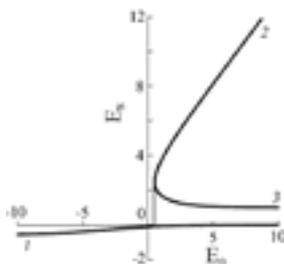
As is seen from Fig.1. a region exists in which the relation between electrode potential and OHP potential is ambiguous. In this electrode potential range, a bistability may arise in an electrochemical system.

Fig.1. The theoretical dimensionless dependence of outer Helmholtz plane potential E_s on electrode potential E_0 for the case of anionic complex formation.

Bistability is of frequent occurrence and corresponds to the situation in which a system can exist in two stable steady states at the same conditions. The presence of several stationary states in the case of anodic dissolution is associated with a complexation reaction at the interface and with mass transfer processes, which determine the potential value on the OHP. The variation of OHP potential through migration may affect greatly the concentration profile in the diffusion layer, which in turn may lead to variation of OHP potential.

In the case of formation of a positive and a neutral complex, the relation between electrode potential and OHP potential is unambiguous.

The behavior of the electrochemical system in the case of anodic dissolution depends very strongly on the ratio of diffusion coefficient and charge values of ions present in the electrolyte and electrochemical reaction constants.

The interface between the electrode and electrolyte is decisive for the kinetics of any electrochemical reaction. Pattern formation in electrochemical systems occurs at the electrode/electrolyte interface and results from the interplay between interfacial kinetics and transport processes near the electrode surface.

Hydrogen diffusion effects on the kinetics of the hydrogen electrode reaction. Frumkin parameter evaluation

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A general consensus exists that the hydrogen electrode reaction (HER) is verified through the Volmer-Heyrovsky-Tafel mechanism. The kinetic parameters are evaluated basically from studies of the cathodic reaction (hydrogen evolution reaction, her) or the anodic reaction (hydrogen oxidation reaction, hor), being the last one much less studied. On this sense, the present work deals with an integral analysis of the HER on the basis that the operative mechanism must be the same in all the range of overpotentials, as well as the values of the elementary kinetic parameters (v_V^e, v_T^e, v_H^e, θ^e). In previous studies [1], these parameters were evaluated from experimental dependences of the hydrogen oxidation reaction on platinum electrodes. Taking into account that the anodic reaction presents a surface coverage of the adsorbed intermediate (θ) very low, the kinetic parameters can be evaluated ignoring effects of coverage on the adsorption energy (Langmuir adsorption). Otherwise, when the cathodic reaction is analysed, θ grows significantly and influences the adsorption energy (existence of lateral interactions, etc.). In this case, the description of the behaviour of the intermediate (H_{ad}) by an adsorption Frumkin process results more suitable [2]. In this context, this work presents a theoretical and experimental study of the hydrogen electrode reaction on a Pt rotating disc electrode in the whole range of overpotentials of applied interest ($-0.3 \leq \eta / V \leq 0.5$). The experimental determinations were carried out in the following range of rotation rate $900 \leq \omega / rpm \leq 8100$, in 0.5 M H_2SO_4 solution of high purity, saturated in H_2 gas at 1 atm and 30 ºC. The theoretical treatment has been derived on the basis of rigorous kinetic expressions previously obtained [3], which take into account the role of the diffusion process of the molecular hydrogen. An extension of this treatment including the adsorption process for the reaction intermediate on the basis of the Frumkin adsorption isotherm has been derived and applied. Therefore, the elementary kinetic parameters, as well as the limiting diffusion current density and the Frumkin interaction parameter, has been evaluated from the analysis of the kinetic behaviour of the cathodic (her) and anodic (hor) reactions. In this way, the complete kinetic description of the hydrogen electrode reaction on platinum electrodes including both the anodic and cathodic domain was obtained through a unique set of kinetic parameters.

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Time Resolved UV-Vis, Raman and EDXAS Data Reveal Oscillating Propane Coverage during Propane Dehydrogenation over Supported MoO$_3$ Catalysts

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Energy Dispersive X-Ray Absorption Spectroscopy (ED-XAS) data combined with UV/Vis, Raman, and gas chromatography data on alumina and silica supported molybdate catalysts under propane dehydrogenation conditions have been obtained [1]. A novel $\Delta\mu$ adsorbate isolation technique was applied to the time-resolved (0.1 min) Mo K-edge ED-XAS data by taking the difference of absorption, μ, at t>1 against the initial time, t=0. Further, full multiple scattering calculations using the FEFF 8.0 code are performed to interpret the $\Delta\mu$ signatures. The resulting difference spectra and interpretation provide real time propane coverages and O depletion at the MoO$_3$ surface (Fig. 1). A surprising oscillatory propane coverage with period of about 1 min. is discovered, that correlates in part with a longer (4 min.) build up of alkene and/or coke product, as exhibited by the UV/Vis, Raman, and GC data. Combined these data give unprecedented insight into the dynamic flow-fields, varying alkane partial pressure at the surface, and kinetics for the propane dehydrogenation. The oscillatory coverage is attributed to two bi-stable autocatalyzed reaction mechanisms, one involving C-H activation by σ-bond metathesis, the other via a reactive H-Mo complex [2]. This is the first evidence that these reactions are autocatalyzed and are stabilized by a varying propane gas pressure at the surface. The coupled differential equations describing the autocatalyzed reaction kinetics have been solved numerically, reproducing the period doubling and onset of chaotic behavior typically seen in autocatalyzed oscillatory reactions brought on by varying pressure.

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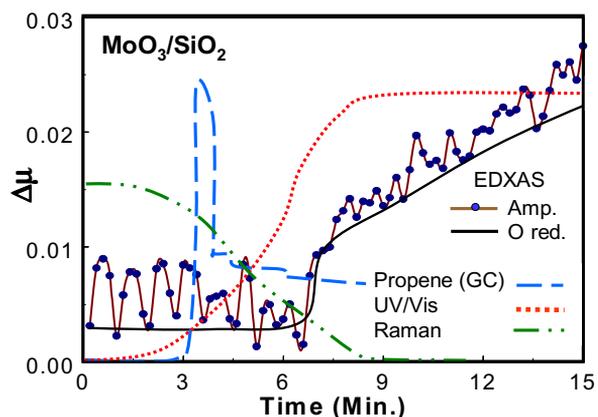
Fig. 1. Plot of EDXAS amplitude, $\Delta\mu = \mu(t)-\mu(t=0)$, and correlation with GC, UV/VIS and Raman amplitudes (the latter 3 amplitudes on an arbitrary scale) for propane dehydrogenation on MoO$_3$/SiO$_2$. The "O red" line follows the lower envelope of the EDXAS minima, and reflects the O reduction of the MoO$_3$. The oscillations in the EDXAS amplitude reflect the propane coverage, and the UV/Vis and Raman data the coke formation.

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Surface Chemistry and Dynamics

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Surface Chemistry and Dynamics

Investigation of the adsorption of fission products on iron, stainless steel and Zr1%Nb by EQCM

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In a nuclear reactor the contamination of structural materials is an important question. Normally the cooling water contains only a very few amount of corrosion product but in case of some leakage uranium and its fission products can be appeared. In this study the sorption properties of cerium, caesium, uranil and iodide ions were investigated on iron, stainless steel, zirconium and zirconium-dioxide surfaces by electrochemical quartz crystal microbalance technique. Iron surface was created by its electrodeposition, while stainless steel, zirconium and zirconium-dioxide were vacuum deposited onto a 1 inch diameter AT-cat 5MHz crystal. The EQCM head was installed into a double-walled all-glass cell cleaned with caroic acid, the counter electrode was a platinum mesh, and reference electrode was a saturated calomel electrode. The solution contained 8g/l boric acid and 5mg/l potassium hydroxide modelling the primary circuit water chemistry of a VVER nuclear power plant. The temperature was controlled by a precision thermostat. Most of the measurements were carried out at the open circuit potential: after the temperature and the mass signal stabilized the solution of the investigated adsorbing ions was injected into the cell in several steps. The mass and potential changes were recorded. This measurement was repeated at 20, 40, 60 and 80°C. After the maximal coverage was reached a cyclic voltammogram was recorded.

In the case of the iron anodic shift of the potential and the decrease of the pH caused dissolution of the electrode metal in uranil and iodide containing solutions. The observed maximum coverage was approximately one monolayer; i.e. less than $0.5\mu g/cm^2$. The sorption on zirconium is a simpler process. No dissolution was observed and maximum monolayer coverages were found with little change in the electrode potential. The stainless steel and zirconium-oxide surfaces showed similar behaviour.

Alternate use of the membranous electrolyzer in voltammetry

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It is known that the treatment of the aqueous solutions by the electric current results in the change of the physical and chemical properties of the solutions such as pH, a redox potential, a superficial tension, viscosity. These properties relax to an initial state for hours, days. Now the treatment of the aqueous solutions by the electric current is employed in many technological processes. The treatment of the aqueous solutions by the electric current are also employed for the sample preparation for the determination of the toxic metals in the natural water and sewage by stripping voltammetry (SVA) [Svinstova L.D., Chernishova N.N J. anal. chem.(Russ) 67 (2001) 11–15] and for the surface cleaning of the indicator electrode [A.S.USSR № 1608560/ A.A. Kaplin, L.D. Svintsova].

The voltamperometric characteristics of the membranous electrolyzer in the range of the concentration of the supporting electrolyte from 0.001M to 1M were obtained. The alternating asymmetrical sinusoidal current (50 hertz) with the amplitude 0,45–0,5A was put through the electrodes of the membranous electrolyzer. The voltamperometric characteristics of this electrolyzer have a form of the S–curve in the certain range of the voltage. Further the solution of 0.05 M *KCL* was treated in the membranous electrolyzer of the flowing type under the leap change voltage. Then the sample of this solution was investigated. The change of the standard properties of the solution such as pH, a redox potential and the following effects were obtained.

1) The shifting of the line of the residual current of mercury-film electrode on 100 mV in the range more negative potentials in the solution supporting electrolyte *KCL* after its treatment of the electric current in the membranous electrolyzer in the cathodic voltammetry (CVA) was shown. The mercury-film electrode prepared by the standard procedure was used.

2) The change of the slope of the line of the residual current of mercury-film electrode and its shifting on 20 mV in the range more positive potentials in the solution supporting electrolyte *KCL* were shown in the stripping voltammetry (SVA). The mercury-film electrode prepared by the standard procedure was used. Further the surface of the mercury-film electrode was prepared by the following technique. The indicator mercury-film electrode was introduced into the anodic chamber of the membranous electrolyzer filled with $0,05$ mol·l^{-1} potassium chloride solution. The alternating asymmetrical sinusoidal current (50 hertz) with the amplitude 0,45–0,5A was put through the indifferent electrodes and the indicator electrode was treated in these conditions during 4–5 minutes. Then the current was switched off, the electrode was removed out of the solution, and rinsed by distilled water, then it was put into the electrochemical cell to register the voltammograms.

3) The decreasing the height of the analytical signal Cd (II) in the solution of supporting electrolyte *KCL* after its treatment by the electric current in the membranous electrolyzer in the CVA was shown. The mercury-film electrode prepared by the standard procedure was used.

4) The increasing the height of the analytical signal Cu (II) in the solution of supporting electrolyte *KCL* after its treatment by the electric current in the membranous electrolyzer in the SVA was shown. The mercury-film electrode prepared by the standard procedure was used.

5) The increasing the height of the analytical signal Cd (II) in the solution of supporting electrolyte *KCL* in the SVA was shown. The mercury-film electrode prepared analogy item 2 was used.

6) The decreasing the height of the analytical signal Cd (II) in the solution of supporting electrolyte *KCL* in the SVA was shown. The mercury-film electrode prepared by the following procedure was used. The silver wire was introduced into the anodic chamber of the membranous electrolyzer filled with $0,05$ mol·l^{-1} potassium chloride solution. The alternating asymmetrical sinusoidal current (50 hertz) with the amplitude 0,45–0,5A was put through the indifferent electrodes and the silver wire was treated in these conditions during 4–5 minutes. Then the current was switched off and the mercury-film electrode was prepared by the standard technique.

7) The increasing the height of the analytical signalCd (II) in the solution of supporting electrolyte *KCL* in the SVA was shown. The indicator mercury-film electrode prepared by the following technique was used. The silver wire was introduced into the anodic chamber of the membranous electrolyzer filled with $0,05$ mol·l^{-1} potassium chloride solution. The alternating asymmetrical sinusoidal current (50 hertz) with the amplitude 0,45–0,5A was put through the indifferent electrodes and the silver wire was treated in these conditions during 4–5 minutes. Then the current was switched off and the mercury-film was prepared by the standard procedure. Then the surface of the mercury-film electrode prerpared additionally on item 2.

8)The improvement of the reproducibility of the analytical signals after treatment of the electric current in the all used regimes was obtained. The improvement of the reproducibility of the analytical signals after treatment of the electric current may be connected with the fluctuation decreasing in the solution or the reproducibility of the active working area of the indicator electrode. The studying of the reason of the improvement of the reproducibility of the analytical signals after treatment of the electric current claim the more detailed investigation.

In-situ External Reflection Infrared and ATR-SEIRAS Study of the Adsorption of Carboxylate Anions at Single Crystal and Thin Film Gold Electrodes

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The adsorption of oxalic and malonic acids at gold electrodes was studied by in-situ infrared spectroscopy. External reflection experiments carried out with gold single crystal electrodes were combined with ATR-SEIRAS experiments with gold thin film electrodes (deposited on silicon substrates either chemically or by argon sputtering). The voltammetric curves obtained in sulfuric acid solutions for the sputtered gold thin films after electrochemical annealing show typical features related to the presence of wide bidimensional (111) domains with long range order. The in-situ infrared data collected for oxalic acid solutions with pH=1 confirmed the potential-dependent adsorption of either oxalate (Au(100)) or a mixture of bioxalate and oxalate anions (Au(111), Au(110) and gold thin films) in a bidentate configuration. The better signal-to-noise ratio associated to the SEIRA effect in the case of the gold thin film electrodes allows the observation of the carbonyl band for adsorbed bioxalate that was not detected in the external reflection experiments. Additional bands are observed between 2000 and 3000 cm^{-1} related to the formation of hydrogen bonds between neighboring bioxalate anions. These bands disappear in pH=3 solutions, for which adsorbed oxalate anions are the predominant species. Similar results are obtained for the gold thin films in solutions containing malonic acid. The analysis of the intensities of the $\nu_s(OCO)$ and

$\nu(C-OH)$ bands for adsorbed oxalate and bioxalate, respectively, suggests that the pK_a for the surface equilibrium between these species is significantly lower than that found in solution. This effect is almost negligible in the case of adsorbed bimalonate for which the non bonded carboxylic group is farther from the electrode surface.
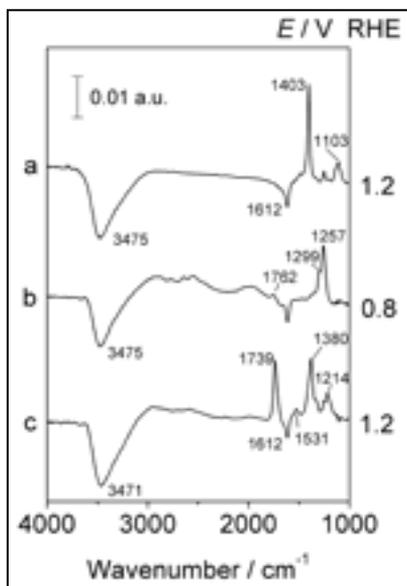
Figure 1. ATR-SEIRAS spectra collected for a gold thin film electrode in 0.1 M $HClO_4$ + 0.01 M acetic (a), oxalic (b) and malonic (c) acid solutions. Reference potential: 0.10 V.

Potential dependence of surface segregation processes at mechanically renewable Au-Ag alloy electrodes

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The phenomenon of the preferential escape of certain alloy components into the surface layer (surface segregation) is of great interest for catalysis, corrosion protection, and also for solving certain problems in microelectronics and other fields of modern science and technology. To date, the studies of this phenomenon at the interface of alloys with vacuum represent a large scientific direction, applying modern experimental techniques and theoretical approaches. Much less number of studies are devoted to the interface formed by alloy electrodes with electrolyte solutions. At the same time, it is evident that the surface segregation processes should have a great effect on the kinetics and mechanism of electrochemical processes that occur at this interface.

We studied the effect of the potential on the kinetics and mechanism of the changes that occur in the surface composition of Au-Ag alloys immersed into the surface inactive NaF electrolyte, based on electrochemical measurements on electrodes with surfaces periodically renewed in situ by mechanical cutting. This method allowed us to equalize the surface and bulk compositions of the metal phase and to create initial conditions for measuring the time effects associated with the preferential escape of atoms of the alloy's surface-active component from the alloy bulk to its interface with solution. Note that this method can be considered as the analog of ionic etching, which is used for studying the surface segregation at the alloy/vacuum interface.

The dependences of the electrical double layer capacitance in the range of ideal polarizability potentials on the time passed from the moment of electrode renewal showed that Ag is the surface-active component of Au-Ag alloys and escapes to the surface layer at a rate "anomalously" high for solid-state processes. It was also found that the rate of the studied process depends on the electrode potential and sharply increases with the transition to the range corresponding to substantial positive charges of the Ag surface ($\sigma > 7$ µC/cm^2). As was shown by special studies, the acceleration of the surface segregation of Ag atoms in this potential range is associated with the chemisorption on them of oxygen atoms.

It was shown that the diffusion model describes the kinetics of the exit of silver atoms into the surface layer of Au-Ag electrodes only under the conditions uncomplicated by the irreversible adsorption of oxygen atoms on the surface. The calculations carried out within the framework of this model allowed us to assess the diffusion coefficient of silver atoms in the surface layer of Au-Ag electrodes excited by mechanical renewal ($10^{-19} - 10^{-18}$ cm^2/s). The results for the electrochemical interface are shown to be in a good agreement with the results of XPS analysis of the surface composition of mechanically renewed Au-Ag alloys at their interface with vacuum.

Reduction mechanism of Schiff base on GCE

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The electroreduction of Schiff base was the subject of several interesting investigations. Presently, our interest is focused on the electrochemical reduction of salicylidenemine schiff base (scheme 1).The cyclic voltammograms of compounds S1-S5 on GCE in B-R buffer solution (pH = 8.2) were shown in Fig.1. The first cathodic peak of S2 was attributed to the reduction of $-NO_2$ group according to the literature[1]. Experimental results revealed that salicylidenemine schiff base compounds can be reduced on glassy carbon electrode, and the electrode reaction process was proved to be irreversible and diffusion-controlled.
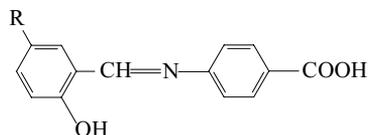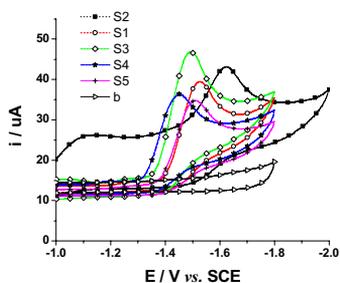
S1: R = –H ; **S2:** R = –NO$_2$; **S3:** R =–OCH$_3$;

S4: R = –Cl ; **S5:** R = –OH

Scheme 1． The molecular formula of Schiff base

Fig.1. Cyclic voltammograms of 3×10^{-3} mol dm^{-3} of S1-S5 in B-R buffer solution, pH = 8.2, v = 100 mV/s , b: B-R buffer solution without schiff base in it

It is kown that Schiff base undergo the two electronic reduction affording corresponding amines [1,2], and based on the experimental results the mechanism of the electrode reaction of compounds S1、S2、S4 is that the N atom of –CH=N– group obtains one electron firstly, then combines with one proton, and in the following fast step one electron and one proton are consumed, The mechanism of S3、S5 follows the sequence H$^+$, e, e, H$^+$, converts the –CH=N– linkage to a –CH$_2$–NH– group.

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Adsorption kinetics of iodide ions on the bismuth single cristal planes

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The electrochemical impedance method has been used for the quantitative study of adsorption kinetics of the iodide ions on Bi(hkl) in aqueus solutions with constant ionic strength $0.1(x$ M KI + $(1-x)$ M KF) from $5 \cdot 10^{-3}$ M KI to $1 \cdot 10^{-1}$ M KI). The electric double layer impedance was measured using an Autolab PGSTAT 30 with a FRA 2 ($0.1 < f < 10000$ Hz, 5 mV modualtion). The Bi(hkl) electrodes are ideally polarizable in the potential range from -1.6 V to -0.5 V (Ag|AgCl) [1].

The complex plane (Z'' vs Z') plots (Nyquist plots) for the system Bi(hkl) | 0.1 M KF aqueus solution results were fitted using various equivalent circuits, good results of fitting were obtined with the Frumkin- Melik- Gaikazyan (FMG) model (Fig. 1). The similar results were gained on Bi(hkl) in LiI solution in ethanol [2]. The same model (FMG) describes the system Bi(hkl) | aqueus KF solution with additions of KI (Fig. 2.). The equivalent circuit parameters were calculated by fitting the impedance function to the experimental impedance curves. There were also calculated phase angle dependence on electrode potential.
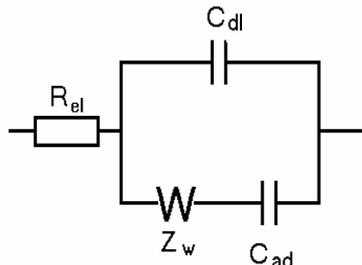
Fig. 1. Equivalent circuit, where R_{el} – electrolyte solution resistance, C_{dl} – double layer capacitance, ΔC – adsorption capacitance, Z_w – Warburg-like diffusion impedance.
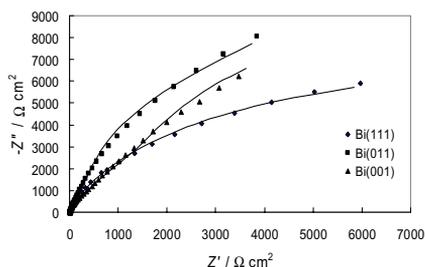
Fig. 2. Nyquist plots for Bi (hkl) planes in 0.1 xM KI + 0.1(1-x) M KF aqueus solitons (x= 100 mM) at the electrode potential E= -0.5V.

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Surface Chemistry and Dynamics

Emission from carbon nanostructures of different morphology at cathodic potentials

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The electrochemical behavior of electrodes containing nanotube carbon materials of different morphology has been studied. The nanotube electrode in the form of so-called nanotube paper – solution deposit was used. The impedance spectra of nanotube paper have been recorded in neutral aqueous electrolyte solutions. A simple model of porous electrode has been demonstrated to be the most suitable to describe impedance changes with frequency [1]. In addition, carbon nanotubes of particular structure with the length from 0.5 to 3 mm and at the nearly constant filament diameter of 100 nm have been studied. The structure of filaments has been revealed to be composed of a single-walled carbon nanotube covered by an outer soot like shell.

The intensive color change of electrolyte near electrodes has been observed just at the moderate cathodic potentials E ≈ -1.0 V for the both nanostructure types in hexamethylphosphoric triamide (HMPA). The above mentioned effect had been earlier observed on smooth metallic electrodes but in the far cathodic potential region (E ≤ 3.0 V) [2]. In this case the electron injection has been shown to occur into the HMPA solution with subsequent formation of almost stable complexes of electrons with the solvent having an intensive deep blue color. The given facts are direct experimental evidence of the autoelectron emission current from carbon nanostructures into electrolyte solutions in the cathodic potential region. A considerable decrease of solvated electrons emission overvoltage on the electrodes containing carbon nanostructures is caused by the presence of atomically sharp parts of the surface in compared with smooth electrodes.

The presence of autoelectron emission current from carbon nanostructure consisting of long parallel columns of about 50 μm in a diameter into the aqueous solution has been studied. The experimental accordance of photo- and autoelectron emission current dependence from acceptor and electrolyte concentration has been shown.

The reduction overvoltage decrease of nitrate sodium has been observed on carbon column electrode in comparison with glass carbon. The reduction overvoltage decrease has been shown to be promising way for electrochemical activation by means the replacement of heterogeneous the first electron transition stage on homogeneous reaction of solvated electrons with the different stable compounds.

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Electrochemistry of supramolecular inclusive complexes of cations

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For recent years investigation of complexes of cations formed by their inclusion into the molecular cavity of macropolycyclic ligand has received special attention. These complexes (cryptates) have very large stability and selectivity, shield effectively included particles from environment. These factors determine wide application of this type macrocomplexes in different fundamental studies and applied branches, however information about adsorption behaviour of cryptates at interfaces and interface electrode/solution is practically absent.

In this work macrobicyclic polyazaether (Cryptand 222, $C_{18}H_{36}O_6N_2$) was choosed as a ligand. Adsorption of cryptates of alcaline earth metals cations (Ca^{2+}, Sr^{2+}, Ba^{2+}) was investigated by impedance measurements on stationary Hg drop in 0.1M water solutions of corresponding chlorides. The obtained data point to a high surface activity of cryptates of two charged metal cations under study. These data are similar to ones for cryptates of alcaline metals cations, which have been investigated by us in previous works [1-3]. The dependencies of differential capacitance of electrical double layer on potential (C,E-curves) were measured for series of solutions with different concentrations of ligand. Mathematical treatment of experimental data was based on the model of two parallel capacitors supplemented by the Frumkin isotherm and was carried out by using the original regression analysis technique. Adsorption parameters of cryptates under study were calculated with use the all set of experimental data for each of systems. It's shown that there is a satisfactorily coincidence between experimental capacitance curves and ones calculated with the parameters found. Essential distinctions of cryptates adsorption behaviour caused by distinctions in their structure and   in the interaction with environment were established in spite of screening of included cations by organic ligand. Correlation between the adsorption behaviour of cryptates and their physical properties is supported by good agreement between dependences   of adsorption parameters of cryptates and their stability constants (literature data) on radius of included cations. Evidently there is a deep mutual relationship between the structure of a complex and the regularities of its adsorption.

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Surface Chemistry and Dynamics

Surface Chemistry and Dynamics

Influence of halide ions on the rate of hydrogen evolution on nickel

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Hydrogen evolution reaction (HER) is one of the most studied electrochemical reactions. Moreover the influence of halide ions on the rate of HER on Ni has been studied only in some works and exceptionally only on polycrystalline electrodes. It was found that bromide and iodide ions considerably decrease the rate (increase the overvoltage) of the HER on Ni [1]. The polarisation and electrochemical impedance spectroscopy (EIS) measurements on the well-defined Ni single crystal planes and polycrystalline Ni electrodes were carried out in this work. In our previous works it was established that some very slow processes take place on the nickel/solution interface in the presence of halide ions. The large amplitude current and potential steps were applied for more detailed examination of these phenomena.

Electrochemical measurements were carried out on polycrystalline and on Ni (111), Ni (110), Ni (100) single crystal planes in $HClO_4$ and H_2SO_4 solutions. The concentration of the halide ions (Cl⁻, Br⁻, I⁻) was in the interval from 10^{-5} to 10^{-1} M. Preparation of the electrodes was similar as described in [1,2]. The quality of the surface was checked by in situ and ex situ AFM/STM methods.

The impedance spectra were measured mainly at ac frequencies from 0.1 to 10 000 Hz using Autolab PGSTAT30 FRA2 measuring system. The experimental results were fitted to various equivalent circuits (EC) using a nonlinear least squares fitting minimisation method. The goodness of the fits was estimated by the value of the chi-square (χ^2) function and by relative errors of each parameter in the EC.

It was established that in the absence of halide ions in solution the results of EIS measurements at relatively high negative potentials presented in complex plane plots (Nyquist plots) are well described by one semicircle. It means that simple 3 element EC (Randels cell) describe behaviour of Ni electrodes in this case quite well. Thus at Ni electrodes HER reaction at high overvoltages is determined by the slow discharge step.

Halide ions studied generally decrease the rate of HER. The value of this effect depends on the nature and concentration of the halide ions, methods used for preparation of the electrode surface, and on the plane structure studied. The results of EIS measurements are possible to fit with 5element EC,
but the goodness of the fits is not very high. The more complicated problem is fitting of Z^{II}, Z^{I} -plots at very low frequencies. Analysis of the potential/current transients after current/potential steps also show that establishing of stationary state of the nickel/electrolyte surface in halide containing solutions is not a quick process.

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Electroreduction of Oxygen on chemically modified glassy carbon electrodes in alkaline solution

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The blocking behaviour of aryl films towards oxygen reduction was investigated. These aspects are essential in order to estimate the influence of covalently attached surface modifiers on the electrocatalytic properties of the substrate material. Glassy carbon (GC) electrodes were grafted by electrochemical reduction of diazonium salts. The diazonium derivatives of benzene, naphthalene, anthracene and biphenyl were used in surface modification. An unexpected order of blocking efficiency of the aryl moieties was observed for O_2 reduction in 0.1 M KOH. The phenyl-modified GC electrode was less active than those electrografted with larger aryl groups (1- and 2-naphthyl, 1- and 2-anthracenyl and biphenyl). The highest blocking efficiency observed for phenyl-modified electrodes is related to a higher surface coverage of phenyl groups. Comparative measurements were carried out in 1 mM $K_3Fe(CN)_6$. A much larger extent of blocking was evident for the $Fe(CN)_6^{3-/4-}$ couple. This effect was explained by a significant difference in size between the $Fe(CN)_6^{3-/4-}$ ions and O_2 molecule. Also, a mixed film of anthraquinone (AQ) and phenyl groups was formed and the kinetics of O_2 reduction on this modified electrode was studied. The kinetic parameters of O_2 reduction were determined using a surface redox-catalytic cycle model for quinone-modified electrodes [1]. The results obtained were compared with those of GC/AQ electrodes [1-6].

The borohydride reduction was used as an alternative method in surface modification and the electrocatalysis of oxygen reduction on the "reduced" GC was studied. This treatment leads to a decrease in the O_2 reduction activity at the prewave potentials, however, this effect is not persistent and the surface regains its initial activity during repetitive potential cycling in the presence of oxygen.

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Surface Chemistry and Dynamics

Electrochemical behaviour of $S_2O_8^{2-}$ anions on the Bi(111) and Cd(0001) single crystal electrodes

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It has been found that electroreduction of $S_2O_8^{2-}$ anions at Bi(hkl) and Cd(0001) planes [1-3] is a complicated reaction and there are noticeable deviations from the simplified version of Frumkin slow discharge theory [4] where the specific adsorptsion of reacting particles has not been taken into account. For the more detailed analysis, the impedance spectroscopy method [5] has been used for studying the electroreduction reaction mechanism of $S_2O_8^{2-}$ anions at the electrochemically polished Bi(111) and Cd(0001) electrodes. The impedance spectra have been measured at ac frequency f from 5×10^{-2} to 1×10^4 Hz and ac voltage amplitude 5 mV within the potential region E from -0.5 to -1.6 V (vs Ag|AgCl|sat.KCl) for Bi(111) and from -1.0 to –1.6 V for Cd(0001) [1-3]. The Milli-Q+ water was used for preparation of the solutions studied. Air was removed from the solution by bubbling argon (Ar, 99.998%) through or over solution prior to or during measurements, respectively. The complex plane impedance Z'',Z' (i.e. Nyquist) plots demonstrate that the reaction mechanism depends on the electrode potential, on the base electrolyte and reactant concentration as well as on the metal studied. The so-called total polarization resistance R_p increases with decreasing the negative potential. The Nyquist plots show complicated behaviour at low f and analysis shows that these effects can be explained by the weak induction effect, which can be simulated with the reaction mechanism taking into account the adsorption of the intermediate species at the electrode [5]. Results of the nonlinear regression analysis of the Nyquist as well as Bode plots show that, to a first very rough approximation, these plots can be simulated by using the classical Randles circuit, which represents the mechanism of mixed kinetics, where both charge transfer and diffusion steps determine the rate of the whole process. However, a better fit of the experimental results has been observed by the equivalent circuit taking into account adsorption of the intermediate particles. [1-3,5]. For more concentrated $S_2O_8^{2-}$ solutions ($c\geq1\times10^{-3}$ M) in the potential region $-1.05\leq E\leq-0.80$ V for Bi(111) plane, a better fit has been achieved by the equivalent circuit where charge-transfer resistance R_{ct} is in parallel to the resistance R_0 and inductance L. Thus, the adsorptsion of $S_2O_8^{2-}$ or reaction intermediate products is possible at Bi(111) as well as Cd(0001) electrodes.

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Surface Chemistry and Dynamics

Comparative in-situ ftir spectroscopic studies of the ethanol oxidation on pt(hkl) surface modified by deposition of osmium nanoislands

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The ethanol oxidation reaction was studied on Pt(100), Pt(110) and Pt(111) modified by different coverage degrees of osmium nanoislands by employing *in-situ* FTIR spectroscopy. The osmium nanoislands were obtained by spontaneous deposition from 1 mM hydrogen hexachloroosmiate solution. Collections of spectra of the ethanol adsorption and oxidation processes were acquired over a series of positive potential steps, in order to determine the intermediate species and the main products that are formed. It is shown that the increase in the catalytic activity of Pt(111)/Os for ethanol oxidation at lower potentials is greater than that observed for Pt(100)/Os and Pt(110)/Os. The mechanistic pathway for this reaction depends directly on the applied potential and the degree of osmium coverage for the three electrodes. For low potential and low osmium coverage, the formation of adsorbed linear CO as an intermediate is favored, and hence the full oxidation of adsorbed ethanol to CO_2 is increased. Adsorbed bridge CO was observed only on Pt(100)/Os. For all potentials and intermediate osmium coverages, the oxidation of ethanol to acetaldehyde and then to acetic acid is favored, although on Pt(111) the formation of acetaldehyde is promoted even with low degrees of osmium coverage. For all potentials and high osmium coverage, the catalytic activity of the electrodes for ethanol oxidation decreases. In addition, the direct oxidation of ethanol to acetic acid at low potentials is observed specially for Pt(111)/Os and Pt(110)/Os. The Pt(110)/Os surface shows the lowest catalytic activity for ethanol oxidation and the Pt(111)/Os is the most active.

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Surface Chemistry and Dynamics

Comparative study of formic acid oxidation on Pt and PtRu supported catalysts

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Oxidation of formic acid has been studied on well characterized PtRu/C and Pt/C catalysts. XRD analysis of PtRu/C shows that the chemical composition corresponds to alloy with ~60% Ru. PtRu particles are predominately in a form of solid solution of Ru in Pt with some amount of Pt in Ru. Average particle sizes calculated by Topas and Scherrer`s equation are 3.9 nm and 3.5 nm, respectively. Using the same methods in XRD analysis of Pt/C, the average particle sizes of 3.1 nm and 2.9 nm has been obtained [1].
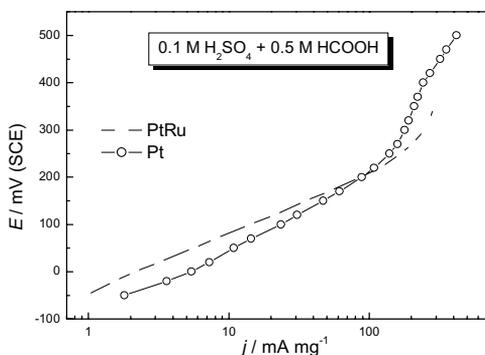
Fig. 1. *Steady-state curves for 0.5 M HCOOH oxidation at Pt and PtRu supported catalyst in 0.1M H_2SO_4 solution. $v = 1$ mV s^{-1}*

The polarization curves recorded under steady-state conditions on both electrodes reveal that formic acid oxidation is inhibited on alloy at low potentials (E < 0.3 V), probably due to the large CO coverage on Ru formed by decomposition of HCOOH {2}. Consequently, it could be assumed that in this potential region the reaction on PtRu/C proceeds predominately on Pt sites.

Kinetic parameters (Table 1) suggest that the transfer of the first electron in dehydrogenation of HCOOH can be rate-determining step in overall reaction on both catalysts.

Table 1: *Diagnostic criteria for the oxidation of HCOOH on Pt/C and PtRu/C catalysts in H_2SO_4 solution*

Catalyst	Tafel slope (mV dec^{-1})	$\left(\dfrac{\partial \ln j}{\partial \ln c_{FA}}\right)_{E,\theta}$	$\left(\dfrac{\partial \ln j}{\partial \ln c_{H^+}}\right)_{E,\theta}$
Pt	~130	0.5	0
PtRu	~120	0.5	0

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Surface Chemistry and Dynamics

Accumulation of uranium compounds on austenitic stainless steel surfaces

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As a result of the breakdown on April 10, 2003 there was a significant uranium contamination (about 4 kg's) in some technological units of the reactor block 2 of the Paks Nuclear Power Plant (PNPP). Some earlier studies attest that the amount of uranium-compound exists on the stainless steel surfaces of the primary cooling circuit is very low at present. However, the limited pieces of information about the quantity and kinetic behaviors of the uranium accumulated on the surface of the main structural materials (stainless steel, Zr-Nb alloy) of the primary cooling circuit may cause difficulties in the better understanding of the material-transport processes. The fact is that the uranium nuclides can present in different chemical forms (molecular, colloidal and/or disperse) in the boric acid coolant enhances the complexity of the problem.

In order to clarify the above issues, comprehensive studies have been performed in order to provide information about the uranium accumulation onto the main constituents of the primary cooling circuit; i.e., onto the 08X18H10T (GOSZT 5632-61) type austenitic stainless steel. In this talk, we give a brief summary of the uranium chemistry, as well as present and discuss some experimental findings on the time and pH dependences of U-accumulation obtained in a semi-plant model system using heat exchanger tube samples. In addition, we have worked out an alpha-spectrometric detection procedure which is suitable for the measurement of the activity-concentrations of both liquid- and surface-phase uranium. In addition, we have analyzed the oxidation state (chemical forms) of uranium sorbed on the inner surfaces of stainless steel tubes by XPS (X-ray Photoelectron Spectroscopic) method. The experimental data have revealed that the significant sorption of uranium onto steel surfaces takes place in the pH range of 4 to 8 where the intense hydrolysis of uranyl-cations in boric acid model solution can be observed. It is probable that the specific adsorption of U(VI)-hydroxo-complexes to be formed in the solution (mainly dissolved and colloidal $UO_2(OH)_2$) prevails over the accumulation of other uranium-compounds. Maximum of uranium-sorption was measured at pH=6; the maximum surface excess approaches to a monolayer coverage (assuming sorption of $(UO_2(OH)_2)$).

Surface Chemistry and Dynamics

Organic additives in the processes of metals deposition from complex electrolytes

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For the purpose of investigation of kinetics and mechanism of metal electrodeposition from complex electrolytes, influence of polyfunctional derivatives of organic acids (acrylamide (A), tartar (TA) and asparaginic (AA) acids) on the electrode process has been studied.

In a perchlorate solution the above-mentioned organic compounds make copper electrodeposition process slow and accelerate zinc electrodeposition. This effect may arise from participation of simple and heteroligand complexes of Cu^{2+} and Zn^{2+} in the electrode process. Earlier we proved existence of these complexes in the investigated solution and determined their stability constants by the potentiodynamic method.

Strong specific adsorption of $Cu(TA)^{2+}$ and $Cu(AA)^{2+}$ complexes which discharge on the electrode has been established by the chronopotentiometry method. This effect has been confirmed by increase of a transient time τ in the presence of the additives with an increase of a current density j as well as by the adsorption values Γ ($0.88\cdot10^{-10}$ mole·cm^{-2} for tartar acid and $1.54\cdot10^{-3}$ mole·cm^{-2} for asparaginic acid) which have been calculated from the measured j,τ-dependence. A corresponding decrease of a chronopotentiometry constant $j\tau^{1/2}$ with time of inputting of acrylamide in the copper perchlorate solution and a linear dependence $\partial(j\tau^{1/2})/\partial j$ on $[A]^{1/2}$ confirm that the electrode process rate is kinetically limited and the CuA^{2+} complexes which are predominant in the solution participate in the slow chemical reaction of dissociation. The character of influence of the composition A+TA+AA on Cu^{2+} ion discharge corresponds to effect of AA and TA. The value of Γ found in this case is $8\cdot10^{-10}$ mole·cm^{-2}. This value exceeds the sum of adsorptions of the individual $Cu(TA)^{2+}$ and $Cu(AA)^{2+}$ complexes and allows to suggest formation of a mixed adsorption layer on the electrode surface.

The values of a Semerano criterion (0.37–0.47) found for zinc electrodeposition confirm that the electrode process rate in the presence of all the additives under investigation is kinetically limited. As Zn^{2+} complexes with the additives are considerably less stable than the analogous Cu^{2+} complexes, it is possible to suppose that the observed chemical reaction preceding discharge is not a process of dissociation of the ZnL^{2+} complex diffusing in the solution but one of formation of ZnL^{2+} in the surface layer.

The carried out study allows to conclude that an approach of copper and zinc reduction potentials from a complex electrolyte can be achieved by combining specific actions of polyfunctional organic acid derivatives on Cu^{2+} and Zn^{2+} ion discharge that allows to deposit high-quality alloys of these metals.

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Surface Chemistry and Dynamics

Study of the electrochemical anodic films / environment interface

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Electrochemical anodic films / environment interface for Ti and its implant alloys Ti-5Al-4V and Ti-6Al-4Fe in Ringer 2 solution of different pH values (2.5; 4.35; 6.98) was investigated in this paper.

Anodic films were prepared by immersion in 10M NaOH at 60^0C for 24 hours and drying at 40^0C during 24 hours. After that, a thermal treatment consisting of heating at 500^0C for 24 hours and then cool in water was applied.

Electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit potential in Ringer 2 solution after different periods (1–60 days). From microhardness measurements were determined the average anodic oxide film depths. Open circuit potentials were monitored during 20 000 exposure hours.

Both Nyquist and Bode plots exhibit two-step processes illustrated by the phase angle at almost -90^0, characteristic for barrier oxide film, and another angle closed to $-20^0 \div -40^0$, due to some diffusion processes through a porous layer. These values are associated with the existence of the inner barrier film of titanium dioxide TiO_2, and another porous layer due to the nucleation of porous apatite. The spectra changed with the exposure time, indicating that the anodic films have grown by the apatite formation. The electrical resistance increased, denoting some thickening processes. So, the apatite on the surface promotes the bounding of implant to the surrounding bone and implant become bioactive.

Microhardness measurements were performed using different loads and the average value, expressed as hardness Vickers degree (HV) were calculated; based on this average values, the corresponding depths were determined. It resulted that the microhardness increased with increasing load, showing the existence of a porous layer on the surface. The average depths of the anodic oxide films, determined by microhardness vary from $1x10^{-3}$mm to $6x10^{-3}$mm

Open circuit potentials were determined in Ringer 2 solution of different pH values but without treatment with the purpose to compare the biomaterial behavior. All open circuit potentials vary around electropositive values, suggesting slow dissolution, re-passivation or ion absorption processes. For all biomaterials it was observed that, the open circuit potentials became slightly more electronegative in the acid pH domain (4.35 respectively 2.5) because of its aggressivity. Their values correspond with the stable state on Pourbaix diagram. Comparing these three biomaterials it resulted that the alloys present a little more active open circuit potentials than titanium, but all values are in the same passive domain, providing a good stability.

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Surface Chemistry and Dynamics

Autocatalytic copper(II) reduction by cobalt(ii) in diethylenetriamine solutions: thermodynamic calculations and kinetic data

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Recently [1], diethylenetriamine (dien) was shown to enhance effectively the anodic oxidation of Co(II) in alkaline solution. The anodic oxidation of a reducing agent is one of the two partial electrochemical reactions of the autocatalytic (electroless) metal deposition process. Therefore, the Co(II)-dien complexes were used at constructing new electroless plating solutions. Co(II) complexes with ethylenediamine [2, 3] and propylenediamine [4] were used for electroless Cu deposition.

The thermodynamic possibility of Cu(II) reduction by Co(II) in dien solutions was demonstrated by calculation of equilibrium potentials of Co(III)/Co(II) and Cu(II)/Cu redox couples using C0(II), Co(III) and Cu(II) distribution among complexes with dien. The redox potentials depend largely on solution pH, and a pH region exists where the Co(III)/Co(II) potential is more negative than that of Cu couple, the potential difference reaching 0.2 V. The experiments using electrochemical quartz crystal microgravimetry (EQCM) showed that the Co(II)-dien complex was able to reduce autocatalytically Cu(II) ions to metal. EQCM measurements provided information on an instantaneous copper deposition rate, mixed potential and copper film build-up kinetics. Using cyclic voltammetry in combination with EQCM, the rate of the partial electrochemical reactions – anodic Co(II) oxidation and cathodic Cu(II) reduction - were obtained. The copper plating process was shown to be very sensitive to solution pH and anions used.

The process rate changes in the sequence: chloride >> tetrafluoroborate > nitrate > sulfate > acetate. The dependence of Cu deposition rate on solution pH was found to be of the same form as that of the reaction free energy change. The Co(II)-dien complex is more active in Cu(II) reduction than the similar complex with ethylenediamine, in spite of a lower redox potential difference.

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A dopamine metabolite adsorption on gold

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The di-hidroxi-fenil-acetic acid is the most important dopamine metabolite. The newrosciene researchers need electronalytical techniques for its determination. To increase the accuracy of this techniques the electrochemical properties of the substance must be known.

The objective of this study was to obtain knowledge on the behavior of di-hydroxy-phenil-acetic acid(DOPAC) on gold as an electrochemical reagent and as an adsorbate. The redox reaction characteristic of the catechol ring allow the study of the substance adsorption under open circuit condition. The procedure include open circuit adsorption, rinsing with the electrolyte, and making cyclic voltammetric scan to determine the amount of adsorbed substance and its electrochemical behavior. For this reason, two cells were employed, one for adsorption, and the other electrochemical, both were thermostatized at 25°C.

From the adsorption isotherms and from the kinetic studies it has been concluded that the DOPAC adsorption is weak. The adsorption bound is strengthening with the time forming a σ bound. The area per molecule of 47 Å^2 , very near of that of the dopamine is obtained.
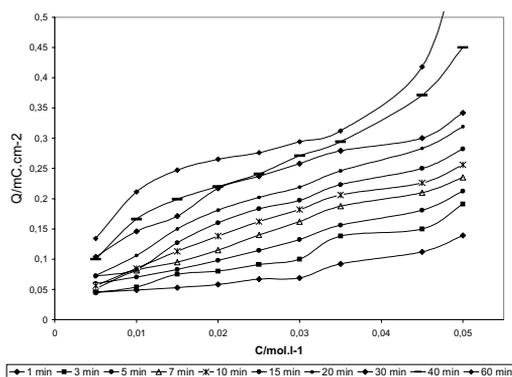
Fig.1: Plot of area per molecule of DOPAC adsorbed on gold in function of adsorate concentration

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Surface Chemistry and Dynamics

Photo-potential in Ag/Ag$_2$O/OH$^-$(H$_2$O) system

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The dissolution of metal is usually accompanied with the formation of insoluble products at the surface (oxides). The electronic structure and semiconductor properties of oxides are defined at first by non-stoichiometry composition that, in its turn, depends on the film formation conditions, metal surface state and so on.

We used in-situ photo-potential V_{ph} measurements in Ag (I) oxide formed on silver in 0.1M KOH under anodic potentiostatic polarization. The polarity of signal determines the type of conductivity. The value of signal is connected with concentration of dominant structure defects in sub-lattices of oxygen or silver. The role of following parameters is examined: oxide formation potential E (0.470 – 0.505 V n.h.e.), film thickness L (6 - 22 nm), intensity of light at the electrode P = 0.2 – 1.3 mWt/cm^2 and crystallographic structure of silver (100, 110, 111, poly). The oxides were grown on compact silver as well as on its microcrystals arising under the cathodic reduction of Ag$_2$O film been formed before.

To generate the photopolarization we used the set of light-diodes radiating the rectangular pulses of quasi-monochromatic light with $\lambda = 375 – 870$ nm. The duration of pulse is 2 ms, the repetition frequency is 5 Hz. In spectral measurements the intensity was constant.

The photo-potential $V_{ph}(t)$ measurements were performed 20s after the polarization switching-off. It is shown that V_{ph} decreases in exponential manner which lets to define $V_{ph}(0)$ by extrapolation the signal to t□0. The digital treatment of a signal and the pre-amplifier with an active filter of frequencies diminish the noise level down to 1–2 μV. We controlled the absence of a noticeable contribution of surface electronic states into the photopolarization signal by impedance measurements.

It is revealed that independently on the conditions of oxide formation $V_{ph}(0) < 0$. It means the n- type conductivity in a crystal Ag(I) oxide, connected with the excess of metal as compared with oxygen in Ag$_2$O structure. The concentration of donor defects (super-stoichiometric atoms of metal) practically does not depend on potential of anodic film formation and is equal to $1.8*10^{-14}$см$^{-3}$ in average. The clear square $V_{ph}(0)$ – L dependence means that $l_D \gg L$, where l_D – Debye's range. With enhancement of light intensity the photo-potential increases linearly.

The shape of spectral dependence of photo-potential and the role of crystal structure of silver are discussed.

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Adsorption of anion of glycine on smooth and platinized platinum electrodes

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At research of electrode processes with participation amino acids the basic task is the study of complex interaction metal - fiber and fundamental definition of a role of various functional groups (-CH - ; -NH$_2$; -COOH; etc.) at their interaction with an electrode surface. However, the skilled data of the different authors on the submitted theme frequently are inconsistent.

The purpose of the given work is the study adsorption of glycine on a surface Pt/Pt - and smooth Pt an electrodes in alkaline medium, where researched amino acid is mainly as anion.

The researches carried out by methods of removal curve loaded on Pt/Pt and complex anodic/cathodic potentiostatic pulses on electrode from smooth Pt. Size of a degree of coverage judged on a charge spent on formation of a monolayer adsorbed of oxygen or hydrogen. Kinetic of adsorption studied at constant potential chosen in area loaded of a double electrical layer, changing time adsorption.

From received thus kinetics and quasistationary to isotherms, reconstructed in half-logarithmic coordinates, the meaning of the factor of power heterogeneity of a surface equal 30 is designed. The similar size received on smooth Pt an electrode has made 28. Let's note, that the received sizes of the factor of power heterogeneity, surface are significant, that specifies essential distinction in energy of internuclear communication metal - adsorbate in system Pt - NH$_2$CH$_2$COO$^-$ on different sites of a surface distinguished on a degree of coverage. On a piece cut on an axis of ordinates stationary isoterms, received on Pt/Pt - and smooth Pt an electrodes, the sizes of a standard constant of balance K$^{(0)}$, equal 6,8$_*$10^{10} and 1,1$_*$10^{11} accordingly are designed. The value of standard change of free energy Gibbs of process exchange adsorption of which meaning very little are determined differ: -59,4 and -62,0 кJ$_*$mol $^{-1}$. The received results testify about appreciable enough chemosorption interaction between molecules of glycine and energetically uniform-non-uniform surface of Pt-electrodes, and also to absence appreciable influence of the form of microparticles of the besieged platinum on this characteristic.

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Surface Chemistry and Dynamics

Electrochemical oxidation of monoaminoacetic acid on platinum

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The researches in the field of electrochemistry aliphatic aminoacids concern to number intensively developing. The interest to the given theme raises because the electrochemical way frequently has a number of advantages before other methods of their reception. However, the opportunity of application of various electrochemical methods can be limited to ability aminoacids to process of electrooxidation on an electrode. It is necessary to note, that the data, available in the literature, on the present problem are superficial and are inconsistent.

The purpose of the present research is the establishment of area of potentials of course of process of electrooxidation the most simple of aminoacid – monoaminoacetic acid (glycine), and also the study his basic kinetic of laws in 0.1M a solution NaOH, where researched aminoacid is mainly as anion. The researches carried out by methods cyclic voltamperogramms on stationary and rotating smooth Pt - electrodes and coulometry on Pt/Pt. Is established, that the process of electrooxidation glycine proceeds in the field of potentials $E_r = 1.2 \div 1.5$ V, passes through a maximum and is imposed on area adsorption of atomic oxygen, that can testify to his direct participation during electrooxidation. The output on a current in the field of potential of a maximum is close to 100 % under condition of "soft" oxidation, proceeds with participation four electrons, and the basic products of oxidation are of ammonia, formiate - ion and CO_2. Is determined, that density of a current in a maximum of electrooxidation and potential, appropriate to it, vary with growth of concentration of researched substance, and as speeds of imposing of potential. The inclination of the received dependences reconstructed in half-logarithmic coordinates has appeared is identical and is equal 0.12 V. The experiences on a rotating disk electrode have shown that density of a current in a maximum remains constant in all intervals of speeds of rotation of an electrode.

Thus, the set of the received data testifies that the process of electrooxidation glycine on a surface of a platinum electrode proceeds in adsorption a condition, and a limiting stage is the carry of a charge from adsorption of a complex to an electrode surface.

The kinetics of anodic destruction of formaldehyde on Au and Ag,Au-alloys in alkaline solution

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It is well known that formaldehyde existing in aqua alkaline solution in a form of methylene glycol oxidizes anodically in the potential range up to 0.5V (s.h.e.) by overall reaction [1,2]:

$$H_2C(OH)O^- + 2OH^- = HCOO^- + 2H_2O + 2e^-.$$
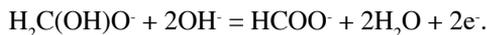
But the details of the kinetic scheme are not established. We have shown before that the initial stage of formaldehyde potentiostatic oxidation in the potential range E = -0.2 ÷ 0.5V on Au and Ag,Au-alloys ($X_{Au} \geq 50$ at.%) is essentially non-stationary. The current efficiency of the purpose reaction is near to 100% in aqua 0.1M NaOH. The aim of this paper is to reveal the nature of non-stationarity and to establish the kinetics of formaldehyde anodic destruction on Au and Ag,Au-alloys in alkaline solution in a wide potential range. The investigations were carried out on stationary electrodes as well as on Au-RDE by means of linear, cycle and multicycle voltammetry, coulonometry, "slow" and "fast" chronoammetry.

It was established that independently on the alloy composition the formaldehyde anodic destruction proceeds in the potential range E = -0.5 ÷ 0.5V including the potential of OH$^-$ specific adsorption. The rate of process on homogeneous Ag,Au-alloys with $X_{Au} \geq 50$ at.% is of the same order as for pure Au. But it sharply diminishes with the growth of silver concentration in the alloys. The formate-ion is the stable product of electrooxidation reaction up to E = 1.4V. The accumulation of this product at the electrode causes the decrease of currents of formaldehyde anodic destruction. In the potential range from -0.2 to 0.5V the kinetics of electrooxidation on the stationary electrodes is volume diffusion one already at t ≥ 0.5s. The non-stationary and then the stationary $H_2C(OH)O^-$ and (or) OH$^-$ bringing up to the electrode but not HCOO$^-$ taking away is the limiting process. After the removing of diffusion limitations the electrooxidation is controlled by some chemical stage. But its rate decreases in time as before presumably because of the adsorption accommodation of intermediates or reaction products at the electrode. The data of currentless chronopotentiometry point indirectly that the $H_2C(OH)O^-$ dissociate chemosorption at the electrodes can play the role of such a stage.

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CATHODIC REDUCTION OF H_3O^+ AT Au, Cu AND HOMOGENEOUS Cu,Au-ALLOYS

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It was established before [1] that the hydrogen evolution reaction (HER) on Ag, Au and Ag,Au-alloys in aqua sulfuric-acid solution proceeds by Volmer-Tafel path. For all examined alloys the stage of H_3O^+ discharge realizes in a barrier-free regime at low overpotentials and turns to usual regime when the overpotential growths. The comparison of data for Cu,Au- alloys with data for Ag,Au-alloys to construct the general scheme of process has a special scientific interest. The aim of this work is to detail the kinetic scheme of cathodic hydrogen evolution on Cu, Au and their alloys in a wide range of alloy compositions.

The experiments were carried out in 0.5M H_2SO_4 and 0.05M H_2SO_4 + 0.45M Na_2SO_4 bubbled with argon by method of cycle voltammetry ($d\eta/dt = 0.5$ mV/s).

It was found that in 0.5M H_2SO_4 at η from 0 to -0.45 V the potentiodynamic curves of direct and reverse scan coincides within the error. Two linear plots appear on voltammograms in semi-logarithmic coordinates. The slope of the first plot on η,lg i-curves (at low overpotentials) is contained between 0.059 and 0.071 V for all examined electrodes. The slope of the second linear plot (in a range of high η) does not depend on alloy composition in a whole. Its value is equal to 0.119 V in average.

It was established that the dilution ten times causes the significant enhancement of overpotential of hydrogen evolution reaction on the second plots of polarization curves for Cu and Cu,Au-alloys. In general, the slopes of II plots remain the same except for Cu and Au, where the values increase to 0.130÷0.135 V. The latter means that H_3O^+ discharge proceeds in usual regime in that range of overpotentials. The values of overpotential in I linear plot does not depend on solution composition for the most of alloys which approves the barrier-free discharge.

The influence of Cu,Au-alloys composition was revealed on the overpotential and current of change for cathodic H_3O^+ reduction. With increasing of Au content in the alloy the overpotential diminishes but the relevant current of change i^0 growths. Even a little concentration of gold (X_{Au} = 4 at.%) lead to the sharp enhancement of the rate of hydrogen evolution on Cu,Au-alloys. However the little amount of Cu in the crystal lattice of Au weakly influences the kinetic parameters of cathodic hydrogen evolution.

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Surface Chemistry and Dynamics

Effect of gaseous nucleation in kineticS of HER on silver, gold and their alloys

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By methods of linear voltammetry and potential transients at current switching off it was established that the hydrogen evolution reaction (HER) on silver, gold and Ag,Au-alloys in sulfuric acid solution proceeds by Volmer-Tafel path [1]. In the course of cathodic reduction of H_3O^+ the bubbles of hydrogen arise at electrode surface, which can make a certain contribution into kinetics of this reaction. The aim of this work is to reveal the effect of gaseous 3D-nucleation in kinetics of HER on these electrodes by method of chronoammetry.

The experiments were carried out at 298K in 0.5M H_2SO_4 bubbled with argon. The solutions were prepared with bidistilled water and reagents of analytical grade. We used the potentiostatic computer complex IPC-Compact. To realize the quasi-equilibrium hydrogen electrode on Ag, Au and their alloys we applied the cathodic pre-polarization by special method for each electrode and saturated the solution with purified H_2.

In overpotential range η = -0.05÷-0.45 V the chronoammograms of H_3O^+ cathodic reduction are obtained. As overpotential increases to certain η_{max} so the current maximum arises on i,t-curves. With growth of η the maximal amplitude of current increases and the peak shifts to less moments of time. The value of η_{max} weakly depends on the alloy composition, slightly increasing at transition from -0.15 V for Cu to -0.27 V for Au.

It is established that the current decay on i,t-curves at $\eta < \eta_{max}$ is connected with non-stationary diffusion of molecular oxygen traces in solution. The appearance of maximum on i-t at $\eta \geq \eta_{max}$ is connected presumably with nucleation of hydrogen at the electrode surface. The analyses of i,t-curves was performed with different models of 3D-nucleation. It was found that latent nucleation centers are activated instantly HER proceeds in a initial-diffusion regime ($i \sim t^{1/2}$), which is caused by surface diffusion of atomic hydrogen. So the scheme of HER – process on Ag, Au and their alloys must be added with stages of formation and growth of phase H_2 nuclei:

$$H_3O^+ + e^- \rightarrow H_{ads} + H_2O \qquad (1) \quad H_{ads} \rightarrow H_{ads}^* \qquad (2)$$

$$H_{ads}^* + H_{ads}^* \rightarrow H_2 \qquad (3) \quad H_2 + \{H_2\}_{n_{cr}} \rightarrow \{H_2\}_{n_{cr}+1} \rightarrow \{H_2\}_{n \gg n_{cr}+1} \quad (4)$$
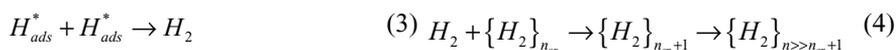
where $\{H_2\}_{n_{cr}+1}$ - critical nucleus arising on electrode surface.

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Quinone Chemistry by Quantum Chemical Models
Redox Properties, Standard Potentials and O_2 Reduction

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Recently, the redox properties of six parent quinones were investigated by means of quantum chemical models.[1] Thermodynamic functions were calculated using DFT/B3LYP for the reduction of the quinones to hydroquinones and semiquinone radicals in the gas-phase. Gibbs energies of reduction and the corresponding standard potentials in water were calculated using the IEF-PCM solvation model. Results are presented for the ortho and para isomers of benzoquinone and naphthoquinone, 9,10-anthraquinone (Figure 1) and 9,10-phenantrenequinone, and the results are compared to experimental values, where available. Although the quantum chemical results are in agreement with experiments within the accuracy limit of the B3LYP method, it was found that a small empirical correction could be used to compensate for the remaining discrepancies. Standard potentials are presented for the stepwise $1e^-$, $1H^+$ reductions via the semiquinone radicals, which have not been determined experimentally, and the experimental uncertainty in some of the $2e^-$, $2H^+$ potentials is addressed.
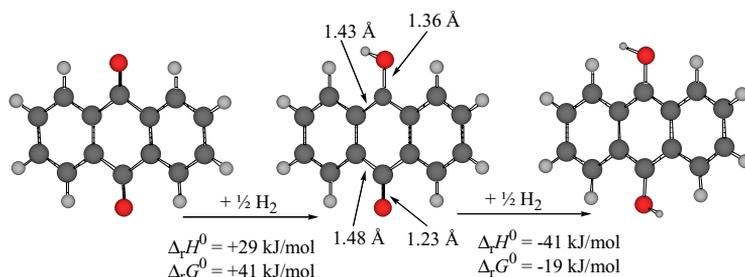
Figure 1. Reduction of 9,10-anthraquinone via the neutral semiquinone radical.

Continued work has focused on the oxygen reduction reaction on different quinones.[2] Results are presented regarding possible intermediates in this process. The overall energetics for O_2 reduction varies due to the differences between the thermodynamic functions of the six quinones. Compounds containing superoxide and hydroperoxide units were found to be more probable reaction intermediates than endoperoxides.

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Symposium 8 - Poster

Surface Chemistry and Dynamics

The influence of quaternary ammonium compound on electroreduction of oxalic acid on the lead electrode

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The production of glyoxalic acid by the electroreduction of oxalic acid has attracted interest for decades, but it has been not widely used in industry so far. The key problem for commercializing the process is the cathode deactivation, which contamination gradually suppresses the surface activity for organic chemical production and allows excessive hydrogen evolution. To solve this problem, addition of certain surfactants to the catholyte is applied in this process to get high activation efficiency. Chemical activators for this purpose are quaternary ammonium compound.

In this paper, the structural effect of the chemical activators on electrode reaction is presented. The results show that the activation efficiency is closely related to the structure of the chemical activator added to the catholyte. How the chemical activator affects the electrode is investigated by difference capacity.

Constant current electrolysis method has been used to investigate current efficiency of different quaternary ammonium compounds, which are tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), tetrapropylammonium hydroxide (TPAH) and tetrabutylammonium hydroxide (TBAH). The results of their concentration range from 0.005 to 0.035 mol·dm^{-3}are shown in Fig 1. The current efficiencies are varied with variety of quaternary ammonium hydroxide and their concentrations.

Compared the differential capacity curve in the same concentration, it can be found that the differential capacity are different in saturated oxalic acid. These curves of 0.005M are shown in Fig 2. It is evident that the capacities are decreasing with increasing the carbon atom number of the alkyl chain of tetraalkylammonium hydroxide. In other words, adsorption quantity of TBAH is the most on the lead electrode. And its potential range of adsorption being close to most becomes wider. It was also investigated that concentrations influenced their capacities in a concentration rang from 0.005 to 0.035 mol·dm^{-3}.

Usually, it is the cation of quaternary ammonium compound to activate deactivating cathode, not the anion. Tetrabutylammonium salts were chosen to investigate the activation effects of anions on cathode. It is also found that their differential capacities nearly kept same value during potential range of -0.5~-1.5v in Fig3.

It can be concluded that the reaction current efficiency are different because of surface adsorption of quaternary ammonium salt.
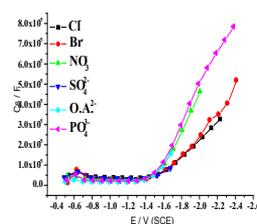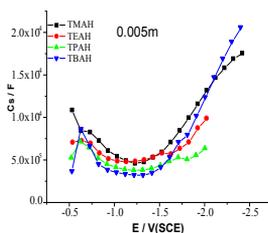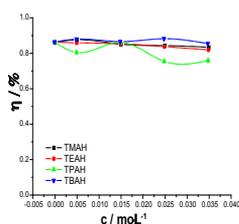
Fig1 the Current efficiency   Fig 2 Differential capacity of 0.005M   Fig 3 Differential capacity of anions

Solutions of the Stefan problem applied to a solid phase growth on substrates of different geometries including the test of the theoretical equations

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The Stefan problem is related to transport phenomena contributions at moving interfaces. These mathematical problems are often called Stefan problems, irrespective of the driving force, and are found in a number of processes occurring in different areas of natural science an technology.

The Stefan problem appears under certain conditions in metal electrodeposition via a mass transport contribution in addition to diffusion, migration and convection. In this work the rate equations for the growth of a solid phase involving a moving front are obtained.

The paper refers to solutions of the Stefan problem in the 2D space for different geometries considering the boundary of a solid phase according to a known displacement law. The solutions for the growth of a solid phase on a plane, a spherical and a cylindrical substrate are given. In all cases, in the absence of convection and surface roughness effects, the phase growth kinetics is determined by diffusion and advection, the latter being due to the linear displacement of the growth front with time. The theory predicts two limiting kinetic situations, namely a diffusion control when the time and/or the radius of the substrate approach zero, and an advection control for the reverse conditions. For the spherical substrate, when its radius tends to infinity, the kinetics of the process approaches that found at the plane plate substrate. Theoretical current transients are tested utilizing growth pattern data for the formation of 2D silver dense branching electrodeposits on a plane plate cathode in a quasi-2D cell, and silver electrodeposits on spherical cathodes employing high viscosity plating solutions. Finally, the contribution of advection in a number of electrochemical processes is explored.

Coupled enzymatic and electrochemical reactions on microstructured template surfaces investigated by scanning electrochemical microscopy (SECM)

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Templated surfaces provide an convenient way of creating spatial patterns of biocatalysts, that allow complex reaction sequences to be carried out by the close proximity of the various active regions. SECM can be used to provide spatial images of the reactivity by also to provide a more detailed analysis of the local kinetics. Our group has used templated self-assembled monolayers (SAM). They have been either produced by microcontact printing of by localized electrochemical desorption using SECM as a tool to surface modification. The templated monolayers have been further processed by covalent attachment of enzymes, by layer-by-layer deposition of polyelectrolytes into which one enzyme was integrated as a polyelectrolete. In this way the templates do not only provide the basis of lateral patterning but also allow a designed combination of crystalline inorganic supports with flexible molecular structures. Alternatively polymer microstructures with immobilized enzymes can be assembled on surfaces.

SECM has been used to monitor the passivating properties of different monolayer systems. While this may be interesting for itself, it allows to navigate an SECM probe on patterns that were created by other techniques such as microcontact printing. A subsequent application of a SECM-based surface modification technique allows to further modify such layers and thus provides a convenient flexible way of their further modification.

Recently we succeeded in quantitatively modelling the SECM response over such structures using the boundary element method (BEM). Steady-state systems of arbitrary 3D geometries can be treated if the boundary conditions can be described as linear functions of the local concentration - a condition that is full-filled for most SECM experiments.

Application of the above concepts can be seen in a number of chemically completely different systems: (i) Similar to artificial structures containing enzymes, also site directed cell adhesion can be directed using microelectrochemical methods to lift the cytophobic character of oligo (ethylene glycol)-terminated SAM and allows for the site directed sequential introduction of different cell populations. (ii) Oxide layers on titanium-based alloys show different passivating properties depending on the composition, crystallographic orientation, and the redox species by which they are probed. (iii) Imaging local enzymes acivity can be used to devise readout procedures for enzyme labels in biochips. It may also serve a signal generation process to read out high-density electrophoresis gels, in particular because this may be compared to sensitive but not selective reading after silver staining.

Symposium 8 - Poster

Surface Chemistry and Dynamics

An Improved Model for the Diffuse Double Layer

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Most electrochemists still use the Gouy-Chapman (GC) model of the diffuse layer in analyzing experimental data for polarizable interfaces.

On the other hand, both Monte Carlo simulations and theoretical studies show that the GC model gives incorrect estimates of the potential drop across the diffuse layer, and of its differential capacity. We present here an empirical model for the diffuse layer which accounts for the effects of ion size and the permittivity of the electrolyte solution. The significance of this model is discussed with respect to the analysis of experimental data.

Symposium 9

Corrosion: from Nanostructure to Structural Failure

Nanoporous de-alloyed metals:
From atomistic modeling to applications

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The literature on electrolytic de-alloying of homogeneous alloys has expanded recently with the realization that the resulting nanoporous metals may have interesting applications. These range from the mundane - filtration membranes, perhaps catalytic or electrically switchable - to the more challenging - actuators or mechanical sensors, specialized coatings, or templates for deposition of electrocatalytic nanoparticles. Bulk metal nanoparticles can be deposited into de-alloyed layers at an underpotential (i.e. above the normal metal/metal-ion equilibrium potential) owing to a curvature effect.

De-alloyed material is nanoporous with close to zero net curvature ; normally the porosity is completely interconnected. The characteristic size scale depends on the surface diffusivity of the more noble alloy component. De-alloyed materials are usually considered as brittle solids; microscopically, they display different types of plastic fracture depending on the thickness of the ligaments.

The mechanism of de-alloying in Ag-Au (for example) involves dissolution of Ag and surface diffusion of Au. The critical electrode potential to form interconnected nanoporosity is set by a balance between the rates of these two processes. Anion adsorption or monolayer Au oxidation influence the size scale of the porosity through their effects on the surface diffusivity of Au. Electrochemically controlled de-alloying in perchloric acid gives the finest porosity, and this may optionally be coarsened by thermal treatment. Another way to make very fine porosity is to use an alloy based on a higher melting-point noble metal such as Pt. The porosity of de-alloyed Ag-Au will continue to coarsen in some applications, but it is relatively stable in air.

Until recently, de-alloyed materials generally had poor mechanical properties and were subject to spontaneous fracture. We find that optimization of the mechanical properties, by increasing the electrolyte temperature and avoiding monolayer Au oxidation, causes strange phenomena to appear that may be related to the surface-charge or 'piezo-electric' effects discovered by Weissmüller et al. De-alloyed layers magnify nanoscale surface effects into macroscopic mechanical behavior.

Symposium 9 - Keynote

Corrosion: from Nanostructure to Structural Failure

Nanoscale Dissolution and Passivation Processes for an Electrochemical Tailoring of Directionally Solidified Eutectics

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It may sound contradictory to apply a process that was initially designed to grow large single crystals in nanotechnology. However, if a eutectic alloy is directionally processed in a Bridgman type furnace both phases are solidifying simultaneously. Bound to the eutectic composition a coupled growth of the phases results. Eutectics with an asymmetric composition form micro or nanowires embedded in a matrix of the mayor phase.

Pseudo-binary NiAl-X (X = Re, Mo, W) eutectics present a structure in which the minor phase (Re, Mo W) is composed of fibres uniformly distributed in a stable NiAl matrix. A comparative study of the Pourbaix diagrams of the 3 elements involved allows selecting conditions under which the NiAl matrix is selectively dissolved to form an array of single crystalline metallic nanowires of identical orientation and diameter [1].

Passivation of the matrix with a simultaneous electrodissolution of the minor phase on the other hand forms nanopore arrays or nanofilters. Careful selection of the conditions used allows controlling the depth of the pores [2].

Subsequently the system can be further used, e.g. by depositing gold into the nanopores that produces various microelectrode arrays [3]. Various other structures can be produced by combining these processing steps, for example Re-nanowire arrays with prominent gold heads.

Pros and cons of processing route as well as possible applications will be discussed.

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Symposium 9 - Keynote

Corrosion: from Nanostructure to Structural Failure

Developing the characteristics and properties of passive metal surfaces

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The passive metal surface is a remarkable entity, controlling much of the stability of metal structures and components in service. Studies of these surfaces over many decades have revealed properties of passive metals which are as unique as they are fascinating: the very nanoscopic nature of the passivating film gives it this uniqueness. Three of the issues which concern the corrosion scientist are addressed in this talk. These matters are as follows. (i) What constitutes passivity and how do we develop total control over it. (ii) Since passivity seems to dominate metals in service, why do they corrode. (iii) What are the properties of the passive surface and how can they be exploited.

Discussion of corrosion centres around pitting corrosion, a form of runaway corrosion reaction with disastrous consequences on engineering structures. However, brought under control, the phenomenon of pitting corrosion can be used to sculpt the surface of metals and generate a known predetermined microscopic morphology.

Discussion is also centred on the properties of the passive metal surface which could be developed for reactive surfaces. Since heterogeneous catalysis involves catalytically reactive interfaces, the passive surface should be exploitable in this fashion. In modern development of the fuel cell, the use of platinum is a prohibitive cost barrier to a wide range of applications. Although several attempts have been made to replace this invaluable electrocatalyst, no major breakthrough has been made. This however, does not mean that there is no such possibility, but rather, that a greater research effort is required. There are several properties of such surfaces that can be usefully developed, and this forms part of the discussion of the present paper.

Symposium 9 - Keynote

Corrosion: from Nanostructure to Structural Failure

Modeling of the Barrier, Electrochemical Protection and Active Corrosion Inhibition Properties of an Al-Co-Ce Amorphous Alloy Coating Protecting AA 2024-T3

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An Al-Co-Ce alloy coating has been developed to protect a 2024-T3 substrate against localized corrosion. The Al-Co-Ce coating can function as a corrosion barrier, a sacrificial anode and a reservoir to supply soluble inhibitor ions to protect defects site exposing AA 2024-T3 to an aqueous environment. In this paper, both experiments and continuum scale modeling investigations are described that identify some of the coating attributes that optimize the ability to perform each function. Additionally, the environmental factors that challenge the ability to perform each function are assessed. Concerning barrier properties, the localized corrosion resistance of the alloy coating was assessed as a function of solid solution alloying content. Quantification of the relationships between solid solution compositions and selected electrochemical corrosion metrics was established by utilizing specialized statistical methods designed for compositional data sets. Electrochemical properties such as pitting and open circuit potential are shown to be tunable, based primarily on cobalt (Co) concentration in solid solution, and secondly on cerium (Ce) content. Therefore, barrier coatings can be tailored for a specific need via choice of alloy composition. Continuum modeling and experiments were performed to assess the sacrificial anodic protection capabilities of these alloy coatings. The geometry is that of an Al-Co-Ce coated surface with the presence of a scratch simulating exposed AA2024-T3. Finite element modeling of current and potential distributions was performed to assess the scratch size that could be cathodically protection via such a sacrificial coating. The criterion used was to achieve a position specific galvanic couple potential that was more negative than the pitting potential associated with 2024-T3. Lastly, the "chemical throwing power" of such an Al-Co-Ce metallic coating under thin electrolyte films representative of atmospheric conditions was also modeled. The chemical throwing power was the distance over which an adequate inhibitor supply could be delivered in a reasonable time period after triggered release of inhibiting ions. Separate experiments identified critical inhibitor concentrations for suppression of corrosion of 2024-T3. The model considered the pH-dependent passive dissolution rate of an Al-Co-Ce alloy to define the inhibitor release flux. Transport by both electro-migration and diffusion were considered. The model calculates the time necessary to accumulate Ce^{+3} and Co^{+2} inhibitors over the scratch when released from the Al-Co-Ce coating under various conditions. The effects of scratch size, initial pH, chloride concentration, and the electrochemical kinetics of the material involved were studied. Sufficient accumulation of the released inhibitor (i.e., when the Ce^{+3} concentration surpassed the critical inhibitor concentration over AA2024-T3 scratches) was achieved within a few hours (e.g., ~ 4 hrs for scratches of S=1500 μm) when the initial solution pH was 6 or less. Coating attributes that optimize both electrochemical and chemical "throwing power" for protection are discussed.

Stress Corrosion Cracking of Severely Deformed Type316L Stainless Steels in High Temperature and High Pressure Aqueous Solution

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Mach attention has been paid for high strength metals and alloys with ultra fine grains that are produced by severe plastic deformation. However, the corrosion property of such materials has not been necessarily well discussed. More recently, on the other hand, stress corrosion cracking has been reported for Type316L stainless steel of not welded but of deformed parts in light water nuclear power generating plants. In the present work, stress corrosion cracking behavior of Type 316L stainless steel cold rolled up to 80 % was examined by slow strain rate test (SSRT) in high temperature and high pressure dilute aqueous solution at 288 C. Solutions employed were 10^{-5} mol/l sodium sulphate with 8 ppm dissolved oxygen and conductivity of 1-2 μS/cm and pure water with dissolved oxygen less than 1 ppb and conductivity of 0.3-1 μS/cm. The strain rate for SSRT was 5×10^{-7} s^{-1}.

Trans granular stress corrosion cracking (TGSCC) was observed for Type316L stainless steels that were deformed more than 20 % (cold rolling). The ruptured surface shows typical brittle fracture of TGSCC. The number of crack initiation increased with increasing deformation ratio for tests in both solutions that are ones with DO 8 ppm and DO 1 ppb. However, the crack development rate that is roughly evaluated by the depth of brittle fracture increased for test in DO 8 ppm but decreased for the test in 1 ppb solutions with increasing deformation. Therefore, the strain at the rapture of specimen decreased with increasing deformation ratio for DO 8 ppm, but showed a minimum at 40 % of deformation for DO 1 ppb. The variation of deformation ratio provides difference in the mechanical strength and the chemical reactivity. In the DO 8 ppm solution in which corrosion potential is more noble than that in the DO 1 ppb solution, the SCC may extends as the active path corrosion mechanism. The larger active dissolution rate for the more severely deformed steel results in the larger crack propagation rate. In DO 1 ppb solution, on the other hand, although the number of crack is larger than that in DO 8 ppm because of unstable passivity at less noble potential, the crack extension is not accelerated electrochemically but suppressed by the larger mechanical strength of more deformed steel.

Symposium 9 - Keynote

Corrosion: from Nanostructure to Structural Failure

Application of Surface Analytical Methods to the Development of Environmentally Friendly Coatings

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A variety of modern, state-of the-art surface analytical techniques such as variable-angle X-ray photoelectron spectroscopy (VAXPS), secondary ion mass spectroscopy (SIMS), Fourier-transform infrared spectroscopy and mapping (FT-IR), Raman spectroscopy, scanning electron microscopy (SEM), laser scanning confocal microscopy; synchrotron based techniques such as X-ray absorption near edge spectroscopy (XANES), synchrotron infrared micro spectroscopy (SIRMS), synchrotron radiation based grazing angle infrared spectroscopy (SR-GAIRS) have been used in conjunction with traditional electrochemical techniques such as open-circuit potential measurements (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) to study systems that range from simple air formed oxide films, oxide films containing various adsorbed species to complex conversion coatings formed on several substrates that include pure metals such as aluminum to complex alloys such as AA2024-T3 and depleted uranium-0.75wt% titanium.

Initial work focused on understanding the effect of surface pretreatment and alloy cleaning procedures on the characteristics of subsequently formed CCC. Mechanism of protection offered by chromate conversion coatings (CCC) to aluminum-copper systems was then studied (1-4). The knowledge gained from these studies was utilized to develop an environmentally-friendly coating for corrosion protection of depleted uranium-0.75wt% Titanium alloy (5-7). The studies starting from alloy cleaning methods to the formation of complex chromate conversion coatings and its application in the development of a new environmentally benign molybdate-based protective coating will be reviewed. The corrosion properties and aging-characteristics of the molybdate coating will also be discussed.

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The Role of Near-surface Microstructure on Corrosion Behaviour of Wrought Aluminium Alloys

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The influence of thermo-mechanical processing conditions on the generation of ultra-fine grain sized near surface microstructures has been investigated for a number of aluminium alloys of the Al-Mn, Al-Mg and Al-Mg-Si alloy families. High shear deformation processes, such as hot rolling, grinding or machining, invariably result in the formation of near-surface layers with dramatically refined microstructures compared to the underlying bulk material. These surface layers typically have grain sizes in the order of 50 to 200 nm and, depending on processing conditions, may also contain significant amounts of second phase inclusions in the form of oxides and carbon containing compounds. The presence and distribution of second phase inclusions have been shown to have a strong effect on the thermal stability of the fine grain structure, but to be of relatively minor importance for controlling corrosion or electrochemical properties. However, during subsequent heat-treatments the precipitation of intermetallic particles is enhanced in the surface layers and this has a dominant effect in controlling corrosion behaviour.

Both electrochemical characterisation and accelerated corrosion testing have been employed to understand the mechanistic relationship between near-surface microstructure and the in-service corrosion performance. Different means of controlling and exploiting the corrosion performance and surface reactivity in terms of choice of alloy, thermo-mechanical processing conditions and optimised cleaning and pre-treatment processes are discussed.

Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Corrosion protection behaviour of new hybrid sol-gel thin films

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The main objectives of this work have been: (i) to design new electrochemically active sol-gel thin films doped with Ce^{3+} salts (environmentally friendly anticorrosive pigments as an alternative to the use of chromates); (ii) to produce doped sol-gel thin films as first chemically active layer for pre-treatments of painted surfaces of mild steel and zinc, and (iii) to study the corrosion protection behaviour of the resulting paint systems.

Sol-gel thin films based on siloxane bonded units were prepared starting from an organic-inorganic hybrid system. The precursors were an alkylalkoxide (γ-methacry loxypropyltrimethoxysilane, MAPTMS) and a silicon alkoxide (tetramethoxysilane, TMOS). Cerium nitrate hexahydrate in three different concentrations was added. Diluted hydrochloric acid and methanol were also added for the sols preparation. These sol-gel thin films were deposited on metal surfaces (pure zinc and mild steel) by applying dip-coating and spin-coating techniques. A model poly vinyl butyral (PVB) was applied on a series of these sol-gel films to simulate the performance of technologically organic coatings. For this matter poly(vinyl butyral- co-vinyl alcohol-co-vinyl acetate) solutions (17% w/w) were prepared in ethanol. Likewise, the remaining sols were kept to gelify at 600C and powdered to obtain suitable samples for analysing them by other characterisation techniques (Si-29 and C-13 NMR, FTIR and DTA).

Electrochemical impedance spectroscopy and cathodic delamination tests were carried out. These techniques allowed to study the role of cerium ions incorporated into the hybrid sol-gel network. The effect of cerium concentration on the impedance spectra was analysed, as well as the system behaviour against the corrosive medium (aqueous NaCl 0.6 M), as a function of exposition time. In parallel studies, cathodic delamination tests were applied on the PVB/sol-gel thin film/metal system. Just before the experiment was initiated, the centre of the sample was damaged with an intentionally scribed circular defect. The metal/paint system was immersed in 0.6 M NaCl aqueous solutions and submitted to a constant cathodic polarization (-0.8 or -1.2V vs. Ag/AgCI) at different immersion time. From the electrochemical point of view, the sol-gel thin film behaved as a passivating layer of the metallic surface. The anticorrosive performance of the hybrid sol-gel thin film is due to an inhibitor effect and a self-repairing mechanism awarded by the Ce3+ ions entrapped in the sol-gel network which is probably associated to the precipitation of insoluble cerium hydroxide at the cathodic sites below the coating.

Acknowledges:

Kinetic Study of Model CO_2 Corrosion Inhibitors

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Internal corrosion of pipelines caused by presence of water and acids like CO_2, acetic acid and H_2S in the fluid from oil and gas wells is a common problem in petroleum production. The use of carbon steel with corrosion inhibitors often constitutes an economically favourable alternative compared to the corrosion resistant materials. Commercial inhibitor products usually consist of mixtures of compounds. Quaternary ammonium salts and imidazoline salts are two major groups of inhibitor components used in such products. The corrosion inhibition performance and the kinetics of inhibition of two model corrosion inhibitors, cetyl trimethyl ammonium bromide (CTAB), and oleic imidazoline salt were investigated on high purity iron at 25ºC, CO_2 partial pressure of 1 bar, pH 4, in 3% NaCl brine. The inhibitor performance was studied at various concentrations and it was discussed in the relation to their critical micelle concentrations (CMC). CMC is defined as the concentration at which a surfactant forms micelles in the bulk solution. Further increase in the surfactant concentration above the CMC does not increase the concentration of the monomer but it increases the number of the micelles. The focus of the presented work was on the kinetics of the inhibition; especially the processes during the initial stage of inhibition occur at a rapid rate. Thus a high frequency impedance measurement technique was developed to determine the rapid changes in polarization resistance and electrode capacitance in approximately 20 seconds interval during the initial stage of inhibition. Furthermore linear polarization resistance measurements (LPR) were used to monitor the corrosion rate during the periods of slow changes. Potentiodynamic polarization curves were measured at the end of the experiment to elucidate the effect of processes involved in CO_2 inhibition on electrode part reactions. The surface of iron specimens at various time of inhibition was analyzed by x-ray photoelectron spectroscopy (XPS).

The inhibition followed the same general trends for both studied compounds. Minimum effective concentration was close to the CMC. The corrosion rate was nearly constant for concentrations above the CMC. The inhibited corrosion rate of the studied compounds was independent on flow. The CO_2 corrosion inhibition was found to be a combination of two processes. First a rapid process (minutes) connected to adsorption of the surfactant. Secondly there is a slower process (hours) leading to a reduction in corrosion rate. The first process was characterized by an increase in the corrosion potential immediately after the inhibitor was added; the corrosion current density remained nearly constant. The inhibitor adsorption was confirmed by XPS; there was an increase in C and N signals for the specimens taken out immediately after inhibitor addition. There was a new N peak detected by XPS for the specimen after long time of inhibition, and there were also changes in the iron peak. This can be interpreted as a bond formation between Fe and N atom of the inhibitor.

Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Corrosion studies of nanostructured composite coatings based on zinc and zinc-cobalt alloys

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Zinc and zinc-based electrogalvanized coatings have attracted remarkable interest and development because of the increasing demand for coatings with better protective ability. The traditional method to improve the corrosion resistance of these layers is their treatment in chromate or phosphate solutions.

A new approach for an increase of corrosion resistance is the formation of nanostructured zinc and zinc alloy coatings containing incorporated polymeric nanoparticles. Their presence in the metal matrix spread the corrosion processes on a greater surface and this holds up the destruction in the depth of the coating. Such layers are relatively new and therefore are object of various investigations.

In this study different types of polymeric nanoparticles obtained from poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide), poly(2-hydroxy-ethyl methacrylate)-b-poly(propylene oxide)-b-poly(2-hydroxy-ethyl methacrylate) or poly(ethylene oxide)-b-poly(2-hydroxyethyl methacrylate) block copolymers are used to prepare the nanostuctured composite coatings of Zn and Zn-Co.

The corrosion resistance of these objects is evaluated using potentiodynamic polarization technique, polarization resistance measurements, scanning and transmission electron microscopy as well as X-ray diffraction analysis. As a model corrosion medium 5 % NaCl solution is used.

It is established that the nanocomposite layers have a higher corrosion resistance compared to the resistance of the matrix coatings, the effect being stronger for pure Zn coating. The incorporation of polymeric nanoparticles in the electrodeposits affects their anodic behaviour and results in increasing of the susceptibility of the coatings to passivation.

In Situ Synchrotron Microtomography Studies of Localised Corrosion of an Mg-Y Alloy

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Synchrotron X-ray microtomography is a method for imaging microstructures in three dimensions with resolution on the micron scale. It can do so non-destructively for samples immersed in water, making it an ideal method for monitoring the evolution of corrosion sites. A further benefit of the use of monochromatic synchrotron radiation for tomographic imaging is that it is possible to obtain tomographic data just above and just below the characteristic X-ray absorption edge, and from the difference in the data sets, obtain a chemical map for the element of interest. This is a particular interest for corrosion of alloys, because chemical inhomogeneity has a major influence on susceptibility to localised corrosion.

Mg-Y-rare earth (Nd) alloys such as WE54 and WE43 are widely used, particularly in aerospace applications, owing to their combination of strength, particularly at elevated temperatures, and corrosion resistance. Yttrium is particularly effective in improving the corrosion resistance of magnesium alloys. In the present work, synchrotron microtomography is used to determine the three-dimensional distribution of Y in as cast WE43, to highlight how Y-rich regions in the matrix influence corrosion, and monitor the three-dimensional evolution of corrosion sites in situ in a corrosive environment. Figure 1(a) shows a Y distribution map for as cast WE43 and Figure 1(b) shows the evolution of a pit measured in situ over a period of 18 hours.
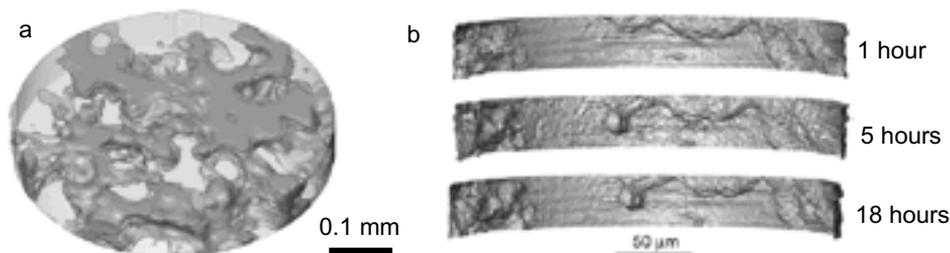
Figure 1 (a) 50 μm thick reconstructed section of as cast WE43 showing the 3D distribution of Y-rich regions determined from tomographic measurements made above and below the Y K edge. (b) Time sequence showing evolution of corrosion for heat-treated (T6) WE43 during exposure to 0.1 M NaCl (pH 10) for 18 hours (in situ measurement).

Mic monitoring in environments containing manganese oxidising bacteria

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Stainless steels show a typical increase of corrosion potential under microbiological induced corrosion (MIC) conditions by manganese-oxidizing bacteria. This potential ennoblement makes corrosive conditions more aggressive. In the present work MIC of several stainless steels was monitored, in laboratory and in field. The experiments were performed on a core of conventional stainless steels supplemented by various steel grades with enhanced corrosion resistance. Laboratory experiments were carried out in an aqueous salt solution matching the chemical composition of the Rhine river water contaminated with manganese oxidizing bacteria. Potentiostatic polarisation was applied to simulate the conditions emerged by manganese oxidizing bacteria. MIC was monitored in a water treatment plant by means of open circuit potential, redox potential and electrochemical impedance measurements.

Electrochemical investigations, performed to simulate the electrochemical conditions emerged by the presence manganese oxidizing bacteria, showed that at potential levels known from MIC-conditions in the synthetic Rhine water and in absence of microbiological activity localised corrosion occurs only under crevice areas.

In waters contaminated with manganese bacteria, an ennoblement of the open-circuit potential was always reached. The potential increases occurred, independent of the materials composition. The surface state plays an important role concerning the onset of the ennoblement.

MIC field experiments carried out in the water treatment plant showed that after 4 weeks of immersion in the water, the highest impedance modulus was showed for the EN 1.4565 and EN 1.4539 stainless steels. The behaviour is in accordance with the higher chromium, molybdenum and nitrogen content of these stainless steels. The behaviour of these steels was followed by the behaviour EN 1.4462 and EN 1.4401 stainless steels. Lower impedance values were obtained for the modified EN 1.4301 and EN 1.4301 steel.

The corrosion process in the water plant was the result of the synergistic action of manganese oxidising bacteria and sulphate reducing bacteria (SRB). Manganese oxidising bacteria produce the biomineralization of MnO_2 through the hydrolysis of Mn^{2+} present in the water. The produced MnO_2 acts as a new oxidising product that can be reduced at the cathodic areas. Anaerobic SRB develop in the inner part of the aerobic film. Sulphide products were formed in the corrosion process by SRB. Sulphide ions produced the acceleration of the anodic dissolution process and decrease the pitting potential of passive alloys.

Mechanism of pure magnesium corrosion in sodium sulphate solutions

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The corrosion behaviour of pure magnesium in aerated sodium sulphate solutions was first investigated using steady-state voltammetry and electrochemical impedance spectroscopy (EIS) with a rotating disc electrode. The analysis of impedance data obtained at the corrosion potential was consistent with the hypothesis that Mg corrosion is controlled by the presence of a very thin MgO oxide film, and that the dissolution occurs only at free-film spots. This hypothesis was substantiated both by the merging of the EIS diagrams obtained for different immersion times and different Na_2SO_4 concentrations into a single one and by scanning electrochemical microscopy (SECM) using the electrolyte resistance as electrochemical sensor. On the basis of the electrochemical results, a model was proposed to describe magnesium dissolution.

(i) It was assumed that Mg^+ is the species that reacts chemically with water to form an oxide/hydroxide layer. These reactions explain the negative difference effect (NDE) and the formation of a partially protective hydroxide layer.

(ii) Mg dissolution occurs only at bare parts of the oxide film whose area depends on potential and pH. The invariance of the EIS diagrams, once normalized by the maximum value of the real part, lead to conclude that the dissolution mechanism is unique in the whole anodic range investigated: it can be described as the exchange of two electrons in two successive electrochemical steps where the adsorption of the intermediate Mg^+ is followed by two parallel paths, one chemical gives rise to the NDE effect and the electrochemical other one to Mg^{++}

Simulation of the EIS diagrams was in good agreement with the experimental results.

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Corrosion: from Nanostructure to Structural Failure

Characterization of Initial Films and Passivating Layers Grown on Magnesium Metal in Alkaline Solution

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Among light metals magnesium presents very interesting engineering properties owing to: its light weight, high specific stiffness, high thermal conductivity, biocompatibility and easy recycling. These potential advantages are counteracted by the poor corrosion and wear resistance of Mg and its alloys due to the high chemical reactivity of MgO surface layer in presence of humidity or water with formation of a poorly protective hydroxide layer having also detrimental effects on the coating procedure. From a fundamental knowledge point of view the debate is still open on the mechanisms of growth and the nature of passivating layers formed on magnesium surfaces during anodizing in aqueous solution. In a complex industrial electrochemical bath containing, among other elements, fluoride ions electric field strengths across the barrier film on the order of $7 \cdot 10^7 \div 1 \cdot 10^8$ V cm^{-1} have been reported during the growth under constant current density of 20 mA cm^{-2}. The presence of such high electric field during the anodizing process has been attributed to the formation of an inner layer of crystalline fluorite covered by an amorphous and porous oxy-hydroxide layer.

As for the kinetics of growth of the passive film in aqueous solution not containing fluoride ions there are very few indications if a barrier layer is formed or not and if the growth of passivating layers occurs in agreement with the Werwey or Cabrera-Mott high field theory.

According to the previously mentioned aspects we have undertaken a detailed investigation on both these aspects. We have focussed our initial study on the characterisation by different techniques (XPS, PCS) of initial films formed on Mg in different conditions of surface preparation. Afterwards we have investigated the anodizing behaviour of Mg in aqueous solutions at high pH values (≥ 13) where a stable passive film is expected to grow. The results of this preliminary study on the composition of initial films based on the analysis of XPS and PCS data together with the experimental findings on the kinetics of the early stage of film growth and breakdown process will be reported. The possible nature of passivating films formed in 1M NaOH solution will be inferred on the basis of kinetic data and fitting of differential admittance plots whilst the information on the solid state properties and nature of corrosion layers gathered by PCS and XPS data analysis will be used to suggest possible mechanisms of breakdown of passive film grown on Mg in aqueous alkaline solutions.

Combination of Surface Gradient Chemistry and Kelvin Probe Studies of Thin Amorphous Conversion Films on Metals

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Conversion layers play a dominant role in providing excellent adhesion and corrosion resistance of polymer/metal interfaces. In the past, detailed electrochemical studies of the classical phophating process on zinc and steel substrates were done by Schultze and co-workers [1]. The authors examined the growth of Zn-phosphate crystals and localised Ni-cementation at the phosphate/metal interface. Today, the Zn-phosphating process including an activation step and the formation of crystalline tri-cation phosphate layers with few micrometer thickness is a well established process in the steel and the automotive industry. However, currently the development of new advanced conversion films is focused on the development of thin amorphous hybrid conversion films with a thickness of only a few tens of nanometers.

In this contribution fundamental investigations on interface reactions of advanced phosphate-containing conversion solutions on ultra-smooth ZnAl-alloy coatings on steel are presented [2-3]. Surface gradient layers on these substrates were realised in order to screen the composition, electrochemical properties and corrosion resistance of the conversion coating as a function of layer thickness and processing time. For this purpose a dip-coating procedure was established yielding well-defined thin amorphous conversion gradient layers from the phosphate-containing conversion bath chemistry. These gradient samples were locally analysed by means of the Scanning Kelvin Probe and localised impedance measurements using an electrochemical capillary cell. Microscopic Infrared Reflection Absorption Spectroscopy (FT-IRRAS) measurements, small-spot XPS and Tof-SIMS were used as complementary surface analytical techniques. All techniques enable a spatial resolution of better than 200 micrometers. The nucleation of thin films was analysed by means of a high resolution AFM. Thereby, a complete variation of thin film properties such as thickness, barrier properties, corrosion resistance and chemical composition could be measured as function of the time of film growth on a sample with some millimetres in length.

It could be shown that this surface gradient film analysis significantly increased the number of parameters that can be analysed per time [4].

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Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

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Corrosion: from Nanostructure to Structural Failure

Corrosion resistance of Cr-free anodised Al 2024-T3 after long term atmospheric exposures

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A great number of studies for aircraft aluminium alloys have lead to some Cr-free anodising baths that might be a reasonable alternative to the traditional chromic baths.

This study aims to evaluate the resistance against atmospheric corrosion of Al2024-T3 alloys etched and anodised with a Cr-free bath.

Samples etched and anodised in a Cr-free bath, a previously developed sulphuric-boric bath, as well as samples treated by the conventional processes, chromic bath, have been submitted to field exposures (long-term exposures), during 30 months in the urban atmosphere of the city of Lisboa (Campo Grande).

The present paper deals with electrochemical data (potentiodynamic polarisation curves and open circuit potential data) of anodised Al2024-T3 material with 3, 6, 12, 24 and 30 months of atmospheric exposure. The electrochemical data is complemented by visual and optical microscopy. Pitting density was evaluated and the crystalline corrosion products formed on the anodised samples during the atmospheric exposures have been identified by X–rays powder diffraction analysis.

Simultaneously to the exposures the level of pollutants in the atmosphere, namely chlorides and SO_2, was monitored.

It was concluded that even after 30 months of exposure both anodised processes lead to surfaces with similar resistance against atmospheric corrosion in spite of the differences found in the morphology of the anodising films.

All the data leads to the conclusion that the sulphuric boric anodising process seems to be a good alternative to the traditional anodising processes.

Applications of a Height-Regulated Scanning Kelvin Probe Blister Test in Corrosion and Adhesion Science

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A new height regulated Scanning Kelvin Probe (HR-SKP) was combined with a Blister Test (BT) to study de-adhesion processes at modified adhesive/metal interfaces under corrosive and mechanical load. The set-up was additionally equipped with a climated chamber and a three electrode set-up, allowing control of the surrounding gas phase and potentiostatic control of the defect.

As an electrochemical technique the SKP measures the electrode potential at buried adhesive/oxide/metal interfaces [1-3]. Thus, it detects changes in the interfacial oxide structure and variations of the interfacial ionic conductivity with high spatial resolution of about 50 micrometer. The height regulation provides a constant distance between the sensing scanning probe and the adhesive surface, even above the spherical blister, while the interfacial electrode potential is measured simultaneous. The liquid for the Blister Test comprises of a corrosive metal halide electrolyte, whose pressure can be varied between zero and 4 bar.

The electrochemical aspects of adhesion loss of adhesives from oxide covered iron and zinc, as model systems for steel and zinc coated steel, were investigated. An epoxy resin free of pigments, fillers and additives was chosen as model adhesive. Selected results illustrate the measurement of pure wet de-adhesion, interfacial corrosive reactions and the acceleration of de-adhesion processes with increasing hydrostatic load of the blister.

The metallic substrates were modified with conversion layers, adhesion promoting organosilanes and thin plasma polymer films prior to the application of the adhesive to reveal the influence of the interface chemistry on the stability of the adhesive/metal joint.

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Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Surface modification of passive iron by alkyl-phosphonic acid layers

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Phosphonate layer formation on passive iron surface has been investigated by electrochemical, conversion electron Mössbauer spectroscopy (CEMS) and atomic force microscopy (AFM) techniques. Electrochemical methods revealed that metallic iron surface is disadvantagous for protective layer formation, while prepassivation of iron surface results in estabilization of the self-assembled layer. The rate of anodic dissolution is continually decreasing due to the time-dependent formation of protective phosphonate layer. The kinetics of phosphonate layer formation on passive iron is determined by the potential applied for preceding passive film formation. CEMS investigations were carried out to evaluate the differences in passive layer composition as a result of phosphonate treatment. The size and shape of iron oxide grains depends slightly on he potential of passivation. Changes in morphology due to the phosphonate layer formation have been recorded by AFM.

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Corrosion: from Nanostructure to Structural Failure

Lifetime extension methods for components in water-cooled nuclear reactor

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There have been well documented instances of environmentally assisted corrosion phenomena in various energy-related industries involving various subcomponents of boilers, steam turbines, piping, pressure vessels, pressurizers, steam generators, deaerators, etc. The common element in these corrosion incidents is exposure to high temperature water of structural materials such as austenitic stainless steels, nickel base alloys, turbine steels, low alloy and carbon steels, and their weld metals. It is known that the water chemistry in nuclear power plants plays an important role in several phenomena that can significantly affect both the cost of operation and the long-term viability of reactors.

The purpose of this paper is to describe advanced novel approaches to address these corrosion issues in water-cooled nuclear plants. This paper provides a fundamental description of the corrosion mechanism and describes various methods for mitigating the risk of stress corrosion cracking of reactor internals and extending the lifetime of components. These approaches are based on modifying the electrochemical nature of the metal surface, such as by the electrochemical catalysis of noble metals and/or the insulating behavior of dielectric materials to protect reactor parts that tend to degrade in the normal reactor environment and eventually to extend plant life beyond 40 years.

Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Simulation of localised corrosion:
a combined probabilistic/finite element approach

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Keywords: stochastic processes, finite element methods, localised corrosion, pitting

In literature localised corrosion processes like pitting, crevice corrosion and stress corrosion cracking are treated both deterministically and stochastically. In case of (metastable) pit and crack generation a stochastic approach seems most appropriate. These localised corrosion phenomena are often described as Poisson processes (e.g. [1]). On the other hand finite element simulations, i.e. deterministic approaches, of localised corrosion exist (e.g. [2]).

In this paper a stochastic and a deterministic approach is combined. The electrochemical stochastic process of pit initiation is simulated using a (discretised) Poisson process, as an initial approach. A realisation of pitting is used for a 3D-finite element simulation: the deterministic part of the approach. In the corrosion of iron or steel, iron dissolution is assumed to be the anodic reaction, which takes place in the pits. Cathodic reactions are the reduction of O_2 and the reduction of H^+. The reduction of O_2 is assumed to be negligible in the pits. For the current densities of the three electrochemical reactions Tafel equations are used. At the electrolyte boundaries the current density in the normal direction is defined to be zero. As a supporting electrolyte 0.1 M NaCl is selected. The Nernst-Planck equation describes the mass transport of species in the electrolyte domain. The electroneutrality condition was applied. The water equilibrium is accounted for using kinetic parameters of the forward and backward reaction of the protolysis reaction: $H_2O \rightleftharpoons H^+ + OH^-$.

Distributions of current density, concentrations and the potential in solution are calculated. It will be discussed whether and when the assumption of independence of (pitting) events is justified. Both stochastic theory and finite element methods are useful instruments in the study and understanding of localised corrosion processes. Finally, possibilities for other combined stochastic and finite element treatments of localised corrosion, including stress corrosion cracking, will be discussed.

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Crevice Corrosion Behavior of Nickel-based Alloys Alloy 600 and Alloy 690 in Acidic Solution Containing Chloride Ions.

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Crevice corrosion is the accelerated attack occurred in the occluded cell under a crevice on the metal surface, which is one of dangerous form of localized corrosion. Crevice corrosion shares many similar characteristics with other type of localized corrosion such as pitting corrosion, in terms of the breakdown of passive film and its repassivation. Crevice corrosion behaviors of nickel-based alloys, Alloy 600 and Alloy 690 were investigated in acidic solution with the variation of chloride ion concentrations. Tests were carried out using the specially designed crevice cell with a very narrow Luginn capillary assembly to measure the potential inside the crevice. It is believed that crevice corrosion in active/passive system such as Alloy 600 and Alloy 690 is highly related with the properties of passive film and its repassivation characteristics. The properties of passive films were measured by the capacitance measurement and the reapssivation characteristics were investigated by the abrading electrode technique. The stability of repassivated film was evaluated considering the results of EIS tests carried out before and after the abrading electrode test. An attempt was made to elucidate the relationship between crevice corrosion behavior of Alloy 600 and Alloy 690, properties of passive film and its repassivation kinetics

Keywords: Alloy 600, Alloy 690, Crevice Corrosion, Passive Film, Repassivation Kinetics,

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Hydrophilic and Hydrophobic Interfaces: the Performance of Functional and Non-Functional Silane-Treated Epoxy-Coated Steel

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This work is concerned with developing model hydrophilic and hydrophobic interfaces on steel by surface treatment using, respectively, 3-glycidoxypropyl (i.e. epoxy-functional) trimethoxysilane and n-propyl (non-functional) trimethoxysilane. Subsequently, the performance of the organic-coated surface-treated steel was determined using electrochemical impedance spectroscopy (EIS), contact (aqueous wetting) angle measurements and pull-off adhesion.

Contact angle measurements confirmed that a non-functional silane produced a significantly more hydrophobic interface (contact angle 105°) than an epoxy-functional silane (contact angle 60°), which was relatively hydrophilic. Both dry and wet adhesion measurements confirmed the expected 20% increase in adhesion for the epoxy-functional treatment but a 40% decrease in adhesion for the non-functional treatment.

EIS measurements were then performed on silane-treated carbon steel substrates (i.e. without epoxy coating). After 20 minutes of immersion in 3.5% NaCl solution, the charge-transfer (polarisation) film resistance was approximately 2000 ohm cm^2 for the hydrophobic treatment compared with about 1000 ohm cm^2 for the hydrophilic treatment; furthermore the film capacitance for the hydrophobic treatment was about one-fifth that of the epoxy-functional treatment indicating a considerably more diffuse double-layer. Over time (about 60 minutes) these values reverted to that of the untreated substrate. EIS results for silane-treated, epoxy-coated steel over the first 50 hours of immersion showed that the initial coating resistance was significantly greater (and the coating capacitance significantly smaller) for the hydrophobic treatment. This confirms that the water uptake into the coating to the interface had been minimised by the hydrophobicity of the interface. However, after 50 hours the coating commenced de-bonding from the non-functional treated substrate due to the considerably lower adhesion strength.

These results imply that if the substrate-coating interface can be made to be both hydrophobic and provide a functional bond between the substrate metal oxide and the organic coating, then the long-term performance of an organic coating is likely to be improved.

XPS and Flow-Cell EQCM Study of Protein Adsorption on Passivated Chromium Surfaces

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The adsorption of proteins (BSA) was studied on passivated chromium surfaces using XPS and a switch-flow cell combined with an electrochemical quartz crystal microbalance (EQCM). The surface was initially passivated in a deaerated, protein-free solution. Subsequently, a protein-containing solution was switched in the cell and the EQCM signals were recorded as a function of time. After protein adsorption the Cr surface was analysed by X-ray Photoelectron Spectroscopy (XPS).

The kinetics of adsorption and the amount of adsorbed protein were investigated as a function of :

- protein concentration in the solution (2-20 mg/l)
- potential in the passive region
- pH

For the interpretation of XPS data obtained after the EQCM adsorption experiments, a 3-layer model was considered : an inner Cr_2O_3 oxide layer and an outer $Cr(OH)_3$ hydroxide layer covered by an adsorbed BSA layer. From the Cr 2p and N 1s core level spectra, the thicknesses of the oxide layer, of the hydroxide layer and of the adsorbed BSA layer were estimated.

The thicknesses of the adsorbed protein layer measured *in situ* by EQCM and *ex situ* by XPS are in excellent agreement.

The data show that the kinetics of adsorption of BSA depends strongly on the protein concentration in the solution whereas the maximum amount of adsorbed protein is similar, and corresponds to ~ 1 monolayer.

Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Fabrication of ultra thick porous oxide films on niobium by anodization

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Recently, fabrication of porous anodic films on various semiconductors such as titanium and indium phosphate has been received significant attention because of its exploitation as photocatalyst and chemical sensors. On the other hand, fabrication of mesoporous oxide of niobium has also special importance in the field of acid catalyst in addition to its potential utilization as a novel capacitor and devise applications. Therefore, an attempt has been done to fabricate ultra thick porous niobia having high specific surface area by anodizing of niobium, which was rarely reported. In the electrolytes containing HF, nano-porous amorphous films with the cell size of approximately 30 nm, pore size of 10 nm and maximum film thickness of 700 nm could be formed at relatively low current density as we reported previously (1). Dimension of the nano-porous film was independent of formation voltage except for the thickness of the barrier layer. To accelerate the oxide growth while preventing surface dissolution of the oxide, addition of some chemicals and cooling of the electrolytes were attempt. As a result, porous oxide films having thickness of 3-5 µm were obtained. However, these oxide films indicate layered structure caused by fluorine ion incorporation into oxide/substrate interface which result in repeated abruption and re-growth of the oxide film as shown in Fig. 1. When a high formation voltage was applied, the thick porous layer up to 35 µm was obtained after 2 hour anodizing. This thickness limitation was caused by substrate thickness of 70 µm. The oxide film was identified as crystalline hexagonal Nb_2O_3 by XRD analysis. The cross section of the film shows granular and cellular oxide, which was grown under the layer-structured amorphous oxide (Fig. 2). Thus, we have succeeded for the first time to fabricate ultra thick porous niobium oxide film by anodization. Details of film growth mechanism and oxide properties will be discussed.

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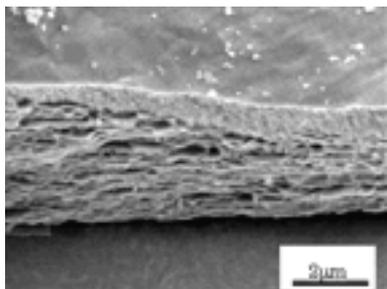

Fig.1 Cross section of anodic film formed on Nb in a fluoride solution at 20V for 2h.
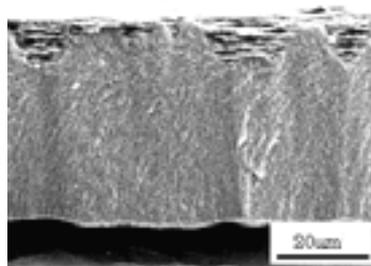
Fig.2 Cross section of anodic film formed on Nb in a fluoride solution at 60V for 2h.

Models of Close-Interval Potential Surveys for Buried Pipelines

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Buried oil and gas transmission pipelines are protected from corrosion by a combination of cathodic protection and coatings that reduce the current requirements for cathodic protection. Regular inspections, such as described in the NACE International Recommended Practice for External Corrosion Direct Assessment (ECDA),[1] are required to ensure the integrity of the pipelines. The methodology behind ECDA relies heavily on close interval surveys of on-potentials (where the CP system is connected) and off-potentials (where the CP system is disconnected).[2,3]

The degree to which a coating holiday is detectable through a close-interval survey is not precisely known. The model CP_3D, developed to model cathodic protection to pipeline networks,[4-6] was extended to allow calculation of on- and off-potentials at arbitrary surfaces. When applied to the soil surface, this model can be used to ascertain the degree to which an arbitrary coating flaw is detectable by such measurements and to thereby guide interpretation of ECDA indications.

This paper will present the methods used to calculate potentials at arbitrary surfaces with the CP system connected and disconnected. These simulations have been used to simulate ECDA measurements and to identify general interpretation strategies. The approach presented illustrates the integration of comprehensive numerical simulation with techniques for assessment of pipe coating condition.

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Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Electrochemical and AFM investigations of dendritic growth and corrosion processes occurring in the course of the "post-CMP cleaning" in microelectronics

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Over the last few years, copper has replaced aluminium in the fabrication process of inter-connexions in microcircuits with the help of the now well-established "dual-damascene" technique. This latter necessitates an intermediate step called chemical-mechanical process (or CMP) aimed at removing the excess metal deposits in order to get very smooth surfaces. The substrates are then subjected first to a thorough cleaning using oxalic acid solutions and finally to a rinsing. Both procedures are grouped in the so-called "post-CMP cleaning" and they are aimed at removing abrasive particles, polishing residues, and at avoiding contamination. This final step, during which acidic solutions are used, is actually highly critical. For example, unintentional dendritic growth phenomena were detected on favourable sites. They were actually found to result from the dissolution of a copper connexion via corrosion followed by the re-deposition of copper on a neighbouring connexion. Among the various sources of copper corrosion involved in the post-CMP procedure, one can cite photo-assisted corrosion, galvanic corrosion involving the tantalum metallic barrier underlying below the copper layer as well as the drawing rules used for the various masks of the integrated circuits.

In order to get a better understanding concerning the dendrite formation, we developed a comprehensive investigation using various electrochemical and imaging techniques. In this work, we relate mainly the precious contribution provided by atomic force microscopy (AFM) imaging carried out either in air or in-situ in oxalic acid containing cleaning solutions. The main results reported hereafter are focused on the morphological aspects of the dendritic growth as well as on the confirmation of a galvanic corrosion process occurring between copper and tantalum.

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Corrosion: from Nanostructure to Structural Failure

Electrodeposition of Alloys with Superior Corrosion Properties

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Tremendous potential exists for the growth of metal finishing industry through the development of processes that are either environmentally friendly or are applicable at the nano scale. The chemical composition and the structure of electrodeposited metals, alloys and composites control their functional properties. This paper will discuss some of the theoretical and experimental studies done to achieve such coatings. Nanostructured alloys and innovative composite materials were developed through adaptation of existing bath chemistries. Process development was based on techniques developed in our laboratories such as: under potential deposition (UPD) of monoatomic metal layers, autocatalytic reduction and potentiostatic pulse (PP) plating of layers of amorphous and crystalline nanostructured metals and alloys. The development processes have been optimized based on superior corrosion properties of the coatings. Further refinement of the coating process was accomplished through the development of first principles based theoretical models.

Electrodeposited nanostructured alloys and composites find applications in metals and surface finishing industry. This paper will feature development of electrochemical deposition processes to synthesize secondary and ternary alloys such as Ni-Zn-X (X=P or SiO_2). These materials were targeted as a replacement for Cd deposition and can inhibit corrosion and completely eliminate the hydrogen induced cracking.

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Corrosion: from Nanostructure to Structural Failure

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Corrosion: from Nanostructure to Structural Failure

Structure and corrosiob resistance of pulse plated nanocrystalline zinc and zinc alloy coatings

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The importance of texture and lattice defects on corrosion behavior of Zn and Zn alloy coatings was revealed in our previous studies [1,2], however, the role of surface morphology remains unclear. It is known that almost all mechanical properties of metals can be effectively improved by refining the grain size. However, the small grain size and the high volume of fraction of grain boundaries may result in corrosion performance different from that of polycrystalline materials. Non-stationary (pulse) electrodeposition can be used as a mean to produce unique structure, i.e. coatings with a structure and properties not obtained by direct current (dc) plating.

The present study was aimed to determine the influence of pulse electrodeposition parameters on the surface morphology, lattice imperfection and corrosion properties of Zn and Zn-Ni (12%) coatings, deposited in alkaline cyanide-free solution. AFM was applied for surface morphology examination, XRD measurements were carried out for phase composition, texture and lattice defects analysis, while electrochemical techniques were used for corrosion performance research.

Pulse electrodeposition yielded a fine-grained and more homogeneous surface appearance of Zn and Zn alloy deposits, with relatively indefinite grain boundaries and smaller grain size. A special attention was given for a precise determination of the latter parameter, which was obtained from AFM studies and XRD line broadening measurements. Line broadening always comprises size and strain broadening components. An attempt has been taken to evaluate separately these two factors, what resulted in attainment of very similar grain size values, obtained by two different (AFM and XRD) methods. Non-stationary electrodeposition yielded the reduction of grain size both for Zn-Ni alloy from ~ 90 nm for dc. plated, to 30-40 nm for pulse plated samples, and for Zn coatings: from ~ 65 nm to ~ 35 nm, respectively.

The corrosion currents of electrodeposited coatings were determined in aerated $NaCl+NaHCO_3$ solution and it appeared that pulse plated Zn and Zn alloy samples possessed from twice to threefold lower corrosion currents with respect to dc plated ones. Zn and Zn-Ni coatings, which possessed lower grain size, higher uniformity of grain distribution and higher number of lattice imperfections exhibited higher corrosion resistance.

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Susceptibility to Stress Corrosion Cracking of Stainless Steels: The Role of Molybdenum

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The role of alloying elements on the susceptibility to Stress Corrosion Cracking (SCC) of stainless steels is well documented in the literature, particularly the effect of molybdenum. However, the role of this element on film properties is not well understood.

The approach used in this work includes the study of high purity austenitic Fe-Cr-Ni model alloys, with and without Mo additions, as well as the effect of deformation. A Mott-Schottky study was conducted complimented with polarization measurements in SCC environments containing chloride ions.

Results show that Mo promotes stress corrosion cracking in the otherwise non-susceptible alloy confirming previous data.

SCC is associated to the presence of a semiconducting film, which is predominantly p-type in character (transport controlled by cationic vacancies).

The doping density estimated for samples with equivalent levels of plastic deformation was found to be larger for the Mo containing alloy.

Mechanisms are discussed focussing the metal/film interface and the possible effect of dislocations on film properties, for the SCC case.

The role of Mo regarding other types of localised corrosion such as pitting will be also discussed, on the basis of phenomena in the film/solution interface.

Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Mechanism of corrosion protection by conducting polymers

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Organic coatings are an efficient way to protect metal based products from corrosion. However, for reliable long-term performance pigments that release corrosion inhibiting substances need to be added to the organic coating. The most efficient pigments are those containing chromates (usually in form of strontium chromate), but because of their toxic and carcinogenic nature their use has to be progressively decreased. But nearly all powerful inhibitors may have detrimental effects on environment, when released in substantial amounts. Since in basically all pigments the release of inhibitors is based on leaching, coatings need to be highly pigmented to ensure a sufficient presence of inhibitors over years, and, of course, inhibitors are constantly released into the environment, even when they are not needed. Hence, novel approaches are desperately sought for.

The potential of conducting polymer coatings for corrosion protection is a topic of current controversy. A number of possible protection mechanisms are proposed. The reason for this is that the efficacy of conducting polymers very much depends on how they are used and on the conditions of the corrosion experiment, i.e. depending on the exact conditions a conducting polymer may have excellent protection capability or may lead to a disastrously enhanced corrosive attack.

This paper will focus on conducting polymer coatings with self-healing capability and on how to counteract the negative properties of the conducting polymer, so as to truly benefit from the positive properties.

Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Effect of composition on the photoelectrochemical behaviour of anodic oxides grown on aluminium alloys

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The study of anodic films grown on Al alloys is of interest for different reasons. From a practical point of view, the presence of small amounts of transition metal solute increases dramatically the pitting potential of the metallic substrate, hence improving the corrosion resistance of the alloy. On the other hand, the possibility of tailor making anodic films with higher dielectric constant with respect to alumina films makes such alloys relevant to the field of electrolytic capacitors. Thus, there is need for research aimed at increased understanding of the physico-chemical properties of amorphous oxide films on Al alloys. Of relevance, it has been proposed recently that the band gaps of crystalline binary oxides correlate with the electronegativities of their constituents, thus suggesting the possibility to predict the band gaps of ternary oxides (1), using an average electronegativity parameter for the cationic group and hence, tailoring of oxide properties. Moreover, the proposed correlation has been extended to amorphous oxides, taking into account the effect of the amorphous structure on the band gap of the corresponding crystalline oxide (1).

In this work, the results of an extensive study on growth and characterisation of anodic films on Al - valve metals alloys, containing niobium, titanium, tantalum and tungsten additions, are presented.

Both in-situ Photocurrent Spectroscopy (PCS) and ex-situ Transmission Electron Microscopy (TEM) and Rutherford Backscattering Spectroscopy (RBS) are applied to the films grown in acidic and quasi-neutral solutions in order to probe the structure, composition and electronic properties.

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Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Assessment of water transport in organic coatings using a.c. impedance in ionic liquids

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Water absorption is a major cause for loss of barrier properties and constitutes the first step to delamination of organic coatings. The process can be monitored by measuring the variations in the coating capacitance, by means of a.c. impedance. These measurements, however, are typically made in an aqueous solution with some salt to make it ionically conductive, which excludes the measurements of the drying processes. The advent of room temperature ionic liquids (IL's) opens new possibilities in this area, particularly in what respects the drying process. The work reported consists of monitoring an epoxy clear coat during the process of water uptake in NaCl 0.05M and of the subsequent drying in an ionic liquid. Estimation of the diffusivity D was made assuming Fickian diffusion, from the slope of a plot of the capacitance, C_t, versus the square root of time: $C_t = C_0 + (C_\infty - C_0)\dfrac{1}{L}\sqrt{\dfrac{4Dt}{\pi}}$, in which C_∞ and C_0 represent the capacitance of the saturated and of the dry coating, respectively, and L the average coating thickness. The study was carried out using a non-pigmented epoxy coating applied on aluminium panels, using as electrolytes either 0.05M NaCl, or an IL. It was observed that the coating capacitance variation was approximately reversible (Fig.1), with the capacitance increasing in the salt solution and decreasing in the IL. With a hydrophilic IL, 1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate, the apparent diffusivity was determined as $7\text{-}8\times10^{-14}$ m^{2}s^{-1} for the absorption step and $\sim19\times10^{-14}$ m^{2}s^{-1} for the drying step, revealing that the diffusion of water in the drying process is an easier process than the absorption step. Repetition of the soaking/drying cycle revealed a nearly total reversibility, although the capacitance was slightly higher in later cycles. This could be due either to irreversible opening of the coating polymer structure caused by water ingress or to trapping of ions from the solution inside the coating matrix. The test was also repeated in a hydrophobic IL, 1-butyl-1 methyl pyrrolidinium tris(pentafluoroethyl) trifluorophosphate. The features were essentially the same, although the diffusivity was lower in the drying step. This new technique opens possibilities to the study of organic coatings and of the processes that affect degradation of coated structures by corrosion.

Copper corrosion inhibiton by amphiphiles in nanolayers

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Special hydroxamic acid amphiphiles (C10-C18) were used in self assembled molecular layers (SAM) as well as in Langmuir-Blodgett (LB) films on copper surface. The importance of the time in the SAM formation as well as of the carbon chain length in the amphiphilic molecules was in the focus of the experiments. The layer formation was characterized by sum frequency vibrational spectroscopy (Fig.1a).The efficiency of nanolayers was measured by different electrochemical techniques (EIS, polarization) and by microcalorimetry. The morphology (Fig.1b.) and the consequence of corrosion processes were visualized by atomic force microscopy. The comparative analysis of data proved that the increase in time of SAM formation up to 1 hour (under the given experimental conditions) and in the layer number in LB films enhanced the stability as well as the efficacy of nanolayers. The length of the carbon chain in the SAM layer has not significant impact on the efficiency in corrosive environment.
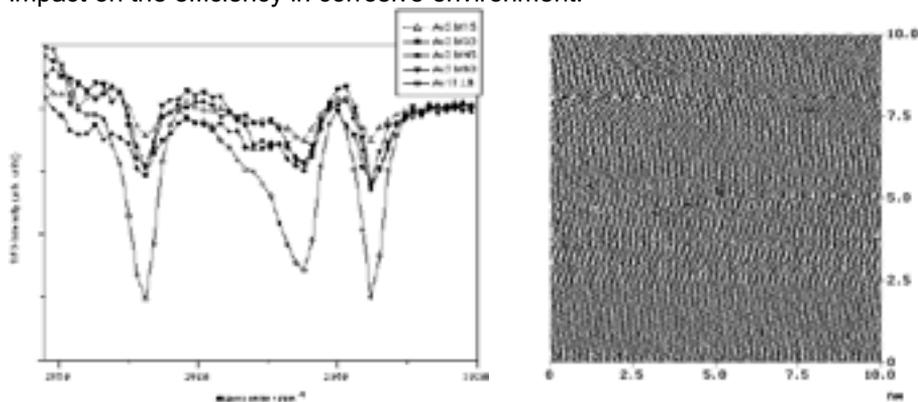
a   b
C18 Hydroxamic acid nanolayer on copper
a: SFG spectra of LB monolayer and of time-dependent SAM formation
b: 2D structure of C18 hydroxamic acid monolayer on copper visualized by AFM

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Corrosion: from Nanostructure to Structural Failure

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Corrosion: from Nanostructure to Structural Failure

Characterization of an oxide film by eis and leis

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A metal or metallic alloy coated by a passive film can be characterized in the high frequency range by an impedance corresponding not to a pure capacitance but to a CPE. The origin of this CPE behaviour is not unique. [1] It was shown that the high frequency dispersion originates from non-uniform current and potential distributions on the disk surface that further lead to a distributed and frequency-dependent ohmic resistance [2,3], whereas, for lower frequencies, global CPE behaviour is always observed.

This CPE behaviour in the medium frequency range can be explained by a gradient of the oxide layer conductivity perpendicularly to the surface. Thus, according to Young's theory [4], the conductivity $\kappa(x)$ within the oxide film decreases exponentially due to non-stoichiometry of the oxide layer: $\kappa(x)=\kappa(0)exp(-x/\delta)$, where δ corresponds to a characteristic length. The Young impedance for such a gradient can be expressed as:

$$Z_Y = \frac{p}{j\omega C_Y}\ln\left[\frac{1+j\omega\tau\exp(p^{-1})}{1+j\omega\tau}\right]$$

where $p = \delta/d$ is the relative penetration depth, $C_Y = \varepsilon_0\varepsilon S/d$ the oxide film capacity, and $\tau = RC_Y = \varepsilon_0\varepsilon/\kappa(0)$ the time constant. [5,6]

LEIS and EIS measurements were performed on a Fe-17 Cr surface immersed in deaerated, pH 4, diluted Na_2SO_4+NaCl solution. The Young impedance was used to regress the experimental LEIS and EIS data. The regression procedure yields for C_Y a value of a few µF corresponding to an oxide film thickness of about 1 nm, which is consistent with the one estimated by XPS.

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Predicting the evolution of stress corrosion cracks from corrosion pits

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The evolution of stress corrosion cracks from pits is important in many industrial applications but continues to be a challenge in both measurement and prediction. Life prediction in these circumstances has to account for pit growth kinetics, the conditions for the transition from pits to cracks, and the growth rate of cracks in the short and long crack domain. An example of importance is the performance of steam turbine discs. Although stress corrosion failures are comparatively rare, the consequences can be severe and occasionally catastrophic. Consequently, considerable effort is being focused on evaluating the effect of operational variables on pitting and crack growth and in developing an improved basis for structural integrity assessment. A mathematical model based on deterministic equations with statistically variable input parameters has been developed for simulating the evolution of the pit depth distribution at different exposure times and the percentage of pits that transform to stress corrosion cracks. It has been shown that the simulation not only reflects the trends in the laboratory experimental measurement but also, uniquely, reproduces the statistical variability or "noise" associated with the measurements. In an extension of this model to consider the early stages of crack growth the distribution of crack sizes in the short crack domain was reasonably simulated.

These varied results will be presented with a discussion of the challenges in model validation and extension of the predictions to service application.

Symposium 9 - Oral

Corrosion: from Nanostructure to Structural Failure

Effect of nickel-aluminium bronze microstructure and crevice solution chemistry on the initiation of crevice corrosion

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Nickel-aluminium bronze (NAB) unlike the other copper alloys is known to be susceptible to crevice corrosion when not cathodically protected. In natural seawater, crevice corrosion rates as high as 0.7 to 1.0 mm y^{-1} have been reported for NAB compared with 0.25 mm y^{-1} for AISI 304. In contrast to stainless steels, crevice corrosion for copper-based alloys, such as for nickel-aluminium is often attributed to the formation of a metal-ion concentration cell. This investigation has studied the evolution of a critical crevice solution and the overall influence of the complex NAB microstructure, principally the $\alpha+\kappa_{III}$ eutectoid, on the initiation of crevice corrosion. The chemical conditions within a Cortest crevice assembly have been studied for NAB in a bulk test solution of 3.5% (0.6M) NaCl. The crevice solution chemistry was assessed intermittently over a period of 6 months using capillary electrophoresis. Capillary electrophoresis is capable of analysing nanolitre solution volumes with widely disparate concentrations of species based on their electrophoretic mobility by applying a voltage (20 kV) across a buffer-filled capillary (50 μm inside diameter and a 93 cm effective length) and provides a means of rapidly and efficiently separating the ionic content of crevice solutions.

A mechanistic model has been established for the physical and chemical mechanism controlling the crevice corrosion. High chloride levels (~100,000 ppm) were only observed in the first month before decreasing back to bulk solution levels, however, the cupric ion concentration showed a more complex behaviour ranging from 1000 to 5000 ppm. The surface corrosion of NAB was initially confined to eutectoid regions with slight attack of the copper rich α-phase within the $\alpha+\kappa_{III}$ eutectoid. In the presence of high chloride concentrations in the crevice, copper and aluminium complexes will be formed and the hydrolysis of these complexes leads to the acidification of the crevice solution chemistry. As the crevice solution becomes increasingly acidic the initial protection of the κ-phases due to their higher aluminium contents is lost and they become anodic to the α-phase. The continuous nature of the κ_{III}-phase makes it especially vulnerable with ~80 μm depth of attack after only the first month and an accompanied copper redeposited at cathodic sites. These crevice cathodic sites can also support further dissolution at areas in contact with low concentrations of dissolved copper-ions, such as the exposed surface immediately adjacent to the crevice, resulting in the characteristic trench associated with crevice corrosion of copper-based alloys. This model has provided further insights in to the development of crevice corrosion experienced by NAB after long-term exposures (3 years) to natural seawater.

Investigation of aluminium pitting corrosion in modified acid solution as a method for controlling surface rougness

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The influence of the addition and concentration of a number of selected additives on the pitting behaviour of an aluminium surface in hydrochloric acid solution was determined by a number of complimentary methods. These measurements included polarisation studies of model samples under cathodic and anodic conditions to ascertain the effect of additive type and strength on the two distinct portions of the corrosion process, analysis of the AC potentials recorded during cycling to determine the impact of additive presence on corrosion product/smut layer formation and weight loss measurements. In addition scanning electron microscopy was also utilised before and after the removal of corrosion product. The results clearly illustrated that smut layer and the underlying surface morphologies are inextricably linked as the presence of additives not only had a profound effect on the on the smut film characteristics but also on the subsequent configuration of the underlying pitted surface. From such experiments an increased understanding of pit initiation and propagation in the presence of different types of additives was achieved allowing the possibility to shift the reactions taking place and produce changes to the surface roughness. These results have importance for the AC electrograining of aluminium, which involves the application of an alternating voltage or current between aluminium electrodes in an appropriate electrolyte - typically 0.34M Hydrochloric Acid- to produce uniformly roughened surfaces that is desirable for modern lithographic printing methods.

(a) (b)
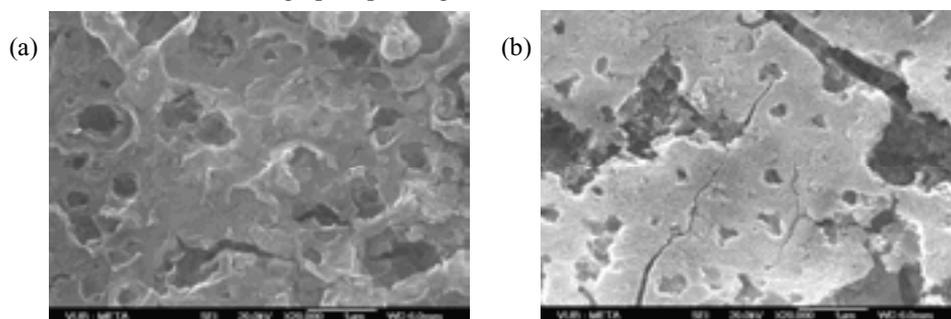
Figure 1: Difference in observed smut layer morphologies (a) with and (b) without additive in the electrograining bath

Pitting corrosion of some superaustenitic Steels in NaBr solution

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Pitting corrosion of stainless steels is one of the most destructive forms of corrosion. Superaustentic steels namely 904L, 254SMO and 654SMO contain high contents of the alloying elements especially molybdenum (Mo > 4.5). These alloys are recommended for using in aggressive environments such as marine applications and oil and gas industries.

The aggressiveness of pitting corrosion of stainless steels caused by halide ions was found to be in the order of chloride > bromide > iodide under different experimental conditions and alloy composition. However, it was reported that the addition of Mo to steel did not always show beneficial effects in lessening pitting in bromide solutions. Therefore, the main goal of this paper is to study in some details the electrochemical pitting corrosion behaviour of 904L, 254SMO and 654SMO in NaBr solutions under different experimental conditions such as, effect of bromide ion concentration, effect of temperature, pH and the potential scan rate. Electrochemical pitting potentials for different stainless steels were determined in NaBr solution and used for determination of the critical pitting temperatures. The results showed that CPT value increases with increasing the alloyed Mo content in the steel. The pitting morphology was inspected by using scanning electron microscope (SEM) at different conditions.

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Adsorption - related Cracking of high strength alloys

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In anhydrous aprotic organic solvent (DMSO) and in its mixtures with water adsorption- or hydrogen-induced SCC of high strength alloys takes place depending on solvent composition and potential [1]. Both subcritical crack growth (SCCG) and threshold stress intensity factor (K_{1SCC}) correlate with solvent adsorption data measured by means of capacitance, radiotracer and AES measurements [2]. It is assumed that strong donor-acceptor bonds between 3d - metals (components of high strength alloys) and DMSO is formed due to interaction of 3d -orbitals with bonding 2π-orbitals and antibonding 2π-orbitals. The strength of chemical bond increases in the series Ni, Co, Fe, Cr, Mn (Table).

Table

Metal	Energy of $DKL_{2,3}$ $L_{2,3}$ auger-line of oxygen, eV	Value of transfered charge
Ni	513,8	0,19
Co	514,0	0,20
Fe	514,5	0,26
Mn	514,6	0,28
Cr	514,7	0,29

Reactivity of oxygen atom in DMSO molecule toward metal atoms is higher in comparison with that one in water molecule. Spatial distribution of stress over surface due to existance of spectrum of chemical bonds and its effect on the kinetics of SCC of high strength alloy in DMSO and DMSO-H_2O mixtures are discussed.

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Chromate free conversion layers on Zn and Zn alloys coatings

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Under the actual trend to use more environmentally friendly electrolytes to process metallic surfaces, a quite important role is assigned to Cr(VI) replacement, especially in the case of Zn and Zn alloys surface treatments both to extend the decorative aspect and to offer at least the same corrosion resistance.

Thus, formation and characterization of chemical/electrochemical conversion layers onto Zn and Zn alloys coatings, respectively: Zn-Fe (0,3-0,6% Fe) and Zn-Ni (10-15% Ni) involving Cr (III), Mo (VI) and W (VI) based iso- or heteropolycombinations are discussed, as ecological alternatives.

They offer a large diversification of decorative aspect by means of an extended range of colors and tones possible to be obtained, as a function of operating parameters.

Some aspects regarding their physical-chemical characteristics (appearance, composition, morphology) against involved solution type and operating parameters, as well as corrosion behaviour as compared with classical Cr(VI) based conversion coatings involving accelerated electrochemical techniques are discussed.

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Sour cherry juice as a green inhibitor for steel corrosion in hydrochloric acid media

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The aqueous juice of the sour cherry is tested as corrosion inhibitor of steel in acidic solution, using the polarization and EIS techniques. Inhibition efficiencies of sour cherry juice were evaluated in the presence of different sour cherry concentrations and also in different temperatures. It was found that sour cherry juice addition decreases the corrosion rate of steel in 1 M HCl even in very low concentration (0.3 % v/v). Inhibition efficiencies of steel corrosion increase from 89.5 to 94.1 when the juice concentration increases from 0.3 % to 4 % concerning the polarization results. Strong inhibition efficiency of sour cherry juice can be explained by the adsorption of different organic compound and especially anthocyanines pigments that present in sour cherry juice. The Corrosion inhibition of sour cherry doesn't change significantly with the temperature increasing but due to thermal degradation, inhibition efficiency decreases suddenly when the temperature rises to 85 °C. Result obtained from both electrochemical methods was in relatively good agreement.

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The Influence of Fluoride Ion in the Phosphating Bath on the Adhesion of Epoxy Coating Electrodeposited on Phosphated Galvanized Steel[#]

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Zinc coatings are widely used for sacrificial cathodic protection of steel parts. Galvanized steel sheets are usually protected from corrosive environments by conversion coatings (phosphate, chromate, etc), and then topcoated with some organic coatings, particuilarly in outdoor applications. The role of a conversion coating is providing more efficient corrosion protection, as well as increasing adhesion of organic coating.

One of the most important factors in corrosion prevention by protective coatings is the coating adhesion loss under enviromental influence. There are many factors influencing the adhesion of organic coatings and in this work an attempt was made to determine the influence of fluoride ion (in the concetration range 0.1-1.0 g dm^{-3}, at 50 ºC) in the phosphating plating bath on the adhesion of epoxy cataphoretic coating on phosphated galvanized steel. Fluoride ion was used since it is well known that its presence thin the oxide layer on the metallic substrate.

The dry and wet adhesion of epoxy coating were measured by a standard pull-off method. The surface roughness of phosphated galvanized steel surfaces was determined, as well as the wettability of the metal surface by polymer solution. The corrosion stability of epoxy coatings on phosphated galvanized steel was investigated by electrochemical impedance spectroscopy.

On the basis of all experimental results it could be concluded that the presence of fluoride ion in the phosphate plating bath in some cases has a beneficial effect on the adhesion, as well as on corrosion stability of the protective system based on phosphated hot-dip galvanized steel epoxy coating. It was shown that the biggest dry adhesion was obtained for epoxy coating on a phosphate coating deposited on hot-dip galvanized steel from a bath containing 0.5 g dm^{-3} NaF. There is a decrease in adhesion of epoxy coating on phosphate coating obtained with about 1.0 g dm^{-3} NaF in the phosphate bath. So it could be concluded that an oxide layer of certain thickness is required for a good adhesion.

[#]Dedicated to the memory of Prof. Aleksandar Despić

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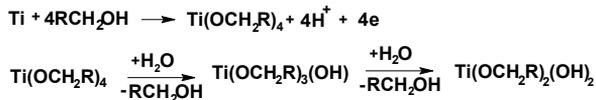# Anodic behaviour of titanium in alcohol – LiClO$_4$ – LiCl solutions

Kamila Banaś, Maria Starowicz, Jacek Banaś

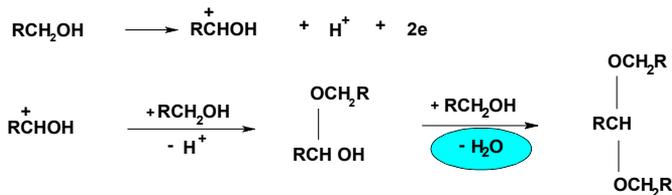*AGH-University of Science and Technology,*
30-059 Kraków Al. Mickiewicza 30, e-mail: banas@uci.agh.edu.pl

Anodic behaviour of titanium was investigated in deaerated anhydrous methanol, ethanol and n-propanol solutions of LiClO$_4$ by means of linear sweep voltammetry (LSV), potentiostatic impedance spectroscopy (EIS) and scanning electron spectroscopy (SEM). The effect of chloride concentration in the above mentioned media was examined.

The primary oxide film, formed in air on the titanium, is stable in alcohol solutions of LiClO$_4$ in the potential range corresponding to the thermodynamic stability of alcohol and alkoxide groups. Oxide layer is covered by adsorbed RO$^-$ and ROH compounds. Adsorbed RO$^-$ outer film stabilizes passive oxide film in similar way as OH$^-$ and water molecules in aqueous media. The impedance spectrum shows capacitive behavior in this potential range. Anodic polarization over the oxidation potential of alcohol leads to activation of titanium and anodic etching of the metal surface. Dissolution of titanium in methanol and ethanol solution of LiClO$_4$ at high anodic overvoltage proceeds with the formation of complex titanium oxide-alkoxide nanoparticles in bulk solutions. The formation of TiO$_x$(OR)$_y$ sol is a result of the hydrolysis of titanium tetraalkoxide according to the following scheme:

$$Ti + 4RCH_2OH \longrightarrow Ti(OCH_2R)_4 + 4H^+ + 4e$$

$$Ti(OCH_2R)_4 \xrightarrow[-RCH_2OH]{+H_2O} Ti(OCH_2R)_3(OH) \xrightarrow[-RCH_2OH]{+H_2O} Ti(OCH_2R)_2(OH)_2$$

Water necessary for hydrolysis can be formed in paralell oxidation process of alcohol molecules on surface oxide:

$$RCH_2OH \longrightarrow R\overset{+}{C}HOH + H^+ + 2e$$

$$R\overset{+}{C}HOH \xrightarrow[-H^+]{+RCH_2OH} RCH\,OH\,(OCH_2R) \xrightarrow[-H_2O]{+RCH_2OH} RCH(OCH_2R)_2$$

The adsorption of alcohol molecules on Ti/TiO$_2$ surface increases according to the row C$_3$H$_7$OH>C$_2$H$_5$OH>CH$_3$OH. In the same way stability of passive film increases.

Chloride ions strongly inhibit anodic dissolution of titanium in methanol and ethanol solutions of lithium perchlorate. The inhibitive action Cl$^-$ is a result of competitive adsorption of these anions. The effect of chlorides is negligible at the presence of strongly adsorbed propanol molecules.

3D and electrochemical characterization of preoxidised TiAlV alloy at different roughness

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Ti6Al4V alloy is widely used in orthopaedic and dental applications due to the excellent corrosion behaviour, mechanical properties and biocompatibility. In addition, a better osseointegration process seems to be achieved as the surface roughness increases.

Hard material coatings obtained by thermal oxidation, mainly based on rutile, have found increasing application in wear- and corrosion-resistant technologies. Ion release studies on oxidized Ti6Al4V alloy have confirmed that the oxidation treatment reduces to the half the Ti ion release in comparison to the as-received ones. In this work, the corrosion behaviour of preoxidised Ti6Al4V alloy at different roughness has been studied by means of electrochemical impedance spectroscopy and anodic polarization curves in order to analyse the influence of the oxidation treatment of the rough surface on the corrosion behaviour of the alloy. To simulate the physiological medium, Ringer's solution was used as corrosive medium. Electrochemical impedance spectroscopy (EIS) was used to evaluate physicochemical characteristics of the surface modifications, i.e., roughness and thermal treatments. The results show in the Bode impedance diagrams two different time constants, associated to the substrate and the oxide layer, as a consequence of the oxidation treatment. Analysis of the EIS results was performed using equivalent circuits. In addition, anodic polarization curves reveal that the oxidation treatment does not impair the excellent pitting corrosion resistance of the Ti6Al4V alloy.

The success in the evaluation of the corrosion resistance of two surfaces with different roughness, it depends strongly on the deep knowledge of the ratio between the true area in contact to the electrolyte and the geometrical projected area. In the present study microstructural studies of sandblasted Ti6Al4V samples with different roughness were carried out by means of field emission scanning electron microscopy (FE-SEM). Based on the analysis of stereopars obtained from the FE-SEM micrographs, a 3D reconstruction of the different surfaces is made. From the 3D-analysis of stereoscopic SEM-images, the roughness and ratio between the true and projected area is obtained. These results allow the correct evaluation of the corrosion performance obtained from electrochemical techniques.

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Selective dissolution of gold silver alloys in halide media

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The selective dissolution of silver from an alloy of gold silver was studied in the presence of chloride, bromide and iodide ions. The rate of selective dissolution of silver from the alloy is several orders of magnitude smaller than that of pure silver. Furthermore, the polarization curves of the alloy show a passive region up to a certain critical potential, Ec, while those of pure silver show simple active dissolution behavior. During this passive region, the current supported by selective dissolution of the alloy is also several orders of magnitude smaller than the limiting current of pure silver.

Beyond Ec, the dissolution rate increases rapidly with potential while the surface develops a nanoporous structure. Furthermore, potentiostatic current transients reveal a power law relationship between the current and the time. The type of halide ion is shown to affect the critical potential, the current and the morphology of the resulting nanoporous structure. The objective of this paper is to document the phenomenon and discuss possible interpretations.

Repassivation Kinetics of Cobalt Chromium Alloy in Aqueous Solution

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In many tribocorrosion systems the passivable materials are used. Tribocorrosion is the process damaging the tribosurfaces by combined action of mechanical wear and corrosion. There is a synergetic interaction between friction and corrosion. Friction induces straining of the material resulting in plastic deformation, residual stresses and, with some materials, in structural transformation. Friction induces also a local destruction of the layers formed by interaction of the material with the surrounding medium. Generally, adsorbed layers are present on the surface. Layers of oxides or corrosion products can also be found. On passive materials, a thin layer (the passive film) protects the material against corrosion. As a result, the reactivity of the surface is deeply changed by friction on the contact areas and the kinetics of corrosion and passivation are completely modified. On the other hand, corrosion or electrochemical reactions occurring on the surface can have a strong influence on the tribological conditions and on mechanical wear. The surface composition is changed by electrochemical reactions and in particular by corrosion, as a result, the surface mechanical properties and consequently the resistance to mechanical wear are also changed. The corrosion products can contribute to the formation of a third body. They can also change the composition and properties of the lubricant. Finally, corrosion affects the geometric characteristics and the roughness of the tribo-surfaces. Consequently, the action of corrosion on tribo-surfaces can change significantly the coefficient of friction, and the wear mechanism and kinetics. Following the tribocorrosions aspects of hard facing coating material of cobalt chromium alloy (stellite6) in aqueous solution [1,2,3] it was studied the repassivation mechanism and kinetics. The specimens for tests were thick layers (1mm) of stellite6 deposited on stainless steel (304L) cylinders. For electrochemical measurements as potentiodynamic diagrams, impedance in active and passive state and the current – time transients, a three-electrode cell set-up was used, with the sample as working electrode, a circular platinum gauze as counter electrode and a „Hg/Hg_2SO_4/saturated K_2SO_4 solution" as reference electrode (SSE=+670mV/ NHE). A mechanism of repassivation is proposed and an estimation of passive layer thickness is done.

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A relation between the structure and properties of functional silver galvanic coatings

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The microstructure of silver films electrodeposited from 4 different types of baths had been studied. The principal formulations of baths were following: (1) cyanide: 0.75M $KAg(CN)_2$ + 1.5M KCN+0.2M KOH; (2) dicyanoargentate-thiocyanate (DCAT): 0.75M $KAg(CN)_2$ + 6M KCNS + 1M K_2CO_3; (3) dicyanoargentate-borate-phosphate-carbonate (BPC): 0.75M $KAg(CN)_2$ +0.82M KH_2PO_4+ 0.41M H_3BO_3 + 0.15M K_2CO_3 + 0.69M KOH; (4) thiocyanate: 0.75M $AgNO_3$ + 6M KCNS.

XRD patterns and intensities of peaks obtained for silver films depend on the current density applied for electrodeposition as well bath type used for films electrodeposition. Regardless on the type of bath utilized for silver films electrodeposition, the obtained silver films are polycrystalline. There is no evident dependency of interplanar distance on the current density applied for Ag films electrodeposition from various baths. However, these distances obtained for Ag films are higher than that obtained for metallurgically prepared silver. The electrodeposited silver films and metallurgic silver are nanocrystalline. The smallest values of grain size as ~60 nm could be obtained at certain current densities (15-40 mA cm^{-2}) for films electrodeposited from cyanide baths, and highest values of grain size (100-120 nm) are obtained for films electrodeposited from thiocyanateand BPC baths [1-2].

The physical-chemical properties of silver coatings electrodeposited from 4 different types of baths at varying current densities was strongly related to their structure. The obtained corrosion current density for bulk silver in 0.2M H_2SO_4 solution is ~2 10^{-5} A cm^{-2} whereas the Ag films electrodeposited from various baths exhibit higher corrosion current densities. The corrosion current density could be correlated with grain size of Ag films that trends to increase in corrosion current density when values of grain size exceed 80 nm [3].

In addition, the effect of various brightening agents for mentioned above solutions (NEONOL, polyvinyl alcohol, derivatives of castor oil, K_2Se) on the structure and corrosion behavior of electrodeposited films also had been studied [4].

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Preparation and characterization of Porous Anodic Alumina Membranes as templates for the growth of metals and semiconductors nanostructures

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The porous structure of alumina membranes, prepared by anodic oxidation of aluminum, is characterized by a highly ordered structure and morphological properties that can be modulated in a rather wide range of thickness (from few to hundreds micron) and porosity (from 10 to 40 %). Moreover it is possible, by simple setting of the anodizing parameters, to tailor the diameter of pores in a wide range of value (20 to 200 nm) [1-2]. These features make PAAM very appealing as templates for the synthesis of nanostructured materials having interesting properties to be exploited in different technological applications.

In a previous work [3] we have shown that PAAM can be used as template for the fabrication of proton conducting thin film membranes, demonstrating their functioning in H_2/O_2 fuel cells. The possibility to be manipulated in micro machining operations makes these membranes very attractive for micro-fuel cell and in general in nanoscale devices.

In this work we would like to extend the potentiality of the anodic alumina membranes to the synthesis of metals and semiconductor nanostructures covering different technological applications. The preparation of nanostructures is realised by electrodeposition into the porous alumina mask, that in contrast to existing nanofabrication methods, is versatile, inexpensive and efficient, and allow fabrication of self-assembled nanoarrays with feature size variable between 20÷200 nm. The templates were prepared according to the potentiostatic conditions studied in previous work [2]: 0.4 M phosphoric acid, 160 V, 10 °C.

Long lasting anodization times were chosen in order to obtain in a simple way highly ordered porous structures at the bottom of the film were the deposition of the nanorods occurs.

In the figure it is shown the Ni electroplated nanorods array prepared into anodic alumina membranes after selective oxide dissolution. In this work the results of a physico-chemical characterization, with different techniques of electrochemically produced nanostructures will be presented and discussed.
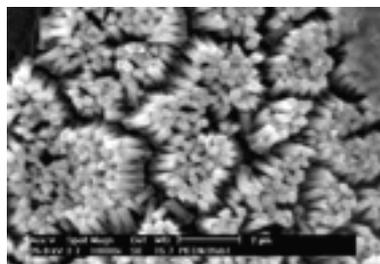
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Investigation of the Kinetics and Mechanism of Oxygen Reduction at Micron-Sized Copper and Iron Intermetallics

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Oxygen reduction is the cathodic process that occurs during corrosion. Intermetallic particles incorporated into aluminium to improve its mechanical strength are susceptible to localised forms of corrosion. Cu and Fe are two metals that are commonly used. In order to enhance our understanding of the process of oxygen reduction at these sites, which are often of micron size or smaller, the mechanism and kinetics of oxygen reduction, was investigated at Fe and Cu ultramicroelectrodes (UMEs). To extract kinetic information a microjet electrode (MJE) arrangment[1]
was employed which is capable of delivering well-defined, variable and high mass transport rates to the UME surface. As the mass transport rate was increased, the oxygen reduction process at the Cu UME was found to move from four electrons to two[2,3] Additionally, confocal microscopy was employed to map the local pH changes which result during cyclic voltammetric reduction of oxygen at both Cu and Fe UMEs[4].

Oxygen reduction has also been investigated on both the 5083 and 2024 aluminium alloys using high resolution scanned probe techniques including scanning electrochemical force microscopy and confocal microscopy. Pitting precursor sites were identified using conducting-atomic force microscopy.

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Dynamical behavior of pitting corrosion of stainless steel in chloride-containing sulfuric acid solutions

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Pitting corrosion of stainless steel (SS) is of important practical interest. It is caused by aggressive ions, such as Cl^-, Br^-, I^- and may result in severe damages of metal structures. Chlorides induce pitting through a local destabilization of the passive oxide film. The pit initiation step is determined by the chemical properties of the oxide film and aggressive ion, as well as, by the ionic and electronic properties of the oxide (i.e. lattice defects, acceptor or donor dopants). Several mechanisms, proposed to explain pit initiation, include the adsorption of halides and formation of surface complexes and/or occupation of oxygen vacancies by halide ions according to the point defect model [1]. Other mechanisms include the influence of halides on the electron energy band structure of the oxide [2]. It seems that the predominant mechanism depends rather on the nature of the oxide film and the factors related to the electrolyte medium and aggressive species. Recent studies show that pitting corrosion may be associated with oscillatory phenomena that might be used to characterize pitting corrosion and distinguish between general and pitting corrosion [3,4].

In this study, the pitting corrosion of stainless steel (SS, AISI 304) is investigated in chloride-containing sulfuric acid solutions. In contrast to the aggressive character of chlorides, sulfates are known for their inhibiting effect on pitting corrosion. It is shown that stable pitting occurs beyond a critical potential, the pitting potential, E_{pit}, whereas repassivation occurs at another critical potential the repassivation potential, E_{rep}. The E_{pit} and E_{rep} were determined as a function of the chloride concentration and potential sweep rate by tracing the current-potential (*I-E*) polarization curves during the forward and backward potential sweeps. The effect of the rotation speed of the SS disc electrode was also examined. Moreover, the dynamics of pitting corrosion was followed through current-time (*I-t*) and potential-time (*E-t*) curves. The experimental results were explained in terms of the point defect model [1,3], which takes into account the absorption of chlorides at local sites of the oxide as well as the formation of surface complexes between metal cations and chlorides. The process that leads to pit initiation is associated with occupation of an oxygen vacancy by a chloride ion. This reaction perturbs the Schottky-pair equilibrium and the steady fluxes of anion and cation vacancies. It is found that increasing the chloride concentration leads to an increase of the cation vacancies that accumulated at the SS|film interface results in the formation of a void. When the void exceeds a critical size, the film breaks down.

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Corrosion: from Nanostructure to Structural Failure

An electrochemical study of the reactions at the metal/ organic coating interface

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The electrochemical impedance spectroscopy has been used to study the reactions at the metal/organic coating interface.

The organic films (20-25 µm) were realized from an alkyd resin on carbon steel substrate.

The experiments were conducted in stagnant, natural aerated 3% NaCl solution under ambient conditions during a 1500 hours period.

Analysis of the impedance spectra has established an electrical equivalent circuit with two time constants (Fig. 1). One time constant concerning the organic coating (C_{pf} and R_{pf}) describes their dielectric and barrier properties and the second time constant concerning the metal/organic film interface (C_{dl} and R_{ct}). The error magnitude between the measured and the calculated data with this electrical equivalent circuit is satisfactory (Fig. 2).
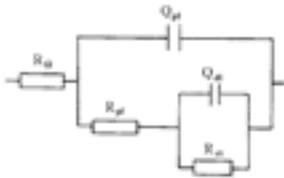

Fig. 1 Equivalent electrical circuit with two time constants
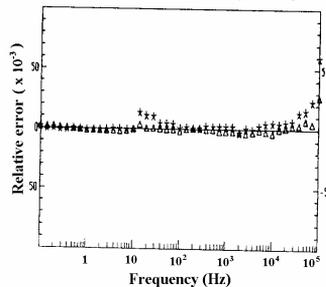
Fig. 2 Comparison of fitting quality (residual error plots: ▵ real relative error; ∗ imaginary relative error)

The time monitoring of the second time constant elements (double layer capacitance and charge transfer resistance) permitted the evaluation of the corrosion process under the organic film as follow:
- the wet area of metallic substrate from the double layer capacitance ;
- the active area of the metal surface and respectively the corrosion rate of the metal under the organic film from the charge transfer resistance.

It resulted that the wet metal area under coating is more reduced (≈ 60 times) in comparison with bare carbon steel and the electrochemical reactions at the metal/organic film interface were slowed down (≈ 50 times) in comparison with those at the uncoated metallic surface.

The mechanism of bronze acceleration corrosion and inhibition method

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Cu-Sn-Pb alloy plated layer with appropriate porosity was used as the simulation sample of bronze ware. Effects of several kinds of corrosion products such as cupric chloride, copper chloride alkali, copper carbonic acid alkali on the corrosion of bronze samples were studied by corrosion paste experiment, and the effects of above cupric salts on the corrosion current of copper micro-electrode in 3% NaCl solution were also investigated by means of copper-cupric salts micro-electrode. The result indicated that the mass losses of bronze samples are 0.209 g, 0.0059 g, 0.0083 g, 0.0034 g and 0.0029 g in turn when the corrosion pastes containing cupric chloride, copper chloride alkali, copper carbonic acid alkali, inert kaoline and nothing respectively, and the corrosion current of copper microelectrode which filled with above solid are $2.5×10^{-6}$ A•cm^{-2}, $4.0×10^{-7}$ A•cm^{-2}, $1.0×10^{-7}$ A•cm^{-2}, $5.6×10^{-8}$ A•cm^{-2} and $1.1×10^{-8}$ A•cm^{-2} in turn. So the catalysis activation of cupric chloride is higher two-amount ranks than bivalent copper salts□ so it has the highest catalysis activation to the depolarization reaction of oxygen and is the most harmful matter to accelerate bronze corrosion. After cuprous chloride powder, bronze samples and bronze artifacts had treated with multicomponent inhibitor which comprised 1,2,3-benzotriazole(BTA), the infrared spectra and Tafel curves testing were carried out. The result indicated that the structure of cupric chloride has been changed after treatment, the corrosion current of bronze samples reduce from $7.24×10^{-7}$A•cm^{-2} to $2.00×10^{-8}$A•cm^{-2} and the inhibitor make the inhibition efficiency of bronze samples reach to 97.2□, and the bronze artifacts have not appear new bronze rusts after 21 months. According to the result of above experiments, we have put forward the mechanism of porous oxygen electrode of bronze acceleration corrosion, and consider that the cupric chloride is a good catalyzer for the depolarization reaction of oxygen.

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Corrosion behaviour of FeCoCrSiB biosensor prototype amorphous materials in phosphate buffered saline solution

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The GMI (Giant Magnetoimpedance) effect was recently considered to create a new type of biosensor for molecular recognition systems and selective detection [1, 2]. Some requirements of this new generation of biosensors are high sensitivity, small size, low power consumption, stability of operation parameters, quick response and resistance to aggressive medium. The purpose of this work was to study the corrosion susceptibility of $Fe_{2.5}Co_{64.5}Cr_3Si_{15}B_{15}$, $Fe_3Co_{67}Cr_3Si_{15}B_{12}$ and $Fe_5Co_{70}Si_{15}B_{10}$ biosensor prototype amorphous materials. The corrosion susceptibility of these materials was studied in a buffered saline solution, PBS, pH 7.4 at 0, 22 and 37ºC, using anodic polarization and electrochemical impedance spectroscopy, EIS. The electrolytes were no de-aerated.

The corrosion potential was measured before the polarization experiments. From the E–log i plots, the pitting potential (E_{pit}) protection potential (E_{prot}) and the perfect and the imperfect passivity regions were obtained [3]. The EIS measurements were taken with an Impedance Analyser Solarton 1255 coupled with a Potentiostat, EGG Par, Model 273. Spectra were obtained at different polarization potentials with a perturbing signal of 10 mV, in the frequency range between 60 kHz to 1 mHz. The corrosion kinetic parameters were calculated from both Tafel extrapolation analysis and ac impedance analysis. The experimental results obtained from different electrochemical techniques were compared and discussed based on the simple Randle equivalent circuit model, modified with a constant phase element, CPE.

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S9·P-17

Development of resistivity sensors for monitoring concrete structures

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The development of new embedded sensors may constitute an alternative method that allows assessing the progress of damage of new and repaired concrete structures.

In concrete the hydration reactions of cement tends to be alkaline (pH 12.5 to 13.6). Under such conditions steel tends to passivity and displays negligible corrosion rates. However aggressive anions may enter into the pores and initiate the corrosion process. Depending on the temperature, resistivity and oxygen levels it may propagate fast leading to the deterioration of the structures in a short time.

It is well known that the electric conductance of concrete is mainly ensured by the electrolyte solution inside its pores (micro and macro pores). Ions, *e. g.* Ca^{2+}, Na^+, K^+, OH^- SO_4^{2-} and Cl^- all contribute to the electrolytic conductance of the solution inside the pores of cement and cementicious materials. Since that those ions that contribute to the electrolytic conductance are the same as those that are involved in its degradation then the measurement of the electric properties of concrete is certainly a useful method to follow its degradation.

In this study small sensors composed by graphite electrodes have been designed and tested in the $Ca(OH)_2$ aqueous solution (simulating the interstitial solution) under various experimental conditions, namely temperatures ranging between 20 and 55ºC, two concentrations of O_2 (5 and 0.4 mg dm^{-3}) and two pH values (9 and 12). The electric resistance, R (Ω), was measured at a fixed frequency of 1000 Hz and also in a frequency domain from $1x10^2$ to $1x10^5$ Hz using the electrochemical impedance spectroscopy (EIS). A very good linear correlation was obtained between the R values measured at 1000 Hz and those obtained from the analysis of EIS spectra (R (1000 Hz) =0.972 R (EIS) +6.314) with R^2 =0.999.

The graphite sensors were calibrated in solutions of known conductivities at five temperatures. A calibration line, described by ϱ (Ω m) = (R+20.77)/16.1, was obtained.

An important and very useful conclusion from this study is that the measurements of the electric resistance can be performed at 1000 Hz instead of using the EIS. Thus with cheap, simples and small sensors the control of damage through the measurements of the evolution of the resistance can be performed *in situ* and continuously.

Studies with sensors to apply in repaired structures, made with graphite powder, are in progress. Their performance will be evaluated in solution and also embedded in concrete samples.

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Corrosion: from Nanostructure to Structural Failure

Stress corrosion cracking and fatigue corrosion of duplex stainless steel and inconel 625 under marine conditions

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The development of technology to petroleum´s borehole in offshore´s platforms leads scientists to researches of new materials or even the revaluation, for each specific situation, of those already existent.

Among many materials projected to work during long periods in highly oxidizing and corrosive atmospheres, LAPEC/UFRGS, with the financial support of the setorial fund CT-PETRO/CNPq, intended to inquire two important superalloys: duplex stainless steel and Inconel 625. Stainless steels and alloys of nickel have been utilized as alternative materials to dress in conventional steels used in "risers" in petroleum extraction. These tubing suffer action of static exertions like their own weight, and they also suffer cyclical exertions like tide movements, which when associated with a corrosive environment (salt water outside the tubing and products with chlorides, "low pH", carbonic acid gas, and perhaps, microbes inside), reduce the limit of exhaustion into very low values, guiding, among another ways of corrosion, to fatigue-corrosion. It may submit all the structure at the risk of suffering failures through this process.

This paper presents the resistance of these two superalloys to stress corrosion cracking and fatigue corrosion combined with synthetic see water, trying to relate the action of an applied stress to the corrosive environment.

The electrolyte used was an aqueous solution of NaCl 18,5%; pH 4,0; $CO_{2\ sat}$ and NaCl 3,5%; pH 7,0; $CO_{2\ sat}$. Besides, they were studied either in air or applying cathodic and anodic potentials, taken from theirs polarization curve. A scheme of the fatigue setup is given in figure 1.
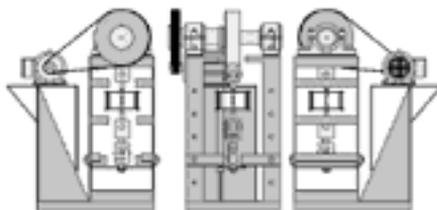
Figure 1. Setup for fatigue corrosion tests used

Results show that both materials are susceptible to stress corrosion cracking and fatigue corrosion. Stress corrosion tests for duplex stainless featured a ductile fracture with the presence of "dimples" in this zone, as seen in SEM and OM, while Inconel featured a fragile fracture. The behavior at fatigue tests observed on these materials showed them to be superior when compared to common steels, because of their high fatigue limit. It indicates that them can be successfully used in petrochemical industry.

New insights into stress corrosion cracking of duplex stainless steel under evaporative conditions

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Stress corrosion cracking of duplex stainless steel in concentrated seawater solutions formed by evaporation is a concern for the oil and gas industry with a number of failure incidents reported in offshore production. Evaporation of seawater occurs on topside pipework as a consequence of exposure to seawater spray, dripping or washing. Research at NPL has focused on optimisation of the drop evaporation test to reflect service conditions and determination of the critical conditions for cracking. To provide a framework for this investigation, complementary chemical analysis of the concentrated solution was undertaken, as the limited published measurements were not in agreement. Based on these results, electrochemical polarisation measurements were carried out on parent and welded specimens in simulated concentrated solution. In the drop evaporation tests, a characteristic damage profile was observed, with patches of general corrosion damage rather than discrete pits, and clusters of microcracks. Linkage of these microcracks led to failure, the location of which was just outside the damp salt layer, where the optimum combination of temperature and wetting conditions occurs. The critical temperature for cracking was determined, the significance of which will be discussed in relation to existing offshore protocols for the adoption of protective coatings.

The chemical composition of the concentrated solutions was determined after boiling ASTM seawater until the water content was reduced in the range 40:1 to 60:1 by mass. Contrary to accepted wisdom, which assumes a dominance of magnesium chloride, the analysis repeatedly showed higher levels of Na^+ than Mg^{2+}, a relatively low boiling point (~ 107 °C), and near-neutral pH (5.7-6.6). Electrochemical polarisation measurements in the simulated concentrated solutions at 130 °C and pH 6.4 indicated an unusually low corrosion potential despite a partial pressure of oxygen designed to give an oxygen concentration in solution of 10 ppm. Impedance of oxygen transfer by precipitation of magnesium hydroxide is a likely explanation. Relatively high pitting potentials with respect to the corrosion potential were observed, except at the lowest pH tested (pH 2). Such low pH values are feasible beneath a deposited salt layer during evaporation due to hydrolysis of chromium and ferric ions, rather than an ionic strength effect associated with magnesium chloride.

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Corrosion: from Nanostructure to Structural Failure

Can tracer redox systems influence microelectrochemical flow measurements?

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Recently we reported on the flow improving properties of long alkyl chain quaternary ammonium compounds like trimethyltetradecylammonium bromide measured with microelectrode arrays under jet impingement flow conditions. This appeared to be in contrast to literature reports which claim that long alkyl chain quats exhibit flow dynamic effects only in the presence of large anions like dimethyl-benzoate or dichloro-benzoate, but not in the presence of bromide as anion. As these conclusions were drawn from rheological experiments our first approach was to explain these discrepancies by the fact that electrochemical measurements give information directly from the interface while rheological measurements derive their data some micrometers away from the interface, somewhere at or in the viscous sublayer of the flow system. If this would be the explanation it would be of utmost importance to get more detailed information on the gradient of flow influenced molecular structures in the space directly adjacent to the electrified interface.

While this appeared experimentally very difficult it was possible to verify the literature findings by own rheological measurements. They proved that aqueous solutions of dimethylbenzoates of alkyl quats exhibit viscoelasticity while aqueous alkyl quat bromide solutions exhibit Newtonian properties. However, further rheological investigations revealed that alkyl quat bromide solutions do exhibit viscoelasticity after adding of hexacyanoferrate(II/III) salts generally used as tracer system in microelectrochemical wall shear stress measurements based on the Levêque equation. From these findings it must be concluded that hexacyanoferrate anions obviously can stabilize micelle aggregates in similar ways as proposed for substituted benzoates.

This is supported by new results obtained with polyimides as additives in electrochemical controlled jet impingement experiments. Using the hexacyanoferrate tracer system polyimides were found to dramatically reduce the wall friction above critical polyimide concentrations. Again rheological measurements proved clearly the contribution of hexacyanoferrate additions to the viscoelastic effect of aqueous polyimide solutions. While these findings may open new doors for the development of taylor-made viscoelastic systems it becomes obvious that the results of microelectrochemical flow measurements may be influenced by the tracer system chosen. First mechanistic approaches will be given in the paper.

Protection of mild steel against corrosion by Polypyrrole-Tangestanate composite film via Galvanostatic technique

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The use of barrier coatings on metal substrates is a common fact in corrosion protection. For the protection of steel substrate, surface treatments like the application of a zinc layer and rinsing with chromate containing agents are often used before the application of the coating to ensure a long-lasting protection and self-healing properties. Unfortunately these techniques involve heave metals which are preferably kept out of the environment. Interest has been recently been focused on the possible use of conducting polymers as either film forming corrosion inhibitors or in protective coatings.

One of the most promising of the conducting polymers for its high conducting, stability and ease of synthesis is polypyrrole (*Ppy*). Application of conducting polymers to corrosion protection of metals is, however subject to some limitations. First, the charge stored in the polymer layer can be irreversibly consumed during the systems redox reactions. Consequently, protective properties of the polymer coating may be lost with time. Also, porosity and anion exchange properties of conducting polymers could be disadvantageous, particularly when it comes to pitting corrosion caused by small aggressive anions (*e.g.*, chlorides). An interesting alternative is to consider conducting polymer-based composite systems.

In the present contribution, we have illustrated fabrication of *Ppy* and *Ppy-* tungstate composite coatings on mild steel from aqueous oxalic acid solution by using galvanostatic technique. The smooth and adherent coatings have been obtained. The protective performance against corrosion of these films is evaluated by using electrochemical impedance spectroscopy and polarization techniques in 3.5% NaCl solution. The results obtained were promising in better protection against corrosion at the present *Ppy-based* composite coating.

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Corrosion: from Nanostructure to Structural Failure

Microstructural and auger microanalytical characterisation of cathodically modified cu-hf and cu-ti catalysts

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Degradation processes occurring at the surface and in the bulk of Cu-based amorphous alloys during cathodic hydrogen charging were used for promoting the catalytic activity of such alloys. These processes modifying the structure, composition, and morphology of the substrate proved to be useful methods for transforming Cu-Hf and inactive Cu-Ti amorphous alloy precursors into active and durable catalysts. Indeed, their catalytic activity for dehydrogenation of 2-propanol increased up to a conversion level of ~60% at selectivities to acetone of about 99% for Cu-Ti and to conversion of ~90% at selectivities of ~95% for Cu-Hf. Previous attempts carried out by aging in air or hydrogen charging from the gas phase resulted in a maximum conversion level up to 15% for Cu-Hf and up to 3% for Cu-Ti. High resolution Auger spectroscopy allowed changes occurring during the activation process to be identified, namely, the formation of small Cu particles on the HfO_2 surface and the formation of highly porous particles containing mostly Cu and some Ti and (Cu-Ti-O) on a Cu-Ti substrate. Differences in the chemistry and structure of both catalysts are discussed, and the implications for catalytic function are considered. A probable configuration of active sites on the Cu-Ti-O/Ti-O-Cu catalyst for dehydrogenation of 2-propanol is proposed. Surface characterizations were performed using a Microlab 350 located at the Physical Chemistry of Materials Centre of the Institute of Physical Chemistry, PAS and of the Faculty of Materials Science and Engineering, WUT.

Inhibition of CO_2 corrosion on anodically polarised carbon steel

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The internal CO_2 corrosion of oil pipelines may be mitigated through proper use of corrosion inhibitors. However, local galvanic cells that influence inhibitor performance can form and may lead to galvanic corrosion. These cells can be due to e.g. welds, or sand or mineral scale deposits in the pipeline causing uneven distribution of the inhibitor [1,2]. The galvanic effect may influence the inhibition in several aspects; inhibitor adsorption can be altered due to the increased dissolution or due to the increased potential.

Here we report some effects of anodic polarisation on the inhibition of CO_2 corrosion of a low carbon steel. The corrosion experiments were carried out on ferrittic-pearlitic, low carbon pipeline steel in a 3 wt-% NaCl solution at 25 °C under 1 bar CO_2 atmosphere. A commercial, amine-based inhibitor was used, in concentrations ranging from 0 to 100 ppm. Current densities in the range of 0 to +0.6 Am^{-2} were applied on the specimens by an external galvanostat. The linear polarisation resistances and electrode potentials were monitored continuously throughout the experiment. A modification of the Stern-Geary equation was developed to calculate the corrosion current densities from the polarisation resistance for polarised specimens. Polarisation curves were recorded to investigate changes in the current-potential characteristics. The metal mass loss was determined, and the specimens were inspected for localised corrosion attacks.

The results showed that the uninhibited corrosion current density was approximately 1.7 Am^{-2} (2 mm/y). With an inhibitor concentration of 30 ppm this was reduced to 0.05 Am^{-2}. However, applying an external current density of e.g. 0.2 Am^{-2} increased the corrosion current density to values higher than the impressed current density. This indicates a reduced inhibitor performance when the metal is polarised. The anodic part of the current-potential curves was shifted toward higher current densities. This corresponded to changes in the Tafel gradients. These changes could be due to changes in the reaction mechanisms, or to irreversible desorption of the inhibitor. The linear polarisation data showed that a minimum concentration of inhibitor must be exceeded to inhibit corrosion for all the applied current densities.

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Kinetics and Mechanisms of the Growth of Thin Oxides on Pt-Group Metals: Combination of Experiments and Data Modeling

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The growth of oxide layers on noble metals has been a subject of extensive research and discussion over several decades. There exists a vastness of papers that report qualitative data but few present a thorough quantitative analysis. Some of our own results show that in the case of several noble metals the very initial oxide growth (sub-monolayer to monolayer range) is limited the *interfacial place-exchange* process treated mathematically by Conway···. On the other hand, the growth of multilayer oxide films is limited by the *interfacial escape of the metal cation* from the metal into the oxide. In this contribution, we present a comprehensive analysis of the growth of thin oxide layers on Pt electrodes at well-defined polarization potential (E_p), polarization time (t_p), and temperature (T) conditions. Although Pt is one of the most studies electrochemical systems, little is known about the influence of T on the oxide growth. In this contribution, we present a comprehensive analysis of the oxide growth at Pt electrodes based on an exhaustive set of experimental data. We relate our results to the early research of Vetter and Schultze···.

Anodic polarization of Pt electrodes in 0.5 M aqueous H_2SO_4 at various E_p values in the 0.90 – 1.50 V range, for $t_p \leq 10^4$ s, and at $278 \leq T \leq 323$ K leads to formation of sub-monolayer and monolayer oxide films. These oxide layers reveal only one feature in the oxide-reduction profiles (OC1 peak), which corresponds to the reduction of PtO to Pt. The oxide growth behaviour is influenced by the experimental conditions such as E_p, t_p, and T, and in general the higher E_p and/or longer t_p and/or higher T, the thicker the oxide layer. An increase of E_p and/or t_p shifts the OC1 peak towards less-positive potentials. On the other hand, an increase of T does not lead to any shift of the OC1 peak. Application of oxide-growth theories and theoretical data treatment indicate that the growth of PtO follows two distinct kinetic laws, each arising from a different growth mechanism: (i) the logarithmic growth for oxide whose thickness is up to 1 ML of PtO, i.e. at $0.9 \leq E_p \leq 1.0$ V for $t_p \leq 10^4$ s, and (ii) the inverse-logarithmic growth for oxide whose thickness is more than 2 ML of PtO, i.e. at $E_p > 1.0$ V for $t_p > 10$ s. The logarithmic growth law originates from the interfacial place exchange between O_{chem} and the top-most Pt atoms that is the rate-determining step, whereas the inverse-logarithmic growth law arises from the escape of the Pt cation, Pt^{2+}, from the metal into the oxide at the inner metal/oxide interface. The dipole moment of the $Pt^{\delta+}$–$O^{\delta-}_{chem}$ surface species that drives the place exchange is consistently 1.30 ± 0.10 D. The electric field, E, which drives the interfacial Pt^{2+} escape is found to be consistently in the $0.33 – 0.46 \times 10^9$ V m^{-1} range.

Potential dependent clustering of interacting electrochemical oscillators

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Coupled electrochemical oscillators are known to interact in an excitatory or inhibitory manner, depending of the geometrical arrangement of the electrochemical network [1] as well as the chemical nature of the interacting electrodes [2]. During excitatory coupling, the oscillators tend to activate each other whereas during inhibitory coupling the active electrode suppresses the neighbor's oscillations. As a result, interacting excitatory electrodes exhibit in-phase synchronization while inhibitory electrodes synchronize out-of-phase.

In the present work, a network of oscillatory electrode pairs is studied under potential controlled conditions. Each oscillatory pair consists of an iron wire, used as an anode, and a copper coil, used as a cathode. At the anode electrodissolution and passivation reactions take place. A specific network geometry is chosen where a combination of excitatory and inhibitory interactions exist among the network members. As a result, clustering in observed among members coupled in an excitatory manner while clusters are synchronized out-of-phase (Fig. 1, left). The clustering pattern depends on the applied potential and thus a desired entrained pattern can be produced by tuning the electrodes' potential (Fig. 1, right).
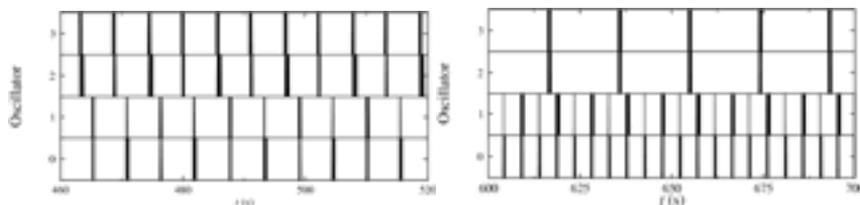

Figure: Clustering among four oscillatory electrodes for V = 260 mV (left) and V = 258 mV.

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Symposium 9 - Poster

Corrosion: from Nanostructure to Structural Failure

Environmentally acceptable nanolayers against zinc corrosion

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Inhibition of corrosion processes of zinc which is in the focus of our work. Though several inorganic and organic additives can decrease the deteriorating processes of zinc but environmentally acceptable alternatives to presently applied protective layers are not solved. The objective of our studies was to form protective layers by α-Ω bis-phosphonic as well as hydroxamic acids (C_5 C_{12}) combined with other additives (mainly bi and trivalent cations) on zinc surface. The effect of different factors such as concentrations, pH, time dependence, solvents, and additives were studied in order to develop a stable, compact protective layer. The efficiency monitored by electrochemical methods (electrochemical impedance spectroscopy (EIS), polarization measurements.). Further experiments using surface analysing techniques (scanning electron microscopy equipped by X-ray analyser (SEM EDX), X-ray photoelectron spectroscopy (XPS), FT-IR spectroscopy) gave information about the chemical composition of the nanolayer. The morphological changes caused by corrosion processes were monitored by atomic force microscopy (AFM).

Based on the results obtained in aqueous and non- aqueous solutions it can be concluded that competitive adsorption of the organic solvent molecules on zinc must be taken into account. 1,5-penthane-diphosphonic acid (DPP) was proved to be the most effective ones among the bi-phosphonic acid inhibitors in neutral aqueous solution. The special roles of the bivalent cations especially calcium and magnesium have been investigated, on the inhibition effect of phosphonic as well as hydroxamic acid because these cations are present in all natural aqueous environments.
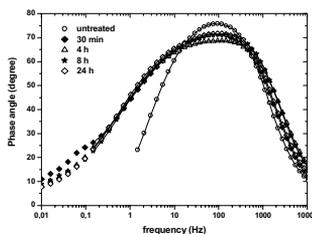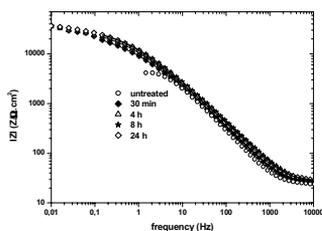
Bode plots of the untreated and DPP treated zinc in neutral 10^{-1} M Na_2SO_4 solution

Effects of Si, Cu, W on the Localized and Stress Corrosion of Austenitic Stainless Steel

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Conventional type 304 stainless steel has been widely used as a material for hot-water tank in Korea due to its good formability, moderate cost, and mass production. However, 304 stainless steel has been reported to be highly susceptible to stress corrosion cracking (SCC) in chloride solution, and therefore incongruent as tank material. Therefore, in recent days, customers require the develpment of new austenitic stainless steel with the excellent resistance to localized and stress corrosion.

Mo, W, Si, and Cu can be emperically alloyed in stainless steels to improve SCC resistance. Nevethless, the addition of Mo is not favored due to its high cost. Thus far, several studies have reported that W, Si, and Cu exhibited beneficial effects on localized and stress corrosion of stainless steels.

The objective of this study is to elucidate systematically the effects of Si, Cu, and W on the localized and stress corrosion of 18 % Cr austenitic stainless steel. $(2^3 + 1)$ full factorial matrix for the alloy was designed varying Si, Cu, and W contents. For the allys, pitting potential (E_{pit}), critical current density (i_c), and the ratio of $\varepsilon_{solution}/\varepsilon_{air}$ were examined in acidified chloride solution.

The follwing regression equations exhibiting the contribution of Si, Cu, and W on the resistance to localized and stress corrosion were obtained from the measured data. In addition, we found an interation between Si and Cu on the localzied and stress corrosin of the alloy.

E_{pit} (V_{SCE}) = 136.8 + 48.8 (% W) + 10.5 (%Si) + 1.12 (%Cu) - 2.25 (%Si)(%Cu)
I_c (μA) = 1684 – 480 (%W) - 293 (%Si) -333 (%Cu) + 105 (%Si)(%Cu)
R_{SCC} = 0.005 + 0.0265 (%W) + 0.0218 (%Si) + 0.008 (%Cu) + 0.0113 (%Si)(%Cu)
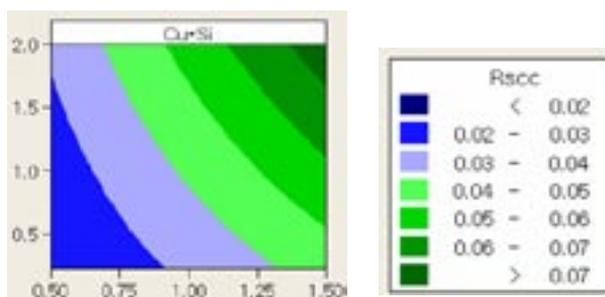
Fig. 1. A contour plot indicating the SCC resistance with varying Cu and Si contents.

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Corrosion: from Nanostructure to Structural Failure

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Anticorrosive properties of the Nafion®-Polyaniline composite films deposited on stainless steel

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Intrinsically electronic conducting polymers (IECPs) are explored intensively during the last years for corrosion control of metal and alloys due to restrictions to the use of chromate-based coatings. IECPs differ from the traditional organic coatings in that they are electroactive materials and hence, as with chromates, redox interactions of IECPs with metal and alloys are expected with concomitant diminution of metal corrosion rates. Indeed, a number of studies suggest that IECPs are promising materials for corrosion control [1]. Moreover, several strategies were implemented aiming to improve the protective performance of IECPs. Some strategies involve the use of polyaniline (PAn)-epoxy or –acrylic blends, pre-treatment of the substrate with chelating agents, copolymerization, or use of large size dopant ions. Recent preliminary results obtained in our laboratory suggest that the Nafion®-PAn composite films show a better protective behavior than the simple PAn films against pitting corrosion of stainless-steel (SS) in chloride-containing acidic solutions [2].

The aim of the present study is to gain a further insight to the mechanism by which the Nafion®-PAn composite films provide protection and to examine conditions that may improve their performance in protection. Towards this goal we investigate the role of: (i) the Nafion®/PAn ratio; (ii) the exposure time of the SS|Nafion® electrode to the polymerization solution prior to the initiation of polymerization, and (iii) the temperature. Nafion®-polyaniline composite films were deposited on stainless steel (SS AISI 304) electrodes in a two-step process. The Nafion® 117 (5% w/v, dissolved in a mixed solution of low aliphatic alcohols and water) was cast at the SS electrode and the PAn was synthesized on the Nafion®-coated SS electrode by cyclic voltammetry in 0.5 M H_2SO_4 containing 0.1 M aniline (An). Monitoring the open circuit potential as a function of time and using cyclic voltammetry experiments the anticorrosive properties of the composite films were evaluated. It is found that: (i) there is a critical Nafion®/PAn ratio that determines the mechanical stability of the composite films; (ii) anilinium monomer diffuses into the film prior to the initiation of polymerization and there is a crucial time for its optimum permeation through the film, and (iii) increasing the temperature results in higher redox currents of the composite film and sufficient protection. The results show that Nafion®-PAn films do not favor chloride exchange between the composite film and the solution. This is attributed to the cationic permeselectiviy of Nafion® and to the Nafion® sulfonate groups that act as inner dopant anions.

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Electrochemical behavior and anticorrosive properties of polyaniline deposited on stainless steel by potentiostatic and potentiodynamic methods

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During the last two decades there has been a significant effort towards the use of intrinsically electronic conducting polymers (IECPs) as protective coatings against the corrosion of several metal and alloys. Polyaniline (PAn) is one of the most widely used IECPs for this purpose [1,2], because it can be easily synthesized by chemical and electrochemical methods and is stable in air. Electrochemical synthesis of PAn on active corrosive metals has the advantage of a controllable synthesis directly on the metal surface, although care has to be taken on choosing the proper polymerization solution and other polymerization conditions. To obtain adequately adherent PAn films the metal substrate has to be in the passive state prior to electropolymerization. Moreover, there are evidences that the protection efficiency of PAn depends on the electrochemical method used for the preparation of PAn films onto the metal substrate.

The aim of this work is to investigate the effect of the electrodeposition method along with associated electrochemical parameters on the protective efficiency of PAn films in chloride-containing solutions. PAn films were electrodeposited on stainless steel 304 (SS) from 0.5 M H_2SO_4 solution containing 0.1 M aniline (An) by using potentiodynamic and potentiostatic techniques as follows: (i) cyclic potential sweep (CPS) deposition upon varying the upper potential limit (E_l) of the polymerization potential region between 0.8 and 1.1 V, while the lower potential limit was equal to -0.2 V. The potential sweep rate (dE/dt) was also varied for the An polymerization during the CPS deposition. (ii) Potentiostatic deposition upon varying the applied potential (E_{appl}) between 0.8 and 1.1 V. Variation of the E_l, dE/dt and E_{appl} seems to affect remarkably the PAn growth leading to films of different redox and structural properties, which, in turn, affect the protection efficiency of PAn against the SS corrosion. The electrochemical properties of the PAn were examined by using cyclic voltammetry. Scanning electron microscopy was used to reveal the structure and morphology of the PAn films. PAn films seem to provide protection against both the general and pitting corrosion of SS, although pits were detected during prolonged immersion of the PAn-coated SS electrodes in chloride-containing solutions. The mechanism of the SS protection provided by the PAn coatings is discussed in terms of the active role of PAn in corrosive environments. The appearance of pits is due to the charge compensation and, therefore to charge transport processes involved proton/anion (i.e. Cl-) expulsion/insertion.

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Corrosion: from Nanostructure to Structural Failure

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Selective dissolution of homogeneous alloys Ag-Au, Cu-Au and Zn-Ag at the solid-phase diffusion kinetic control

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Limiting stage of selective dissolution (SD) of a homogeneous alloy at the certain stage is the solid-phase interdiffusion of components. Revealing the solid-phase diffusion kinetics and correct determination of diffusion zone parameters for an alloy is usually seriously complicated because of adsorption of alloy components in the surface layer prior to SD, roughness of an electrode surface, mixed kinetic mode, displacement of interphase border, relaxation of the nonequilibrium vacancy subsystem of an alloy.

The purpose of the work is to establish the kinetics of formation and to find parameters of solid-phase diffusion zones formed at anodic selective dissolution of homogeneous alloys Ag-Au, Zn-Ag and Cu-Au, within the framework of the stage-by-stage account of the basic complicating factors of the process.

Theoretical models of anodic selective dissolution of a homogeneous binary alloy is constructed. Solutions of problems of non-stationary bidimentional interdiffusion in an alloy as modified Cottrell and Sand equations are obtained. The technique of correct determination of interdiffusivity, solid-phase diffusion zone thickness, concentration of superequilibrium vacancies and parameters of capacity of vacancy sinks is developed and proved. The role of each factor in current recession and potential relaxation is revealed. It is shown, that in conditions of solid-phase diffusion kinetics an electrode surface roughness and relaxation of the nonequilibrium vacancy subsystem can lead to a curvature of chronoammograms and chronopotentiograms of an alloy. It is established, that influence of a roughness on mass-transfer parameters is not specific to conditions of polarization and to the form of separate microroughnesses. This influence is determined only by the ratio between the roughness factor, interdiffusivity and average distance between microroughnesses.

The relative contribution of all major factors of selective dissolution to the formation of curves of current recession of Ag,Au-alloys in acid nitrate solution, and also curves of an overpotential relaxation of Zn,Ag- and Cu,Au-alloys in acid chloride solution is determined. It is shown, that the account of a roughness in calculating all parameters of solid-phase diffusion zones in investigated alloys is reduced to use a true (instead of geometrical) area of an electrode surface. It is confirmed that ionization of zinc and copper from Zn,Ag- and Cu,Au-alloys is quasi-equilibrium. The basic channel of injection of non-equilibrium vacancies in Ag,Au-alloy is dissolution of silver, but not change of a surface tension at various shift from potential of a zero charge. Generation of superequilibrium vacancies in Ag,Au-alloys proceeds in the mixed kinetic mode when rates of charge carrying and surface diffusion of ad-atom are comparable. Sinks of vacancies in all investigated alloys are ineffective.

Critical dealloying potential of Ag-Au and Cu-Au alloy

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Selective corrosion of an electronegative component A from homogeneous A,B-alloy is the basic channel of injection of vacancies in its surface layer. If concentration of metal A in an alloy is great, then at certain, critical potential E_c process of accumulation of superequilibrium vacancies starts to dominate over their assimilation by sinks. Thus on an electrode surface there are extended destructions owing to that the true area sharply grows. The morphology of an alloy determines the rate of its corrosion, hence, the kinetics of selective dissolution at $E < E_c$ and $E > E_c$ can be various. Thus, determination of the critical potential of an alloy, and also studying of its dependence on an alloy structure and the corrosion environment are obligatory investigation phases of the mechanism of alloys destruction.

In this work the model of a surface development [1] at anodic selective dissolution of a homogeneous A,B-alloy with prevalence of an electronegative component is specified. The basis of this model is an idea about the disbalance between the electrochemical dissolution flow of the component A and its surface-diffusion flow. Theoretical expressions for E_c, taking into account the various nature of kinetic limitations of selective dissolution at $E > E_c$ (electrochemical, liquid-phase diffusion, solid-phase diffusion, and also mixed liquid-solid phase diffusion and electrochemical-diffusion control) are obtained.

The critical potentials corresponding to infringement of morphological stability of Ag,Au-alloys (molar fraction of silver 0.65-0.95) in an acid nitrate solution with the different contents of ions Ag^+, and also Cu,Au-alloys (molar fraction of copper 0.70 and 0.96) in an acid sulphate solution with addition of ions Cu^{2+} are experimentally found. It is revealed, that the critical potential sharply grows with the growth of atomic fraction of electropositive component (gold), i.e. dissolution of an alloy is slowed down. The analysis of dependences E_c from activity of metal ions allows to conclude, that the kinetic control of selective dissolution of Ag,Au- and Cu,Au-alloys in the acid environment at $E>E_c$ belongs to mixed liquid-solid phase diffusion.

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Corrosion: from Nanostructure to Structural Failure

PANI layers of different degrees of protonation in corrosion protection of stainless steel

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It has been shown that PANI can be effective in corrosion protection of steel [1] and of some other metals like copper [2] and aluminium [3].

In corrosion protection different states of polyaniline were tested, mostly protonated emeraldine, but also emeraldine base was used. There are speculations about protecting properties of PANI base. Good protecting properties with PANI base were obtained in some papers [2], while in other [4] it was reported that PANI base does not offer corrosion protection.

In this work the aim was to study protecting properties of PANI layers of different degrees of protonation in 0.1 mol dm^{-3} NaCl solution. Methods of testing, used in this work, were open circuit potential monitoring and Electrochemical impedance spectroscopy. Different degree of PANI protonation was obtained by keeping the layer during one day in different solutions, like 3 mol dm^{-3} phosphoric acid solution (pH=0.4), or in buffer solutions (pH=4.3, pH=7.8). Depending on a degree of protonation different protecting properties were obtained. Corrosion protection of stainless steel with PANI layer, in solutions containing chloride ion, is not based on the previously proposed electrochemical mechanism [5]. In this case PANI imposes a physical barrier for the diffusion of chloride ions through the layer. The best protecting properties, in solution containing Cl^-, were obtained with the layer kept before testing during one day in buffer solution of pH=7.8 where a complete deprotonation was obtained. It was shown that better corrosion protection is not a consequence of the improved oxide quality but of deprotonation that is followed by a change of a polymer structure.

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Electrodeposition of functional gold films

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In this work was studied morphology and physic-mechanical properties of gold coatings electrodeposited from the phosphate acid bathes at varying deposition regimes and bath composition. These coatings are widely used in microelectronics. Thin gold films (1-5 microns) were deposited by the stationary and non-stationary regimes. The morphology obtained coatings was studied by SEM. Texture formation in gold electrodeposition on a brass substrate was studied by X-ray diffractometry. A relation between the texture and mechanical stresses in the deposits was considered. Size of crystallites of the gold deposits was of 0.8 - 1.6 mkm.

The deposits structure is depend on electrolyses regime. We will be able to build the thin structure of gold films, if we make changes of deposition regime. The optimal conditions for obtaining of compact, fine-grained, bright golden coatings are $f = 250$ Hz; $q = 3 – 5$; $j_\kappa, = 0.25$ A dm^{-2} [1].

The physic-mechanical properties of gold coatings electrodeposited from the phosphate acid bath on brass substrate at varying current densities was strongly related to their morphology. The corrosion stability of obtained gold coating is depending on the deposition conditions. Non-stationary regimes of electrolyse have positive influence. The decrease of corrosion current (in the case of direct regime is linear shape: from 35 till 12 mkA; and in the case of pulse regime is hyperbolic shape: from 120 till 6mkA) with increase of coating thickness from 1 to 5 microns under equal value of anodic potential (φ=150mV) was established. The rate of corrosion process for obtained by pulse electrolyses coating with thickness 5 micron is 0.6mkA mV^{-1}. Whereas the rate of corrosion process for coating obtained by direct electrolyses is 1.1mkA mV^{-1}. With increase of frequency and porousness of pulse current we can observe of intensification of the protection properties of gold coatings. At the same time the dissolution currents are decreasing.

Influence of different specific additive surfactants H$_4$Oedph (oxyethylidendiamin phosphonic acid) and EDDNP (ethylendiaminedinitrilpropionat) on the not-porous coatings formation was studied. The presents of surfactants to increase surface microroughness. The microhardness of gold coatings growth is the result of the grain size decrease with cathode current density increasing. Maximum microhardness has a plating which was formed at current density 0.5 A dm^{-2} in phosphate baths contain additives. The gold coatings electrodeposited from phosphate bath with additives surfactants H$_4$Oedph and EDDNP at range current densities 0.2 – 0.5 A dm^{-2} may be using for microelectronic industry [2].

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Corrosion: from Nanostructure to Structural Failure

Initiation and Repassivation of Crevice Corrosion of Type 444 Stainless Steel in Chloride Solution

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Type 444 ferritic stainless steel with the chemical composition of Fe-19Cr-2Mo-(Ti,Nb) is atractive as a structural material, because it has higher mechanical strength and exhibits higher resistance to localized and stress corrosion than type 300 series austenitic stainless steels at a comparible cost. However, crevice corrosion can occur in the crevice betewen the insetsion and the stainless steel sheet in bolt type water storage tank containing tap water.

The objective of the present work is to examine the efforts of the chloride ion concentration and crevice-forming material (Silicone and EPDM) on the repassivation of artificially creviced type 444 stainless steel sheet. In addition, the concenpt of repassivation potential is discussed from the perspective of the stability of metastable pitting corrosion.

Potential for initiation and repassivation of crevice corrosion was measured accoridng to the JIS G0592 standard method. In addition, electrochemical noise analysis was conducted to investigate the correlation between crevice repassivation potential and the initiation of metastable pitting corrosion.

Critical crevice potential (E_{crev}) and repassivation potential (E_r) of the creviced alloy decreased with an increase in chloride concentation [Cl^-], satistying the logarithmic relationship between E and [Cl^-]. In addition, E_{crev} and E_r of the alloy with silicone crevice former were measured to be higher than those of the alloy with EPDM (Ethylene Propylene Diene Monomer) crevice former, suggesting that silicone was more effective in preventing water from penetrating crevices between a stainless steel sheet and the crevice former. In electrochemical current transient measuments with an applied potential, the intensity of current transients corresponding to the initiation of metastable pits increased abruptly near the E_r of the alloy, indicating that the stability of crevice corrosion is associated with
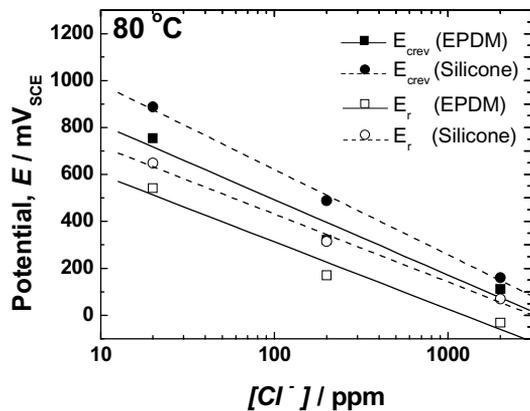

Fig. 1. Effect of [Cl^-] on the E_{crev} and E_r of the type 444 alloy.

Study on the Corrosion Behavior of Reinforcing Steel by EIS and Electrochemical Noise

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Corrosion of reinforcing steel in concrete is the major cause of failure of reinforced concrete structures. Various techniques have been developed to study corrosion behaviors of reinforcing steel in concrete. Electrochemical impedance spectroscopy (EIS) has been widely used to study the corrosion process of reinforcing steel, and electrochemical noise (EN) measurement has shown to be possible to be applied in corrosion fields. However, only a few of studies of EN for corrosion of reinforcing steel in concrete are reported.

The corrosion behavior of reinforcing steel in concrete mortar was studied by EIS along with EN. The mortar specimens was subjected to a cyclic immersion and drying test which the specimens were immersed in 3.5% sodium chloride solution for four days and then dried in air for three days.

The impedance spectra show one time constant related to the corrosion process at an early stage, and from the 6th cycle, a diffusion process appears in the spectra. The results obtained from EIS measurements show that the corrosion of reinforcing steel is slight at beginning, and serious after about the 6th cycle. The time records of current show the different stages of corrosion process of reinforcing steel. At beginning of the cyclic test, the noise current fluctuates in a more regular pattern. With the time, a large direct current (DC) trend dominates the time records, and the fluctuations decline and disappear. The EN data are also analyzed by statistical methods. The standard deviation of current (σ_I) reflects the magnitude of fluctuation of current and estimates the activity of corrosion. The σ_I values are very low at beginning, indicating the low activity of reinforcing steel in mortar. Then the σ_I values increase largely, indicating the increasing activities of reinforcing steel. The noise resistance R_n is defined as the ratio of the standard deviations of the potential and current noise. R_n shows the similar trend with the charge transfer resistance (R_{ct}), which decreases largely at beginning, then keeps very low values.

The results obtained from EN measurements show the different stage of corrosion process of reinforcing steel in mortar. It agrees with the results obtained from the EIS measurements. EN measurements is useful for studying the corrosion process of reinforcing steel in mortar.

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Photoelectrochemical Anticorrosion Effect of the TiO$_2$-SnO$_2$ Composite Films on 316L Stainless Steel

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A uniform TiO$_2$-SnO$_2$ composite film coated on 316L stainless steel was obtained via sol-gel and dip-coating techniques. The morphologies and crystallinity of the films were investigated with SEM and XRD. The photo-generated cathodic protection property of TiO$_2$-SnO$_2$ composite coatings under UV illumination and dark conditions was evaluated through the electrochemical measurement techniques. It is indicated that the photoactivity is optimal when the composite coating bearing TiO$_2$ and SnO$_2$ in a 1:1 molar ratio. Such a desirable photoeffect was obtained after a sequential thermal treatment ending with 120 min at 450°C in air. The prepared films exhibited a maximum lowering of potential and a continued cathodic protection to the metallic substrates even in the absence of ultraviolet illumination, due to a charge storage of the photogenerated electrons from TiO$_2$ to SnO$_2$, which could be released to the substrate after cessation of illumination. The performance of photogenerated cathodic protection was carried out in 0.5 molL^{-1} NaCl solution by measuring the open circuit potential (OCP) of the samples (vs.SCE) in a three-electrode system built in a transparent photoelectrochemical cell. The result in Fig.1 shows that there is a rapid decline of the potential as soon as the photoanode exposured to UV light, the potentials continually become more negative and finally reach value of -285 mV which is sufficiently more negative than the corrosion potential of 316L (~ -137 mV). On turning off the UV light, the OCP switches back slowly to less negative value (~-283 mV) due to the fast charge recombination, and remains at such values for a long period of time. It is noted that the recovery extent of the OCP is small even in 2 mV. The present investigations shows that the TiO$_2$-SnO$_2$ composite films coated on 316L stainless steel is possible to remain a remarkble effect of phot-generated cathodic protection even in a dark conditions.
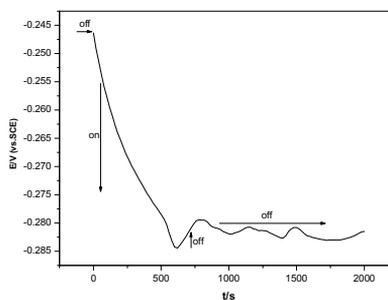

Fig.1 Variation of photo-generated potential with time for TiO$_2$-SnO$_2$ composite caoted on 316Lss under UV illumination and dark condition.

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Surface Chemistry of Oxidised ZnSe ATR Crystals

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The transport of small infrared active molecular species through a paint film can be measure using the ATR-IR (attenuated total reflection – infra-red spectroscopy) method. In this case, an organic coating is applied onto an infra-red transparent crystal such as silicon, germanium or diamond. One problem with this method is that many ATR substrates are chemically different from the metal substrates where the paint will be applied. However, zinc selenide (ZnSe) is possibly a realistic substrate for zinc. Consequently, the aim of this work was to study the surface chemistry and electrochemistry of zinc, selenium and zinc selenide in order to compare their properties.

Conventional polarisation was carried out for zinc and selenium in a range of electrolytes. Experimentally, selenium was difficult to measure due to its high intrinsic resistivity however it was shown to be a relatively noble consistent with its calculated thermodynamic data (Pourbaix Diagram).

Subsequently, various treatments were applied to a typical ZnSe crystal in order to identify whether the surface chemistry could be modified in order to mimic that of zinc. The surfaces were then analysed using X-Ray Photo-Electron Spectroscopy (XPS) and the results are shown in the table below:

Element	As Received	Thermally Oxidised	Oxidised in Iodate	Oxidised in H_2O_2	Immersed in pH 10
Zn	11.0%	11.4%	12.7%	12.3%	13.5%
Se	37.4%	35.5%	56.4%	45.6%	62.0%
O	51.6%	53.1%	30.9%	42.1%	24.5%

This data demonstrate that the surface of as-received ZnSe crystals have a mixed oxide containing zinc and selenium in an approximate 3:1 ratio (Se:Zn) and in an approximately 1:1 stoichiometry metal:oxygen. This is not affected significantly by thermal oxidation at 250°C in air but may be altered by solution phase oxidising agents. The potential for preferentially oxidising zinc, but not selenium, in order to provide a substrate analogue for galvanised steel, is clearly present.

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Corrosion: from Nanostructure to Structural Failure

Lactic acid influence on CoCrMo alloys

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Cobalt–chromium based alloys are known to have excellent corrosion resistance[1] connected with a thin passive oxide film which consists of a mix of cobalt, chromium and molibdenum oxides. However, it was suggested[2] that patients with an extensive exposure to the studied metals may develop immune disfunctions, with an increased risk of infection and inflammation. Because of their outstanding mechanical properties these alloys are mainly used for the fabrication of removable partial dentures. However, their high hardness[3] does not guarantee the biocompatibility which is greatly influenced by reactions at the tissue-implant surface. In the region where passive layer dissolution/ repassivation take place, it is difficult to avoid the release of cobalt and chromium ions into body fluids associated with CoCrMo implants.

In order to simulate the severe corrosion conditions of decreased pH in oral cavity, the present study was undertaken in a solution of artificial saliva with 0.1% lactic acid (LA) added. The corrosive effect of this agent on dental metallic materials has not been well documented. It was an objective of this *in vitro* study to evaluate electrochemical behavior of ten experimental CoCrMo alloys (Figure 1) and compare them to the commercially available dental alloy WIRONIT®.

Electrochemical corrosion measurements were performed by polarization in Tafel region and by the method of cyclic potentiodynamic anodic polarization at a scanning rate of 2 mVs^{-1} in aerated solutions (30 L/h) at $37 \pm 0.5°C$.
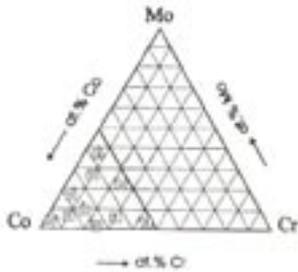

Fig.1. The composition of the tested alloys from ternary CoCrMo system

Fig.2. Optical micrograph of the as-cast experimental alloy $Co_{60}Cr_{30}Mo_{10}$

It was shown that LA made the passivation layer on the metallic materials unstable. Some of tested alloys suffered severe pitting attack depending on the microstructure (Figure 2) and on Cr -content. The presence of LA in solution significantly decreased E_{corr} - and E_b- potentials, while j_{corr} was increased comparing to artificial saliva.

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Crystal lattice distortion in steel charged with cathodic hydrogen

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The requirements on modern steels include not only the high mechanical performances but also the improved resistance to hydrogen induced cracking[1] (HIC). Appropriate steel making technologies are established[,2] in order to produce microstructures with low HIC susceptibility. In order to investigate the influence of hydrogen on some microstructural characteristics, in this study the hydrogenation of steel was performed at high cathodic overpotential. Detrimental effects of hydrogen absorption and diffusion within the metal were traced by permeation technique, metallographic observations, and by X-ray diffraction measurements, Figure 1. The mechanical testing revealed that investigated coupons made from metallurgically clean, cathodically hydrogenated steel have low hydrogen embrittlement susceptibility, but metallography of charged specimens displayed characteristic internal stepwise cracks and surface blisters. Fractured surfaces also were characterized by quasy-cleavage and cleavage appearance typical for brittle cracking mechanism.
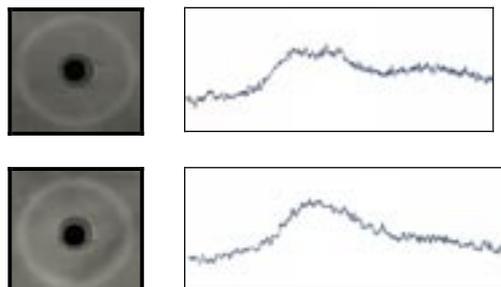

Figure 1. Diffraction patterns of Debye ring 310 Fe and adequate microphotometer records in
(a) noncharged pipeline steel

(b) H-charged pipeline steel

Increased diffusivity in Debye ring 310 Fe as well as the widening of the microphotometer record registered in H-charged steel are the result of hydrogen absorption within the metal. The observed changes are the consequence of microdeformations in crystal lattice. XRD examinations have shown that HER at high cathodic overpotential accelerated hydrogen trapping in steel and subsequent lattice distortion appears. Therefore, the residual stresses on the basis of XRD-data were calculated. It was shown that trapping of hydrogen at imperfections in steel matrix resulted in significant increase of residual stresses. In accordance to this, dislocation density have been increased upon charging too.

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Corrosion: from Nanostructure to Structural Failure

The mechanism of copper and silver dissolution under cathodic polarization in sour solutions

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According to electrochemical kinetic the rate anodic dissolution of metals should to decrease at displacement of potential in area cathodic of meanings but in practice the appreciable dissolution of metals is observed. This phenomenon has received the name of anomalous (chemical) dissolution. Basically it is investigated on iron and is explained by chemical interaction of metal with an acid.

Copper and silver are dissolved only at the presence of oxygen. Even in very sour deaerated solutions (1M HCl) the oxidation copper under cathodic polarization is insignificant a little, but in the area of potentials of allocation of hydrogen the appreciable growth of speed of dissolution is observed. The introduction in a working solution peroxide of hydrogen or also results others oxygen-containing of oxidizers in increase of rate of dissolution in several times.

It is supposed, that the oxidation of silver and copper at cathodic potentials is possible only at cathodic restoration of oxidizers, as a result of which the concentration adsorption of hydroxide-ions is increased, as causes oxidation of metal at negative cathodic potentials. Thus, under cathodic polarization three electrochemical processes take place: reducing of an oxidizer, and simultaneous oxidation of metal. By virtue of that products of oxidation copper and silver are easily reduced, first two processes become complicated them cathodic by restoration.

Corrosion Protection of AA2219 via Anodic Oxide Formation

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Al-Cu alloys, such as AA2219, are highly desirable in the aerospace industry due to their high strength to weight ratios. In order to increase corrosion resistance, these alloys are typically anodised with DC currents in acidic solutions. However, this process frequently results in the dissolution of Cu-rich areas of the metal surface. To resolve this problem, an AC/DC spark anodisation method utilising an alkaline silicate bath has been developed. The research presented here has focussed on the optimisation of the anodising bath parameters, namely the pH and silicate concentration.

The anodically formed films have been chiefly evaluated using three techniques. Scanning electron microscopy (SEM) has been used to characterise the film morphology, and to determine the loss or retention of the Cu-rich constituents. Cyclic voltammetry in a pH 7 borate solution has given information on the surface coverage and quality of the as-formed oxide films. Finally, accelerated corrosion testing has been carried out by immersion in 5 % NaCl and tracking the changes in the film resistance and capacitance with time using electrochemical impedance spectroscopy (EIS).

Cross-sectional SEM imaging has determined that the Cu-rich constituents of AA2219 are retained during the spark anodisation process, while top-down images show that the oxide is quite porous (Figure 1). The electrochemical experiments have shown that the corrosion resistance of spark anodised AA2219 can be improved by increasing the silicate concentration in an anodising bath of optimised pH.
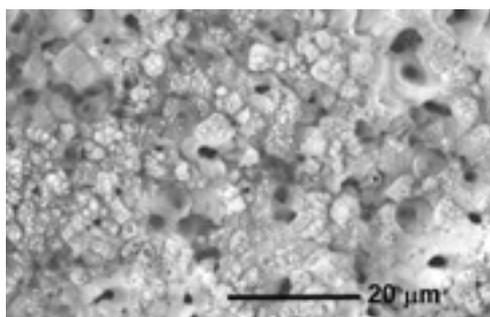
Figure 1: Top-down SEM Image of Spark Anodised AA2219 at 1600 X.

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Corrosion: from Nanostructure to Structural Failure

Halide ions as initiators of corrosion of Cu and Zn metals and Cu-xZn alloys in alkaline solution

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The polarization behaviour of copper and zinc was examined in slightly alkaline solutions containing various halide ions in order to determine whether the type of halide has an effect on the electrochemical behavior. Secondly, the effect of zinc content on the corrosion resistance of the Cu-xZn alloys was investigated.

The passivity of copper-zinc alloys with zinc content up to 40 wt. % is mainly governed by the copper component and is based on the formation of copper oxide. The formation of zinc oxide becomes more pronounced with increasing zinc content in the alloy. The addition of F^-, Cl^- and Br^- ions to borate buffer promotes the localized breakdown of the passive oxide film of all the materials investigated. The susceptibility to localized corrosion was expressed quantitatively by the dependence of breakdown potential on the concentration of halide ions. E_b vs. log c (NaX) diagrams are constructed for Cu, Zn and four Cu-xZn alloys. In general, the breakdown potential shifts towards more negative values with increasing concentration of halide ions. The most aggressive halides, in terms of localized breakdown of the passive film, are chloride ions, followed by bromide and then fluoride. Prolonged oxidation is accompanied by the formation of cupric oxy-halide compounds. For a constant type and concentration of halide ion, the breakdown potential shifts to more negative values with increasing content of zinc in the alloy. The slopes of the related curves are relatively small indicating that, for a given concentration of halide, the type of ion plays a more important role in corrosion resistance than the zinc content in the alloy.

The effect of iodide ion on copper and copper-zinc alloys differs from that of other halide ions. The formation of a passive oxide layer is prevented due to the formation of very slowly soluble copper iodide. Due to the low solubility this layer partially inhibits further oxidation, as evidenced by the independence of current density on potential. At more positive potentials it becomes unstable due to oxidation of I^- to I_3^- and/or I_2.

In the case of zinc metal, all halide ions promote localized breakdown of the zinc oxide layer. This effect was considered to be related to the low stability constants of complexes between zinc and halide ions.
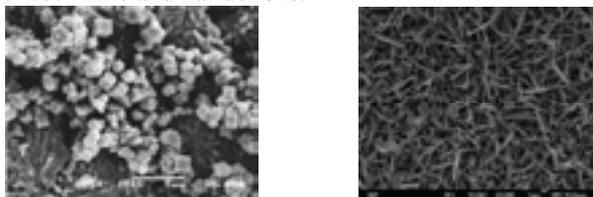

Fig. 4. SEM images of the corrosion products formed on Cu in borate buffer containing (a) 0.1 M NaCl and (b) 0.1 M NaI.

The inhibition effect of some amino acids towards lead-alloy corrosion in sulfuric acid solution

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Corrosion is one of the main reasons of surface damage and it strongly influences instruments lifetime. Therefore, study of surface modification is important to prevent corrosion. An important method for protection of metals against deterioration from corrosion is using inhibitors [1-3]. Unfortunately, many common corrosion inhibitors are health hazards for the inhibition of corrosion in aqueous media [4, 5]. To solve this problem, some of researchers investigated the inhibition effect of amino acids on corrosion of metals. These inhibitors are nontoxic, low cost and easy to produce in purities greater than 99% [6, 7].

In this work, the inhibition effect of some amino acids such as cysteine, towards the corrosion of lead-alloy in H_2SO_4 solution was investigated by potentiodynamic polarization, impedance, weight loss measurement and SEM methods. Corrosion data such as corrosion current (i_{corr}), corrosion potential (E_{corr}) and corrosion resistance (R_p) were determined from cathodic and anodic branches of Tafel plot. The effect of temperature, inhibitor and acid concentration against inhibitor action was investigated. Recording impedance spectra show that by increasing adsorption time, charge transfer resistance was increased. SEM images present that with increasing inhibitor concentration, corrosive surface area was decreased. The inhibition efficiency (IE) depended on the type of amino acid and its concentration. The IE for 0.1 M cysteine in 0.5 M H_2SO_4 is more than 95%.

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Corrosion: from Nanostructure to Structural Failure

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The role of microstructure in local corrosion of carbon steels in alkaline solution

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The regularity of carbon steels passivation and local corrosion processes in 0.2M H_3BO_3 +0.05M $Na_2B_4O_7$ + XM Na_2SO_4 (X = 0 ÷ 0.05 mpl) at room temperature were analyzed. Carbon mass fracture was changed within g_C = 0.005 (microstructure includes grains of ferrite α-Fe and cementite Fe_3C) and g_C = 0.297 ÷ 0.910% (microstructure includes grains of ferrite α-Fe and pearlite – eutectoid mixture of α-Fe and Fe_3C).

The results have shown that passive film composition doesn't depend on microstructure of all investigated alloys and includes inner layer Fe_3O_4 and hydrated outer layer γ-Fe_2O_3. At the same time it was obtained that the increase of carbon content was lead to stabilization of the Fe-C alloys passive state. This effect was connected with presence of more active H_2O molecules on interface high carbon steel/solution due to increase of heterogeneity it's surface in comparison with mild steels [1]. As the result of this process there is the concentration adsorbed OH^- -ions rise and increase of passive surface part of alloy.

The addition in borate solution of 0.01 mpl sodium sulphate causes carbon steel local corrosion. The individual behavior of iron in local corrosion processes in comparison with other carbon steel was observed. This effect was connected with iron microstructure. So pits on iron are initiating on ferrite/cementite interface. They are representing damage of right form with spherical and shining metal bottom. At the same time the spots on carbon steel surface are representing the uniformly dissoluble pearlite grain. It is necessary to note that high carbon content in alloy decrease their corrosion stability.

The received at the present investigation results of aggressive ion concentration influence on local corrosion, corresponding the literature data [2, 3], permitted to do the conclusion about the adsorption mechanism of pit initiation with formation of two-dimensional $FeSO_4$ salt islands on passive layer, as it has been postulated for iron in halide-containing solutions.

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Role of Foreign Species in Nucleation and Growth of Crystalline Oxide in Amorphous Anodic Niobia

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In anodizing of niobium and tantalum at relatively high voltages of more than 50 V and at increased electrolyte temperatures field crystallization of amorphous anodic oxide occurs. The crystallization is detrimental for electrolytic capacitor application of the anodic oxides due to increased leakage current. Our recent studies have found that the air-formed oxide, which should be located at about 30% of the film thickness in the anodic niobia, becomes a nucleation site, with its growth proceeding toward the metal/film interface by inward migration of oxygen species in the crystalline oxide. The field crystallization can be suppressed by incorporation of foreign species from electrolyte as well as substrate. In the present study, two-layered films of Nb/Nb-Si and Nb-Si/Nb were anodized in order to examine the influence of silicon species on nucleation and growth of crystalline oxide separately.

Two types of specimens were prepared by magnetron sputtering: a thin layer of Nb-12 at% Si alloy superimposed on Nb (Nb-Si/Nb) and a thin layer of Nb superimposed on Nb-12 at% Si alloy (Nb/Nb-Si). They were anodized at a current density of 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K to 100 V with current decay for 3.6 ks. The outer superimposed layer was consumed by anodizing to about 55 V and 75 V for the Nb/Nb-Si and Nb-Si/Nb specimens respectively. Some specimens were annealed in air prior to anodizing to examine the influence of thermal oxide on field crystallization. Crystallization was examined by current transients as well as surface observations by SEM. The anodic films were also examined by GDOES and RBS.

No field crystallization occurred on the Nb/Nb-Si specimen. Even after thermal treatment at 523 K, which caused accelerated crystallization for niobium, uniform amorphous oxide was formed without growing crystalline oxide. Since no silicon species were present at the nucleation site, growth of crystalline oxide was effectively suppressed by the incorporation of silicon species in the inner layer of the anodic film. However, when prior thermal treatment was performed at 623 K, crystalline oxide was developed throughout the surface. The thermal treatment at this temperature formed crystalline thermal oxide. Once a certain size of crystalline oxide was developed, growth of crystalline oxide might not be suppressed by incorporation of silicon species.

Effective suppression of field crystallization was also observed for the Nb-Si/Nb specimen. Although crystalline oxide was found in the anodic film, but the number of the crystalline oxide was markedly reduced by the presence of the superimposed layer. The crystalline oxide might be formed at flaw regions of the anodic film. The silicon species are present even in the air-formed oxide such that nucleation of the crystalline oxide should be impeded during anodizing. It was also found that no accelerated field crystallization occurred even after thermal treatment up to 623 K.

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Corrosion: from Nanostructure to Structural Failure

Strengthening the corrosion protection properties of polyaniline based coatings

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Polyaniline and other conducting polymers continue to be of considerable interest as components of corrosion-resistant coating systems. Earlier we detected different extents of corrosion protection of mild steel [1], and aluminum alloy [2] by polyaniline doped with different organic sulfonic acids. In this study we investigated a possibility to strengthen the corrosion protection properties of polyaniline due to doping with nitric acid.

In order to estimate an influence of nitrate anions on the indicated properties we compared the corrosion protective performance of polyanilines doped with nitric, sulphuric, and phosphoric acids. An anticorrosion performances of coatings, made of 20/80 wt./wt. % polyaniline salt/ poly(vinylbutyral) compositions, at mild steel samples when exposing to aqueous 3.5% NaCl and 0.1 N hydrochloric acid solutions were evaluated. Potentiodynamic polarization studies were used to determine changes in the corrosion current and corrosion potential of mild steel.

Samples of mild steel coated with compositions of polyaniline, which was doped with nitric acid, exhibited corrosion rates in aqueous 3.5% NaCl solutions about 10 times less, and in 0.1 N HCl solutions, about 100 times less than observed for identical samples coated with compositions of polyaniline, which was doped with sulphuric or phosphoric acids. It was supposed that the substantial improvement of corrosion protection properties of polyaniline results from redox properties of nitrate anion possessing high standard redox potential.

The corrosion protective performance was characterized also by the anodic shift of corrosion potential in aqueous 3.5% NaCl solutions by about 100 mV and in 0.1 N HCl solutions, by about 150 mV. The obtained results indicate that mechanism of the corrosion protection of polyaniline doped with nitric acid is based on the anode process braking.

The promising results, which were shown by polyaniline doped with nitric acid, allow to hope for a substitution of the classical toxic corrosion inhibitors by this polymer.

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Formation of Porous Anodic Alumina Films in Hot Glycerol Solutions Containing Phosphate

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Non-thickness-limited growth of barrier-type anodic films on valve metals in hot dehydrated glycerol solution containing a dibasic potassium phosphate was reported by Melody et al. in 1998 [1]. Later, it was found that the anodic film formed were porous [2, 3]. The porous films can be formed on several valve metals, including aluminium, niobium, tantalum and titanium, in this electrolyte. Porous film growth in this electrolyte is of great interest from fundamental as well as practical points of view, since porous film cannot be formed easily on valve metals except for aluminium. In order to clarify the characteristic feature of the growth of porous films in hot glycerol solutions, we have examined the growth behaviour, structure and composition of porous anodic films on high purity aluminium in hot glycerol solution at constant formation voltages using scanning electron microscopy, transmission electron microscopy, glow discharge optical emission spectroscopy.

When aluminium was anodized in the freshly prepared hydrated glycerol solution containing 10 wt% dibasic potassium phosphate at 433 K, many cracked, non-porous films were developed. In contrast, anodizing in dehydrated solution resulted in the formation of porous anodic films with the morphology being similar to those formed in acid aqueous solutions at ambient temperature. The cell size increases with the formation voltages. The porous films formed in this electrolyte were almost free from the phosphorus species, in contrast to the anodic films formed in aqueous electrolytes. On repeated anodizing at a certain formation voltage in the same solution, the current density increased every time. This was associated with increased basicity of the electrolyte during anodizing. In fact, the addition of K_3PO_4 into the electrolyte enhanced the dissolution of alumina films formed. The use of the glycerol solution containing a mixture of KH_2PO_4 and K_2HPO_4 allowed to get reproducible results. The porosity of the anodic films, measured by re-anodizing in a borate buffer aqueous solution, was little influenced by the formation voltage.

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Corrosion inhibition of poly(n-vinylimidazole) and derivatives for copper and stainless steel

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The corrosion of the stainless steel and the copper is one of the most important processes as these materials are commonly used in industry. The polymeric coatings provide corrosion   inhibition by acting as a barrier layer between the substrate material and the environment [1-3]. The conductive polymers and the resins have been widely used for this purpose in the literature [4,5]. In this study, effect of N-vinylimidazole monomer, polymer (Scheme 1) and their carboxyl containing derivatives on corrosion inhibition of metals such as stainless steel (PC) and copper (Cu) was investigated in acidic medium. Corrosion rates were determined in the absence and presence of monomers and polymers. Polymers have also been coated on metal electrode as a thin film by dipping method. Corrosion currents were obtained by Tafel extrapolation from anodic and cathodic polarization curves of these films (Figure 1). Impedance measurements were used for characterization and polarization resistance was obtained from these measurements. The stability of polymeric coating was tested with time in acidic medium.
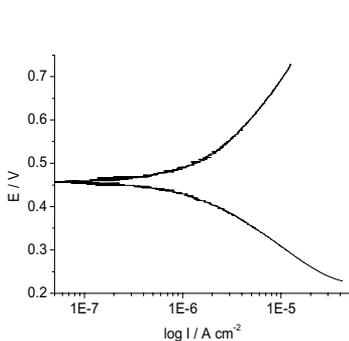
Figure 1: Tafel Plot of Stainless Steel in the presence of NVI in 1 N H_2SO_4
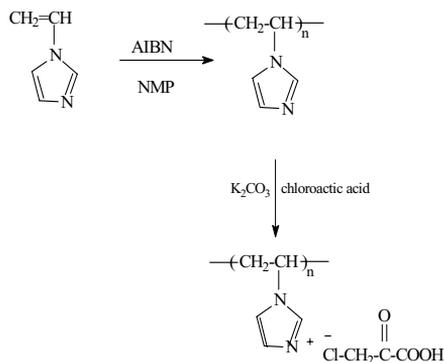
Scheme 1: Polymerization of N-vinylimidazole (NVI)

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Control of Gas Emission in Vacuum from the Surface of Anodized Aluminum Alloys

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Aluminum alloys are used for vacuum gas chambers in which various semiconductors or liquid crystal devices are chemically processed. For this purpose, aluminum alloys are anodized to give thick porous oxide films in sulfuric or oxalic acid solutions and sealed by dipping in a boiling water to prevent corrosion in an active gas atmosphere such as fluorine. However, thick porous layer emitted water vapor and other gases including chemical regent used for the processing. A barrier type oxide film would be beneficial for the suppression of gas emission although commercial Al alloys produce not a few amounts of defects in anodic films because of dispersed elements such as Si, Mg and Fe. The purpose of this study is to clarify gas emission property of anodized aluminum surfaces and to develop new barrier films having minimized defects and reduced gas emission property.

Figure 1 shows gas emission properties measured by mass spectrometry of anodized A5052 specimens associated with elevating temperature at 0.1 ˚C / s up to 300 ˚C. A porous type / barrier type composite anodic film was formed in oxalic acid at 20 V for 90 s or 120 s subsequent to re-anodization in adipate at 200V for 3 h. As it is clearly shown, the gas emission of composite films was effectively reduced with prolonged anodization time compared with the simple barrier type film formed in adipate. When a porous film was formed in sulfuric acid at 10V, the suppression effect was higher. The reduction of gas emission was occurred only when the porous film was thinner than the barrier film. As shown in Fig.2, SEM images of the cross section of composite films on 6061 indicate that capsulated porous film effectively prevents voids formation in the composite anodic film. Thus, it is clarified that the porous film growth in acid solutions on practical Al alloys controls the defect generation induced by alloy elements at the barrier film growth.
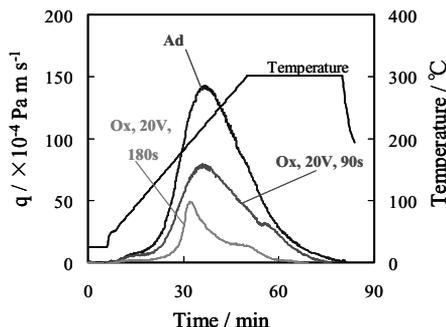

Fig.1 Emission property (H_2O) of anodized A5052 alloy. Ad : Barrie film in adipate, Ox : Composite film
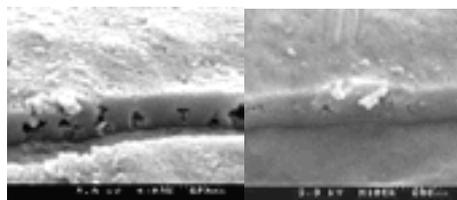

Fig.2 SEM images of anodized A6061 alloy. Left: Barrie film in adipate Light: Composite film

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Corrosion: from Nanostructure to Structural Failure

Electrochemical Corrosion Behavior of Carbon Steel with Phosphate Inhibitor in Drinking Water

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Although phosphate inhibitor has been used for over 60 years, there are controversies on the effect of the inhibitor in corrosion protection. The same debate has been applied to the issue of zinc addition. OCP (Open circuit potential) of the carbon steel specimen was measured for a given retention time of 5, 30, 60, and 80 minutes. According to the results, the deviations for 30 and 60 minutes were the smallest. Although OCP decreased to 0.5 mg/L with the change of residual chlorine concentration, it showed a trend of increasing with the concentration of 0.5 mg/L and higher. The results from Tafel test by adding 1) Phosphoric acid and 2) Phosphoric acid + Zinc suggested that corrosion is inhibited little under stagnant condition. After stirred thoroughly for 1 hr, the corrosion rate could be decreased to 61% and 81% with the addition of phosphoric acid and phosphoric acid + zinc, respectively.
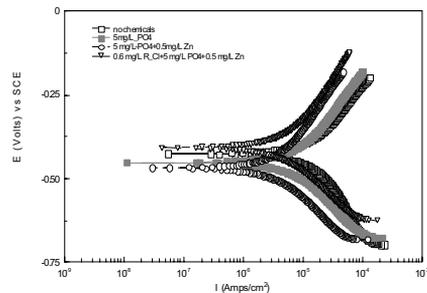
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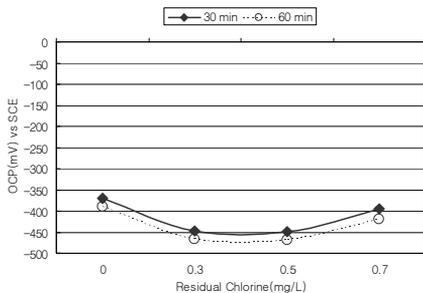
Fig. 1. **Open circuit potential Plots with residual chlorine concentration for stagnant time**

Fig.2. **Potentiodynamic plots on carbon steel specimens with residual chlorine and phosphate concentration in drinking water**

Impedance spectroscopy on micro cell array in crevice configuration

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In corrosion testing conventional electrochemical methods yield mean parameter values of heterogeneous surfaces. Information about localized parameters during the corrosion process is not available, especially in crevice corrosion. For the localisation of measurements micro techniques such as scanning electrochemical microscopy or scanning reference electrode technique have been developed. These methods use single or double electrodes to detect different parameters while scanning the electro-active surface. The main limitation of such methods is that the micro positioning systems cannot be applied in the usual corrosion testing devices such as salt spray or VDA testing chamber to gain the parameters during a simulated corrosion process.

A multiple micro cell array was constructed using double Pt disc electrodes of 50μm diameter placed in a 2-dimensional plane with a distance of 5 mm between the separate double electrodes. The electrodes are fused in glass and fixed with epoxy resin into a printed circuit board. The electrodes are connected to a multiplexer/frequency analyzer measuring system. The control program for this equipment consists of three parts: The graphical user interface, a database containing parameters and data and the control of the scanning instruments.

The microelectrode array is bonded to the strip steel sample leaving a crevice with a width of 150μm-250μm. With this setup the in situ detection of solution parameters during a crevice corrosion process is possible without any influence caused by electrode movement inside the gap. The local conductivity is measured by recording impedance spectra between all twin electrodes connected subsequently by the multiplexer. The conductivity stands as a parameter for the wetting of the crevice and the concentration changes of the conducting electrolyte.. The mapping of the conductivity shows wetted areas. At these electrolyte borderlines the corrosion process started as optical inspection proved.

This method allows conclusions about the start of a corrosion process over several wetting and drying cycles Furthermore examinations for the understanding of the mechanism of crevice corrosion can be gained as different parameters of the solution can be recorded in situ with a very robust electrode setup of this multicell arrangement.

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Corrosion: from Nanostructure to Structural Failure

Nanoscale characterisation of anodic oxide films on Ti-6Al-4V alloy

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Titanium and titanium alloys are widely used as biomedical materials because of their attractive properties such as high strength, low Young modulus and good biocompatibility. However, they are unable to meet all the clinical requirements. Therefore, in order to improve their biological, chemical and/or mechanical properties, they are subjected to surface modification processes. In industrial practice, anodic oxidation in acidic solution is frequently used since it is a simple and effective method to modify the surface of titanium and its alloys (biocompatibility in vivo and corrosion immunity). Depending on applied voltage (i=const.) various thickness of anodic oxide films can be produced. A detailed knowledge of chemical composition of oxide layer on a nanometer scale may help to understood their good corrosion resistant. Surface analytical techniques like AES or XPS combined with Ar+ ion sputtering allow to investigate the interface/interphase region and examine its chemical properties. The aim of the present work is to characterize in nanoscale anodic oxide film obtained at different voltages on Ti-6Al-4V alloy and to determine its influence on corrosion resistance of this alloy.

Surface characterizations were performed using a Microlab 350 located at the Physical Chemistry of Materials Centre of the Institute of Physical Chemistry, PAS and of the Faculty of Materials Science and Engineering, WUT.

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Corrosion: from Nanostructure to Structural Failure

Electrocatalytic processes at the formation of chromium deposits from Cr(III) electrolytes with organic additives

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From the environmental viewpoint, the replacement of toxic Cr(VI) electrolytes by Cr(III) electrolytes in Cr electroplating is of great practical interest. Recent studies (including those by our group) have shown that chromium coatings of high quality as regards their corrosion resistance and physicochemical, mechanical, decorative and other characteristics can be obtained from Cr(III) electrolytes containing certain organic substances, particularly, formic and oxalic acids. At the same time, these deposits exhibit certain characteristic features, which distinguish them from the deposits formed in conventional Cr(VI) electrolytes. Thus, it was shown that their composition involves considerable amounts of carbon-containing species (up to 7 wt. %), they have the crystallographically amorphous structure, and their corrosion potential in 0.5 M H_2SO_4 is shifted by $0.3 – 0.4$ V in the positive direction as compared with electrodes of crystalline chromium and falls in the passivity range.

To elucidate the role played by organic additives in the electrodeposition of chromium from Cr(III) electrolytes, we carried out detailed studies of the composition, structure, and properties of these deposits. For this purpose, we used basic electrochemical methods as well as XPS, X-ray emission spectroscopy (XES), XRD, and chromatography mass-spectrometry (CMS).

To determine the composition of organic products incorporated into Cr deposits, the latter were dissolved in 6 M HCl and the organic products were extracted from the resulting solution with chloroform and analyzed using the CMS method. It was found that no more than 10% of the total amount of carbon in the deposits was in the form of polymerization products of initial organic substances. The information of basic importance was obtained using the XES method. Based on the analysis of the spectrum of the Kβ satellite line of Cr, it was found that the main amount of carbon is in the form of a carbide compound of chromium. It should be noted that the possibility of so deep (in fact, the extreme) electrochemical reduction of organic substances up to the state carbon takes in the carbide compounds of metals was never mentioned earlier. This result suggests that crystalline chromium nuclei formed during its electrodeposition should be characterized by very high electrocatalytic activity.

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Corrosion: from Nanostructure to Structural Failure

Effect of anodizing on corrosion of al-zn alloy coated steels in chloride environments

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Coated steels are widely used, because of their excellent corrosion protection characteristics in atmospheric environments. The coated usually uses after Cr conversion treatment to improve adhesiveness of organic coating and increasing corrosion resistance. However, this treatment will not be used in near future, because of ill effects for environment and human body. Many researchers try to develop new Cr free treatment. Aluminum and its alloys are usually used after surface treatment processing, such as anodizing and painting. There are three types of anodic oxide films, a porous type, a barrier type and a composite type that can be formed on aluminum. The purpose of this study is to examine the effect of anodic oxide film structure on corrosion protection of Al- 45 mass% Zn coated steels.

The Al- 45 mass% Zn coated steel sheets (coated layer thickness of about 15 μm, Nippon Steel Co.) were cut into 15 x 20 mm coupons. Porous type anodic oxide films were formed by anodizing in 0.22 kmol/m^3 oxalic acid solution at 293 K and 3.72 kmol/m^3 sulfuric acid solution at 273K with a constant current density, i_a = 100 A/m^2. Composite type anodic oxide films were formed after formed porous type anodic oxide films in oxalic acid solution and then anodizing at 293 K in 0.5 kmol/m^3 H$_3$BO$_4$ / 0.05 kmol/m^3 Na$_2$B$_4$O$_7$ solution with a constant applied current density of i_a = 10 A/m^2. Some anodized specimens were sealed in boiling doubly distilled water for 900 s. Polarization curves of the specimens were measured by a potential scanning method, 0.33 mV/s in 0.5 kmol m^{-3} H$_3$BO$_3$ - 0.05 kmol m^{-3} Na$_2$B$_4$O$_7$ (pH = 7.4) with 0.01 kmol m^{-3} NaCl solutions. A corrosion potential in this study is the potential of current became higher than 100 mA cm^{-2} while polarization.

Table 1 shows summary of rest potentials and corrosion potentials of anodized specimens. The rest potentials do not change with treatments. The corrosion potential of anodized specimens almost same as without anodized specimens except for anodized in sulfuric acid solution. The most effective treatment is first anodized in sulfuric acid solution and then pore sealed.

Table 1 Corrosion potentials of anodized coated steels (mV vs. Ag/AgCl)

	Rest Potential	Corrosion potential
As-received	- 809	- 672
Porous type (Oxalic acid)	- 758	- 677
Porous type (Sulfuric acid)	- 997	- 375
Composite type	- 711	- 661
Pore Sealing(Sulfuric acid)	- 956	397

Effect of temperature on oxide film reformation of titanium in vitro with photon rupture

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Titanium and its alloys show a very good corrosion resistance and excellent medical compatibility. These remarkable properties are because of the oxide films formed on the surface of it. There are a large number of papers dedicated to the corrosion and passivity of titanium and its alloys. Analysis of abrupt destroyed of passive oxide films and its repair is important to understand the localized corrosion of titanium and its alloys. Analysis of this behavior has been carried out by monitoring potential- or current- transients after mechanically stripping of the oxide films. The mechanical film stripping poses problem in film stripping rate, contamination from stripping tools, and stress or strain on the substrate. Recently, film stripping by photon rupture (focused pulsed Nd-YAG laser beam irradiation) method, which resolves many of the problems has been reported. The irradiation of a pulsed laser beam is able to strip the oxide film at extremely high rate without any contamination from film removing tools.

In the present investigations, anodized titanium specimens were irradiated with one pulse of pulsed Nd-YAG laser beam in phosphate buffer solutions at constant potentials measuring the current transients to investigate the effect of solution temperature on initial stage of localized reformation of oxide films.

Titanium sheets (99.5 mass %) were cut into 10 x 10 mm^2 and then anodized. The anodized specimens were immersed in 8.1 mol/m^3 Na$_2$HPO$_4$/ 5 mol/m^3 KH$_2$PO$_4$ with 140 mol/m^3 NaCl + 50 mol/m^3 KCl solutions and irradiated by a pulsed Nd-YAG laser through a lens and quartz window at constant potentials. Current transients after the laser irradiation were measured by a computer through an A/D converter.

Figure 1 shows changes in current with time after laser irradiation at 1.5V. By laser irradiation, the current increases instantaneously through a maximum at about 0.4 ms, and then decreases exponentially with time at every temperature. The current increases with increasing temperature.
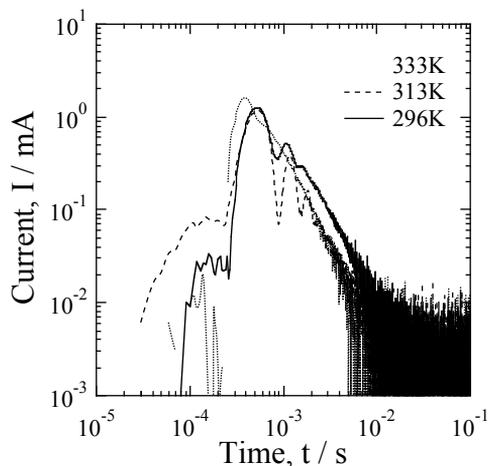

Fig. 1 Changes in current with time after laser irradiation at 1.5 V vs. Ag/AgCl.

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Corrosion: from Nanostructure to Structural Failure

Cathodic disbondment of different paint coatings on powder metallurgical steels

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The main goal of the present work has been to evaluate the cathodic disbondment experienced by two different paint coatings on various powder metallurgical (PM) steels obtained by the conventional pressed and sintered process. For this purpose, a commercial primer and an antirust paint (electrolytic minium) were applied on both Astaloy Mo + 0.5%C and Distaloy AE + 0.5%C PM steels. After that, cathodic protection was simulated by imposing a voltage of -1V on the coated samples at variable exposure time in 3.56% NaCl solution. Just before the cathodic delamination test was initiated, the centre of the painted metal sample was damaged with an intentionally artificial rounded defect in order to accelerate coating disbondment. The time required for the coating to disbond (delay time) as well as the evolution with time of the coating disbondment area were characterized according to ASTM G8 tests.

Results showed that, in general, disbondment occurred earlier and in greater extension on Astaloy Mo coated samples than on the Distaloy AE ones, for the case of the two studied coatings.

Open surface porosity was quantified by applying scanning electron microscopy (SEM) and an image processing program on both Astaloy Mo and Distaloy AE sintered samples, resulting greater for the former. This feature could be probably associated to a major and quicker adhesion loss for the Astaloy Mo sample compared to the Distaloy AE one.

On the other hand, a visual inspection of the samples after the tests revealed the existence and the absence of oxidation products on the surface of the Astaloy Mo and distaloy AE, respectively. In this sense, the compositional analysis of both metallic substrates, examined by Energy-Dispersive X-ray analysis (EDX), showed the presence of nickel in the Astaloy samples, which could improve the corrosion protection performance of these systems by impeding the oxidation of the surface exposed to the electrolyte trough the coating defect.

Size-controllable formation of Pore array into Si wafer using Electrochemical etching

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High-aspect-ratio etching is necessary to form nano- and micro-scaled pores, tubes and needles for various micro-systems. We have developed electrochemical etching process with aqueous HF solution to form high-aspect-ratio pores at selected areas on Si wafer [1]. In this process, arrayed inverted-pyramid-shaped micro-pits were preformed on the Si wafer. During the electrochemical etching, holes were diffused to the micro-pits arrayed areas and dissolved Si, forming micro-scaled pores, whose diameters were determined by that of the micro-pits. In this study, we attempted to focus holes at the tip of micro-pits to form pores with smaller diameters.

N-type Si(100) wafer with 5 Ωcm or 50 Ωcm of specific resistance was thermally oxidized to form SiO_2 layer. After the SiO_2 layer on the front surface was patterned to form 10-μm-squre array with photolithography and reactive ion etching, inverted-pyramid-shaped micro-pits were formed by anisotropic alkaline etching. Following removal of the SiO_2 layer on the back surface, a Au/Cr layer was evaporated there for electric contact. Then, the electrochemical etching was carried out with 1.0 wt% of aqueous HF solution at anodic over potential of 0.5 - 5.0 V.

At interface between Si wafer surface and electrolyte, space charge region (SCR) preventing hole pass is formed, whose depth is controllable with specific resistance and applied potential. Therefore, we investigated the influences of such parameters on the pore formation, aiming to adjust the depth of SCR with the depth of micro-pit to focus holes at the tip of micro-pit. With the low-resistivety Si wafer, the pores were not formed but the surface was roughened regardless of applied over potential. The SCR was suggested to be too shallow to prevent the hole pass. In order to expand the SCR, the high-resistivety Si wafer was used. By applying the voltage higher than 2.0 V, high-aspect-ratio pore with ca. 500-nm-diameter was formed at every tip of the micro-pit. In this case, the depth of SCR is theoretically estimated to be 5.7 - 8.5 μm, which is closed on that of the micro-pit. From these investigations, it is considered that the depth-adjusted SCR focused holes at the tip of micro-pit forming the submicron pore. In this pore formation, the diameter will be controlled by adjusting the depth of SCR and other electrochemical parameters.

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Corrosion: from Nanostructure to Structural Failure

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The role of chlorate and perchlorate ions on the iron passivity breakdown and its associated oscillatory phenomena in sulfuric acid solutions

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Oscillatory phenomena associated with localized corrosion of iron in halide-containing sulfuric acid solutions has been the subject of numerous studies. It was shown that oscillations are closely related with the breakdown/repair processes of the passive oxide film and the susceptibility of iron to pitting. Using a point defect model for the oxide growth and breakdown for the Felx M H_2SO_4+Cl⁻ system it was shown that simple periodic current oscillations are associated with general corrosion, which involves a uniform dissolution of the passive oxide film through a gradual removal of the oxide layer due to the formation of soluble surface complexes. On the other hand, complex periodic and aperiodic current oscillations indicate pitting corrosion induced by the occupation of an oxygen vacancy by halides and a localized attack of the passive oxide film [1,2]. Moreover, current oscillatory phenomena were used for the characterization of early and late stages of pitting as well as for the distinction between passive-active sate dissolution and polishing state dissolution [3,4].

In this study, oscillatory phenomena are used to explore the role of chlorate and perchlorate ions on the passivity breakdown of Fe in sulphuric acid solutions. There are different opinions about the effect of these anions on the stability of the oxide film. Some studies [5,6] report that, both chlorates and perchlorates, may induce pitting corrosion and others suggest that pechlorates induce a rapid increase of anodic current at transpassive potentials due to oxidation of iron and iron oxides from the passive film to hexavalent iron [7]. It is shown in this work that perchlorates are associated with simple periodic current oscillations across the passive-active transition indicating general corrosion. On the contrary, chlorates induce complex current oscillations. Characterization of the Fe surface by scanning electron microscopy reveals pits over the entire surface. Pitting was attributed to the presence of chlorides that are released by a chemical reaction during which chlorates oxidize ferrous ions resulting in chlorides and ferric ions. Studying the influence of ferrous ion additions in the solution and analyzing the current oscillations the occurrence of this reaction was confirmed.

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Performance of drag reducing additives in disturbed two-phase flow - a microelectrochemical approach

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Drag reducing additives are used in many industrial flow systems to decrease the wall friction between the flowing liquid and the solid and, thus, minimize energy losses. Flow induced localized corrosion (FILC) can be mitigated as well. The efficiency of such additives has been proven in one-phase and two-phase flow, even under conditions of disturbed flow. Measurements in the authors' lab already demonstrated that such additives can be effective under conditions of e.g. uneven wall surfaces and horizontal slug flow and can reduce the likelihood of initiation of FILC in sweet and sour oil & gas production systems. The maximum interaction energies between turbulent flowing liquids and the solid wall have been quantified only recently for the first time in terms of "freak energy densities", available by Wavelet diagnosis of microelectrochemical current noise data.

This method was used in the present paper to investigate the magnitude of local surface impacts arising from a gas pulsed impinging jet. This small laboratory device was tested in order to find out whether it could simulated the flow pattern and the flow intensities generally encountered in disturbed two-phase flow, e.g. under slug flow conditions. This would avoid using large, expensive and difficult-to-decontaminate high diameter slug flow loops.

The paper will first demonstrate the applicability of a specifically designed jet impingement flow rig for microelectrochemical quantification of local flow intensities under one-phase liquid flow up to high jet nozzle flow rates. It will be shown that the data obtained are comparable with results of former investigations using the same or similar drag reducing additives in different jet cells.

First results will be given for gas pulsed jet impingement of gold microelectrodes. The nitrogen gas is pulsed into a continuously flowing liquid jet stream (containing the hexacyanoferrate(II/III) tracer system) with pulse durations in the order of 50 milliseconds at pulse frequencies of 1 Hz. The current noise data were measured with a sampling rate of 100 kHz and subjected to a Wavelet analysis in order to evaluate the magnitude of local freak energy densities during the gas pulse periods. Data will be provided for the additive-free system and for the performance of additives composed of quaternary alkyl ammonium compounds and polyimines with different average molecular weights.

The unexpected effects arising from the presence of drag reducing additives are discussed with respect to the supermolecular structures formed by the additives and with back-up of rheological findings.

Corrosion: from Nanostructure to Structural Failure

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Corrosion: from Nanostructure to Structural Failure

Cathodic reactions on steel in aqueous solutions containing REM salts

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Rare earth metal (REM) salts are often used as a green alternative for chromium species during surface treatments of different metals and alloys, such as carbon steel, galvanized steel, zinc, aluminium and magnesium alloys. The main effect of the rare earth metals is to decrease the rate of the cathodic process, particularly of the oxygen reduction reaction, at the cathodic areas of the metal, at which local alkalinisation leads to precipitation of REM hydroxide. Nevertheless, according to Aldykiewicz *et al* [1], oxygen reduction is not necessary to obtain REM oxide/hydroxide precipitation, since precipitation can be observed in deaerated solutions as well, yet in form of thinner films than under aerated conditions. An other unexplained result from the literature is that cathodic-activation methods, applied in order to reduce the required treatment time for REM hydroxide precipitation lead sometimes to a loss of protective properties of the film [2].

The aim of this work is thus to analyse the whole cathodic process occurring at steel in REM salts containing solutions and to study its influence towards the corrosion rate of steel in a 0.5 M NaCl solution. The results of potentiodynamic experiments performed under different hydrodynamic conditions using a rotating steel disk electrode, and as a function of the concentration of REM in the solution are discussed. In addition, an electrochemical microbalance (EQMB) coated with gold, with or without a steel over layer, was used to follow the mass increase due to REM hydroxide precipitation, in the whole cathodic range.

It clearly appears that REM salts in aqueous solutions activate the reaction of water reduction, due to the formation of a REM-aqua-complexe [3]: the overpotential for the reduction of water bounded to REM is strongly decreased at a potential close to the equilibrium potential for water reduction. In the absence of oxygen, the reduction of activated water gets then the main cathodic reaction at the open-circuit potential, leading to polarization resistance values which are lower in the presence than in the absence of REM ions [4].

The cathodic processes at steel in a 0.5 M NaCl solution are compared and discussed for three different rare earth metals: Y(III), La(III) and Ce(III) salts.

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Effect of a chemical decontamination procedure on the corrosion state of the heat exchanger tubes of steam generators

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In this work, we present some findings obtained by the comprehensive investigation of the general corrosion state of 32 stainless steel samples, cut out from various locations of the steam generators of the Paks NPP (Hungary) in the time period of 2000-2005 [1]. In addition, surface properties (morphology, chemical and phase compositions) of the passive layer formed on the inner surface of above heat exchanger tubes were discussed, too.

The passivity of the inside surface of the stainless steel specimens was investigated by voltammetry, the morphology, chemical and phase compositions of the oxide layer formed on the surface were analysed by SEM-EDX, XRD and CEMS methods.

Based on the measured corrosion characteristics (corrosion rate, thickness and chemical composition of the protective oxide-layer) the steel tube samples can be classified into two groups. The samples that were never subjected to decontamination exhibit favourable corrosion behaviour. In contrast, the samples decontaminated by the AP-CITROX procedure (AP: alkaline permanganate; CITROX: citric and oxalic acid) have less favourable classifying. It is assumed that the chemical decontamination of the heat exchanger tubes does exert a detrimental effect on the morphology and corrosion state of steel surfaces. As an undesired consequence of the decontamination technology, a "hybrid" structure of the amorphous and crystalline phases is formed in the outermost surface region. It is important to pay attention for the tendency of the structure and morphology of protective oxide-films formed in the long run on decontaminated surfaces of heat exchanger tubes under normal operation conditions.

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Corrosion: from Nanostructure to Structural Failure

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Corrosion: from Nanostructure to Structural Failure

Studies of the Formation and Reduction of Oxide Layers at Au Electrodes in Acidic and Basic Media

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The growth of oxides on noble-metal electrodes involves a mechanism and a rate-determining step that depend on the experimental conditions. The electric field that develops across the metal-electrolyte interface gives rise to either *logarithmic* or *inverse-logarithmic* growth kinetics. The applicability of a given growth mechanism depends on the oxide thickness. Our previous research on the growth of oxides on noble metals shows that they possess a two-layer structure [1]; the inner layer grows to a limiting thickness, whilst the outer layer develops without reaching any limit and the metallic species is in a higher oxidation state. In the case of Au, the inner layer (AuO) grows to a limiting thickness of 3 MLs in acid electrolyte and 1 ML in basic ones [2]. In addition, the process is limited by an interface place exchange between the Au atoms and the O-containing species. The outer layer (Au_2O_3) grows without reaching any limit and the escape of the Au cation from the metal into the oxide is the rate determining step [3]. In this work we present new data on the growth of surface oxides on Au in aqueous acidic and basic electrolytes under well-defined polarization potential (E_p) and time conditions (t_p). Such formed oxide layers are then reduced in both acidic and basic media. We analyze the oxide growth in basic media and reduction in acidic ones, and vice versa. We observe three overlapping oxide-reduction peaks in CV profiles for films formed and reduced in acidic media at 2.15 V. There is a significant peak separation when the oxide formation and reduction is performed in basic electrolytes, as also observed for oxide layers grown in acid and reduced in alkaline medium. An opposite behaviour is observed for oxides formed in basic electrolytes and reduced in acid ones. These results suggest that oxides formed in acid and basic media have the same chemical composition. The observed peaks displacement is only associated to the pH of the electrolyte in which the oxide layers are formed or reduced.

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New thiadiazole derivatives as corrosion inhibitors of bronze artefacts

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The conservation and preservation of the cultural heritage is one of the main concerns today. From the family of ancient and historical metals, copper and bronze artefacts are unstable in oxygen-containing electrolytes and substantial improvement in their passivity is needed. To this regard, a range of organic compounds can offer a good protection against corrosion to the exposed copper and bronze surfaces in different aggressive media. Among them, benzotriazole (BTA) is widely used, but it is highly toxic [1].

In an attempt to find non-toxic alternatives to the conventional BTA, the efficiency of 2 mercapto-5-R-acetylamino-1,3,4-thiadiazole (**I**) and 2 mercapto-5-R-amino-1,3,4 thiadiazole (**II**) on the bronze corrosion was studied by electrochemical impedance spectroscopy and potentiodynamic polarization (Tafel extrapolation). The composition of the investigated bronze sample, Cu-6Sn (wt %) was chosen very close to that of different Bronze Age artefacts discovered in Transylvania, Romania, after a preliminary investigation by SEM-EDS.

The effect of thiadiazole derivatives on bronze corrosion was examined in different electrolytes (0.2 gL^{-1} Na_2SO_4 and 0.2 gL^{-1} $NaHCO_3$) and compared with that exerted in a solution simulating an acid rain (0.2 gL^{-1} Na_2SO_4+0.2 gL^{-1} $NaHCO_3$, pH=3) in an urban environment.

The calculated corrosion parameters showed that the thiadiazole derivatives reduce the rate of bronze corrosion (figure), their inhibiting action being attributed mainly to the blockage of the bronze surface by a protective film consisting of a polymeric Cu(I)-inhibitor complex in which the inhibitors acts as bidentate ligands through the aminic nitrogen atom and the closed ring nitrogen [2].
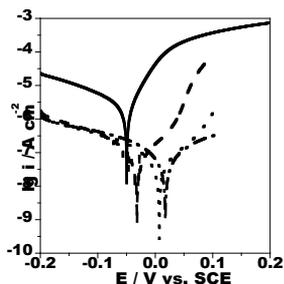
Figure. *Polarization curves of bronze in 0.2 gL^{-1} Na_2SO_4 in the absence (_) and in the presence of different concentrations of 2 mercapto-5-R-amino-1, 3, 4 thiadiazole (mM): (- - -) 0.01; (_____) 0.1; (-___) 1.*
Experimental conditions: scan rate, 0.33 mV s^{-1}; electrode rotation speed, 1000 rpm.

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Corrosion: from Nanostructure to Structural Failure

Monitoring, evolution and prediction of passivation processes on titanium materials

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Titanium and its Ti-6Al-7Nb alloy are used in dental and orthopedic implantology for their high corrosion resistance and mechanical properties. In conditions of long-term service, the pH changes on some zones of the implant can generate potential gradients that can initiate galvanic cells; the ions released into the surrounding tissues can affect the mineralisation process at the implant surface. Surface roughness allows the tissue growth into pores, contributing to the osseo-integration process and the biocompatibility increase.

The evolution of the passivation processes at the Ti or Ti-6Al-7Nb alloy / Ringer 2 solution or Carter-Brugirard artificial saliva interface was monitored for 4000 exposure hours. In time evaluation of material stability was studied by: a) monitoring of the open circuit potentials (E_{oc}) after different immersion periods during 4000 hours; statistical treatment of these potential values with Medcalc. Program provides histograms, scatter diagrams with corresponding regression equations which permit the prediction of the E_{oc} values for longer periods than experimental time; if the determination coefficients (D) have values from 0.7 to 1, the credibility of the prognosis is very good; b) analysis of the ion release quantity and its variation in time, using atomic absorption spectroscopy (AAS); c) determination of the surface roughness, applying atomic force microscopy (AFM).

Monitoring of the open circuit potentials during 4000 hours in Ringer 2 solution and Carter-Brugirard artificial saliva shows that these potentials oscillate around some electropositive values placed in the passive domain of titanium on Pourbaix diagram, denoting very good stability. The computing of scatter diagrams and regression equations presents a good percent of credibility. So, the calculated E_{oc} values with this Program were in concordance with the experimental results and the statistical treatment proved a valid method for prognosis. But, such predictions need more precautions because of the human body complexity.

The open circuit potential gradients $\Delta E_{oc}(c)$ due to the composition non-uniformity (with and without fluoride ions) of Carter-Brugirard artificial saliva which can appear along the implant surface were simulated and calculated; $\Delta E_{oc}(c)$ present low values during 4000 exposure hours and can not generate galvanic cells or local corrosion.

Ion release quantity increased in the first 400 - 600 immersion hours and tend to a constant level, due to the adsorption processes from solution: hydroxyl (OH^-), calcium (Ca^{2+}) or phosphorus (HPO_4^-) ions. These processes have a beneficial effect both for the osseo-integration process and the improvement of the passivation processes.

Oxygen reduction on brass is slightly alkaline solutions

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The corrosion resistance of Cu alloys, particularly brasses, strongly depends on the quality of their protective passive film. This study focuses on the influence of Zn as alloying element in the improvement of the corrosion resistance of brass (UNS 68700), using boric-borate buffer (pH = 7.8) as electrolyte.

The film growth rate and composition was evaluated spectrophotometrically, using reflectance spectroscopy. The spectral features are similar to those of copper.

Oxides were grown a various characteristic potentials. Potential affects both the thickness and the composition. The oxides reduction current is influenced by the zinc content in the alloy. This is also reflected in the reflectance spectra. Characterisation by means of impedance spectroscopy is also presented.

The effect of the presence of zinc in the oxygen reduction on brass is also analysed. This is investigated for both pre reduced and pre oxidised substrates. The differences in the number of electrons exchanged and in the Tafel slopes are presented and interpreted in terms of the passive film composition.

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The Corrosion Resistance of Electroless NiZnP Alloy

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The elements states on the electroless NiZnP deposit surface exposed in the air and immersed in 3.5 Wt% NaCl solution(pH 7.0) were comparatively studied by scanning electron microscope (SEM), X-ray energy dispersive spectrometry (EDX) and X-ray photoelectron spectroscopy (XPS). The each element on the NiZnP deposit surface mainly exist in high valence of compounds owing to having been oxidated in the air. The NaCl solution could accelerate to oxidate the deposit and formed the passivated film, which consists mainly of Ni_2O_3 and Zn^{2+} compounds. The corrosion resistance of the deposit in the NaCl solution relates to the passivated film which possesses the effect of obstruct. The anodic polarization behavior of the deposit in 3.5 Wt% NaCl solution(pH 7.0) was examined by electrochemical polarization, scanning electron microscope and X-ray energy dispersive spectrometry. The results show that the deposit can work as dissolving anodic deposit to protect steel, and the mechanism of the anodic polarization for the deposit in NaCl solution has been put forward.
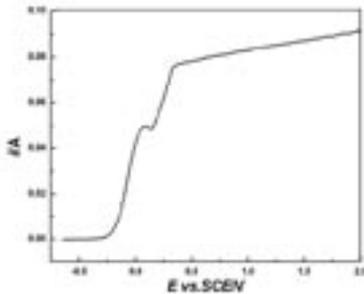
Fig.1 The anodic polarization curve of the NiZnP deposit in NaCl solution.
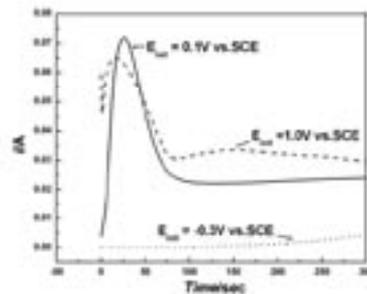

Fig.2 The curves of the current vs. time at different fixed potential: -0.3, 0.1, 1.0 V (vs.SCE).
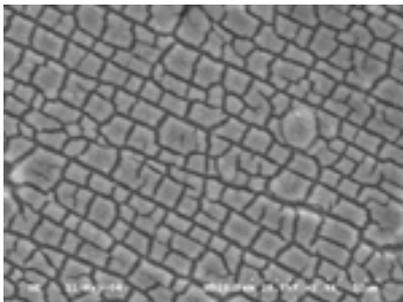

Fig.3 The Surface photo of the NiZnP deposit after anodic polarized in NaCl solution.

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Corrosion: from Nanostructure to Structural Failure

Optimal internal corrosion control method of drinking water distribution systems in Korea

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The internal corrosion of water distribution pipeline systems is the main cause for the problem of the pulbic health threat as well as water leakage in the deteriorated pipeline, red water, and odor and taste of the water. Especially, applications and investingations have been rarely studied and practiced on corrosion control by water agents and facilities for corrosion control of water distribuion systems in Korea although the public drinking water is relatively corrosive because of low hardness and alkalinity. After Lead and Copper Rule (LCR) was established in 1991 in the US, the application of proper corrosion inhibitors in the water treatment plants has been one of the most effective and economic corrosion control measures in combatting the corrosion problems in the water distribution pipeline systems.

This study has examined the effect of chemicals for pH and alkalinity control and corrosion inhibitors for producing the optimal corrosion control method. Corrosion study at different pH and alkalinity indicated that these control using alkaline chemicals was effective in corrosion rate, deposition rate, Fe release reduction, but an increase of turbidity was observed and corrosion-by-products (THMs) problems were caused. The turbidity showed a slight increase requiring caution in use of the control agent $Ca(OH)_2$. At pH 9.0, THMs concentration increased two times compared with non-control of pH. Using the pipe which had experienced 28 years of exposure, iron release was decreased with the corrosion inhibitor.

Consequently, pH, Alkalinity control method using alkaline chemicals must be complemented by corrosion inhibitor application for more efficient corrosion control. Apart from the type of chemicals, there are other factors to be considered such as water quality, pipeline corrosion condition, chemical concentraion and chemical costs.

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Corrosion: from Nanostructure to Structural Failure

Current Transients from Type-185N Stainless Steel Observed during Micro-indentation Test in pH 8.4 Borate Buffer Solution

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Type-185N stainless steel (0.009mass%C, 0.38Si, 0.31Mn, 0.025P, 0.0005S, 17.73Ni, 20.01Cr, 6.07Mo, 0.78Cu, 0.187N, bal. Fe) is gathering much attention because of its superior resistance against pitting corrosion. Micro-indentation test[1], in which a conical micro-indenter is driven downward to penetrate into and upward to remove from the passive metal surface under potentiostatic condition, is unique to analyse rupture and repair of passive film mechano-electrochemically. Here it was applied to type-185N stainless steel in order to investigate corrosion behaviour in pH 8.4 borate buffer solution. A couple of anodic current peaks emerged during downward and upward drives of the indenter as shown in Fig. 1. When the indenter traveled with a depth of 50 µm, the surface was deformed plastically with a depth of 11 µm. The intensity of the current peak during the upward drive was larger than that during the downward, suggesting that areas of ruptured film and substrate exposed to solution were larger during the upward drive. Current peaks during both drives depended on indenter-driving rate, v, as well as polarization potential, E. Comparison with type-304 and -316L stainless steels revealed that type-185 stainless steel emerged significant larger current peak than others in the case of relatively noble potential and high rate. It was considered due to selective dissolution of alloying element, i.e. molybdenum.
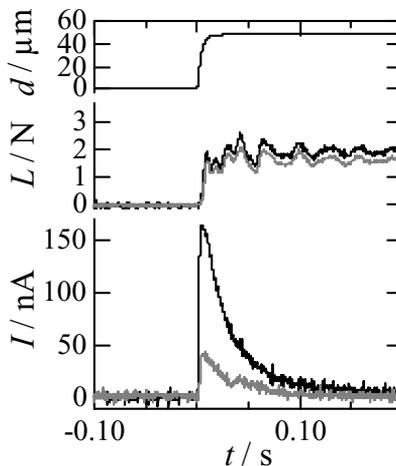
Fig. 1   Time-transients of indentation depth, **d**, load, **L**, and current, **I**, during downward driving of micro-indenter at v = 8 mm s^{-1} for the 316L and 185N stainless steel electrodes passivated at E = 0.4 V(SHE),

Reference

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Corrosion: from Nanostructure to Structural Failure

Study of organic anti-corrosion polymer on zinc-electroplated steel

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Polyaniline films were successfully synthesized on zinc-electroplated steel sheets in sodium salicylate aqueous medium in which silane was added by single-step electro-oxidation process, Corrosion behaviors of the films mentioned above is studied by salt spray test, anodic polarization experiment and electrochemical impedance spectroscopy (EIS) method. Experimental results show that of polyaniline coatings are close to the anticorrosion properties of chromating films because of its good shielding and inhibiting properties. Their formation   mechanisms were discussed and it was found that the sodium salicylate and silane inhabited the zinc dissolution and favoured the electropolymerization of polyaniline by passivating the substrate. The polyaniline films, whose corrosion behaviors were improved by using silane as passivate sealers, are a promising , environment-friendly technique for replacing the chromating films.
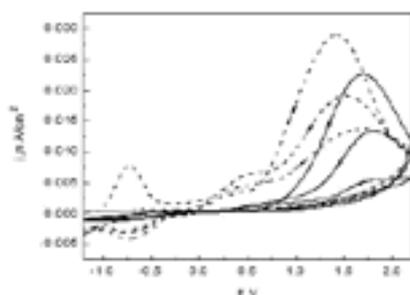

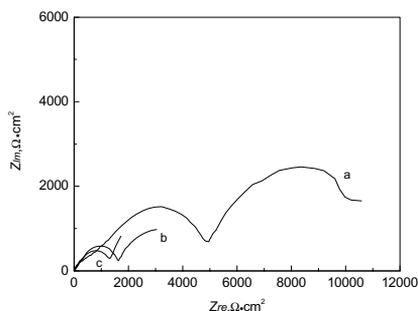Fig 1 Voltammetric curves electropolymerization of aniline on zincated steel

Fig.2   EIS of different samples in 3.5％ NaCl solution

The voltammetric behavior of the working electrode in a 1 mol·dm^{-3} sodium salicylatc and 0.5mol·dm^{-3} aniline solution obtained by sweeping the potential between -1.30V and 2.20V with 0.l/V • s^{-1} scan rate is presented in Fig.1. The peak at 1.5V, which corresponds to the anodic electropolymerization of   aniline. The current peak(-0.7V) results from the dissolution of zinc, and the adding of silane prevents the dissolution, making the films uniform and compact. Comparing the three sample, the Rct values of steel coated by PANI with silane added were larger than the two other samples, and among the three samples, the Rct values of chromating film was smallest, which showed the silane could improve the film's corrosion resistance effectively.

The Pani films were measured by observing the SEM micrographs of sever side The films(b) with silane added were more compact and uniform than that without silane(a), with no pits be found.

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Corrosion: from Nanostructure to Structural Failure

Hot corrosion of Fe-Cr alloys covered with a fused $(Na,K)_2SO_4$ film at 900^0C in air using electrochemical impedance

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Hot corrosion is the accelerated oxidation of metals and alloys covered with a thin film of fused salt deposit in an oxidizing gas atmosphere at elevated temperatures. Fused salts are usually ionically conducting electrolytes, thus hot corrosion is an electrochemical process in nature as aqueous corrosion. Some electrochemical techniques widely used in aqueous corrosion have been employed to study hot corrosion. However, most of up to date electrochemical studies of hot corrosion were conducted in deep melts. The establishment of electrochemical measurements under a thin film of fused salts is necessary for the eventual understanding of hot corrosion kinetics. In present paper, hot corrosion behavior of Fe-5Cr, Fe-10Cr and Fe-20Cr (in mass%) alloys in the presence of a fused $(Na,K)_2SO_4$ film has been examined by electrochemical impedance. The results indicated that the impedance spectra for the corrosion of both Fe-5Cr and Fe-10Cr showed the typical characteristics of a Warburg resistance. The alloys were attacked severely, forming a porous scale. However, the corrosion of Fe-20Cr included two different stages. In initial stage, a Cr-rich scale was formed on the alloy surface and the impedance spectra were composed of two capacitive loops. With extended reaction, the impedance spectra presented the features of a diffusion-controlled reaction, relating to the degradation of the protective scale caused by the fluxing of the oxide scale together with internal sulfidation of Cr. Equivalent circuits were proposed to describe the hot corrosion of the alloys, and the electrochemical parameters in the equivalent circuits were calculated. Hot corrosion mechanism of the alloys was also discussed in accordance with the changes of some parameters.

The corrosion performance and hardness of Zn-Ni-Al$_2$O$_3$ nanocomposite coatings

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Zn-Ni-Al$_2$O$_3$ nanocomposite coatings with uniformly dispersed nano α–alumina were synthesized with the aid of ultrasound [1]. The surface morphology of composite coatings observed by scanning electron microscopy (SEM) indicates that the ultrasound technique is an effective method to reducing the agglomeration and improving the amount of α-alumina particles embedded in the Zn-Ni alloy matrix. Their corrosion protection performance in 3.5% NaCl was investigated by using the AC impedance spectroscopy (EIS) technique and immersion test (5% NaCl regulate pH3.2 with acetic acid), which showed that Zn-Ni-Al$_2$O$_3$ coating exhibited a significant barrier property against the attack of corrosive products. The result of hardness showed that only a very low weight percent (5g/L) of Al$_2$O$_3$ nanoparticles in Zn-Ni-Al$_2$O$_3$ electrolyte would result in higher hardness of the coatings under ultrasound condition. The hardness of Zn-Ni-Al$_2$O$_3$ nanocomposite coatings and Zn-Ni alloy coatings were 439 and 223 HV, respectively. The hardness value of the former composite coatings was nearly 2 times higher than that of the later. The further study indicates the hardness increasing of Zn-Ni-Al$_2$O$_3$ coatings is attributing to the incorporate of nano scale α–alumina not the ultrasonic vibration [2].

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Corrosion: from Nanostructure to Structural Failure

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Corrosion: from Nanostructure to Structural Failure

A Numerical Model of Rupture and Repair of Passive Film on Iron in pH 8.4 Borate Buffer during Micro-indentation

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Micro-indentation test, in which a conical micro-indenter is driven downward to penetrate and upward to remove from the passive metal surface immersed in solution under potential controlling condition, is effective to gain an insight into healing ability of the surface as well as mechanical parameters. In the previous paper[1], it was applied to passive iron surface in pH 8.4 borate buffer solution and a couple of anodic current peaks and inconsistent changes in load corresponding to rupture and repair of passive film on the surface were observed. However, regardless of its importance for well understanding of the mechano-electrochemistry of passive surface, it was difficult to correlate load change with current transients during both downward and upward driving of the indenter. Here the numerical model for rupture and repair of the passive film during the downward driving indentation is proposed to discuss the correlation between load and current transients. In the model, the current flowing differential surface area is integrated all over the surface by using the following assumptions;

1) effective contact area of the indenter with the surface is proportional to load,
2) the area of total ruptured film is also proportional to load,
3) a part of ruptured sites is covered with the indenter penetrating into the substrate,
4) anodic current to repair the film can flow only at the exposing site, with which the indenter is uncovered, to solution, and
5) film repair is following with high field model under potentiostatic condition.

It was also considered parameters resulted from the comparison between current transients measured experimentally and estimated from load transient.

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The Influence of Organic Acids on the Corrosion of Pipeline Steels

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The importance of organic acids for the corrosion of pipeline steels can be expected in two situations, concerning respectively the external and internal corrosion of the pipeline: As soluble humic substances present in turf soils and as water soluble organic matter extracted from the transported oil by decanted water. To simulate these situations, corrosion experiments with different API steels were preceded in humic and fulvic acids extracted form different soils, as well as in water extractions from crude oil and in pure naftenic acids solutions. It was observed that naftenic acids strongly promote the corrosion of steels, while humic acids show a slight increase of the localized attack. In both cases the attack is related to presence of complex round inclusions, as showed by SEM and AFM analysis. Fulvic acids, in the other hand, were observed to act as natural corrosion inhibitors. Fig.1 shows the corrosion attack of API 5LX65 in a pure aqueous naftenic acid solution and voltammograms in naftenic acids extracted from crude oil.
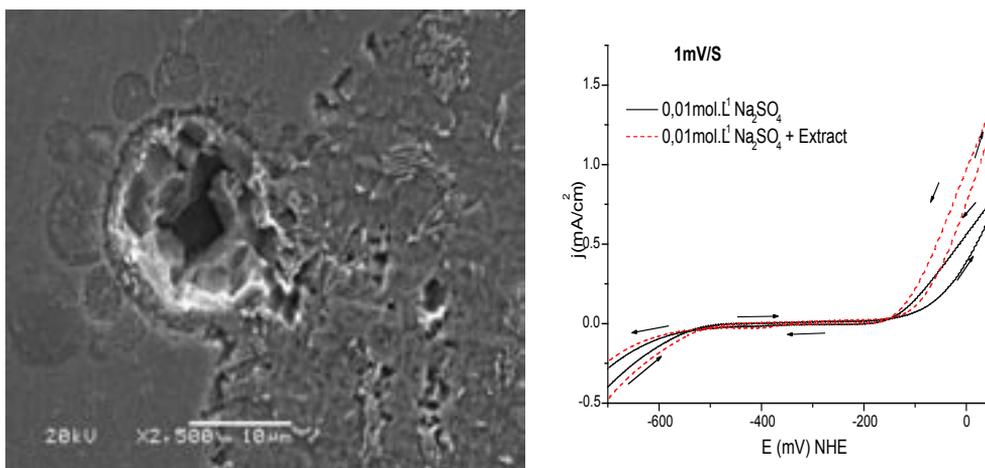

Fig. 1: Inclusion attack of API steel in aqueos solution of cyclopentanecarboxylic acid (1g/L) + Na_2SO_4 (0,01mol/L) and voltammograms showing the corrosivity of aqueous extracts of crude oil.

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Symposium 10

Fuel Cells and Sustainable Energy

Characterizing Novel Electrocatalytic Surfaces: Combined Electrochemical and Nuclear Magnetic Resonance Studies

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We have produced new platinum-lanthanide alloys for use in direct alcohol fuel cells (DAFCs) through a novel synthesis technique developed in our laboratories [1]. The $PrPt_2$ and $CePt_2$ catalysts exploit the lanthanide elements' favorable oxidation behavior to promote a bi-functional mechanism with platinum in the direct electrochemical oxidation of methanol and ethanol [1,2]. Through electrochemical and spectroscopic studies of these new catalysts and other commercially available catalysts, we seek a more complete, molecular-level understanding of the electrochemical oxidation of alcohols.

Details of the synthesis and characterization of the new catalysts, including transmission electron microscopy (TEM), x-ray diffraction (XRD), and x-ray absorption spectroscopy (XAS) will be presented. We also provide performance curves for the electrocatalysts in a PEM fuel cell. $PrPt_2$ and $CePt_2$ show improved performance over Pt-black in the direct oxidation of methanol [1]. In addition, both catalysts show similar activity to PtRu in the direct oxidation of ethanol [1]. Nuclear magnetic resonance (NMR) spectroscopy is used in conjunction with cyclic voltammetry (CV) to explore the surface chemistry of the new electrocatalysts. $^{13}CH_3OH$ was electrochemically adsorbed to $PrPt_2$, $CePt_2$, PtRu, and Pt catalysts in H_2SO_4 electrolyte at various electrode potentials. ^{13}C-NMR of the resulting surface species provides direct insight into the surface electronic structure of the catalysts. CV illustrates the relative activities of the four electrocatalysts via the onset potential of the oxidation peak for the adsorbed intermediate. In addition, quantitative treatment of ^{13}C-NMR signal and proper accounting of oxidation currents in CV suggest that the surface intermediate in the electro-oxidation of methanol on Pt-based electrocatalysts is a mixture of linear and bridged CO [3].

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Fuel Cells and Sustainable Energy

Symposium 10 - Keynote

Fuel Cells and Sustainable Energy

Electrochemical and electrocatalytic properties of supported mono- and bimetallic Pd nanoparticles.

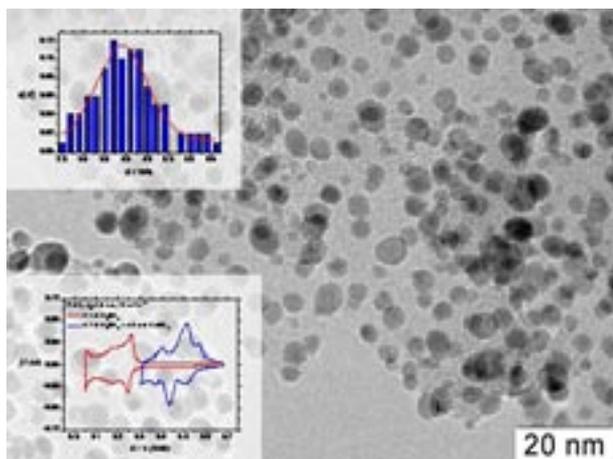Sergey N. Pronkin[1,2]*, Pavel S. Ruvinsky, Pavel A. Simonov, Elena R. Savinova

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Tailored nanoparticles supported on inert substrates are generally used as model systems in electrocatalysis linking well-defined single crystalline surfaces and real-type electrodes with complex structure. Fine tuning of structural parameters of tailored nanoparticles, such as size distribution, surface and bulk composition, inter-particle distances, grain boundaries formation, allows elucidation of the effect of these parameters on the electrochemical properties. This approach is especially attractive for Pd-based particles due to unique properties of Pd among other Pt-group metals. Low Pd-Pd interaction energy allows formation of wide variety of Pd-based bimetallic systems: alloys and pseudomorphic overlayers. Mixing with foreign metals and/or formation of α- and β-hydrides allows fine tuning of Pd structure in relatively wide range. Pd-based catalysts are cheaper and more abundant alternative to Pt due to their significant tolerance towards CO-poisoning and "soft hydrogenation" properties.

We present the study of electrochemical properties of tailored Pd nanoparticles, supported on low surface area (~6 m^2/g) carbon substrate of Sibunit family and their electrocatalytic performance in hydrogen oxidation and nitrate/nitrite reduction. Samples with different mean size (from 2 to 6 nm) were used to study size effects. Nanoparticles were characterized ex situ by HRTEM and in situ by electrochemical methods. Underpotential deposition of foreign metals (Cu, Sn) was used for Pd surface

20 nm

characterization and modification. The electrocatalytic properties of tailored nanoparticles were studied by conventional electrochemical techniques, as well as by rotating disk electrode and electrochemical impedance measurements.

We discuss the influence of the mean particle size and surface composition on the electrochemical properties (hydrogen ad- and absorption and metal underpotential deposition), and electrocatalytic activity in hydrogen oxidation and nitrate/nitrite reduction.

A Combinatorial Approach to the Study of Particle Size and Substrate Effects in Electrocatalysis

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A Physical Vapour Deposition system has been designed and built for thigh throughput materials synthesis, with adjustable source shutters that achieve a controllable gradient of depositing elements across a substrate or array of masked fields[1]. In an earlier paper, the system was employed to produce a compositional library of Pd/Pt/Au alloys on a 10 x 10 array of individually addressable Au electrodes (1 mm x 1 mm) on a silicon nitride substrate and it was shown that such arrays allowed the simultaneous recording of 100 electrochemical experiments[2]. In this paper, the same approach has been used to allow a detailed investigation of particle size and support effects on electrocatalysts. Here, the procedures are illustrated by a study of the kinetics of oxygen reduction at gold centres deposited onto both carbon and sub-stoichiometric titania and the results are compared with those obtained employing a RDE technique with disc surfaces also prepared within the PVD system. TEM analysis shows that on each pad in the array there is a distribution of gold centre sizes and in these experiments, the mean particle diameters on the pads of the single array ranged from ~ 1.4 nm to ~ 7 nm. The actual diameters and number density were used to estimate the real surface area of gold on each pad (assuming hemispherical growth of centres). The results indicate that there is a strong particle size effect on the catalytic activity of the gold centres supported on titania or carbon for oxygen reduction. Loss of activity is observed for very small centres with diameters below 2.5 nm and the trend implies that centres below 1 nm are totally inactive. In the case of titania supported Au particles, a maximum in oxygen reduction activity is also observed at particle sizes of ca. 3nm.

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Symposium 10 - Keynote

Fuel Cells and Sustainable Energy

Proton Generation and Transport in the Fuel Cell Environment

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Unlike in polymer electrolyte fuel cells (PEFCs) where hydrogen gas is used as protonic source, the hydrogen atoms in direct methanol fuel cells (DMFCs) are produced 'in situ' by dissociation of methanol on precious metal catalysts (Pt, Pt/Ru) in an aqueous environment. The abstraction of the first hydrogen atom via C-H bond cleavage is generally considered to be the rate-limiting step of dissociative methanol adsorption on the catalyst surface. This oxidation reaction on platinum alloys in a fuel cell is investigated by means of a combined approach of classical molecular dynamics (MD) simulations and ab initio calculations. Representative starting configurations for quantum-mechanical density functional theory calculations are chosen from MD simulations in order to include well-equilibrated solvation shells around the reactants. The main interest is to understand the role of the solvent for the stabilization of intermediates and for the enhancement of proton desorption from the catalyst surface and subsequent transfer into the nearby PEM [1]. The approch is currently extended to include the influence stepped surfaces.

The anodically generated protons in PEFCs and DMFCs need to migrate efficiently through the membrane to the cathode were they are consumed. At the same time water and methanol (in a direct methanol fuel cell) transport should be slow. Humidified PEMs are considered to consist of a nanometer-scale phase-separated bicontinuous network of polymer regions providing structural integrity and of aqueous regions providing the pathways for proton conduction. Molecular dynamics (MD) simulations provide a powerful theoretical tool for the investigation and clarification of the relationship between molecular structure and these transport phenomena. In recent years transport through individual pores of membranes were investigated by MD simulations [2]. These studies have been extended recently towards a more realistic description of the transport process in the membrane as a whole [3]. In order to atomistically model larger fractions of a humidified PEM, a coarse-grained model of humidified polymer electrolyte membranes has been developed. The repeat unit of Nafion 1100 is described by only 11 connected sites. By omitting the side chain, materials with main-chain sulfonation such as sPEK or sPEEK can be modelled. With the simple model large systems can be simulated over the long time periods needed to study pore dynamics.

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S10·KN-5

Investigation of bimetallic Pt-M/C as DMFC cathode catalysts

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Direct methanol fuel cells (DMFCs) have good potentialities for transportation applications and as portable power sources. Several drawbacks have hindered the large-scale diffusion of this technology. These mainly concern with significant device costs and methanol cross-over through the electrolyte membrane. Methanol cross-over results in a significant loss of efficiency for the DMFC because of two reactions compete on the Pt cathode, i.e. oxygen reduction and methanol oxidation. One possibility to solve this drawback is to use a selective oxygen reduction catalyst, characterized by a high methanol tolerance. Thus, it is necessary to develop novel Pt based electrocatalysts that promote oxygen reduction and reduce methanol oxidation at the cathode. Carbon-supported nanoparticles of Pt-Cu, Pt-Fe and Pt-Co were prepared for this purpose and characterized in terms of structure and morphology by XRD and TEM analyses. X-ray diffraction data showed a moderate degree of alloying in the as-prepared nanosized Pt-Fe, Pt-Cu and Pt-Co alloy catalysts. TEM analysis of the catalysts showed a good dispersion of the Pt particles on the carbon support with a relatively narrow size distribution. Oxygen reduction properties of these bimetallic catalysts were investigated by single cell DMFC polarizations. An improvement of the DMFC performance was observed in the activation controlled region in the presence of bimetallic catalysts. These catalysts appear to combine enhanced oxygen reduction properties to methanol tolerance characteristics.

Symposium 10 - Keynote

Fuel Cells and Sustainable Energy

DMFC: Towards understanding cell and stack function

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At small air flow rate DMFC enters the bifunctional regime (BFR) of operation: part of the cell at the inlet of the oxygen channel produces current, while the rest part of the cell consumes current to yield hydrogen. This phenomenon was discovered in experiments by Mueller and Dohle (as quoted in [1]) and independently by Ye et al [2].

Mueller—Dohle and Ye et al used the standard DMFCs with non—segmented electrodes; the onset of BFR in their experiments was detected by hydrogen evolution on the anode. We report the first direct observation of this novel phenomenon made with specially designed single—channel DMFC with segmented electrodes [3]. We present the shapes of local current along the channel at different operating conditions (Figure 1) and explain the physics of BFR using model of DMFC [1].

We also report the first model of a quasi—1D DMFC stack [3], which is based on single—cell model [1]. Analysis shows that dimensionless local potential of the bipolar plate (BP) satisfies Poisson equation $\Delta \widetilde{V} = \tilde{j}_A - \tilde{j}_B$, where $\tilde{j}_A, \tilde{j}_B$ are dimensionless current densities in the adjacent cells. Local cell voltage in turn equals the voltage drop between the adjacent BPs. Model of a stack is thus a self—consistent problem of current and voltage distribution in cells and BPs. We discuss voltage loss in the BPs and the effect of local resistive spots on the stack performance (Figure 2).
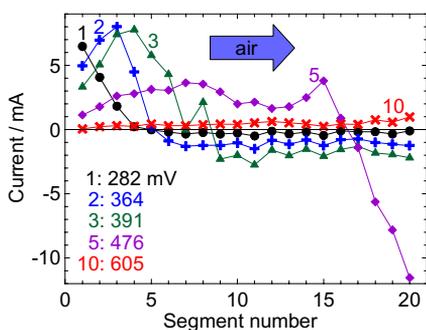

Figure 1. The distribution of local current along the single-channel DMFC for indicated air flow rates (ml min-1). Current in the external load is fixed at 8.5 mA. The electrolytic domain (negative current) is clearly seen.
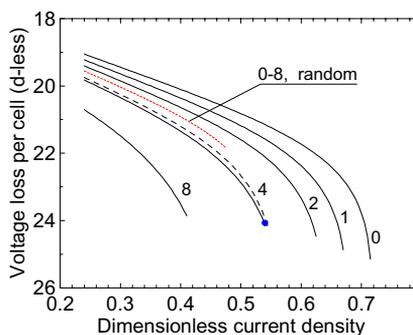
Figure 2. Polarization curve of 100-cell DMFC stack with the indicated number of resistive spots in each cell. Shown is the dimensionless voltage loss per cell as a function of mean current density.

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Aspects of Materials Research for Polymer Electrolyte Fuel Cells

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In recent years, Polymer Electrolyte Fuel Cell Systems have been demonstrated in various applications. In particular, demonstration projects related to transportation have shown that these fuel cell systems can be operated under the respective conditions. However, these demonstration projects also have shown that cost and reliability are still issues of paramount importance. Hence, materials research for this technology will still be an important challenge for the years to come.

We report on work carried out our in our laboratory, related to i) polymer membrane and ii) catalyst development.

i) Radiation grafting, followed by a subsequent sulfonation step, is a method to prepare potentially low-cost proton-conducting membranes. Introducing new monomer combinations to be grafted onto commercially available pre-formed polymer films allows enhancing the stability and performance during fuel cell operation, comparable to commercial products [1].

ii) Today Platinum, an essential cost factor, is still the choice for the electro-catalyst to be used in this technology. Partially substitution of Platinum may be achieved by Platinum oxide compounds, like $Bi_2Pt_xIr_{2-x}O_7$. Fundamental investigations of these Platinum containing oxide electrodes in contact to an aqueous electrolyte were carried out, to understand the influence of activation parameters on the Oxygen Reduction (ORR) and Methanol Oxidation Reaction (MOR) [2, 3].

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[2] N.K. Beck et al, Fuel Cells 6 (2006) 26-30

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Novel lscm based sofc for direct electrochemical oxidation of lpg

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In this study, we report on the suitability of $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) perovskite anodes for use of liquefied petroleum gas (LPG) fuels. Different methods of internal reforming of LPG have been studied. The anode material has been prepared by sol-gel method; they were optimized to obtain a single phase with high purity and crystallinity. Microstructural studies were carried out by SEM and the microstructure was related to the solid oxide fuel cell electrochemical properties. A slurry of LSCM/YSZ was deposited onto fully dense YSZ electrolyte. Fuel cell tests were performed for the fuel cell using different fuel mixtures such as steam reforming of C_3H_8 and a mixture of propane with oxygen at 900ºC temperature. The polarization resistances are about 0.5 Ωcm^{-2} under operating conditions. Different steam and POX reforming conditions were studied varying ratios of propane to steam and oxygen, according to viable operation conditions to avoid coke formation. Moreover polarization studies have been carried out under LPG atmosphere demonstrating the suitability of the LSCM anode component to run under such fuel.

Symposium 10 - Oral

Fuel Cells and Sustainable Energy

CO monolayer oxidation on Pt nanoparticles

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The electrochemical oxidation of CO adsorbed on platinum surfaces is a widely studied reaction in electrocatalysis because to the fact that CO is almost universally present as a surface poison, not only in the direct oxidation of organic fuels, in which CO is produced in a side reaction, but also in the oxidation of hydrogen coming from the reforming of these fuels, in which CO is present in the feed gas.

In this paper, CO monolayer oxidation on platinum nanoparticles with different shapes (semi-spherical, cubic and tetrahedral-hexagonal nanoparticles) and different sizes has been studied. The results obtained show a great dependence between bidimensional (111) and (100) ordered domains present on the surface of the nanoparticles and their CO electrocatalytic activity, specially for Pt nanoparticles in the size range 10 ± 2nm although similar tendencies can be also found for smaller Pt nanoparticles ≈ 4 nm.

In addition CO monolayer oxidation has been shown as a very sensitive reaction to the influence of the experimental parameters such as electrochemical activation of the surface, effect of the sweep rate, effect of the successive CO adsoption-oxidation. Thus, adsorbed CO oxidation has been revealed as an extremely structure sensitive reaction useful to establish correlations with the surface properties of platinum nanoparticles.
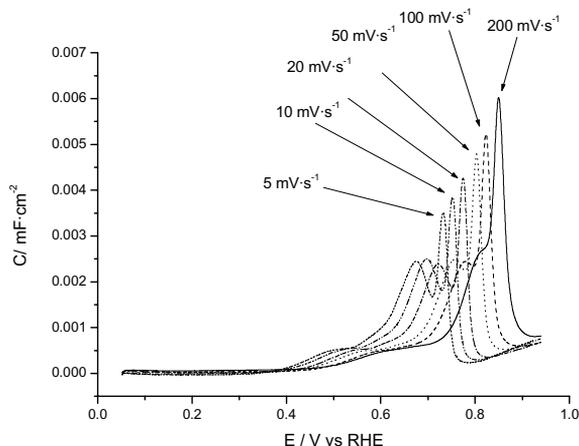
Figure 1. CO stripping voltammograms for preferential (100) Pt nanoparticles at different sweep rates. Particle size 9 ± 3 nm. Test solution: 0.5 M H_2SO_4.

Symposium 10 - Oral

Fuel Cells and Sustainable Energy

Electrocatalysis and electrochemical promotion of CO oxidation in PEM fuel cells: The role of oxygen crossover

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The electrochemical promotion of catalysis (or NEMCA effect) was studied for the CO oxidation and water gas shift reaction on a Pt anode in a PEM fuel cell. It was found that this phenomenon plays a significant role in a normal fuel cell operation (fuel mixture – air) but not in a hydrogen pumping operation (fuel mixture – H_2). This implies that the role of oxygen crossover in the electropromotion (EP) of CO oxidation is vital. The increase in the rate of CO consumption is 2.5 times larger, in fuel cell operation, while for oxygen bleeding conditions (fuel mixture + O_2 - air) the increase is 5 times larger than the electrochemical rate, I/2F of CO oxidation. This shows that the catalytic properties of the Pt anode are significantly modified by varying catalyst potential. In order to confirm the role of oxygen crossover, Nafion membranes (117, 1135) with different thickness, were studied. The results show that upon decreasing the membrane thickness the crossover is increased and thus the electrochemical promotion effect becomes more pronounced.

S10·O-3

Symposium 10 - Oral

Fuel Cells and Sustainable Energy

Can CO stripping voltammetry be used as a quantitative method for in situ fuel cell catalyst characterisation?

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CO stripping voltammetry is often used for fuel cell catalyst characterisation since commencement, peak potential and shape of CO stripping wave are surface sensitive [1] or the CO stripping charge is integrated and used for an estimation of the electrochemically active surface area. This latter procedure is connected with many uncertainties. Some of them arise from unknown type of CO bonding on the catalyst surface. The other uncertainty is connected with accurate CO stripping charge correction in respect to other contributions like double layer charging and charging due to metal oxide formation. This problem is significant since oxide formation on PtRu catalyst overlaps with CO oxidation. For this reason most of the studies in literature use CO stripping voltammetry only in a qualitative way and state that the surface area is only given (if it is given) as a relative and not absolute value. It was shown recently that the CO charge can be accurately determined by using IR (Infra-Red) [2] or DEMS (Differential Electrochemical Mass Spectroscopy) [3]. These techniques have one major advantage compared to voltammetric CO charge determination, namely CO charge determined in this way is free from other faradaic and non-faradaic contributions. However there are some disadvantages, like applicability of these techniques in the fuel cell labs and on real catalysts. In this study an attempt is made to overcome the difficulties in voltammetric CO charge determination by using a mathematical model of CO stripping and to show how this method can be used for surface area determination of fuel cell catalyst in a membrane electrode assembly.

The influence of temperature (20 – 60 °C) and of sweep rate (2 – 200 mV s^{-1}) was studied in a series of experiments. As model catalyst supported PtRu catalyst (Johnson Matthey) of nominal Pt : Ru composition 1 : 1 was used and tested in a three electrode electrochemical cell and also in a real fuel cell configuration. A mathematical model was developed assuming CO adsorption to take place on both the platinum and the ruthenium surface, water dissociative adsorption to take place mainly on the ruthenium surface and the surface reaction occurring between CO adsorbed either on platinum or ruthenium and reacting with OH adsorbed on the ruthenium surface. The model shows a good agreement with an experimental data.

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Symposium 10 - Oral

Fuel Cells and Sustainable Energy

Studies of Electrochemical Kinetics by Time-Resolved FTIR Reflection Spectroscopy

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In situ time-resolved reflection FTIR spectroscopy (TR-FTIRS) can provide both structural and transient information, and is a powerful tool for studying widely electrochemical kinetics at molecular level. Unfortunately, the large time constant of the thin-layer IR cell has greatly hampered its application for investigating fast kinetics. We have developed recently the TR-FTIRS to enhance its ability in time-resolving power, which consists in combining an IR microscope with a microelectrode to improve significantly the transient response of thin-layer configuration. Two techniques of in situ TR-FTIRS have been developed, namely the in situ step-scan time-resolved microscope FTIR spectroscopy (in situ SSTR-MFTIRS) [1,2] and the rapid-scan time-resolved microscope FTIR spectroscopy (in situ RSTR-MFTIRS) [3]. The former can reach a time resolution as fast as 10 μs, while that of the latter is about 13 ms.

In the current paper, we have put emphasis upon surface kinetic processes of the spontaneous dissociative adsorption and the electrocatalytic oxidation of methanol on PtRu catalysts. The figure shows the time-dependence CO species generated from dissociative adsorption of methanol on PtRu electrode in 0.5 M CH_3OH + 0.1M H_2SO_4 at different potential. It illustratesd clearly that the quantity of CO species increases

rapidly to a maximal value within 2 seconds. As the potential increases, the quantity of CO species then decreases gradually due to the oxidation. When the potential is exceeded 0.40V (SCE), the PtRu electrode is essentially free from the poisoning by CO species at steady state. The studies of time-resolved IR spectroscopy have gained an insight into the interaction between electrocatalysts and methanol in direct methanol fuel cell system.
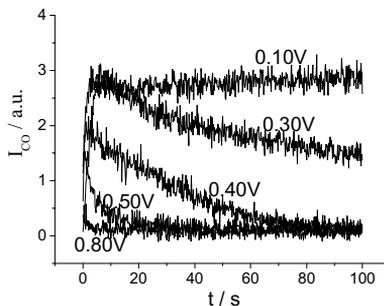
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Model studies in electrocatalysis: oxygen reduction at Ruthenium and Gold nanoparticles

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The electrocatalytic reduction of oxygen to water has attracted much interest in the last decade since it constitutes the cathode reaction in PEM-fuel cells. Much effort has been undertaken to replace the rare and expensive Pt, which, as metal or ally nanoparticle, is the current state-of-the art catalyst for this reaction. One route pursued in this regard is the use of Ru-based catalysts, which are prepared by thermolysis of Ru carbonyls [1] or via colloidal preparation [2]. The nature of these catalysts is still under debate. One hypothesis is that the Ru nanoparticles are superficially modified; this modification leads to enhanced stability and activity [3]. However, other models are also under discussion [4].

Our approach to investigate oxygen reduction at Ru nanoparticles is to deposit these on highly ordered pyrolytic graphite (HOPG). Different ways for depositing Ru have been used, including electrodeposition, thermal decomposition of Ru carbonyls and deposition of preformed colloids. The oxygen reduction activity has been investigated using rotating disc electrode measurements. Characterisation has been carried out using XPS and STM. The oxygen reduction activity of the deposited nanoparticles is considerably lower than that of carbon-supported Ru nanoparticles, indicating that the nature of both maybe different. Preliminary results on the modification of the ruthenium nanoparticles with catalytically active centres based on iron phtalocyanines will also be presented. This approach has been chosen, since we have shown, that modification of carbon-supported Ru nanoparticles with active centres based on the FeN_4C_x motif leads to enhanced oxygen reduction activity [5].

Similar investigations have also been carried out using Au nanoparticles. In this case, the oxygen reduction activity of nanoparticles deposited on HOPG is similar to that of carbon supported ones. However, interestingly, the oxygen reduction activity (in terms of peak potential in cyclic voltammograms) on carbon-supported Au nanoparticles strongly depends on the potential applied to the electrode before the oxygen reduction experiment. This is interpreted in terms of slow gold oxide reduction on the carbon-supported Au nanoparticles.

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Symposium 10 - Oral

Fuel Cells and Sustainable Energy

Anode and Fuel Cell Performances of CO Tolerant Pt Composite Catalysts with Organic Metal Complexes

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In reformate type polymer electrolyte fuel cells, the anode catalysts often suffer from CO poisoning, and thus the level of CO in the fuel gas must be lowered to less than 10 ppm before entering into the anode catalyst layer. Moreover, CO tolerant anode catalysts such as Pt-Ru alloy are used in practical operation. In order to reduce the cost in the future catalyst market, substitutes are desired that can reduce precious metal loading in the alloy. In this paper we report that some composite catalysts composed of Pt and organic metal complex co-catalysts can be good candidates for such purposes.

The composite catalysts were made from platinum precursor and organic metal complexes supported on carbon black (Vulcan XC-72R), then heat-treated in Ar at temperatures 300 to 600 °C. As the organic metal complexes, nitrogen containing ligands with transition metal are synthesized and screend by electrochemical half cell experiments, using half-MEA that was made by hot-pressing catalyst supported carbon paper (Toray TGP-H-090) on Nafion 115. Good candidates of complexes such as VO(salen) [oxo-vanadium N,N'-(salicylidene) ethylenediamine] or Ni(mqph) [nickel N, N'-mono-8-quinolyl-o-phenylenediamine] were tested for single cell experiments, where MEA of 4 cm^2 area was installed in fuel cell test station, and operated at 70 °C with CO containing H_2 (anode) and Air (cathode), humidified through water rervervoir.

Figure 1 shows polarization curves measured for MEA of Pt-VO(salen)/Nafion 115/Pt at single cell. It seems that except for the high polarization region, the catalyst shows good CO tolerance even at high level CO. A specific problem with this new catalysts is the MEA fabrication technique, in which the catalyst ink should carefully be prepared in order to guarantee good 3-pahse boundaries with the polymer electrolyte membrane. Search for additives to improve the properties of the paste of catalyst ink to facilitate good contact with the membrane is now under way.
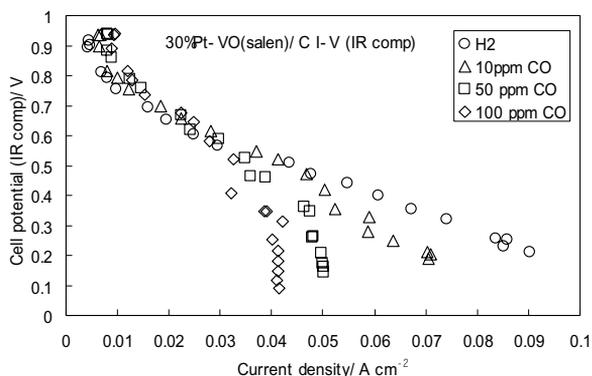

Fig. 1 Single cell experiment with the Pt-VO(salen)/Nafion 115/Pt MEA. Anode: 0.46mg cm^{-2} Pt+VO(salen), cathode: 1mg cm^{-2} Pt.

Reference: H. Yano, C. Ono, H. Shiroishi, T. Okada, Chem. Commn. **2005** (2005) 1212.

Platinized Carbon Nanotube-Modified Carbon Material for Fuel Cell Applications

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The amount of noble metal catalysts used in fuel cells is still limiting their application. Moreover, missing electrical contact between catalyst nanoparticles and the underlying carbon material and between adjacent carbon flakes severely prevents the productive use of the total catalyst loading. Carbon nanotubes are increasingly used as support material due to their excellent conductivity, chemical stability and high surface area.

In order to assure electrical contact to the noble metal catalyst nanoclusters we are proposing to grow carbon nanotubes on carbon fibers or carbon cloth. The modified carbon material is then simultaneously used as catalyst support, electrical contact and gas diffusion layer and provides a basis for a highly dispersed noble metal loading. Iron complexes were electrochemically deposited as catalyst for the growths of carbon nanotubes which was performed in a furnace in the presence of volatile carbon containing materials (Fig. 1). The obtained nanotube-modified carbon fibers were further modified with Pt micro- and nanoparticles using a variety of protocols.
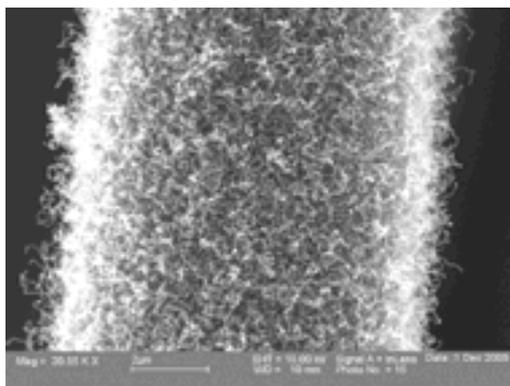

Fig. 1   PAN fiber modified with carbon nanotubes

The obtained catalyst modified carbon materials were evaluated using cyclic voltammetry and chronoamperometry for elucidating their electrocatalytic properties demonstrating the enhanced activity caused by the nanotube modification.

In addition, scanning electrochemical microscopy (SECM) in a newly developed oxygen-competition mode was used for evaluating the localized catalyst activity on the modified carbon material with high spatial resolution.

The obtained catalyst modified carbon material showed a tremendously increased catalytic activity for the electrocatalytic O_2 reduction both in cyclic voltammetry and in SECM visualization. The formation and evaluation of platinized nanotube-modified carbon materials for potential applications in fuel cells will be explained in detail.

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Highly-Active Non-Platinum Electrocatalysts for Oxygen Reduction Reaction

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Electrocatalysts for oxygen reduction reaction have attracted attentions of electrochemists and electrochemical engineers, because of their increasing importance in various applications, such as air cathode in fuel cells, metal/air batteries, and energy-saving brine electrolytic processes. Pt and Pt-based catalysts have been most widely used because of their high activity and stability. However, less expensive catalysts, if available, are preferred over precious metal catalysts. Many efforts have been made to explore non-precious metal catalysts, such as transition metal oxides, transition metal macrocycles, and alternative catalysts.

Recently, we have found that a highly active non-platinum catalyst for oxygen reduction whose activity is comparable to that of Pt/C can be prepared from the inorganic precursors consisting of transition metal hexacyanometallates (Prussian blue analogs) by heat-treating the precursors under an inert atmosphere[1, 2]. In this paper, we report oxygen reduction activity and methanol tolerance of the new electrocatalysts. The catalytic activity for oxygen reduction was examined with floating electrode and rotating ring-disk electrode techniques. Among a series of catalyst samples, the catalyst prepared from cobalt hexacyanoferrate and copper hexacyanoferrate precursors showed prominent catalytic activity for oxygen reduction.

Fig. 1 shows rotating ring-disk electrode data for oxygen reduction on HT(800)-Cu[Fe]PB/C in 1 M potassium phosphate buffer solution saturated with oxygen. Steep disk polarization (oxygen reduction) curves with well defined limiting current plateau were obtained together with small ring-current irrespective of a large collection efficiency of 0.48 from the RRDE dimensions. Apparent number of electrons transferred to O_2 for oxygen reduction reaction was calculated to be somewhere between 3.9 and 4.0 from the disk and ring current data shown in Fig. 1.

From these results together with IR and XPS measurements, the evolution of the high catalytic activity for oxygen reduction and the applicability of the present catalyst to fuel cell cathode will be discussed.

Fig. 1   Ring-disk polarization curves for oxygen reduction on HT(800)-Cu[Fe]PB/C in O_2 saturated phosphate buffer solution (pH 7.6).

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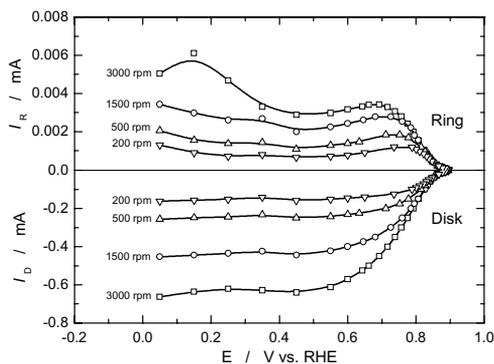# Co-sputtering: a novel approach for low pt loading fuel cell electrodes

A. Reiner*[a], F. Hajbolouri[a], M. Doebeli[b], S. Abolhassani-Dadras[a]
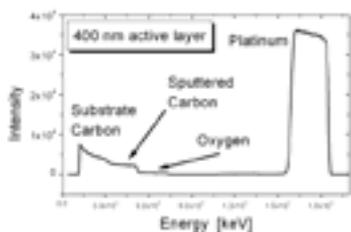A. Wokaun[a], G.G. Scherer[a]

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The reduction of the noble metal content in the catalyst layers of polymer electrolyte fuel cells (today mostly platinum) pose one of the challenges on the way to make fuel cell technology cost competitive. For reaching this goal the catalyst utilisation has to be increased to compensate for the desired decrease in total Pt content without performance penalty. Srinivasan [1] et al. investigated the Pt sputter technique to create a low Pt loading catalyst layer with high specific electrochemically active surface. In this work, we describe a new approach of co-sputtering Pt and C, covering all the aspects from fundamental investigations to fuel cells testing.

Simultaneous deposition of Pt and C via co-sputtering onto a substrate offers the possibility to create Pt particles in a carbon matrix. Pt particles are generally favoured in comparison to a Pt layer, due to the potentially higher surface to volume fraction and the principally lower mass transport limiting effects. Investigations by Transmission Electron Microscopy revealed [2] that Pt particle sizes of about one to two nanometer can be obtained. Applying Rutherford Backscattering Spectrometry, it can be seen from Figure 1 that both, platinum and carbon, are uniformly distributed throughout the layers. We deposited 100 nm to 700 nm thick films onto glassy carbon for characterisation purposes, corresponding to Pt loadings in the range of 0.023 mg/cm^2 to 1.225 mg/cm^2. Further, Pt/C-layers were also co-sputtered onto uncatalyzed gas diffusion electrodes and onto ion conducting membranes, taking advantage from the flexibility of the co-sputter process concerning layer thickness and substrate variation. Electrochemical characterisation via cyclic voltammograms was performed and the charge related to the hydrogen desorption reaction was used to determine the active surface area. The comparison to conventional fuel cell catalysts showed that comparable and even superior specific electrochemically active surface values can be achieved via co-sputtering. Finally, fuel cell electrodes with an area of 29.2 cm^2 have been prepared and tested, applying standard operating conditions, showing encouraging performance values, which will be given in the presentation.

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Fig. 1. Rutherford Backscattering Spectrometry measurements of a co-sputtered film with a thickness of 400 nm.

Interaction of methanol and formic acid with preliminarily adsorbed oxygen on polycrystalline platinum electrode at open-circuit conditions

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Investigations on the kinetics and mechanism of the interaction of HCO-substances with adsorbed oxygen (O_{ads}) are not only of scientific but also practical interest in connection with the problem of fuel crossover in fuel cells.

In this work, a monolayer (ML) of O_{ads} was formed on smooth polycrystalline Pt-electrode (pc Pt) in 0.5M H_2SO_4 by varying the electrode potential (E) under a certain program. To investigate the interaction of CH_3OH and HCOOH with O_{ads} ML, the method of open-circuit potential transients coupled with cathodic potentiodynamic pulses [1] was used. The latter made it possible to determine the shift of the surface coverage of O_{ads} (θ_O) and chemisorption products of investigated HCO-substances in the course of potential transient. The region of high θ_O (~1.0–0.8) was determined to account for the major part of time necessary to completely remove O_{ads} ML both in HCOOH and CH_3OH solutions. In this θ_O region, the process was suggested to be limited by direct interaction of HCOOH and CH_3OH molecules from the bulk with O_{ads} (Eley-Rideal mechanism). At the same time, the rates of O_{ads} interaction with HCOOH appeared to be ~5–6 times greater than with CH_3OH (at the same concentrations).

Cathodic potentiodynamic pulses showed that the chemisorption products of HCOOH and CH_3OH were not accumulated in substantial amounts on the sites that get free of O_{ads} (up to θ_O~0.2) in the course of potential decay. In the region of medium θ_O (~0.8–0.2), the interaction of CH_3OH and HCOOH with O_{ads} corresponds to the "conjugated reactions" mechanism [1]. However, good agreement of experimental and calculated E,t-dependencies (E – potential, t – time) was obtained only after introducing the corrections that taken into consideration the dissociative character of HCO-substances adsorption [2] into the equation used earlier (equation (4) in [1]). The optimal n value (the amount of particles into which the organic molecule splits) for CH_3OH appeared to be greater than for HCOOH (4 and 2, respectively), which agrees with the literature data for the chemisorption of these substances on Pt.

Thus, the mechanisms of CH_3OH and HCOOH interaction with O_{ads} on pc Pt at open-circuit conditions were determined to be analogous; however, substantial differences in kinetic parameters were observed.

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Enhancement of the oxidation of methyl formate at multifunctional electrocatalyst composed Pt/Pd and Pt/Ru nanoparticles

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Among organic compounds for anodic reactions in fuel cells, methanol has been most extensively studied. It is commonly accepted that binary Pt-Ru metallic centers are practically the most effective electrocatalysts for methanol oxidation. The ruthenium addition is expected to activate more readily water molecules on the metal surface and to produce Ru oxo species capable of interacting with the poisoning chemisorbed CO intermediate to yield CO_2 . Also the electrooxidation of formic acid at Pt/Pd nanoparticle catalyst has also been demonstrated to be a promising anodic process for fuel cell technology. The formic acid oxidation proceeds via so-called dual path mechanism comprising direct fast formation of CO_2 in addition to the generation of CO intermediate. Thus, when compared to methanol, the extent of CO-poisoning is less pronounced and the anodic current densities are higher in the case of formic acid. Electrooxidation of methyl formate (CH_3OCOH), a volatile ester with low boiling temperature (31.5 ºC), involves ideally eight electrons per molecule to produce carbon dioxide. The ester molecule consists of two (methanolic and formate) components, and the overall oxidation mechanism requires breaking of different bonds around two carbon atoms. The formate component of the ester is expected to be oxidized more rapidly than methanolic component. In the present work, we propose a multifunctional electrocatalytic system in which both Pt/Ru and Pt/Pd nanoparticles are assembled within tungsten oxide support. While Pt/Ru is expected to induce oxidation of primarily the methanolic part and secondary of the formate part of the ester, the Pt/Pd binary system should be particularly effective during electrooxidation of formate or formic acid. The ultra-thin layers of ruthenium oxo-species should also have some activating properties on noble metals nanoparticles during electrooxidation of methyl formate in 2 mol dm^{-3} H_2SO_4.. Comparison is made to the electrochemical behavior of methanol and formic acid under analogous conditions. It is rationalized that not only Pt/Ru is catalytic towards oxidation of methyl formate (or products of its hydrolysis) but also Pt/Pd is capable of promoting effectively the oxidation of formic acid or formate component of the ester. This multifunctional activity of co-deposited Pt/Ru and Pt/Pd centers is supported by good electronic and protonic conductivities of hydrated tungsten oxide matrix.

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Particle size and particle size distribution effect on the metanol and ethanol oxidation.

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Oxidation of methanol and ethanol has been studied on gas diffusion electrodes using DEMS to follow the oxidation products. In this work we report the results of the oxidation of methanol and ethanol on Pt and Pt-Rh nanoparticles dispersed on high area carbon (Vulcan XC-72). The nanoparticles were characterized by HRTEM. For the low metal loading, the particles present a relatively sharp distribution, but for high metal loading the size dispersion increases. Increasing the metal loading very large particles surrounded by very small particles was observed. We show that this kind of distribution has an important effect on the product distribution, mainly for methanol oxidation.

As a general trend, it is observed that the particle size has an effect on the reaction selectivity. It was found that partitioning of methanol products depends on the platinum nanoparticles. The intermediate size particles (3 to 10 nm) are more effective for the full oxidation to CO_2. It can be also postulated that coupling among the particles of different size in the same catalyst by the soluble products must be considered to understand the particle size effect on selectivity. The loss in CO_2 efficiency is due mainly to the formaldehyde production.

For ethanol oxidation the smaller particles are the most effective for the full oxidation to CO_2. It must be considered that ethanol oxidation to CO_2 entails the C-C bond scission and the smaller platinum particles are more effective to carry out this step with high efficiency. The thickness of the catalyst layer affects both the current density and the product distribution, again showing that connection between the particles inside the catalyst layer is important for the ethanol oxidation.

Pt-Rh bimetallic nanoparticles present a poor current density, compared to bulk Pt-Rh bimetallic electrodes for ethanol oxidation. This effect can be ascribed to the rhodium segregation to the particle surface. In spite of the low current density the Pt-Rh bimetallic nanoparticles present a good CO_2 efficiency, as observed for pure rhodium electrodes.

Structure-Reactivity Relationship of Metallic Nanoparticles

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We will present a novel approach to vary the size of supported platinum nanoparticles. Our new method enables the preparation of particles in the interval of 1 – 5 nm. Due to the combination of two preparation paths we can prepare particles with a very narrow size distribution. Furthermore we will discuss the structure-reactivity relationship.

A vast number of works try to understand the relationship between size, morphology and structure of nanostructured noble metal particles and their associated electrocatalytic activity.

For that purpose a preparation method which achieves two requirements is necessary.

(1) Nanoparticles with the particle size above 4 nm do not show significant size effects [1]. Therefore it is essential to prepare particles smaller than 4 to 5 nm.

(2) The thorough investigation of model catalyst systems demands supplementary a very narrow size distribution.

With the combination of the electrochemical and the chemical deposition we are now able to accomplish both of these requirements. We generate very small nuclei in the range of 0.7 to 1.2 nm by chemical deposition on glassy carbon. In a following step we use a low overpotential (η_{dep} = 14 mV) to grow the particle very slow and even up to 5 nm. TEM investigations allow the precise determination of the particle size and size distribution. The high resolution mode offers the possibility to get structural information of single particles. For the investigation of the reactivity we have chosen the CO monolayer oxidation because of its surface sensitivity and its relevance for fuel cell applications. We found a linear correlation between the particle size and the CO oxidation potential.

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Acknowledgment

Understanding the Implications of Doping PFSA Ionomers with Heteropoly Acids

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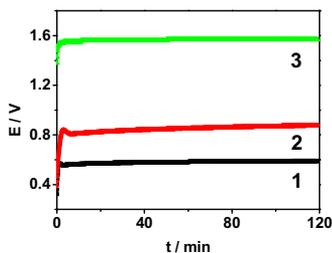*Colorado School of Mines, Golden, CO 80401-1887*
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Water electrolysis is one technique for hydrogen production alongside production from catalytic cracking of natural gas, methanol and ammonia reformation, pyrolysis and gasification processes [1-4]. The main obstacle to commercial exploitation of water electrolysis for large scale hydrogen production is the high electricity consumption, which makes the process economically unattractive offsetting the associated technical and environmental advantages [5]. Here an economic way to produce hydrogen by alcohol electrolysis is reported, a process that requires lower voltages than water electrolysis (*e.g.* E^o = 0.02 V *vs.* NHE for methanol compared to 1.23 V for water).

Figure 1 Voltage response at 20°C from galvanostatic electrolysis at a current density of 60mA cm^{-2} of: (1) 2 mol dm^{-3} methanol, (2) 2 mol dm^{-3} ethanol and (3) water at constant.

Fig.1 compared typical voltage responses with time for the electrolysis of methanol, ethanol and water at constant current density. A ratio of 1.3 was observed for the electrolytic voltages of methanol to water. This significant reduction in the electrolytic operation voltage will reduce the electricity consumption and the level of investment in the associated infrastructure. In economic terms for hydrogen production, the electricity plus methanol cost for production of 1 dm^3 H_2 is less than half of the cost when employing water electrolysis. The effects of the concentration of methanol and temperature on the electrolytic voltage were tested. The novelty of this technique is the inherent simplicity and substantially lowered cost. Different scale requirements can easily be achieved by using modified these PEMFC-MEAs as electrolyzers.

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New proton conducting semi-IPNs from PVA/PAMPS composites with plasticizer variants

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In DMFCs, although membranes that show high proton conductivity, and at the same time, low methanol permeability are strongly desired, there is achieved only a little progress because of trade-off relations between these parameters. We successfully proposed new families of cost-effective proton-conducting membranes based on chemically cross-linked PVA-PAMPS [poly(vinyl alcohol) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid)] composites.[1-3] In this work, we attempt to establish a concept of PVA-PAMPS based semi-interpenetrating polymer network (semi-IPNs) by incorporating plasticizer variants R (R = poly(ethylene glycol)(PEG), poly(ethylene glycol) methyl ether (PEGME), poly(ethylene glycol) dimethyl ether (PEGDE) and poly(ethylene glycol) diglycidyl ether (PEGDCE)) as the third components.

PVA-PAMPS-R semi-IPNs were prepared by a simple solution casting method where PVA (Mw = 124,000~186,000, Aldrich), PAMPS (Mw = 2,000,000, Aldrich) and plasticizers (R) were separately prepared and mixed to cast a membrane at ambient temperatures. Membranes were then soaked in 10% glutaraldehyde (GA, Wako) solution in acetone at 25°C. The cross-linking proceeded between the -OH of PVA and the –CHO of GA in the membrane due to an acid-catalyzed reaction by PAMPS.

PVA-PAMPS-R semi-IPNs showed high proton conductivity comparable to Nafion 117, while a low methanol permeability (P_M) with only 1/2 of Nafion 117 (Table 1). Thus a high selectivity (σ / P_M) was attained for these semi-IPNs that was 2 fold of Nafion 117. It is important to note that PVA-PAMPS-R semi-IPNs exhibited higher water uptake value in comparison with Nafion 117 (4-fold higher than that of Nafion 117), but the opposite trend was observed for methanol permeability. This may suggest that the microstructure of the membranes is highly improved by incorporating plasticizer variants. Incorporation of plasticizer variants promoted the hydrolytic and the oxidative stability of these semi-IPNs. These results are very promising, because the semi-IPNs are all hydrocarbon membranes made only of aliphatic skeletons, which is unique structure compared to most of the proposed membranes for DMFC applications.

Table 1 Proton conductivity (σ), ion exchange capacity (IEC), water uptake (WU), methanol

R	Composition PVA/PAMPS/R	Cross-linking time	σ/Scm^{-1}	IEC/m eq g^{-1}	WU/g g^{-1}	P_M/10^{6} cm^2 s^{-1}	σ/P_M/10^{4} Scm^{-3} s
PEGDCE	1:1:0.5	1 h	0.099	1.78	1.41	1.01	9.80
PEG	1:1:0.5	1 h	0.109	1.85	1.49	1.17	9.06
PEGME	1:1:0.4	1 h	0.103	1.96	1.43	1.02	11.8
PEGDE	1:1:0.3	40 min	0.099	1.43	1.48	0.96	10.3
Nafion 117			0.1	0.92	0.34	2.13	4.96

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PBI-based Membrane as Proton Conductor in HT-PEMFC. Synthesis, Physico-Chemical Characterisation, and Performance

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During the recent years, great efforts have been made to develop high-temperature (T>100ºC) proton exchange membrane fuel cells (HT-PEMFCs). These cells show an enhanced CO tolerance and the high operation-temperature also enables a better connection between the hydrogen storage and the fuel cell systems. Literature shows that polybenzimidazole (PBI) based membranes are one of the best candidates for its use in HT-PEMFCs[1].

The authors have proposed recently a new method to synthesise PBI[2]. This method allows synthesising reproducible polymer batches, reducing the reaction times and avoiding the appearance of polluting reaction by-products. In this work, the method has been improved in order to obtain polymer batches with intrinsic viscosities about 1.5. This polymer can be efficiently used to make a direct casting of the membrane so as to enhance the properties of the membrane. The influence of the ratios of the different raw materials (monomers, catalysts, polycondensating agents), the media, the temperature and reaction times on the synthesis of the PBI has been evaluated. It has been observed, that the temperature is the most significant parameter in the synthesis process. Once the synthesis procedure was optimized, membranes have been cast and then they have been characterised. It has been measured the phosphoric acid uptake; the kinetic of absorption; X-ray pattern; FTIR spectra and thermal stability as a function of the doping level; methanol permeability; the proton conductivity at different temperatures, relative humidities, and doping levels, obtaining the parameters of Arrhenius' law. Finally, doped membranes have been tested in a fuel cell set-up at temperatures between 100 and 175ºC, confirming their good predisposition for being a high temperature polymer electrolyte.

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Composites of functionalized polysiloxanes and nanostructured porous silicas as novel fuel cell membranes

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Hybrid materials based on functionalized polysiloxanes and highly ordered mesoporous host systems are developed as novel highly proton conducting fuel cell membranes operating at temperatures of 120-150°C. Compared to Nafion based membranes this class of hybrid materials promises improved thermal and mechanical stability and easier water management.

As porous hosts SiO_2-based mesoporous structures, called e.g. Si-MCM-41 or Si-SBA-15, are highly suitable due to their highly ordered and uniform pore systems. The diameters of their pores can be tailored in the range of 3-20 nm. Such materials are well-known for practical applications in adsorption, catalysis and nanotechnology. A high number of OH groups on the inner surface of the pores enables the anchoring of functional groups and/or the cross-linking of modified polysiloxanes.

After anchoring electrochemically active groups or ions on mesoporous silica layers via amino or ammonium functionalization in order to create as electrode layers or ion-permselective pH-switchable layers [1], we now expanded our method to the covalent anchoring of carboxylic acid groups (-COOH) or sulfonic acid groups (-SO_3H) on the inner walls of Si-MCM-41 or Si-SBA-15. Carboxylic acid groups were introduced with 2-cyanoethyltriethoxysilane, sulfonic acid groups via grafting with 3-mercaptopropyl-trimethoxysilane. In both cases an oxidation with H_2O_2 is the final step. Depending on the content of sulfonic acid groups, different proton conductivities could be measured by impedance spectroscopy. Optimum proton conductivity along the channels is achieved for about 15 wt-% of SO_3H groups. Fully hydrated Si-MCM-41 materials with anchored sulfonic acid groups exhibited proton conductivities above 0.01 S/cm placing them among the most promising solid electrolytes. The proton conductivity is strongly affected by the presence of water with the porous host matrix helping to store water at temperatures above 100°C.

By effective coupling and cross-linking with functionalized polysiloxanes, which by their own achieve proton conductivities of about 0.01 S/cm a further improvement in the proton transport is expected, measurements are currently under way.

In a second approach functionalized polysiloxanes are linked together with nanocrystals of Al-rich zeolites. In the pores of the latter proton hopping between the Al centers is easily possible. In the composites the zeolite nanoparticles help to improve the mechanical stability without loosing significantly proton conductivity.

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Development and evaluation of the pore-filling electrolyte membrane using aromatic hydrocarbon polymer

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Reduction of methanol crossover is required for practical use of direct methanol fuel cell (DMFC). Here, we propose the pore-filling polymer electrolyte membrane (Fig. 1). Polymer electrolyte is filled inside the pores and substrate matrix suppresses polymer swelling. High proton conductivity is achieved through the electrolyte polymer, and swelling suppression enables significant reduction of methanol crossover [1-3]. For high durability, we employed polyimide and SPES, which show excellent heat resistance and durability, as substrate and electrolyte. The pore-filling membrane was developed in our laboratory by polymerizing SPES inside the pore of porous substrate and the membrane reduced the methanol permeability to 1/300 of commercial Nafion[®]117 [4]. However, polymerization inside the pores requires severe condition.

In this presentation, we report on novel preparation method of the pore-filling membrane by introducing SPES polymer into the pores of polyimide membrane. Table.1 shows the methanol permeability and proton conductivity. The methanol permeability of this electrolyte membrane was reduced to 1/60 of Nafion[®]117 while retaining proton conductivity. This electrolyte membrane is more practical compared to previous method, as easy preparation and sufficient reduction on methanol crossover was achieved simultaneously. Also, the oxidative durability was much improved from a SPES membrane prepared with casting method. We will also report on fuel cell performance of a MEA with the pore-filling membrane.
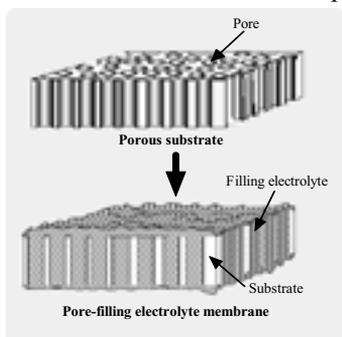

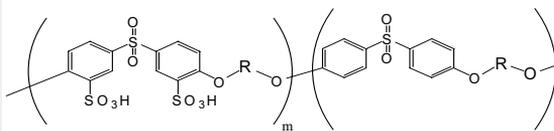Fig. 1 Concept of pore-filling membranes

Fig. 2 Structure of sulfonated poly(ether-sulfone) (SPES)

Table 1 Proton conductivity and methanol permeability

Membrane	Proton conductivity (S/cm)	MeOH permeability (kg_£ m/m^{2}h)
Pore filling membrane	0.06	**1.7**
Nafion[®]117	0.08	103

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First principles computation of the conductivity of hydrated Nafion membranes

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A first principles model is developed to describe analytically the protonic conductivity of fully hydrated Nafion membrane and its peculiar non-linear dependence[1,2] on membrane thickness, potential and P_{H_2} The model focuses on the surface migration of protons between adjacent sulfonate groups and utilizes the Poisson-Boltzmann charge distribution around each proton combined with the basic Gamow equation of quantum mechanics for proton tunneling. It is shown that the proton tunneling distance equals the proton wavelength[2] and that each proton surrounded by its Debye-Hückel cloud behaves as a leaking nanobattery.[2]

The model, which contains no adjustable parameters, is solved analytically and its predictions are in semiquantitative agreement with experiment, including the magnitude of the conductivity, its linear increase with membrane thickness, its exponential increase with potential and its strong dependence on P_{H_2}.

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Symposium 10 - Oral

Fuel Cells and Sustainable Energy

New polymeric proton conductors for water-free and high temperature fuel cells.

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Due to the considerable interest in PEM fuel cells for transportation purposes there has arisen a need to examine the feasibility of proton conducting membranes that do not depend on the presence of water for their performance. The most attractive option would involve a true solid-state material that contains no free solvent, can tolerate the presence of water, is conductive at low temperatures as well as high temperatures and can be tailored to provide desired gas permeabilities for both the separator and the membrane-electrode assembly.

The object of this work is to devise an easily modified polymer structure that will allow rapid elucidation of the role of the polymer structural features in the determination of the properties of the membrane, bearing in mind that the needs are different in the separator and the MEA. We have chosen to study imidazole as the proton solvating group due to the successful development of the Polybenzimidazole-phosphoric acid system, the recent advances reported by Kreuer et al. and reports of remarkable stability of imidazole-containing polymer membranes that have been used for oxygen separation. The base polymer structure has been under development for use in lithium polymer batteries and uses a grafting chemistry that allows easy modification of the nature and length of the side chains, the nature of the backbone, the nature and concentration of the anions and the nature and density of cross-links. This chemistry has been recently reported and the strategy is extended to include proton conducting units in this work. The concentration of imidazole groups relative to that of the acid groups is critical not only for the possible operation of a Grotthuss-type mechanism but also to control possible poisoning interactions with the platinum electrocatalysts. Conductivities of imidazole-containing polyelectrolyte membranes are sufficiently high to be of interest for fuel cell operation. The conductivity of membranes swollen with unsubstituted imidazole is higher than that of the N-methyl imidazole which may provide support for the participation of a Grotthuss mechanism of proton transport. Tethering of the imidazoles to the polymer matrix results in a solid state membrane with no mobile solvent that have the same conductivity as the the solvent swollen systems. The polyelectrolyte structures are presently under construction and their conductivities will be reported on. The preliminary indications are that the stronger imide acid will provide higher conductivities and that optimization of the imidazole: acid ratio and the morphology of the polymer will provide conductivities that are of interest to fuel cell engineers.

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# Humidity dependent surface diffusion on Pt and its implication to PEMFC electrodes

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It has been previously noted that the hydrogen and oxygen-containing species on Pt surfaces can diffuse fairly quickly [1, 2], rendering Pt surfaces electrochemically detectable (e.g. by CV) even without contact with electrolyte. Recently we found that the said surface diffusion is strongly humidity dependent and the Pt surface not in contact with Nafion network in the catalytic layer of PEMFC electrodes can still contribute to current generation.

In a miniaturized PEMFC, one electrode was fed with wet hydrogen to serve as counter and reference electrode and the other electrode was used as the working electrode (WE). The WE had two versions: WE1 was a layer of Nafion bonded Pt back hot-pressed on a Nafion 117 membrane and WE2 was the same WE1 overlaid with plain Pt back (without Nafion). The two WEs were tested by CV in Ar, hydrogen oxidation (HOR) in H_2 and oxygen reduction (ORR) in O_2. The plain Pt back was found to produce large current in CV in wet Ar but not in dry Ar, exhibiting humidity dependence of the surface diffusion of adsorbed hydrogen and oxygen containing species. The additional current output due to the plain Pt back overlay for HOR and ORR was enhanced in wet atmospheres, indicative of the contribution of the humidity-dependent surface diffusion. The possible mechanism and implication the humidity dependent surface diffusion to PEMFC electrodes will be discussed in presentation.
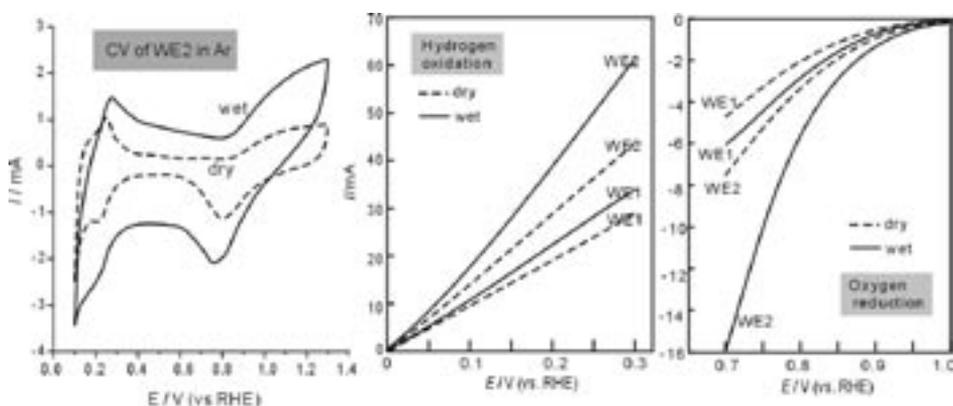
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Preparation of Pt/polypyrrole Loaded Carbon Composite for Improvement of Electrode Durability for PEFCs

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Polymer electrolyte fuel cells (PEFCs) have attracted enormous interest as a primary power source for electric vehicles (EVs) and a portable power source for electric devices as well as an onsite type with the cogeneration system. We have attempted optimization of the reaction condition of Pt/PPy composite and measured the catalytic activity for oxygen reduction in order to make a high dimensional structure of the gas diffusion electrode. The oxidation of pyrrole(Py) into polypyrrole and the reduction of Pt(IV) to Pt(0) is proceeded using H_2PtCl_4 by the following reaction at room temperature[1].

$$3 \;\text{(pyrrole)} + {}^{7}/_{4}\,[Pt(NH_3)_4]^{2+} \longrightarrow \text{(polypyrrole)} + {}^{7}/_{4}\,Pt + 7NH_3 \quad [1]$$

Applying this method, the Pt catalyst can be supported simultaneously during the polymerization of PPy. In this study, the Pt/polypyrrole was loaded on the surface-oxidized carbon support using the similar reaction of the onestep synthesis of Pt/PPy composites. The durability and diffusion of Pt catalyst are discussed.

Vulcan XC-72R carbon powder was oxidized by high concentrated $KMnO_4$ and HNO_3 aqueous solution for 4 hours[2]. Surface oxidized active group on carbon was ion-exchanged by the aqueous HCl solution for 20hrs. Resulting material has a ca 0.8 meq/g-carbon of the ion-exchange capacity. The surface acidic group was ion-exchanged by $[Pt(NH_3)_4]OH_2$ aqueous solution during neutralization. After drying, the Pt ionized carbon was put into the pyrrole aqueous solution. Immediately, the oxidation of platinum and polymerization of pyrrole proceeded simultaneously. The distribution of the platinum particles was measured by EDX equipped scanning microscope. In order to evaluate of catalytic activity of the composite, a cyclic voltammogram was measured for the Pt/PPy composite samples. Nafion® solution (5 wt%, Aldrich) was added to Pt/PPy-carbon composite as a binder. The composite was supported by the glassy carbon electrode. The electrode is set into 1mol/l H_2SO_4 aqueous solution with N_2 or O_2 bubbling. Size distribution of loaded platinum particle ranged at 3-8 nm by TEM image observation. As a result of the reaction, Pt was loaded on carbon surface combined by the polypyrrole as shown in Fig.1. The Pt and N profiles were observed with existence of carbon particles. It is suggested that the platinum particle was dispersed on the carbon paticles with polypyrrole polymer. We measured electrocatalytic activity of Pt particles before and after the oxygen reduction reaction. For the system using the Pt/PPy carbon composite, the reduction peak assigned oxygen reduction was observed during O_2 bubbling at 1.0 V vs Ag/AgCl which corresponded to the open curcit voltage of PEFCs. It is suggested that the platinum catalytic activity was kept during high potential reaction circumstance.

This study was supported by Development of Elemental Technology for Polymer Electrolyte Fuel Cells of NEDO project in Japan.

Fig.1 HRTEM image of Pt/PPy loaded carbon composite.

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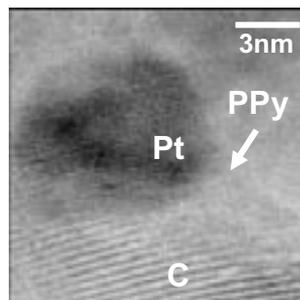K. Amine et al., *J. Chem. Soc. Faraday Trans.*, **91**, 4451 (1995).

Symposium 10 - Oral

Fuel Cells and Sustainable Energy

PEDOT as catalyst support and methanol barrier for DMFC applications

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The direct methanol fuel cell (DMFC) is a promising candidate for energy supply of mobile, stationary and portable applications. However, its performances are limited by low kinetics of the methanol oxidation at Pt compared to that of hydrogen and high methanol crossover rate that induces a mixed potential and a fuel loss at the cathode. In the last decade, conjugated conducting polymers such as polyaniline, polypyrrole and poly(3-4ethylenedioxithiophene)-polysterensulfonate (PEDOT-PSS) have been intensi-vely studied as anti-static, semi-conducting, conducting and catalyst support material, as well.

Since conducting polymers are ionic and electronic conductors, a priori only a two-phase boundary is needed for the electron and proton transfer during the electrochemical reaction, compared to the three-phase boundary when carbon is used as catalyst support. For this reason, better utilization of the noble metal catalyst is expected. Chemical polymerization of EDOT (Bayer AG) was carried out in $Na_2S_2O_8$. After Pt catalyst deposition on PEDOT and PEDOT-PSS powder, ink preparation and deposition on Toray carbon paper, gas diffusion electrodes (GDE) were tested in half-cell by means of cyclic voltammetry and impedance spectroscopy. PEDOT-PSS systems exhibited higher impedance values than PEDOT alone. Preliminary results in half-cell showed similar activity for methanol oxidation at Pt-PEDOT/C and Pt-C/C while performances in fuel cell were about 10-20% lower for Pt-PEDOT/C.

Conducting polymer-based membranes are used for ions and neutral species separation, as well. Their efficiency depends on adequate pore size, embedded counter-ion, temperature and degree of oxidation. In this work, Nafion117 membranes were modified by chemical diffusion-controlled polymerization of EDOT diluted in 0.1M NaPSS. $FeCl_3$ and H_2O_2 were used as oxidizing agents. PEDOT modified membrane were character-rized regarding ionic conductivity, methanol permeability and impedance in a two-compartment diaphragm cell. Two different polymerization behaviours were observed: methanol permeation and ionic conductivity of membranes prepared with H_2O_2 decreased proportionally to reaction time, whereas membranes prepared with $FeCl_3$ showed a $t^{-1/2}$ dependence. First deposition method led to PEDOT deposition within the Nafion membrane while second one resulted in film growing. PEDOT modified membranes were tested with two commercial GDEs in DMFC. Comparable proton exchange properties by lower methanol permeation rate were registered at PEDOT-modified membranes for polymerisation time under 2h, compared to pure Nafion.

In conclusion, the feasibility of PEDOT as catalyst support and methanol barrier for DMFC applications was demonstrated for the first time in this work.

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Cryogel carbon supports for DMFC-PtRu catalysts

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Carbon supported PtRu is the catalyst of choice for the DMFC anode and, given the high cost of noble metals, much research effort is focusing on the development of high catalytic activity electrodes. One of the pursued strategies to provide high catalytic surface at low noble metal content is that of developing new carbon supports with high electric conductivity, high surface area and high mesoporosity in the 20-40 nm region for a high accessible surface area to catalyst and to monomeric units of Nafion and to favour the diffusion of chemical species involved in methanol oxidation [1]. Cryogel carbons which are high conducting carbon networks featuring a high surface area and a high tunable mesoporosity along with the advantage of a low-cost preparation procedure based on freeze drying and pyrolysis of resorcinol-formaldehyde gels, should be suitable supports [2, 3].

Thus, we pursued the strategy of developing PtRu catalysts supported on mesoporous cryogel carbons and we deposited PtRu on carbon-Nafion substrate electrochemically, which is a promising technique because it provides the catalyst at the electrode's three-phase boundary [4]. Here we present and discuss preparation and characterization data of different mesoporous cryogel carbons as well as we report the catalytic activity of PtRu catalyst electrodeposited on cryogel carbon-Nafion supports for methanol oxidation in DMFC.

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Novel Electrode Structures for Direct Methanol Fuel Cells

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Up to now, the electrodes for direct methanol fuel cell (DMFC) have been developed mostly on the basis of the gas diffusion electrodes employed in proton exchange membrane fuel cells. Typically, the structure of such electrodes comprises a catalyst layer and a diffusion layer, the latter being carbon cloth or carbon paper. However, unlike other fuel cells, the liquid feed DMFC suffers from mass transport limitations predominantly at the anode due to the low diffusion coefficient of methanol in water. In addition, carbon paper is fragile and expensive and carbon cloth is soft compared with metal material, such materials are not as versatile as metals.

In our present work, new structures based on metal meshes for both the anode and the cathode of DMFC have been developed. The preparation procedures and the main characteristics of the anodes and cathodes studied by SEM, EDAX, *in-situ* FTIR spectroscopy, half cell and single cell tests will be reported.

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Investigation of Coupling Phenomena in PEFC Stacks

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In an *ideal* fuel cell stack geometry, components and mechanics of every single cell, as well as the operating conditions for all individual cells are identical. In a *real* stack however, individual cells may operate at different working conditions because of differences in manufacturing tolerances and/or location in the stack. Differences in local working conditions lead to performance changes at individual cell level. These performance variations are often not confined to individual cells only, but are accompanied by coupled performance of adjacent cells.

Experiments in 200 cm^2 short stacks with local current recording have been conducted [1]. Starvation of air at single cell level was emulated in 1+1 and 1+2 stacks by gradually reducing air stoichiometry in the anomalous cell only, while keeping the operating conditions of adjacent cells unaltered (coupling cells). Substantial voltage and current density coupling is then observed for the coupling cells (Fig, 1). For the studied cell geometry and material, changes in local current density propagate to an adjacent cell with a coupling factor of 0.64. The coupling behaviour is different when the anomalous cell is subject to a temperature distortion.

A theoretical analysis, elucidating the underlying mechanisms will also be presented.
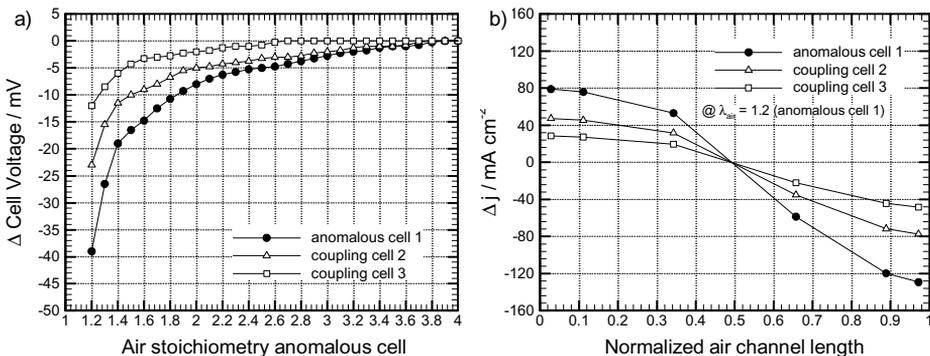

Fig. 1: 3-cell short stack: a) voltage changes of the anomalous cell 1 and coupling cells 2 and 3 as function of the air stoichiometry in the anomalous cell 1; b) changes in local current density j in the anomalous cell 1 and coupling cells 2 and 3 as function of the normalized air channel length. Changes are given with reference to values obtained at an air stoichiometry of 4.0 .

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Measuring the Current Density in PEFCs with Sub-Millimetre Resolution – Fundamental Insights

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By introducing a new measurement principle a method has been developed that enables for measuring the current density distribution in PEFC with a resolution smaller than the channel / rib scale [1]. It delivers for the first time measured and therefore reliable current distributions on this scale without the uncertainties of modelling calculations that have been the only way to get insight in phenomena on that scale so far.

Results for a cell with 2 mm channel and rib width are given in Fig. 1. The general pattern of the small scale current distribution was found to be strongly current dependent. An important finding is that parts of the cell have already reached the limiting current density whereas the integral *j-U* curve is still far away from its limiting current. This "back folding" of the local curves lowers the integral curve already at currents, where the shape of the latter one does not give rise to assume strong transport losses. In depth analysis of the measured distributions reveals the underlying transport phenomena on the crucial scale of flow field channels and ribs to be critical for PEFC performance. Analogies can be drawn to the effect of O_2 starvation in the along-the-channel direction [2].
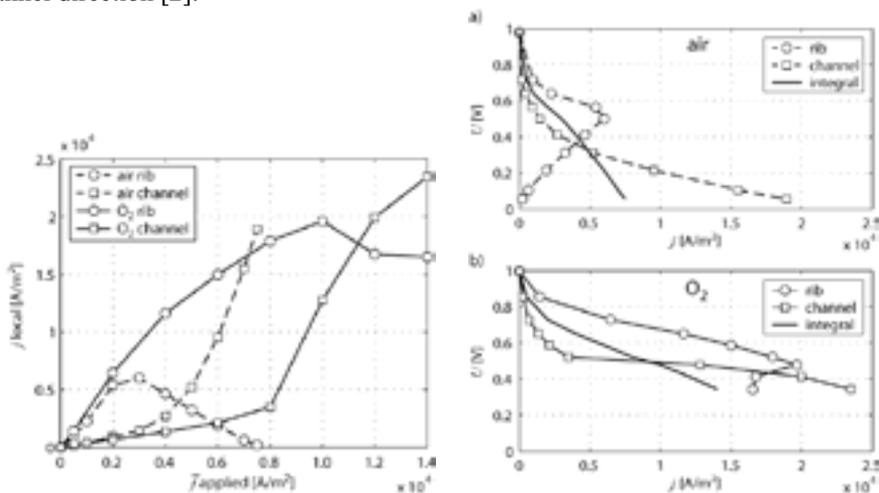

Fig. 1: Left: Local current density in the centre of rib and channel as a function of the average current density for air and oxygen operation. Right: Corresponding local current density - voltage curves in comparison with the integral one.

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Dissolution of Pt under stationary and accelerated conditions

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Platinum is one of the most widely used catalysts and considered as an extremely durable material. In the fuel cell system, however, even small magnitude of the Pt degradation is not ignored for long time operation. In this sense, the dissolution phenomena have been investigated from the point of stationary and accelerated conditions.

2. Experimental

First platinum black powder was dipped in sulphuric acid solution under nitrogen, air and oxygen condition. The solution was periodically sampled and the amount of Pt dissolved into the solution, Pt^{2+} and Pt^{4+}, was analysed by spectroscopic and also ICP methods.

As for accelerated method, a rotating ring disk method was applied. In consideration of the actual fuel cell operation, the potential was rifted to higher potential and decreased to lower potential at various conditions. During such potential cycling, Pt surface was oxidized and reduced and the Pt surface degraded to Pt ions in the electrolyte.

3. Results and discussion

Dissolution of Pt black under air at various pH and temperature is shown in Fig. 1. The solubility of Pt in pH 0 solution at $80^{o}C$ got to ca. 6 ppm. Platinum was considered to be firstly oxidized to PtO which dissolves into the acidic medium as Pt^{2+} and is then further oxidized to Pt^{4+}. The solubility increased with decrease of pH and with increase of temperature. After the surface oxidant was reduced at 0.4V vs. RHE, the potential of Pt was kept open. Under N_2 and O_2 atmosphere it reached shortly to 0.9V and 1.1V, respectively. Even in N_2 atmosphere, Pt would

**Fig .1 Relationship between log(Pt solubility)
and pH in H_2SO_4 under air atmosphere.**

be oxidized to PtO with extremely low pressure of oxygen included in N_2.

Dissolution of Pt under potential cycling was examined by a rotating ring disk electrodes. During potential rifting of the disc electrode from 0.05 to 1.5V, Pt was oxidized to PtO and PtO_2 . Under potential return to 0.05V, some of them was reduced to Pt^{2+} which was detected by the ring electrode.

Acknowledgement

The development of a direct formic acid fuel cell power system for lap-top computer operation

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In the last ten years there has been a resurgence of interest in the development of direct fuel cell power system for the portable application. Of late, LG Chem, NEC, Toshiba and Samsung SDI have reported a direct methanol fuel cell (DMFC) system to operate lap-top computer and showed the possiblity of the commericalization of DMFC system.. We first present here the development of a direct formic acid fuel cell (DF^{2}C) power system for a lap-top computer operation. The system consists of a 15 MEA stack capable of 30 W at $60 \sim 70$ mW/cm^2 and power management system (PMS) including high efficienct DC-DC converter. The initial start-up, dynamic response and long-term performance of the DF^{2}C system were extensively investigated. In addition, further developments needed for the miniaturization of DF^{2}C will be introduced.

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Performance of Direct Ethanol Fuel Cells

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The main prerequisite of a liquid fuel for polymer electrolyte fuel cell applications is a high electrochemical reactivity at relatively low temperatures. Furthermore, the fuel should be reasonably cheap, non-toxic and largely available. At present, mainly methanol and natural gas are actively investigated as a alternative to hydrogen in fuel cells. Among other possible candidates, ethanol appears to fulfill many of the above requirements. Although the oxidation of ethanol to carbon dioxide requires the cleavage of the C-C bond, previous studies have shown interesting electrochemical reactivity at temperatures above 100 °C [1]. The main bulk products in the electrochemical oxidation of ethanol are CO_2, acetaldehyde and acetic acid. The latter determine low electrical energy yield and environmental problems. Such drawbacks are addressed by increasing fuel cell operating temperature and/or developing highly selective catalysts. Nanostructured materials such as nanosized catalysts and nanocomposite membranes offer unique properties for enhancing the performance   of PEMFCs [2]. Since the state-of-the-art membranes dehydrate at temperatures above 100°C, new membranes, capable of sustaining higher temperatures (150 °C), need to be developed. There are evidences that this drawback can be overcome by composite membranes including nanosized hygroscopic oxides dispersed in the polymeric matrix. An operating range for direct ethanol fuel cells (DEFC) between 110°C and 150°C appears suitable for distributed generation, whereas, for portable uses the maximum temperature should be not higher than 60 °C. A further severe problem for DEFCs is the fuel crossover through the membrane. This effect lowers the FC efficiency markedly.   In the present work, an investigation of direct ethanol fuel cells based on composite polymer electrolytes for both low and high temperature applications is presented. The fuel cell systems have been studied in terms of performance, efficiency, cross-over and CO_2 yield. A significant increase of performance and electrical yield is achieved by operating the DEFC in the presence of composite membranes containing appropriate ceramic fillers. Furthermore, ethanol cross-over through the membrane is reduced by effect of an increase in tortuosity factor caused by the filler and ethanol consumption due to enhanced reaction kinetics at the anode-electrolyte interface.

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Performance of a Direct Alcohol Fuel Cell Stack

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Fuel cells are clean and efficient energy conversion devices, capable of competing with established technologies for energy generation.   The potential benefits of fuel cell technology include energy saving, low carbon dioxide emissions, low pollutant production and low noise. One of the current leading fuel cells is based on a solid polymer membrane electrolyte and using hydrogen as fuel operates at temperatures below 100°C. An emerging technology uses liquid alcohols, typically methanol. Direct alcohol fuel cells (DAFC) generate power through the direct oxidation of alcohol in conjunction with the reduction of oxygen (in air).

The paper describes a compact direct alcohol fuel cell stack for applications in portable and stationary power. The cell design uses membrane electrode assemblies (MEA) connected (electrically) by thin metal mesh with a conductive coating. The research will result in improvements in the performance of selective oxygen reduction catalysts, fabrication of electrodes with the new catalysts and their incorporation into a direct alcohol fuel cell stack using coated mesh structures inter-cell connectors.

Performance of the cell stack with low catalysts loading for both methanol and ethanol fuels is described.
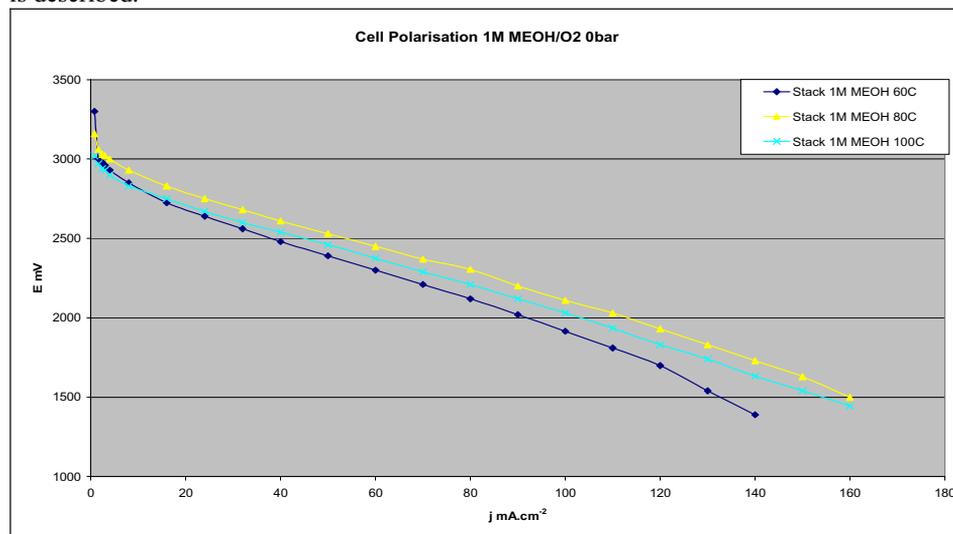
Keywords: Direct alcohol fuel cell, Portable and stationary power, Stack, Coated Mesh.

A "proton pump" concept for the evaluation of proton transport and electrode kinetics in PEM fuel cells

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A novel concept for the measurement of proton transport properties and electrode kinetics in PEM fuel cells is presented. The concept makes it possible to distinguish between the kinetics of proton transport in the membrane, anode reaction and cathode reaction under realistic conditions.

Base of the concept is a "proton pump" setup, which is essentially a fuel cell with N_2 instead of O_2 gas on the cathode side. If negative potentials are applied to the cathode with respect to the anode, ohmic behaviour, i.e. a linear relationship between current and voltage, is observed. Since it was found that $I - \log p(H_2)$, which can be attributed to the Nernst equation, it is proven that the current is determined by the proton transport in the membrane. The setup therefore allows the measurement of the conductivity of the proton exchange membrane (PEM) under realistic working conditions, which is in most cases not possible in a fuel cell setup with O_2 at the cathode, where the current is often limited by the oxygen reduction reaction. The ohmic behaviour was found over a wide range of temperatures, showing that even at high temperatures, where the conductivity of the membranes increased, hydrogen oxidation at the anode as well as the back reaction at the cathode are not limiting the current.

The oxidation of H_2 at the anode has been studied in detail in the "proton pump" setup by impedance measurements under variation of parameters such as $p(H_2)$, temperature and potential. The semicircles caused by hydrogen oxidation and back reaction can be easily distinguished in the Nyquist plots, since the resistance attributable to hydrogen becomes lower with increasing $p(H_2)$, while the semicircle caused by the back reaction totally disappears towards negative potentials of the cathode due to the high electron concentration and the high proton flux towards this electrode.

Having investigated the anode reaction and the proton transport in the PEM in detail, oxygen reduction is added to the investigation by returning to the normal fuel cell setup with O_2 at the cathode under otherwise unchanged conditions. In I-V-curves the current was found to follow a law with $I - p(O_2)^m$, proving that oxygen reduction has become the limiting step. Knowing the impedance of the hydrogen oxidation, semicircles caused by the oxygen reduction in the Nyquist plots can be easily identified. In accordance and conjunction with the results from the I-V-curves, it has been found that, while a low resistance attributable to the membrane is a *sine qua non* condition for a high fuel cell power, the sufficient condition is a low resistance attributable to the oxygen reduction.

Analysis of membraneless micro fuel cell using decomposition of hydrogen peroxide in a Y-shaped microchannel

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A novel design of fuel cell technology based on microfluidic devices has received much attention recently due to its promising applications in portable power sources and MEMs related devices such as "Lab-on-a-chip" systems. This microfuel cell utilizes the occurrence of laminar flow in a Y-shaped microchannel at low Reynolds number. Both anodic and cathodic liquid streams flow in parallel through the microchannel without turbulent mixing. Such a novel design removes the membrane used in conventional proton exchange membrane fuel cells (PEMFCs) and possesses many merits: the ohmic losses and fouling problems due to the membrane are eliminated, the fabrication and water management are simpler, the size of fuel cell can be greatly reduced, and the liquid fuels have higher energy densities.

Many experimental studies had been performed in developing membraneless microchannel fuel cells. Several kinds of fuel were used in these investigations such as formic acid, methanol, and hydrogen solutions. However, since they all used oxygen solution as the oxidant stream, it had been found that the performance of these micro fuel cells is restricted severely by the low transport efficiency of oxygen in the cathode electrolyte. Recently, an experimental study using hydrogen peroxide has been proposed for a Y-shaped microchannel fuel cell. The hydrogen peroxide is used not only as a reductant but also an oxidant. The decomposition of hydrogen peroxide in both anode and cathode streams can generate electric power comparable to a typical air breathing direct methanol fuel cell (DMFC) at room temperature and produce no carbon dioxide. Therefore, it is quite important to understand the characteristics of this kind of membraneless micro fuel cell using hydrogen peroxide in both fuel and oxidant streams. In this study, we develop a theoretical model to simulate this membraneless Y-shaped microchannel fuel cell and perform a numerical study to investigate the species transport in both streams and their influences on cell performance. The effects of geometrical factors of microchannel and electrodes are also examined in detail. Results provide physical insights for transport phenomena and electrochemistry reactions in this system, and benefit the optimal design of this membraneless micro fuel cell for the fulfillment of practical application in portable sources.

Symposium 10 - Oral

Fuel Cells and Sustainable Energy

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Miniature, Potentially Implantable, Batteries and Glucose-O$_2$ Fuel Cells

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All presently used batteries contain reactive, corrosive, or toxic components and require strong cases, usually made of steel. As a battery is miniaturized, the required case dominates its size. Hence, the smallest manufactured batteries are of about 20 mm^3, much larger then the integrated circuits or sensors of functional analytical packages, exemplified by implantable glucose sensors for diabetes management. Progress made in the 2004-2006 period in the miniaturization of the power sources of such packages will be reviewed. In one route to miniature batteries, all components would be made harmless,[1] enabling their packaging in thin plastic films, metallized to prevent the drying of the electrolyte. In a second, the case and the electrolyte would be eliminated through forming the battery of a harmless, implantable, miniature Zn anode and an also harmless and also implantable, biocompatible hydrogel-shielded, Ag/AgCl cathode, with the subcutaneous interstitial fluid serving as the electrolyte.[1] In the third, the power source would be a miniature glucose-O$_2$ biofuel cell. Glucose of the subcutaneous interstitial fluid would be electrooxidized on a miniature glucose oxidase microanode and O$_2$ would be electroreduced on an also implanted wired bilirubin oxidase microcathode. [2, 3]

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Symposium 10 - Oral

Fuel Cells and Sustainable Energy

Co-generation of hydrogen peroxide and energy in fuel cells

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There have been rapid developments in the hydrogen-oxygen fuel cell for use in traction and the technology has advanced to the point where vehicles with fuel cell engines are being actively road-tested. This represents one of the most important practical applications of modern electrochemistry and its use relies on achieving quantitatively the 4 e$^-$ reduction of oxygen to water. The purpose of the work described is to transpose this technology to achieve quantitatively the reduction of oxygen to H_2O_2 in a fuel cell, i.e. to stop the reduction of oxygen at the two electron stage, in order to produce an important chemical and at the same time, attempt to generate energy. The reaction is:

$$O_2 + 2\,H^+ + 2\,e^- \quad H_2O_2$$
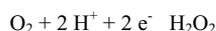
The strategy followed was to transpose the well known current industrial synthesis of reacting chemically a reduced quinone with atmospheric oxygen, to an electrochemical environment.[1-7] Thus, the reaction studied was the electrocatalytic reduction of O_2 on carbon surfaces chemically grafted with quinones.[8] The reaction sequence considered in this case is:

$$Q + e^- \rightarrow Q^{\bullet -} \tag{I}$$

followed by:

$$Q^{\bullet -} + O_2 \xrightarrow{k_c} O_2^-(ads) + Q \rightarrow H_2O_2 \tag{II}$$

This reaction sequence has been investigated using a glassy carbon rotating disk electrode functionalised by the reduction of the corresponding diazonium salt. It has been found that for anthraquinone (AQ) derivatives, the rate of Reaction (II) depends on the substituents present in the AQ molecule. In particular, electron withdrawing groups lead to an increase in the rate of this chemical step. These problems are analysed in terms of the Marcus theory. Dispersed carbon can also be readily functionalised and fuel cell electrodes made.

The pH dependence of the kinetic parameters shows that the radical anion is the reactive species. The possibility of using quinones as electrocatalysts requires an alkaline environment and the industrial implementation of the ideas discussed above depends critically on the availability of robust alkaline membranes. These practical problems will be discussed and a prospective for potential applications will be presented.

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Development of a Three-Dimensional Porous Structure Simulator and Its Application to Fuel Cells

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Ni-YSZ (Y_2O_3 stabilized ZrO_2) is used as standard anode for solid oxide fuel cell (SOFC). Traditional view of anodic reactions is that the reaction occurs at the triple-phase boundary (TPB) of gas phase, metal and oxide particles. However, the actual anodic reaction is governed by various transfer processes such as gas-phase diffusions, surface diffusions of adsorbed species, electron and oxide ion conduction in particles. Microstructure is empirically controlled by changing fabrication conditions experimentally, while no theoretical method for optimizing microstructure can be found so far. In this study, we developed a theoretical method for optimizing the three-dimensional microstructure of porous electrodes and applied it to the evaluation of microstructure and overpotential characteristics of SOFC anode.

Methods

We developed a simulator for constructing porous structure on the computer, a program to quantitatively evaluate the microstructure of porous electrode, a simulator of the anodic overpotential. These developed simulators are applied to the study of SOFC anode.

Results and Discussion

Porous structure model Fig. 1 shows structures of various porous structures constructed by the developed simulator; multi-component structure, layered structure, tubular strucuture, structure with surface coating, and secondary particle structure. We can see that the developed simulator can construct various types of porous structures.

Quantitative evaluation of microstructure Fig. 2(a) shows a structure of Ni-YSZ anode constructed by the developed
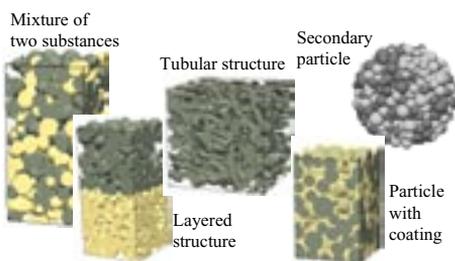
Fig. 1 Porous structures constructed by the developed simulator

Distribution of the active sites for oxygen reduction in composite electrodes for IT-SOFC

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Half-cells consisting of YSZ electrolyte pellets and slurry-coated cathodes were tested with a three- electrode configuration. The composite cathodes considered in this study had a fixed LSM/YSZ volume ratio equal to 1 and variable apparent surfaces, ranging from 0.05 to 0.25 cm2. Electrochemical Impedance Spectroscopy and potentiodynamic polarisations were used to evaluate the main electrochemical parameters. The results obtained with the two techniques showed a good agreement. The slope of the lnRp/lnd lines moves monotonically from 2.3 at 700°C to 3.3 at 900°C (Fig. 2). These values suggest that at lower temperatures increases in the cathode diameter produce an active surface that has some dependence on the cathode volume. As the temperature increases and the slope approaches 3 the entire volume of the cathode is involved in the oxygen reduction. The composite cathode has a preferential ionic path for oxygen ions through the YSZ particles dispersed in the LSM/YSZ mixture. The sintering temperature of the cathode was 1100°C and measurements performed on porous LSM cathodes with a YSZ electrolyte pellet sintered at 1100°C showed an electrolyte ohmic resistance about ten times higher than that obtained when porous LSM cathodes were applied to a YSZ electrolyte sintered at 1500°C. When the oxygen reduction proceeds at a low rate (low T) the active area is mainly concentrated at the cathode/electrolyte interface. As the charge transfer reaction rate increases (high T) the cathodic polarisations and the faster ionic transport, even in partially sintered YSZ, within the cathode involves the entire cathode volume in the electrodic reaction.A theoretical model that describe the behaviour of the composite cathode as a function of temperature has been developed The model simulations compared satisfactorily with the experimental data, and also they show that, at low temperatures, the reaction zone in the cathode is confined to the electrolyte interface. When the temperature is increased, the retarding effects of mass transfer and conduction in the electrolyte become negligible, and the reaction zone progressively extends through the electrode.

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Investigations on the electronic, ionic, and thermal conductivity of nickel and cobalt substituted lathanum strontium ferrous oxides

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The electrochemical processes that take place in solid oxide electrochemical cells, such as in solid oxide fuel cells, involve electrons, oxygen ions and the gas phase. Therefore, mixed electronically and ionically conductive materials such as perovskites are used to form porous electrode layers as air electrode (cathode) and fuel electrode (anode) materials, respectively. In view operating temperatures as high as 750°C, La-Sr cobaltates and ferrites have become interesting materials for the air electrode for they exhibit a higher electrochemical activity then the well established La-Sr-manganates. We now present some results from our recent activities, including structural and electrochemical data on the aforementioned materials systems. Perovskite powders were prepared by spray pyrolysis and investigated by X-ray diffraction. Impact of substitution of La-Sr-ferrites (LSF) with 3d Elements such as Co, Ni and Cu was investigated with respect to their crystallographic structure and the electrical properties and also their thermal properties. The solubility limit of Ni and Cu was found to be below 20mol% indicating the limited tolerance of the perovskite B-site for 2 valance cations such as Ni^{2+} and Cu^{2+}. From their positions in a simplified structural field map, the substitution of Fe by the 2-valent cations should change the conductivity from semi conducting to metallic, which may have an impact on the oxygen exchange properties. The temperature dependence of LSF substituted by Ni and Cu will be presented and discussed with respect to the crystal structure and the materials position in the structural field map. The thermal and electric conductivity are discussed in terms of Wiedemann-Frans' Law.

Direct Electrochemical Oxidation of Propane in Solid Oxide Fuel Cells

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Solid oxide fuel cells have attracted significant interest in the last decades due to their high efficiency and performance to convert chemical into electrical energy. Generally, these systems operate at temperatures higher than 800°C. Recently, the development of electrolytes alternative to stabilised-zirconia have opened new perspectives for operating these devices at lower temperatures. This allows to increase SOFC lifetime, reduce the occurrence of cracking processes in the presence of hydrocarbon-based fuels and the use of cheap metallic interconnectors. The direct oxidation of hydrocarbons in intermediate temperature solid oxide fuel cells (IT-SOFCs) has been intensively investigated in the last years due to the high intrinsic efficiency of the direct electrochemical oxidation process. In the present work, a Ru/CGO electrocatalyst was investigated in combination with a Cu current collector for the direct electro-oxidation of propane in a solid oxide fuel cell. Comparable electrochemical power densities for both direct oxidation and internal reforming have been measured at 750°C. The electrochemical performance in the presence of propane was significantly affected by the polarization resistance. The charge transfer resistance for a SOFC based on the direct propane oxidation was about four times larger than that obtained for the SOFC fed with hydrogen. Out-of-cell steam reforming experiments showed a C_3H_8 conversion to syngas approaching 90% at 750-800°C. Accordingly, significant efforts have been addressed to the anode structure optimization to achieve suitable catalytic conversion efficiency. No formation of carbon deposits was observed upon operation of the anode in the direct oxidation mode at 750°C.

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Fuel Cells and Sustainable Energy

Relationship between the overpotential and the structure of ni-sdc anode for solid oxide fuel cell

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Solid oxide fuel cell (SOFC) is expected as one of the important power generation systems of the future. However, there are many problems to overcome for practical use. One of them is to develop a high performance electrode of low overpotential. To reduce the overpotential, not only the material but also the morphological structure is important. Anodic reaction consists of several elementary steps such as gas diffusion, ion and electron conduction, electrochemical reaction, etc. The effective reaction zone should differ if the rate determining step is different. In this study, the structure of a cermet anode of Ni and Sm doped ceria (SDC) has been investigated.

SDC disk was used as an electrolyte, and Ni-SDC and $Sm_{0.5}Sr_{0.5}CoO_3$ were pasted and sintered as an anode and a cathode, respectively. Two types of anode with particle size of 7µm and 0.5µm (NS7, NS0.5) were used. Anode with different thickness was prepared for each type. Current density vs. terminal voltage was measured by using H_2 as fuel and O_2 as oxidant. Overpotential of the anode was measured by current interruption method.

Figure 1 shows the overpotential of the anode of NS7 and NS0.5 when the current density was $1A/cm^2$. The dependence of the overpotential to the thickness of the anode was different for anode with different particle size. The thickness dependence was large for NS7 but was small for NS0.5. The overpotential of NS7 showed the minimum at 120µm, and there is a possibility that it can be reduced even more by further increasing the anode thickness. The large thickness dependence for NS7 can be attributed to the relatively small reaction zone per unit area, which results from the large particle size. On the other hand, NS0.5 showed smaller thickness dependence. It is expected that the reaction zone per unit area of NS0.5 was large since the particle size was small, resulting in the small thickness dependence.
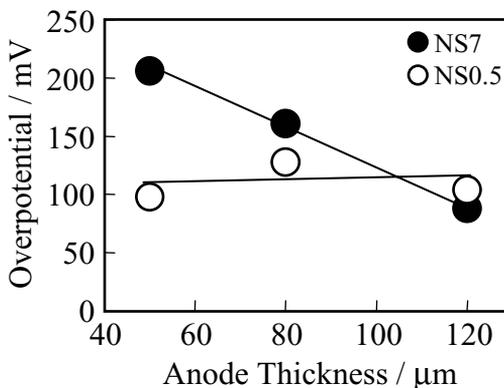
Fig. 1. Anode thickness dependence of overpotential at $1A/cm^2$ (800°C)

Symposium 10 - Oral

Fuel Cells and Sustainable Energy

Electrocatalytic behaviour of molybdenum modified platinum electrodes for electrooxidation of ethanol in acid medium

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In this work we investigated the electrooxidation of ethanol on various Pt based electrodes, prepared by two methods:

Pt-Mo alloy electrocatalysts were prepared by arc-melting furnace. Compositions such as (50:50) and (80:20) were chosen in two different zones of a binary phase diagram where they are supposed to form a pure alloy mixture either a solid solution.

Elsewhere, we prepared electrodes containing Pt and Mo oxides with different compositions by thermal decomposition of polymeric precursors. The precursor solutions were prepared by dissolving $H_2PtCl_6.6H_2O$ and $MoCl_5$ in a solution of citric acid and ethylene glycol. The final solution was obtained by mixing appropriate mass of the precursor solutions in order to obtain the desired composition of $Pt_{(1-x)}Mo_xO_2$, where $0.50 < x < 0.8$. The oxide layers were obtained after calcination at 400 $^\circ$C.

The atomic composition of the catalysts by EDX analysis performed on different zones of samples was close to the target. Pt-Mo alloy catalysts showed higher activity than Pt-alone. Gradual dissolution of Mo at the electrode surface was observed after voltammetry and chronoamperometry measurements. This dissolved Mo could keep its catalytic effect in the bulk solution by its behaviour as underpotentially deposited (upd) adatoms. Another assumption which is highly likely is that this dissolution involves an increase of the roughness of the electrode surface. When increasing molybdenum content in the catalyst composition, a pure Pt-Mo alloy formation stabilizes the catalyst and the activity for ethanol oxidation was better in terms of performance with time.

During chronoamperometry measurements at 0.6V vs. RHE for electrocatalysts prepared by thermal decomposition, the reaction products were analyzed by liquid chromatography. Acetaldehyde and acetic acid were successively formed. Carbon dioxide was also determined showing Pt-Mo catalysts are active for breaking the C-C bond.

FTIR spectroscopy results showed that Pt-Mo (50:50) electrocatalyst was an attractive way to modify the kinetics of specific steps of a reaction mechanism for CO pre-adsorbed oxidation.

Diamond-supported binary and ternary nano-sized catalysts for advanced direct-alcohol PEM fuel cells

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Typical sp2-bonded carbon support materials, such as activated carbon and carbon black, are susceptible to micro structural and morphological degradation and loss of catalytic activity under oxidizing conditions. Moreover, this carbon support leads to a reduction of the metallic oxides prepared by Sol-gel techniques, an undesirable fact due to the high electrocatalytic activity shown by hydrous ruthenium oxides for methanol oxidation [1]. Advances in the chemical vapour deposition (CVD) technology have made conductive boron-doped diamond (BDD) materials (mainly composed of sp3 type carbon) a feasible alternative as support material. This is due to its chemical inertness and excellent physical stability even under demanding electrochemical conditions. Moreover, the use of BDD as substrate allows the production of metallic oxides by the Sol-gel method. Recently, Fischer et al. [2] reported the production of conducting diamond powder (ϕ = 8-12 μm) using microwave plasma-assisted CVD. In fact, the future of advanced anodes for direct-alcohol fuel cell systems is focused on the use of this advanced carbon powder as a new dimensionally stable support material for electrocatalyst. Thus, studies of the methanol and ethanol oxidation reactions on Sol-gel modified BDD electrode surfaces using Pt, Pt-RuO2 and Pt-RuO2-RhO2 are reported here. XRD analyses show that the proposed method produces nano-sized (4-6 nm) particles. These deposits also form nano-clusters with a size of ca. 100 nm as observed by SEM and AFM. EDX maps revealed that the metals are homogeneously distributed on the BDD surface and have a composition close to the expected one thus confirming the effectiveness of the preparation method. Cyclic voltammetry revealed that the CO poisoning response for the methanol and ethanol oxidation reactions in acid media is largely inhibited on the Pt-RuO2-RhO2/BDD electrode. This shows the good performance of the RhO2 to either promote the oxidation to CO2 or to produce a weakening of the CO adsorption on the neighbouring Pt atoms in the composite. Steady-state polarization curves showed that the addition of RuO2-RhO2 to Pt/BDD produces a more reactive electrocatalyst for methanol and ethanol oxidation reactions that changes the reaction onsets by 120 mV or 180 mV towards less positive potentials, respectively. As a consequence, the stationary current density determined at a fixed potential of 0.57 V vs. HESS to the ethanol oxidation reaction is over 12 times higher on Pt-RuO2-RhO2 /BDD electrodes than on Pt/BDD. Consequently, this ternary catalyst containing Pt-RuO2-RhO2 is a very promising material to be used in fuel cell anodes.

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Symposium 10 - Poster

Fuel Cells and Sustainable Energy

Solid Oxide Fuel Cells: Enhancing Their Performance and Lifetime

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Fuel cells are highly efficient devices that cleanly and quietly convert chemical energy into electricity. Indeed, certain types of fuel cells have theoretical fuel-to-electricity conversion efficiencies close to 100% and have realizable efficiencies approaching 50%. There are a number of types of fuel cells that are currently in various stages of development, but it is generally accepted that proton exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs) offer the most promise of flexibility of application, fuel options, and the potential to realize high fuel conversion efficiencies. However, PEMFCs are hindered by their need for high purity H_2, while SOFCs are significantly more flexible in terms of fuels. Also, as they can co-generate both electricity and heat, SOFCs are ideally suited for a wide range of stationary applications.

At the same time, there are still a number of key factors that are holding back the commercial implementation of SOFCs. For example, the anode performance can be compromised by such factors as sulfur poisoning, the deposition of coke, and other problematic morphological changes. The cathode performance is limited by the slow kinetics of the oxygen reduction reaction, while its lifetime can be negatively affected by factors related to the corrosion of stainless steel interconnect materials, currently used in planar SOFC designs. This talk will present an overview of these challenges and some possible solutions to these problems. In addition, recent promising research efforts directed towards performance enhancement (cost reduction) of SOFCs through the use of nanoscale electrocatalyst fabrication will be discussed.

Thermal Imaging and Stress Analysis Modeling of Solid Oxide Fuel Cells

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Solid oxide fuel cells (SOFCs) are highly efficient devices for converting chemical energy directly into electrical energy. The SOFC is particularly attractive for combined heat and power (CHP) applications. The high temperature operation of SOFCs (500-1000ºC) allows high grade heat to be generated and also facilitates operation on hydrocarbon fuel where internal reforming or simplified external reforming can be used.

Temperature gradients within SOFCs are a major cause of failure both during production and use. One of the main design considerations for SOFC developers is the minimisation of thermal gradients within the cell and stack structures. Excessive temperature gradients can result in cracking or delamination of electrodes and electrolyte, sealing material integrity can become compromised and non-uniform current distribution can result.

This study uses an infrared camera operating at a wavelength of 4 µm to determine the temperature distribution of SOFC systems. Figure 1 shows the temperature distribution across a 5 cm wide electrolyte supported SOFC when exposed to a cold stream of nitrogen at the centre of the component. Results show that temperature gradients of over 25ºC cm^{-1} can easily be tolerated without breakage.

Empirical measurements are compared with a finite element stress analysis model to predict the failure point of selected SOFC samples. Results of temperature distribution across the cathode of an operational 'pellet' SOFC are presented along with recommendations for ensuring uniform and accurate temperature control of SOFCs under test.

Figure 1. Temperature distribution across the surface of an electrolyte supported SOFC when subjected to a 'cold' stream of nitrogen in the centre of the plate.
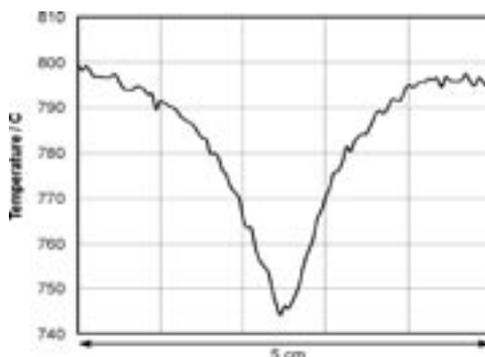
PBI fuel cell catalysts prepared by colloidal routes

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A new generation of polymer electrolyte fuel cells, operating at elevated temperatures, are very promising energy conversion systems for future clean energy plants. Such systems utilize polymeric membranes (e.g. polybenzimidazole, PBI), which in comparison with perfluorosulphonic acid ones (e.g. Nafion), can be operated at temperatures up to 200 °C. An increased operating temperature significantly increases the catalysts' tolerance towards contaminations in the fuel cell feed, especially CO [1], thus reducing the extensive and expensive pre-treatment of the fuel as required in low-temperature PEM fuel cells.

Highly effective carbon nanofibre supported catalytic powders were prepared by a modified polyol method [2]. The platinum loading was in the range 5-55w% (with control of the platinum particle size) and the active surface area of platinum was 50-140 m^2/g. The catalysts exhibit good electrocatalytic properties as part of PBI-containing electrodes tested in a half cell with phosphoric and sulfuric acid electrolytes. Modeling of XRD data shows that the distribution of primary crystals is narrow, with a maximum size of about 2-4 nm. These data correlate well with results from TEM investigations, which show particles with a size less than 5 nm. The stability of the prepared catalyst was investigated by temperature programmed oxidation. The results show higher stability compared to commercially available catalyst on Vulcan XC-72.

For comparison of catalyst preparation and properties, other methods involving deposition of preformed colloids onto carbon supports were investigated. Citric acid is well known for its dual function as a reducing and stabilizing agent in nanocolloidal chemistry [3]. In the citric acid method, a Pt precursor, H_2PtCl_6, is reduced in an aqueous solution of sodium citrate at elevated temperature and a suitable pH. Deposition of Pt onto carbon supports was attempted, giving catalysts with low loading 1.6 wt% Pt (nominal 20 wt. %). The difficulties in platinum deposition are believed to be caused by incomplete reduction of Pt^{+4}, as reported by Gou et al.[3] They claim that additional reducing agents like $NaBH_4$ is needed for full reduction. By optimization of preparation parameters we are now able to produce Pt/C electrocatalysts with 36 wt% Pt by the citric acid method without any additional reducing agents. XRD measurements show a narrow particle size distribution centered around 4 nm.

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Electrochemical characterisation of LSM/YSZ cathode in an anode supported cell configuration: considerations on the mechanism of oxigen reduction.

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Sr-doped LaMnO3 (LSM) and yttria stabilized zirconia (YSZ) composites are widely studied as cathodic materials for high temperature solid oxide fuel cells. The oxygen reduction (O.R.) mechanism of these electrodes is still uncertain. In previous works we suggested the existence of a "critical" temperature for the activation of the entire composite cathode volume close to 750°C and the presence of transport limitations. The LSM/YSZ composite cathode is screen printed on a Ni/YSZ cermet anode-supported half-cell with yttria stabilized zirconia (8YSZ) electrolyte. The cell is characterized by Electrochemical Impedance Spectroscopy in different fuel and oxygen partial pressure conditions in the temperature range between 650 and 850°C using a two-electrode configuration. The results confirm that between 700 and 800°C the rate determining step of the oxygen reduction reaction changes. In this paper, the behaviour of the system in a two-electrode configuration is analyzed, with the aim to individuate and extract the cathodic contribute from the overall impedance response of the anode-supported cell, varying the partial pressure of the reactant gases. Finally, the main features to interpret the kinetic mechanisms which control the O.R. process in the different temperature ranges are presented and discussed.

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Photoelectrochemical Fuel Cell for Water Remediation

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Environmental remediation of wastewater streams has been reported using TiO_2 suspensions in the presence of UV light. Similarly organic components in wastewater streams have been mineralised using microbial fuel cells where the organics are oxidised at an anode while oxygen is reduced at typically a precious metal based cathode. In this work we report the synergy of the above two systems in order to improve efficiency of mineralization of organic compounds.

We report on two systems. The first system was based on a glassy carbon electrode coated with a TiO_2/PVC composite in a two compartment cell with a Pt foil as cathode. The light source was a 150 W xenon arc lamp. Using this configuration it was possible to mineralise ethanol and isopropanol. Furthermore, it was also possible to degrade acetone and starch which cannot be degraded by using TiO_2 with UV light alone. In this way we show that the combination of the photo and electrochemical processes result in a greater mineralization efficiency. Such a cell has also been used with a 60 W tungsten lamp to show that mineralization can be carried out with visible light.

The second system is based on carbon ink electrodes; the anode was a carbon ink electrode with a surface deposit of TiO_2 and the cathode was carbon ink combined with cobalt phthalocyanine. Both of these were placed in a one compartment cell in a Q sun chamber and the effect of exposure of the resulting model sunlight on the current was monitored.

Optimised systems based on the Photoelectrochemical Fuel Cells, (PEFC), mentioned above will simultaneously reduce the COD of wastewaters while yielding a useful current.

Electrochemical characterisation of ruthenium chalcogenides for direct methanol fuel cells

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Carbon-supported ruthenium-based chalcogenide materials were prepared and characterised using cyclic voltammetry, steady-state polarisation and rotating disk electrode techniques (Figs. 1 and 2). Kinetic parameters of the reaction and the dependence of the activity for oxygen reduction and methanol tolerance on the material composition were established in acid media. The materials were compared to Pt cathodes.
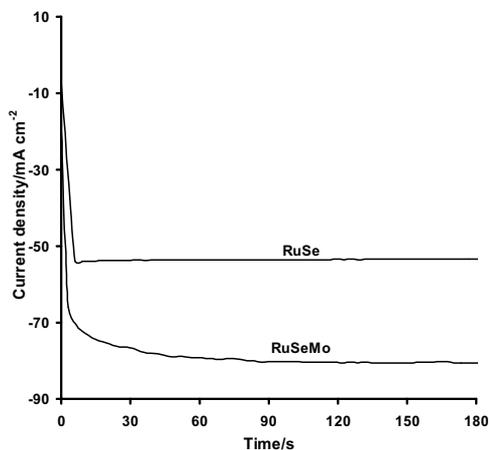

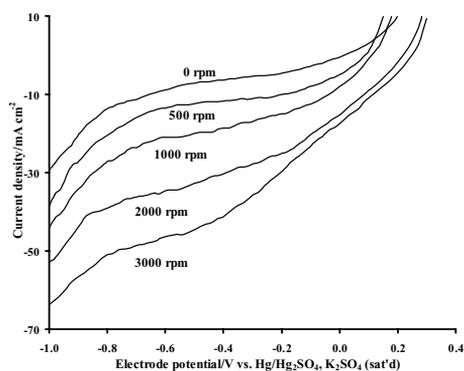Figure 1. Steady-state polarisation behaviour.

Figure 2. RDE characterisation.

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Novel anode structure for direct ethanol fuel cells

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Direct methanol fuel cells are projected as potential power source for portable and static power applications. Methanol as a liquid fuel has been receiving increased attention due to its advantages of easy transportation, storage, high energy efficiency. Nevertheless, methanol has the disadvantages of toxicity, low boiling point, and is not a primary fuel. Therefore, other alcohols are being considered as alternative fuels. Ethanol is an interesting and attractive fuel for portable application. Ethanol is non toxic, less volatile, inexpensive and also renewable. However, the oxidation of ethanol is more difficult than that of methanol with the necessity of breaking the C–C bond for complete oxidation. To increase the electroactivity of ethanol together with its complete oxidation to carbon dioxide is a challenging area. In addition, the liquid feed alcohol fuel cell suffers from mass transport limitation predominantly at the anode due to the low diffusion coefficient of alcohol in water and the formation of CO_2 bubbles.

In Newcastle, we have developed a novel electrode; a hydrophilic anode coated with platinum based catalyst on to a mesh electrode structure. Titanium mesh was selected as the substrate due to its chemical stability, and can support diverse electrocatalyst deposit. The advantage of the mesh based support includes versatile cell design, and low cost anode fabrication. The hydrophilic nature of the anode facilitates alcohol transport throughout the electrode and enables efficient gas release from the electrode structure. Thermal decomposition and electrodeposition were used to deposit platinum based catalysts onto the mesh substrate. The development of anode electrocatalysts was associated with the introduction of a more oxidisable metal, such as W, Sn, Pd, Ir etc. to Pt and PtRu involving binary and ternary electrocatalyst system. Cyclic voltammetry and single direct ethanol fuel cell tests indicate that the novel anodes prepared with platinum based catalyst show a competitive performance in comparison with the conventional ethanol fuel cells.

# Polymer Coated PTFE Proton Exchange Membrane for High Temperature PEMFC

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Synthesis and characterizations of polymer coated on porous PTFE membrane were utilized by the polymer multi-layer (PML) process. The PML process is usually employs flash evaporation techniques for various types of monomer fluids onto the surface and internal structure of porous substrates[1-3]. Depend on different types of monomers or ionomers these PML processed polymer films have shown characteristics of proton exchange capability. In our laboratory, we have coated sulfonic acid, phosphonic acid functional monomers and various types of cross-linking agents for increase mechanical and thermal properties. After PML process, as shown in the figures, the porous polymer membrane still contains large portions of pores either in the surface and internal threads which will help proton migration from one side to the other. The coated ionomer will be swelled by phosphoric acid media and all open pores will be closed by swelled ionomer. Then proton will migrate through the swelled ionomer which are much soft and flexible portion of the membrane. As a result polymer coated porous membrane showed conductivity of 2×10^{-2} S/cm at 150˚C while unchanged film formation neither mechanical properties.   The obtained proton exchange membranes were characterized by scanning electronic microscopy (SEM), ionic conductivity, thickness and I-V (current-voltage) curves from MEA test
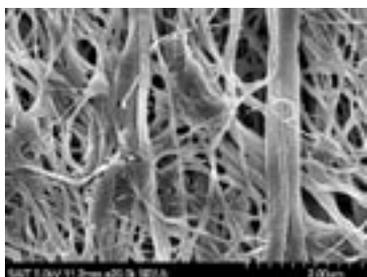
Bare porous membrane
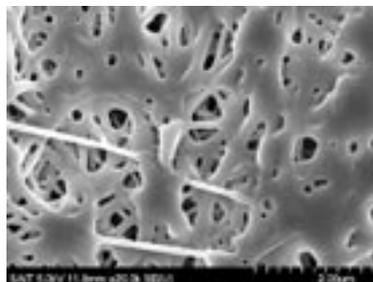
Ionomer coated membrane

New High Temperature Polymer Electrolyte Membranes and their Fuel Cell Performance

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Polymer electrolyte membrane fuel cells are the most promising renewable power generators for zero-emission vehicles and portable applications. High-temperature (>120ºC) PEMFCs have recently drawn attention due to their certain advantages. Increased tolerance of the anode to carbon monoxide (>0.1 CO at 150ºC), enhancement of reaction's rate, electrochemical performance relatively independent of humidity are some of them.

At the heart of the PEM fuel cell is the membrane electrode assembly (MEA). MEA consists of a proton exchange membrane, catalyst layers and gas diffusion layers (GDL). Starting with the membrane, the requirements that should be met concerning its properties are the following: (1) high doping ability with strong acids, (2) high ionic conductivity, (3) low electronic conductivity, (4) low gas permeability, (5) chemical and oxidative stability, (6) thermal stability, (7) good mechanical properties and (8) low cost.

Polybenzimidazole, PBI, has been studied by several research groups and seems to be the most promising electrolyte for high temperature PEMFCs. Our approaches to the development of new polymer membranes include the synthesis of new aromatic polyethers containing polar units in the main chain and the preparation of PBI based as well as PBI free blends. Aromatic polyethers were chosen due to their good mechanic properties and high thermal stability. The insertion of polar pyridine units was done with the view of having sites that could interact with phosphoric acid giving thus good doping ability. Characterization of the prepared materials showed that in most cases they fulfilled the prerequisites of a polymer electrolyte.

Further more, different MEAs were constructed and tested in a single 2x2 cm[2] fuel cell. There are many parameters involved in the construction of the MEAs. The Pt loading, the ionomer type, the ratio Pt/ionomer, the doping level and the thickness of the membrane, the temperature and pressure of the hot pressing surely affect the final fuel cell performance.

The conductivity of the polymer membrane as well as the different electrode's and MEA's performance were tested by means of A.C. impedance and Tafel plots measurements at various temperatures. Conductivities in the range of 10^{-2} s/cm were obtained while the single cell performance is slightly lower than the one reported for the PBI membranes since the system is not yet optimized.

Electrocatalysts for Solid Alkaline fuel Cells (SAFC): beneficial effect of adding bismuth to Pt/C and PtPd/C based catalysts

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Solid Alkaline Fuel Cells (SAFC) are promising devices for power generation for small power units working under ambient conditions, such as electronic portable devices. Comparing SAFC with PEMFC (Proton Exchange Membrane Fuel Cell), the kinetics of the ORR (Oxygen Reduction Reaction) is easier in alkaline medium than in acidic medium[1]: thus using non-noble metals as electrocatalysts is possible[2]. Furthermore, the crossover of fuels[1] (alcohols, such as methanol, ethanol and ethylene glycol) by the electro-osmotic effect will be limited, as a consequence of the hydroxyl ion conductivity across the membrane. Moreover, the highest activity of electrocatalysts in alkaline medium for alcohol oxidation will allow us to build anodes with low level of platinum. These facts may reduce the cost of the fuel cell, particularly that using ethylene glycol (EG) as a fuel.

Production units of EG already exist. This product is used in resins, polyester fibers, anti-freeze, heat transfer fluid, hydraulic fluid, …[3] Ethylene glycol is less toxic than methanol and their volumetric energy densities are close (3840 Ah dm^{-3} for EG oxidation to oxalic acid and 3960 Ah dm^{-3} for methanol oxidation to CO_2). Then EG seems to be a good candidate as a fuel for a SAFC.

The aim of this work is to prepare and to characterize the activity of Pt/C and PtPd/C based catalysts, modified by bismuth, for the oxidation of EG in alkaline medium. Moreover, PtBi/C catalysts have shown a good activity for oxygen reduction in alkaline medium and a good EG tolerance. Results concerning the composition, the preparation route and tests in a single fuel cell will be discussed.

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Removal of liquid water from PEMFC structure: effect of the bipolar plate design

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The pattern of bipolar plates consists often of series of sets of parallel channels grooved in the plate. However other distributor designs have been suggested, in particular for liquid fuel injected into the cell. The effect of the design on the two-dimensional gas distribution in the diffusion layers and in the electrode structure, have been investigated through CFD modelling. However the issue of liquid water formed in the fuel cell structure, and its possible blocking in the grooved pattern of the plate has been scarcely investigated, and is discussed in the present paper.

Two 25 cm^2 bipolar plates (Electrochem ™) have been considered here: in addition to the usual "serpentine" design with 0.8 mm channels, the other design called column-flow pattern, consists in 2 mm cubic plots placed regularly on the plate surface, with two rows of squared orifices at the inlet and outlet. Experiments were conducted in the cell fed with hydrogen and air at ambient pressure, with various humidification conditions. 112 and 115 Nafion ™ membranes were used. With the thicker membrane, liquid water could be formed in the cathodic compartment for high humidification of the air injected, as confirmed by mass balances: experiments showed the slow, regular decrease of the cell voltage with the current for the column-flow pattern; in contrast, the voltage recorded with the other design decreased far more rapidly for current densities over 0.1 – 0.2 A cm^{-2}, probably due to flooding phenomena. Use of thinner membranes favoured the diffusion of vapour from the cathode side to the anode compartment, as expected: the performance afforded by the two plate patterns differed to a lower extent.

Visualisation experiments of gas-liquid flow in bipolar plates have been carried out with condensation of vapour injected in the feeding gas. High-speed camera has been used for observation of the liquid flow through the Perspex layer of the modified cell: the column-flow pattern allows more regular removal of the liquid, whereas plug flow of water was observed in the serpentine pattern. Interpretation of the data collected, sare discussed in the paper.

This conclusions obtained in the investigation are essential in the design of bipolar plates, with respect to both the circuit design and the material of the plate.

Preparation and activity of Pt-TiO$_2$/C composite catalyst for electrooxidation of methanol

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The direct electro-catalytic oxidation of small organic molecules (SOMs) for potential use as fuels in so-called direct fuel cells has been studied in recent years. Electrocatalysts having higher activity for methanol, ethanol and fomic acid oxidation are critically needed to achieve enhanced fuel cell performance. Poisons such as CO_{ads}, which is often an intermediate on Pt surface of such SOMs electrooxidation reactions, resulting in a dramatic decrease in efficiency. Recent studies of developing catalysts with transition metal oxides such as SnO_2, WO_3, TiO_2 have shown improvement electrocatalytic properties in SOMs electrooxidation. Thus, the purpose of this work is to study the influence of some parameters in the preparation of Pt-TiO$_2$/C composite catalyst to methanol electrooxidation.

Effects of different aging temperature, aging time and t Ti/Pt molar ratio are researched in our experiment. Through the comparison of current by CV, we found the sample prepared by higher aging temperature (353K) and longer aging time (24h) shows better electro-performance proving its influence in the process of this sol-gel reaction. Also there exists an optimal molar ratio of Ti:Pt at 1:2.

Catalyst sintered at different temperature, comparing with commercial Pt/C have been tested in our work using CV. With the increase of scan cycles, the current of catalyst increase ring-by-ring which differ from commercial Pt/C whose current reduce with the increase of scan cycles.[1] At the same time, the current changing with different temperature shows an apparent formula which consistent with the ratio the forward anodic peak current (If) to the reverse anodic peak current (Ib) which is used to describe the catalyst tolerance to accumulation of carbonaceous species.

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Application of Heme Proteins and Enzymes as Biocathodes for Biofuel Cells

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Biofuel cells utilise biocatalysts, electrically "wired" to the electrodes, for the conversion of raw materials such as methanol or glucose to electrical energy using O_2 or H_2O_2 as an oxidiser, thus offering a reasonable energy alternative for e.g. *in vivo* medical applications. Enzymes accelerate the equilibrium formation of chemical reactions by a factor of 10^8-10^{20} compared to un-catalysed reactions, thus enhancing the transformation of traditionally used "fuel" compounds. Hitherto, the glucose-oxidase-based glucose/O_2 and glucose/H_2O_2 redox systems were mostly used to convert glucose to electricity; at present whole organism-based fuel cells are proposed to convert sugars to electricity.

For the development of biofuel cells, biocathodes providing the 4e$^-$ electroreduction of oxygen to water are essential (for more than a century the reference catalyst of this reaction has been Pt in 0.5 M H_2SO_4). In addition to intensively studied copper enzymes, heme enzymes and proteins enabling both O_2 and H_2O_2 bioelectrocatalytic reductions are of evident interest. By itself heme demonstrates strong electrocatalytic properties, e.g. in the reaction of O_2 and H_2O_2 reductions at potentials of its $Fe^{3+/2+}$ redox conversion close to 0 V (NHE) pH 7. In a polypeptide environment and upon interactions with various ligands, the heme active site in proteins can exhibit a wide 800-mV range of the redox potentials due to its Fe^{2+}/Fe^{3+}- redox couple (from 0.4 V to -0.4 V), and the redox potentials exceeding 1.4 V for higher oxidation states of heme in a number of peroxidases. Bioelectrocatalytic activity of heme promotes bioelectrochemical applications of heme proteins and enzymes as biocathodes in biofuel cells. Principal applicability of cyt *c*-cytochrome *c* oxidase complex and microperoxidase in biocatalytic cathodes has already been demonstrated (*Katz et al., J. Electroanal. Chem. 479 (1999) 64; Wilner et al., J. Chem. Soc., Perkin Trans. 2 (1998) 1817*). The question is how efficiently heme proteins and enzymes can be used in biofuel cells, where electrically "wired" heme will work as a biocathode, transforming oxidising energy of O_2 and H_2O_2 in electricity?

In this paper the bioelectrocatalytic properties of the other heme proteins and enzymes that are necessary for constructing biocathodes are discussed. Possibility and prerequisites for application of peroxidases, catalases, some multi-cofactor heme enzymes, as well as heme-containing globins, which, being not catalysts under biological conditions, exhibit pseudo-enzymatic activity under conditions of electrode reactions, are analysed.

Influence of the Cooling Strategy on the Local Performance of PEFC

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System efficiency concerns limit the coolant flow rate and restrict the energetically costly gas humidification to an extent well below cell temperature. Limited coolant flow leads to temperature inhomogeneities in the cell-plane. Due to the influence of the temperature sensitive water condensation/evaporation equilibrium on membrane conductivity, temperature inhomogenieties have a serious impact on the *local* current generation and performance.

Experiments in 200 cm^2 cells with local current recording have been conducted in counter flow operation of dry hydrogen and differently humidified air, with different temperature profiles along the air path and (Fig. 1). The current at the dry H$_2$ inlet (right) rises steeply, even at increased temperature. In contrast heat up at the air inlet shows a much stronger response in local performance. This is because air becomes saturated by product water towards the H$_2$ inlet, which is then humidified by water exchange through the MEA. In contrary, dry air at the inlet cannot be humidified the same way due to the low volume stream of hydrogen.

A theoretical analysis [1, 2], systematically elucidating the underlying loss mechanisms of the different cooling strategies will also be presented.
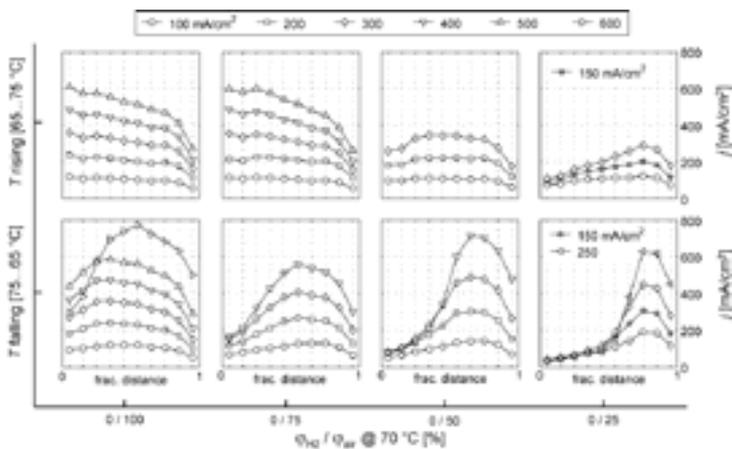

Fig. 1: Current density distribution for counter flow operation of dry hydrogen and air at different total current. Air enters on the left side. Upper row: temperature rises along the air path from 65 to 75 °C. Right column: Inverse profile with decline from 75 to 65 °C. Air humidification decreases from left to right.

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Novel supporting materials for Pt nanoparticles in electrooxidation of alcohols

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This work is dedicated to the memory of Prof. Aleksandar Despi_

For applications in PEMFCs, high area carbons are usually employed as the supporting materials. Their alternative are titanium suboxide ceramics having formula Ti_nO_{2-n} ($4<n<10$). The composite consisting mainly of Ti_4O_7 and Ti_5O_9 is registered as Ebonex®. Ebonex posses metallic conductivity and corrosion resistance superior to carbon. Additionally, owing to its hypo-d-electron character, Ebonex is capable to interact with metallic particles. The goal of this work was to investigate the activity of Pt nanoparticles supported on Ebonex for the electrooxidation of lower alcohols.

BET surface of starting Ebonex powder was found to be 1.6 $m^2 g^{-1}$. The impregnation method has been applied to synthesize platinum nanoparticles on it. Rather uniformly dispersed Pt particles of 5±3 nm were obtained. Pt/Ebonex catalyst was dispersed in mixture of water and Nafion (v/v 20:1). A drop of the suspension was placed on Au disk electrode. Electrooxidation of methanol, ethanol and 2-propanol was investigated in acid media by slow sweep polarization of 1 mV s^{-1}.

Onset potential of electrooxidation of alcohols shifts in negative direction with the increase in the chain length. In the entire potential region up to the maximum on the polarization curve current densities for oxidation of 2-propanol are the highest and for oxidation of methanol are the lowest. The current densities (calculated with respect to the real surface area determined from cyclic voltammetry) were compared to those on the smooth Pt electrode and no substantial synergetic effect of the Pt particles and Ebonex support was found.

Nanostructured bimetallic CATHODIC catalysts for pemfc

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The performance of hydrogen-air fuel cells are known to be limited by slowness of cathodic oxygen reduction reaction (ORR). It's common accepted now that the best electrocatalysts are multi-component, in particular binary, especially nanosized metallic systems [1]. Of late fundamental problems concerning size effects in ORR at Pt-alloys nanoparticles deposited onto carbon supports are still very much in vogue.

Modern methods of mutual reduction of metals from mixed solutions fail to obtain proper binary systems due to difference in reduction rates for different metals. It stands to logic to prepare some precursors in which atoms of Pt and another metal (M) being in stoichiometric relation have direct bonds Pt–M and are surrounded by organic groups. This approach gives a possibility to impregnate a support, e.g. carbon black by solution of such a precursor, and then to extract organic constituents by heat treatment at 350–500 ^{o}C. In result, very even heterometallic coating will be applied onto the support surface. It must be stressed that the relation Pt:M can be varied in a wide range. The thermodestruction process can be controlled with DTA, TGA and DSC.

As initial substance for precursor synthesis, ethoxydicyclopentenyle-platinum-ethoxide $(C_{10}H_{12}OC_2H_5)_2Pt_3(OC_2H_5)_4$ was used. Binuclear complex of cobalt __2(__)6(____2____2__) and cyclopentadienyltricarbonyls of chromium and tungsten $[C_5H_5M(CO)_3]_2$ (M = Cr, W) were used as heterometallic counterparts. Three versions of bimetallic catalysts, specifically of Pt–Co, Pt–Cr and Pt–W systems supported at carbon black with surface area ca. 600 m^2/g were synthesized. Atomic relation Pt:M was equal to unity in all cases. It came to pass that the performances of all catalysts are barely differ. Open circuit potential at all catalysts studied was close to +0.36 V vs. Hg/HgSO$_4$, that points to their high catalytic activity in ORR.

Fig. 1 shows polarization curves for ORR at gas-diffusion electrodes with catalysts of the systems Pt–Co, Pt–Cr and Pt–W. Current density at potentials +0,2, +0,1 and 0,0 V amounted, correspondingly to 35, 350 and 1500 mA/cm^2 for electrodes with Pt–Co and Pt–Cr catalysts. Some fading of catalytic activity of Pt–Co system was found in the course of prolonged testing. This phenomenon could be explained by selective Co leaching. Other systems have much more stability. The specific activity of catalysts was close to 1500 A/g at the potential of 0.0 V.
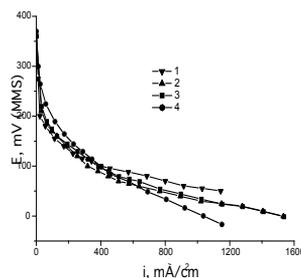

Fig.1 Polarization curves for electrodes with Pt (1), Pt-Co (2), Pt-Cr (3) and Pt-W (4). Electrolyte - 2,5 _ H$_2$SO$_4$.

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Comparision of different ternary pt-ru-x catalysts dispersed on poly(3-methyl) thiophene conducting polymer towards the electrooxidation of methanol

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Direct Methanol Fuel Cell (DMFC) is an ideal power source for electric vehicles because of favourable properties of methanol as a fuel. Methanol is a liquid which can be easily stored, handled and produced from oil,natural gas,coal or biomass. Thus,it should be widely available and cheap. Morever,the DMFC can run at low temperatures (around 100^0C) and does not require fuell processing.

For a long time, platinum was considered as the best electrocatalyst in acidic medium for methanol oxidation in terms of fuel cell application. However, the methanol oxidation at a platinum electrode is a self-poisoning reaction, owing to strongly adsorbed CO_{ads} or COH_{ads} by chemisorption of methanol. In order to enhance the performance of the platinum electrode, one way is to increase the active surface area by dispersion of the catalyst as small particles on a convenient conducting support. This can be achieved by the use of a conducting polymer such as polythiophene, polypyrrole or poly aniline.

The use of bimetallic catalysts such as Pt-Ru improves the performance of practical electrodes and decrease poisoning. Moreover, the preliminary experiments have shown that the incorporation of a third metal to the binary catalyst enhanced the performance of methanol oxidation compared to Pt-Ru, at low potentials.

In this study, the electrochemical oxidation of methanol was investigated on Pt-Ru-X ternary metallic catalysts (with X= Mo, Cr or V). The catalysts were prepared by electrochemical deposition and dispersed in a conductive three-dimensional matrix, an electronic conducting polymer, poly 3-methyl thiophene (P-3MeT). The performance of ternary catalyst on methanol oxidation was compared to that of binary catalyst under the same experimental conditions. The anode compositions were verified using XRD and XPS technique.

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"Cross-Talk" in Carbon Corrosion of PEMFC/DMFC

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Carbon corrosion is a fundamental issue in PEMFC/DMFC fuel cells. Carbon is currently the major material component in the electrodes and flow-plates; degradation of these components will seriously influence the performance and lifetime of the fuel cell. In the course of our work, we have found that corrosion occurs in both components, resulting in material degradation.

Indeed, corrosion of the carbon in the electrodes influences the performance of the flow plates and *vice versa*. Such "cross-talk" will be discussed in detail on the basis of results obtained using a DMFC test set-up. The effect of the corrosion products on the proton-conducting membrane will also be discussed. Corrosion products from the carbon components in the electrodes and flow-plates can perturb ion transport through the membrane. The effect of this on fuel-cell performance and lifetime will also be discussed.

All flow-plate and Membrane Electrode Assembly (MEA) examinations were made using SEM, EDS and XPS.

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Validation of a 2D-MCFC model to an industrial plant

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High temperature fuel cells such as MCFC and SOFC are devices for combined stationary power and heat supply. Although several industrial companies have successfully operated field trial plants based on these concepts and have thereby proven their technical feasibility, there are still some issues that need to be dealt with on the way to commercialisation. Many of these issues are closely correlated to the spatially distributed temperature profile in the cells. Thus, knowledge and understanding of this state is important for the further development of these systems.

Unfortunately, temperature measurement inside high temperature fuel cells is difficult, so sufficient direct information on the actual temperature field is not available. In order to reproduce actual temperature profiles and predict them under arbitrary operating conditions and varying design parameters, a spatially distributed model for a cross-flow MCFC has been developed. This model consists of highly linear, coupled partial differential equations of hyperbolic and parabolic type and an integral equation. The complexity of the model leads to a high effort for its numerical solution. To ensure good quantitative agreement of the model with measurement data, an extensive model validation is carried out using a 250 kW industrial MCFC plant.

This validation process requires an elaborate strategy for several reasons. Firstly, although the plant is equipped with a large array of sensors, measurement information is incomplete and not always reliable. Secondly, with more than 20 unknown parameters, the number of fitting parameters is rather high. Thirdly, the parameters must not only be fitted to a single operating point, but to a whole range of load cases. The last reason is the complexity of the model, which impedes the simultaneous adaptation of all parameters with a least squares method.

To handle this challenge, a threefold strategy is applied. First, a black box modelling of several compartments of the system is used to complete and correct the measurement data obtained from several load cases covering a whole operating range. In this step, compliance of the measurement data with the conservation laws of mass and energy is established and the reliability and uncertainty of each single measurement source is taken into account. The second aspect is a parameter sensitivity analysis, which has to be performed repeatedly as parameter values are changed during the validation process. This analysis helps to eliminate insensitive parameters which can be set to arbitrary high or low values, depending on the parameter. The third aspect is a separation approach, where parts of the model containing single parameters or small parameter groups are isolated and fitted independently from the rest of the model. Even in those cases where a total isolation of a part of the model is not possible, this approach helps to identify parameter groups that can be fitted alternately.

In this contribution, after a short overview over the mathematical model, the authors focus on the various aspects of the validation strategy and finally demonstrate a comparison of the validated model with measurement data.

Characterization of Proton Selectivity through Poly(vinyl alcohol) Based Polymer Electrolyte Membranes for Direct Methanol Fuel Cell

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A direct methanol fuel cell (DMFC) using polymer electrolyte membranes (PEMs) are one of the most attractive power sources due to the stable operation at a low temperature, the high energy generation yield and energy density, the simplicity of system. PEMs for DMFC have been developed in order to reduce methanol crossover as well as to reach high proton conductivity. In this study, PEMs were prepared by casting mixed solution of poly(vinyl alcohol) and poly(vinyl alcohol-co-2-acrylamido-2-methylpropane sulfonic acid) (AP-2) on a glass plate and drying it at 50^oC. The PEMs obtained were annealed at various temperatures for 20 min and then were cross-linked chemically by immersing them in a glutaraldehyde solution at 25^oC for 24h to control their water content. The ionic conductivity, mechanical strength and methanol permeability of the membranes have been measured as a function of the AP-2 content.

The water content of the PEMs increases with AP-2 content because osmotic pressure in the PEMs increases with increasing the number of the charged groups. The water content decreases with increasing annealing temperature because the degree of crystalinity in the PVA matrix increases with increasing annealing temperature.

The proton conductivity (σ) and methanol permeability (P) of the PEMs increase with increasing AP-2 content because the water content of the PEMs increases with increasing AP-2 content. Fig. 2 shows the proton permselectivity (ϕ) of the PEMs, which is defined as $\phi = \sigma/P$, as a function of AP-2 content. The proton prmselectivity increases with increasing AP-2 content. The PEMs annealed at 170^oC have higher proton permselectivity than Nafion®117.
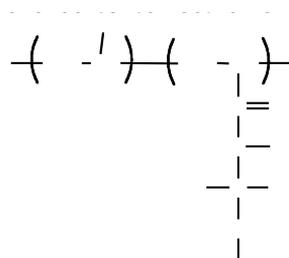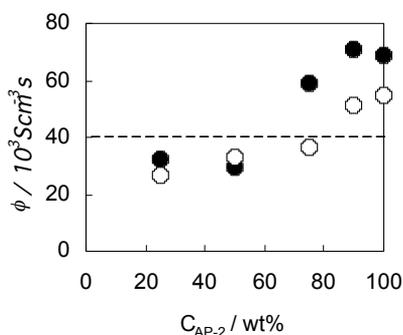

Fig.1 Chemical structure of AP-2.

Fig.2 The proton permselectivity, ϕ, as a function of AP-2 content, C_{AP-2}. Temp.: 25^oC MeOH: 10M.
Annealing temperature : ●,170^oC ; ○,160^oC
Dotted line: ϕ of Nafion®117 under the same conditions.

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Anhydrous Nafion-Bz Proton Conducting Membranes for High Temperature PEFCs

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Currently, PEFCs (polymer electrolyte fuel cells) are expected that energy conversion devices in the future that have higher energy efficiency than membrane fuel cells will become a leading alternative to internal combustion engines. However, the high materials cost and complicated water management are major obstacles for PEMFCs. Moreover, CO, which is contained in the hydrogen gas reformed by hydrocarbons at the ppm level, can severely poison the anode catalyst of membrane electrolyte assemblies (MEAs) and can cause significant loss in energy efficiency. On the other hand, the operation of PEMFCs at intermediate temperatures (100-200°C) has been considered to provide many advantages such as improved CO tolerance of the Pt electrode, reduction of the amount of Pt electrode materials, higher energy efficiency, better heat management, and co-generation. Many temperature tolerant polymer materials have been synthesized, and protonic conductivity and cell performance at elevated temperature ranges have been investigated intensively.

Here we synthesized anhydrous Nafion-Benzimidazole (Bz) composite proton conducting membrane. The thermal stability and chemical structures of these composite membranes are investigated by thermogravimethric analysis (TG) and FTIR. The proton conducting membrane showed the excellent proton conductivity of $10^{-3} - 10^{-2}$ S/cm at the high temperature of 140 – 200°C under anhydrous conditions. The proton in the acid-base membrane can transfer from deprotonated anions to protonated cation with proton hopping mechanism. The cell performance of the membrane is on going.

Characteristics of Al-reinforced γ-LiAlO$_2$ matrices for molten carbonate fuel cells

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Al-reinforced γ-LiAlO$_2$ matrices for molten carbonate fuel cells (MCFC) were fabricated to improve their mechanical strength, longevity, and efficiency. The fine γ-LiAlO$_2$ powders (average size of 2μm) and the pure Al (average size of 3 / 20 / 50μm) / Li$_2$CO$_3$ (average size of 1μm) particles were used as matrix and reinforcing materials, respectively. The phase transformation and the mechanical strength were measured after sintering at operation temperature of 650℃ for MCFC. The Al phase transformed completely into γ-LiAlO$_2$ at 650℃ within 10 h (4Al + 2Li$_2$CO$_3$ + 3O$_2$ → 4LiAlO$_2$ + 2CO$_2$). The mechanical strength of these matrices (283.48g$_f$/mm^2) increased about three times higher than that of the pure γ-LiAlO$_2$ matrix (104.01g$_f$/mm^2). The mismatch of the thermal expansion coefficient between the matrix and electrolyte phases might be also controlled by adding Al particles, which resulted in the improvement of the thermal stability in the initial heating-up step. The unit cell and thermal cycling tests showed a promising performance in comparison with the pure γ-LiAlO$_2$ matrices.

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Formic acid oxidation on glassy carbon supported platinum nanoparticles – strustural effect

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Electrochemical oxidation of formic acid is well known as the structural sensitive reaction. While Pt (111) shows negligible poisoning over the whole potential region where the reaction occurs and proceeds with almost same rate in both sweep directions, Pt (110) and Pt (100) are completely blocked with poisoning species up to high potentials where these species can be oxidised and the reaction reaches high rates upon the reversal sweep at both planes[1]. Formic acid oxidation, although not extensively, has been studied at Pt nanocatalysts as well[1-4]. We examined this reaction on Pt particles electrochemically deposited on polished and on electrochemically oxidised glassy carbon.
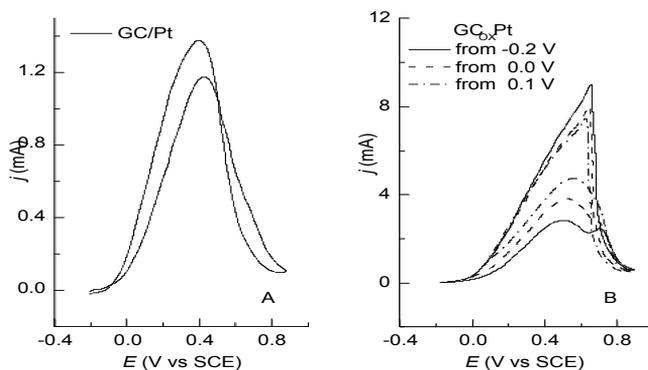

Fig. 1: Cyclic voltammograms for oxidation of 0.5 M HCOOH in 0.1 M $HclO_4$ at GC/Pt (A) and GC_{OX}/Pt (B) electrodes (sweep rate 50 mV/s).

Based on cyclic voltammogram for formic acid oxidation at Pt deposited on polished GC (Fig. 1A) it could be assumed that the predominant fraction in the particle has Pt(111) crystal facet. If GC is oxidised prior to Pt deposition, the shape of CV (Fig. 1B) suggests that this reaction still proceeds predominantly at Pt(111) at low potentials (E < 0.5 V vs SCE), but the second anodic peak at E = 0.7 V vs SCE and sharp increase in currents in reverse sweep indicate the increase in fraction of Pt(110) and Pt(100) facets.

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Prepration and characterization of ternary carbon-supported platinum-tin based nanosized electrocatalysts for direct ethanol fuel cell

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As an alternative fuel, ethanol is safer and exhibits higher energy density than methanol. As well known, ethanol electrooxidation is more difficult than that of methanol. So far, it is difficult for the state of the art PtRu catalyst to oxidize ethanol completely, with many intermediates produced which lead to electrocatalyst poisoning [1-4]. The electrocatalytic activity of Pt can be greatly enhanced by using Pt-Sn/C for ethanol oxidation (5-7). In the present work, several carbon supported nanosized PtSnMn and PtSnCu catalysts were synthesized and characterized by X-ray diffraction (XRD). Their electrocatalytic activities toward ethanol were also investigated in function of working temperature.

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Preparation and characterization of bimetallic carbon-supported platinum-palladium based nanosized electrocatalysts for direct methanol fuel cell

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DMFCs have been studied and considered as possible power sources for the portable electric apparatus and electric vehicles and it has benefits such as high energy density of methanol, availability and portability (1,2). Poor efficiency of platinum at the anode was observed due to the slow kinetics methanol oxidation. Pt-Pd system have been reported to be promising catalysts and tolerant toward CO formation during the electro-oxidation of methanol in direct methanol fuel cells (3). In this work, typical catalyst metals are platinum, palladium and typical support particles are Vulcan XC-72. The method of making carbon supported Pt-Pd catalyst is provided comprising the steps of providing the solution of metal chlorides of catalyst metals in solvent system containing at least one polyalcohol(ethylene glycol), forming a colloidal suspension of catalyst metal nanoparticles by raising the pH of the solution and heating the solution, adding support particles to the colloidal suspension, depositing the catalyst metal nanoparticles on the support particles by lowering the pH of the suspension (4).

Methanol electrooxidation was investigated using this catalyst. The results were compared to commercially use Pt-based E-TEK catalysts. The surface characterization was made by XRD.

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Comparison of electrocatalytic activity towards oxygen reduction of some metallophthalocyanines incorporated carbon and ultra dispersed diamond electrodes

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Stability, oxygen reduction reaction activity and methanol resistivity of some different transition metals (Co, Fe, Cu....) based 2,916,23 - Tetrakis (4'-carbohexyloxybiph enyloxy) phthalocyanines were investigated. Transition metal based catalysts were prepared either on carbon (Vulcan XC-72) supported or diamond (Alit Co.) supported carbon papers using potentiometric methods. The effect of heat treatment was investigated. Their catalytic activities were tested for oxygen reduction reaction as a function of working temperature. The results were compared to commercially use Pt-based E-TEK catalysts. The methanol tolerance of catalysts was also tested under the same experimental conditions. The surface characterization was made by XRD. Complex structure has been characterized by FTIR, NMR, UV-visible spectroscopy.

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Thin film electrodes and PVDF-g-PSSA membrane for direct methanol fuel cell

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In this work, the applicability of manufacturing membrane-electrode assemblys (MEA) by painting the electrode on an experimental poly(vinylidene fluoride) membrane grafted with polystyrene sulfonic acid (PVDF-g-PSSA) is investigated. The price of PVDF-g-PSSA is significantly lower than that of commonly used Nafion® because of its simple manufacture process by radiation grafting [1]. The goal of the experiments is to find the best method to prepare MEAs for the direct methanol fuel cell (DMFC) by changing the composition of the electrode layer and hot-press conditions.

The results show that even during a short test period the electrode layer with Nafion matrix breaks off from the PVDF-g-PSSA membrane. This decreases the performance of the fuel cell radically, e.g. at 60°C 90% decrease in performance after 5 days. This is quite the opposite, when compared to electrodes painted on Nafion. The performance of the Nafion MEA actually improved during the first days of testing by 10% at 60°C. The electrode remained firmly on the membrane. However, when each test was started, the performance of the PVDF-g-PSSA MEA was 5% better than the Nafion MEA showing it has good potential to replace Nafion, if durability is improved. When the hot-pressing temperature of the PVDF-g-PSSA MEA was increased, its performance generally improved but the decay over time was only slightly affected. The optimum value of the anode's Nafion content was determined to be 60% of the amount of the metal catalyst. Lowering the temperature of the fuel cell to 30°C slowed the degradation so that the decrease of performance was 10% after 5 days.

According the measurements it can be concluded that the decline of performance has two stages: first a quick and steep decrease over a couple of days and after that a slow decay. The former can be attributed to the failing of the electrode structure. This causes proton and electron conductive channels and diffusion routes to be cut off or blocked. The active amount of catalyst decreases strongly. The latter can be attributed to the solvent action of methanol that slowly removes both Nafion and catalyst from the electrodes. The cause of decomposition is probably the mechanical incompatibility between the membrane (PVDF-g-PSSA) and the matrix material of the electrode (Nafion). The membrane also curls up when wetted so that it may have strong tension when it is spread out and put in the fuel cell.

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Dimethoxymethane (DMM) as an alternative fuel for direct oxidation fuel cells

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Among fuel cells working at low temperatures, the PEMFCs (Proton Exchange Membrane Fuel Cells), DMFCs (Direct Methanol Fuel Cells) and DEFCs (Direct Ethanol Fuel Cells) are mostly considered. But each of them displays some limitations due to either storage, safety issue, toxicity, or reactivity of the fuel. In order to find an alternative to these problems, electrooxidation of others organic fuels such as ethers without carbon-carbon bonds are studied. Electrooxidation of the simplest one, dimethyl ether (DME) [1-4], proceeds through its hydrolysis to produce CO_2 and HCOOH. A maximum power density of 30 mW cm^{-2} can be obtained, compared to that with methanol (60 mW cm^{-2}). DME is a gas at room temperature, but, as a liquid is more convenient for fuel cell applications, dimethoxymethane (DMM) appears as a good candidate. DMM, which is also called formaldehyde dimethyl acetal, formal or methylal ($CH_3OCH_2OCH_3$), can be an alternative fuel for such applications. This ether is a stable liquid except in an acidic electrolyte and/or at elevated temperatures; its boiling point is 45.5°C under atmospheric pressure. This compound has an interesting theoretical energy density (7 kWh kg^{-1}). The performances in a Direct Oxidation Fuel Cell (DOFC) using DMM are higher than those of a DMFC, in agreement with its energy density higher than that of methanol, i.e., 4.89 Ah/mL (5.62 Ah/g) for DMM compared to 3.97 Ah/mL (5.02 Ah/g) for methanol. The Gibbs energy change associated with the full combustion of DMM (CH_3-O-CH_2-O-CH_3 + 4 O_2 → 3 CO_2 + 4 H_2O) is $\Delta_r G° = -1903.2$ kJ mol^{-1} under standard conditions. The corresponding equilibrium potential is 1.23 V, with a number of exchanged electrons equal to 16. This communication will compare electrochemical results of DMM oxidation at the three platinum basal plane electrodes and some stepped surfaces in the series Pt[n(111)x(111)] and Pt[n(111)x(100)] to observe structural effects. Comparison with polycrystalline platinum electrodes is also discussed. Effect of several other parameters, such as anion nature, DMM concentration, scan rate, have been studied to better understand the reaction mechanism of the electrooxidation of DMM.

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The influence of pt-ru catalysts structure on their activity in dmfc

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The influence of binary catalyst structure on its electrocatalytic activity is widely discussed in literature. A high activity of Pt-Ru/C E-TEK catalyst is usually accounted for by the uniform distribution of Pt and Ru atoms on the surface of carbon nanoparticles. Pt and Ru form an alloy that has fcc lattice of Pt, Ru being dissolved in the alloy solid solution. Pt-Ru electrodeposited catalysts developed earlier in our laboratory had as high electrocatalytic activity as conventional Pt-Ru/C E-TEK catalyst. The EXAFTS data for electrodeposited Pt-Ru electrodes indicated the presence of Pt-Ru alloy structure. The catalyst consisted of small (1-2 nm in diameter) particles, Ru atoms being present mainly on the particle surface. At the same time the promising results for decorated Pt/Ru and Ru/Pt catalysts show that alloy formation is not the only factor that provides high catalytic activity.

In this research nanostructured carbon supported Pt-Ru catalyst was prepared from Pt ethoxy-complex and tetracarbonyl of Ru by thermal destruction at 500° C in Ar atmosphere. The real surface area was measured by oxidative stripping of preadsorbed CO in 0.5 M H_2SO_4. The kinetics of methanol oxidation was investigated by steady state polarization curve measurements in 1 M CH_3OH + 0.5 M H_2SO_4 at 60° C. Bulk and surface ratio of Pt and Ru was determined using EDX and XPS analyses. Phase composition and lattice parameters were characterized by XRD.

The data obtained in this research show that Pt-Ru/C catalyst as prepared is so highly active as conventional E-TEK catalyst but loses its activity during storage. The total currents of methanol oxidation decreased by 7-8 times during storage, the real surface area of the catalyst decreasing only by two times. That means that the catalyst gradually loses its intrinsic activity. The current maxima and the region of CO_{ads} stripping shifted to more positive potentials testifing to the loss of the catalyst activity in CO oxidation reaction.

XRD analyses of the catalyst samples have shown the absence of Pt-Ru alloy structure. XPS analysis of Pt-Ru/C electrode manufactured with this catalyst has shown the decrease in Ru content on the surface after electrochemical testing. The preliminary conclusion can be drawn that the alloy formation does not considerably influence the initial activity of binary catalyst but is important for its stability during storage and electrochemical testing.

Structure of diffusion electrode for air breathing operation in direct methanol fuel cells

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Direct methanol fuel cells (DMFC) are attractive power for the portable electronic devices. However, using the pump or fan for supplying the air and liquid methanol was improved [1-4].

In this study, structure of diffusion electrode for air breathing condition without pump or fan was developed. To operate of air breathing conditions for DMFC, cathode electrode has two functions. One is supplying the air in the catalyst active site and the other is exhausting the water that was produced by electrochemical reaction. Size and surface area of the pore of catalyst layer was controlled in the range of 10-50 nm and below 10 m^2/g because big pore was advantage of supplying air in the catalyst don't prevent from the produced water. On the other hand, anode electrode has 3-6 nm pore size for control the amount of liquid methanol in order to prevent from methanol crossover to cathode electrode.

MEA was prepared by this electrode using the hot press and performance was tested. Fig.2. shows current density profile and performance achieved above the 150 mA/cm^2 at 0.4V operation.
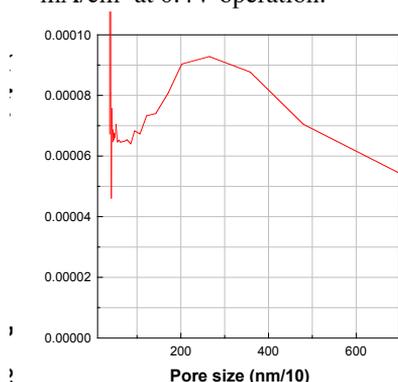

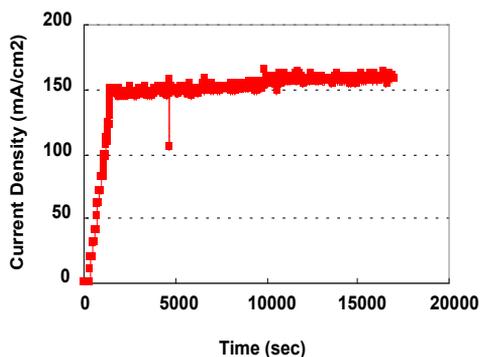Fig.1. Pore size distribution of cathode and anode electrode.

Fig.2. MEA performance at the air breathing conditions. (0.4V, 50 $^{\circ}$C)

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Electrochemical Behavior of Co/Ce Coated Ni cathode for Molten Carbonate Fuel Cells (MCFCs)

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The dissolution of the state of the art cathode material NiO into electrolyte is one of the major technical obstacles to the commercialization of the MCFC [1]. To solve this problem, many studies carried out. Surface modification by more stable materials than NiO in MCFC cathodic condition is one of them.

In this study, we studied about the electrochemical behavior of Co/Ce coated Ni cathode. We prepared the coated materials by Pechini method [2] and the coated cathodes by tape-casting process. We confirmed that these coated cathodes were more stable than NiO cathode in MCFC cathode conditions. And also these cathodes have electricalcatalytic activity for the oxygen reduction. We employed SEM/EDX, XRD and ICP-AES to characterize. And Electrochemical Impedance Spectroscopy and Cyclic Voltametry were measured to verify electrochemical behavior of these cathodes.

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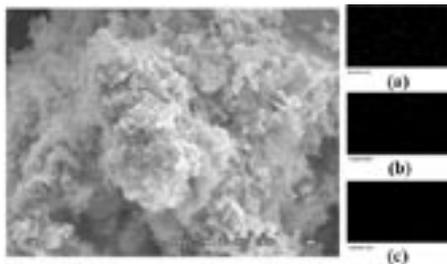[2] M.P. Pechini, US Patent No. 3330697, July 11, 1967.
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Fig.1 SEM and mapping images of Co/Ce coated Ni powder.(a) Ni (b) Co (c) Ce

Ni/YSZ composite electrodes for high performance and durability of solid oxide fuel cells

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NiO-YSZ composite powders, which composed of nano-sized NiO and YSZ coated on YSZ particle, were synthesized by the Pechini process for improving the performance and durability of solid oxide fuel cell (SOFC) anodes, and their microstructures and electrical properties have been investigated. Ni-YSZ electrodes were manufactured by sintering the die-pressed NiO-YSZ pellet at 1400°C for 3 h, followed by reducing it at 800°C under hydrogen atmosphere. The NiO/YSZ composite anode with high homogeneity and large three phase boundaries (TPBs) showed an excellent tolerance against the redox cycling and the thermal aging. The maximum power density of a single cell using this NiO/YSZ anode was found to be over 1 W/cm^2 at 800°C in reactive gases of humidified hydrogen and air. The cell shows also excellent initial (<12 h) stability of 0.905~0.907 V at 0.3 A/cm^2 under galvanostatic tests. It can be concluded that the functional NiO/YSZ composite powder will suppress the degradation of anodes and enhance the long-term and redox stability of the unit cell at elevated temperatures. Further, functional electrodes composed of active thin layer between large porous Ni-YSZ support and YSZ electrolyte layer using composite powder is being investigated for improving the performance of the IT-SOFCs.

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Fuel Cells and Sustainable Energy

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Electrochemical Conducting of PVDF/SPEEK Composite Membrane with Surface Treated for DMFC

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In the last decade, the development of the direct methanol fuel cell (DMFC) had gained much interest mainly for portable power application. A key component of (DMFC) is the proton exchange membrane, which is required to have low liquid uptake at water and methanol. The SPEEK is typically obtained by either directly introducing sulfonic acid groups onto the polymer backbone or direct polymerizing sulfonated monomers.

In this study, poly(vinylidiene difluoride)/Sulfonated poly(ether ether Ketone) hybrid membranes were prepared to evaluate the possibility of use as a proton exchange membrane for direct methanol fuel cell (DMFC). PVdF and Sulfonated poly(ether ether ketone) was use to increase proton conductivity, and simultaneously to prevent methanol transport through the cross linked membrane. The Nafion-PVDF/SPEEK-Nafion(NPSN) composite membrane was prepared by immersing the SPEEK in the Nafion-containing casting solution.

Furthermore, in order to improve the composite properties for DMFC applications, the single phase pure polymer method was discussed.

SPEEK/ TiO_2 10.0% membrane with exhibit performances comparable to that of SPEEK/ TiO_2 2.5% membrane due to lower methanol crossover, and the performance of SPEEK/ TiO_2 10.0% membrane at high current densities with methanol (2M) high than SPEEK/ TiO_2 2.5% membrane due to lower methanol permeability. Increasing the titanium oxide content in the SPEEK composite membranes leads to a decrease of the MeOH permeability. The reason for these results is related with the increasing amount of inorganic filler in the membranes, which increases the membranes barrier properties in terms of mass transport.

However, separations of the electrodes from the SPEEK membrane were observed after 2 hour of operation in DMFC due to the poor adhesion and bonding properties. Further work is needed to overcome this problem and fully assess the long term stability. Nevertheless, the lower cost and methanol crossover compared to that of Nafion make the SPEEK membranes promising alternatives for DMFC.

Nanoporous materials growth and transport

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Nanoporous materials have wide applications in the energy research. For example, in the processing of micro fuel cells, the gas diffusion layers and the current collectors can be fabricated using the nanoporous conductive layers. Gold nanoporous layers on porous alumina substrates were prepared by co-evaporating silver/gold metals and subsequently dealloying the composition by selectively removing the silver metal leaving a nanoporous gold film. Using a similar process, patterned gold nanoporous layers were also prepared on a silicon substrate with prefabricated micro holes. XPS analysis was performed to analyze the deposited alloy composition as well as the dealloyed film compositions. Pressure drop across the membrane and gas permeability were measured for the nanoporous gold films. The influence of alloy composition (Ag/Au ratio), dealloying etch times and the influence of thermal annealing on the structure of the porous film were studied. Application of these nonporous films for the fabrication of micro fuel cells will be discussed.

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Utilising Impinging Jet measurements to characterize oxidation of small organic molecules on platinum

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Platinum based catalysts for the electrooxidation of hydrogen and small organic molecules are very important for fuel cell applications. Carbonaceous intermediates (for instance CO) are potent poisons in hydrogen fuel cell, or poisoning reaction intermediates within the direct methanol fuel cell, requiring the anode catalyst to operate at high over potential, reducing the efficiency of the cell. Therefore, the ability of a fuel cell catalyst to promote the oxidation of such intermediates at lower over potentials has always been seen as a significant step towards commercialising fuel cells. In order to design better catalysts a complete understanding of these intermediates we have developed approaches utilising an impinging jet to characterise the surface coverage and composition of species adsorbed on the electrode surface.

The impinging jet approach is useful as it allows rapid variation of electrolyte composition whilst maintaining full electrochemical control of the system and is thus ideally suited to studying electrochemical surface modification and the resultant effects on reactions or processes[1]. The main issue with the impinging jet approach is associated with the non-uniform access of wall-jet type cell configurations[2]. We have developed a critical improvement to this technique which allows us to attain uniform access across the entire electrode surface. This is accomplished by utilising a sufficiently small electrode (Ø≈100μm), and position that electrode above the point at which the boundary layer is thinnest.

We have used the impinging jet approach to measure the electrooxidation of hydrogen on a platinum surface with different coverages of CO and other carbonaceous species. Specifically, we find that the hydrogen oxidation reaction (hor) is very sensitive to CO coverage, and we can use the hor to study the early stages of CO oxidation.

Results showed significant differences in the structure of CO admitted at potentials within the hydrogen region and the double layer region, consistent with the literature. Significant differences in the structure of CO monolayers prepared by incomplete dosing compared to complete dosing followed by partial stripping, were also seen, again consistent with the literature. The different CO submonolayer structures influenced the hydrogen electrooxidation reaction in different ways, from which it is possible to extract insight into the mechanism and kinetic data for the hydrogen electrooxidation reaction.

The impinging jet system has also been used to examine the electrooxidation of methanol, formaldehyde and formic acid, and allows the determination of the reaction intermediates for those oxidation processes.

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Sulfonated poly(arylene ether)s/poly(1-vinylimidazole) for high temperature pemfc applications

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Acid-doped poly[2,2_-(*m*-phenylene)-5,5_-bibenzimidazole] (polybenzimidazole, PBI) and poly(2,5-benzimidazole) (ABPBI) have been studied to substitute for Nafion-type polymers [1,2]. They show high proton conductivity and high CO tolerance at high temperature and under low relative humidity conditions

In this study, novel membrane was prepared by blending ionically two different type of polymers based on the sulfonated poly(arylene ether)s and poly(1-vinylimidazole) in order to operate PEMFC at high temperature above 150°C without humidification. The acid/base blend membrane was impregnated in phosphoric acid with excess P_2O_5 to transfer protons. This membrane was characterized by FT-IR, SEM/EDX, and XPS. Line scanning of cross-section of the membranes showed uniform distribution of phosphoric acid. XPS data confirmed that the nitrogen atom of imidazole was involved in the ionic interaction in the blend membrane [3]. The blend membrane had the high proton conductivity and good cell performance being suitable for high temperature PEMFC.

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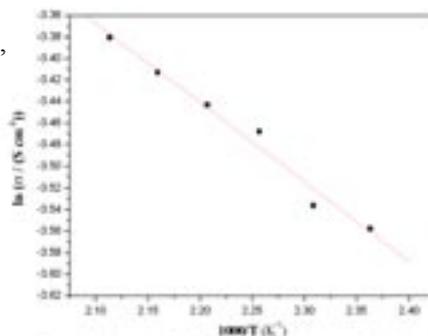Macromol. Chem. Phys. 200, 874-880 (1999).

Fig. 1. Conductivity of acid doped blend membrane with increasing temperature (150-200 °C), without external humidification

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Fuel Cells and Sustainable Energy

Fuel-cell Electrodes based on PAMAM-Dendrimer-encapsulated Platinum Nanoparticles Immobilized on a Carbon-paper Support

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The development of new nanostructured materials with high surface area represents one of the most important and active research topics in the world today. Their importance derives from the large number of potential applications, as in catalysis, chemical sensors, and others[1-2]. Dendrimer-metal nanocomposites have been widely studied from the point of view of their catalytic properties. These materials are prepared by sorbing metallic ions into hydroxyl- and amine-terminated poly(amidoamine) dendrimers where they complex with interior amine groups. After that, chemical reduction of the metal ions yields dendrimer-encapsulated metal nanoparticles[3-4]. These structures have been immobilized on various supports. A strategy was recently reported for grafting dendrimer-encapsulated platinum nanoparticles to glassy carbon electrodes by cycling the potential, which resulted in very stable films[5].

In this work, we report preliminary studies on the construction and evaluation of a fuel cell based on porous-carbon substrates modified with PAMAM G4-OH-dendrimer-encapsulated platinum nanoparticles. The porous-carbon surface was first functionalized with anhydride-like species by means of electrochemical treatment[6], and then platinum-encapsulating dendritic material was incorporated following the literature report[5]. Electrochemical studies revealed the presence of platinum nanoparticles on the porous carbon surface as well as their catalytic activity for the oxygen reduction reaction. Finally, a hydrogen-oxygen fuel cell was constructed from two plates of the previously modified commercial carbon paper separated by a Nafion 115® proton-exchange membrane. The fuel cell was evaluated by means of voltage-current profiles and power-density plots. Preliminary results indicate that this new fuel-cell-electrode concept offers the potential for efficient energy generation.

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Development of anode catalyst in HCOOH oxidation: Electrochemical characteristics and fuel cell operation

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Platinum nanoparticles are usually used as the base anode catalyst in fuel cells. However, platinum is easily poisoned by carbon monoxide (CO), a reaction intermediate, and the poisoned surface is no longer active. Therefore, various Pt-based binary catalysts have been investigated with the view of enhancing the catalytic activity by eliminating or inhibiting the CO poisoning effect on the basis of a bifunctional mechanism, an electronic effect, or third-body effect [1]. Whereas many kinds of metals such as ruthenium, tin, palladium, tungsten etc. are widely researched as additive metals to platinum for the oxidation of methanol, appropriate materials to be added to the anode for the oxidation of formic acid has not yet been examined sufficiently. Especially, as gold has not been examined fairly as the anode of direct formic acid fuel cell, this investigation would prepare and compare the behavior of platinum black, gold, and platinum-gold nanoparticles as the anode.

In this work, we investigated electrochemical characterization of Pt-based catalyst were synthesized by conventional impregnation reduction method. for the electrocatalytic HCOOH oxidation. Enhanced electrooxidation was observed in the cyclic voltammetry and current-potential polarization curve was showed possibility as anode catalyst for direct formic acid fuel cell (DFAFC). In order to identify the structural characteristics and the alloy formation of nanoparticles, X-ray diffraction (XRD) analyses were carried out.

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A structured Co-B catalyst for H_2 extraction from $NaBH_4$

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Of late, the occurrence of increasing demand of portable electronic devices with high power density immediately raises the intention of low temperature fuel cells as an alternative power source of lithium ion batteries. Obviously, among the various types of fuel cell, direct liquid fuel cell (DLFC) using methanol, formic acid, methyl formate, dimethyl ether etc., has been developed as a strong candidate mainly due to availability of fuel supply and easy handling. Even though the PEMFC using hydrogen as a fuel has a higher efficiency and power density than DLFC, H_2 supply has been an obstacle to the application of PEMFC to portable power sources. Therefore the hydrogen storage and generation systems are important for the application of PEMFC. Hydrogen has been stored in tanks of compressed or liquefied H_2, in hydrogen-storing alloys, and on activated carbon or carbon nanotubes or graphite nanofiber, or in a hydrogen-adsorbing alloy. However, all the methods are not appropriate for portable applications due to its low volumetric and gravimetric efficiency of hydrogen storage and the safety issue should be also considered. Instead of those hydrogen storage methods, liquid hydrocarbons (propane, methanol, gasoline, etc.) and chemical hydrides ($NaBH_4$, KBH_4, $LiBH_4$, etc.) could be employed as hydrogen sources for portable PEMFC. In the case of the liquid hydrocarbons, high-temperature reforming processes are complex in PEMFC operation. On the other hand, simple hydrolysis of hydrogen complex compounds represented by the general formula was suggested by Suda. Among the chemical hydrogen complexes, the hydrolysis of a sodium borohydride ($NaBH_4$) has been of great interest in terms of various advantages: nonflammable and stable in air, easy control of hydrogen generation rate, the possible recycling of the side products and large theoretical hydrogen content of 10.9 wt% ($NaBH_4$ 30% ~ 2500 Wh/L). A base-stabilized $NaBH_4$ solution hydrolyzes to hydrogen and water soluble sodium metaborate ($NaBO_2$) only when in contact with selected catalysts.

During the reaction time, the outlet of the flow reactor contains both the solution with trace amount of Co-B catalyst powder. Co-B catalyst powder in the flow reactor would not give the constant H_2 generation due to the continuous loss of Co-B powder. In order to avoid this problem as well as the efficient utilization of Co-B catalyst, we used dipping method to make Co-B catalyst coated Ni-foam support because of its porous nature, better thermal and chemical stability. In addition, we tried to find stable structure of Co-B/Ni support with different heat treatment and calcination temperature and the amount of cobalt precursor were parameters of choice.

Manufacture of Phosphated Polymer Electrolyte Membrane for High Temperature PEMFC

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Perfluorinated copolymers such as Dupont Nafion are the most commonly utilized PEM materials. Although these materials possess excellent mechanical properties, chemical stability and high proton conductivity, the loss of proton conductivity at temperatures 80 and high cost inherent in fluorinated polymers, limit their application in fuel cells operated at elevated temperatures. The hydrocarbon PEM materials, especially the H_3PO_4-doped PBI exhibits excellent thermal stability, good conductivity, even in the anhydrous state. However, its relatively weak chemical resistance at high temperature in acid doping system raised a pinhole trace problem which resulted in gas crossover. In order to this drawback, hydrophilic porous polytetrafluoroethylene (PTFE) was selected as a substrate.

In acid-doped system, the compatibility of acid is the most important thing to improve the proton conductivity and cell performance. So, polymeric blending with the phosphate-containing monomer, ethylene glycol methacrylate monophosphate (EGMP) has been carried out. The effect of blending phosphate monomer into the substrate has been attributed to improve the capability of holding phosphoric acid. Monomer EGMP has been in-situ polymerized via free radical solution polymerization by UV and heat into porous substrate. In this study, we used hydrophilic porous PTFE membrane as substrate with phosphated polymer electrolyte, being chosen to hold and prevent the leakage of acid. To increase the holding capacity of acid, novel research with pores are coated with phosphate or sulfate functional groups by using flash evaporation coating method has been in progress.

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H_3PO_4 doped Polybenzimidazole based High Temperature PEMFC – Temperature Effects on Cell Performance and Catalytic Stability.

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The challenge of increasing the polymer electrolyte membrane fuel cell operating temperature is very interesting for several reasons, such as reduction of the impact of fuel impurities on cell performance, improvement of the electrode kinetic, easier water management, faster heat rejection rates and better system integration [1]. However, this implies the use of a suitable polymeric electrolyte, capable of withstanding temperatures higher than 100ºC without losing mechanical and chemical stability, and having high enough conductivity. Among the proposed materials, one of the most interesting ones is H_3PO_4 doped polybenzimidazole (PBI), firstly proposed as polymer electrolyte membrane by Savinell et al. [2], since it fully fulfils the previous mentioned conditions. Previous work of this research group showed a synthetic route to produce PBI, and subsequently, membranes were cast and characterised [3]. Therefore, the next step is to test the membranes in an actual fuel cell setup, analysing the influence of some operating parameters.

In this line, this work studies the effect of the temperature (100, 125, 150 and 175ºC) on PBI based PEMFC system. For that, authors have set a protocol to collect data consisting of keeping the cell at a constant potential (0.5 V) for 24 hours at one of the temperatures, recording the evolution of the current vs. time. Afterwards, polarization curves and impedance spectra (at 0.5 V) were recorded at the four temperatures. It was observed that working above 150ºC had no beneficial effect on cell performance. The behaviour of the conditioning curves (current vs. time), polarization curves, impedance spectra (Nyquist and Bode plots) and thermogravimetric analyses performed on the acid doped membrane seem to indicate that a severe acid dehydration within the electrolyte was responsible for the performance decay at 150 and 175ºC. Possible reasons have been proposed in order to explain these results. It is believed that since lower current densities were drawn from the cell when compared to literature, lower amounts of water was produced in the cathode which were not able to counteract the electrolyte dehydration, with the consequent drop in the electrolyte conductivity and global cell performance. Also, it has been evaluated the stability of the catalyst by mean of cyclic voltammetry (CV) studies, revealing a loss of activity as consecutive cycles went by. X-Ray diffraction patterns showed an agglomeration and migration phenomenon taking place in the system, which may explain the activity drop. In consequence, this fact must not be rejected in order to explain the performance losses, since higher temperatures will promote the agglomeration/promotion process in a harsh environment such as highly phosphoric acid doped membrane (similar to that of phosphoric acid fuel cells).

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Modification of carbon substrate

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Activated carbons play a basic role in industrial and environmental applications. Reasons can be traced to structural and morphological features (high surface area and microporosity), high adsorption power and complex surface chemistry. Moreover, carbons can be used to support catalyst and electrocatalyst in many chemical and electrochemical processes.

Improved performances of these materials are desirable and can be obtained by modifying the nature and number of the native functional groups of the carbon surface and by adding new surface species, as metallic centres, oxide particles, etc..

In this work we present some modifications of carbon that were adopted to obtain new materials of use as intermediates in the preparation of catalysts for oxygen reduction. A main attention is given to carbon characterization by physical, chemical and electrochemical methods.

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Fuel Cells and Sustainable Energy

Use of Methanol Tolerant Cathode Materials in Direct Alcohol Fuel Cell Stack

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One of the major problems, limiting further improvements of direct alcohol fuel cells (DAFC), is the crossover of alcohol through the polymer electrolyte membrane to platinum based cathodes. Methanol crossover from anode to cathode in a direct methanol fuel cell (DMFC) causes a loss of fuel for the anode reaction, decreases the active area of the cathode catalysts and introduces parasitic currents. A potential loss of 0.2-0.3 V and 25% of reduction in efficiency from the cathode loss is typically observed in a DMFC. The resulting oxidation of methanol can be alleviated by the use of Ru chalcogenide cathode materials. In this work, in-house made carbon-supported Ru materials were pre-treated at several temperatures and then characterised by scanning electron microscope, an energy-dispersive X-ray system and X-ray diffractometer and tested in half-cells and fuel cells.

A direct methanol fuel cell stack has been designed and constructed based on coated metal mesh inter-cell connectors and carbon Graphoil seals. The effect of temperature and pressure were investigated and data compared with that obtained with Pt based catalysts. The performance achieved is inferior to that of Pt based catalysts. The cell stack has been operated with Ru based methanol tolerant cathode catalysts. The 5 cell stack has demonstrated generated power at the level of approximately 2 W. The stability of the cell is good and with optimisation of catalyst synthesis and treatment for large scale cells it is expected that the stack will achieve power densities per cell of 20 mW cm^{-2}. A single cell therefore produces 1.0 W @ 50 cm^2 area. With the compact cell design this equates to a power production between 150-200 W/litre

Keywords: Direct methanol fuel cell, Ruthenium cathode, Methanol tolerance, Stack.

Development of SOFC Anode-supported Thin Electrolytes via Tape Casting and Co-firing

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The anode-supported thin electrolytes have been fabricated by the tape casting and co-firing technique, which could be cost-effectively applied for mass production of SOFC(Solid Oxide Fuel Cell) unit cells. The optimum slurry compositions of anode(about 40μm thickness) and electrolyte(about 7μm to 20 μm thickness) green tapes, such as the weight ratio of powder to binder solution and the amount of dispersants, were determined by the analysis of the slurry viscosity, the tensile strength/stain of green tapes, and their green microstructures. The unique technique for manufacturing perfect anode-supported thin electrolytes (about 5 um thickness) via laminating the green tapes, isostatic-pressing, burning-out of binder, and then co-firing has been developed in this work. The porosity, fracture strength, gas permeability, electrical conductivity, microstructure, etc. of the anode and the anode-supported thin electrolyte were evaluated as a function of sintering temperature (1200~1400℃). The anode-supported thin electrolytes showed excellent electrical, electrochemical, and mechanical properties as well as the SOFC unit cells composed of theses electrolytes much improved the cell performance at the relatively low temperature region.

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Grätzel photoelectrochemical solar cells: an electrochemical education outreach project

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The RSC Electrochemistry Group's primary mission is to provide a central focus for the development of basic, strategic and applied electrochemistry. The Group realise that in order to ensure the future supply of enthusiastic electrochemical researchers and educators, it is essential to stimulate interest in the subject in schools. In 2002, the Group's Executive Committee, through the Chairmanship of Professor Phil Bartlett, had a vision to supply schools with electrochemical educational demonstration kits, that could be used to both illustrate a wide range of scientific principles and to interest school students in contemporary research topics. We here describe the progress of an initial project that has focussed on the distribution of Grätzel photoelectrochemical solar cell kits.

Grätzel photoelectrochemical solar cells use dye-sensitised nanoparticulate titanium dioxide to directly convert sunlight energy into electrical energy. Distribution of 'Man Solar' (www.mansolar.com) educational kits has allowed school students to make their own Grätzel solar cells and to investigate the use of various organic dyes from, *e.g.*, blackcurrants, cranberries and hybiscus tea. The assembled solar cells are then used to power small electronic devices. The original target was to reach 10 schools in each of the Loughborough/Leicester and Bristol regions. However, following successful publicity, the interest from school teachers has been substantial and educational kits have been placed in over 35 schools. Each school has been sent 5 kits, with support provided through presentations, practical demonstrations, workshops and an instruction manual. The scope for linking the UK national curriculum and GCE AS/A2 science specifications to Grätzel solar cells is extensive, and extends beyond electrochemistry to numerous scientific principles from chemistry, biology and physics, which can be illustrated by appropriate practical investigations. The anticipation is that through studying a real research topic and meeting actively involved researchers, the project will encourage school students to choose science in education options and as a career.

Funding has been through the award of an EPSRC 'Partnerships for Public Engagement' grant, that has allowed a research associate to work full time for 18 months on this outreach project. The project team has included the RSC Electrochemistry Group (now under the Chairmanship of Professor Pat Unwin), which contributed towards the costs of the kits, Dr Jason Riley (University of Bristol) and Dr Nicola Shaw (Brimsham Green School, Bristol). The longer-term plan is to extend the Grätzel solar cell project to additional schools and to introduce other electrochemical education tools, such as fuel cell demonstration kits, for the further inspiration of school students.

Ionic liquid-based proton membranes

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An increasing interest is being devoted to polymer electrolyte fuel cells (PEMFCs) for their role in the energy renewal and clean transportation areas. However, to be efficient, PEMFCs require the use of membrane electrolytes having properties which are not totally satisfied by the present technology based on perfluorosulfonic acid polymer membrane, e.g. Nafion. Although having good chemical stability, Nafion-type membranes suffer of fuel permeability (i.e. methanol) and experience a conductivity decay close to 100 °C, due to dehydration. Both these drawbacks limit the overall fuel cell efficiency and, thus, significant research efforts are currently directed either to improve the conventional membranes or to develop alternative systems.

In our laboratory, we have focused on a novel approach which consists of the development of composite gel-type membranes formed by trapping an acidic component into appropriate polymer matrices [1].

In this work we report on a new type of gel membrane designed for relatively high temperature operation [2]. The quoted membranes are formed by the gelification of a poly(vinylidene)fluoride, PVdF polymer in a highly stable ionic liquid solvent, i.e. 1,2-dimethyl-3-*n*-propylimidazolium *bis*(trifluoromethylsulfonyl)imide (DMPI-Im). The protonic transport is assured by the addition of a strong organic acid, i.e. trifluoromethanesulfonic acid (TFA), which is chemically compatible with the ionic liquid because of the equality between the anionic parts.

The results of physico-chemical and electrochemical characterisations have highlighted the key role of the ionic liquid component, so far rarely used in fuel cell electrolytes, in providing highly favourable properties to the membrane. A good thermal stability has been reached and all the samples have shown a total weight loss less than 5% at 200 °C. An excellent methanol crossover control can be realised in virtue of the hydrophobic properties of the matrix (i.e. ionic liquid and polymer), obtaining very low permeability values ranging from zero to 10^{-7} cm^{2}s^{-1}. In addition, a fast proton transfer, due to the confinement of a suitable acid, guarantees conductivity values in the order of 10^{-2} Scm^{-1} stable at 100 °C for prolonged time.

The results here described, together with a further investigation actually in progress (e.g. fuel cell tests), make the membranes under study of interest for practical applications.

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Effect of Mo on the adsorption/desorption and electrooxidation of CO on Pt

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The synthesis and development of highly active and CO tolerant anode electrocatalysts is a sought goal for the succesfull implementation of low temperature PEM fuel cells. Anodic electrocatalysts that operate under reformate H_2 gas must be able to oxidize both CO and H_2 at low anodic overpotential not exceeding 200mV.

In the present study CO adsorption/desorption and electro oxidation was studied on Pt_xMo/TiO_2 and Pt_4Mo/C by means of combined TPD-FTIR and cyclic voltametry respectively. The TPD-FTIR experiments under H_2 flow had shown that CO desorbs from Pt_4Mo/TiO_2 at 390 K ie. 70K below the desorption temperature from the Pt/TiO_2 catalyst (Fig. 1). This shows that primarily Mo contributes to the weak adsorption of CO on the Pt surface. As it is also shown in Fig. 1 Corresponding experiments under He flow resulted in the desorption and complete depletion of CO from the surface at temperatures below 375K. This was attributed to CO chemical oxidation at the boundaries of the Mo oxide nanoclusters by the OH species supplied by $MoO(OH)_3$ which was detected by XPS as the most abundant oxidation state.

Fig. 2 shows a cyclic voltamogram of the Pt_4Mo/C interfaced with NAFION membrane under continuous CO flow. Very interestingly it is observed that CO is being oxidized in two potential regions along the anodic sweep of the cyclic voltamogram. In region I the oxidation starts at potentials close to the H_2 oxidation potential and is attributed to the effect and OH formation on the lower oxidation states of Mo in the form of oxyhydroxides. The reactivity of the catalyst depends on the stability of $MoO(OH)_x$ (x=2 or 3). The oxidation in region II is attributed to Pt surface atoms far from the MoO_x boundaries.
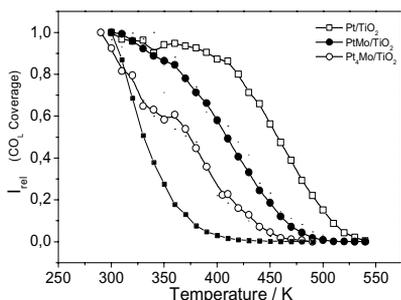

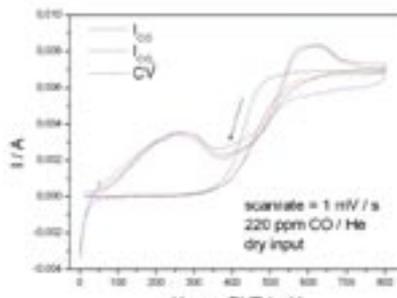Fig. 1. Combined TPD-FTIR experiments. Ramp rate 20K/min

Fig. 2. Cyclic voltamogram of Pt_4Mo/C under He/CO flow at 333K.

EQCM and CFDE Study on Platinum Dissolution in 1N H_2SO_4 and HCl Solutions

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Dissolution of platinum has been investigated in H_2SO_4 and HCl solutions using electrochemical quartz crystal microbalance (EQCM) and channel flow double electrode (CFDE) to clarify the degradation mechanism of platinum catalyst in PEMFC.

Both solutions of 1N HCl and 1N H_2SO_4 were used as electrolytes at 25 ºC for the EQCM study and at 25 and 80 ºC for the CFDE. A quartz crystal of 6 MHz with Au film electrode (6 mm diameter) was used for the EQCM. Platinum was electroplated in a 1.58 % H_2PtCl_6 solution on the Au film electrode surface before experiment. In the CFDE system, a Pt plate (1 x 4 mm^2) for the working electrode (WE) and an Au plate (1 x 4 mm^2) for the collector electrode (CE) were embedded in an acrylic block (155 x 40 x 15 mm^3) in parallel with a gap distance of 0.5 mm. A 0.5-mm-high channel was constructed on these electrodes by covering with another acrylic block. The test solution flowed on these electrodes through the channel at a rate of 10 cm/s with a pump. Platinum ions dissolved into the flowing solution at the WE (upper stream electrode) were electrochemically detected on the CE (down stream electrode), the electrode potential of which was set at 0.6 V vs. SHE so that Pt (II) and Pt(IV) ions were reduced into Pt (0). The dissolved platinum ions were determined by ICP analyses of the test solutions after anodic polarization. The potentials were measured with respect to a saturated KCl-Ag/AgCl (SSE) at 25 ºC and are shown here vs. SHE.

The EQCM results showed that the mass loss due to anodic dissolution of Pt was observed at 0.85 V vs. SHE in 1N HCl solution and the rate was still higher at 0.9 V. A large mount of dissolved Pt ions was detected in 1N HCl solution at 80 ºC with the CFDE system. On the other hand, the mass gain due to formation of Pt oxide (PtO) was observed in the range of 0.9 - 1.1 V in 1N H_2SO_4 solution and a trace amount of platinum ions was detected with the CFDE system. The dissolution of platinum in both solutions was confirmed with ICP analyses. From the above results, it was found that platinum is oxidized to mainly PtO and slightly Pt^{2+} in more positive potential than 0.8 V in 1N H_2SO_4 solution, and the dissolution is strongly enhanced under the presence of chloride ions probably due to the formation of $PtCl_4^{2-}$.

The mass change of Pt electrode was also measured in 1N H_2SO_4 solution, carrying CV at the scan rate of 10 mV/s. The return potentials of the anodic and cathodic were varied, A:(0.6-1.2V), B:(0.9-1.2V), C:(1.0-1.2V) and D:(0.6-0.9V), and the potentials were cycled 50 times. The results indicated that the Pt dissolution is enhanced by the potential scan, except for the case of D. The acceleration was remarkable for the case A, where the formation of PtO in the anodic scan and the reduction of PtO to Pt in the cathodic scan took place.

Characteric Change of Water Molecules in PEFC Membranes on Increase of Temperatures

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Polymer electrolyte fuel cells (PEFC) are promising as a device for clean and efficient energy conversion. However, there are several problems to be surmounted for the development of PEFCs. Although the polymer electrolyte membranes employed for PEFCs show superior conductivity in the wet state, they deteriorate when they are dry or under low humidified conditions. Therefore, water managements to protect the membranes from drying is a major concern during fuel cell operations. For this purpose extensive efforts have been made in terms of modeling water transport and its management [1, 2]. In this study, in order to provide some insights into the various models proposed so far, we attempted to characterize the water molecules confined in the PEFC membranes by means of ^{1}H-NMR spectroscopy.

Commercially available Nafion 112, 115, and 1135 (DuPont; thickness: 50, 125 and 88 μm) were used. The membranes are composed of poly(tetrafluoroethylene) main chain with sulfoperfluoroalkyleneether side chains. The ^{1}H-NMR spectra of the membranes were measured in the form of a single sheet. The[1]H-NMR spectra of water molecules in the PEFC membranes presented broad resonance lines. From the spectral change of the samples measured under flowing dry air in a NMR probe and the field dependence of the resonance line, the resonance lines at room temperature were found to be composed of the signals of water molecules in different chemical enviroments in the membrane, reflecting the structural heterogeneity of the polymer membranes. By the analysis of the change of the spectral feature at various hydration states and temperatures, it was found that at a certain critical temperature, the structural conversion took place, so that the mobility of water molecules become higher and the chemical environments around the water become more homogeneous. The sturucture would be favored to realize the high ion conductivities because the water mobility is considerd to be highly promoted. The attained structure is considered to be highly stabilized by the interaction of water molecules with polymer, since the transition did not take place under less humidified conditions. In adddition, it must be stable at room temperature for fairly long time since the homogeneous spectral feature of water molecules remained more than 18 days at 297 K.

Acknowledgement

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Evaluation of suitable coatings on separator plates for polymer electrolyte membrane fuel cells

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Due to its high efficiency, fast start up and relatively low working temperature of 80 ºC, the polymer electrode membrane fuel cell (PEMFC) is considered a promising power source for portable and transport applications.

While research is still being carried out trying to develop membrane technology and lower platinum catalyst loadings, special attention is given to the plates which count for 60% of the total cost and represent 88% of the bulk of the stack.

Graphite plates have been used in the past, however it is an expensive material and lacks mechanical strength increasing the size of the fuel cell and therefore limiting the volumetric power density.

Metals constitute an alternative to graphitic materials as they can be manufactured at a low cost, are easy to shape and thin plates can be machined offering low volume and weight. Unfortunately, most of these metals ie. stainless steel, aluminium and titanium tend to form a passive oxide layer which acts as an electrical insulator between the MEA and the substrate, reducing the total voltage output and consequently decreasing the fuel cell performance. To overcome this problem metallic and non-metallic low surface resistance coatings have been employed and selected according to their ability to be non permeable to the reactant gases, be chemically inert, provide low contact resistance and offer good corrosion resistance in order to stand the oxidising and reducing media.

This paper reviews the different materials and coatings used in separator plates for PEMFC stacks outlining advantages, disadvantages and evaluating their suitability when working in the aggressive fuel cell environment.

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Electrochemical analysis of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$ cathodes with different porosities supported on $Ce_{0.2}Gd_{0.8}O_{1.9}$ Electrolyte.

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Solid oxide fuel cells (SOFC) as promising energy production systems for the 21st century with high total efficiency and environmental friendliness have been studied by many workgroups looking for different aspects [1]. Recently, the SOFC with a medium-temperature operation (600…700°C) have been focused on by several groups. Perspective cathode electrolyte systems for medium-temperature SOFC are $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ | $Ce_{0.8}Gd_{0.2}O_{1.9}$ and $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$ | $Ce_{0.8}Gd_{0.2}O_{1.9}$. As shown in previous works the mass transport limitations connected with porosity parameters of cathode increase significantly in medium and low temperatures [2]. Cathode structure – performance dependences has been studied in the case of yttria stabilized zirconia | La (Sr)MnO3 systems [3] but not much in $Ce_{0.8}Gd_{0.2}O_{1.9}$ supported systems. The main aim of this work is to synthesise porous cathode materials with different porousities and characterize these systems to clarify the porosity – performance dependences.

The complex impedance plane (-Z'',Z') plots at different T and ΔE in the *ac* frequency range from 0.01 to 10000 Hz have been obtained. In the region of *ac* frequences $0.1 \leq f \leq 10000$, the number and shape of arcs was dependent on porosity characteristics as well as corresponding time constants characterizing limiting processes prevail in different frequencies. Analysis of relaxation time constant dependencies on temperature, polarisation, chemical composition and porosity parameters has been carried out. The Nyquist plots were fitted using different equivalent circuits and the corresponding dependencies of the circuit parameters on potential and temperature. Significant dependencies of the polarisation resistance on ΔE and T as well as on the chemical composition and porosity of the cathode have been established.

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Controlled synthesis of catalyst – nanocarbon compositions for fuel cells

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Nanostructures composed of nanodimensional catalyst and support material particles are widely used as electrode materials for electrochemical energy sources, particularly fuel cells. Compositions based on catalysts and carbon nanotubes (CNT) are among the most efficient electrode materials. As is known, some metal containing compounds react with activated carbons to form metal particles supported on the carbons [1]. As well, redox reactions of metal compounds with carbon materials can result in formation of carbon-supported nanodimensional metal-oxide particles which possess high catalytic activity.

We have synthesized and studied some composite metal-containing nanomaterials with use of CNT as a support. CNTs used in this work were obtained by CVD method as described in [2] and purified by treatment with acids. Surface area of the CNT samples used was 200-500 m^2/g. Synthesis of the catalyst – nanocarbon compositions was performed with use of redox reaction of potassium permanganate solution with CNT. This reaction resulted in formation of manganese dioxide nanoparticles supported on CNT. As it was determined by transmission electron microscopy method the size of MnO_2 particles formed was of the order of several nanometers. If other reducing agent (formic acid) was added to the reacting system much more large MnO_2 particles were formed.

Electrochemical characteristics of the composite electrode materials obtained were measured with use of model low-temperature hydrogen-oxygen fuel cell with alkaline electrolyte. The composite materials were studied as oxygen electrode. It was found that the most catalytically active are composite materials obtained by reduction of potassium permanganate by CNT containing 50% of MnO_2. Increasing of MnO_2 content above 50% resulted in deterioration of electrochemical characteristics because of formation of large MnO_2 particles. Decreasing of the MnO_2 content below 50% also resulted in decrease of catalytic activity.

Another composite material was obtained by reduction of palladium chloride on CNT. Size of palladium particles supported on CNT as estimated by XRD method was near 20 nm. This composite material appeared to by highly effective as hydrogen electrode.

Thus, catalyst – nanocarbon compositions developed are highly efficient as electrode materials for electrochemical devices.

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Effect of mesoporous silica on proton conductivity in CsH_2PO_4/SiO_2 composites

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Cesium dihydrogen phosphate, CsH_2PO_4 (CDP), is a hydrogen-bonded proton conductor that exhibits a superionic phase transition at T_c = ca. 230 °C leading to an abrupt increase in conductivity by four orders of magnitude from 10^{-6} S cm^{-1} to 10^{-2} S cm^{-1}. CDP is therefore one of the prospective materials for proton conducting electrolyte membranes of solid electrolyte fuel cells working at intermediate temperatures between 200 °C and 300 °C. In this presentation, we address the investigation of proton conduction in CDP/SiO$_2$ composites that consist of polycrystalline CDP and mesoporous SiO$_2$ powder. An SiO$_2$ volume ratio in the CDP/SiO$_2$ composites strongly influenced on the proton conductivity in the composites. Figure 1 shows temperature dependence of conductivity in neat CDP and CDP/SiO$_2$ composite (molar ratio CDP: SiO$_2$ = 0.4:0.6). The results regarding neat CDP showed that the conductivity suddenly jumped up around 230 °C from a low-conducting phase to a high-conducting phase, and it changed reversibly during a heating-cooling cycle. In the case of CDP/SiO$_2$ composite, an enhancement in conductivity was observed at the low-conducting phase. An interfacial phase of structurally disordering CDP that forms between CDP and SiO$_2$ surface will contribute to the conductivity-enhancement [1,2]. Also, it should be noted that a hysteresis loop appears in the CDP/SiO$_2$ composite in the heating-cooling cycle, which will be related with the volume ratio of the interfacial phase to a bulky CDP phase in the composite, i.e., the proton conduction networks of the interfacial phase and the bulky CDP phase in the composite will govern this hysteretic behavior.
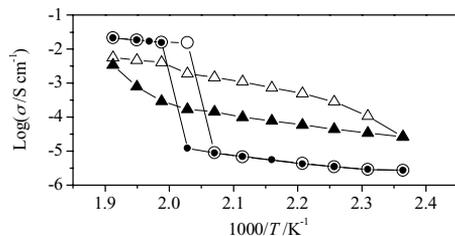

Fig. 1. Temperature dependence of conductivity in neat CDP and CDP/SiO$_2$ composite in 30mol%H$_2$O/70mol%Ar. Filled symbols: heating process; open symbols: cooling process; circle symbols: neat CDP; triangle symbols: CDP/SiO$_2$ composite.

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[1] J.Otomo et al., Solid State Ionics 156 (2003) 357.
[2] S. Wang et al., Solid State Ionics 176 (2005) 755.

Effect of mesoporous silica on proton conductivity in CsH$_2$PO$_4$/SiO$_2$ composites

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Cesium dihydrogen phosphate, CsH$_2$PO$_4$ (CDP), is a hydrogen-bonded proton conductor that exhibits a superionic phase transition at T_c = ca. 230 °C leading to an abrupt increase in conductivity by four orders of magnitude from 10^{-6} S cm^{-1} to 10^{-2} S cm^{-1}. CDP is therefore one of the prospective materials for proton conducting electrolyte membranes of solid electrolyte fuel cells working at intermediate temperatures between 200 °C and 300 °C. In this presentation, we address the investigation of proton conduction in CDP/SiO$_2$ composites that consist of polycrystalline CDP and mesoporous SiO$_2$ powder. An SiO$_2$ volume ratio in the CDP/SiO$_2$ composites strongly influenced on the proton conductivity in the composites. Figure 1 shows temperature dependence of conductivity in neat CDP and CDP/SiO$_2$ composite (molar ratio CDP: SiO$_2$ = 0.4:0.6). The results regarding neat CDP showed that the conductivity suddenly jumped up around 230 °C from a low-conducting phase to a high-conducting phase, and it changed reversibly during a heating-cooling cycle. In the case of CDP/SiO$_2$ composite, an enhancement in conductivity was observed at the low-conducting phase. An interfacial phase of structurally disordering CDP that forms between CDP and SiO$_2$ surface will contribute to the conductivity-enhancement [1,2]. Also, it should be noted that a hysteresis loop appears in the CDP/SiO$_2$ composite in the heating-cooling cycle, which will be related with the volume ratio of the interfacial phase to a bulky CDP phase in the composite, i.e., the proton conduction networks of the interfacial phase and the bulky CDP phase in the composite will govern this hysteretic behavior.
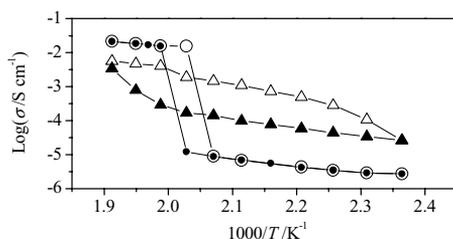

Fig. 1. Temperature dependence of conductivity in neat CDP and CDP/SiO$_2$ composite in 30mol%H$_2$O/70mol%Ar. Filled symbols: heating process; open symbols: cooling process; circle symbols: neat CDP; triangle symbols: CDP/SiO$_2$ composite.

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[2] S. Wang et al., Solid State Ionics 176 (2005) 755.

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Fuel Cells and Sustainable Energy

Steady State Thermal Study of the planar solid oxide fuel cells

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the study of thermal stresses within solid oxide fuel cells is an essential aspect in the development of the fuel cell systems. Various reactions occurring across the planar components of the fuel cell, thermal energy transport, heat exchange, electrocatalytic reactions, mass transport owing to the oxygen ionic conduction across the electrolyte and property involved in current generation are significantly temperature dependent. Therefore local temperature plays an important role in determining local current density, which, in turn, determines the local heat flux. Temperature distribution is modeled by formulating the energy balance equations which describe the heat transfer processes occurring in the local heat balance.

Heat transfer occurs in the solid and fluid region of SOFC and between the fuel cell and its ambiance. Heat is generated at the electrolyte-electrode interface due to electro-chemical reactions and ohmic heating occurs within the electrolyte.

These physiochemical processes constitute a mathematical model which can be used to predict the temperature distribution using numerical methods.

We use the software (FORTRAN 90) to solve the equations system corresponding to the model developed. Numerical methods are usually employed in such situations to solve the equations.

The model calculate the distribution of temperature and species concentrations inside the SOFC.

Modified IrO$_2$ supported electrodes for regenerative fuel cells

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To improve the water electrolysis performance of unitized regenerative fuel cells, ultrafine IrO$_2$ was deposited by sputtering on carbon paper. An active electrode support for oxygen evolution and reduction was prepared by modifying the IrO$_2$ surface with a conductive polymer. IrO$_2$ treated carbon paper electrodes are modified with polyaniline by electrochemical methods. Their ability to catalyze and the kinetics of oxygen evolution and reduction reaction in acid electrolyte with their stabilities were investigated. Active electrodes were prepared applying different transition metal complexes over these supporting materials. The results were compared to commercially use Pt-based E-TEK catalysts. The surface characterization was made by XRD.

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Fuel Cells and Sustainable Energy

Influence of conducting polymer presence in MEA on PEM fuel cell performance

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Fuel cells (FC) as a perspective source of electric energy are drawing an increasing attention of scientific community during the last two decades. With respect to the wide range of possible applications PEM fuel cells are expected to reach broad widespreading. However, there still exist serious drawbacks. One of most critical problem is low utilisation of catalyst together with its high sensitivity to poisoning by carbon monoxide. Second important problem represents the penetration of the fuel through membrane to cathode compartment causing decrease in a FC performance. The application of conducting polymers is expected to be a possible solution of both problems. These materials exhibit parallel electronic and ionic conductivity. Thus, theirs application as a catalyst support is supposed to increase probability of the three-phase contact occurrence. Moreover, modification of the Nafion membrane by a thin conducting polymer layer was reported to reduce penetration of the fuel through membrane substantially [1]. Nevertheless, it is necessary to verify function of conducting polymers utilising MEA in real FC environment. Two methods of conducting polymer incorporation into the MEA were used. The properties of prepared composites were tested in the laboratory hydrogen/oxygen fuel cell.

In the first instance Nafion/conducting polymer composite was prepared by the diffusion method [2]. Laboratory fuel cell based on this composite equipped with commercial ELAT (E-TEK, USA) electrodes was tested. As it was found, the presence of conducting polymer film on the membrane surface negatively influences the cell water management. As a consequence its performance decreases with time of operation under constant as well as cyclically changed current load was observed. From the two conducting polymers studied polypyrrole shows better performance and polyaniline higher stability.

The conducting polymers have been alternatively tested as a anode catalyst support. The polyaniline was anodicaly synthesised in the bulk of the gas difusion layer (GDL, E-TEK, USA). Subsequently, platinum as catalyst was electrodeposited on this composite. Alternative approach was to cover by polyaniline platinum electrodeposited on GDL. Both polyaniline modified composites have shown in comparison to the GDL with the only electrodeposited platinum fast fuel cell performance decrease. Main reason is probably the conducting polymer drying out connected with ionic conductivity loss or its degradation connected with the loss of electronic conductivity.

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$(NiNb)_{99}(PtX)_1$ amorphous alloy electrodes for fuel cells DMFC

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The presente work describes of modified carbon paste electrodes (MCPEs), working in percloric acid solutions, have been made by adding amorphous alloys powders with compositions $(NiNb)_{99}PtX_{(1)}$ and obtained by mechanical alloying, to the mixture of powdered graphite and paraffin.

It was observed that both $Ni_{59}Nb_{40}Pt_{0.6}Ru_{0.4}$ and $Ni_{59}Nb_{40}Pt_{0.6}Sn_{0.4}$ containing MCPEs, shift the onset potential for CO (ca. 0.23 V) to lower potentials compared to $Ni_{59}Nb_{40}Pt_1$ electrodes. While ruthenium promoted the catalytic activity for methanol and CO electrooxidation, tin showed the same enhancing behaviour for a shorter period of time, probably due to the facile dissolution of tin from the surface[1].

The determination of the oxidation activity of methanol, the current density is drastically decreased with the presence of tin, susceptible to the potential range, followed by the $Ni_{59}Nb_{40}Pt_1$ and $Ni_{59}Nb_{40}Pt_{0.6}Ru_{0.4}$ alloys. However, these new electrodes show a very interesting behaviour, taking into account their high tolerance to CO molecules, and the decrease of the onset potential for methanol electrooxidation, which are the main causes of poisoning of anode materials in fuel cells.

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Oxygen reduction electrocatalysts based on polynuclear aminoethylate complexes of 3D metals

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Oxygen reduction electrocatalysts based on organometalic polynuclear complexes have promise in the creation of air-metal power sources, electrochemical generators and sensors. In polynuclear aminoethylate organometalic complexes the central ions of metals are bound to ligand through the atoms of nitrogen or oxygen. Such arrangement makes for the fact that by the modification of carbon carriers it is possible to create nanostructured directed compositions of d-metals, which are electroactive in the reaction of oxygen reduction and bound to the carbon surface through atoms of nitrogen or oxygen.

Electrocatalytic nanostructures active in oxygen reduction reaction have been obtained by adsorption from dimethylformamide solutions of polynuclear complexes of some 3d-metals $[Co(2TEA-3H)] \cdot MCl_2$, $[Co(2TEA-3H)]_m \cdot n \cdot NiCl_2$, $[Co(2DEA-3H)]_m$ $n \cdot NiCl_2$ ($M = Co^{2+}$, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cr^{2+}; m=1,2 and n=1,2, DEA-diethanolamine and TEA-triethanolamine) to activated carbon AG-3 with subsequent heat treatment in the temperature range of 200-800°C in argon atmosphere. By thermogravimetric analysis and the method of thermodesorption with mass spectrometric analysis of desorbing particles thermal properties of complexes have been investigated and electrochemical characteristics of catalysts on "floating" gas-diffusion electrode in 1M KOH have been obtained.

It has been demonstrated that electrocatalysts obtained by the pyrolysis of aminoethylate heteropolynuclear complexes of 3d-metals at 600°C are the most active. Based on electrochemical measurements and results of the thermal analysis it is suggested that the active centers of oxygen reduction electrocatalysts are spinels or oxides with nonstoichiometric composition. Based on potentiostatic measurements of catalysts have been shown that making Cr atoms a part at the structure of electrocatalysts significantly worsens their electrocatalytic properties in oxygen reduction reaction. Increasing the cobalt content of the catalyst based on diethanolamine and triethanolamine heteropolynuclear complexes with various ratio of Co^{2+} and Ni^{2+} improves their electrocatalytic properties in oxygen reduction reaction, but increasing the nickel content worsens them. Series of catalytic activity in oxygen reduction reaction in catalysts under investigation have been established:
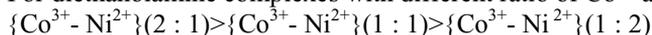
For triethanolamine heteropolynuclear complexes
$\{Co^{3+}-Co^{2+}\} > \{Co^{3+}-Fe^{2+}\} > \{Co^{3+}-Cu^{2+}\} > \{Co^{3+}-Ni^{2+}\} > \{Co^{3+}-Zn^{2+}\} > \{Co^{3+}-Cr^{2+}\}$
For triethanolamine complexes with different ratio of Co^{3+} and Ni^{2+}
$\{Co^{3+}-Ni^{2+}\}(2:1) > \{Co^{3+}-Ni^{2+}\}(1:1) > \{Co^{3+}-Ni^{2+}\}(1:2)$
For diethanolamine complexes with different ratio of Co^{3+} and Ni^{2+}
$\{Co^{3+}-Ni^{2+}\}(2:1) > \{Co^{3+}-Ni^{2+}\}(1:1) > \{Co^{3+}-Ni^{2+}\}(1:2)$

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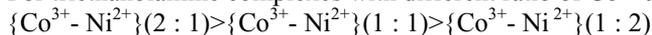
Ruthenium Selenide Catalysts for the Cathodic Oxygen Reduction Reaction in Direct Methanol Fuel Cells

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Sluggish kinetics of the oxygen reduction reaction (ORR) is the major source of efficiency losses in low temperature proton exchange membrane (PEM) type fuel cells. The situation becomes even worse for direct methanol fuel cells (DMFC), where efficiency is further reduced due to the cross-over of methanol to the cathode and establishment of mixed potentials on Pt-based catalysts and the water transfer from anode to cathode. Further development of DMFCs and their introduction to the market requires highly catalytically active and methanol tolerant cathode materials.

Ruthenium-based cluster catalysts containing selenium have been introduced by Alonso-Vante [1, 2] as methanol tolerant oxygen reduction catalysts. In this talk we report on different methods of preparation for carbon supported ruthenium selenide catalysts (RuSe/C), as well as structural and kinetic investigation of these materials. Structural characterisation was performed using TEM, TEM-EDX and XRD partly in cooperation with partners from the "O2RedNet". In addition STEM EDX technique was used to characterise some single nanoparticles on the RuSe/C catalyst sample. ORR kinetics on RuSe/C and commercial Pt/C catalysts were investigated using thin-film rotating (ring) disk electrode method. Still the overpotential is around 150mV higher compared to Pt/C catalysts. The electrochemical active surface areas of the catalysts were determined using Cu-UPD and CO-Stripping technique.

Finally for further evaluation of the catalysts they were incorporated into a fuel cell. Results of the catalyst characterisation will be presented.

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The Importance of Platinum Alloy Electrocatalysts to PEM Fuel Cells

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The rapid development of PEM fuel cells is making increasing demands on the performance of MEAs, including that of Pt alloy on carbon electrocatalysts. Candidate electrode materials and their characteristics (obtained using a wide variety of physical and spectrosopic techniques) are concisely reviewed. Binary alloys have become established as high performers and we consider examples used for oxygen reduction and methanol oxidation to illustrate successes yet continuing challenges.

A series of binary Pt-M alloy catalysts (M = Ni, Cr, Fe, Ti) was prepared on PTFE-treated porous carbon paper with a Pt content of 0.5 mg cm^{-2}. The catalysts were characterised by cyclic voltammetry in 1 mol dm^{-3} H$_2$SO$_4$ at 25°C, TEM/EDS, XPS and EPMA. High utilisation, high specific surface area (30-96 m^2 g^{-1}) electrocatalysts were compared to a Pt single metal catalyst. Oxygen reduction kinetics were examined in 1 mol dm^{-3} H$_2$SO$_4$ at 25°C. Polarisation data were used to calculate kinetic parameters and the effect of potential cycling (<4000 cycles) was quantified.

There is significant demand for anode catalysts that are more active for methanol electrooxidation. Even with Pt-Ru alloys there is an overpotential of ca. 300 mV before sufficient CO electrooxidation to CO$_2$ occurs to provide 'free' Pt sites for methanol electrooxidation. A number of binary Pt-M alloy catalysts (M = Ir, Pd, Os, Rh, Ga, W) have been investigated for their ability to form OH$_{ads}$ at lower cell potentials and to adsorb methanol. The ternary catalyst systems Pt-Ru-Sn and Pt-Ru-Rh have also been examined. The performance of the catalysts for methanol electrooxidation has been examined in a half-cell operating on 2 mol dm^{-3} CH$_3$OH in 0.5 mol dm^{-3} H$_2$SO$_4$ at 80°C.

Current challenges to the development of Pt-alloy catalysts for PEM fuel cells are considered and important approaches are highlighted.

Electro oxidation of alcohols at gas diffusion electrodes: a DEMS study

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The ethanol and ethylene glycol electro oxidation at gas diffusion electrodes (GDE) made of different catalysts, Pt/C, PtRu/C and PtSn/C, were both studied by on-line differential electrochemical mass spectrometry (DEMS) in a wide temperature range (30-90 °C) as a function of the anode potential, the fuel concentration and catalyst loading. Doubly ionized CO_2^{2+} molecular ion at m/z = 22 for CO_2, CHO^+ fragment at m/z = 29 for acetaldehyde, were used to monitor both products simultaneously as proposed in [1]. The CO_2 current efficiency (CCE) for ethanol oxidation reaction (EOR) shows a strong dependence on the anode potential, decreasing rapidly with increasing potentials $> 0.6V$ vs. RHE. But the CCE for ethylene glycol oxidation reaction (EGOR) is almost potential independent. The CCE for the EOR goes down with increase in concentration of ethanol. CCE for both reactions shows a strong dependence on the catalyst layer thickness or catalyst loading, respectively. It increases with increasing catalyst loading. The formation of CO_2 in both reactions is a temperature-activated process with apparent activation energy of 21 kJ/mol. The apparent activation energy for ethanol oxidation is estimated to be 31 kJ/mol while 25 kJ/mol for ethylene glycol oxidation, for Pt/C catalyst. The CCE increases with increasing temperature, exceeding 90% at 90 °C, 0.1 M fuel, ethanol or ethylene glycol, and 5 mg/cm^2 Pt catalyst loading. PtSn/C, which has been reported to be the most active catalyst for ethanol oxidation in e.g. [2], also shows high CCE, like Pt/C. But PtRu/C shows very small CCE. The majority product in case of PtRu/C seems to be acetic acid, as the signal for acetaldehyde is also relatively small in comparison to Pt/C. Experimental tests on the electro oxidation of acetic acid revealed that acetic acid is fairly resistant to electro oxidation with all three of the tested catalysts (Pt, PtSn/C, PtRu/C), with almost zero oxidation current in relevant potential region. This has been found both for tests at gas diffusion electrodes and for catalysts applied to a planar gold electrode and immersed into sulfuric acid. Our results indicate that the C-C bond scission observed for the ethanol electro oxidation with CO_2 current efficiencies in excess of 50% has to proceed in parallel with ethanol oxidation to either acetaldehyde or acetic acid, and not sequentially from acetic acid further on, as acetic acid can not be oxidized any further.

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Impact of Flow Field Geometry on Local Current Distribution on the Sub-Millimeter Scale in PEFC

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In today's PEFCs current distribution on all scales is of high interest for the improvement of power density, which is associated to performance and costs. To understand and optimize a fuel cell on the technical level, fundamental knowledge of the processes occurring on the micrometer scale is indispensable. Considering processes on this scale, cell performance decreases with an inhomogeneous current distribution across single gas channels and flow field ribs. Therefore, efforts to homogenize the current by the means of flow field design and material properties will contribute to the reduction of the integral cell losses. Although experiments on this sub-millimeter scale are also valuable input and validation for numerous simulations (*e.g.* [1]), up to now experimental efforts have been restricted to the correlation of integral performance to channel and rib spacing [2].

At PSI, a novel technique for measuring the local current with a resolution finer than the flow field structure has been developed. The method employs voltage probes at the reaction layer interface for *in-situ* measurements of the potential distribution (see Fig.1a). The electron conductors in the plane perpendicular to the membrane are considered as two-dimensional shunt resistors. Current density is therefore obtained by solving Laplace's equation with the potentials measured as boundary conditions. In order to examine the influence of flow field structure and reactant gas composition on the current distribution, the method is applied on a test cell with different geometry and operating parameters. Results show that electrical resistances govern the current distribution in the low current regime, while mass transport limitations hamper current production under the rib at high loads (see Fig.1b & c).
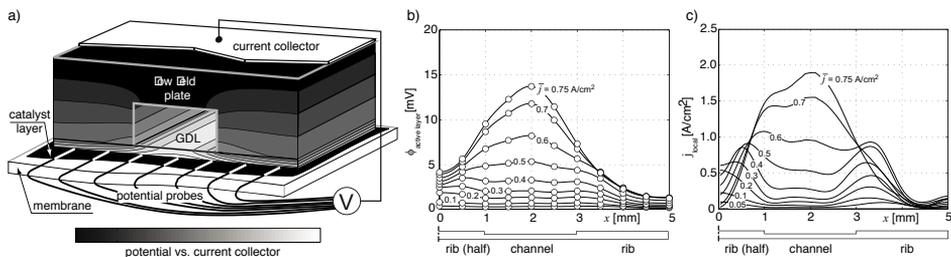

Figure 1: (a) Scheme of measurement principle. (b) Local potentials measured at catalyst layer. (c) Current density distribution calculated from (b).

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Nafion - zeolite composite membranes for Direct Methanol Fuel Cells

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The challenge of reducing methanol crossover while maintaining proton conductivity is a major obstacle inhibiting the commercialization of direct methanol fuel cells (DMFCs). Composite membranes were fabricated using zeolites (such as zeolite A, Mordenite, zeolite X) as an inorganic filler, with the intention of reducing the transport of methanol and protons within the DMFC membrane. The hydrophilic zeolite crystals allow solvated protons to pass but repel methanol, thus methanol crossover may be significantly reduced. However, as-synthesised Nafion-zeolite composite membranes often exhibit high methanol permeability, probably due to poor interfacial bonding between the fillers and Nafion matrix, creating new paths for methanol transport. In order to solve this problem, the surfaces of the zeolite crystals were functionalized to improve the adhesion between the zeolite and polymer phases. A range of composite materials have been synthesised, varying the type of zeolites, the particle size, the zeolite loading and the degree of functionalisation. The fabricated composite membranes have been characterised by measurements of methanol crossover and proton conductivity. The performance of an operating fuel cell has been evaluated with different membrane materials.

In addition to the effect on methanol crossover, composite membranes can also offer improved proton conductivity at elevated temperatures. Nafion membranes lose their proton conductivity at high temperature due to severe water loss; while the water retention ability of these zeolites in composite membranes can maintain the proton conductivity of the membrane at high temperatures. The proton conductivity of the composite membranes has been measured under a range of temperature and humidity conditions.

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Evaluation of membranes for direct methanol fuel cells

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The performance of direct methanol fuel cells (DMFCs) can be significantly affected by the transport of methanol through the membrane, depolarising the cathode. A wide range of membrane materials have been developed which aim to address this problem. While these membranes can be effective in reducing methanol permeability, this has usually been combined with a reduction in proton conductivity. Measurements of methanol permeability and proton conductivity are relatively straightforward, and these parameters (or a membrane 'selectivity' based on the ratio between them) are often used to characterise DMFC membranes. However, we have carried out one-dimensional simulations of DMFC performance for a wide range of membrane properties, and the results indicate that DMFC performance is normally either limited by methanol permeability or proton conductivity. Thus use of a 'selectivity' is not appropriate for comparison of membrane materials, and results from the model can be used to compare different membranes. The results also show that Nafion 117 has an optimum thickness, where DMFC performance is equally limited by both methanol permeability and proton conductivity. The model indicates that new composite membranes based on Nafion can only offer significant improvement in DMFC performance by enabling operation with increased methanol concentration in the fuel. A number of composite membrane materials that have been reported in the literature are shown to deliver significant reduction in DMFC performance due to reduced proton conductivity, although improved performance at high methanol concentration may be possible.

Production of electricity from a municipal wastewaster using a microbial fuel cell

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Energy can be obtained from the pollutants contained in a wastewater by the anaerobic fermentation (biomethanization) of the organic matter, and the later incineration of the gases. An alternative to methane production is the direct generation of electricity in a microbial fuel cell. This is an emergent technology that in the present moment is far away from industrial application, but it could be very interesting in future. In this work, a lab-scale two chamber microbial fuel cell has been used to treat a domestic wastewater. This wastewater came from the affluent to the municipal wastewater treatment facility of Ciudad Real (Spain) and it had a Chemical Oxygen Demand (COD) in the range 50-300 mg dm^{-3} and a conductivity around 120 μS cm^{-1}. The two chambers in the experimental setup are separated by a salt bridge. The anode and the cathode were made of graphite. Air was supplied to the cathodic chamber by means of a small pump at a flowrate of 3 dm^3 min. The influence of the organic load on the power density has been studied. It was found that a linear relationship exists between the influent COD and the power generation rate. The maximum power density obtained in this treatment is slightly over 20 mW m^{-2}, which is similar to those reported in literature [1-3] for the same kind of wastewaters. Efficiencies in the COD removal are over those expected for a pure microbial fuel cell operation. This means that other microorganisms contributes to the COD removal and competes with those fixed on the anodic surface. A mathematical model is proposed to explain the obtained results.

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A new PtCo/C electrocatalyst with highly crystalline graphite support

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For residential PEMFC the choice of the catalyst support is crucial, affecting both nanoparticles morphology and catalyst performance at temperatures higher than 120^0C. Among all materials used for electrocatalysts the carbon supports are most suitable, well-studied and the cheapest. However, amorphous carbons are usually used for conventional Pt and Pt alloy supported electrocatalysts. On the other side, the carbons with perfect graphitic structure can provide good electrical contact between the platinum nanoparticles and between the catalyst and the current collector. Such Pt-loaded carbons also demonstrate the high thermal stability in short-term corrosion tests [1,2]. However, graphitization of amorphous carbon up to around 3000°C leads to reduction of the carbon surface area. As a result, it is difficult to apply high metal loadings with uniform Pt and/or Pt alloy nanoparticles distribution on the surface of graphitized carbons.

The objective of this work was to accommodate the standard polyol process for high loaded PtCo/C catalyst preparation with highly crystalline synthetic graphite support (TIMREX HSAG 300).

The polyol process in aqueous-ethylene glycol solution containing chloroplatinic acid under refluxing conditions at 110-150^0C was applied during first stage of electrocatalyst preparation. The obtained catalyst demonstrates high thermal stability (see Fig.), but Co content in the alloy was not enough. To increase Co in PtCo alloy we applied gaseous reduction in H_2 atmosphere after polyol synthesis.

It was shown that such approach allows preparation of 40-55%PtCo alloy catalyst with 3-5nm nanoparticles size. The regularities of catalyst preparation will be discussed.
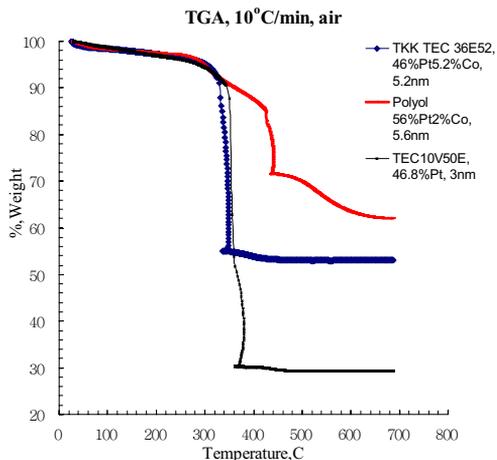
Fig. Thermal stability of in-house and commercial electrocatalysts.

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Measurement and interpretation of oxygen diffusion and surface exchange data for $La_{1-x}Sr_xCoO_{3-\delta}$

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Improved understanding of surface properties is crucial for the development and application of mixed ionic electronic conductors (MIEC) such as membranes, sensors, reactors and SOFC electrodes. Different measurement methods are used, data are evaluated by various numerical techniques, and these are finally correlated with one another to obtain reliable information about parameters determining oxygen surface exchange and bulk diffusion rates. The methods used were oxygen permeation, conductivity relaxation, electrochemical potential step technique and electrochemical impedance spectroscopy. The data were evaluated by use of direct numerical fitting to solutions of Fick's law and analysis of Fourier-transformed relaxation data in the complex plane, and consistency checks were performed by near-equilibrium asymptotic analyses and Kramers-Kronig transformation of impedance and Fourier-transformed data. Glass-sealed Belzner-type cell was used for the electrochemical measurements. The electrochemical measurements gave consistently lower first-order surface exchange k_{chem} coefficients than the other methods used, and this was attributed to the contamination of the specimen surface in the Belzner cell. Furthermore, the D_{chem} and k_{chem} coefficients assessed by conductivity relaxation varied significantly for oxidation and reduction processes at low oxygen partial pressures. While it is possible that the oxidation and reduction kinetics of surface exchange can differ, bulk diffusion should, in principle, not be affected. However, the calculated chemical diffusion coefficient D_{chem} can be in error if the model for surface exchange kinetics is oversimplified. The reason for the discrepancy as well as the advantage of using more advanced models are discussed.

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Unravelling the complexities of CO_2 tolerance at PtRu/C and PtMo/C

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We have previously reported a difference in the CO_2 tolerance exhibited by PtRu/C and PtMo/C catalysts 80 ºC in 40 ppm CO and 25 % CO_2 in H_2 [1]. In contrast to the trend in CO tolerance, the PtRu/C catalyst was found to have better CO_2 tolerance than the PtMo/C catalyst. Voltammetric studies have indicated that deactivation of the anode in the presence of CO_2 is caused by the build up of a CO-like poison [2]. Two mechanisms have been proposed to account for the conversion of CO_2 to CO under PEM FC anode conditions; the reverse water gas shift reaction

$$CO_2 + H_2 \rightarrow CO + H_2O$$
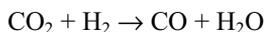
and/or the electrochemical reduction of CO_2

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O.$$
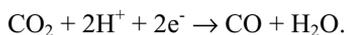
It is interesting to note that the potential at which adsorbed CO is oxidised is typically 0.5 V vs. RHE at PtRu/C catalyst electrodes, whilst two peaks are observed for PtMo/C; a broad peak between 0.15 and 0.5 V and a second at 0.78 V. The former has been attributed to oxidation of adsorbed CO promoted by turn over of the $Mo^{+4/+6}$ redox couple [3] and overlaps the potential window at which H is adsorbed at Pt at its lower limit. We, therefore, propose that the mechanism of CO_2 poisoning at PtMo/C electrodes proceeds via the electrochemical mechanism, whilst at PtRu/C the RWGS reaction is dominant. Results from a study of single cell MEAs operated under potentiostatic control and connected to a mass spectrometer will be presented to test this hypothesis. The implications of the relative contribution of electrochemical CO_2 reduction in determining the optimum anode potential for reformate PEM FCs and the continued search for bimetallic Pt catalysts with ever lower CO oxidation potentials will be discussed.

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Combining extensive characterization data of membranes for fuel cell applications

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The commercial Nafion® membranes and the recently developed ETFE-SA membranes (sulphonated poly(ethylene-*alt*-tetrafluoroethylene)) were investigated with sophisticated characterization techniques. An extensive characterization enables fast feedback to the membrane and electrode development and the complicated connections between different manufacturing parameters can also be studied. The thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) were used to find out the thermal behavior of the membranes and during those measurements the ETFE-SA membrane was observed to be suitable for the direct methanol fuel cell (DMFC) at low temperatures. In earlier research, the ETFE-SA membrane was already proved to be chemically stable during a continuous 2000 h test in the DMFC.

The electrochemical inhomogeneity of the membranes was investigated with the scanning electrochemical microscopy (SECM) by mapping proton distribution across the membrane surface. The atomic force microscopy (AFM) was used, when the surface morphology and morphology changes originating from swelling were studied, while with the (SEM), the composition and structure of the membranes was clarified in detail. Those measurements showed that the surface of ETFE-SA differs significantly from the surface of Nafion□. Surface roughness of the ETFE-SA membrane was higher, which originates from the manufacturing process and it also varied as a function of manufacturing parameters. The surface hydrophobicity properties were investigated by water contact angle (CA) measurements and the surface hydrophobicity of ETFE-SA was observed to decrease as a function of sulphonation degree, resulting from the increasing amount of the hydrophilic sulphonic acid groups.

The drawback of the membranes based on poly(perfluorosulphonicacid), e.g. the Nafion® membranes, is especially their high methanol permeability (MeOH crossover). The MeOH permeabilities through the ETFE-SA and different Nafion□ membranes were measured in a diffusion cell and analyzed with a gas chromatograph (GC). According to those measurements, the MeOH permeability through ETFE-SA was less than 2% of the corresponding value of the Nafion□ membranes. The sulphur profile along the membrane cross-section gives information about the distribution of sulphonic acid groups and it was detected with the SEM combined with an energy dispersive X-ray spectrometer (EDX). A smooth sulphur profile proved that the sulphonic acid groups were evenly distributed and the sulphonation process was succeeded. The homogeneous sulphur profile will lead further on to good proton conductivity and high performance in the DMFC.

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Fuel Cells and Sustainable Energy

Analysis of an alkaline fuel cell performance by using a modeling approach

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Much research has been done in the area of fuel cell system control to study and optimize the system performance under different conditions. The relationships between cell current (I) and voltage (V) are usually depicted as polarization curves and these are based on fuel cell's steady state performance, which can be analyzed by using appropriate models for providing the required informations for the system optimization. In this work, experimental polarization results of an alkaline fuel cell were analyzed by using the Chemical Engineering Module of the Multiphysics 3.2 software [1]Experimentally obtained I-V characteristics were analyzed by fitting an empirical equation ($V = E_0 - b \log I - RI - exp(nI)$), through which b, R and n were obtained as a function of cell temperature and gas concentrations. These data were combined with a model describing mass transport phenomena of H_2, and O_2 along the flow channel of the electrode to predict the current and gas concentration distributions. The polarization curves and limiting current obtained using this model agreed well with experimental data. The simulation results showed that some flooding control strategy can be designed to prevent or reduce the flooding effect. A full simulation is being carried out to characterize the overall dynamic system performance at the different fuel cell operating conditions.

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# Exploring Single Electrode Reactions in Polymer Electrolyte Fuel Cells

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Electrochemical impedance spectroscopy (EIS) is a powerful tool to characterise polymer electrolyte fuel cells (PEFCs) and understand the fundamental processes therein. However, one has to bear in mind an important implication in interpreting the impedance spectra: due to the nature of the *solid* polymer electrolyte membrane one cannot easily introduce a reference electrode into the cell, as it is done with cells containing a liquid electrolyte, and therefore determine single electrode behaviour. Hence, integral impedance spectra, measured over the complete active area and across the entire cell do not allow detection of local processes, neither at the anode nor the cathode.

We introduce a *pseudo* reference electrode into the solid electrolyte of a 1-dimensional cell, and therefore we can separate the integral impedance of the cell into anode and cathode contributions. In particular, the anode impedance allows identifying different processes, which we attribute to the hydrogen adsorption, proton generation, and proton transport process, the latter includes water transport in the aqueous phase within the polymer morphology [1]. In a first step, the anode impedance for the hydrogen oxidation reaction (HOR) was measured and fitted with a kinetic model which allows for the determination of the kinetic parameters for single reaction steps.

The cathode impedance for the oxygen reduction reaction (ORR) indicates several steps, e.g. a charge transfer reaction with an apparent intermediate. A model based on the kinetic reactions of the ORR is proposed for low current densities. First results of
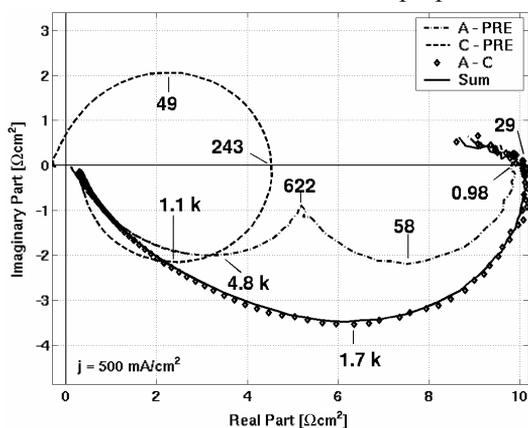
EIS measurments of the ORR in an operating PEFC will be compared to theoretical predictions derived from the kinetic model [2]. It is demonstrated that a chemical step has to be considered in the ORR pathway.

Fig. 1: Measured impedances of the single electrode reactions and across the entire cell, compared with the summarised impedance of the single electrodes. Units of given frequencies are in *rads^-1*.

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Investigation of Pt/RuO$_2$xH$_2$O /CNT as Catalyst in DMFC Anodes

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High costs due to high noble metal loadings are a major obstacle for market introduction of DMFC. One way to reduce the metal loading is to increase the utilisation of noble metal in the catalyst layer. In a previous work it could be shown that a higher catalyst utilisation can be achieved using RuO$_2$·xH$_2$O as catalyst support [1]. The higher activity has been attributed to the support's intrinsic proton conductivity. Carbon nanotubes (CNT) are also frequently discussed as catalyst support for fuel cells, because they have good electronic conductivity and form open porous structures facilitating mass transport in liquid feed operation. In this contribution the combination of the both approaches is described. Catalysts were prepared by coating a thin layer of hydrous ruthenium oxide onto multiwalled carbon nanotubes which have been surface treated with sodium dodecylsulphate beforehand. On this support platinum nanoparticles were deposited using the ethylene glycol reduction method. A high dispersion of particles was achieved. Membrane electrode assemblies using this catalyst on the anode side were produced by hot-spraying. On the cathode side unsupported Pt black catalyst by Johnson & Matthey was used. The electrochemical active surface area (ECA) was determined by CO stripping measurements and compared to the ECA which was achieved using commercial (ETEK) PtRu/C catalyst.

The results show that a significantly higher ECA per gram of noble metal is achieved compared to the reference. Unfortunately the oxidation onset is positively shifted by some ten mV. Overall the approach proved to be quite promising but will need further optimisation. Full cell tests are currently performed and will be presented as well.
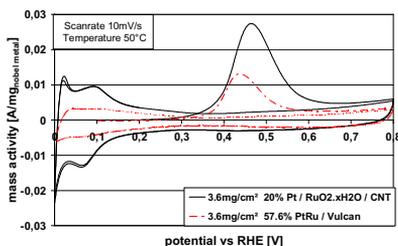
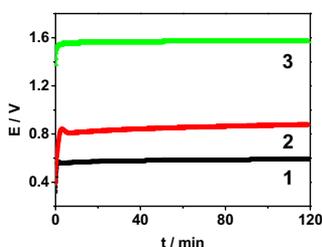**Fig 1: CO-stripping at MEA with new and reference anode catalyst**

[1] F. Scheiba, M. Scholz, L. Cao, C. Roth, C. Cremers, X.Qiu, U. Stimming, H. Fuess, Fuel Cells (accepted for publication)

Economic production of hydrogen by Alcohol Electrolysis

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Water electrolysis is one technique for hydrogen production alongside production from catalytic cracking of natural gas, methanol and ammonia reformation, pyrolysis and gasification processes [1-4]. The main obstacle to commercial exploitation of water electrolysis for large scale hydrogen production is the high electricity consumption, which makes the process economically unattractive offsetting the associated technical and environmental advantages [5]. Here an economic way to produce hydrogen by alcohol electrolysis is reported, a process that requires lower voltages than water electrolysis (*e.g.* E^o = 0.02 V *vs.* NHE for methanol compared to 1.23 V for water).

Figure 1 Voltage response at 20°C from galvanostatic electrolysis at a current density of 60mA cm^{-2} of: (1) 2 mol dm^{-3} methanol, (2) 2 mol dm^{-3} ethanol and (3) water at constant.

Fig.1 compared typical voltage responses with time for the electrolysis of methanol, ethanol and water at constant current density. A ratio of 1.3 was observed for the electrolytic voltages of methanol to water. This significant reduction in the electrolytic operation voltage will reduce the electricity consumption and the level of investment in the associated infrastructure. In economic terms for hydrogen production, the electricity plus methanol cost for production of 1 dm^3 H$_2$ is less than half of the cost when employing water electrolysis. The effects of the concentration of methanol and temperature on the electrolytic voltage were tested. The novelty of this technique is the inherent simplicity and substantially lowered cost. Different scale requirements can easily be achieved by using modified these PEMFC-MEAs as electrolyzers.

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Fuel Cells and Sustainable Energy

Water splitting in pem electrolyser using Pt-Co-Ebonex catalysts

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The recent intensive development of PEM fuel cells imposes the need of analogous electrochemical systems for efficient and cost-effective generation of hydrogen. Proton Exchange Membrane Electrolysers (PEMEL's) are the newest development in the electrolyser technology with high potential for further improvements. In this work composite Pt-Co-Ebonex nanomaterials, synthesized by BH method have been investigated as catalysts for water splitting in a polymer electrolyte membrane (PEM) electrolytic cell. A commercial Nafion 117 polymer membrane has been used as a proton conducting electrolyte. The Me:Ebonex® weight ratio was fixed to 0.6 at varying content of both metals. The primarily role of Ebonex, which is a commercial mixture of titanium oxides with general formula Ti_nO_{2n-1}, has been to suppress the agglomeration of catalyst particles during the synthesis. In addition, inter electronic and/or inter ionic interactions with the metallic components, affecting the catalytic efficiency of the composite material have been expected. The phase composition of the synthesized catalysts, their morphology and surface structure were studied by physical methods for bulk and surface analysis, such as electron microprobe analysis (EMPA), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and BET technique. The electrocatalytic activity towards HER and OER has been investigated by the conventional electrochemical techniques of cyclovoltametry and steady state polarisation. It has been found that Pt-Co-Ebonex facilitates essentially both partial reactions which start at lower overpotentials and proceeds with higher rate compared both to the individual metals and the bi-metallic PtCo catalysts, as it is illustrated on the presented figures. The enhanced catalytic activity has been prescribed to the formation of surface oxides and electronic interactions between the hyper metallic and oxide components of the composite catalyst.
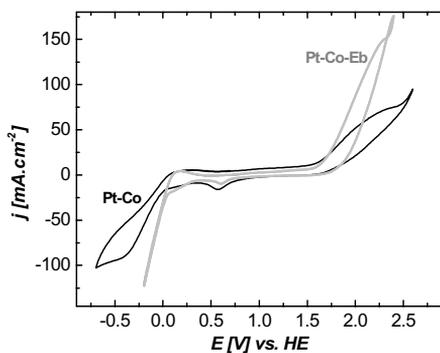

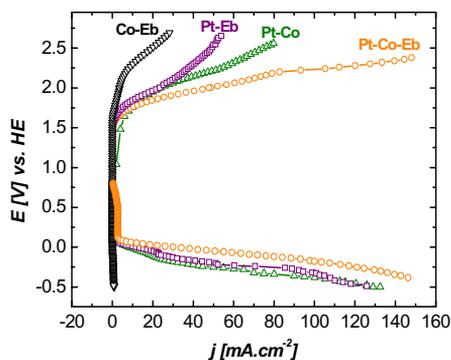Fig. 1: Cyclovoltammetric curves of synthesized catalysts (20°C, scan rate 20 mV/s)

Fig. 2: Steady state polarization curves of the catalysts under study at 20°C

Modeling of Diffusion Electrodes and Fuel Cells

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In this laboratory, modeling studies of usual diffusion electrodes and PEM biochemical fuel cells are being developed. In this stage of the work, a mechanistic model of an air cathode was developed. It can provide details of the physical system (as in Fig. 1). Mechanistic models of methanol and ethanol (in an association with Université de Poitiers, France) anodes will also be developed.
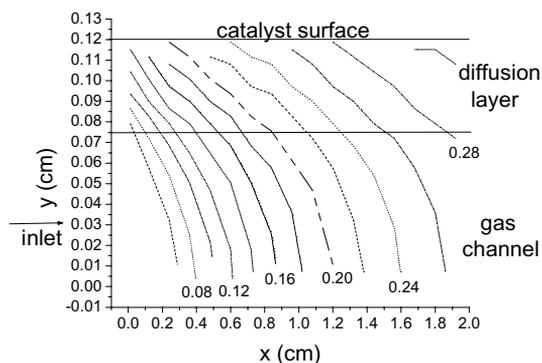

Fig. 1. Water mass fraction contours in an air cathode at 0.83 A cm^{-2} and 0.77 V.

Regarding biochemical fuel cells, a semi-empirical model based on Michaelis-Menten kinetics could predict the performance of a Pt-H_2/H_2O_2-peroxidase fuel cell:
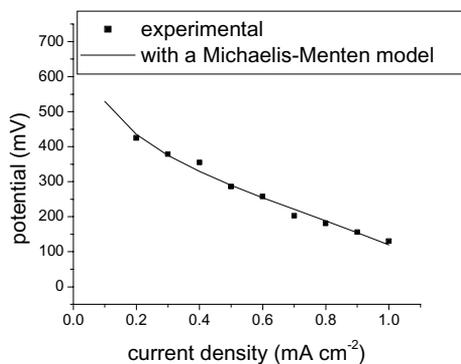

Fig. 2. Potential/current relationship for a Pt-H_2/H_2O_2-peroxidase fuel cell. T=24°C, P=1atm, [H_2O_2]=0.8mM.

Energy Efficient Direct Alkaline Fuel Cells for Liquid Organic Compounds

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xThe low temperature alkaline fuel cells (LTAFC) have been found to be promising for operating with liquid organic compounds as a fuel, especially, when compared to PEM fuel cells. Also, the use of the liquid organic compounds as a fuel in alkaline fuel cells should avoid the problems in transport and storage, when the gaseous hydrogen is used as a fuel for LTAFC. This investigation with laboratory-scale testings will concentrate in the liquid organic organic compounds as a fuel for being used in LTAFC. The research includes the use of several liquid organic fuels (i.e., glucose, ethanol, biodiesel and methanol), which are fed directly in alkaline electrolyte of LTAFC. The different anode-side catalyst materials are studied for finding the effective applications of LTAFCs with high current densities enough together with acceptaply high operation capacities for enabling the use of LTAFCs as current sources.

Keywords: Glucose, ethanol, biodiesel, AFC, anode catalyst material, current density, power density, capacity and laboratory-scale testing.

Anionic membranes based on poly(epichlorhydrin) matrix for alkaline fuel cells

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Many researches are currently focused on electrochemical energy sources, in particular fuel cells, to find out an efficient alternative to the internal combustion engine. PEMFC are among the most promising systems. One of the major disadvantages of the PEMFC is the MEA cost, related (i) to an expensive polymeric membrane and (ii) to the use of platinum catalysts [1]. Alkaline Fuel Cells (AFC) might compete with the PEMFC, at least in some application domains. The main drawback of current AFC consisting of a liquid electrolyte (KOH) deals with their sensitivity to carbon dioxide pollution. Consequently the output of the fuel is drastically reduced. One attractive solution should be the replacement of KOH solution by an anion-conducting polymer electrolyte. The study of these promising electrolytes was initiated by the laboratory of industrial electrochemistry (CNAM) [2, 3]. Thus, a series of ionomers were prepared and characterised. A special attention was paid to the required chemical and electrochemical properties of the cationic function, i.e. a quaternary ammonium [4]. The polymer backbone was based on poly(epichlorhydrin) polymer. Quaternary amination processes were carried out using 1,4 Diazabicyclo [2.2.2] octane (Dabco) and 1-Azabicyclo[2.2.2]octane (Quinuclidine), two cyclic amines not very sensitive to Hofmann elimination. In order to avoid their dissolution in water or a too huge swelling, the membranes were cross-linked either by UV insolation or by heat treatment. To improve still more their thermomechanical properties, the membranes were reinforced by poly(propylene) or nylon supports. Exchange ionic capacity, swelling ratio, glass transition temperature, ionic conductivity, ageing stability, were evaluated. Moreover electrochemical characterizations were performed on these membranes. As a result these membranes appeared as promising candidates for AFC.

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Fuel Cells and Sustainable Energy

Methanol and CO Electro-oxidation on RuO$_2$ Nanosheet Modified Pt/C

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Carbon supported platinum-ruthenium alloys (PtRu/C) are one of the most promising anode catalysts for direct methanol fuel cells. One of the problems associated with such electrocatalysts is the instability of the co-catalyst Ru, initiating catalyst de-activation as well as membrane failure. The possibility of ruthenium oxides (RuO$_x$ or RuO$_x$H$_y$) acting as co-catalysts has attracted recent interest. We recently succeeded in the preparation of crystalline H$_{0.2}$RuO$_{2.1}$ nanosheets (HROns) with thickness of 0.4 nm. HROns have exceptional electrochemical stability and excellent proton-electron conductivity. Here we report the use of crystalline HROns as a co-catalyst for platinum towards CO and CH$_3$OH electro-oxidation in an acidic environment.

The effect of the modification of Pt/C with crystalline HROns towards the electro-oxidation of CO and methanol at 60°C was studied using the thin film electrode technique. CO stripping voltammetry indicated that the modification of Pt/C with HROns decreases the overpotential for CO$_{ad}$ oxidation by ~200 mV. Voltammetry in a 0.5 M H$_2$SO$_4$+1 M CH$_3$OH electrolyte indicated that the threshold for CH$_3$OH electro-oxidation on HROns modified Pt/C was ~150 mV lower than Pt/C. A four-fold increase in methanol electro-oxidation activity was obtained by chronoamperometry at 500 mV. The increase in the activity is suggested to be a result of the bi-functional characteristic of the surface of the HROns. Furthermore, HROns modified Pt/C provided superior durability compared to conventional catalysts under fuel cell operating conditions due to the electrochemical stability of HROns.

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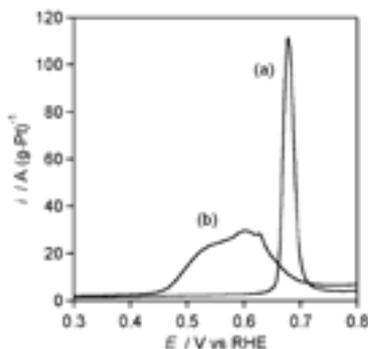

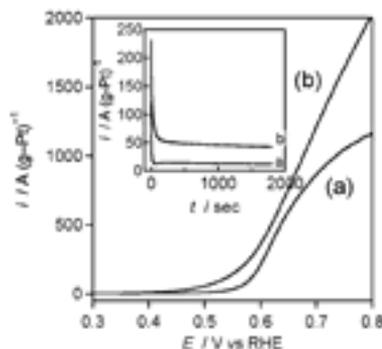Fig. 1. CO stripping voltammogram of (a) Pt/C and (b) HROns modified Pt/C.

Fig. 2. Methanol oxidation on (a) Pt/C and (b) HROns modified Pt/C.

Niw/tiox composite layers as cathode material for hydrogen evolution reaction

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Composite NiW +TiOx layers were obtained by electrolyte containing nickel sulphamate with high concentration of W and nonstoichiometric Ti oxides particles. The codeposition of NiW layers with TiOx particles was carried out under potentiostatic conditions on pristine and oxidized carbon fibers at different rate stirring. Comparatively, NiW layers were obtained under the same experimental conditions. The morphology of the deposits was examined by means of scanning electron microscopy (SEM). Secondary crystallization of NiW layers on the surface of the embedded Ti oxides particles was observed. The electrochemical impedance spectroscopy (EIS) was used to study the electrocatalytic activity of these materials for hydrogen evolution reaction (HER) in acid solution. This reaction is very important in industrial hydrogen production for the fuel cell technology. The results showed that NiW +TiOx layers on oxidized carbon fiber electrodes possess the highest electrocatalytic activity for HER compared with NiW +TiOx layers on non-oxidized carbon fiber electrodes and NiW layers on oxidized carbon fiber electrodes. This behaviour may be attributed not only to the developed electrode surface from the presence of nonstoichiometric titanium oxides but also to the nature of the interaction between the composite and oxidized carbon fibers.

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Electrochemical Impedance Spectroscopy Analysis for Catalyst Layers of DMFC Anode

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We have applied electrochemical impedance spectroscopy (EIS) to analyze catalyst layers, especially anode, of direct methanol fuel cells (DMFCs). To evaluate individual electrodes in a similar condition to DMFC operation, we applied a proposed electrochemical cell named 'half-MEA cell' [1]. The half-MEA cell enables electrochemical evaluation of catalyst layers in a solution without electrolyte. Thus, especially, conditions of polymer electrolyte in the catalyst layers can be evaluated clearly.

In this study, we prepared and evaluated catalyst layers in different condition of polymer electrolyte. To prepare such catalyst layers, we prepared catalyst suspensions containing catalyst powder (Pt/C), polymer electrolyte (Nafion), and different dispersing solvents. As the solvents with different propeties, we applied ethylene glycol dimethyl ether (EGDE) or isopropyl alcohol aqueous solution (IPA aq.). Thus the dispersed condition of Pt/C and Nafion in each solvent could be different [2]. Subsequently, the catalyst layers prepared from the suspensions could obtain different condition of Nafion.

To evaluate the catalyst layers, we prepared single electrode and electrolyte membrane assemblies, named 'half-MEAs', using different catalyst layers. The catalyst layers of these half-MEAs were evaluated with EIS and the half-MEA cell.

As the results of EIS, complex-plane impedance diagrams are shown in Figure 1. Figure 1 apparently indicated that the impedance of IPA aq. was bigger than that of EGDE. In addition, the result corresponded to the result of current-voltage result (figures were omitted).

Furthermore, precise analysis based on our equivalent circuit [1] could suggest that the most significant drawback of the catalyst layer using IPA aq. was low ionic conductivity in secondary pores, which were pores containing Nafion.
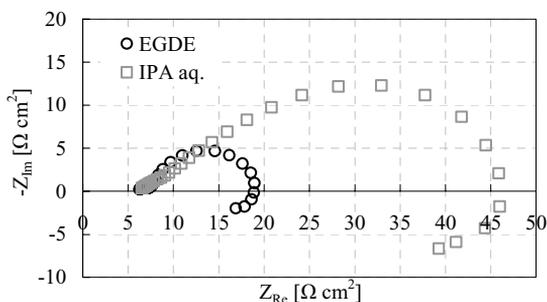
Figure 1, Complex-plane impedance diagrams of methanol oxidation on the catalyst layers using EGDE (○) or IPA aq. (□) as solvents.

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Preparation and characterization of Pt/CNF electrocatalysts for high temperature PEM fuel cells

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Fuel cells with high temperature polymer electrolytes, like phosphoric acid doped PBI are very promising energy conversion systems for future clean energy plants. In comparison with conventional polymer electrolyte (Nafion) fuel cells, they work at temperatures up to 200°C. At these conditions electrochemical processes are less dependent on mass-transport, and catalysts are more tolerant to contaminations in reagents. One problem is the stability of the catalyst, especially the catalyst support, at quite strong operation conditions [1].

Monodisperse platinum nanoparticles were prepared by reduction of H_2PtCl_6 in ethylene glycol [2]. The particle formation was controlled by precursor concentration and reduction reaction conditions (temperature and time). Solution changed color during the heat treatment from light yellow to dark brown usually attributed to platinum colloid formation. Kinetics of the platinum particle formation and prepared intermediates structure were investigated by XAS. The XANES spectra at Pt L_3-edge of the nanoparticles were compared with initial precursor solution and bulk Pt standard (foil) as well as with PtO_2 powder.

Prepared platinum colloidal nanoprecursor was deposited on a carbon nanofibre having a herringbone structure. Prepared electrocatalysts were characterized by ex-situ X-ray techniques, HR-TEM and by in-situ electrochemical XAS in H_2SO_4 and H_3PO_4.

Analysis of the XANES spectra shows rapid exchange of the Cl- ligands of $(PtCl_6)^{2-}$ precursors to oxygen bonds, formed during the interaction between OH- groups of the polyol and the precursor. EXAFS region shows that Pt –Pt bonds start to form during refluxing. No significant changes in platinum colloidal particle structure were detected even after 5 minutes of heating. That indicates formation of Pt first shell structure; the further heating gives no significant rise of signals from higher Pt-Pt shells.

Electrocatalysts on carbon nanofibres shows amorphous structure even after heat treatment with cluster sizes in a range 3-5 nm. High platinum loading in a range of 40-55 wt% was achieved keeping the electrochemical active surface area in a range 50-80 m^2/g. The cluster formation conditions and structure changes at the annealing stage strongly affects the fuel cell electrode behaviour.

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Fuel Cells and Sustainable Energy

Electrochemical Conducting of PVDF/SPEEK Composite Membrane with Surface Treated for DMFC

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In the last decade, the development of the direct methanol fuel cell (DMFC) had gained much interest mainly for portable power application. A key component of (DMFC) is the proton exchange membrane, which is required to have low liquid uptake at water and methanol. The SPEEK is typically obtained by either directly introducing sulfonic acid groups onto the polymer backbone or direct polymerizing sulfonated monomers.

In this study, poly(vinylidiene difluoride)/Sulfonated poly(ether ether Ketone) hybrid membranes were prepared to evaluate the possibility of use as a proton exchange membrane for direct methanol fuel cell (DMFC). PVdF and Sulfonated poly(ether ether ketone) was use to increase proton conductivity, and simultaneously to prevent methanol transport through the cross linked membrane. The Nafion-PVDF/SPEEK-Nafion(NPSN) composite membrane was prepared by immersing the SPEEK in the Nafion-containing casting solution.

Furthermore, in order to improve the composite properties for DMFC applications, the single phase pure polymer method was discussed.

SPEEK/ TiO_2 10.0% membrane with exhibit performances comparable to that of SPEEK/ TiO_2 2.5% membrane due to lower methanol crossover, and the performance of SPEEK/ TiO_2 10.0% membrane at high current densities with methanol (2M) high than SPEEK/ TiO_2 2.5% membrane due to lower methanol permeability. Increasing the titanium oxide content in the SPEEK composite membranes leads to a decrease of the MeOH permeability. The reason for these results is related with the increasing amount of inorganic filler in the membranes, which increases the membranes barrier properties in terms of mass transport.

However, separations of the electrodes from the SPEEK membrane were observed after 2 hour of operation in DMFC due to the poor adhesion and bonding properties. Further work is needed to overcome this problem and fully assess the long term stability. Nevertheless, the lower cost and methanol crossover compared to that of Nafion make the SPEEK membranes promising alternatives for DMFC.

Self-Discharge Mechanisms in the Vanadium Redox Flow Battery

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The vanadium redox flow battery (VRB) is one of the most promising energy storage systems for coupling with intermittent renewable energy supplies (photovoltaic, wind turbine and so on) and for load levelling [1, 2]. Flow batteries in general have several advantages over other storage systems, namely:
•Power and energy can be independently specified.
•Extra energy can be added by adding more electrolyte.
•The battery weight can be easily distributed in different ways, by choosing different tank designs.
•Very rapid electrical response.
•The battery can be recharged electrically or by refilling the electrolyte.
•Very low emissions (especially with respect to diesel generators).
•Accurate, simple state-of-charge measurement.
•Cells can be deep-discharged without damage.
•No memory effect.
•No need to perform 'equalisation' charging.
•Very high cycle life.
Another often quoted advantage is the low self-discharge rate. However, self-discharge may proceed by many mechanisms, especially with respect to discharge in the tanks and reactors. These have not been well documented in the literature. Therefore, this work aims to elucidate and quantify the self-discharge mechanisms in the VRB.

One unusual feature of our design of VRB is the use of an oil layer to protect the negative electrolyte from aerial oxidation and both electrolytes from evaporative water loss. In general an inert glass blanket over the electrolytes has been used in commercial systems. The efficacy of the oil layer was anticipated from laboratory measurements using a spectroscopic technique and validated after a 12 month field trial.

In contrast to aerial oxidation, which represents an 'irreversible' loss of capacity in the tanks, shunt currents represent a route to 'reversible' self-discharge in the reactor. Shunt currents arise through many electrodes at different potentials being in contact with a common electrolyte. All bipolar flow batteries exhibit shunt current losses to some extent, dependent on the design of flow frame and manifold. A simple mathematical model of the shunt currents in the VRB is compared with experimental measurements as determined by several different techniques.

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Photoelectrochemical kinetics of Eosin Y-sensitized zinc oxide films investigated by scanning electrochemical microscopy

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Among the approaches towards inexpensive renewable energy sources dye-sensitized solar cells (DSSC) constitute a main effort that is based on a combination of a nanocrystalline wide-band gap semiconductor, an adsorbed dye with an absorption band in the visible region and an appropriate electrolyte system. Remarkable conversion efficiencies have been demonstrated while avoiding photocorrosion of the semiconductor material. While initial work was mainly performed on nanocrystalline titania in the anatase form and ruthenium coordination complexes as sensitizers, present experimental studies also include a range of other semiconducting metal oxides. Particular appealing are semiconductor systems that can be processed to functional films with very few processing steps or on a variety of substrates, preferably low- cost, light and mechanically flexible polymers. Zinc oxide is electrochemically deposited on a transparent electrode from an aqueous electrolyte in the presence of the dye Eosin Y. Eosin Y not only is an efficient sensitizer, it also acts as a structure-directing agent (SDA) to shape the morphology of the deposited nanocrystalline ZnO [1]. Highly porous yet crystalline sensitized ZnO is obtained in one step and at temperatures below 70 °C.

Eosin Y is used as a sensitizer for nanoporous zinc oxide films for prospective applications in photoelectrochemical solar cells. The kinetics for the reduction of the intermittently formed photooxidized dye molecules by iodide ions in the electrolyte phase was investigated using the feedback mode of a scanning electrochemical microscope (SECM). The bulk phase of the solution contained triiodide as mediator, from which the ultramicroelectrode generated iodide ions acting as electron donors for photooxidized Eosin Y molecules (D^+_{ads}) at the zinc oxide sample. From SECM approach curves effective rate constants for the dye regeneration could be extracted. The effective rate constants at different triiodide concentrations could be related to the rate constant for the reaction of the dissolved donor with photooxidized Eosin Y bound to ZnO as well as to the overall rate of the photosensitization process. For the reaction $D^+_{ads} + 3/2\ I^- \rightarrow D_{ads} + 1/2\ I_3^-$ a rate constant of $k_{ox} = (1.4 \pm 0.8)\ 10^8\ cm^{9/2}\ mol^{-3/2}\ s^{-1}$ was determined.

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Microscale analysis of cathode electrocatalytic reaction on active MEA electrode surface of PEMFC

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High overvoltage of oxygen reduction reaction (ORR) is considered to be one of the problems for achievement of theoretical cell performance in polymer electrolyte membrane fuel cell (PEMFC). In order to conqure this problem, comprehensive analysis of ORR on three-phase boundary in fuel cell operation is necessary. In low cathode overpotential region, PEMFC cathode polarization property per electrochemically active Pt surface area (A_{Pt}) was lower than theoretical current obtained using Tafel equation. As reported in a previous study of ORR with Pt planer electrode in acid media[1], different adsorption conditions of the reaction intermediates cause the change of Tafel slope from $-2RT/F$ to $-RT/F$. We focused on adsorbed oxygen species on active electrode in investigation of the ORR mechanism on membrane electrode assembly (MEA) cathode in fuel cell operation.

The A_{Pt} of the cathode electrode was ascertained by cyclic voltammetry. From the cathode polarization curve, we obtained the exchange current density (i_0) using the Tafel equation with transfer coefficient (α) 0.5. Coverage with oxygen containing species on active electrode was determined by stripping voltammetry[2]. The electric charge required for stripping oxygen species (Q_{Ox}) showed linear correlation with positive electrochemical potential above 0.7 V vs. RHE ($V_{adsorption}$). Therefore, we defined the coverage of oxygen species on electrode (θ) as Eq. 1, where q_{Pt} represents the charge for the desorption of oxygen species on unit Pt surface. Furthermore, we developed a novel cathode catalytic reaction model including the effect that oxygen species adsorbed to reaction sites inhibited the reactivity of cathode reaction, and modified the Tafel equation as Eq. 2, which represents the relationship between cathode overpotential ($\eta_{cathode}$) and current density (i).

$$V \quad V_{adsorption} \qquad \theta = 0, \quad V > V_{adsorption} \qquad \theta = Q_{Ox} / (q_{Pt} \times A_{Pt}) \quad 1 \qquad \text{Eq. 1}$$

$$i = i_0 (1 - \theta) \exp (0.5 F \eta_{cathode} / RT) \qquad\qquad \text{Eq. 2}$$

We simultaneously fitted the Eq. 1 and 2 to all experimental data using q_{Pt} as single fitting parameter. The result of model calculation showed high correspondency with experimental polarization data with various Pt loadings. Result of model calculation for potential dependency of coverage is shown in Fig. 1, which A_{Pt} is fully covered with oxygen species above 1.05 V vs. RHE.

A novel ORR mechanism to analyze the poisoning of active Pt surface with oxygen species, which causes a low MEA cathode catalytic performance in fuel cell operation, has been proposed.

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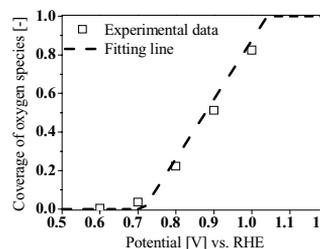
Fig. 1   Potential dependency of coverage. (q_{Pt} = 450 µC/cm²-Pt)

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Electrocatalytic Role of Eosin Y during Electrodeposition of ZnO/Eosin Y Hybrid Thin Films

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Recently, we have succeeded in one-step heat treatment free synthesis of ZnO/dye hybrid thin films by cathodic electrodeposition from aqueous mixed solutions containing Zn^{2+} ion and xanthene dye molecule in the presence of oxygen. Porous crystals of ZnO are formed due to the surface adsorption of dye in the course of the film growth. In addition to such an effect as structure directing agents, these dye molecules act as electrocatalysts to improve the charge transfer kinetics for the oxygen reduction reaction, and hence accelerate the rate of ZnO growth. Modeling of the hybrid film growth taking thermodynamic stabilities of Zn^{2+} / dye interaction as well as the influence of dyes to the kinetics into account should lead us to a comprehensive understanding of the process. Here we employed ZnO/eosin Y hybrid as the model system for the discussion.

The reduction of dissolved oxygen in the presence of Zn^{2+} ions and variable concentration of eosin Y molecules was analyzed by using a rotating disk electrode (RDE). CV curves measured at 500 rpm are shown in Fig. 1. A plateau current of oxygen reduction limited by mass transport is reached only in Zn^{2+} free solution. The current becomes kinetically limited in the presence of Zn^{2+} ions. The addition of eosin Y, however, increases the reduction current significantly due to its electrocatalytic activity. It is further noticed that the enhancement of cathodic current follows different rules depending on the redox state of eosin Y molecule ($E^0_{eosin Y}$ = ca. –0.9 V vs. SCE).

When it is in the oxidized state, the relationship between reductive current and the concentration of eosin Y could be described by Langmuir type adsorption of electrocatalyst, namely, charge transfer rate constant being proportional to the surface coverage of ZnO with eosin Y. When eosin Y is reduced, it forms a complex designated as $[2Zn^{2+}\cdots EY^-]$ whose stability constant (pK_{Zn}) was measured as 3.88. Because the increment of the reductive current becomes proportional to the concentration of eosin Y, an electrocatalysis by redox mediation is considered for the complex of reduced eosin Y as shown above.
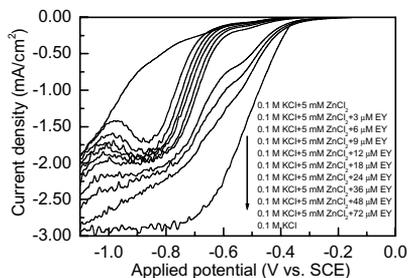

Fig.1 CV polarization curves recorded on ITO rotation disk electrode (500 rpm) in different electrolyte bubbled by O_2 at 70 °C. Scan rate 5 mV/s

Acknowledgement

Direct fabrication of Pt-supported porous carbon catalyst for PEM fuel cell

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Pt-based electrocatalysts are usually employed in proton exchange membrane fuel cells (PEMFC) and direct alcohol fuel cells (DAFC) as electrocatalysts in relatively low temperature. Conventional preparation techniques based on wet impregnation and chemical reduction of the metal precursors. There conventional synthesis methods based on impregnation-reduction [1], microemulsions [2], sonochemistry [3, 4], and microwave irradiation [5–7]. However, it is rather tedious to prepare the Pt-supported carbon catalOxygen Reduction on Carbon Supported Iron Electrocatalysts: Effects of Iron Loading on the Activity

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The electrochemical reduction of oxygen is one of the most important reactions in various energy conversion systems. Platinum, as an active catalyst, is too expensive to be used widely for commercialization. Thus, non-noble metal electrocatalysts with high catalytic activity have received great concern in recent years [1, 2]. Although the work of G. Lalande, G. Faubert et. al. has demonstrated that a carbon black, a source of iron and nitrogen are necessary to obtain catalytic activity for oxygen reduction[3, 4], the optimum loading of iron on the substrate hasn't been studied in detail in the literatures.

In this publication, the effects of iron loading on their activity for oxygen reduction are studied. Catalysts were prepared by heat-treating Turnbull's Blue deposited on conducting carbon black at 800°C under nitrogen atmosphere. Before loading with the precursors, the carbon black was first treated by concentrated HNO_3, filtered, washed with deionized water and then dried at 80°C for 3hs. The quantification of iron on the catalysts was performed by ICP. The catalysts were evaluated electrochemically in a three-electrode one-compartment cell, in which 0.5 mol/l H_2SO_4 was used as the electrolyte, saturated calomel electrode (SCE) and platinum foil were used as reference and counter electrode, respectively. The working electrodes were prepared by coating a glassy carbon disk (4 mm diameter) with a suspension containing the catalysts and Teflon. The measurements were performed at 25°C.

The cyclic voltammograms show that both the peak potential and peak current of oxygen reduction increase with iron loading on the carbon black and reach a maximum of ca. 0.4V at 23 wt% Fe then decrease. The higher peak potential is an indication of

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Oxygen Reduction on Carbon Supported Iron Electrocatalysts: Effects of Iron Loading on the Activity

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The cyclic voltammograms show that both the peak potential and peak current of oxygen reduction increase with iron loading on the carbon black and reach a maximum of ca. 0.4V at 23 wt% Fe then decrease. The higher peak potential is an indication of a higher catalytic activity. In another experiment, the stead state polarization curves give the lowest Tafel slop of ca. 82 mV/dec at 23 wt% Fe loading. The change of Tafel slop means that the mechanism of oxygen reduction reaction changes with iron loading on the catalysts [5]. The results indicate that iron loading of ac. 23 wt% on the catalysts favours either the thermodynamics or the kinetics for electrochemical reduction of oxygen.

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Spillover of primary oxides as a dynamic catalytic effect of interactive supports

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The reversible peaks of primary oxides (M-OH) usually appear on voltammograms of Pt, Au and some other metals at fixed potential and immediately merge into broader irreversible peaks of the stable surface oxide (M=O) growth. Primary oxides play a decisive catalytic role both in anodic CO oxidation (CO tolerance) and cathodic oxygen reduction (ORR). Hypo-*d*-electronic oxides, on the first place anatase titania, impose two catalytic effects on supported nanostructured electrocatalysts: (i) Strong Metal Support Interaction (SMSI) with hyper-*d*-electronic catalytic metal, and (ii) The spillover effect of the primary oxides. Hypo-*d*-oxides feature the exchange membrane properties, and the higher the altervalent capacity, the higher the spillover effect. Experiments have been carried out with: (a) Magneli phases as highly electronic conducting and rather stable Ti-suboxide support of developed surface area; (b) Submonolayer anatase titania sol-gel deposited on carbon carrier of surface area above 250 m^2 g^{-1}; (c) The latter with $3 - 7$ mol.% of colloidal tungstenia ingredient; (d) Moderately developed Magneli phases with sol-gel deposited submonolayer of anatase titania to increase the overall surface area for metallic electrocatalyst SMSI deposition, and (e) As the reference state, Pt and Au upon plain, but highly developed carbon carrier. The reversible peak of the primary oxide growth on Pt and Au becomes shifted at remarkably more negative potential values and starts even within the range of H-adatoms desorption, while its reduction extends up to the UPD of hydrogen atoms. With wet titania supported Pt catalyst in membrane cells these peaks dramatically increase in their charge capacity and almost reversibly become shrunk with decreased moisture content in the feeding indifferent gas mixture. Such potentiodynamic scans are the best as comparable experimental evidence of the spillover effect for primary oxides, confirmed also by the formaldehyde oxidation. The latter is even more pronounced with the rather fast reaction of formaldehyde when its anodic oxidation approaches rather high limiting currents of concentrated solutions within a broader potential range practically between hydrogen and oxygen evolving limits.

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