Program of the

20th Topical Meeting of the International Society of Electrochemistry

Advances in Lithium and Hydrogen Electrochemical Systems for Energy Conversion and Storage

19-22 March 2017
Buenos Aires, Argentina

Organized by:
Division 3 Electrochemical Energy Conversion and Storage
Division 4 Electrochemical Materials Science
ISE Region Argentina

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Sunday 19 March 2017 - Afternoon

Opening Ceremony & Welcome Reception

18:00 to 20:00

Chaired by: Agustin E. Bolzán and Ezequiel Pedro Marcos Leiva

Monday 20 March 2017 - Morning

Lithium Batteries

Auditorio 1 Valsecchi

Chaired by: Ezequiel Leiva and Silvia Bodoardo

09:00 to 09:30 Invited

Alejandro A. Franco (Laboratoire de Réactivité et Chimie de Solides (LRCS), Université de Picardie Jules Verne & CNRS (UMR 7314), Amiens, France)

Mesostructure-performance relationships in rechargeable batteries: challenging the dogma with multiscale computations and immersive visualization

09:30 to 09:50

Pierre Bernard (LITEN, Université Grenoble Alpes, CEA, Grenoble, France)

Analysis of Si-based Anode in Li-ion Batteries Combining Electrochemical Characterization and Multi-Scale Modeling

09:50 to 10:10

Steen Brian Schougaard (Chemistry, NanoQAM and UQAM, Montreal, Canada)

Methods for Determining the ¨Ultimate¨ Lithium Insertion/Extraction Kinetics

10:10 to 10:30

Mario El Kazzi (ENE - Energy and Environment, Paul scherrer Institute (PSI), Villigen, Switzerland), Daniela Leanza, Petr Novák, Carlos A.F. Vaz

Monitoring the Chemical and Structural Surface Changes on Single Particles of Commercial-Like Li-Ion Battery Electrodes

10:30 to 10:50

Coffee Break

10:50 to 11:10

Janine Mauzeroll (Chemistry, McGill University, Montreal, Canada), Malak Dayeh, Steen Brian Schougaard, Michael E. Snowden

Properties of Lithium Battery Particles from Electrochemical Micro-Pipets Measurements

11:10 to 11:30

Xinhua Zhu (Department Materials and Chemistry, SURF Group, Vrije Universiteit Brussels, Brussels, Belgium), Lucia Fernandez Marcia, Rahul Gopalakrishnan, Annick Hubin, Noshin Omar, Joeri Van Mierlo

Advanced Electrochemical Impedance Spectroscopy for the Aging Study of Commercial Li Ion Batteries

11:30 to 11:50

Daniel Bélanger (Chimie, Université du Québec à Montréal, Montréal, Canada)

Improving the Performance of Energy Storage Materials by Chemical Modification

11:50 to 12:10

Thierry Djenizian (Flexible electronics Department, Ecole Nationale Superieure des Mines de Saint-Etienne, Gardanne, France)

Electropolymerized Electrodes for High Performance Thin-film Li-ion Microbatteries

12:10 to 12:50 Keynote

Khalil Amine (Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, USA)

Advanced next Generation Lithium Ion batteries and beyond

Hydrogen Electrochemical Systems

Aula Magna Cardenal Pironio

Chaired by: Andreas Friedrich and Sara Cavaliere

09:00 to 09:30 Invited

Dario R. Dekel (Chemical Engineering, Technion, Haifa, Israel)

Anion Exchange Membrane Fuel Cells: State-of-the-Art

09:30 to 09:50

Deborah Jones (ICGM Aggregates, Interfaces and Materials for Energy, CNRS - Université de Montpellier, Montpellier, France), Sara Cavaliere, Nicolas Donzel, Stefano Giancola, Luca Pasquini, Jacques Rozière, Rakhi Sood, Marta Zaton

High Durability Composite Fuel Cell Membranes

09:50 to 10:10

David Zitoun (Department of Chemistry, Bar Ilan University, Ramat Gan, Israel)

Low PGM Electrocatalyst for Alkaline Exchange Membrane Fuel Cells

10:10 to 10:30

Aldo Gago (Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany), Philipp Lettenmeier, K. Andreas Friedrich, Jan Majchel, Li Wang

Synthesis of Highly Active Iridium Catalysts for Anodes of Proton Exchange Membrane Electrolyzers

10:30 to 10:50

Coffee Break

10:50 to 11:10

Katrin F. Domke (Molecular Spectroscopy Department, Max Planck Institute for Polymer Research, Mainz, Germany), Mischa Bonn, Xiao Ling, Sapun H. Parekh

Nanoscale Distribution of Sulfonic Acid Groups Determines Structure and Binding of Water in Nafion Membranes

11:10 to 11:30

Annika Carlson (Applied Electrochemistry, KTH Royal Institute of Technology, Stockholm, Sweden), Carina Lagergren, Göran Lindbergh, Rakel Wreland Lindström

Performance limitations in anion-exchange membrane fuel cells

11:30 to 11:50

Thomas Jahnke (Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany), Georg Futter, Arnulf Latz

A transient 2D PEMFC model to investigate cell performance and degradation

11:50 to 12:10

Iryna Zenyuk (Mechanical Engineering, Tufts University, Medford, USA)

Understanding Water Management in Polymer Electrolyte and Anion Exchange Membrane Fuel Cells through *in-operando* X-ray Computed Tomography

12:10 to 12:50 Keynote

Sanjeev Mukerjee (Chemistry and Chemical Biology, Northeastern University, Boston, USA), Qingying Jia

Enabling Sustainable Non Noble Metal Electrocatalysts for Oxygen Reduction Reaction

Monday 20 March 2017 - Afternoon

Lithium Batteries

Auditorio 1 Valsecchi

Chaired by: Robert Dominko and Daniel Bélanger

14:30 to 15:00 Invited

Kristina Edstrom (Department of Chemistry, Angstrom Laboratory, Uppsala University, Uppsala, Sweden)

Silicon as negative electrode material for Li-ion batteries – what have we learnt through interface studies

15:00 to 15:20

Robert Kostecki (ESDR, LBNL, Berkeley, USA), Maurice Ayache, Hans A. Bechtel, Angelique Jarry, Michael C. Martin

IR spectroscopy and Imaging Interfaces in Silicon Anode

15:20 to 15:40

Jong-Sung Yu (Energy Systems Engineering, DGIST, Daegu, Korea), Tong-Hyun Kang, Chunfei Zhang

3D graphene-functionalized silicon anode for lithium ion battery with excellent cycle stability and rate capability

15:40 to 16:00

Tony Jaumann (Institute of Complex Materials, Leibniz IFW Dresden, Dresden, Germany), Eike Ahrens, Holger Althues, Juan Balach, Susanne Dörfler, Lars Giebeler, Andreas Krause, Markus Piwko, Walter Weber

In situ Synchrotron XRD of Silicon Nanowires on 3D Carbon Substrates for Li-Ion- and Li-Sulfur-Batteries

16:00 to 16:20

Andreas Krause (Nanowire Group, NaMLab gGmbH, Dresden, Germany), Lars Giebeler, Matthias Grube, Tony Jaumann, Ulrike Langklotz, Alexander Michaelis, Thomas Mikolajick, Steffen Oswald, Walter Weber

Influence of Ultrathin Carbon Coatings on Silicon Nanowires to Capacity and Cycling Stability in Li-Ion Batteries

16:20 to 16:40

Coffee Break

16:40 to 17:00

Giulio Ferraresi (Energy and Environment Research Division (ENE), Paul Scherrer Institut, Villigen, Switzerland), Lukas Czornomaz, Mario El Kazzi, Petr Novák, Claire Villevieille

Thin Films of Si/Sn and SiO_2/SnO_2 as Model Anodes in Li-Ion Batteries: Understanding the Electrode/Electrolyte Interface Reactions

17:00 to 17:20

Emiliano Primo (IFEG, FaMAF-Universidad Nacional de Córdoba, CONICET, Córdoba, Argentina), Daniel Barraco, Guillermina Luque

Comprehensive understanding of aqueous polymers as effective binders for silicon nanoparticles-based anodes for lithium-ion batteries

17:20 to 17:40

Meruyert Karim (School of Engineering, Nazarbayev University, Institute of Battery, Astana, Kazakhstan), Moulay-Rashid Babaa, Zhumabay Bakenov, Azhar Moldabayeva, Anara Molkenova, Yongguang Zhang, Anar Zhexembekova

Development of SiO_2 based Composite Anode Material for Li-ion Batteries

Hydrogen Electrochemical Systems

Aula Magna Cardenal Pironio

Chaired by: Enrique Herrero and Stanko Brankovic

14:30 to 15:00 Invited

Simon Thiele (Institute of Microsystems Engineering, University of Freiburg, Freiburg, Germany), Matthias Breitweiser, Matthias Klingele, Carolin Klose, Riko Moroni, Severin Vierrath

Direct Membrane Deposition: a New Way in Membrane Electrode Assembly Manufacturing for Fuel Cells

15:00 to 15:20

Baptiste Verdin (DEHT/STP/LCP, CEA-LITEN, Grenoble, France), Frédéric Fouda-Onana, Pierre Millet

Current Distribution in Large-Surface Area PEM Electrolysis Cells

15:20 to 15:40

Jin-Soo Park (Department of Green Chemical Engineering, Sangmyung University, Cheonan, Korea), Moon-Sung Kang, Mun-Sik Shin, Chan-Ho Song

Porous Polybenzimidazole Membranes for High Temperature Proton Exchange Membrane Fuel Cells

15:40 to 16:00

Plamen Atanassov (Center for Micro-Engineered Materials (CMEM), University of New Mexico, Albuquerque, USA), Kateryna Artyushkova, Ivana Matanovic, Alexey Serov, Michael Workman

Platinum Group Metal-Free Catalysts Integration in MEA: Catalytic Layer Design for PEMFC and AEMFC

16:00 to 16:20

Kenichiro Ota (Green Hydrogen Research Center, Yokohama National University, Yokohama, Japan), Akimitsu Ishihara, Koichi Matsuzawa, Shigenori Mitsushima, Takaaki Nagai

NPGM Oxide Cathode with Oxide Support for Advanced PEFCs

16:20 to 16:40

Coffee Break

16:40 to 17:00

Adam Weber (Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, USA), Huai-Suen Shiau

Modeling Water Management: Alkaline-Exchange-Membrane Fuel Cells

17:00 to 17:20

David Levitan (Instituto de Tecnologias de Hidrogeno y Energias Sostenibles, UBA - CONICET, Ciudad de Buenos Aires, Argentina), Pablo Daniel Giunta, Miguel Angel Laborde

Numerical modelling of CO poisoning induced sustained oscillations in the anode potential of a PEM fuel cell

17:20 to 17:40

Wolfgang Schmickler (Institute of Theoretical Chemistry, Ulm University, Ulm, Germany)

Oxygen Reduction in Alkaline Media - a Theoretical Study

Tuesday 21 March 2017 - Morning

Lithium Batteries

Auditorio 1 Valsecchi

Chaired by: Ernesto Calvo and Alejandro Franco

09:00 to 09:30 Invited

Robert Dominko (Department of Materials Chemistry, National Institute of Chemistry, Ljubljana, Slovenia), Giulliana Aquilanti, Iztok Arcon, Sara Drvaric Talian, Lorenzo Stievano, Alen Vizintin

The role of polysulfides in Li-S batteries

09:30 to 09:50

Alar Janes (Faculty of Science and Technology, Institute of Chemistry, University of Tartu, Tartu, Estonia), Enn Lust, Thomas Thomberg, Tauno Tooming, Ronald Vali

Synthesis and Characterization of D-Glucose Derived Nanospheric Hard Carbon Negative Electrodes for Lithium- and Sodium-Ion Batteries

09:50 to 10:10

Ulrike Langklotz (Institute of Materials Science, TU Dresden, Dresden, Germany), Christian Heubner, Michael Schneider, Mathias Weiser

Direct electrochemical synthesis of 3D-nanostructured titania anodes for high power lithium ion batteries

10:10 to 10:30

Guillermina Luque (Departamento de Química Teórica y Computacional, Universidad Nacional de Córdoba, Córdoba, Argentina), Daniel Barraco, Paula Bercoff, Victoria Bracamonte, Emiliano Primo, Lisandro Venosta

Dual lithium uptake anode materials: crystalline Fe_3O_4 nanoparticles supported over graphitic matrices for lithium-ion batteries

10:30 to 10:50

Coffee Break

10:50 to 11:10

Mariela Gisela Ortiz (Electrochemistry, INIFTA-UNLP, La Plata, Argentina), Silvia Real, Arnaldo Visintin

Synthesis and Electrochemical Properties of Nickel Oxide as Anodes for Lithium Ion Batteries

11:10 to 11:30

Florencia Marchini (INQUIMAE - CONICET, University of Buenos Aires, Buenos Aires, Argentina), Ernesto Julio Calvo, Santiago Herrera, Nataliia Mozhzhukhina, Alvaro Y. Tesio, Walter Ramón Torres, Federico J. Williams

Solvent and electrolyte instability during Oxygen Reduction Reaction in Li-O_2 battery cathodes

11:30 to 11:50

Usman Zubair (Department of Applied Science and Technology, Politecnico di Torino, Turin, Italy), Mojtaba Alidoost, Julia Amici, Silvia Bodoardo, Carlotta Francia, Nerino Penazzi

rGO Wrapped Activated Microporous Carbon from β-Cyclodextrin Nanosponges for Li/S Batteries

11:50 to 12:10

Amangeldi Torayev (Laboratoire de Reactivite et Chimie des Solides, University of Picardie Jules Verne, Amiens, France), Alejandro A. Franco, Caroline Gaya, Clare P. Grey, Pieter Magusin, Celine Merlet, Yinghui Yin

Understanding the role of Li_2O_2 particle size on Li-O_2 battery charge process

12:10 to 12:30

Helmut Baltruschat (Institute of Physical and Theoretical Chemistry, University of Bonn, Bonn, Germany), P. P. Bawol, P. Koenigshoven, P. Reinsberg, A. Weiss

ORR and OER in Li+-Containing DMSO: Further Mechanistic Insights and the Action of Redox-Mediators as Probed by DEMS

Hydrogen Electrochemical Systems

Aula Magna Cardenal Pironio

Chaired by: Dario Dekel and Katrin Domke

09:00 to 09:30 Invited

Sara Cavaliere (Aggregates, Interfaces and Materials for Energy, Institut Charles Gerhardt - University of Montpellier, Montpellier, France), Giorgio Ercolano, Filippo Farina, Ignacio Jiménez-Morales, Deborah Jones, Jacques Rozière

Pt Thin Film Deposition on Nanofibrous Supports: PEMFC Electrodes with Enhanced Performance and Stability

09:30 to 09:50

Renate Hiesgen (University of Applied Sciences, Department of Basic Science, Esslingen, Germany), K. Andreas Friedrich, Michael Handl, Tobias Morawietz

Quantitative *in Situ* Analysis of Ionomer Structure in Fuel Cell Catalytic Layers

09:50 to 10:10

Oran Lori (Chemistry, Bar Ilan University, Ramat Gan, Israel), Lior Elbaz, Shmuel Gonen, Oran Lori

Highly Active, Corrosion-Resistant Cathode for Fuel Cells, Based on Platinum and Molybdenum Carbide

10:10 to 10:30

Josef Schefold (Distributed Energy Group, European Institute for Energy Research, Karlsruhe, Germany), Annabelle Brisse

Stability of Solid Oxide Cells for Steam Electrolysis Analysed in the 10 to above 20 Thousand Hours Range

10:30 to 10:50

Coffee Break

10:50 to 11:10

Elizabeth Santos (Theoretical Chemistry, Ulm University, Ulm, Germany), Milagros Avila, Maria Fernanda Juarez, Ezequiel Leiva, Oscar Oviedo, Andres Ruderman

Hydrogen Oxidation on Nanostructures Electrodes – A Scenario on Stepped Silver Surfaces

11:10 to 11:30

Enrico Pizzutilo (Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GMBH, Düsseldorf, Germany), Simon Freakley, Graham J. Hutchings, Karl J.J. Mayrhofer

Hydrogen peroxide on-site production: a fundamental study on the direct synthesis and electrocatalytic synthesis using Au-Pd catalysts

11:30 to 11:50

Konstantin Petrov (Electrocatalysis, IEES-BAS, Sofia, Bulgaria), Konstantin Petrov, Dzhamal Uzun

The Black Sea and Hydrogen Energy

11:50 to 12:10

André Dourado (Fundamental Chemistry, Instituto de Química, USP, São Paulo, Brazil), Matthias Arenz, Susana Cordoba de Torresi

H_2 Generation by Electrocatalytic Oxidation of SO_2

12:10 to 12:30

Fernando Zinola (Universidad de la República, Montevideo, Uruguay)

The role of electrochemical hydrogen evolution at platinum nanoparticles on carbon monoxide oxidation in fuel cells

Tuesday 21 March 2017 - Afternoon

Lithium Batteries

Auditorio 1 Valsecchi

Chaired by: Kristina Edstrom and Thierry Djenizian

14:30 to 15:00 Invited

Silvia Bodoardo (Applied Science and Technology, Politecnico di Torino, Torino, Italy), Julia Amici, Christophe Aucher, Carlotta Francia, Paulina Marquez, Motjaba Alidoost, Francesco Trotta, Juqin Zeng

Lithium air batteries: can this be the future for electric vehicles?

15:00 to 15:20

Ernesto Julio Calvo (INQUIMAE, DQIAyQF, CONICET, University of Buenos Aires, Buenos Aires, Argentina), Maria del Pozo Vázquez, Santiago Herrera, Florencia Marchini, Nataliia Mozhzhukhina, Alvaro Y. Tesio, Walter Ramón Torres, Federico J. Williams

From the sustainable extraction of lithium to advanced lithium air batteries: An electrochemical approach

15:20 to 15:40

Sergio Brutti (Dipartimento di Scienze, Università della Basilicata, Potenza, Italy)

1,2-dimetoxyethane degradation chemistry in Li-O_2 batteries

15:40 to 16:00

Julia Amici (DISAT, Politecnico di Torino, Torino, Italy), Mojtaba Alidoost, David Amantia, Silvia Bodoardo, Fabrizio Caldera, Carlotta Francia, Sandra Martinez Crespiera, Nerino Penazzi, Francesco Trotta

O_2 Selective Membrane Based on a Dextrin-Nanosponge in Polymer Matrix for Li–air Cells Actually Working in Ambient Air

16:00 to 16:20

Gabriela Horwitz (Physics, Comisión Nacional de Energía Atómica, San Martin, Argentina), Henry Andres Cortes Páez, Horacio Corti, Matias Factorovich, M. Paula Longinotti

Transport of Lithium Ions and Oxygen in Cathodes of Lithium-Air Batteries

16:20 to 16:40

Coffee Break

16:40 to 17:00

Kwangjin Park (Energy Lab, Material Group, Samsung Advanced Institute of Technology, SAIT, Suwon, Korea), Jin-Hwan Park, Byungjin Choi, Suk-Gi Hong, Jun-Ho Park

Enhancement in the electrochemical performance of zirconium/phosphate bi-functional coatings on $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ by the removal of Li residuals

17:00 to 17:20

Pablo Jiménez Manero (Institut des Matériaux Jean Rouxel, CNRS, Nantes, France), Olivier Aleveque, Franck Dolhem, Joël Gaubicher, Dominique Guyomard, Bernard Lestriez, Eric Levillain, Philippe Poizot

Properties and performance of a novel lithium-doped state of polyaniline as positive active material and conducting additive for lithium-ion batteries

17:20 to 17:40

Tomáš Kazda (Department of Electrical and Electronic Technology, Brno University of Technology, Brno, Czech Republic), Lubomír Kubáè, Marie Sedlarikova, Lucie Syrová, Tomáš Syrový, Jiøí Vondrák

Cathode material for Li-Ion batteries prepared by screen printing for smart textile applications

Hydrogen Electrochemical Systems

Aula Magna Cardenal Pironio

Chaired by: Simon Thiele and José L. Fernández

14:30 to 15:00 Invited

K. Andreas Friedrich (Electrochemical Energy Technology, German Aerospace Centre (DLR), Stuttgart, Germany)

Achieving Cost Reduction in PEM Electrolysis by Material Development

15:00 to 15:20

Yasna Acevedo Gomez (Applied Electrochemistry, KTH Royal Institute of Technology, Stockholm, Sweden), Carina Lagergren, Keyvan Raeissi, Hamed Rashtchi, Morteza Shamanian, Rakel Wreland Lindström, Mohammad Zhiani

Study of electroplated Ni-Mo and Ni-Mo-P coated stainless steel as bipolar plates in PEM fuel cell

15:20 to 15:40

Klaus Wippermann (IEK-3, Forschungszentrum Jülich, Jülich, Germany), Carsten Korte, Susanne Kuhri, Werner Lehnert, Jürgen Wackerl

Aminoalkylsulfonic Acids as Electrolytes for High Temperature PEM Fuel Cells

15:40 to 16:00

Belen Molina Concha (LEPMI, Grenoble-INP, Grenoble, France), Marian Chatenet, Yasser Ahmad, Nicolas Batisse, Sandrine Berthon-Fabry, Laetitia Dubau, Marc Dubois, Katia Guérin, Frédéric Maillard

Fluorination surface treatment to mitigate carbon corrosion and improve the durability of Pt electrocatalysts in proton-exchange membrane fuel cells

16:00 to 16:20

Enn Lust (Institute of Chemistry, University of Tartu, Tartu, Estonia), Eneli Härk, Rutha Jäger, Rait Kanarbik, Piia Ereth Kasatkin, Jaak Nerut, Silver Sepp, Indrek Tallo, Thomas Thomberg, Kersti Vaarmets, Peeter Valk

Development of Novel Catalysts for Polymer Electrolyte Membrane Fuel Cells

16:20 to 16:40

Coffee Break

16:40 to 17:00

Tania Benedetti (School of Chemistry, University of New South Wales, Sydney, Australia), Yibing Li, Lucy Gloag, J. Justin Gooding, Nickson Perini, Edson A. Ticianelli, Richard D. Tilley, Chuan Zhao

3D Ru-Au branched nanoparticles for OER with enhanced activity and stability

17:00 to 17:20

Lucy Gloag (School of Chemistry, University of New South Wales, Sydney, Australia)

Structural characterization and growth study of Au-Ru branched nanoparticles for oxygen evolution catalysis

17:20 to 17:40

Ariel Friedman (Department of Chemistry, Bar Ilan University, Ramat-Gan, Israel), Lior Elbaz, Zeev Gross

Electropolymerization of Metallo-Corroles: Towards a Synergistic Electrocatalyst for Oxygen Reduction Reaction

Wednesday 22 March 2017 - Morning

Lithium Batteries

Auditorio 1 Valsecchi

Chaired by: Guillermina Luque and Brett Lucht

09:00 to 09:30 Invited

Nuria Garcia-Araez (Chemistry, University of Southampton, Southampton, United Kingdom), James Dibden, James Frith, Noramon Intaranont, John Owen, Luyi Yang

Using redox mediators for $Li-O_2$ and Li-S batteries and Li recycling

09:30 to 09:50

Johan Hagberg (Department of Applied Electrochemistry, KTH Royal Institute of Technology, Stockholm, Sweden), Kayne Alvim, Alexander Bismarck, Göran Lindbergh, Henry Maples

Electrophoretic Deposition of $LiFePO_4$ on Carbon Fibres for Structural Battery Applications

09:50 to 10:10

Aleksei Llusco (Department of Chemical Engineering and Mineral Processing, University of Antofagasta, Antofagasta, Chile), Mario Grageda, Svetlana Ushak

Synthesis of $LiMg_xMn_{2-x}O_4$ cathode using lithium compounds with high magnesium content from natural brines

10:10 to 10:30

Chinwe Ikpo (Department of Chemistry, University of the Western Cape, Bellville, Cape Town, South Africa), Ntuthuko Hlongwa, Emmanuel Iwuoha, Zolani Myalo, Miranda Ndipingwi

Microscopic, Spectroscopic and Electrochemical Properties of Nanocomposite Li_2MnSiO_4/Al_2O_3 : a Promising Lithium Ion Battery Cathode

10:30 to 10:50

Coffee Break

10:50 to 11:10

Candace Chan (Materials Science and Engineering, Arizona State University, Tempe, USA), Zachary Gordon, Ting Yang

Synthesis and Characterization of Nanostructured $Li_7La_3Zr_2O_{12}$ Solid Electrolytes using Electrospinning and Nanocellulose Templating

11:10 to 11:30

Roberto M. Torresi (Insituto de Química, São Paulo, Brazil), Tania Benedetti, Vitor L. Martins, Nedher Sanchez-Ramirez

Transport properties in ionic liquids and poly(ionic liquids) and its lithium mixtures

11:30 to 11:50

Helene Rouault (CEA-French Alternative Energies and Atomic Energy Commission, Liten, Grenoble, France), Anass Benayad, Ewelina Bolimowska, Jorge E. Morales-Ugarte, Catherine C. Santini, Jesus Santos-Pena

Impregnation Study of Graphite Electrode by Vinylene Carbonate Doped Ionic Liquid Electrolyte

11:50 to 12:10

Marcelina Pyschik (MEET Battery Research Center, University of Münster, Muenster, Germany), Sascha Nowak, Martin Winter

Decomposition and Reaction of the Additive 1,3-Propane Sultone with Electrolyte Compounds

12:10 to 12:50 Keynote

Doron Aurbach (Chemistry, Bar Ilan University, Ramat, Israel), Michal Afri, Aryeh Frimer, Daniel Hirshberg, Wonjin Kwak, Daniel Sharon, Yang-Kook Sun

Recent Insights related to $Li\text{-}O_2$ Battery Technology

Hydrogen Electrochemical Systems

Aula Magna Cardenal Pironio

Chaired by: Elizabeth Santos and David Zitoun

09:00 to 09:30 Invited

Stanko Brankovic (Cullen College of Engineering, ECE Department, Houston, USA), Hieu Doan, Lars Grabow, Dongjun Wu, Qiuyi Yuan

Finite Size Effects in Pt Monolayer Catalysts

09:30 to 09:50

Loic Assaud (Chemistry, ICMMO, University Paris-Sud, University Paris-Saclay, Orsay, France), Joumada Al Cheikh, Manuel Antuch, Julien Bachmann, Pierre Millet, Alireza Ranjbari

Materials and Nanostructures in Electrochemical Energy Conversion: Functionality Understood at the Atomic Level

09:50 to 10:10

Adriana Serquis (Caracterizacion de Materiales, CNEA - CONICET, Bariloche, Argentina), Mauricio Arce, Alberto Caneiro, Afra Fernandez Zuvich, Diego Lamas, Federico Napolitano, Analía Soldati, Horacio Troiani

Nanostructured Ni/(Ce,Gd)$O_{2-\delta}$ Anodes For Intermediate-Temperature Solid-Oxide Fuel Cells (IT-SOFC)

10:10 to 10:30

Paola Dager (Caracterizacion de Materiales, Centro Atomico Bariloche, S.C. de Bariloche, Argentina), Alberto Caneiro, Liliana Mogni, Sergio Soria, Guillermo Zampieri

Influence of Mo-site doping on the electrochemical properties of $Sr_2MgMo_{0.9}A_{0.1}O_{6-\delta}$ (A = Co and Mn)

10:30 to 10:50

Coffee Break

10:50 to 11:10

Enrique Herrero (Instituto de Electroquimica, Universidad de Alicante, Alicante, Spain), Valentín Briega-Martos, Adolfo Ferre-Vilaplana

Understanding the ORR in Nitrogen-Doped Graphitic Materials

11:10 to 11:30

Javier Recio (Inorganic Chemistry, Pontifical Catholic University of Chile, Santiago de Chile, Chile), Mónica Ortiz, Ricardo Venegas, José H. Zagal, César Zúñiga

Study of formal potential of pyrolyzed catalysts as reactivity index for oxygen reduction reaction in basic media

11:30 to 11:50

Gonzalo Montiel (Procesos Superficiales, INTI, San Martín, Argentina), Mariano Bruno, Horacio Corti, Eduardo Fuentes Quezada, Federico Viva

Optimized mesoporous carbon supports for Pt-Ru catalyst. Synthesis and characterization

11:50 to 12:10

Federico Calle-Vallejo (Leiden Institute of Chemistry, Leiden University, Leiden, Netherlands), Aliaksandr S. Bandarenka, David Loffreda, Marcus D. Pohl, David Reinisch, Philippe Sautet

How Concavities Enhance the Activity of Platinum Nanostructures for the Oxygen Reduction Reaction

12:10 to 12:50 Keynote

Edson A. Ticianelli (Institute of Chemistry of Sao Carlos, University of Sao Paulo, São Carlos, Brazil), João Victor P. Godoy, Ana M. Gómez-Marin, Nickson Perini, Gabriel C. Silva, Victor M.P. Silva

Activity and Stability of Carbide- and Oxide-based Electrocatalysts for the H_2/O_2 Evolution Reactions in Acid and Alkaline Electrolytes

Wednesday 22 March 2017 - Afternoon

Lithium Batteries

Auditorio 1 Valsecchi

Chaired by: Roberto Torresi and Nuria Garcia Araez

14:30 to 15:00 Invited

Brett Lucht (Chemistry, University of Rhode Island, Kingston, USA)

Development of novel electrolyte additives for designed surface modification

15:00 to 15:20

Babak Rezaei Rad (IEK-12, Helmholtz-Institut Münster, Forschungszentrum Juelich GmbH, Muenster, Germany), Serife Kaymaksiz, Martin Winter

Aluminum dissolution preventing additive for LiTFSI based liquid electrolytes in lithium ion battery application

15:20 to 15:40

Bao Kou Xiong (Université de Tours, France)

Measurement of Oxygen and Hydrogen Solubilities in Electrolytes for Lithium-ion Batteries

15:40 to 16:00

Nicolas Jäckel (Energy Materials, INM- Leibniz Institute for New Materials, Saarbrücken, Germany), Doron Aurbach, Mikhael D. Levi, Volker Presser, Netanel Shpigel

In situ monitoring of elastic properties of common binders *via* electrochemical quartz microbalance with dissipation and dilatometry

16:00 to 16:20

Abdilbari Mussa (Chemical Engineering and Technology, KTH Royal Institute of Technology, Stockholm, Sweden), Matilda Klett, Göran Lindbergh, Rakel Wreland Lindström

Fast Top-up Charging of Lithium-ion Batteries - A Comparative Ageing Study

16:20 to 16:40

Coffee Break

16:40 to 17:00

Ken Darcovich (Energy, Mining and Environment Portfolio, National Research Council of Canada, Canada), Yacine Hazaz, Steven Recoskie, Hajo Ribberink

Battery Pack Thermal Management in Vehicle-to-Grid Applications

17:00 to 17:20

Elodie Guyot (CP2S, CEM, Institut Jean Lamour Université de Lorraine CNRS, Metz, France), David Bonina, Clotilde Boulanger, Samuel Kenzari

From End-of-life Lithium Based Batteries to Lithium Value-creation by a Green Electrochemical Innovative Process

17:20 to 17:40

Fabian Benavente (Instituto de Investigaciones Químicas, Universidad Mayor de San Andres, La Paz, Bolivia), Cesario Ajpi, Mario Blanco, Saul Cabrera, Naviana Leiva, Göran Lindbergh, Anders Lundblad, Eduardo Palenque, Max Vargas

Development of Lithium ion Battery Components in Bolivia: Towards Renewable Energy Applications

Hydrogen Electrochemical Systems

Aula Magna Cardenal Pironio

Chaired by: Ana Castro Luna and Wolfgang Schmickler

14:30 to 15:00 Invited

José H. Zagal (Chemistry of Materials, , Santiago, Chile)

An overview of the reactivity indexes of MN_4 and MN_2 molecular catalysts for the reduction of O_2

15:00 to 15:20

Ting He (Energy and Environment Science and Technology, Idaho National Laboratory, Idaho Falls, USA), Dong Ding

Perovskite Proton Conductors for Energy Conversion and Storage at Intermediate Temperatures

15:20 to 15:40

Federico Tasca (Quimica de los Materiales, Universidad de Santiago de Chile, Santiago, Chile), Karinna Neira, Francisco Javier Recio, Jorge Riquelme, Ricardo Venegas, José H. Zagal, César Zúñiga

Comparison of the Catalytic Activity Towards the O_2 Reduction of Fe MN_4 Catalysts Simply Adsorbed or Coordinated to Pyridine Anchored to Carbon Nanotubes

15:40 to 16:00

Earving Arciga Duran (Materiales Compuestos y Recubrimientros, CIDETEQ S.C., Santiago de Querétaro, Mexico), Juan Carlos Ballesteros Pacheco, Gabriel Trejo Córdova

Electrodeposition of Co_3O_4 thin films for their application in the Oxygen Evolution Reaction

16:00 to 16:20

Lior Elbaz (Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel)

Electrocatalysis of Oxygen Reduction with Metallocorroles: Identification of the Parameters Affecting the Catalyst Activity and Stability

16:20 to 16:40

Coffee Break

16:40 to 17:00

Maria Retuerto (Instituto de Catalisis y PetroleoquÃmica, CSIC, Madrid, Spain), Miguel Antonio Peña, Sergio Rojas

Perovskite-oxide electrocatalysts with high OER activity and durability in acid media: $Sr_{1-x}Na_xRuO_3$

17:00 to 17:20

Federico Viva (Department of Condensed Matter Physics, Comisión Nacional de Energía Atómica, San Martín , Argentina), Ana Katherine Diaz Duran, Federico Roncaroli

Metal Organic Frameworks as Catalyst Precursors for Oxygen Reduction in Fuel Cells

17:20 to 17:40

Ricardo Venegas (Inorganic Chemistry, Pontificia Universidad Católica de Chile., Santiago, Chile), Luis Lemus, Karina Muñoz-Becerra, Javier Recio, Alejandro Toro-Labbé, José H. Zagal

Reactivity predictors for oxygen reduction reaction (ORR) on substituted Cu(I) 1,10-phenanthroline-modified electrodes

Poster Presentations

Session 1 on Monday 17:20 to 19:00
Session 2 on Tuesday 17:20 to 19:00

Session 1: Poster Presentations - Lithium Batteries

s1-001

Paulina Marquez (Química de los Materiales, Usach, Santiago, Chile), M.J. Aguirre, Julia Amici, Silvia Bodoardo, Carlotta Francia, Juan Luis Gautier, F. Herrera

Effect of binder on performance of aprotic Li–O_2 cells

s1-002

Graciela Abuin (Procesos Superficiales, INTI-Instituto Nacional de Tecnología Industrial, San Martín, Argentina), Roxana Coppola, Guido de Titto, Liliana Diaz, Patricia Eisemberg

Preparation and Characterization of Nanofibrillated Cellulose Separators for Lithium-Ion Batteries

s1-003

Daniela Alburquenque (Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Chile), Juan Luis Gautier, José Francisco Marco, Loreto Troncoso

Synthesis, Characterization and Cathodic Behavior of Nanostructured Mixed Oxides $LiNi_xCoyMn_2$-x-y$O_{4+\delta}$ (x, y = 1/3, 1/4)

s1-004

Analia Natali Arias (San Salvador de Jujuy, Centro de Investigaciones y Transferencia de Jujuy- CONICET, San Salvador de Jujuy, Argentina), Victoria Flexer, Gabriel A. Planes, Alvaro Y. Tesio

Electrochemical and spectroscopic studies of carbon-based porous electrodes for lithium-sulfur batteries

s1-005

Violetta Arszelewska (Fundamental Aspects of Materials and Energy, Delft University of Technology, Delft, Netherlands)

Graphite Encapsulation of Silicon Particles Using Different Metals as Template For Negative Electrode in Lithium-Ion Batteries

s1-006

Loic Assaud (Chemistry/ICMMO, University Paris-Sud, University Paris-Saclay, Orsay, France), Anshuman Agrawal, Jean-Claude Badot, Olivier Dubrunfaut, Sylvain Franger, Nicolas Gauthier, Bernard Lestriez

Charge Transport Limitations in Hierarchical Composite Electrodes of Lithium-ion Batteries

s1-007

Sergio Brutti (Dipartimento di Scienze, Università della Basilicata, Potenza, Italy)

A carbon-coated mixed olivine $Li(Co_{1/3}Fe_{1/3}Mn_{1/3})PO_4$ material as positive electrode in lithium cells

s1-008

Cecilia Calderón (Instituto de Física Enrique Gaviola, Universidad Nacional de Córdoba, Córdoba, Argentina), Daniel Barraco, Ezequiel Leiva, German Lener, Karim Sapag, Arnaldo Visintin

Carbonaceous Separators Modified to Improve the Cyclability of Lithium Sulfur Batteries

s1-009

Susana Chauque (Instituto de Investigaciones en Fisicoquimica de Cordoba, Universidad Nacional de Cordoba, Cordoba, Argentina), Daniel Barraco, Osvaldo R. Camara, Ezequiel Leiva, Fabiana Oliva

Lithium Titanate Synthesized by Sol-Gel Method: Influence of the Final Calcination Temperature in the Lithium-Ion Storage

s1-010

Susana Chauque (Instituto de Investigaciones en Fisicoquímica de Córdoba, Universidad Nacional de Córdoba, Córdoba, Argentina), Osvaldo R. Camara, Fabiana Oliva, Roberto M. Torresi

Importance of the binder on the electro-activity of lithium titanate as negative materials in LIBs using ionic liquids as electrolyte

s1-011

Melina Cozzarin (YPF Tecnología S.A., CONICET, Berisso, Argentina), Alejandra Calvo, Antonela Canneva, Miguel Sanservino, Jorge Thomas, Arnaldo Visintin

High-voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ for lithium-ion batteries: synthesis improvement using different thermal treatment

s1-012

Giulio Ferraresi (Energy and Environment Research Division (ENE), Paul Scherrer Institut, Villigen, Switzerland), Mario El Kazzi, Petr Novák, Chih-Long Tsai, Sven Uhlenbruck, Claire Villevieille

All-Solid-State Li Battery Based on c-$Li_7La_3Zr_2O_{12}$ Solid Electrolyte and Alloy Anode Materials

s1-013

Eduardo Fuentes Quezada (Physics, Comisión Nacional de Energía Atómica, San Martin, Argentina), Mariano Bruno, Horacio Corti, Matias Factorovich, Gonzalo Montiel, Federico Viva

Synthesis and Characterization of Mesoporous Carbon Electrodes for Lithium-Air Batteries

s1-014

Nuria Garcia-Araez (Chemistry, University of Southampton, Southampton, United Kingdom), James Dibden, John Owen

A Quantitative Tool to Predict the Phase Composition of Lithium-Sulfur Batteries

s1-015

Christopher Heim (Electrochemical Energy Storage, German Aerospace Center, Stuttgart, Germany), K. Andreas Friedrich, Ezequiel Leiva, Manuel Otero, Norbert Wagner

Design-Considerations regarding Silicon/Graphite and Tin/Graphite Composite Electrodes for Lithium-Ion Battery

s1-016

Eduardo Rubén Henquín (INGAR - FAC. de ING. QCA., CONICET - UNL , Santa Fe, Argentina), Pio Antonio Aguirre

Solar microgeneration and accumulation in Lithium ion Batteries. Simplified phenomenological model

s1-017

Ezequiel Leiva (Facultad de Ciencias Químicas, Universidad Nacional De Cordoba, Villa el Zanjón, Argentina), Maximiliano Gavilan, Beatriz López de Mishima, Oscar Oviedo, Eduardo Perassi, Oscar Pinto

Computer Simulations of Lithium Ion Storage in Graphite

s1-018

German Lener (Laboratory of Sustainable Energy, IFEG-Conicet, National University of Cordoba, Cordoba, Argentina), Daniel Barraco, Ezequiel Leiva, Manuel Otero

Energetic and Phonon Dispersion of Lithium Silicates Formed *in Operando* Reduction of SiO_2 with Li in Lithium-ion Battery. A Theoretical and Experimental Study

s1-019

Brett Lucht (Chemistry, University of Rhode Island, Kingston, USA), Jason Dwyer, Jiyeon Kim

Electrochemical research efforts on lithium batteries, catalysis and nanostructures

s1-020

Guillermina Luque (Departamento de Química Teórica y Computacional, Universidad Nacional de Córdoba, Córdoba, Argentina), Daniel Barraco, Andrea Calderón, Ezequiel Leiva, Patricio Vélez

Computational studies of polysulfides interaction with graphene oxide structures

s1-021

Pablo Martinez (MMyN, Instituto Balseiro CONICET CAB CNEA, S.C. Bariloche, Argentina), Enio Lima Jr, Mario Sergio Moreno, Fabricio Ruiz

Synthesis and characterization of $LiFePO_4$ prepared by high temperature thermal decomposition of organometallic precursors

s1-022

Pablo Martinez (MMyN, Instituto Balseiro CONICET CAB CNEA, S.C. Bariloche, Argentina), Gustavo Morales, Mario Sergio Moreno, Fabricio Ruiz, Maximiliano Zensich

FeOOH/graphene oxide composite as anode for lithium ion battery

s1-023

Rodrigo Montoya López (SURF, Vrije Universiteit Brussel, Brussels, Belgium), Johan Deconinck, Annick Hubin, Nils Van den Steen

Simplification of the Porous Electrode Theory for an Efficient 3D Isothermal-Electrochemical Lithium-Ion Battery Model

s1-024

Nataliia Mozhzhukhina (Institute of Physical Chemistry of Materials, Environment and Energy Chemistry, University of Buenos Aires, Buenos Aires, Argentina), Ernesto Julio Calvo, Lucila Mendez de Leo, Alvaro Y. Tesio

$PYR_{14}TFSI$ Ionic Liquid for Li-air Battery

s1-025

Pedro Muñoz (Facultad de Ciencias Exactas Físicas y Naturales, Universidad Nacional de Córdoba, Córdoba, Argentina), Gabriel Correa Perelmuter, Arpit Maheshwari, Massimo Santarelli

Thermal behavior investigation of a $LiFePO_4$ battery cell determined by optimum power management of fuel cell electric vehicles

s1-026

Manuel Otero (Departamento de Química Teórica y Computacional, Universidad Nacional de Río Cuarto, Río Cuarto, Argentina), María B. Suarez, Estefanía Baigorria, M. Belen Ballatore, Edgardo N. Durantini, Miguel Gervaldo, Ezequiel Leiva, María E. Milanesio, Luis Otero, Agustín Sigal, Claudia Solis

Tetrapyrrolic Organic Polymers Cathodes for Lithium Ion Batteries

s1-027

Manuel Otero (Departamento de Química Teórica y Computacional, Universidad Nacional de Córdoba, Río Cuarto, Argentina), Daniel Barraco, Segio Ceppi, Ezequiel Leiva, Guillermina Luque, Carla Robledo, Guillermo Stutz

Inelastic X-ray scattering spectroscopy of Li stage intercalation in graphite

s1-028

Kwangjin Park (Energy Lab, Material Group, Samsung Advanced Institute of Technology, SAIT, Suwon, Korea), Byungjin Choi, Suk-Gi Hong, Jun-Ho Park

Synergistic effect of Al_2O_3 and LiF dual coating process for structurally stable Li-ion battery cathodes

s1-029

Jun Peng (Faculty of Chemistry, Northeast Normal University, Changchun, Jilin, China), Yanhong Ding, Shifa-Ullah Khan

Polyoxometalate-assisted Synthesis of Polydopamine Composite as Anode Material for Binder-free High-performance Lithium Ion Batteries

s1-030

Eduardo Perassi (Dto. Química Teórica y Computacional, Fac. de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina), Daniel Barraco, Ezequiel Leiva

Shedding Light on the Entropy Change Found for the Li-ion Storage in Graphite

s1-031

Konstantin Petrov (Electrocatalysis, IEES-BAS, Sofia, Bulgaria), Borislav Abrashev, Dzhamal Uzun

Bi-functional Air electrodes for a Li-Air accumulator

s1-032

Fernando Pignanelli (Centro NanoMat, Catedra de Fisica, DETEMA, Facultad de Quimica, UdelaR, Montevideo, Uruguay), Veronica Diaz, Ricardo Faccio, Alvaro W. Mombru, Mariano Romero, Erika Teliz, Fernando Zinola

Structural Characterization and Theoretical Modelling of $LiFe_{1-x}Co_xPO_4$ cathodes for Li-ion Batteries

s1-033

Facundo Quiñones (Electrotecnia, Universidad Nacional del Comahue, Neuquen, Argentina), Ruben Milocco, Silvia Real

Modeling, Parameterization, and Identification of Rechargeable Lithium-Ion Batteries

s1-034

Pierre Ranque (Chemical Engineering, Delft University of Technology, Delft, Netherlands), Rémi Dedryvère, Wolter F. Jager, Erik M. Kelder, Frans G.B. Ooms, Ernst J.R. Sudhölter

New Electroactive Polymer Binders for Li-battery Si-anodes

s1-035

Silvia Real (Electrochemistry, INIFTA-UNLP, La Plata, Argentina), Mariela Gisela Ortiz, Arnaldo Visintin

Electrochemical Characterization of Carbon/Sulfur as Lithium-Sulfur Battery Cathodes

s1-036

Silvia Real (Electrochemistry, INIFTA-UNLP, La Plata, Argentina), Mariela Gisela Ortiz, Arnaldo Visintin

Study of the Electrochemical Behavior of Different Carbon Materials as Anodes for Lithium Ion Batteries

s1-037

Valeria Carolina Estefania Romero (CIT CONICET Universidad Nacional de Jujuy, San Salvador de Jujuy, Argentina), Ernesto Julio Calvo, Victoria Flexer

Electrochemical reactor modeling and simulation for electrochemical extraction process of lithium chloride from brine

s1-038

Nedher Sanchez-Ramirez (Chemistry, University of São Paulo, São Paulo, Brazil), Daniel Bélanger, Birhanu Desalegn Assresahegn, Roberto M. Torresi

High-performance Silicon Anodes Using Ionic Liquid as Electrolytes

s1-039

Elizabeth Santos (Theoretical Chemistry, Ulm University, Ulm, Germany), Maria Fernanda Juarez, Leila Mohammadadze, Wolfgang Schmickler

Storage of Ions in Various Forms of Carbon – a Theoretical Investigation

s1-040

Sacha Smrekar (IFEG, Famaf, Cordoba, Argentina), Daniel Barraco, Guillermina Luque, Emiliano Primo, Jorge Thomas

Characterization and comparison between different binders applied to Sn-based anodes for lithium ion batteries

s1-041

Jiyong Soon (Chemical and Biological Engineering, Seoul National Universtiy, Seoul, Korea), Seulki Chae, Seunghae Hwang, Hyejeong Jeong, Jongjung Kim, Tae Jin Lee, Seung M. Oh, Ji Heon Ryu

Grafting of Nitrophenyl Group on Carbon Surface by Diazonium Chemistry to Suppress Irreversible Reactions

s1-042

Cintia Terny (Departamento de Quimica, Universidad Nacional del Sur-INQUISUR- CONICET, Bahia Blanca, Argentina), Marisa A. Frechero

Study of doped-Phosphate Polyanion electrode and bismuth-phosphate glassy electrolyte. Lithium ion solid state batteries

s1-043

Jorge Thomas (INIFTA, CONICET-UNLP, La Plata, Argentina), Lisandro Giovanetti, Felix Requejo, Miguel Sanservino, Arnaldo Visintin

Design and Optimization of *In situ* Cell for Lithium Ion Batteries X-ray Absorption Studies

s1-044

Walter Ramón Torres (INQUIMAE, Universidad de Buenos Aires, Ciudad Autónoma de Buenos Aires, Argentina), Ernesto Julio Calvo, Maria del Pozo Vázquez, Santiago Herrera, Nataliia Mozhzhukhina, Alvaro Y. Tesio

Oxygen Reduction Reaction in DMSO Lithium Containing Electrolyte

s1-045

Libuse Trnkova (Department of Chemistry, Masaryk University, Faculty of Science, Brno, Czech Republic), Klara Castkova, Ondrej Cech, Libuse Trnkova, Petr Vanysek

Nanostructured Sodium Titanate for Lithium and Sodium Ion Insertion

s1-046

Claudia Zech (X-ray Spectrometry, Physikalisch-Technische Bundesanstalt, Berlin, Germany), Burkhard Beckhoff, Markus Boerner, Andreas Bund, Marco Evertz, Olga Graetz, Daniel Groetzsch, Svetlozar Ivanov, Wolfgang Malzer, Matthias Mueller, Sascha Nowak, Marcelina Pyschik, Ivan Raguzin, Manfred Stamm

Traceable chemical analyses of new liquid and solid battery components by X-ray spectrometry in UHV environment

s1-047

Martin E. Zoloff Michoff (Departamento de Química Teórica y Computacional, Fac. de Cs. Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina), Ezequiel Leiva

Underpotential Deposition of Sn on Defective Graphene and its Relevance as Active Material for Li-ion Batteries

s1-048

Henry Andres Cortes Páez (Buenos Aires, Comisión Nacional de Energía Atomica, Buenos Aires, Argentina) Andrea Barral, Veronica Vildosola, Horacio Corti

An ab Initio Calculation of the Effect of Halogen Dopants on Li_2O_2

Session 2: Poster Presentations - Hydrogen fuel cells

s2-001

Graciela Abuin (Procesos Superficiales, INTI-Instituto Nacional de Tecnología Industrial, San Martín, Argentina), Roxana Coppola, Liliana Diaz, Ricardo Escudero, Daniel Herranz, Pilar Ocón

Composite Polyvinyl Alcohol - Polybenzimidazole Membranes for Alkaline Water Electrolysis and Ethanol Fuel Cell

s2-002

Ali Akbari-Fakhrabadi (Mechanical Engineering, University of Chile, Santiago, Chile), José Ignacio Canales Lemus

Structural and mechanical properties of $La_2NiO_{4+\delta}$ synthesized by sonochemical method

s2-003

Gustavo Andreasen (Inst. de Investigaciones Fisicoquimicas Teoricas y Aplicadas, Universidad Nacional de La Plata, La Plata, Argentina), Hernan Peretti, Silvina Ramos, Walter E. Triaca

Development of a Thermally Coupled Hydrogen Storage and Fuel Cell System

s2-004

Mauricio Arce (Caracterización de Materiales, Centro Atómico Bariloche - CNEA, San Carlos de Bariloche, Argentina), Juan Basbus, Alberto Caneiro, Liliana Mogni, Qing Su, Horacio Troiani, Haiyan Wang

Study of $BaCe_{0.8}Pr_{0.2}O_{3-\delta}/BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ Bilayer Proton Conductor Electrolytes

s2-005

Earving Arciga Duran (Materiales Compuestos y Recubrimientos, CIDETEQ S.C., Santiago de Querétaro, Mexico), Juan Carlos Ballesteros Pacheco, Gabriel Trejo Córdova

Efficient Co_3O_4 electrocatalyst for the Oxygen Evolution Reaction (OER): Role of Co-Glycine complexes

s2-006

Mariela Brites Helu (PRELINE-FIQ, Universidad Nacional del Litoral, Santa Fe, Argentina)

Metal-glass interactions during the hydrogen oxidation reaction sensed by scanning electrochemical microscopy on Pt microelectrodes

s2-007

Ana Castro Luna (Universidad Tecnologica Nacional, La Plata, Argentina), Mariano Asteazaran, German Cespedes

Evaluation and Characterization of Bipolar Plates Printed by 3D Technology for a Fuel Cell

s2-008

Ana Castro Luna (Universidad Tecnologica Nacional, La Plata, Argentina), Mariano Asteazaran, German Cespedes

Passive Direct Methanol Fuel Cell Catalysts

s2-009

Angela Contreras (Inst. de Investigaciones Fisicoquimicas Teoricas y Aplicadas, Universidad Nacional de La Plata, La Plata, Argentina), Diego Barsellini, Rene Calzada, Barbara Lombardi, Silvina Ramos, Alberto Scian, Walter E. Triaca

Development of Oxide Modified Nanostructured Carbon Materials for using as Electrocatalyst Supports in Hydrogen/Oxygen Fuel Cell Electrodes

s2-010

Paola Dager (Departamento Caracterizacion de Materiales, Centro Atomico Bariloche, S.C. de Bariloche, Argentina), Alberto Caneiro, Liliana Mogni, Alejandra Montenegro-Hernandez, Horacio Troiani

Impregnation strategy to improve Solid Oxide Cells (SOC) cathode materials: Gadolinium doped Ceria on La-Sr cobalt-ferrite

s2-011

Liliana Diaz (Centro de Procesos Superficiales, INTI - Centros de Investigación, San Martin, Argentina), Graciela Abuin, Roxana Coppola, Ricardo Escudero, Daniel Herranz, Pilar Ocón

Evaluation of Polybenzimidazole-c-PVBC/OH as Anion Exchange Membrane for Alkaline Conversion Systems

s2-012

Veronica Diaz (Instituto de Ingeniería Química, UdelaR, Montevideo, Uruguay), Ricardo Faccio, Estefania German, Erika Teliz, Fernando Zinola

Density Functional Theory Study of Structural and Electronic Properties of Hydrogenated $ZrCr_2$ and $ZrMo_2$ Phases

s2-013

Joaquin Diez (Laboratorio de Electroquímica Fundamental, UdelaR, Montevideo, Uruguay), Veronica Diaz, Ricardo Faccio, Fernando Pignanelli, Fabricio Ruiz, Erika Teliz, Fernando Zinola

Titanium effect in electrochemical hydrogen storage in $Zr_{1-x}Ti_xCr_{0.7}NiMo_{0.3}$ alloy

s2-014

Joaquin Diez (Fac. de Ciencias, UdelaR, Montevideo, Uruguay), Veronica Diaz, Joaquin Diez, Ricardo Faccio, Maximiliano Melnichuk, Erika Teliz, Santiago Vazquez, Fernando Zinola

Electrochemical and gaseous hydrogen storage in $LaNi_{5-x-y-z}Al_xCo_yMo_z$

s2-015

Tomás Falagüerra (CITCA, CONICET-UNCA, FACEN-UNCA, San Fernando del valle de Catamarca, Argentina), Gabriel Correa Perelmuter, Héctor Fasoli

Sensitivity analysis of water management in cathode side PEMFC varying structural and operational parameters by computational simulation

s2-016

Omobosede Fashedemi (Chemistry, Augustine University, Ilara-Epe, Lagos, South Africa)

Oxygen reduction reaction at MWCNT-modified nanoscale Iron (II) tetrasulfophthalocyanine: Remarkable performance over Platinum and tolerance to methanol in alkaline medium

s2-017

José Fernández (PRELINE - Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santa Fe, Argentina), Mariela Brites Helu

Recent advances in the application of scanning electrochemical microscopy for studying the hydrogen electrode reaction mechanism

s2-018

Sirlane Gomes da Silva (IPEN-Instituto de Pesquisas Energéticas e Nucleares, CCCH, USP- Universidade de São Paulo, São Paulo, Brazil), Monica H.M.T. Assumpcao, Almir O. Neto, Júlio César M. Silva

Electrochemical and Fuel Cell Evaluation of PtIr/C Electrocatalysts

s2-019

Melisa Julieta Gómez (INFIQC - CONICET, FCQ, Universidad Nacional de Córdoba, Córdoba Capital, Argentina), Esteban Andrés Franceschini, Gabriela Inés Lacconi

Synthesis and characterization of hybrid nickel/mesoporous TiO_2 catalysts for hydrogen evolution reaction

s2-020

Melisa Julieta Gómez (INFIQC - CONICET, FCQ - Universidad Nacional de Córdoba, Córdoba Capital, Argentina), Esteban Andrés Franceschini, Gabriela Inés Lacconi, Luis Alberto Perez

Synthesis and properties of a hybrid nickel/nitrogenated-GO for hydrogen evolution reaction

s2-021

Eduardo Rubén Henquín (INGAR, Fac. de Ing. QCA., CONICET - UNL , Santa Fe, Argentina)

Reactors with N^{+1} bipolar electrode. Simplified mathematical model

s2-022

Moon-Sung Kang (Department of Environmental Engineering, Sangmyung University, Cheonan, Korea), Do-Hyeong Kim, Jin-Soo Park

Development of pore-filled ion-exchange membranes for efficient electrochemical energy storage and conversions

s2-023

Mariela Lescano (Instituto de Energia y Desarrollo Sustentable, Comision Nacional de Energia Atomica, San Carlos de Bariloche, Argentina), Aurelien Gasnier, Daniel Pasquevich, Maria Laura Pedano, Maria Belen Prados, Mauricio Pablo Sica

Development and characterization of graphene-based electrodes for microbial electrolysis cells

s2-024

Andrew Lin (Dept. Chem. & Materials Eng., Chang Gung University, Taoyuan, Taiwan), Chih-Ping Chang, Yingjeng James Li

Performance of catalysts coated Nafion as membrane electrode assembly using at hydrogen oxygen polymer electrolyte fuel cell

s2-025

Maria de los Angeles Montero (PRELINE, Universidad Nacional del Litoral, Santa Fe, Argentina), Abel Cesar Chialvo, Maria Rosa Gennero de Chialvo, Carlos Alberto Marozzi

Hydrogen Electrode Reaction: a General Description of the Equilibrium Polarization Resistance

s2-026

Maria de los Angeles Montero (PRELINE, Universidad Nacional del Litoral, Santa Fe, Argentina), Abel Cesar Chialvo, Maria Rosa Gennero de Chialvo

Study of the Hydrogen Electrode Reaction on Iridium Electrodes Covered by a Hydrous Oxide Film

s2-027

Federico Nores Pondal (Renewable Energy Area, Y-TEC, Berisso, Argentina), Nicolás Fortunato, Pablo Daniel Giunta

Numerical Simulation of a PEM Fuel Cell: Electrochemical Double Layer Capacity

s2-028

Jin-Soo Park (Department of Green Chemical Engineering, Sangmyung University, Cheonan, Korea), Moon-Sung Kang, Mun-Sik Shin, Chan-Ho Song

Anion Exchangeable Polybenzimidazole Ionomers for Solid Alkaline Fuel Cells

s2-029

Ignacio Schmidhalter (Chemical Engineering, INGAR, Instituto Desarrollo y Diseno (CONICET-UTN), Santa Fe, Argentina), Pio Antonio Aguirre

Definition of Operational Regimes for PEMFC through Dimensionless Numbers

s2-030

Ignacio Schmidhalter (Chemical Engineering, INGAR, Instituto Desarrollo y Diseno (CONICET-UTN), Santa Fe, Argentina), Pio Antonio Aguirre

Phenomenological Modelling of GDL in LT_PEMFC

s2-031

Erica Schulte (PRELINE, FIQ-UNL, Santa Fe, Argentina), Gustavo Daniel Belletti, Paola Quaino

Oxygen reduction reaction on different materials: theoretical studies

s2-032

Erica Schulte (Facultad de Ingenieria Quimica, Universidad Nacional del Litoral, Santa Fe, Argentina), Paola Quaino, Elizabeth Santos

Development of theoretical models of bimetallic nanostructures for hydrogen electrocatalysis

s2-033

Adriana Serquis (Caracterización de Materiales, CNEA - CONICET, Bariloche, Argentina), Laura Baqué

Degradation of Oxygen Reduction Reaction Kinetics at $La_{0.6}S_{r0.4}Co_{0.2}Fe_{0.8}O3$-d Cathodes Aged at Different Temperatures

s2-034

Illia Shypunov (Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark)

Oxygen Reduction Non-Precious Metal Catalyst Synthesis *via* High Temperature and Pressure Pyrolysis

s2-035

Erika Teliz (Fac. de Ciencias, UdelaR, Montevideo, Uruguay), Veronica Diaz, Joaquin Diez, Ricardo Faccio, Fernando Zinola

$ZrCr_{1-x}NiMo_x$: Microsegregated Phases Study

s2-036

Jorge Torrero (Instituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain), Miguel Antonio Peña, Sergio Rojas

IRRAS study of ethanol electrooxidation in alkaline media

s2-037

Federico Viva (Departamento de Materia Condensada, Comisión Nacional de Energía Atomica, San Martin, Argentina), Bradley Easton, Gonzalo Montiel, Christopher Odetola, Liliana Trevani

Synthesis and characterizxation of $Pt/TiO_2/C$. DEMS study for the methanol oxidation reaction

s2-038

Hsiharng Yang (Graduate Institute of Precision Engineering, National Chung Hsing University, Taichung, Taiwan), Wan-Ting Fang, Yi-Ta Wang

The Circulatory System Study for Glucose Oxidase Enzymatic Fuel Cells

s2-039

Jong-Sung Yu (Energy Systems Engineering, DGIST, Daegu, Korea), Tong-Hyun Kang, Hyean-Yeol Park

N-doped Carbon Electrocatalysts Treated by Fe: Surface Properties and Electrocatalytic Activity

s2-040

Fernando Zinola (Universidad de la Republica, Montevideo, Uruguay)

Preferentially oriented platinum nanoparticles modified by electrochemical hydrogen evolution

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Zúñiga, César, *(Wed s2)11:10*, *(Wed s2)15:20*

Platinum-Niobium Materials for H_2/O_2 Fuel Cells

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Traditional Polymer Electrolyte Fuel Cells (PEFC) are fed with hydrogen in the anode and oxygen in the cathode. This type of fuel cell is especially attractive because of the high efficiency at low temperature. Our work was divided into two parts. In the first part, the performance of a fuel cell with Nafion 115 as the polymer electrolyte was evaluated. The anodes were composed of Pt/C and/or Pt_3Nb/C, which were fed with H_2 containning 100 ppm of CO, while the cathode (Pt/C) was fed with O_2. For the Pt_3Nb/C (20 % metal/C) synthesis, the metals were impregnated on carbon, followed by heat treatment in a reducing atmosphere.[1] X-Ray Diffraction results showed evidence of a Pt_3Nb-Nb_xO_y structure. The Transmission Electron Microscopy data indicated that even after heat-treating the material at 1000°C, it is possible to obtain a good nanoparticle size distribution. X-Ray Absorption results for Pt_3Nb/C showed that electronic levels in the Pt 5d band are filled, mainly because of the better size distribution of the nanoparticles in this material, and because of the Nb presence in the structure. The later has a significant influence on the electrochemical responses observed for the CO electrooxidation reaction. The data obtained from the fuel cell coupled to a mass spectrometer definitely showed that Pt_3Nb/C is much more CO-tolerant than Pt/C. Figure 1 displays the corresponding polarization curves with the fuel cell at 70 °C and 90 °C with Pt_3Nb/C in the anode.

In the second part, two materials composed of Pt supported on Nb_2O_5/C were synthesized by reducing ions with formic acid.[2] The performance and stability of these materials as cathodes of a fuel cell were evaluated. In this case, the fuel cell with Nafion 115 as the polymer electrolyte was fed with H_2/O_2. The anodes were composed of Pt/C, and cathodes of Pt/C and/or Pt-Nb_2O_5-C. The X-Ray Absorption data reveled a decrease in the electronic density of the Pt 5d band, due to the presence of oxide, leading to a small increase of the absorption observed for the synthesized materials when compared to the commercial Pt/C. Transmission Electron Microscopy images showed nanoparticles agglomeration and corrosion of the carbon support in the cathode, decreasing the performance of the fuel cell over time.

In terms of the stability, the better performance of the materials supported on Nb_2O_5/C in relation to the oxygen reduction reaction, over long periods of the fuel cell operation, is due to a smaller loss of the active areas of these materials. Figure 2 shows corresponding polarization curves with the fuel cell at 85 °C and Pt-Nb_2O_5-C in the cathode before and after durability test.[3]

ACKNOWLEDGEMENTS

Authors thank FAPESP, CNPq and CAPES, Brazil, for the financial support.

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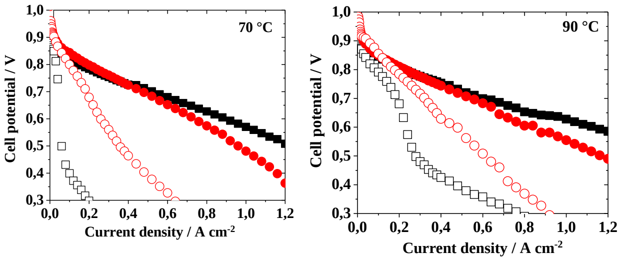

Figure 1. current density vs. cell potential curves at 70 °C and 90 °C. (■ Pt/C H_2, □ Pt/C H_2/CO, ● Pt_3Nb/C H_2, ○ Pt_3Nb/C H_2/CO). Currents normalized to electrode geometric area (4.62 cm^2). Anode and cathode with 0.4 mg Pt cm^{-2}.

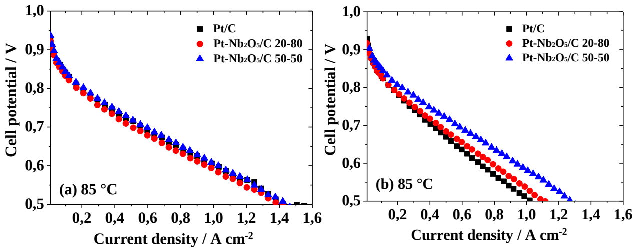

Figure 2. current density vs. cell potential curves at 85 °C (a) cathode before durability test, (b) cathode after durability test. Currents normalized to electrode geometric area (4.62 cm^2). Anode e cathode with 0.4 mg Pt cm^{-2}.

Enabling Sustainable Non Noble Metal Electrocatalysts for Oxygen Reduction Reaction

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Enabling concerted charge transfer at the inner Helmholtz plane of an electrochemical interface is a prelude to higher selectivity and activity for electrochemical processes hitherto not possible with conventional highly dispersed metal and metal alloy electrocatalysts. This presentation will focus on recent shifts away from conventional supported metal and metal oxide based catalysts to organo-metallic and composite metal oxides based structures, which promise orders of magnitude higher turnover frequency and selectivity. Taking oxygen reduction as a theme, this presentation will provide clear comparison of electrrochemcal response between supported metal catalysts (alloys and oxides), especially on noble metals in acidic pH and catalyst based on transition metal nitrogen coordinated systems and multi-phase composite oxides. Electrochemical data will be discussed in the context of spectroscopy, especially *in situ* synchrotron x-ray absorption spectroscopy (XAS). Here the conventional bulk averaged XANES and EXAFS spectroscopy will be further embellished by unique use of subtractive method referred to as '$\Delta\ \mu$ technique'. This specially designed subtractive technique using the near edge part of the spectra (x-ray absorption near edge spectra, XANES) has been previously validated and has unprecedented ability to elucidate nature of adsorbed species on transition metals. The unique element specificity and the in situ and operando capability of the XAS spectra in close conjunction with electrochemical data will be used to provide insight on steady state electrocatalytic pathways as a function of various operating conditions and associated applications. Unique structural features of the active sites determined in situ using the extended part of the spectra (i.e., extended x-ray absorption spectra, EXAFS) will be invoked to explain activity difference based on pH and water activity.

Advanced Next Generation Lithium Ion batteries and Beyond

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In other to enable 40 miles PHEVs and long electric drive range EVs, there is a need of developing advanced battery systems that offer at least 250 to 300 wh/kg energy density. The most significant technical barrier to developing commercially viable Plug-in Hybrid Electric Vehicles (PHEV) is the energy storage system. The challenge is to develop batteries that are able to perform the requirements imposed by a PHEV system and yet meet market expectations in terms of cost and life. In this case, the PHEV battery will experience both deep discharge, like an electric vehicle, and shallow cycling necessary to maintain the battery for power assist in charge sustaining HEV mode. Conventional lithium-ion batteries based on metal oxides and graphite have made significant progress in recent years for HEV applications, however, durability with the PHEV duty cycle and the ultimate cost and safety of the technology remain key challenges. To achieve a very high all electric drive range, a new battery system with advanced high capacity cathode materials and stabilized high capacity anode is needed. . In this talk, we will disclose several strategies to increase significantly the energy density of lithium battery trough the development of high energy cathode material coupled with high voltage electrolyte. We also describe some new approach of improving the cycle life of Si/carbon composite anode by impregnating nano-silicon particles within graphene sheets or making a new composite system. We also disclose a new pre-lithiation technology that is very effective in eliminating the large irreversible loss in Si based. Anode. Finally, we will disclose new battery system based on SeS7 and lithium superoxide based battery that offer the potential of high energy for automotive applications.

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Recent Insights related to Li-O_2 Battery technology

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Li-O_2 batteries can be considered as a promising future technology that might be integrated in electric vehicles as high energy density power sources. Due to the infinite supply of oxygen from air, Li-O_2 cells have a notably high theoretical energy density which can compete with that of internal combustion engines. However, it is now clear that the instability of the components in any relevant Li-oxygen cell toward the extreme conditions existing during operation, leads to many difficulties in bringing these systems to a practical level. All Li-oxygen cells tested so far in conditions approaching those existing in real batteries, demonstrated early too early failure situations.[1]

An obvious problem may be the need to apply too high over potential in order to oxidize the Li-peroxide formed by the ORR, back to oxygen, what challenges the stability of both the cathode and the electrolyte solution. The use of redox-mediators in Li-oxygen cells may reduce the over-potential and, therefore, improve the efficiency and cyclability of Li-O_2 cells. Their use in Li-oxygen cells is mandatory. We have previously shown that LiI can indeed behave in such a manner; however, it also promotes the formation of side products during cell operation.[2] We have therefore carried out a comprehensive study of lithium halides as electrolytes or additives for use in Li-O_2 cells. Based on the electrochemical behavior and the identity of the final cells' products under various conditions, we can provide a clear information regarding the detailed operation mechanisms for each specific case. We have concluded that low concentration of LiBr in diglyme based solutions can improve the performance of Li-oxygen cells with only minor possible side effects. LiBr is superior in this respect than LiI.[3]

Another challenge facing researchers in this field is the use of lithium metal as an anode in Li-O_2 cells. We have examined the replacement of metallic lithium anode in Li-O_2 cells with lithiated hard carbon (HC) electrodes.[4] HC anodes have many benefits that are suitable for oxygen reduction in the presence of solvated lithium cations. Although there are still many challenges to tackle, this study seems to offer a more practical direction for Li-oxygen battery technology and sets up a platform for further systematic optimization.

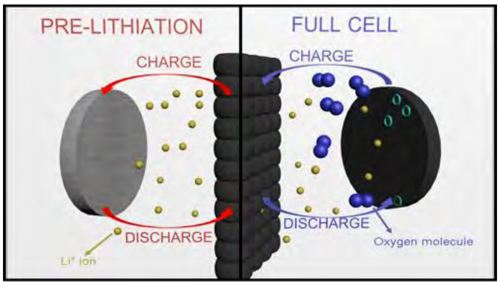

Figure 1: Illustration of the (Li-ion)-O_2 cell concept

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Synthesis and characterizxation of Pt/TiO_2/C. DEMS study for the methanol oxidation reaction

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For long, TiO_2 has shown to be an interest material due to its property of photocatalyze the oxidation of a wide range of molecules. A clear example was the use of TiO_2 in the water splitting process for the generation of H_2 and O_2 [1]. Recently, the combination of TiO_2 with carbon nanotubes (CNTs) was envisioned as a way to obtain a synergetic effect on the properties of both materials for photo-electro-catalysis [2]. The addition of Pt as a co-catalyst to TiO_2 is proposed as a way to suppress recombination of electron-hole pairs and enhance photocatalytic activity in both the UV and visible regions [3]. The combination of Pt-TiO_2/C could enhance the H_2 oxidation reaction in fuel cells as well as the water oxidation reaction in in the water splitting anodes. Recently, a combination of Pt/TiO_2 supported on carbon has shown enhancement in the methanol oxidation reaction (MOR) for its use in direct methanol fuel cell (DMFC) [4].

Pt supported on TiO_2 over carbon black was prepared by a non-oxidative approach. Pristine Vulcan carbon was used to prepare TiO_2/C substrate as catalyst support. TiO_2 nanoparticles were deposited on glucose modified carbon using a sol-gel solvothermal method [5]. Pt nanoparticles were deposited on this substrate using a chemical impregnation method to produce Pt/TiO_2/G-PV catalyst.

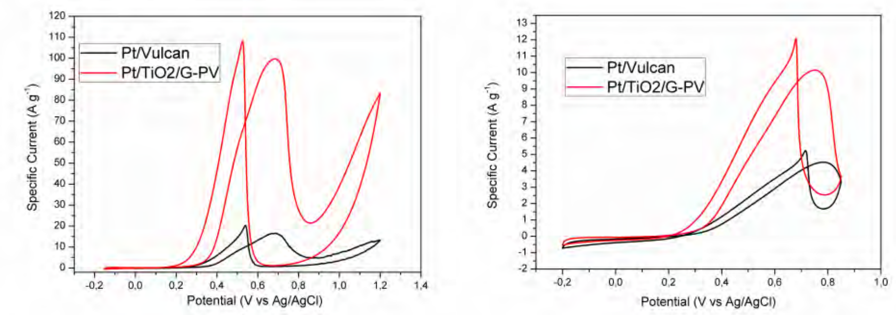

Figure 1: Cyclic voltammogram in 0.5M CH_3OH + 1.0 M H_2SO_4 at 5 mV sec^{-1}. A) Three electrode cell configuration. B) DEMS cell configuration.

The electrochemical performance toward the MOR was evaluated by cyclic voltammetry (CV), chronopotentiometry and differential electrochemical mass spectrometry (DEMS) (Figure 1). DEMS, has been used extensively to follow and quantify the reactions products of methanol oxidation [6]. The obtained average current efficiency toward the CO_2 formation was 72% for Pt/TiO_2/G-PV and 46% for Pt/Vulcan. Illumination of the catalyst during CV measurements showed further enhancement of the catalytic activity and therefore steps are being taken to evaluate the catalyst in a DEMS cell under light.

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Synthesis of Biomass Derived Carbon Supported Metal Oxides for Biofuel Cells and High Performance Supercapacitor Applications

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Supercapacitors (SCs) are the electrochemical energy storage devices which stored the energy as either double layer capacitance or pseudo capacitance. Most of the electrochemical double layer supercapacitors (EDLC) are demonstrated by the carbon or carbonaceous supported manganese and ruthenium oxide catalysts. In this aspect, we have described both EDLC and pseudo capacitor by the biomass derived carbon and metal oxide nanocomposites. For instance, the dopamine-derived carbon was used to prepare the flower-like nickel─cobalt oxide and carbon composite for the high performance supercapacitor applications. The ruthenium nanoparticles decorated curl-like porous carbons were demonstrated for the EDLC supercapacitors. The functional porous carbon–ZnO nanocomposites were derived from the sugarcane bagasse and activated by zinc chloride. This activated functional porous carbon- zinc oxide composite was exhibited the good supercapacitance behavior. To improve the specific capacitance, the functional porous carbon was synthesized from guava leaves and composite with nickel oxide nanocomposites, which act as a binder-free electrode for supercapacitors. The honeycomb-like porous carbon─cobalt oxide nanocomposite was synthesized by chemical activation of Pongam seed shells and successfully applied to the high-performance supercapacitor applications. The aforesaid activated carbons are prepared from the various biomass derivatives and activated by the chemical process cum thermal annealing. The metal oxide composites are simultaneously prepared by *in-situ* activation process with biomass derivatives. The as-prepared biomass derived carbon and metal oxide composites are exhibited good specific capacitance, superior cycling stability and acceptable capacitance retention. These electrochemical energy storage properties of aforementioned materials were revealed better performances when compared with previously reported works.

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Electrocatalysis of Oxygen Reduction with Metallocorroles: Identification of the Parameters Affecting the Catalyst Activity and Stability

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The most active non-precious metal catalysts (NPMCs) for oxygen reduction (ORR) to date are the pyrolyzed catalysts, inspired from heme-like complexes. These are usually composed of iron and/or cobalt coordinated by nitrogens, claimed to resemble the structure of porphyrins and phthalocynines, on the surface of a carbon support. Unfortunately, the exact structure of the catalytic sites remains a mystery and the solution for this conundrum seems be almost impossible. The advantages of using such catalysts are: (1) their high activity and (2) low price, which is derived from the cost of their precursors. The disadvantages are: (1) low durability compared to precious metal catalysts, and (2) their unknown structure, which limits their further improvement in order to obtain both the activity and durability benchmarks needed to become good alternatives for precious metals.

One of the most promising options to resolve these issues is to find non-pyrolyzed molecular non-precious metal catalysts for ORR that could be tuned to match the necessary requirements. Recently, Metallocorroles, a relatively new family of molecular catalysts was reported to have very good potential as non-precious metal catalysts for ORR, comparable to platinum as shown in figure 1. The effect of the different metal centers, the substituents on the meso- and beta-positions, interactions with the support and with neighboring catalytic centers may have a significant impact on the way we design and utilize non-precious metal catalysts as a whole, and metallocorroles in particular. In this talk, all of these parameters will be discussed. In particular, we will show how different substituents on the meso-positions affect the ORR activity and mechanism, and answer the question: Is it important to have electron-withdrawing functionalities near the catalytic center? and if so, what is their effect? We will show how covalently attached centers work synergistically towards ORR electrocatalysis, and try to shed some light on the importance of the surface functionalities in carbonaceous supports.

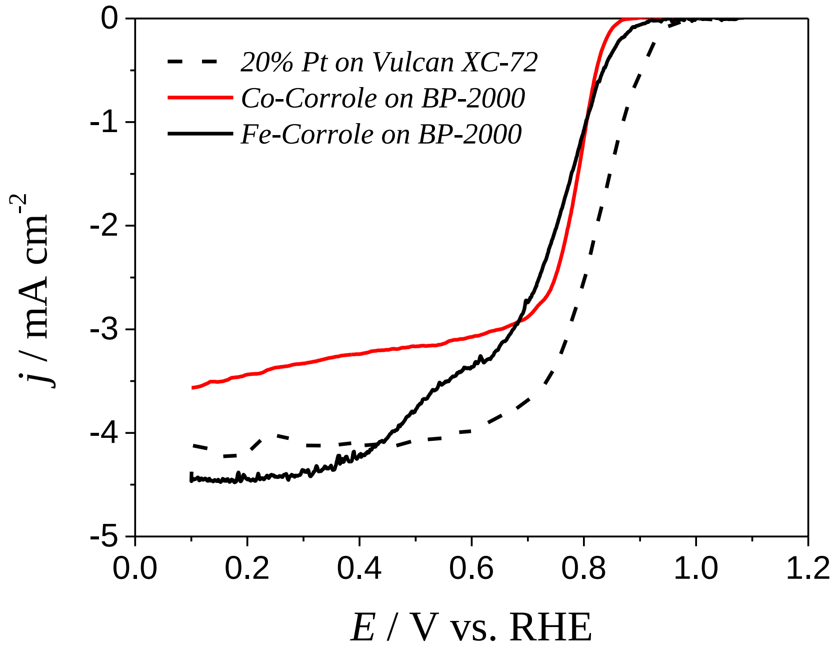

Figure 1: Rotating disk electrode measurements at 900 rpm showing electrocatalysis of oxygen reduction with Fe- and Co-corrole in 0.1 M KOH with comparison to commercial Pt/C catalyst.

Photoelectrode for solar hydrogen production with copper bacteria

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Fuel cell technology is considered essential part of the hydrogen economy. While fuel cells are usually perceived in the context of fuel-to-electricity conversion, the questions arises "*Where does the fuel come from?*" [1] Certainly the fuel can also come from fuel cells, i.e. photo electrochemical cells [2]. We present a photo-electrochemical cell for hydrogen fuel production which is based on photoelectrodes with bio-organic components [3,4]. We have recently developed water oxidation photoanodes with light harvesting protein phycocyanin from cyanobacteria[5]. In particular will we use a Cu2O photocathode, which is functionalized at the surface with cupredoxins such as azurin or plastocyanin, which are known for their charge transfer properties in living organisms. In there, the central copper atom plays a vital role for charge transport. Moreover, we consider the electrode surface functionalization with heavy metal resistant bacteria such as the streptoymces [6], or more specifically, of the copper resistant *Amycolatopsis tucumanensis* bacteria [7], which is an extremophile particularly found in the Tucuman region in Argentina and currently under consideration for use in biotechnology [8]. We demonstrate how electrochemical impedance spectroscopy and synchrotron based resonant valence band spectroscopy is utilized for the functional and quantitative assessment of complex photoelectrode assemblies with bio-electric interfaces under realistic electro-photophysiological operation conditions.

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Corrosion Testing of Metallic Bipolar plates

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Polymer electrolyte membrane fuel cells (PEMFCs) are holding the most promise for low carbon transport applications. However, the commercialization has been hindered by the relatively high cost of materials and manufacturing. As for the price – below \$25/kW according to the 2020 US Department of Energy (DoE)[1] – PEMFCs should afford a significant durability to ensure massive market uptake. A low cost approach would provide cheap materials without sacrificing the lifetime of the stack.

Traditionally, bipolar plates are made out of impregnated graphite and account for 45-60 % of the stack cost, 80 % of the weight, and almost all the volume of the PEM fuel cell stack. They are in charge of supplying the fuel to the MEA as well as exhausting water produced at the cathode side[2]. Graphite is resilient at fuel cell operating conditions, non-porous, conductive with a low contact resistance. However, the cost of machining is above the 2020 DoE targets. The technical plan states that the corrosion rate must be below 1 $\mu A.cm^{-2}$ and that an interfacial contact resistance must be below 10 $m\Omega.cm^{2}$ at a compaction pressure of 140 $N.cm^{-2}$. These condition has to be attained with a cost below 3 $\$kW^{-1}$.

The flexiplanar approach uses a metallic substrate mounted on a printed circuit board (PCB) in order to produce a low cost cell. Copper is a strong candidate for this purpose: it is robust, has a high conductivity and a low contact resistance as well as a possibility of scalable hydroforming or stamping[3], which is an important feature in order to produce a flow field plate. Unfortunately, metallic substrates corrode under realistic operating conditions i. e. 1.2 V and up to 120°C. More recent attention has focused on coatings[4,5], yet a new approach has been developed in order to avoid the use of a metallic substrate.

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Improving the Performance of Energy Storage Materials by Chemical Modification

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The improvement of the performance of current energy storage systems such as batteries and electrochemical capacitors is attracting a lot of attention worldwide. Other important aspects of these devices are their long-term stability and safety, especially because of their crucial contribution to the electrification of transport. Consequently, an approach to improve stability and safety rely on the surface modification of active electrode materials. To this end, a large variety of approaches have been investigated such as the deposition of inorganic and organic coatings in order to mitigate the abovementioned issues.

Our laboratory has developed in the past two decades an expertise in surface modification by the diazonium chemistry (1). Relevant to energy storage, we have developed procedures to modify the surface of carbons for electrochemical capacitor applications (2-4) and cathode battery materials of lithium-ion batteries (4-7). The chemical modification of active materials (eg. porous carbon, anode and cathode materials) involves the spontaneous reduction of the suitable diazonium ion, which leads to the formation of the corresponding radical species that react with the surface to form a covalent bond with active sites on the electrode. Another approach that has been investigated is based on the formation of a film at the surface of an electrode material by oxidative processes (7).

The talk will present the basic principles of the modification methods that were developed in our laboratory and some important recent findings.

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Electropolymerization of Metallo-Corroles: Towards a Synergistic Electrocatalyst for Oxygen Reduction Reaction

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Finding a substitute to the platinum-based catalysts, based on precious group metal-free (PGM-Free) catalysts is one of the biggest challenges in fuel cell research. One PGM-Free catalyst that shows great promise is metallo-corroles. In the past year we investigated several variations of metallo-corroles. The best catalytic performance was obtained for the Co^{III} corrole which was comparable with that of Pt. However, the limiting current measured with rotating ring-disk electrode in acidic environment is relatively low compared to platinum, hinting on a reaction mechanism leaning towards the 2-electron reduction to peroxide which is considered the less desirable path (as opposed to the 4-electron reduction to water) Inspired from biological system which usually contain several metal/catalytic centers working in tandem (e.g., Hemoglobin and Laccase), in order to increase the catalytic activity and durability, cobalt(III)-tris(4-aminophenyl) corrole (Fig. 1) was electropolymerized at various polymerization conditions directly on a glassy carbon electrodes and tested for oxygen reduction reaction (ORR) in both acidic and alkaline conditions. The electropolymerized corroles formed three-dimensional structures which may also serve as a sort of all-in-one electrodes for ORR. They were tested in acidic solution, the number of electrons involved in the reaction was improved and the half-wave potential, $E_{1/2,}$ shifted by 120 mV more positive while in alkaline solution the reaction number of electrons was further improved leaning towards a four-electron mechanism and the $E_{1/2}$ shifted even more significantly by 200 mV more positive. In agreement with previous studies with amino substituted porphyrins, the accepted polymerization mechanism is similar to that of polyaniline. Indeed, FTIR-ATR analysis shows transition of the primary amine substitutes to secondary and tertiary amine, indicate on formation of dihydrophenazine and phenazine unit linkage respectively. In this talk we will discuss this unique electrocatalytic polymer, the synergistic effects between the catalytic centers and present its full characterization.

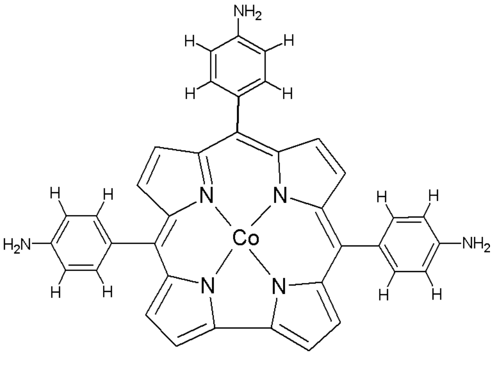

Figure 1: structure of cobalt(III)-tris(4-aminophenyl) corrole

Phenyl sulfonated graphene/sulfur electrodes with excellent electrochemistry performance for lithium sulfur batteries

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Elemental sulfur has been extensively investigated as a promising candidate for cathode material for next generation lithium secondary batteries. Despite for its high theoretical specific capacity of 1675 mA h g^{-1} and high theoretical specific energy of 2600 Wh kg^{-1}, several troublesome issues associated with the sulfur cathode severely limits the practical use of sulfur in an electrode, such as, the highly electrical insulating nature of sulfur, the redox shuttle of dissolved polysulfide ions and the volume expansion of sulfur cathode materials. In our work, phenyl sulfonated functional groups ($PhSO_3$–) were anchored on the graphene surface to increase the conductivity and water solubility of the carbon matrix. With surface modifications, graphene was not only very soluble in water but also existed as individual carbon sheets exhibiting excellent electrical conductivity, Furthermore, although there has been some progress on cathode materials for lithium sulfur cells in recent years, the results for the volumetric energy density are unsatisfactory. It is well known that the volumetric energy density of sulfur is low because the density of sulfur is low compared to those of transition metal oxides and phosphates. When more additives (conductive carbon+binder) are added for the operation of sulfur cathodes, the volumetric energy density is further decreased. In our study, large amounts of conductive carbon additives and binder were not required when carbon-coated aluminum foil was used as the substrate during the preparation of electrodes because of the excellent electrical conductivity of $PhSO_3$-RG and the adhesive force of the composite material itself. We obtained phenyl sulfonated graphene sheets/sulfur ($PhSO_3$-RG/S) via an in situ redox reaction in aqueous solution and applied it as the cathode material of lithium sulfur battery, the additive-free $PhSO_3$-RG/S electrodes had a high initial discharge capacity, a good cycling life at a current density of 0.2 C, and an excellent rate capability.

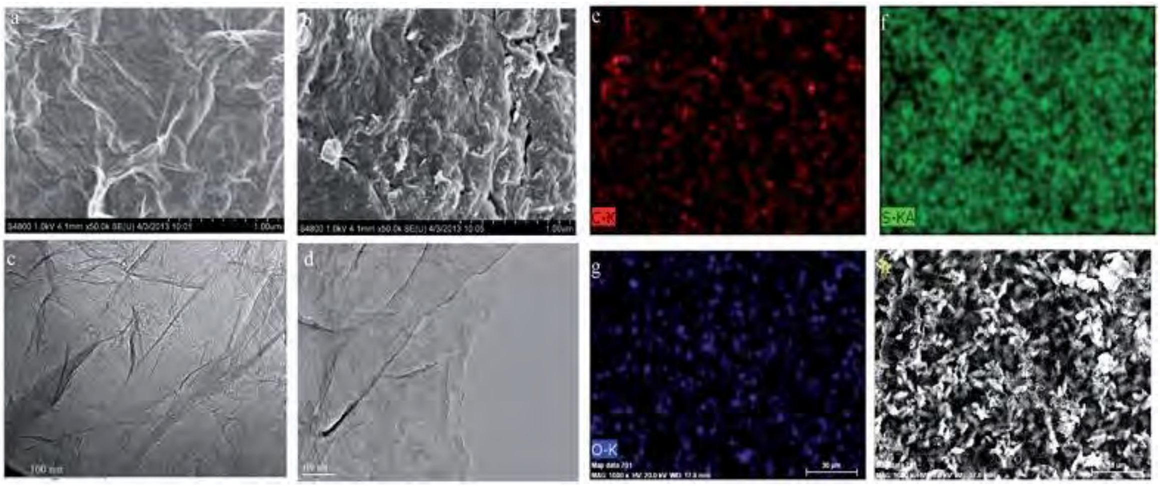

Fig. 1 A FESEM image (a) and a TEM image (c) of $PhSO_3$-RG; a FESEM image (b) and a TEM image (d) of $PhSO_3$-RG/S; a FESEM image at low magnification of $PhSO_3$-RG/S (h) and the corresponding element mapping of C/S/O (e/f/g).

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Transport properties in ionic liquids and poly(ionic liquids) and its lithium mixtures

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This work presents the physicochemical characterization of ionic liquids (ILs) and poly(ionic liquids) (PILs) with different cations, and their mixtures with Li^+. We discuss properties as electrochemical window, density, viscosity and ionic conductivity. We have measured the diffusion coefficient by two different techniques, PGSE-NMR and Li electrodeposition with microelectrodes. In addition, we have calculated the Li^+ transport number by the PGSE-NMR technique and by an electrochemical approach. We use Raman spectroscopy and molecular dynamics simulations to evaluate the short-range structure of the liquids. The results found in this work suggest that these Li^+ mixtures present outstanding have promising potential as electrolytes for lithium batteries.

Lithium-ion batteries are one of the most popular types of batteries, especially for its high charge density and being rechargeable. These batteries are used extensively in portable devices such as cell phones, laptops, digital cameras. Mixtures of aprotic organic solvents and $LiPF_6$ are used in these batteries. However, the flammability of organic solvents and low thermal stability of LiPF6 makes it prohibitive to build lithium-ion batteries using such systems for large devices. ILs have been widely studied due to the unique properties that they display, such as low vapor pressure, non-flammability, thermal stability.

The polarity and hidrophilicity or lipophilicity can be varied through a suitable choice of the anion. The phosphonium ionic liquids, are thermally stable and they are interesting for use in electrochemical systems. With the strongly electron-withdrawing phosphonium groups, the anion is expected to possess several desirable properties, such as resistance to oxidation and weak cation coordination. In the present study, two ionic liquids, triethylpenthylphosphonium bis(trifluoromethanesulfonyl)imide ([P2225][Tf2N]) and (2-methoxyethyl)trimethyl phosphonium bis(trifluoromethanesulfonyl)imide ([P222(2O1)][Tf+N]) were studied. Related to PILS, we have studied the poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide. The results found in this work suggest that these Li^+ mixtures present outstading transport properties. In the case of PILs, they can be used as solid electrolytes or as binders. All liquids are stable till over 400°C and it is observed that adding the lithium salt, there is an increase in the viscosity and density, but surprisingly a slight increase in the ionic conductivity is observed. This result is unusual compared with other ILs derives from other anions and it shows that it is a promising result considering the application as electrolyte for lithium ion batteries.

Current distribution in large-surface area PEM electrolysis cells

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Hydrogen production by water electrolysis is considered as a key process for large scale storage of renewable energy sources. Polymer Electrolyte Membrane (PEM) water electrolysis technology is promising in terms of performances, but cost and durability still need improvement[1]. Internal cell components (such as membranes and catalysts) have been extensively described and characterized. However, little information is available in the literature regarding current distribution at the local scale in electrolysis cells, similarly to what have been carried out on PEMFC[2]. Current distribution is a topic of major interest in view of process optimization and cost~~s~~ reduction. Heterogeneous distributions can be highlighted and then addressed, leading to better cell design and improvement on MEAs design and conception (e.g. optimal material use). As a result, better global performances can be obtained and stack lifetime can be significantly extended. In this communication, we report for the first time on an experimental set-up used for current and temperature distribution measurements over a 250cm² single PEM water electrolysis cell. We also provide results related to mechanical compression and first data from ageing study.

A Current Scan Shunt measurement card (from S++ Co.) has been designed and developed for measurements in a PEM water electrolysis single cell. Segmented graphite plates have been added on each side of the sensor plate to simulate downstream and upstream cells and avoid current line recombination in the plane of the current collecting plate (a situation that would lead to current maldistribution compared with normal operation in a stack). In-house MEAs were manufactured using Nafion 117, commercial IrO_2 (2mg/cm² loading at anode, Surepure Co.), commercial Pt/C 46% (1mgPt/cm² loading at cathode, Tanaka Co.). MEAs were assembled using the decal-transfer method.

Compression pressure distributions over the active surface area of the cell have been measured under different operating conditions, using a pressure sensitive film (Fuji Prescale LLW), digitalized and compared with experimental current distributions measured with the S++ card. Strong correlations were observed between pressure fields and local current distributions (Fig. 1). In order to homogenize current distribution over the entire cell area, it was found that the peripheral ring of the cell requires more compression. This was confirmed by measuring current distribution over single current collectors: current circulation is privileged near current collecting pads and at the center of the cell. Thus, we reached the conclusion that homogeneous pressure distribution does not necessary lead to homogeneous current distribution. Furthermore, a three-steps ageing protocol (24h current cycling 0.1-0.4A/cm² - 300h 0.4A/cm² stationary – 100h current cycling) has been applied to a fresh MEA (Fig. 2). It was found that during cycling tests, the current distribution changes with time (current tends to flow gradually towards the center/upper part of the cell), while stationary operating conditions do not significantly affect current distribution. Current evolution and ageing phenomena can be explained by considering that either catalyst degradation (leading to lower local current) or membrane thinning (leading to higher local currents) prevails depending on the area. Additional results obtained by SEM analysis and MEA samples characterization will be reported to support the discussion, as well as MEA design improvement routes.

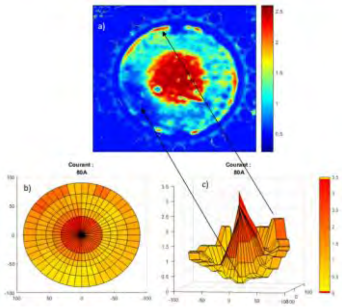

Figure 1: Link between clamping pressure distribution and current distribution

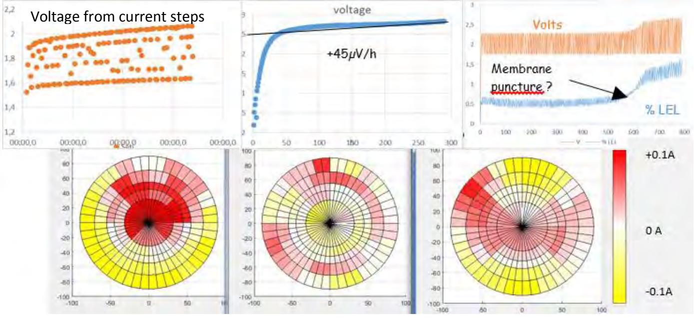

Figure 2: Voltage (top) and current mapping (bottom) evolutions between EoT and BoT for each ageing phase.

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Direct membrane deposition– a new way in membrane electrode assembly manufacturing for fuel cells

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The membrane is one of the very central polymer electrolyte membrane fuel cell components. At the same time it must conduct protons and inhibit transport of electrons and cross-over of reactant gases. Additionally, degradation effects have to be small to ensure a long lifetime. While traditionally consisting of pure Nafion, up to date membranes contain nanofiber reinforcements and radical scavenger packages to decrease degradation effects. Thus, seminal membranes are multi-layer, multi-component structures.

In the state of the art, membrane electrode assemblies (MEA) are manufactured as catalyst coated membranes (CCMs). To form a CCM, electrodes are deposited either by the decal method, or by another deposition method.

In this talk we present a novel approach for MEA manufacturing (Figure 1). In the so called 'direct membrane deposition' (DMD) approach, liquid ionomer is deposited on the catalyst layers of two gas diffusion electrodes which are successively dried and pressed together to form an MEA. Interestingly, this approach enabled power densities more than two times higher than traditional CCM based approaches which are commercially available [1]. Also this approach allows for a simple fabrication of thin multi-layer membranes and improves the water management [2]. DMD applied to low Pt loading electrodes revealed very high power densities per gram Pt of up to 88 kW/g Pt [3]. An analysis of the underlying reasons for the improved performance values revealed a small influence of membrane resistance but mainly an influence in mass transport and charge transfer phenomena [4,5].

In this talk we highlight our latest developments in the field of DMD based manufacturing and give an insight on degradation and durability aspects.

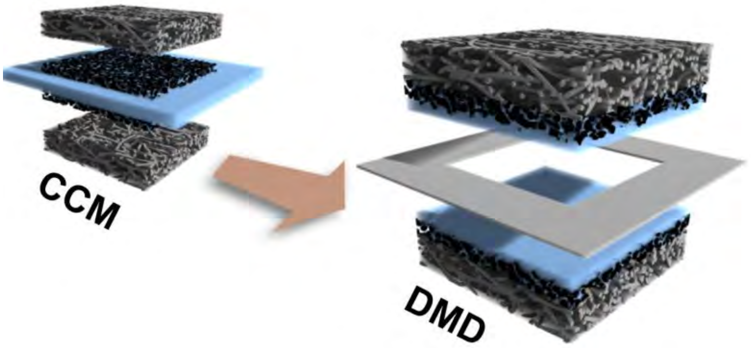

Figure 1 The traditional catalyst coated membrane (CCM) manufacturing approach for membrane electrode assemblies and the novel direct membrane deposition (DMD) approach. For the DMD approach, a thin layer of membrane material is deposited on both sides of gas diffusion electrodes.

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Pt Thin Film Deposition on Nanofibrous Supports: PEMFC Electrodes with Enhanced Performance and Stability

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To overcome the degradation of component materials over time that is still hindering the widespread adoption of Proton Exchange Membrane Fuel Cells (PEMFC), novel materials and original methods of elaboration are needed.

Our approach uses electrospinning of nanofibres or nanotubes and their multiscale assembly to produce innovative energy materials with specific architectures and improved properties [1]. The nanometre size and the high aspect ratio of the 1 D obtained materials and their highly porous structure are expected to bring associated advanced properties, in particular with regard to directional, mechanical and mass transport properties, with beneficial effects on the performance and lifetime of the resulting membrane-electrode assemblies. Due to its inherent adaptability and applicability, electrospinning can be applied to all stages of the preparation of PEMFC materials, from electrolyte membranes to electrodes [1].

Here we will discuss the development and characterization of electrocatalyst supports including carbon, metal (Ni), metal carbide (NbC, WC) and oxide (Nb-TiO_2, Nb-SnO_2, Sb-SnO_2) nanofibres and nanotubes with extended durability and high electrical conductivity [2, 3].

In parallel, we are developing Pt deposition techniques - including Ni and Cu galvanostatic displacement [4], high overpotential pulsed Pt electrodeposition and electrochemical atomic layer deposition - leading to extended metal surfaces on the electrospun materials. This 2D morphology enables higher platinum exploitation and increased stability compared to nanoparticulate electrocatalysts [5], leading to ultra-low loaded electrodes with high activity and durability.

This association of deposition techniques opens up a broad range of opportunities for tuning materials composition and architecture.

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Using redox mediators for $Li-O_2$ and Li-S batteries and Li recycling

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Lithium-oxygen and lithium-sulfur batteries have the potential to revolutionize the energy storage market, since they can in principle store >5 times more energy than the current lithium-ion battery technologies. However, the performance of $Li-O_2$ and Li-S batteries is currently limited by several fundamental issues.

We have recently shown that redox mediators can solve the two more important issues associated to $Li-O_2$ batteries, i.e. electrode passivation and degradation reactions.[1] Degradation reactions are initiated by superoxide radical species that are formed as intermediates in the pathway of the reduction of oxygen:

$O_2 + e^- + Li^+ \rightarrow LiO_2$

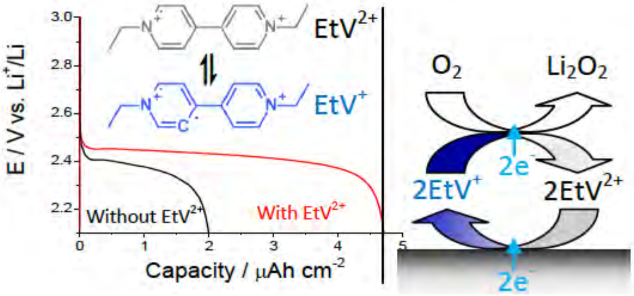
$LiO_2 + e^- + Li^+ \rightarrow Li_2O_2$

On the example of ethyl viologen, EtV^{2+}, we demonstrated that redox mediators can be used to decrease the lifetime of superoxide species by promoting the fast reduction of superoxide to peroxide:

$EtV^{2+} + e^- \rightarrow EtV^+$

$LiO_2 + EtV^+ + Li^+ \rightarrow Li_2O_2 + EtV^{2+}$

where EtV^{2+} acts as homogeneous catalyst and it is not consumed in the reaction. Furthermore, EtV^{2+} also acts as an electron shuttle, preventing electrode passivation by displacing the location of the reduction of oxygen from the electrode surface to the solution. Indeed, a major increase in capacity is obtained upon addition of EtV^{2+} to a $Li-O_2$ cell.

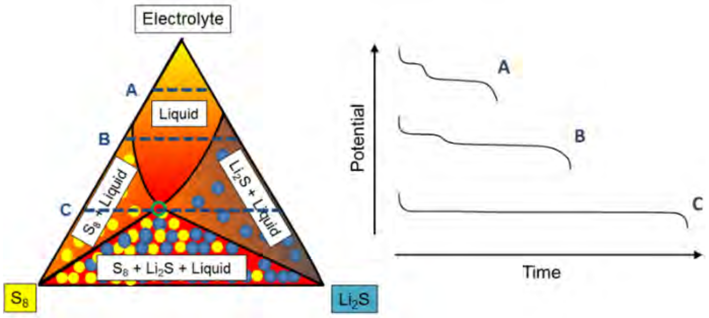


In Li-S batteries, a variety of polysulfides, Li_2S_n, are formed in the pathway of the reduction of S to Li_2S:

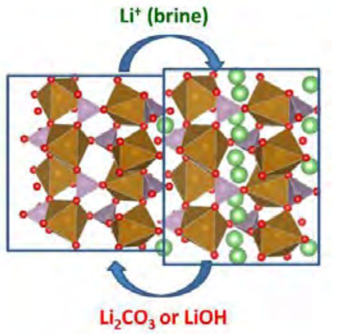
$n\ S + 2e^- + 2Li^+ \rightarrow Li_2S_n$

$Li_2S_n + (2n-2)\ e^- + (2n-2)\ Li^+ \rightarrow n\ Li_2S$

We hypothesize that polysulfides can act as redox mediators and shuttles in Li-S batteries, and their action can be optimized via a selection of suitable electrolytes. We have recently developed a new method that allows predicting the equilibrium concentration of polysulfides in Li-S cells, as well as the theoretical electrochemical response of the cell as a function of the amount of electrolyte.[2] This new approach, based on the construction of an experimental phase diagram, will be used for the rational screening of electrolytes for Li-S batteries.



Redox mediators are also a promising tool for Li recycling. We have shown that the reaction of battery materials (e.g. $LiFePO_4$) with redox agents is a fast, selective and efficient new method to extract lithium from natural brines and for recycling spent batteries.[3]



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Enhancement in the electrochemical performance of zirconium/phosphate bi-functional coatings on $LiNi_{0.8}Co_{0.15}Mn_{0.05}O_2$ by the removal of Li residuals

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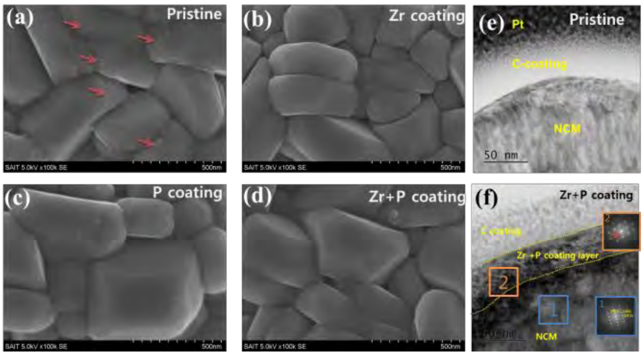
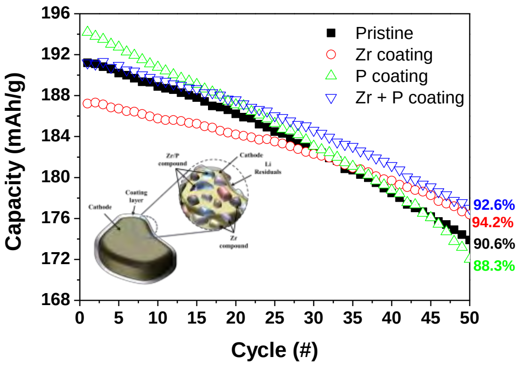
The effect of bi-functional coatings consisting of zirconium (Zr) and phosphate (P) on the electrochemical performance of Ni-rich cathode material has been investigated. $Li_{1.0}Ni_{0.8}Co_{0.15}Mn_{0.05}O_2$ (NCM) was used. The coating quality has been investigated by TEM, SEM, XRD, and XPS analyses and the electrochemical performance has been systematically characterized by electrochemical measurements using 2032 coin cells. The covered particles on the surface in Figure (a) could be Li residuals composed of LiOH and Li_2CO_3.The presence of various types of Zr and P compounds such as oxides (ZrO_2 and Li_2ZrO_3) and phosphates ($Zr_2P_2O_9$, ZrP_2O_7 and $LiZr_2(PO_4)_3$) in the coating was confirmed by experiments as well as density functional theory (DFT) calculations. A uniform coating layer was achieved after coating the cathode surface with Zr/P, as confirmed from the TEM images shown in Figure (e)-(f). The results of EDS analysis indicate not only that the Ni-rich active material was successfully coated by two coating materials, but also that the two materials were mixed homogeneously on the surface without separation. The results of the study show that NCM samples coated with Zr alone show a drop in the initial capacity and inefficient removal of Li residuals, but exhibit improved cycle retention. That might be due to low electronic conductivity of ZrO_2 in coating layer. On the other hand, poor cycle retention is observed in samples coated only with P, owing to decrease in Li^+ mobility due to the presence of P_2O_5 in the coating layer. When the NCM samples were coated with the Zr/P hybrid material, the cycle retention and amount of removed Li residuals (LiOH, Li_2CO_3) were enhanced by the synergistic effect from Zr and P. The NCM sample coated with a Zr/P layer with a Zr/P ratio of 1:1 exhibited an increase in the initial capacity (209.3 $mAh \cdot g^{-1}$) compared to the pristine sample (207.4 $mAh \cdot g^{-1}$) at 0.1C, owing to the formation of the coating layer. That might be due to improved ionic diffusion resulting from the $LiZr_2(PO_4)_3$ formed at the surface and from the reduction of Li residuals, similar to the effect from P coating. The capacity retention of the Zr/P coated sample (92.6% at the 50th cycle) was also improved compared to that of the pristine NCM sample (90.6% at the 50th cycle). Moreover, the amount of Li residuals in the Zr/P coated NCM sample was greatly reduced from 3693 ppm (pristine NCM) to 2525 ppm (Zr/P = 5:5).





Synergistic effect of Al2O3 and LiF dual coating process for structurally stable Li-ion battery cathodes

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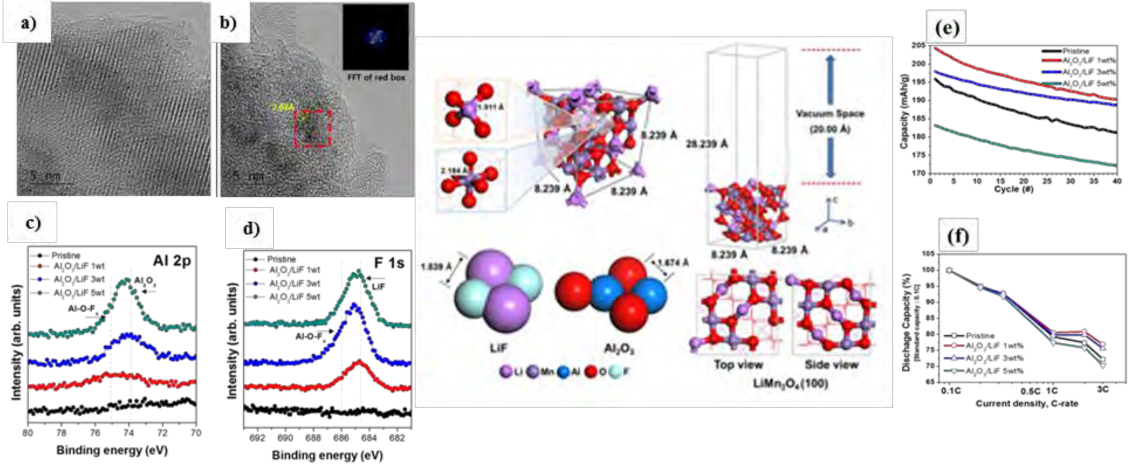
The simultaneous encapsulation of Al_2O_3 and LiF (Al_2O_3/LiF) on over-lithiated layered oxide (OLO) was investigated. TEM images show the pristine (Figure a) and 5 wt.% coated OLO materials (Figure b), which exhibit a well-ordered layered phase, even after the dual coating process. The ordering pattern of the pristine OLO structure is uniform with a clear surface, whereas the coated sample shows a rough surface due to the coating material. Interestingly, we observed crystal structure changes of OLO from a layered structure to a cubic-like structure after the co-precipitating procedure, as shown in the red box of Figure 1b. Furthermore, we found that the dual coating process leads to the formation of $LiMn_2O_4$ over OLO, as measured by the lattice parameter of 2.08 Å of the $LiMn_2O_4$ (400) phase, because the lattice parameters of the Li_2MnO_3 (440) and (006) are 2.15 and 1.57 Å, respectively (Figure b). The phase transformation was also confirmed by powder conductivity data, since the electrical conductivity of the Li_2MnO_3 powder was lower than that of $LiMn_2O_4$. The electrical conductivities of the pristine, 1, 3, and 5 wt.% Al_2O_3 and LiF-coated OLOs were 2.07×10^{-9}, 1.46×10^{-8}, 1.24×10^{-6}, and 4.1×10^{-6} $S{\bullet}cm^{-1}$, respectively. For the 5 wt.% dual coated sample in synchrotron high-resolution powder diffraction (HRPD) and Rietveld analysis, the additional peaks detected located at 2θ values of 18° and 43° correlate to the LiF phase. The weight percent of LiF was approximately 3.6%, less than the expected 5 wt.%, but was noticeable on the surface as calculated by Rietveld analysis. The XPS spectra of the Al 2p core levels allow the accurate characterization of two such oxidation states of Al_2O_3 at 73.9 eV, with a strong peak intensity, and Al-O-F_x near 75.2 eV, with small shoulder peak intensity. For better understanding the coating reaction, we carried out density functional theory (DFT) calculations to investigate the structural arrangement and binding affinity between Al_2O_3/LiF coating and $LiMn_2O_4$(100). The optimized structure of the LiMn2O4 spinel unit cell provided a cubic lattice parameter of 8.239 Å (Figure), which is in good agreement with the 8.247 Å experimentally measured length from Joint Committee on Powder Diffraction Standards (JCPDS), No. 35-782 for $LiMn_2O_4$. The $LiMn_2O_4$ spinel structure is a cubic (isometric) close-packed (face-centered cubic, fcc) crystal phase with Mn2+ and Li+ occupying octahedral and tetrahedral sites in the lattice. We optimized the geometries for the binding of Al2O3 or LiF to $LiMn_2O_4$(100), which shows that favorable binding takes place with strong binding energy (Ea > -1.53 eV) in accordance with the modest interactive bond lengths between Al_2O_3 or LiF and the surface (Figure). The presence of such a favorable electronic attraction between Al_2O_3 or LiF and $LiMn_2O_4$ (100) is responsible for coating formation on the OLO surface. At a cutoff voltage of 2.5 V, the cells delivered reversible capacities of near 251.32, 255.67, 248.11, and 236.6 mAh $\bullet g^{-1}$ for pristine, 1, 3, and 5 wt.% Al_2O_3/LiF-coated OLO samples, respectively, which is the best battery performance of 1 wt% Al_2O_3/LiF-coated OLO. The capacity retention for the pristine, 1, 3, and 5 wt.% Al_2O_3 and LiF coated samples were 92.4, 93.3, 95.6, and 94.4% at the 40th cycle, respectively.



Battery Pack Thermal Management in Vehicle-to-Grid Applications

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In recent years, electric vehicles (EVs) have successfully been gaining a market foothold in many countries around the world. The total number of plug-in vehicles on the road is forecast to grow steadily to over 10 million vehicles before 2024. Concurrently, the growing amount of electricity from renewable sources will require an ever increasing effort to balance supply and demand on the grid, as well as costly grid upgrades. EVs could provide a cost effective alternative to grid stabilization done with conventional spinning reserves by feeding the power stored in their batteries back into the grid through Vehicle-to-Grid (V2G) applications.

Of course, any supplemental use of an EV beyond driving will inflict additional wear on the battery pack. Some preliminary data on additional battery degradation due to V2G is available from [1], as well as on the specific application of vehicle-to-home [2], where a number of modeling and simulation procedures were coordinated to enable investigation of the impact of V2G on EV battery life. Experimentally measured discharge curves of LiNMC cells established the basis of the previous work. Using Doyle's classical battery model [3], coupled with experimentally determined electrochemical parameters, a series of discharge curves at currents higher than could be measured in the lab, but which occur in automotive applications, were simulated. The full range of discharge current data fed an empirical equivalent resistance battery ageing model which incorporated capacity loss mechanisms and could track the service life of a battery pack. The ageing model was then used to study the battery life impact of various usage scenarios defined by driving cycle and various V2G power provision events in comparison to base cases of regular driving and charging. Aggressive driving and fast charging were found to have the greatest impact on EV battery life.

More recently, a coupled electrochemical-thermal model [4] has enabled the determination of time-temperature profiles of various battery operations for packs comprised of prismatic cells. The thermal states of the suite of activities considered in [1] could now be simulated in much more detail, encompassing 50 km drive cycle trips, V2G discharges, and recharging at industry standard rates of 1.3 kW through 50 kW, all as a function of the evolving extent of cell degradation. Boundary conditions reflecting both forced-air and liquid cooling systems were simulated. These temperature profiles were then overlaid on V2G scenarios as considered in [1] to note the effect of how realistically varying thermal states affect the battery pack lifetime estimates compared to the initial simulations done isothermally, as well as showing performance differences between air and liquid cooled battery systems. Finally, recommendations were given for necessary pack cooling in V2G applications.

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Modeling Water Management:
Alkaline-Exchange-Membrane Fuel Cells

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Mathematical modeling is ideally suited for exploring the inherent tradeoffs in water management of polymer-electrolyte fuel cells (PEFCs). In this talk, we will explore such tradeoffs in PEFCs, with a focus on alkaline exchange membrane fuel cells (AEMFCs). Their major advantage is the possibility of using non-noble catalysts due to more facile oxygen-reduction reaction (ORR) kinetics in alkaline than in acidic media. However, water management is a more serious concern in AEMFCs because OH^- conductivity is more highly dependent on water content and the ORR consumes water. Compared to PEMFCs, the lower performance of AEMFCs is mostly caused by extremely nonuniform distribution of water in the ionomer phase between the anode and cathode as well as the increased overpotential for the hydrogen oxidation reaction. In this presentation, we will discuss the performance-limiting mechanisms specific to different operating conditions (e.g. varying inlet relative humidity (RH)) based on a cell-level mathematical model. For example, low AEMFC performance at high current is not simply due to mass transport issues with vapor/membrane water, but a consequence of poor water distribution leading to sluggish OH^- conduction and ORR kinetics. A sensitivity analysis of design and component parameters will be discussed to identify the most significant factors controlling performance. In addition, the impact of CO2 and resultant bicarbonate formation in the membrane will also be explored.

Acknowledgements

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Porous Polybenzimidazole Membranes for High Temperature Proton Exchange Membrane Fuel Cells

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High-temperature proton exchange membrane fuel cells (HT-PEMFCs, working at 150-200 °C) nowadays become attractive for the application of tri-generation (heat+cooling+electricity) in Korea due to their operating temperature. In addition, in order to solve some of the problems of low temperature PEMFCs based on Nafion® (CO tolerance, kinetics, water management, etc.) the development is being accelerated. HT-PEMFCs operated at no external humidification and high temperature have been proven to provide several benefits compared to low temperature operation, such as increased kinetics of the oxygen reduction reaction, greater tolerance of the platinum catalyst to CO and better heat management as the cooling and hydration system can be simplified. The main difficulty in commercialization for HT-PEMFCs is, however, to develop a proton-exchange membrane with high proton conductivity, high chemical stability, and high mechanical strength at high temperatures and low humidification. Development of thermally stable polymer electrolyte membranes with higher proton conductivity as well as mechanical stability is a key challenge in commercializing PEM fuel cells operating above 100 °C. Polybenzimidazole (PBI) membranes exhibit good electrochemical and physicochemical characteristics at temperatures up to 200 °C. The proton conductivity of phosphoric acid (PA) doped PBI membranes highly depends on the acid doping level (ADL) of the membranes, defined as the mole number of PA per molar repeating unit of the polymer. Many methods have been explored to increase the ADL to improve the conductivity of PA-doped PBI membrane. Mecerreyes et al. reported a method to fabricate porous PBI membrane using soft template such as dibutyl phthalate, dimethyl phthalate, diphenyl phthalate and triphenyl phosphate as porogen. However, high doping levels often cause excess swelling or even complete loss of the mechanical strength of the membranes due to the strong plasticizing effect of the dopant. In this study, dead-end porous PBI membranes (means that the one side of membranes is porous and the other side of ones is dense) were prepared in order to increase the mechanical strength than porous PBI membrane as well as proton conductivity for high proton conductivity. The ADL of the PA doped dead-end porous PBI membranes has been increased up to 23.8 (9.5 for dense *m*-PBI) by keeping tensile strength above 12 MPa. The dead-end porous PBI membranes were investigated in terms of ionic conductivity, ADL, SEM, mechanical strength, etc. Finally, the membrane-electrode assemblies (MEAs) introducing the dead-end porous PBI membranes were fabricated and evaluated in terms of I-V polarization curve.

ACKNOWLEDGEMENT

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P-doped Carbon Nanosheets from Carbon Dots for Advanced Sodium-Ion Batteries

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Lithium-ion batteries (LIBs) have been widely utilized as power source for various electrical devices, including consumer electronics, electric tools and electric vehicles. The market demand of LIBs is growing rapidly, leading to the large consumption of lithium resource. Since the lithium resource reserve is quite low on the earth, which will hamper the the development of LIBs. Recently, sodium-ion batteries (SIBs) has attracted more and more attentions due to the abundant sodium reource reserve and the similar physicochemical properties to lithium.

The earth-abundant, cost-effective, eco-friendly, thermally stable and electrically conductive carbon-based materials have been reagarded as promising candidate for SIBs anode. In this work, carbon dots (CDs, Figure 1a) are directly prepared from acetaldehyde solution and NaOH in large scale within short time. The obtained CDs can be transformed into amorphous P-doped carbon nanosheets (Figure 1b) with large area through calcining the mixture of CDs and NaH_2PO_4. P-doped carbon nanosheets show the thickness of 2.1 nm, interlayer distance of 0.42 nm, specific surface area of 549.8 m^2 g^{-1} and P content of 1.39 at%. The sodium storage performances of P-doped carbon material are evaluated by cyclic voltammetry and galvanostatic charge-discharge methods. The P-doped carbon nanosheets exhibit excellent electrochemical performances due to the synergistic effect of ultrathin sheets with large area, expanded graphite layer and P-doping. When cycled at 100 mA g^{-1}, the it exhibited a high reversible capacity of 328 mAh g^{-1}, even at a high current density of 20 A g^{-1}, a considerable capacity of 108 mAh g^{-1} can still be maintained. Besides, this material also showed excellent cycle stability, at a current density of 5 A g^{-1}, the reversible capacity can still reach 149 mAh g^{-1} after 5000 cycles (Figure 1c), no obvious capacity decay is observed.

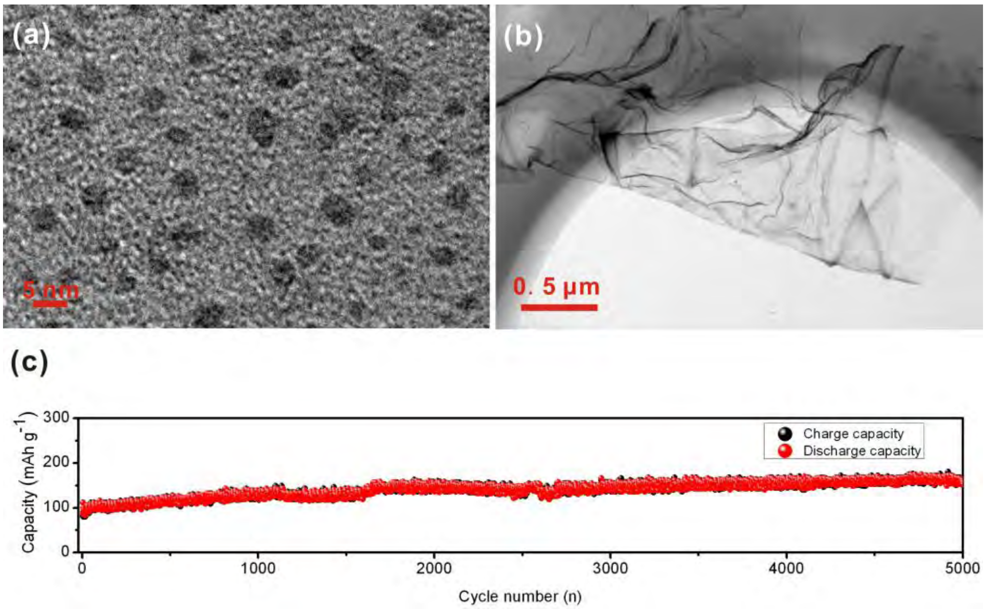

Figure 1 TEM images of carbon dots (a) and P-doped carbon nanosheets (b); cycling performances of P-doped carbon nanosheets (c)

Provide of excellent expanse Reduced Graphene Oxide Modified with Carboxymethyl Cellulose for Highly Sensitive Detection of ultra trace Zn (II) in Water

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Abstract: In this article, reduced graphene oxide (RGO)/ carboxy methyl cellulose (CMC) composites (RGO/CMC) were synthesized by a hydrothermal method through in-situ reduction and modification of graphene oxide (GO) in the presence of CMC. An electrochemical sensor for the determination of Zn (II) by differential pulse anodic stripping voltammetry (DPASV) was constructed by an electrode modified with RGO/CMC. The fabricated electrochemical sensor shows a linear range of 0.01–1.4μmol L^{-1}, a detection limit of 3.25 nmol L^{-1} (S/N = 4) and a sensitivity of 132.85 μA.μmol L^{-1}. Cm^{-2}, indicating the sensor has an excellent detection performance for Zn (II) ions in aqueous solutions.

Porphyrins and Cobaloximes:
Molecular Photocatalytic Systems for Hydrogen Evolution

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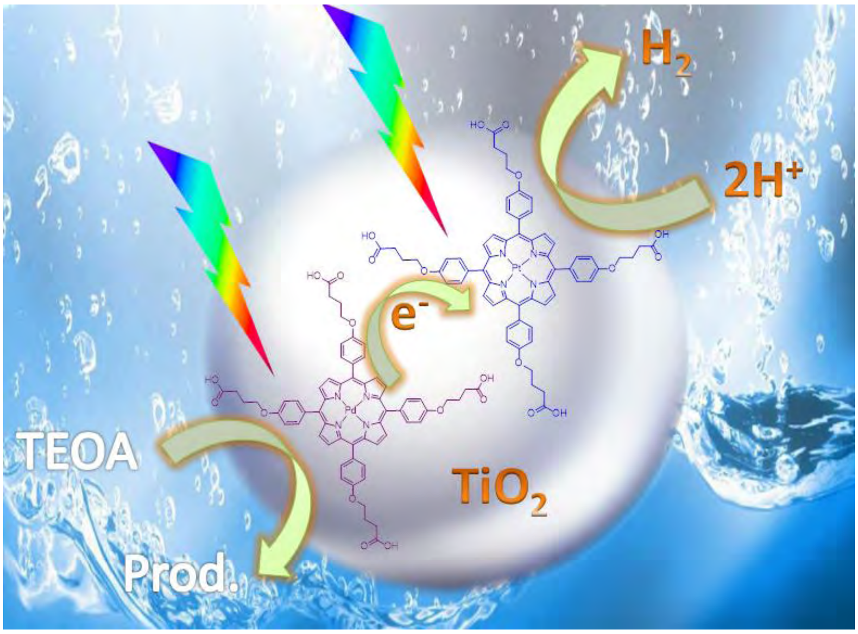
The research for the development and optimization of methods of using sunlight as an energy source is a major challenge to tackle the problem of reducing stocks of fuel and the ecological problem of burning hydrocarbons [1]. A fairly promising path for the efficient conversion of solar energy is to develop efficient photocatalytic systems for H2 production from aqueous protons, which constitutes the reductive side of water splitting. Hydrogen is the ideal fuel for the future because it is clean, energy efficient, and abundant in nature. While various technologies can be used to generate hydrogen, only some of them can be considered environmentally friendly. The great challenges as far as concern the field of photocatalytic hydrogen production involve the development of systems, which use earth-abundant bioinspired materials, and the enhancement of the activity and durability of the systems. Water soluble porphyrins and metallated porphyrins, due to their similarity to the natural photosynthesis dyes, are excellent candidates for efficient absorption of photon and electron transfer in the photocatalytic system. Also, cobaloximes Co(dmgH)2Cl(L), where L a substituted pyridine, in combination with a water soluble porphyrin photosensitizer both noble-metal free components, could increase dramatically their photochemical hydrogen production when L is replaced by imidazole ligand. We focused our research on the synthesis of a series of new and old Cobalt dimethylglyoxime based catalyst [CoIII(dmgH)2(L)Cl] with different pyridyl and imidazole derivates as axial ligands which has been performed and tested for hydrogen production in the presence of zinc meso-tetrakis (1-methylpyridinium-4yl) porphyrin chloride [ZnTMPyP4+]Cl4 as photosensitizer (PS) [2]. Also, we present, for the first time in the history of artificial photosynthesis, the combination of two porphyrins for high efficient H_2 production. Specifically fully studied the system include water soluble porphyrins Pt (as a catalyst) and Pd (as a photosensitizer) [3]-[5] to produce H_2.



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Development of novel electrolyte additives for designed surface modification

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An investigation of the effect of electrolyte on performance of in lithium ion batteries will be presented The electrochemical performance of common electrolyte formulations will be discussed along with detailed ex-situ surface analysis of the cycled electrodes. The ex-situ analysis allows the development of an understanding of the role of the electrolyte and common additives in the structure of interfacial electrode films on both the anode (solid electrolyte interphase, SEI) and on the cathode. Correlation of the structure of the surface films with the performance limiting reactions in lithium ion batteries affords insight into the mechanism of interfacial film formation and function. The mechanistic insight is used to systematically develop novel additives designed for specific electrode surface modification to afford optimized electrochemical performance. The electrochemical performance and ex-situ surface analysis of electrodes cycled with novel Additives for Designed Surface Modification (ADSM) will be presented.

Quantitative in Situ Analysis of Ionomer Structure in Fuel Cell Catalytic Layers

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The investigation of the nanostructure of fuel cell electrodes, especially the analysis of the ionomer component in the electrode has proven to be exceptionally difficult [1]. With high-resolution electron beam-based techniques, the contrast between carbon and ionomer phase is small and the analysis has to be performed under vacuum, where the ionomer is dry and shrunken [2]. Atomic force microscopy (AFM) has the advantage to work in humid environment and at elevated temperatures, close to operational conditions [3]. Using material-sensitive tapping mode AFM, a large contrast in adhesion force and stiffness values between Pt particles, mesoporous carbon, and ionomer is existent.

In this contribution, results from the investigation of cross-sections of electrodes cut from differently prepared membrane-electrode-assemblies (MEAs) are presented and changes due to fuel cell operation are presented. The size and ionomer coverage of Pt/agglomerates was analyzed, and the distribution of thickness of ionomer layers around Pt/C particles/agglomerates was evaluated.

Before operation, differences in distribution and average layer thickness ranging from 6-13 nm were observed. After operation, a significant thinning of the layers was found, depending on the position in the MEA. Possible reasons for the observed thinning will be discussed [4].

Conductivity through and along ultra-thin ionomer films with thicknesses comparable to ionomer films inside the electrodes was analyzed. A dependence of cell degradation on electrode ionomer thickness was observed.

Consequences of the results for fuel cell durability and possible degradation factors will be discussed.

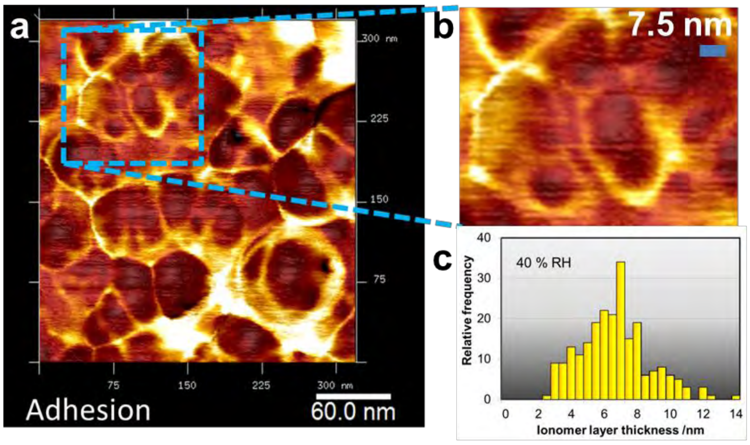

Figure 1: (a) AFM adhesion force mapping of electrode cross-section with bright ionomer phase, (b) zoomed-in view on encapsulated Pt/C agglomerates, and (c) distribution of ionomer layer thickness.

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Achieving Cost Reduction in PEM Electrolysis by Material Development

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Hydrogen is expected to play an important role as a crosslinking technology between power generation on one hand and transport and industry on the other hand. It can directly replace fossil fuels in transport and industry when produced by water electrolysis renewable energies such as solar or wind, which are converted with low efficiencies. The relevant technologies are either the mature alkaline electrolysis or the newer proton exchange membrane (PEM) water electrolysis. The PEM system is one of the most promising technologies for a sustainable and emission-free hydrogen production due to its high power density and high efficiency, with potential for performance enhancement and cost reduction [1]. Recent studies have analysed in detail the cost structure of the different electrolysis technologies [2]. For PEM electrolysis in particular, key components that determine the stack cost are the titanium-based contact elements, such as the bipolar plates (BPP) and the current collectors (CC), and the high iridium loading of electrocatalyst for the OER in state of art membrane electrode assemblies (MEA). However, the cost structure depends on the specific design of the electrolyser.

This presentation will discuss strategies for cost reduction by synthesizing unsupported and supported IrO_x and IrRuOx electrocatalyst with the aim of lowering the high loading [3-5]. Our synthesis procedure consists of producing nano-sized iridium particles by reducing iridium chloride ($IrCl_3$) with conventional sodium borohydride at room temperature and in water-free environment. This concept can also be applied to supported and alloy electrocatalysts. The supports need to be highly stable and exhibit sufficient electronic conductivity. The enhancement of activity achieved with improved electrocatalyst reaches a factor of about15 with respect to the best commercially available electrocatalyst.

Additionally, the cost reduction achieved by a titanium coating for stainless steel BPPs or CCs for PEM electrolysis will be discussed. We use vacuum plasma spraying (VPS) to coat either dense coatings for corrosion protection of stainless steel components or build up titanium diffusion layers with defined porosity as contact elements for the MEA [6-8]. The conductivity of the titanium coating can be improved by well-known Pt or Au additions; however, we have also developed promising non-noble conductivity enhancement elements. Furthermore, the VPS coating and production procedure is adaptable to large-scale industrial production.

This contribution will discuss the state-of-art of these material developments as well as their potential for future improvements.

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Acknowledgements
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New Electrolyte Systems for Li-S Cells with pPAN@S Cathode and Li-O_2 Cells

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Lithium metal based Li-S and Li-O_2 batteries have been intensively investigated in recent years due to their high energy densities, of which Li-S battery is in the more advanced development state towards practical application. Nevertheless, several technical challenges still limit their commercialization. Among these, the instability of Li anode has become a dominant factor limiting the cycle life and safety of these battery systems. For Li-S cells, dissolution of polysulfide ions from elemental sulfur based cathodes in ether based electrolytes and the consequent shuttle reaction are very difficult to be avoided, which lead to the poor cyclability and serious self-discharge. We have designed and developed novel pPAN@S cathode materials, in which molecular (or even atomic)-level sulfur distribution and embedding in the conducting matrix avoids the shuttle reaction and self-discharge[1,2]. Moreover, this cathode can be used in carbonate based electrolytes. However, the cycle life of the Li-pPAN@S cell is still limited in conventional $LiPF_6$/EC+DMC electrolyte, mostly due to the poor cycle stability on the anode side. In this presentation, we report new electrolyte systems for Li-pPAN@S and Li-O_2 batteries.

Using 1M lithium oxalyldifluoroborate (LiODFB)/EC+DMC+FEC (4.5:4.5:1 v/v/v) electrolyte, even and compact lithium deposition can be obtained in a Li/Li symmetric cell as shown in Fig. 1, and the stable Li cycle efficiency reaches more than 98%, far higher than that in $LiPF_6$/EC+DMC. Moreover, the LiODFB based electrolyte significantly improves the cycle and rate performances of Li-pPAN@S cell. 93% and 88% of the capacity can be retained after 1000 cycles, respectively at 2C and 4C (Fig. 2). The Coulombic efficiency of the cathode approaches 100% during cycling except the first cycle. Even at 10C rate, stable cycling is realizable with a capacity of ca. 1100 mAh/g $_{\text{sulfur}}$. The positive co-effect of LiODFB and FEC on the SEI layers on both lithium anode and pPAN@S cathode results in the excellent performance.

On the other hand, many lithium salts, such as $LiPF_6$, $Li[N(SO_2CF_3)_2]$, $LiCF_3SO_3$, $LiClO_4$, $LiBF_4$, and $Li[B(C_2O_4)_2]$ (LiBOB), have been tested in electrolytes for the non-aqueous Li–O_2 batteries. Here we design a new electrolyte system with high Li^+ conductive and chemically stable LiFSI as the lithium salt for the non-aqueous Li–O_2 battery, in which less-volatile and frequently used TEGDME is chosen as the basic solvent, and 1,4-dioxan (DX), (a symmetrically structured cyclic ether for its probably improved chemical stability) as the 2nd solvent. In the proposed electrolyte, the reversible oxygen electrode reaction with Li_2O_2 product can be realized as shown in Fig. 3. Moreover, Li dendrites formation on anode can be prevented.

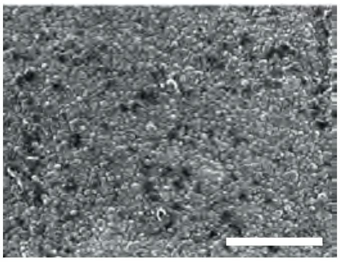

Fig. 1 SEM image of Li electrode in Li/Li cell with 0.28 mAcm^{-2} after 100 cycles. Scale bar: 10μm

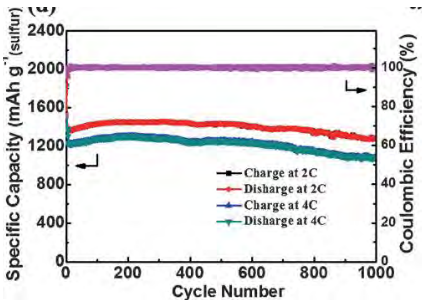

Fig. 2 Charge/discharge capacities and Coulombic efficiency of Li/S cells

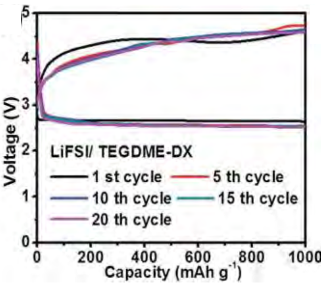

Fig. 3 Charge-discharge profiles of Li–O_2 cell at 500 mA g^{-1} to the fixed capacity of 1000 mA h g^{-1}

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The role of electrochemical hydrogen evolution at platinum nanoparticles on carbon monoxide oxidation in fuel cells.

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Carbon monoxide is the origin of more than half of human poisonings worldwide by carboxyhemoglobin formation. Incomplete combustion of carbon monoxide oxidation requires higher catalyst efficiencies, so we propose a modification of oriented platinum nanoparticles electrodes by extreme hydrogen evolution to enhance this reaction.

We have diagrammed a new preparation method of platinum nanoparticles comprising electrogenerated Pt(II) and Pt(IV) soluble species at mildly pHs with a final reduction either by bubbling hydrogen for different times and/or electrogenerated hydrogen under potential control. Depending on the selected reduction methodology (111), (100) or (110)-oriented nanoparticles can be obtained. After stationary overnight stabilization a modification of the preferentially oriented surfaces by a strong cathodization was conducted. We have formerly found [1] that long-lasting hydrogen evolution on platinum produces the underpotential deposited OH_{ads} species as a pre-monolayer due to the increase of pH. Besides, the formation of (111) stepped planes on platinum leads to a much lower onset potential for OH_{ads} species formation. We have also found a considerable catalytic effect for carbon monoxide oxidation claiming for the ability of platinum to oxidize CO_{ads} at lower potentials (Figure 1) [1]. Other authors observed diffusion limited oxidations at 0.47 V on this kind of “activated” surfaces [2]. We have considered that the facile oxygen transfer capability of platinum at such low potentials is due to OH_{ads} species formation with low coordination to platinum atoms located at stepped (111) sites. Similarly to Burke [3] we have reported at least two regions of OH_{ads} formation commencing at 0.20 V and 0.40 V, in contrast to the generally regarded onset of monolayer oxide formation on platinum in acid ca. 0.80 V. We explain these results by a large accommodation of surface platinum sites to low-coordinated platinum atoms in certain sites, many of them in overlayers of stepped (111) domains [4].

The use of platinum nanoparticles in fuel cells has been proven to be very useful due to their large dispersion and optimum size on carbon substrates. In this work we disperse them on polyoriented platinum to avoid contamination. A lower 0.20 V onset potential for the anodic stripping of CO_{ads} oxidation is observed on cathodically treated (111)-oriented platinum nanoparticles. The reaction involved first, the formation of oxygen species at low coordinated large active area platinum of stepped (111) plane orientations. Second, the diffusion of CO_{ads} toward neighbored sites with adsorbed oxygen-containing species. Third, the Langmuir-Hinshelwood surface reaction between them. After then, and with the decrease of CO_{ads} coverage, a final formation of oxygen species on terraces as well as diffusion of CO_{ads} toward (111) steps occurs. The enhanced active area defines a 25 % larger anodic stripping charge density and the persistence of surface morphology even when cycling up to 1.60 V.

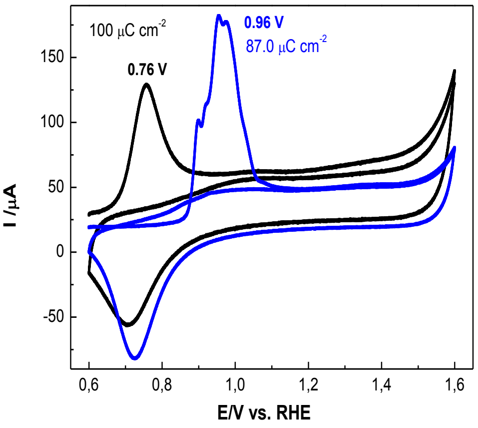

Figure 1.- First anodic *stripping* voltammetries of saturated carbon monoxide adsorbed at 0.60 V for 2 min on cathodically treated (111)-oriented (black lines) and (111)-oriented (blue lines) platinum nanoparticles run at 50 mV/s between 0.60 to 1.60 V in 0.1 M perchloric acid.

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Atomic Insights into Surface Structure and Electrochemical Performance of Nanostructured Spinel LTO ($Li_4Ti_5O_{12}$) Anodes

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Spinel lithium titanate $Li_4Ti_5O_{12}$ (LTO) is regarded as promising alternative to carbon-based materials for the application as anode material in lithium-ion batteries (LIBs) according to its high safety and cycling stability. However, the weak electronic conductivity and the low lithium-ion diffusion coefficient limit the performance of LTO as anode material in LIBs. In order to optimize the performance of LTO, various strategies such as nanostructuring or doping with other elements have been carried out in recent years **[1]**.
In this contribution, we present a combined experiment-theory approach, in which the morphology and the electrochemical performance of ultra-small LTO nanoparticles (NPs) with crystallite sizes smaller than 10 nm is studied by high-resolution transmission electron microscopy (HRTEM) and cyclic voltammetric (CV) measurements, respectively while density functional theory (DFT) calculations are employed to gain atomic insights into the surface structure of LTO model anodes.
The HRTEM measurements reveal that LTO NPs reveal an abundance of the (111) facet in agreement with previous studies **[2]**. Consequently, a LTO(111) model electrode may be envisioned as an appropriate model system in the corresponding DFT calculations. Applying a first principles thermodynamics approach **[3,4]** the surface structure of a LTO(111) model electrode is resolved under constrained reaction conditions **[5]**, in which depending on the NP size a delithiated oxygen-rich ($y = 0$), a lithiated oxygen-poor ($y = 3/8$) or a fully-lithiated oxygen-poor interface ($y = 1$) mainly covers the NP surface. Here, y describes the content of lithium on interfacial 16*d* sites ($0 \leq y \leq 1$). These thermodynamically stable surfaces are proposed as active phases within the interfacial intercalation reaction and exhibit different stabilities and interfacial capacities **(**cf. Figure 1).
The CV measurements yield that the optimized NP size amounts to about 7 nm, since NPs of this size show distinctly larger interfacial charge storage properties compared to commercial LTO (67 nm), whereas the stability remains unchanged. This finding is confirmed by the calculated stability diagram (cf. Figure 1), which enables to discuss the NP size as function of stability and interfacial capacity **[6]**.

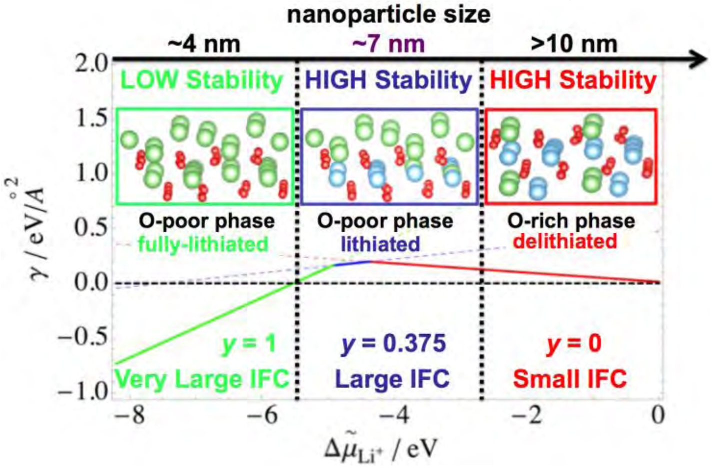

Figure 1: Stability diagram of a model LTO(111) electrode as function of the surface energy (stability) and the change in the electrochemical potential of lithium, which directly scales with the NP size **[6]**. IFC denotes the interfacial capacity corresponding to the lithium concentration on interfacial 16*d* sites.

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How Concavities Enhance the Activity of Platinum Nanostructures for the Oxygen Reduction Reaction

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The surface of an electrocatalyst is usually composed of numerous types of sites: open facets and defects such as steps and kinks coexist with close-packed surfaces. Importantly, if the catalytic reaction is structure sensitive, all those sites contribute differently to the overall activity. To obtain the highest possible catalytic activities, the most active sites need to be identified and their abundance maximized using suitable synthesis protocols. Thus, the rational design of catalysts is based on the challenging task of elucidating the active sites for the reaction of interest.

In particular for hydrogen fuel cells, the structure sensitivity of the oxygen reduction reaction (ORR) catalyzed by platinum is puzzling. On the one hand, it has been consistently reported that stepped Pt(111) electrodes are more active than the pristine ones [1, 2]. On the other hand, the activities of convex Pt nanoparticles, in which step-like defects are abundant, are never as high as that of pristine Pt(111) [3, 4]. These two observations suggest opposite effects of Pt defects on the ORR and, in more general terms, raise concerns on the use of conclusions obtained from model surfaces to design nanoparticle catalysts.

In this talk, I will offer a solution to this apparent contradiction by means of "coordination-activity plots" [5], which establish a correspondence between the geometric configuration of catalytic Pt sites and their ORR activities. The plots are based on generalized coordination numbers, which capture trends in adsorption energies for a variety of sites on extended surfaces and nanoparticles of different sizes and shapes [6, 7]. Enhanced Pt sites for the ORR need larger coordination than pristine Pt(111), which can be found at concavities on extended surfaces but not on convex nanoparticles. Coalescent, cross-shaped and frame nanostructures contain such overcoordinated sites and are shown to outperform Pt(111) [8].

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Identifying low temperature aging behaviours in lithium-ion batteries

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The success of electric vehicles (EVs) is related directly to the development of high performing, long lasting, low-cost and safe batteries. A particular challenge in the Canadian market, are the extreme low ambient temperatures that lithium ion battery (LIB) packs are exposed to during Canadian winters. These temperatures reduce driving range and performance, reduce battery lifetimes and also present a cell safety risk. Fast charging at low temperatures can cause the formation of metallic lithium on the negative electrode which leads to internal short circuits. The lack of field data with large-scale LIB aging has led manufacturers to impose to stringent, heuristic-based, operating constraints in order to meet the warrantied service life of the pack (8-10 years for EVs). These constraints are typically in the form of voltage limits, temperature limits and temperature gradient limits. The overly conservative operating window reduces the exploitable battery capacity and limits cell performance through excessive control applied by the thermal management system. A better understanding of low temperature capacity loss mechanisms can lead to improved design, more flexible operation and reduced cost of the complete battery management system.

This study investigates the performance and life cycle endurance characteristics of lithium-ion cells under different operating conditions through experimental evaluation on lithium ion (NMC) 18650 cells. It identifies the onset conditions of capacity loss mechanisms that are accelerated by low temperatures, such as lithium plating on the anode. Capacity loss data are presented for cells tested at a variety of charge/discharge rates, voltage limits, and operating temperatures. At ambient (or elevated) temperatures and standard (or below standard) charge/discharge current rates, cell degradation rates are dominated by thermally activated parasitic chemical and electrochemical side reactions. Under these conditions, cell degradation stabilizes over time as the SEI layer formation and the driving forces for the loss of active lithium equilibrate. However, test results show that at certain combinations of high current charging and low ambient temperature causes the capacity loss functionality to accelerate over time, indicating that an additional capacity loss mechanism becomes important. Teardown failure analysis was performed to confirm and qualitatively assess the presence of metallic lithium on the negative electrode. The threshold that defines this transition was defined as an empirical function of both factors. Results demonstrating the effects of the operating environment expressed in terms of current and temperature on the presence and extent of lithium plating are given and discussed. Although this function is specific to the chemistry and geometry of the cells tested, it represents the first steps towards optimizing thermal management strategies to effectively control these unfavorable conditions.

Separating Hydrogen and Oxygen Evolution in Alkaline Water Electrolysis Using Nickel Hydroxide Electrode

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Compared with PEM water electrolysis, alkaline water electrolysis exhibits inherent low cost characteristic because it can employ non-precious catalyst and porous separator [1, 2]. However, alkaline water electrolysers are difficult to shut down/start up and their output cannot be ramped quickly because the pressure on the anode and cathode sides of the cell must be equalized at all times to prevent gas crossover through the porous cell separator [1]. Therefore, it is quite difficult to efficiently utilize the intermitted and fluctuating power from renewable energy for conventional alkaline water electrolysis.

In this talk, I will introduce our recent work on decoupled H_2 and O_2 in alkaline water electrolysis [3]. By using nickel hydroxide as a redox mediator, we decouple H_2-production and O_2-production in alkaline water electrolysis, which well overcomes the gas mixing issue and increases the utilization of renewable energy. In this architecture, the H_2-production occurs on the cathode by H_2O-reduction, and the anodic $Ni(OH)_2$ is oxidized into NiOOH simultaneously. The subsequent O_2-production involves a cathodic NiOOH-reduction ($NiOOH \rightarrow Ni(OH)_2$) and an anodic OH^- oxidization (Figure 1). Alternatively, the formed NiOOH during H_2-production can be coupled with a Zinc anode to form a NiOOH-Zn battery, and its discharge product (i.e. $Ni(OH)_2$) can be used to produce H_2 again. This architecture brings a new solution for facilitating renewables-to-hydrogen conversion.

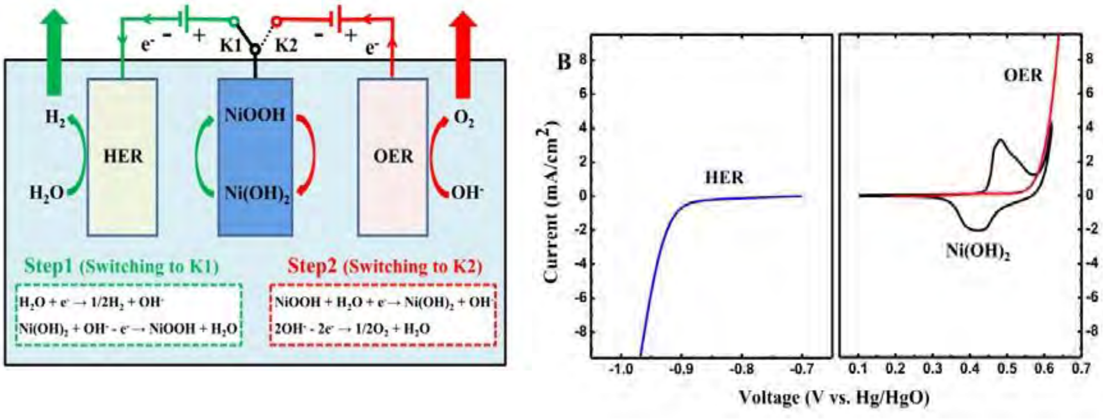

Fig.1 Electrode reaction of two-step alkaline water electrolysis

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NPGM Oxide Cathode with Oxide Support for Advanced PEFCs

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Polymer electrolyte fuel cells are expected for the residential and transportable applications, due to their high power density and low operating temperature. Many ENEFARMs (micro CHP) are operating and fuel cell vehicles are also commercially available in Japan. However, the estimated amount of Pt reserve is limited and its cost is high. The dissolution of Pt cathode might be the final problem to be solved related to the stability in the present PEFC system. Additionally, the instability of carbon support is also a big problem especially for fuel cell vehicles. Carbon including graphite is thermochemically unstable at room temperature in air or oxygen containing atmosphere. A stable non-precious metal oxide cathode with stable metal oxide support might be the final goal for the cathode of PEFC for fuel cell vehicles.

We have reported that partially oxidized group 4 and 5 metal carbonitrides and organometallic complexes are stable in an acid solution and have definite catalytic activity for the oxygen reduction reaction (ORR) (1-4). In this paper we will report our recent advancement of the group 4 and 5 metal oxide catalyst with metal oxide support without carbon.

Recently, we published the results of precious-metal-free and carbon-free cathodes based on oxides and demonstrated the superior durability of oxide-based cathodes by preparing titanium-niobium oxides mixed with Ti_4O_7 ($Ti_xNb_yO_z + Ti_4O_7$) (5). The ORR activity of the $Ti_xNb_yO_z + Ti_4O_7$ is higher than that of the Ti_4O_7, indicating that the $Ti_xNb_yO_z$ might have active sites for the ORR. The highest onset potential of the $Ti_xNb_yO_z + Ti_4O_7$ was over 1.1 V with respect to reversible hydrogen electrode. No degradation of the ORR performance of $Ti_xNb_yO_z + Ti_4O_7$ was observed during both start-stop and load cycle tests. We successfully demonstrated that the precious-metal and carbon-free oxide-based cathodes had superior durability under the cathode conditions of a polymer electrolyte fuel cell.

In order to qualify the role of Nb oxide for ORR, we used TiO_2-Nb rods with different Nb concentrations as working electrodes. TiO_2-Nb rods were heat-treated at 800 °C in air and 4%H_2/Ar to examine the effect of heat-treatment. All electrochemical measurements were performed in 0.1 mol dm^{-3} H_2SO_4 at 30 °C with a 3-electrode cell. Chronoamperometry (CA) was performed from 0.2 to 1.2 V vs. RHE under O_2 atmosphere to obtain ORR current. The ORR current density was normalized by the electric charge of the double layer capacitance under N_2 atmosphere.

From the results of the potential-ORR current curves from 0.2 to 1.0 V of TiO_2-Nb electrodes, the ORR activity of the TiO_2-Nb(0.5atm%) electrode was highest. Although Nb doping is necessary to have some electric conductivity, small amount of Nb doping might be enough to get high ORR activity. In addition, the ORR activity of the TiO_2-Nb(0.5atm%_800°C reduction) was higher than that of the TiO_2-Nb(0.5atm%). The reduction of oxide at high temperature might be a key to get high ORR activities of oxide cathode.

Acknowledgement

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Electropolymerized Electrodes for High Performance Thin-film Li-ion Microbatteries

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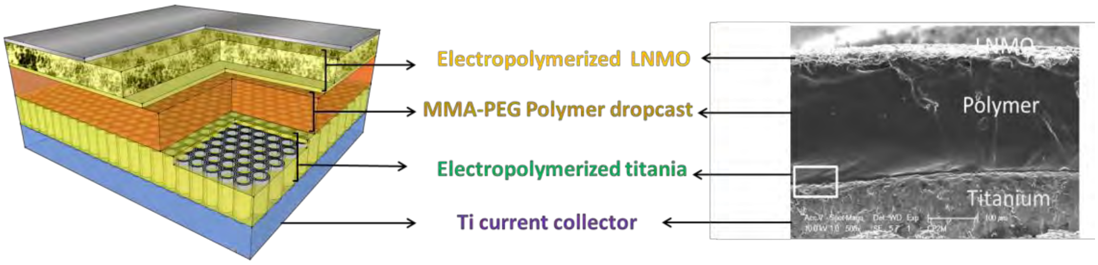
Lithium-ion batteries (LIBs) are widely used to power portable devices, microelectronics, vehicles, etc. With many advantages such as high surface area and improved charge transport, self-supported 3-D nanostructured metal oxides such as titania nanotubes (TiO_2nts) are promising electrode materials for LIBs and their impact is particularly significant when considering the miniaturization of energy storage systems and the development of 3D microbatteries.

This talk will review the concept and fabrication of all-solid-state Li-ion microbatteries using TiO_2nts as negative electrode. Effects of material selection and processing on the performance and reliability are presented as a means to develop conceptual guidelines to understand and improve microbattery designs. Fundamentals such as electrode reactions, lithium ion diffusion and the conformal electrodeposition mechanism of polymer electrolytes onto the nanostructured electrodes will be presented. The fabrication of a full 3D microcell showing high electrochemical performance will be presented (See Fig. 1) and the development of the next generation of 3D microbatteries will be discussed.



(a) (b)

Fig. 1. (a) Schematic representation and (b) cross-sectional SEM image of the all-solid-state microbattery.

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Biography

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Hydrogen peroxide on-site production: a fundamental study on the direct synthesis and electrocatalytic synthesis using Au-Pd catalysts

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Hydrogen peroxide (H_2O_2) is an important chemical, commonly employed for disinfection, water treatment and bleaching. Whilst H_2O_2 itself is considered as an environmental friendly chemical oxidant, whose sole side product is water, its current synthesis method, the anthraquinone process, can be considered less so. Considering that most of end-use applications require concentrations between 2 to 5 wt%, a continuous on-site production of H_2O_2 would provide an attractive alternative and is therefore highly desirable. Both the electrochemical reduction of oxygen to hydrogen peroxide [1] and the direct synthesis in an autoclave [2] have attracted considerable research interest into catalysts which could provide a more efficient alternative to the current industrial process. Despite the state of the art characterization techniques, being applied to determine the surface structure of mono and bimetallic catalysts, there is still a lack of detailed understanding of the active sites of the metal nanoparticle and the actual reaction mechanism.

In this work different molar ratio of Au/Pd catalysts were synthesized [3] with a final metal loading of 10 wt% on activated carbon and the influence of bimetallic nanoparticles composition for Oxygen Reduction Reaction (ORR) and Hydrogen Oxydation Reaction (HOR) is studied.

The change in activity, selectivity towards H_2O_2 as well as in H_2O_2 decomposition is characterized in both an electrochemical cell (electrochemical synthesis), using a Rotating Ring Disk Electrode (RRDE), and in an autoclave (heterogeneous direct synthesis). Whilst the addition of Au to Pd increases the overall selectivity, the results for pure Au showed low H_2O_2 productivity during direct synthesis. Furthermore, the stability of these catalysts in acidic media and the catalyst degradation consequences on the performances for H_2O_2 synthesis represents also a major interest of this work. The online dissolutionas characterized with a Scanning Flow Cell and Inductively Coupled Plasma Mass Spectrometer (SFC-ICPMS), while the microscopic stability was studied with Identical Location TEM (IL-TEM).

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Perovskite-oxide electrocatalysts with high OER activity and durability in acid media: $Sr_{1-x}Na_xRuO_3$.

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In the last years functional oxides have being reported as promising catalysts for the electrochemical dissociation of water into H_2 and O_2 [1]. In particular, they show good results in the oxygen evolution reaction (OER), $2H_2O \rightarrow O_2 + 2H^+ + 4e^-$. This semi-reaction is kinetically very slow so catalysts are needed to conduct the reaction at low overpotentials. The benchmarking catalysts are based on noble metals, expensive, scarce and not very robust. For that reasons many attempts are addressed to designing improved catalysts. While in alkaline media some oxides have been reported active for the OER[2], active and stable electrocatalysts in acid electrolyte are scarce. In this work we unveil a new family of perovskites, $Sr_{1-x}Na_xRuO_3$, with very high activity and durability for the OER in acid electrolyte. Whereas parent $SrRuO_3$ has been reported to be one of the most active oxides in media, with activities even higher than RuO_2 [3], its durability is very limited, deactivating within very few cycles. It has been reported that the lack of stability is related to the change from Ru^{4+} to $Ru^{>4+}$ when the voltage increases during OER. $Ru^{>4+}$ oxidation state is unstable inside the perovskite, destroying the oxide and losing the activity. We synthesized $Sr_{1-x}Na_xRuO_3$ (x= 0.05, 0.10, 0.15) with partial oxidation of Ru^{4+} to $Ru^{>4+}$, trying to avoid the destabilization caused by the formation of $Ru^{>4+}$ inside the oxide, enhancing OER activity and durability.

The samples were prepared by citrates method and subsequent high temperatures. By Powder Neutron Diffraction we determined crystal structures, oxygen vacancies, positions, distances (related to oxidation states), angles and Na content (Fig. 1a). We performed X-ray Absorption Spectroscopy: Na K-edge confirms the presence of Na and Ru K-edge verifies a partial oxidation. The electrochemical activity was determined by measuring current densities between 1.1-1.5 V *vs.* RHE in 0.1M $HClO_4$. Fig. 1b summarizes the current densities obtained during 20 cycles, observing that Na enhances enormously the durability (Fig. 1c). Also we observed an enhancement of the intrinsic activity (normalized by the electrochemical surface areas (ECSA)) with x (Fig. 1d). We ascribed the increment of durability to the partial oxidation of Ru inside the compound which avoids the rapid decomposition of the sample. By TEM we proved that after 10 cycles of OER, $SrRuO_3$ decomposes almost completely while Na samples remain stable. The enhancement of the activity has been verified theoretically by DFT, showing that $SrRuO_3$ is a very active perovskite for OER. Moreover, the introduction of Na increases the activity even more. We believe that it could be an effect of a change of structure since $SrRuO_3$ has a more distorted structure than $Sr_{1-x}Na_xRuO_3$ and we are currently studying if there is a change in the spin state of Ru^{4+}. RuO_6 octahedra become more regular and could change from low spin $Ru^{4+}(d^4{:}t_{2g}\uparrow^3\ t_{2g}\downarrow^1)$ in $SrRuO_3$ to high spin $Ru^{4+}(d^4{:}t_{2g}\uparrow^3\ e_g\uparrow^1)$ when it is Na doped, and e_g^1 spin state has been reported as the most active state for perovskites [1].

In summary we have discovered a new family of OER catalysts in acid media, with higher activities (onset potential) and durability than the benchmarking activities reported until date.

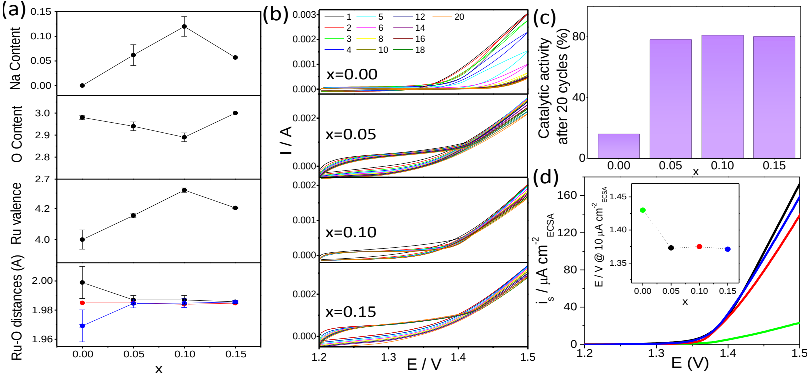

Fig. 1: (a) PND results, (b) 20 cycles of current densities between 1.2-1.5V, (c) Percentage of the catalytic activity after 20 cycles, (d) intrinsic activity normalized by ECSA.

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Stability of Solid Oxide Cells for Steam Electrolysis Analysed in the 10 to Above 20 Thousand Hours Range

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Steam electrolysis with solid oxide cells (SOCs) at high temperature can provide electrical-to-chemical energy-conversion efficiencies for hydrogen production exceeding those of the more classical Alkaline and PEM technologies. The efficiency gain is largest, if thermal energy is available for water evaporation, e.g., from the downstream exothermal reaction of hydrogen and CO_2 to hydrocarbons in 'power-to-gas/liquid' converters ('Sunfire' research project [1]). All three technologies are currently under consideration for the storage of surplus renewable electrical energy such as from wind or solar.

Apart from the electrolysis application, the low electrode overvoltages at SOCs are favourable for reversible fuel cell/electrolysis cell operation (so called r-SOCs). This application is subject of a presently running demonstration project on a larger scale, sponsored by the European Union ('GrInHy' [2]). The planned output is 40 Nm^3/h hydrogen (electrolysis or SOEC mode) and 30 kWel (SOFC mode).

The focus of EIFER work in the mentioned research projects was and is the analysis of the lifetime of the core component, the cells, under electrolysis operation. Cells from different suppliers using different structures are included (electrolyte- and hydrogen-electrode supported cells). Moreover, stack testing is done up to, at present, a power range of about 10 kWel. In the testing, impedance spectroscopy serves as diagnostic tool for *in-situ* degradation analysis while maintaining steady state operation conditions. A benchmark test with an electrolyte supported cell was finished early 2016 with 23 000 h total operation time and a voltage degradation of 0.57 %/1000 h or 7.4 mV/1000 h for j = -0.9 Acm^{-2} [3-5] (Fig. 1). This test approaches in a satisfying way the operation conditions required for industrial application, which implies around 50 000 h usable operation time at current densities exceeding those of the fuel cell operation (of typically 0.5 Acm^{-2}).

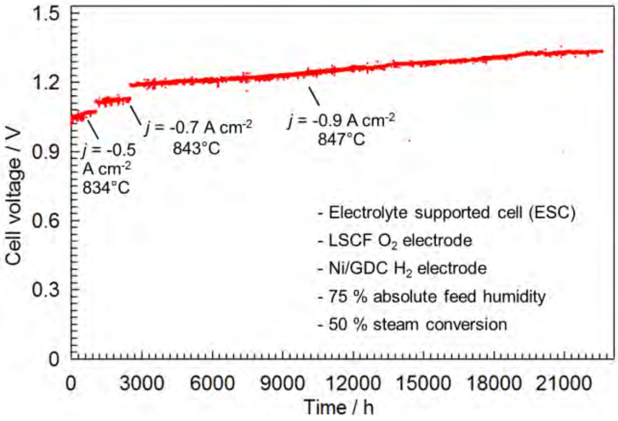

Fig. 1: Cell voltage during long-term steam electrolysis.

An overview on our recent long-term cell-testing results will be given. The evaluations rely on the mentioned benchmark test and further experiments in the 5000 to above 10 000 h time range. Main points of interest are the evolution of long-term degradation and its dependence on the operation parameters, the identification of the degrading elements (electrolyte, electrodes, barrier layers, contacting…), potential sudden cell failure, and also the influence of feed-gas purity and periods of de-rated operation (e.g., under steam starvation). A further issue is the comparison of the different existing SOC technologies in the electrolysis mode (i.e. electrolyte [3-5] and electrode [6,7] supported cells). The technologies yield specific advantages and drawbacks, which do not necessarily coincide with the ones known from the fuel cell application.

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Highly Active, Corrosion-Resistant Cathode for Fuel Cells, Based on Platinum and Molybdenum Carbide

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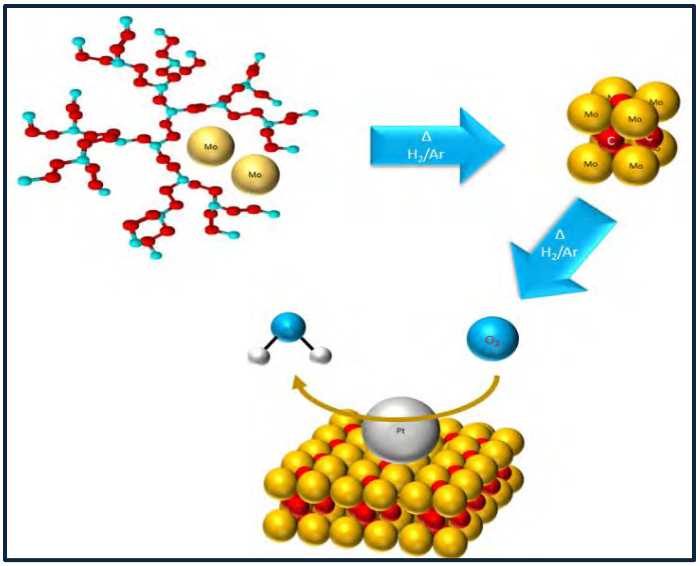
ABSTRACT

Considering the need for alternative and efficient energy sources, fuel cells might possibly be a viable and cost-effective solution. One of the more acute setbacks in the commercial distribution and utilization of this technology is the lifetime of the fuel cell which is limited by the stability of the electrode.[1] In this regard, carbon-based materials are not suitable as an electrode material.

Consequently, nano-crystallites of Mo_2C were synthesized via modified polymer-assisted deposition (mPAD) and utilized as support material for the deposition of Pt catalyst in order to be studied as a durable, corrosion-resistant ceramic-based system for the oxygen reduction reaction (ORR). The synthesized ceramic compound was found to include no free amorphous carbon, making it potentially compatible for fuel cell electrode material. The molybdenum carbide appeared to improve both the electro-catalytic activity of Pt catalyst, showing an increase in both the mass activity, three times higher at 0.9 V vs. RHE, and in the half-wave potential by 70 mV, when compared to commercial Pt/C catalyst. As anticipated, the durability was also increased, showing 40% more resistance to chemical and physical corrosion than standard commercial Pt/C catalyst/support system.



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Electrochemical Synthezis of Nanocrystalline NiPd Alloys of Catalytic Activity Towards HER - alkaline $Ni^{2+} – Pd^{2+} – Cl^{-} – NH_3 – H_2O$ system

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Synthesis of NiPd alloy is investigated in many research centers in the world mainly due to its interesting properties making possible its application as magnetic and catalytic materials. NiPd alloys were investigated also as catalysts in autothermal reforming of methane (1), counter electrode electrocatalyst in liquid-junction solar cells (2), utilization of CO_2 and methane in dry reforming process (3), anodes in methanol oxidation (4) and toluene hydrogenation (5). Exchange current density versus the enthalpy of hydrogen adsorption ($Log(i_0)$-dG_{Me-H}) dependence allows on assumption that material composed of Ni and Pd will exhibit high catalytic properties towards hydrogen evolution reaction (HER). Previously we reported studies on electrochemical co-deposition of nickel with palladium from acidic solutions containing aquachloro- complexes of both elements (6) as well as palladium with cobalt (7, 8) and nickel with molybdenum (9). In literature, in spite of its wide application range, few reports exist concerning electrodeposition of NiPd alloys. Existing reports are focused on synthesis of NiPd alloys from suplphate-chloride (5), ethylenediamine (4) and chloride (6) based baths. In present work authors reported studies focused on electrochemical deposition in alkaline ammonia based system for first time.

Described studies were started from thermodynamic and UV-Vis analysis enabling qualitative description of analysed system. Electrochemistry of $Ni^{2+} – Pd^{2+} – Cl^{-} – NH_3 – H_2O$ system was analyzed based on results of differential pulse voltammetry (DPV), cyclic (CV), linear (LV) and linear stripping voltammetry (LVS) combined with electrochemical quartz crystal microbalance (EQCM). In further step synthesized alloys were characterized towards their compositions (WD-XRF), morphology (SEM, AFM), structure (XRD) and catalytic properties towards HER.

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Finite Size Effects in Pt Monolayer Catalysts

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The ultimate configuration of ultra-thin Pt catalyst overlayers in terms of their specific activity is the 2D Pt monolayer (ML). According to modern theoretical considerations[1], the energy of d-band center relative to Fermi level is the main descriptor of Pt ML catalytic behavior. In the case of the substrate which has weak electronic effect (weak ligand), the energy of d-band center is mainly affected by the coherent strain in Pt ML [2]. For substrates which are stronger ligands, the electronic and strain effects are coupled and the energy of d-band center is function of both[1,3].

At room temperature, Pt is very difficult to deposit in a true continuous ML configuration[4]. The functional Pt ML catalysts have morphology consisting of compact 2D nanoclusters with certain size distribution and coverage of the substrate[5-8]. Due to the *finite size effects*[9,10], each 2D Pt nanocluster in the ML experiences size-dependent compressive stress[11]. Because of that, the active strain in Pt nanocluster (ε_a) is the linear combination between the coherent strain (ε_{cho}) and the strain caused by the finite size effects. The ε_a has a radial dependence being always more compressive at the periphery than in the center of the Pt nanocluster[11]. Recent study[12] shows that the finite size effects can significantly influence the activity of Pt ML deposited on Au(111) (Pt_{ML}/Au(111)). Pt_{ML}/Au(111) consisting of smaller nanoclusters were found less active for hydrogen oxidation reaction. The observed trend has linear correlation with the value of the average strain in Pt.

In the case of substrate that has stronger electronic effect on Pt, the importance of the *finite size effects* on the Pt ML activity has not been evaluated yet. System that falls into this category is Pt ML on Pd substrate (Pt_{ML}/Pd(hkl))[1,3]. It has been identified as one of the best oxygen reduction catalyst[13] with significant practical application in fuel cell technology[14]. Therefore, it is of fundamental and practical significance to better understand the relative contribution of the *finite size effects* on the catalytic behavior of Pt_{ML}/Pd(hkl). The presented work addresses this challenge by studying the carbon monoxide (CO) ML adsorption on well characterized Pt_{ML}/Pd(100) electrode morphology using subtractively normalized interfacial furrier transform infra-red spectroscopy (SNIFTIRS) and density functional theory (DFT) calculations. Experiments and calculations do suggest that the finite size effects in Pt/Pd(hkl) system represent the main contribution to their overall electrosorption behavior. This means that electronic effect of substrate even if it is a strong ligand does not have dominant role in catalyst ML behavior as long as its morphology is consisting of 2D nanoclusters rather than as continuous ML. Other examples of *finite size effects* in a system such as 2D core-edge Ru-Pt ML catalyst will be discussed as well.

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1,2-dimetoxyethane degradation chemistry in Li-O_2 batteries

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Li-O_2 batteries are extraordinary energy devices able to exploit the outstanding properties of the Li/O_2 redox couple to reversibly store energy. Nowadays they represent one of the most promising device for electric carriage (especially for electric vehicles), massive green energy storage and the new generation electronics. In fact from the point of view of the general public, the implementation of an effective Li-O_2 battery in current technological devices may have an extraordinary impact on common life ranging from sustainable electron mobility, green smart use of renewable energy sources, de-carbonization of industrial processes and thus drastic reduction of the CO_2 emission related to human activities.
However, despite the enormous R&D effort spent worldwide in the last decade, the best state-of-the-art non-aqueous secondary Li-O_2 cell is still a lab scale demonstrator and the complete comprehension of the based mechanisms that rule these devices is far. In particular, the stability of the materials in the high oxidation environment of the Li-O_2 cell is not cleary demonstrated just as the possible degradation routes for the compounds of the device. In fact, carbonaceous materials, i.e. amorphous cathode matrix (porous SuperP) and the ether-based solvent (e.g. TEGDME, DME), may undergo oxidation from the superoxide radical anion O_2^-.
Here we discuss the degradation chemistry in Li-oxygen electrochemical cells of ether-based electrolytes as well as on carbonaceous cathodes. To this aim electrochemical tests have been performed in galvanostatic conditions and electrodes have been recuperated for post mortem analysis by XPS, FTIR and TEM techniques. Results show that reversible accumulation and decomposition of organic and inorganic precipitates occur upon discharge and charge, respectively. These precipitations and decompositions are likely driven by electrochemical and chemical parasitic processes due to the reactivity of the cathode carbonaceous matrix or by the degradation of the electrolyte. The two effects have been decoupled by studying also gold-based electrodes without carbon catalysts in parallel to the usual carbonaceous-based electrodes.
The comprehension of the ether degradation mechanisms has been complemented by quanto-mechanic computations of the potential energy surfaces of the reactivity of DME in Li-O_2 environments.

Decomposition and Reaction of the Additive 1,3-Propane Sultone with Electrolyte Compounds

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Sulfur based additives, such as 1,3–propane sultone (PS), were reported for graphitic anode protection and the accompanying formation of the solid electrolyte interphase (SEI). The SEI was generated on the anode surface in the first cycles. [1] PS which is often applied in propylene carbonate (PC) based electrolytes in lithium ion batteries (LIB), suppressed the decomposition of PC. [2] In combination with PC, ethylene carbonate (EC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC), PS inhibited cell swelling after cycling at higher temperatures. [3] Furthermore, the combination of PS and vinylene carbonate (VC) was reported for providing better performance and reducing gas production inside the cell during cycling. [4]

Fischer described the cycle opening of PS where 3-hydroxypropane-1-sulfonate or hydroxypropanesulfonic acid, was formed. This took place in combination with different reaction partners like water, ammonia, phosphorus compounds, carboxylic acids and many more. [5] As PS was described as very reactive [5], it would be interesting if and how PS reacted in a commercially used LIB electrolyte.

In this study, the fresh and aged electrolyte of a cell containing the PS additive, was investigated. The cells were calendric and electrochemically aged. After that, the electrolyte samples were investigated by gas chromatography (GC) for analyze the volatile electrolyte compounds and by capillary electrophoresis (CE) for the investigations of ionic compounds and decomposition products.
Overall, the combination of the analytical methods resulted in a good overview about the aging of the electrolyte and it was found out that PS opened the cycle and polymerized with different compounds from the electrolyte.

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A New Pb (II)-Selective Membrane Electrode Based on Thiophene-2-aldehyde Thiosemicarbazone (TATS) Schiff base in Polymer Metrix

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ABSTRACT

A new lead (II) selective electrode has been constructed with thiophene-2-aldehyde thiosemicarbazone (TATS) ligand as a neutral carrier and PVC as membrane matrix. The electrode gave Nerstian response over a wide concentration range (1.0×10^{-7} to 1.0×10^{-2} M) lead(II) with a slope of 29.4 ± 0.1 mV decade^{-1}. It has releatively fast reasponse time (<15 s) with an improved selectivity in presence of various interfering ions. The best performance was recorded with a membrane composition of PVC: DOP: Ionophore: NaTPB as 33: 59: 3.4: 4.6 (w/w %). The detection limit of the electrode was approximately 4.0×10^{-8} M and the electrode works well in the pH range of 2.4–8.0. The electrode can be used for at least 3 months without any significant divergence in potential. The proposed electrode has found application as an indicator electrode for potentiometric titration of Pb(II) with EDTA. It can also used to determine Pb(II) ion concentration in wastewater samples.

Keywords: PVC Membrane, Lead(II) ion-selective electrode, Membrane electrode, Schiff Bases.

Aminoalkylsulfonic Acids as Electrolytes for High Temperature PEM Fuel Cells

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The fundamental suitability of 2-Sulfoethylammonium triflate ([2-SeA$^+$][TfO$^-$]) for application as a protic electrolyte in high temperature PEM fuel cells (HT-PEFCs) has recently been proven [1]. [2-SeA$^+$][TfO$^-$] represents a novel class of proton conducting ionic liquids (PILs) based on aminoalkylsulfonic acids. Compared to phosphoric acid, the state-of-the-art electrolyte of HT-PEFCs, [2-SeA$^+$][TfO$^-$] shows superior kinetics in terms of oxygen reduction reaction (ORR) on polycrystalline Pt at elevated temperatures [1].

Water is produced on the cathode side, consequently, under fuel cell operating conditions, the presence of water is unavoidable. At an operating temperature of 160 °C, synchrotron radiography measurements of HT-PEFC MEAs with phosphoric acid as electrolyte resulted in an average water content of 5 – 15 vol%, depending on current density [2]. It is therefore appropriate to study mixtures of aminoalkylsulfonic acids and small amounts of water. In this work, we investigate the influence of water content (0.7 – 6.1 wt%) and temperature (70 – 110 °C) on the double layer properties and the ORR kinetics for the example of 2-Sulfoethylmethylammonium triflate ([2-SeMA$^+$][TfO$^-$]). The [2-SeMA$^+$] cation is a methyl derivate of [2-SeA$^+$]. The methylation should reduce the intermolecular forces and thus decrease the viscosity.

For the investigation of double layer properties, cyclic voltammograms and series impedance spectra were recorded in a potential range of 0 – 1.6 V (RHE). By fitting the impedance spectra as complex capacitances, up to four differential double layer capacitances and corresponding time constants are obtained, depending on potential, water content and temperature. In the whole potential range investigated, a high frequency capacitance, C_1, and a low frequency capacitance, C_2, can be calculated. Moreover, in the HUPD region, C_1 can be separated in two parts, C_{1a} and C_{1b}. Whereas the high frequency capacitive processes are mainly attributed to ion transport processes in the double layer, the low frequency process is ascribed to changes of the interfacial layer, including ad-/desorption and Faradaic processes. The role of water in a network of hydrogen bonds in the double layer is discussed.

The ORR kinetics were investigated by means of a hanging meniscus rotating platinum disc electrode (HMRDE). Distinct limiting currents are visible and $j_{\mathrm{lim}} \sim \omega^{0.5}$ follows the Levich equation. It turned out, that the ORR current is virtually independent of the water content. The b factors (135-148 mV/dec.) are close to theoretical value (144 mV/dec.@90 °C). The ORR current density is about three times higher than that of phosphoric acid.

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Organic-phase Synthesis of $Li_3V_2(PO_4)_3$@Carbon nanocrystals and Their Lithium Storage Properties

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Reduction the particle size is a efficient strategy for improving lithium storage properties of $Li_3V_2(PO_4)_3$ (LVP) due to a shorter pathway for lithium ion and electron transport. However, designing and synthesizing LVP nanocrystals (NCs) smaller than 30 nm remains a challenge. In this work, we have developed a facile approach for the fabrication of the monodisperse LVP NCs electrode materials through a robust high-temperature organic-phase reduction method. The thermodynamics of synthesis and the possible reaction mechanism were investigated. The results showed that organic-phase reduction environment (at 320 °C) may not be thermodynamically allowed to crystallization of LVP. Nevertheless, oleic acid (OA) and oleylamine (OAm) is essential to hinder the agglomeration and growth of the particles as a capping agent. For meeting the requirement of thermodynamics, the calcination is essential to prepare the LVP. The surface electronic conductivity of LVP NCs was enhanced through a succedent carbon-coating treatment. The optimum design of size reduction combined carbon coating is very favorable for kinetics of electron transfer and lithium ion diffusion. Therefore, LVP@C NCs exhibit superior lithium storage properties with excellent rate capability (84 mA h g^{-1} at a rate of 20 C) and superior cyclic stability (96.2 % capacity retention after 200 cycles at 5 C), demonstrating their potential application in high-performance lithium-ion batteries.

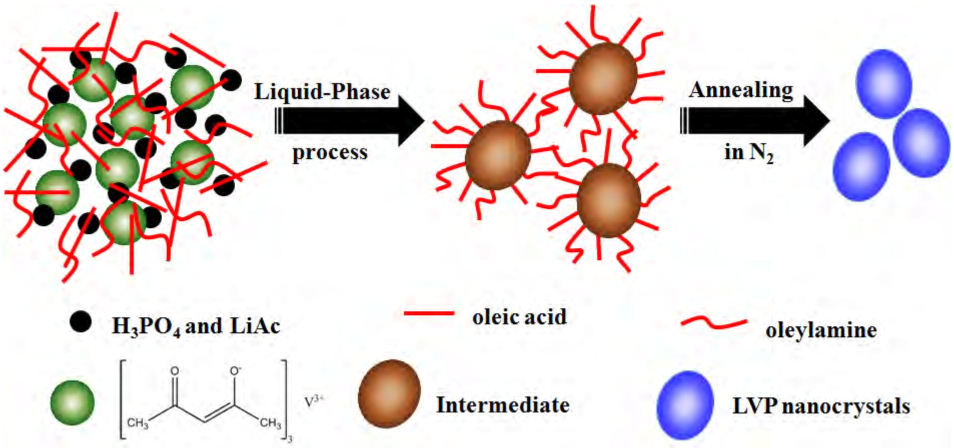

Fig. 1. Principle schematic illustration of the fabrication of LVP NCs.

Analysis of Si-based Anode in Li-ion Batteries Combining Electrochemical Characterization and Multi-Scale Modeling

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In the past years, Silicon has drawn attention among li-ion batteries technology as a promising material for negative electrodes. It is abundant, not toxic and displays a significantly higher specific capacity than more commonly used materials. However, this material is well known to be prone to large volume changes upon lithation and delithation (up to 320 %). This phenomenon causes particles cracking, SEI instability and electrode delamination, dramatically affecting the cycle performance of such batteries. To overcome those problems, several strategies have been tested such as the use of submicronic particles (i.e.< 150 nm) and/or the use of composite material with carbon. Recently, Si/C core-shell nanoparticles have been proposed as a promising anode material. To optimize the design of such and similar Si/C composite electrodes an in-depth understanding of their performance and chemo-mechanical degradations remains critical.

In this work, we analyze the performance of electrodes composed of Si-based nanoparticles combining both electrochemical characterization and multi-scale modeling. The Si-based nanoparticles are synthesized in a two stages laser pyrolysis reactor, which allows to obtain carbon coated silicon nanoparticles in one single step, mitigating oxidation and particle degradation [1]. The techniques also allows to control the particle size and the coating thickness, and both crystalline and amorphous silicon core have been synthesized. Several electrochemical techniques such as GITT, galvanostatic cycling and Electrochemical Impedance Spectroscopy (EIS) have been used to characterize the battery performance and to provide physical parameters to a mathematical model of the Si electrode based on the porous-electrode theory [2]. In particular, the EIS study, carried out at various cell states of lithiation of Si material, allows to track the evolution of several critical parameters of the mathematical model (figure 1). For non-coated nanoparticles, the results shows that the lithium ion concentration at the electrolyte/particle interface drops drastically after 30% of lithiation, while the SEI resistance seems to breathe, being maximum between 40% and 80% of lithiation. Experimental and modeling results suggest significant heterogeneities through the electrode thickness in term of particles state of lithiation as well as electrolyte ionic concentration, caused by Si large volumic expansion and competition between insertion and diffusion processes.

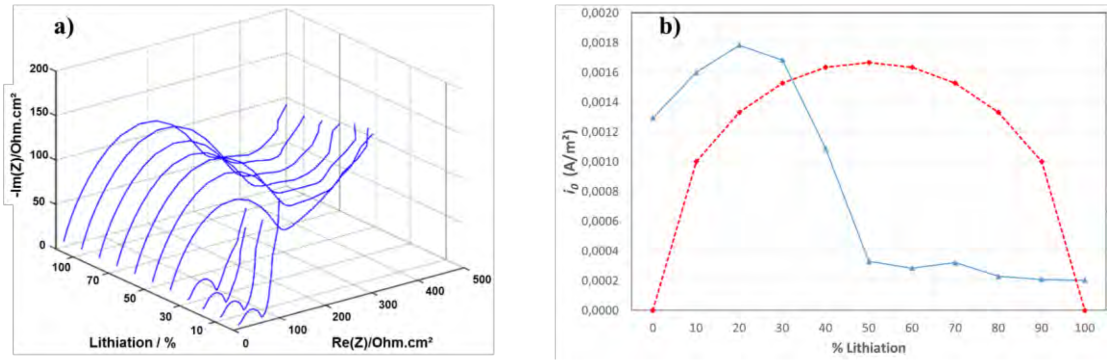

Figure 1:a) Impedance spectra during the lithiation of a non-coated crystalline silicon electrode and b) exchange current density (i_0) calculated from spectra fitting (solid blue) compared to theoretic evolution of i_0 according to the Butler-Volmer equation (dotted red)

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ORR and OER in Li^+-Containing DMSO: Further Mechanistic Insights and the Action of Redox-Mediators as Probed by DEMS

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The underlying mechanism of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in Li^+-containing electrolyte is still not fully understood. To add to the mechanistic picture, the dependence of the ORR and OER on the oxygen concentration have been examined using the rotating ring-disc electrode assembly (RRDE) for different electrode materials (gold, glassy carbon and platinum). One advantage of this method is that the contribution of superoxide formation, which is considered to be soluble, and that of peroxide formation, which is insoluble, to the overall current can be separated: The ring current is expected to be only due to the oxidation of superoxide. While the electrochemical reaction order with respect to oxygen is close to unity for the superoxide formation, it is significantly lower for peroxide formation, indicating adsorption phenomena or a nucleation hindrance (1). Astonishingly, the amount of peroxide deposited on the surface does not vary too much with the oxygen concentration or rotation rate. Furthermore, additional evidence for the occurrence of a direct reduction of oxygen to peroxide at gold electrodes has been found investigating the rotation dependence of the collection efficiency via Damjanovic's diagnostic equation (2).

The extent of superoxide formation, which somewhere in the electrolyte disproportionates into peroxide, depends on potential, the electrolyte composition and possible additives.(3, 4) To make such peroxide particles reoxidizable, soluble redox mediators were introduced. For the experiments with redox mediators a new thin-layer cell for DEMS experiments with an in situ oxygen saturation in the working electrode compartment has been constructed. This cell has an electrode area to electrolyte volume ratio comparable to batteries. Therefore it could be used to investigate the stability of electrolyte systems for metal-air batteries. In this study, the activity of tetrathiafulvalene (TTF) (5) and LiI (6) was compared. The thin-layer cell enables the direct, mass-spectrometric observation of evolved oxygen parallel to the oxidation of the redox mediators. In the case of TTF, it was found that small concentrations of TTF^+ in the cell volume are sufficient to observe higher ionic currents for oxygen evolution as compared to the OER in absence of TTF^+. After the redox mediator activity starts an increase of the number of electrons transferred per O_2 molecule is observed for higher overpotentials which leads to the conclusion, that parasitic secondary reactions take place at higher overpotentials. In the case of LiI the electron number is close to 2 e^-/O_2 for the whole potential window of the redox mediator activity which is in agreement with the oxidation of Li_2O_2.

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Simplification Of The Porous Electrode Theory For An Efficient 3D Isothermal-Electrochemical Lithium-Ion Battery Model

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The porous electrode theory has been used for modeling lithium-ion batteries since the first works of Newman's group[1,2,3]. Since then, several publications have been written providing improvements to those original models. They deal with the numerical analysis of salt concentration and potential distribution in the solid active particles, in both negative and positive electrodes, and in the electrolyte of both electrodes and the separator. Nevertheless, the completeness and complexity of the model result in a heavy numerical code demanding a huge computing time. Therefore, most of these models have been implemented just in 1D.

In this work we propose a set of simplifications on the governing equations, deduced from porous electrode theory for lithium-ion batteries, in order to obtain a reduction in the computational time used for finding time dependent profiles of potential and salt concentration in the electrolyte of both electrodes and the separator. Instead of solving numerically the partial differential equations in the electrolyte, proper simplifications gave the chance to find analytical solutions.

It is important to point out that the made simplifications were always carried out taking into account the physics of the battery, which provided a well posed frame of reference for the new governing equations. Results show that good and proper approximations can be obtained with such considerations reducing computational time importantly.

Although the model can be adapted to different chemistries in the electrodes, for this work graphite was considered as negative electrode and a NMC type as positive electrode.

Finally, a set of 1D domains -where the 1D model was solved- were coupled with two surfaces (representing metallic collectors) generating a 3D model that provides the potential distribution in the collectors and allows distinction of local battery behavior.

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Charge transport limitations in hierarchical composite electrodes of lithium-ion batteries

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Despite the significant benefits that offer Li-ion batteries as an energy storage system, the electrode technology suffers of limitations with regard to the power and energy densities. As a result, 50% of batteries weight and volume are non-electroactive parts (collectors, separators, electrolyte). The limitations mainly originate from charge transport in these complex and hierarchical materials. The present study aims at better understand the strong interactions existing between the liquid electrolyte and the materials of the composite electrode. Our study presents the charge transport characterization at different scales, from electronic to ionic, by combining a high-frequency analysis performed by ex- and in-situ broadband dielectric spectroscopy[1] (BDS, up to 10 GHz), with a low-frequency analysis performed by electrochemical impedance spectroscopy[2] (EIS, down to 1 mHz). In particular, we focused our study on the limitations occurring at the carbon black/electrolyte interface. To do so, we substituted the active material ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ or $LiFePO_4$) by an insulating compound (e.g. γ-Al_2O_3). The electronic percolation threshold and the kinetics of impregnation by the electrolyte have been determined with respect to the carbon black content in the composite electrode (see Figure). The various contributions were assigned and modelled. In addition, the morphology as well as the porosity/tortuosity effects on the ionic mass transport will be discussed.

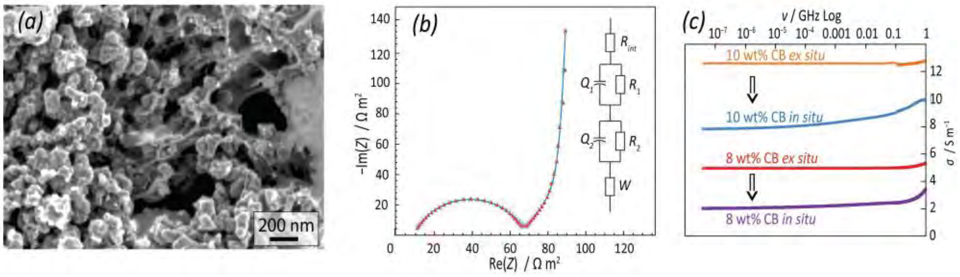

Figure : Characterization of a γ-Al_2O_3/PVdF/CB. (a) SEM micrograph, (b) electrochemical impedance spectrum and (c) broadband dielectric spectroscopy ex-situ (dry samples) and in-situ (samples wetted by the electrolyte) measurements.

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H_2 Generation by Electrocatalytic Oxidation of SO_2

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The sulfur hybrid cycle (HyS) is a process that can be used to electrochemically generate H_2 from electrolysis, but using a lower voltage (0.158 V) than water decomposition (1.229 V), by using the oxidation of SO_2 to H_2SO_4 as the counter reaction of interest[1,2]. HyS is called a hybrid cycle because it consists two steps, the thermal one, that is the generation of SO_2 by thermal decomposition of H_2SO_4 and the electrochemical one[1]. This work presents the study of SO_2 oxidation in H_2SO_4 0.50 mol L^{-1} using different catalysts, aiming to contribute to the optimization of HyS.

SO_2 from Air Liquid, was bubbled for 30 min in H_2SO_4 (suprapur) solution. The working electrodes were Au and Pt disks, a Pt mesh and SCE as counter and reference electrodes respectively. The systems were studied by cyclic voltammetry (CV) in static and hydrodynamic conditions (rotating disk electrode – RDE).

Previous calculations[3] suggested that the oxidation of SO_2 onto Pt should take place at less anodic overpotential than onto Au, both electrodes presenting the same pathway: oxidation by chemical steps, with the metal oxides as oxidants and oxygen donors[3]. So, it is expected to obtain the same CV shapes for both electrodes, differing just by the potential, but it was not the case. When Au electrode is used, the oxidation started at more cathodic conditions than the surface oxidation itself, which can be an indication that the mechanism for the reaction onto this catalyst would be different, involving at least one direct electron transfer process between the SO_2 and the surface. Also, a well-defined oxidation peak was observed onto Pt while onto Au a peak followed by a plateau was observed.

Both systems presented an increase of current proportional to the scan rate, but especially for the Pt electrode, the potential peak was shifted to more positive values, strongly indicating activation control.

For a better understanding of the diffusion dependence of this process, the RDE technique was used. The rotation rate was varied and CV experiments, at a constant scan rate, were performed. For the Pt catalyst, not many changes were observed, just a small increase of current and a small shift to more negative potentials, corroborating the idea that the process being mainly activation controlled. For the Au electrode the results were pretty different, showing a well-defined diffusion limited region, allowing a better analysis of the reaction. Also, the conventional Koutékey-Levich plot was not the best linearization obtained. Instead, a linear $-j_L/f^{1/2}$ *vs.* j_L was obtained indicating a diffusion dependent chemical step influencing the charge transfer process.

It was possible to infer that the mechanism already proposed SO_2 oxidation[3] does not seem to be applied to all electrodes. Gold, expected to be the less active[3], presented a higher current density and a possible different pathway, since the oxidation started earlier than the oxide formation, even before than on Pt electrode.

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Oxygen Reduction in Alkaline Media – a Theoretical Study

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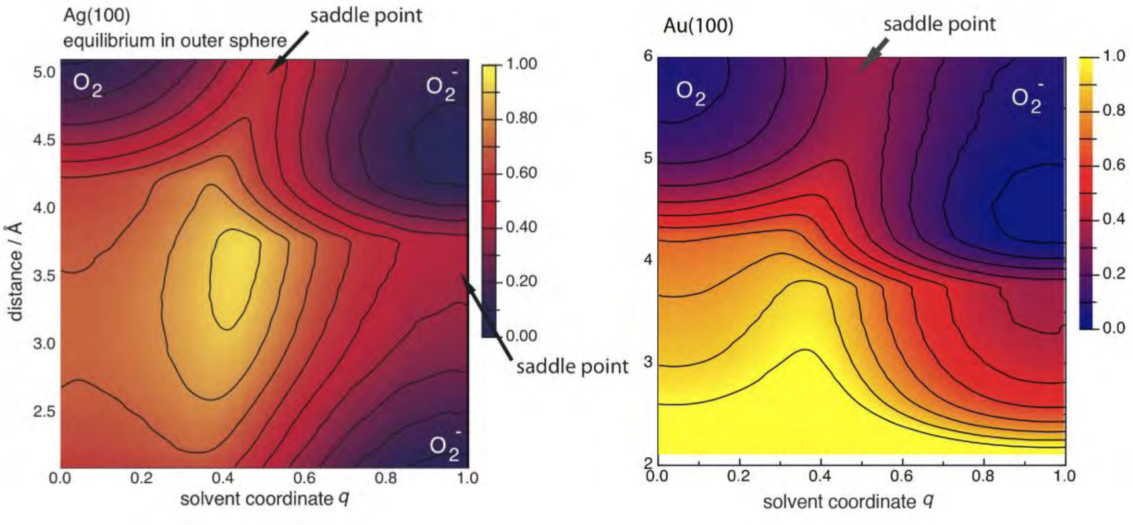
Oxygen reduction is slow and limits the efficiency of fuel cells. It is faster in alkaline than in acid solutions, and it does not require such expensive catalysts as platinum. Indeed, the fuel cells used by NASA in the Apollo mission were alkaline cells, and they proved to be reliable and efficient. However, the advent of the PEM gave an advantage to acid cells, which can only be reversed once a similar membrane has been developed for alkaline media.

Independent of any technological applications the mechanism of oxygen reduction is of great scientific interest. With focus on gold and silver electrodes, we propose a detailed mechanism of four electron transfer steps that reduce O_2 to OH^-. For each step we determine the reaction free energy and the activation energy as a function of potential by a combination of DFT and our own theory. The first and rate-determining step is:

$$O_2 + e^- \rightarrow O_2^-$$

which usually takes place in the outer sphere mode. We have calculated explicit free energy surfaces for Au(100) and Ag(100) (see figure); the activation energy is about the same on both metals. The subsequent steps involve reactions with water, and the generation of adsorbed OH. The latter is a crucial step and determines, if the reaction goes all the way to OH^-, or if it stops at peroxide. In particular we explain, why Au(100) is such a good catalyst, while on Au(111) the reaction stops after the transfer of two electrons.



Free energy surfaces for the reaction $O_2 + e^- \rightarrow O_2^-$ on Ag(100) and Au(100).

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Storage of Ions in Various Forms of Carbon – a Theoretical Investigation

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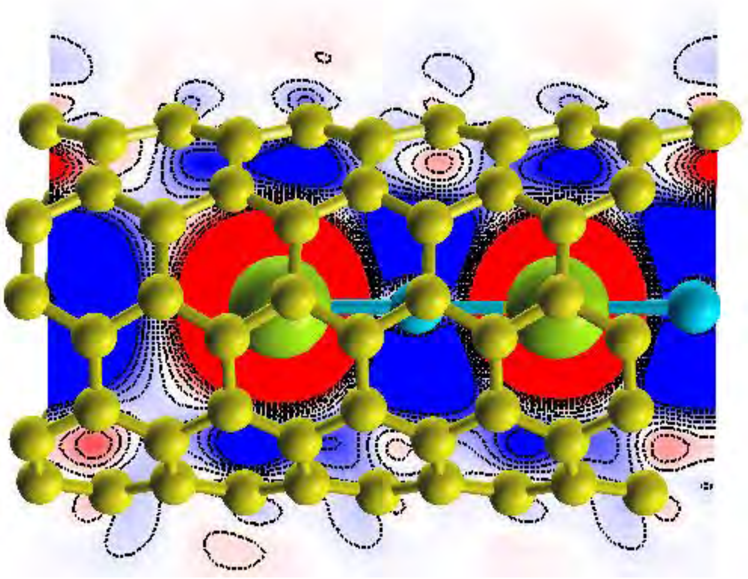
Various forms of carbon, such as graphite, graphene, or carbon nanotubes are excellent materials for the storage of ions in batteries and supercapacitors. In order to explore the interaction of ions with the carbon materials, we have performed DFT calculation for alkali and halide ions both in various kinds of carbon nanotubes (CNT) and between sheets of graphene by density functional theory; both chiral and non-chiral tubes have been considered. The atoms are stored in the form of ions; the transferred charge resides on the carbon in the form of an image charge; the concomitant charge transfer affects the band structure and makes originally semiconducting tubes conducting. The electrostatic interaction between a charge and the walls of the tube or the graphene sheets has been calculated explicitly. The insertion energies and the positions of the ions are determined by a competition between the electrostatic energy and Pauli repulsion.

A particularly intriguing problem is the interaction of ions within carbon structures. Following an idea of Kondrat and Kornyshev [1] we have investigated the Coulomb interaction between two ions in a carbon nanotube. It is strongly screened by the formation of image charges on the walls of the tube – see figure. Consequently, the energy of formation of cation-anion pairs within the tube is substantially reduced.

Intuitively one would expect that the interaction of ions *across the wall* of a tube, or across a graphene layer, is screened by the intervening carbon. Two Li+ ions on opposite sides should at best experience a weak repulsion. However, experimental evidence [2] suggests that in some circumstances the interaction can be attractive. We discuss the possible origin of this effect on the basis of our DFT calculations.



A chain of sodium (blue) and chloride (green) ion within a carbon (golden) nanotube. The red and blue colors indicate the positive and negative image charges induced in the carbon lattice.

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Hydrogen Oxidation on Nanostructures Electrodes – A Scenario on Stepped Silver Surfaces

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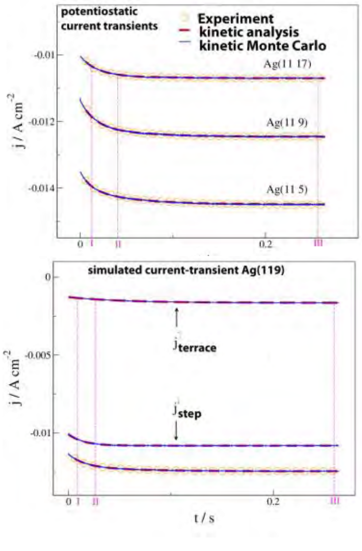
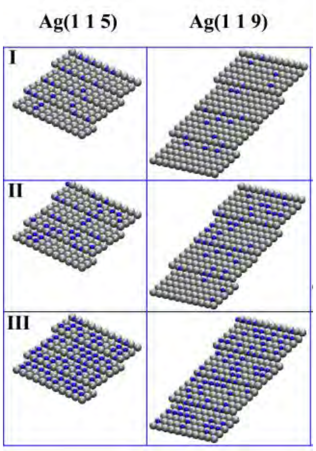
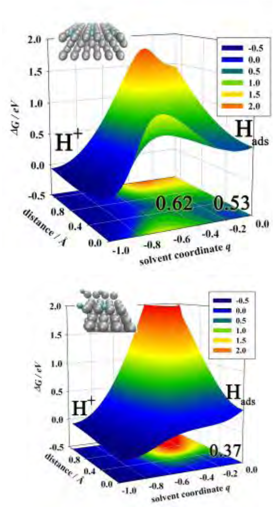
The fuel cell is a promising alternative for the development of new methods of production, conversion, and storage of clean energy. It employs a device in which hydrogen, through reaction with oxygen, produces water and heat as the only products. However, there are still many problems to be solved to ensure that hydrogen-based systems become a competitive force. It is a challenge to describe the hydrogen reactions (evolution and oxidation) in an electrochemical environment. We chose silver because this material shows an intermediate reactivity, and are therefore well suited to investigate in detail different effects. The use of well-defined stepped surfaces has early been recognized as an approach to understand the behavior of nanoparticles. Within this scenario, we have focused on the hydrogen reactions using different approaches. Experimentally, we obtained the kinetic parameters for the Volmer and Heyrovsky steps by potentiostatic current transients. The energetics for the adsorption on different sites and the electronic interactions with the electrode were obtained by Density Functional Theory calculations. The electrochemical environment (electron transfer) was described by the electrocatalysis theory [1,2]. The reorganization of the solvent when the proton approaches the surface was modeled by steered-molecular dynamics (SMD) simulations using a canonical ensemble (constant NVT). Finally, kinetic Monte Carlo (KMC) simulations were performed to obtain the nanoscopic description of the reactions on step and terrace sites.

After this detailed analysis, we can understand which are the most important issues involved in the electrocatalysis of the hydrogen reactions. The sites at the steps are considerably more active than those on the terraces. In this case, the rate constants for both Volmer and Heyrovsky on steps are more than two orders of magnitude larger.







kinetic Monte Carlo Simulations

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The role of polysulfides in Li-S batteries

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Li-S batteries are considered as a next generation of post lithium ion batteries with improved energy density. Electrochemical reactions in the Li-S batteries are multistep reactions with at least 2–3 equilibrium states. Different equilibrium steps can be correlated to a different degree of polysulfide dissolution and to the parasitic reactions which are determining life time in the Li-S batteries. By understanding the mechanism of the electrochemical reactions and by understanding the influence of different parameters one can introduce appropriate modifications in components design which can effectively suppress or completely stop polysulfide migration or even their formation. The ideal solution would be a system with a direct conversion from sulfur to Li_2S and backwards. Other options are trapping of polysulphides in the porous matrix or/and iono selective membranes with selectivity only for lithium. In this talk a special attention will be paid to development of different components within the battery. Additionally, mechanism(s) of Li-S battery operation will be discusses based on the analytical work using operando XAS, EIS and UV-Vis measurements.

Acknowledgements:

Access to synchrotron radiation facilities of ELETTRA is acknowledged. This research has received funding from the Slovenian Research Agency research programs P1-0112, P2-0148, and the European Union Seventh Framework Programme under grant agreement No. 314515 (EUROLIS) and No. 666221 (HELIS)

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A Comparative Study of the Effects of Metal-Support Interactions on Oxygen Reduction on Pt and Pd Nanoparticles

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The electronic properties of an active metal may alter adsorption energies, which, in turn, would affect the catalytic activity for electrochemical reactions involving adsorbed reactants and/or intermediates. In this work, we analyze the variations of the electronic occupancy of the active metal d band, which is the relevant band for adsorption processes, promoted by metal-support interactions and their influence in the electrocatalytic activity for oxygen reduction. Pt and Pd nanoparticles were prepared by a modified polyol method directly onto nanopowders of transition-metal oxides that were added to the reaction medium. After separation and washing, these materials were mixed with Vulcan XC-72 carbon to obtain the catalysts. The electronic occupancy of the active metal d band was studied by *in situ* X-ray absorption spectroscopy for all catalysts containing Pt nanoparticles. Because of the low energy of the Pd L3 edge, experiments for materials containing Pd were carried out in vacuum using soft X-rays energy. Results show that different transition-metal oxides have different effects on the electronic occupancy of the metal d band, indicating that charge transfer is in some cases from the oxide to the metal and in others from the metal to the oxide. XPS analysis showed that for the catalysts investigated in this work metal-support interactions are not strong enough to significantly change the binding energies of core level electrons. The reduction of oxygen was studied by polarization curves taken in O_2-saturated 0.5 M H_2SO_4 solution by the rotating ring-disk electrode technique. In a general manner, results show that the catalytic performance, assess by the kinetic current density at 0.9 and 0.8 V (RHE) correlates well with the electronic occupancy. In the case of Pt, the oxygen reduction activity is enhanced by transition-metal oxides that promote an increase in the 5d band electronic occupancy. The charge transfer effects are different for Pd. In general, data shed new light on the role of electronic effects on oxygen reduction electrocatalysis.

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In situ monitoring of elastic properties of common binders via electrochemical quartz microbalance with dissipation and dilatometry

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The cycling performance of composite lithium ion batteries and hybrid supercapacitor electrodes is strongly influenced by significant dimensional changes (deformation) of the active electrode material while the reversible lithium ion intercalation and deintercalation.[1,2] Typical composite cathodes are composed of an active material (i.e., lithium iron phosphate) with conductive additives and a polymeric binder.[3,4] Dimensional changes apply stress not only on the active material, but also on the binder. The viscoelastic properties of the different binders in a certain electrolyte influence the swelling and shrinkage.[5] We employ a new complementary approach of a non-invasive in-situ monitoring of the dimensional changes via electrical quartz crystal microbalance with dissipation monitoring (EQCM-D) and electrochemical dilatometry.[6] This approach combines in situ probing of single-particle effects measured with EQCM-D and bulk in operando testing on composite electrodes via electrical dilatometry measurements over several orders of magnitude.

The monitoring of elastic properties of three different polymeric binders was carried out in an aqueous electrolyte (0.1 M $LiSO_4$). While monitoring EQCM-D using a hydrodynamic admittance model, we can see changes in frequency and dissipation during cycling voltammetry which are related to single particle effects. Measuring the same system with in situ dilatometry, we can see an average effect of the bulk electrode, which results in dimensional changes less for rigid binder types and much larger for soft ones. We find the combination of both, EQCM-D and dilatometry, as a unique tool to track the structural behavior of the binder in-situ and non-invasive during (de-)intercalation of Li ions into lithium iron phosphate composite electrodes.

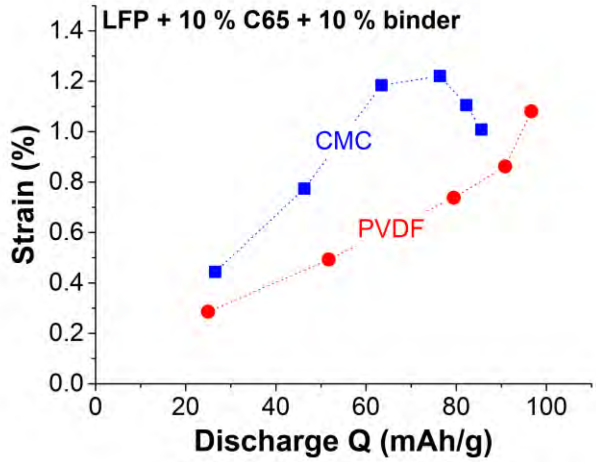

Figure 1: Behavior of binder influences the properties of the composite electrode

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Microscopic, Spectroscopic and Electrochemical Properties of Nanocomposite Li_2MnSiO_4/Al_2O_3: a Promising Lithium Ion Battery Cathode

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Lithium metal orthosilicates attract great attention as high capacity cathodes for new generation Li-ion batteries due to the possibility of exchanging more than one Li-ion per redox-active transition metal ion. However, the capacity of Li_2MnSiO_4 is not fully exploited in practical galvanostatic tests due to its low intrinsic electronic conductivity and the instability of the delithiated material which causes excessive polarization during cycling [1-3]. In this research, Li_2MnSiO_4 nanoparticles were prepared hydrothermally followed by a coating process with Al_2O_3 nanoparticles through a wet chemical pathway. Morphological, phase compositions and the surface chemistry of the synthesized materials were investigated using High Resolution Scanning and Transmission Electron Microscopies (HRSEM, HRTEM), X-Ray Diffraction (XRD), Solid-State Nuclear Magnetic Resonance (SS-NMR) Spectroscopy and X-ray Photoelectron Spectroscopy (XPS). Electrochemical measurements were conducted using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). Morphological and XRD studies revealed spherical particles and a $Pmn2_1$ orthorhombic crystal pattern for the pristine Li_2MnSiO_4 and nanocomposite Li_2MnSiO_4/Al_2O_3, respectively. Electrochemical studies of the materials in aqueous 1 M $LiNO_3$ electrolyte showed higher charge and discharge capacities of 209 mAh/g and 107 mAh/g for the nanaocomposite cathode material over 159 mAh/g and 68 mAh/g for the pristine material. CV results showed the diffusion of Li^+ ions to be higher in the nanocomposite cathode material with a coefficient of $3.06 \ x10^{-6} \ cm^2s^{-1}$ compared to that of the pristine material at $6.79 \ x \ 10^{-7} \ cm^2s^{-1}$. This enhanced performance can be ascribed to the uniform Al_2O_3 surface coating which considerably reduced the structural instability intrinsic to the pristine Li_2MnSiO_4 cathode material and improved the charge transfer kinetics.

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From End-of-life Lithium Based Batteries to Lithium Value-creation by a Green Innovative Electrochemical Process

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Lithium supply and its price in the future is expected to be impacted by a number of factors, such as additional demand from consumer electronics (cellular phones, laptop, remote controllers, digital cameras…), geo-political relationships, environmental impact of mining, new modes of mobility solutions gaining large acceptance such as electric two-wheelers or vehicles. Recycling lithium is consequently essential to avoid harmful substances in the environment, to recover some valuable elements having scarce natural resources or to limit the risk due to the accessibility of the raw material available only in a specific geography.

In this context, a process of cation recovery, based on their intercalation properties into a host matrix was developed. It consists in a selective extraction of a cation from a source electrolyte (spent batteries leachates, industrial effluents…) to a recovery electrolyte, separated by an Electrochemical Junction Transfer (ETJ) by a galvanostatic regulation [1]. The ETJ is composed of a porous support coated with a slurry of a host matrix and binder. The global phenomenon of intercalation, diffusion and de-intercalation is represented by the reaction:

$$[Li_{1-x}RH] + x\ e^- + x\ Li^+ \leftrightarrow [LiRH]$$

The amount of lithium possibly recovered is directly linked to the surface of junction and the applied current density.

First studies concerned the choice of the appropriate host matrix for lithium intercalation ($LiCoO_2$, $LiWO_3$, $LiMn_2O_4$, $LiFePO_4$…). Then, different parameters were investigated: selectivity towards other cations (Na^+, K^+…), chemical and electrochemical stability in different media (acidic, basic, containing metallic cations, different kinds of anions…). The spinel $LiMn_2O_4$ was finally selected.

After this analytical study, the transfer from synthetic solutions (Li_2SO_4 or $Li_2SO_4/CoSO_4$) was performed successfully [2], whereas the transfer from industrial leachates evidenced some problems. After chemical or thermal pre-treatments, the recovery of lithium from such leachates becomes possible. The black mass (batteries crushed) was thermally treated for 3 days at 500°C and the leachate was basified with soda to pH=5[3]. The global transfer yield and the selectivity rate were near 100% with a current density of 5 mA/cm² (or 50 A/m²).

The second step was scaling-up to be compatible with the considered applications. A surface of about 1 m² was required. Larger porous supports were produced by a new process based on additive manufacturing allowing some advantages (no shape restriction, controlled micro-porosity…). The target area of 1 m² was reached by accumulating 20 cells of 1/20 m². First experiments on this larger surface showed a selectivity of about 100%, a transfer yield above 90%.

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Stable carbon cathodes for potassium-oxygen batteries

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Among energy storage technologies beyond lithium-ion, alkali metal-oxygen batteries stand out for their unparalleled theoretical energy densities. Based on the reaction between dioxygen and alkali metal ions in non-aqueous electrolytes, metal-oxygen batteries could store up to 10 times more energy per unit mass (in the case of Li-O_2) when compared to today's lithium-ion batteries[1]. Despite extensive efforts elucidating the mechanism of the reaction between alkali cations and dioxygen, this technology is still far from maturing into a commercial device. The main drawbacks of Li-O_2 systems are electrolyte and cathode instability, low conductivity of lithium peroxide (Li_2O_2) leading to poor cycleability. In contrast to Li-O_2, potassium-O_2 discharge reactions proceeds via a one electron reduction leading to potassium superoxide (KO_2) as the sole discharge product[2]. Here, different carbon based cathodes were investigated in K-O_2 cells. Furthermore the stability of the K metal anode with different non-aqueous electrolytes were compared. The cell capacity varied depending upon the cathodic carbon structure employed (Fig. 1a). KO_2 was the only discharge product identified via Raman spectroscopy (Fig. 1b) and powder X-ray diffraction. FTIR spectra taken of the cathodes after first discharge, showed no evidence of carbonate species or other parasitic reaction products.

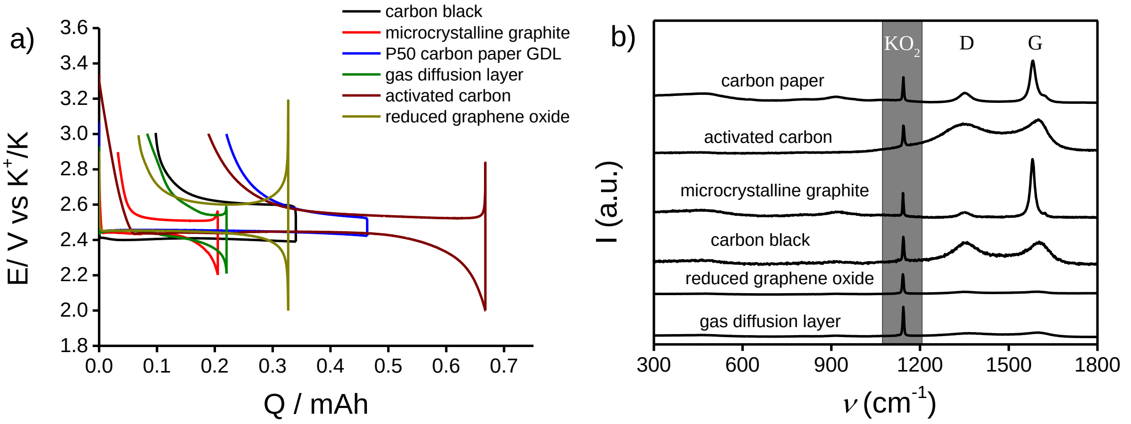

Figure 1. a) Discharge and charge potential hysteresis for potassium-oxygen cells with different carbon cathodes (rate 120 μA cm^{-2}). b) Raman spectra of discharged cells with different carbon cathodes.

These results are encouraging, since the large overpotential observed within Li-O_2 cells was found to be related to side reactions on the carbon electrode surface[3]. The voltage gap in K-O_2 cells was lower than 100 mV, and round trip efficiency, as high as 98%. The cycleability of the cells was found to be limited by side reactions between the potassium metal anode and ether-based electrolyte in the presence of dioxygen reduced species, rather than side reactions within the carbon cathode. The main components of this insulating anode surface layer were K_2CO_3, KOH and KO_2. Similar anode surface layer composition was found for different combinations of ether electrolytes and potassium salts. However, while using super-concentrated electrolytes (3M and 5 M KTFSI in dimethoxyethane), O_2 crossover was inhibited, and no KO_2 was detected on the potassium metal anode surface. As a result, these cells were able to be cycled over 50 times under shallow cycling of 50 mAh/g. The superconcentrated electrolytes had no effect on the cathode reaction product, and the battery cycled through KO_2 formation and oxidation. Capacity fade eventually occurred, as repetitive stripping/plating of K metal anode caused the disruption of the protective layer. This work highlights that once a suitable electrolyte has been selected, a metal-O_2 cell can indeed be cycled numerous times. The challenge is to increase the cycleable capacity to more appealing values, whilst maintaining cell stability.

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Monitoring the Chemical and Structural Surface Changes on Single Particles of Commercial-Like Li-Ion Battery Electrodes

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Understanding the electrode/electrolyte interface evolution during cycling as well as the surface structural change of the active materials is crucial to improve the safety and the life-cycle of Li-ion batteries. Despite all the significant efforts attempted to elucidate the nature and origin of the surface reactivity of the electrodes in liquid organic electrolytes, a fundamental knowledge is still lacking to definitively assess the various mechanisms taking place with respect to the applied voltages. The lack of agreement in the reported findings is caused mainly by the surface complexity of the commercial electrodes (multiple particles, high roughness, and porosity) and by the intrinsic limitations of the commonly used surface characterization techniques (poor lateral resolution). Thus, in this contribution we propose the implementation of X-Ray Photoelectron Emission Spectroscopy (XPEEM) in battery research as a surface technique able to gain localized information on single particles of composite anode and cathode materials, while preserving their working environment (as in commercial-like electrodes). The unique combination of the high lateral resolution and the spectroscopic capabilities confined within the depth analysis range of 3-4 nm will finally provide the missing piece of the exact mechanism of the electrolyte/electrode interactions. The surfaces of two types of electrodes are investigated and will be presented, $Li(Mn,Ni,Co)O_2$-Li_2MnO_3 (NCM) and $Li_4Ti_5O_{12}$ (LTO), as promising positive and negative electrodes, respectively, for Li-ion batteries. A systematic study of the potential dependency of the surface evolution was performed during the early stage and after long cycling. The contrast images in Figure 1a,d attest the good lateral resolution of the XPEEM and its capability to localize the different particles present on the surface. The local XAS spectra (Figure 1b) at the Mn-L edges acquired on NCM particles allow monitoring its oxidation states and the surface structure modification as confirmed by the reduced Mn after full delithiation. At the same time the C-K edge provides direct information regarding the chemical change and the electrolyte decomposition. Thanks to the XPEEM, valuable knowledge was accumulated, providing better insight on the mechanism of the electrolyte/electrode interaction on the positive and negative electrodes. Moreover, the origin of the surface layer present on LTO as well as the oxidation states of the dissolved transition metals were elucidated, alongside the impact of the high potential on the NCM structure stability.

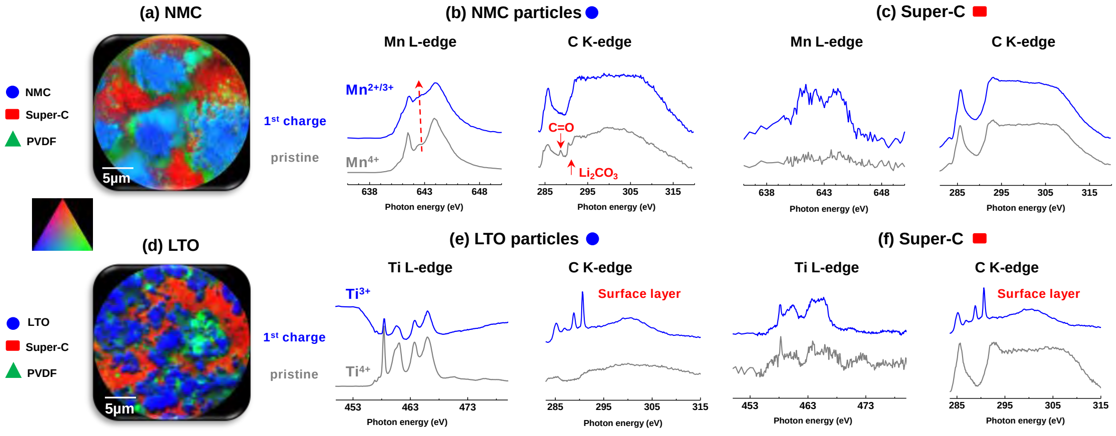

Figure 1: Element-specific XPEEM contrast images performed on (a) NCM and (d) LTO pristine electrodes. Local XAS evolution upon the delithiation of the NCM performed at the Mn-L edge and C-K edge acquired on (b) NCM particles and (c) carbon particles. Local XAS evolution upon the lithiation of the LTO at the Ti-L edge and C-K edge acquired on (e) LTO particles and (f) carbon particles.

High-performance Silicon Anodes Using Ionic Liquid as Electrolytes

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Nanostructured silicon (Si) is a promising anode for the next-generation of high-energy lithium-ion batteries [1,2]. An important issue for the implementation of silicon is the control of the chemical reactivity at the electrode/electrolyte interface during lithiation and delithiation [3]. Given their relevant physicochemical properties, such as high stability, good transport properties and nonvolatility, modulated by changing the cation or anion, ionic liquids (ILs) hold the possibility to alleviate the instability of the solid electrolyte interface (SEI) layer due to the large volume changes of Si upon cycling. Here, we report the performance of triethyl-n-pentylphosphonium bis(fluorosulfonyl)imide (P_{2225}FSI) and bis(fluorosulfonyl)imide N-methyl-N-butylpyrrolidinium (BMPYRFSI) ILs as outstanding electrolytes for Si/PAN composite electrode. The Si/PAN electrode was prepared by using a published procedure [2]. After 1000 charge/discharge cycle, these composite-IL systems exhibit a specific charge capacity of about 1000 mAh g^{-1} attained at 1.0 A g^{-1} with a coulombic efficiency approaching 100%. Such performance makes these electrolytes promising materials for use in lithium-ion battery.

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Platinum Group Metal-Free Catalysts Integration in MEA: Catalytic Layer Design for PEMFC and AEMFC

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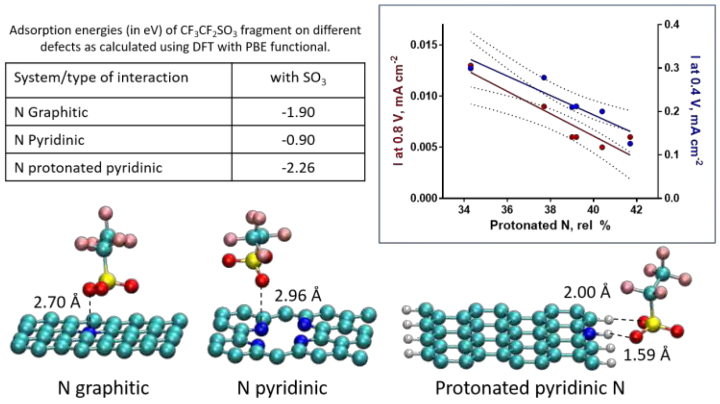
Over the last decade, our group has been developing a new type of platinum metal-free (PGM-free) catalyst based on the sacrificial support method (SSM). The oxygen reduction reaction (ORR) catalysts of metal–nitrogen–carbon (MNC) type developed at UNM has reached the level of industrial scale-up and deployment as the first commercially available PGM-free cathode catalyst.[1] Applications of such MNC catalyst in proton-exchange membrane fuel cells (PEMFC) and anion-exchange membrane fuel cells (AMFC) requires the development of technology for membrane / electrode assembly (MEA) design with different approaches in making catalyst layers. We assume that the active sites in these catalysts (we consider that there are multiple, chemically different but kinetically similar active sites[2]) include atomically dispersed Fe (II), integrated into a graphene-like carbonaceous “backbone” and incorporated in it trough association with pyridinic N defects.[3] It is necessary to understand the effect of the interaction of ionomer and catalyst at the active site (micro-scale), morphology (meso-scale) and layer structure (macro-scale) level. Such understanding will help us fill the gap between understanding activity and durability parameters as well as chemical and morphological changes that occur inside the catalyst layer during the oxygen reduction reaction in an operational fuel cell.

In this paper, we will present a series of MNC electrocatalysts synthesized by SSM and their performance in MEA. Surface chemistry of the electrocatalysts and catalyst layers is studied by XPS. The types of N and Fe-N functionalities that are present in these materials are in-plane defects such as graphitic N and edge defects, such as hydrogenated, pyridinic or protonated N as well as Fe-coordinated to two, three or four N defects resulting in Fe-N_2, Fe-N_3 or Fe-N_4 sites. In the catalyst layers, overall activity is affected by the interactions of the active site(s) with negatively charged sulfonate group of Nafion or positively charged quaternary ammonia group of the anion-exchange ionomer.



Adsorption energies (in eV) of $CF_3CF_2SO_3$ fragment on different defects as calculated using DFT with PBE functional.

System/type of interaction	with SO_3
N Graphitic	-1.90
N Pyridinic	-0.90
N protonated pyridinic	-2.26

DFT calculations were used to evaluate the strength of the interaction between different types of nitrogen-containing defects and sulfonate groups and to calculate binding energy shifts of N1s spectra upon ionomer binding (see Fig.). It was found that protonated N defects ani-correlate with the MEA performance.

The pore structure is critical in oxygen and water transport in the catalytic layer. The change in pore structure induced by the chemical changes introduced during fuel cell operation has to be understood in order to design PGM-free electrocatalyst with highest possible lifetime. The morphology of catalyst layers has been analyzed by focused ion beam/scanning electron microscopy (FIB-SEM) sectioning. Evolution of structural parameters such as: surface area, porosity, connectivity will be discussed in the context of catalysts degradation and fuel cell durability.

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Mesostructure-performance relationships in rechargeable batteries: challenging the dogma with multiscale computations and immersive visualization

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Optimized design of composite electrodes for batteries is recognized to be of crucial importance, in particular to reach automotive application expectations in terms of performance gain and cost reduction. Such electrodes are currently made of active material or catalysts, additives and binder and the resulting complex porous structure contains an electrolyte. Several conceptual pictures have been developed attempting to capture the influence of these composite electrodes structural properties on the overall cell response: approaches consisting of building up artificial structures capturing the main features of the actual electrodes and approaches based on computer-aided reconstruction of the electrode structure. These two approaches have provided progress on the understanding of batteries operation, but there is still a significant lack of understanding of their structural features (e.g. exact location of the binder) and the impact of the three-dimensional structural anisotropies on the effective transport properties at multiple scales, from the pore and/or particle to the percolated aggregates and/or agglomerates. Defining an appropriate structural picture for the composite electrodes is crucial for a correct interpretation of experimental characterizations but also for optimizing the full cells.

In this lecture I discuss novel computational modeling approaches describing the interplays between electrochemical and transport processes at multiple spatial scales.[1,2] The predictive capabilities of these approaches on establishing and optimizing electrode mesostructure-performance relationships are presented within the context of three application examples:

- discharge and charge mechanisms in Li-O_2 batteries;[3,4,5]
- cyclability of Li-S batteries;[6]
- discharge of lithium ion batteries with Si/C suspensions electrodes.[1]

Finally, the tremendous opportunities opened by the combination of these models with three-dimensional immersive Virtual Reality software for data analysis are discussed on the basis of our recent experience on integrating these aspects in our teaching activities at the University of Picardie Jules Verne within the Master Programme M.E.S.C.[7]

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Understanding Water Management in Polymer Electrolyte and Anion Exchange Membrane Fuel Cells through *in-operando* X-ray Computed Tomography

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For polymer-electrolyte fuel cells (PEFCs) and anion exchange membrane fuel cells (AEMFCs) effective water management is critical, especially at lower operating temperatures. During start-up and at operating conditions, where water is present in a liquid form water can block reactant delivery to electrocatalyst sites, resulting in significant mass-transport losses, flooding and associated cell low power densities. Using synchrotron X-ray computed tomography (CT) we have previously shown the dependency of water transport properties on porous materials morphology and chemical composition, as well as cell compression.[1-3] These *ex-* and *in-situ* studies isolate specific porous membrane / electrode assembly (MEA) component's effect on water management (such as micro-porous (MPL) or gas-diffusion layer (GDL)). Addressing and understanding water transport issues, however, is made possible only by introducing the capabilities for *in-operando* tomography.

In this work *in-operando* single serpentine channel (1x1 mm) fuel cell testing hardware (see Fig. 1) for synchrotron X-ray CT was designed with active area of 1 cm^2. Steady-state water generation and removal is observed in PEFCs and AEMFCs for temperature of 30°C with chronoamperometric holds at current densities ranges of 20 – 100 mA/cm^2. Furthermore, comparison of water distribution in PGM and PGM-free catalysts for both type of fuel-cells will be presented. Conditions studied also include varying GDLs and reactant flow-rates. In all of these systems water pooling was observed at the component interfaces, where larger voids were present due to specifics of fabrication methods.

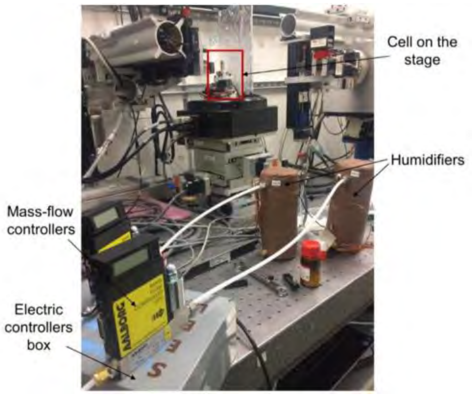

Fig. 1. Experimental set-up at the Advanced Light Source at DOE Argonne National Laboratory.

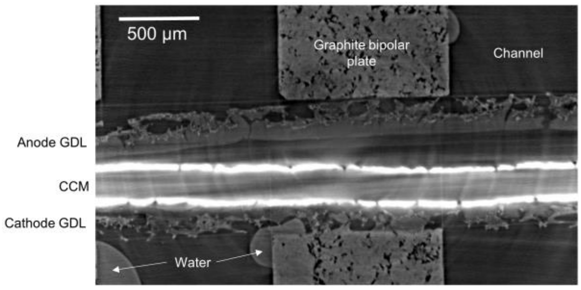

Fig. 2. Cross-section tomograph of in-operando PEFC at 30°C, 50 mA/cm^2, air- H_2 at 0.1 slpm.

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Robust benzimidazole based electrolyte overcomes high-voltage and high-temperature applications in 5V class lithium ion batteries

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Electric vehicles (EV) will be the key to dominate the next generation of transportation. In order to obey the power requirement of EV, lithium ion battery used in high temperature and high voltage suffers great challenge. One of the specific problems is the electrolyte, the $LiPF_6$ and carbonates are not appropriate under extreme conditions. Lithium benzimidazole salt is a promising electrolyte additive that was used to stabilize $LiPF_6$ by Lewis acid base reaction. However, the imidazole ring is not eligible for the applications at high voltage owing to its resonance structure. In this research, electron withdrawing ($-CF_3$) and donating ($-CH_3$) substitutions on imidazole ring have been investigated. According to the calculation results, the CF_3 substitution facilitates high electron cloud density on imidazole ring structure in order to resist the electron releases from bezimidazole in oxidation (anodic) reaction. In addition, the CF_3 substitution is used to accept the electrons from lattice oxygen (O^{2-}) in lithium rich cathode and is great quantity converted to O^-, which accompanies the electrolyte reduction and forms SEI. Furthermore, the cycle performance tested at 60^{o}C and 4.8V conditions shows that the CF_3 substitution well maintains the battery retention and almost no fading compares with the blank electrolyte.

Understanding the ORR Reaction in Nitrogen-Doped Graphitic Materials

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Nitrogen-doped graphitic materials exhibit activity for the ORR, especially in alkaline conditions. Although the overpotentials are higher than those measured for the reference material (platinum) in the same conditions, there is still room for improvement of these materials. Thus, the understanding of the role of nitrogen atom in the graphitic network is a key element in order to design better electrocatalytic materials. For these materials, the nature of the sites and the mechanisms explaining the observed activity are still under discussion. The measured ORR activity has been mainly attributed to graphitic and pyridinic nitrogen. In this communication, we will explore by means DFT calculations, in combination with some experimental results using model materials, the role played by the nitrogen dopant. For the DFT calculations, it will be considered that the relevant step is the monodentate adsorption of oxygen on the material, since it is the initial step in the ORR mechanism. This adsorbed species can evolve to other intermediate species leading to the formation of water or hydrogen peroxide. Additionally, explicit water molecules have been included in the calculations. The hydrogen bonds formed between the adsorbed oxygen species and the water molecules are key elements in the stabilization of the adsorbed oxygen. Graphitic and pyridinic nitrogen dopants in a graphene lattice have been considered as model systems for these calculations. In all cases, a stable sate for the monodentate adsorption of oxygen has been found, provided that some requirements are fulfilled. First, the adsorption of oxygen always occurs in a carbon atom that is able to change its hybridization state from sp^2 to sp^3. This is only possible in a carbon atom neighboring a nitrogen dopant. Second, the studied system should be able to provide charge to stabilize the adsorbed state. This additional charge can come from an additional graphitic nitrogen dopant included in the graphene network or from the adsorption of a proton in a pyridinic nitrogen dopant and its neutralization. From all the studied configurations, the most active site is a carbon atom neighboring pyridinic nitrogen dopant (protonated and neutralized) located in an arm-chair border. The presence of a graphitic dopant in the graphene network further stabilizes the adsorbed state. If the pyridinic nitrogen dopant is located in a zig-zag border, the stabilization of the adsorbed monodentate oxygen molecule significantly decreases. An intermediate stabilization energy of the monodentate adsorbed oxygen between these two previous configurations is obtained for the adsorption on a carbon adjacent to a graphic nitrogen dopant with an additional nitrogen dopant in the lattice.

Thin Films of Si/Sn and SiO_2/SnO_2 as Model Anodes in Li-Ion Batteries: Understanding the Electrode/Electrolyte Interface Reactions

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The continuous need of Li-ion batteries with higher energy density has motivated the community to replace the current commercial electrodes with materials providing higher specific charge. In particular, the graphite-based negative electrode (theoretical capacity of 372 $mAhg^{-1}$) can be substituted with much higher capacity materials such as intermetallics- (i.e. Si, Sn, Sb) or oxide-based materials (i.e. SiO_2, SnO_2, ZnO)[1]. These materials show practical restrictions related to the low efficiency and the rapid fading during cycling caused by the volume expansion preventing their commercialization. In this context, fundamental understanding is required to elucidate the alloying reaction mechanisms and the various reactions taking place at the electrode/electrolyte interface. Owing to the complexity of the commercial-like electrodes composed of active materials, binder and conductive additives, the investigation and interpretation of the different interfacial reactions is very challenging.

Using thin film electrodes composed of only the active material is an effective method to simplify the system. Thin films lead to an enhanced adhesion at the current collector/active material interface, improving both the electronic conductivity and the mechanical stability of the active material. For X-ray photoelectron spectroscopy (XPS) surface analysis this is an ideal system because it avoids the signals interference from binder and conductive carbon additives by probing exclusively the active material/electrolyte interface reactions.

Based on this approach, we present a systematic study on various negative electrodes made of Si, Sn, SiO_2 and SnO_2 investigated during the early stages of cycling in organic electrolytes. Combining electrochemical characterization (Figure 1a) with surface techniques, such as postmortem XPS (Figure 1b) and scanning electron microscopy (SEM) (Figure 1c), we report the potential dependency of the intermediate phases formed during reversible reactions together with the mechanism of electrolyte decomposition and SEI formation/decomposition[2]. Among the accomplishments, the detection of the early lithiation of SnO_2 film forming Sn^0 during first charge, as well as the complete SEI dissolution from the Si surface after the first discharge. Thanks to this approach and work methodology, significant knowledge and understanding was achieved in the electrode/electrolyte interface and alloys reactions.

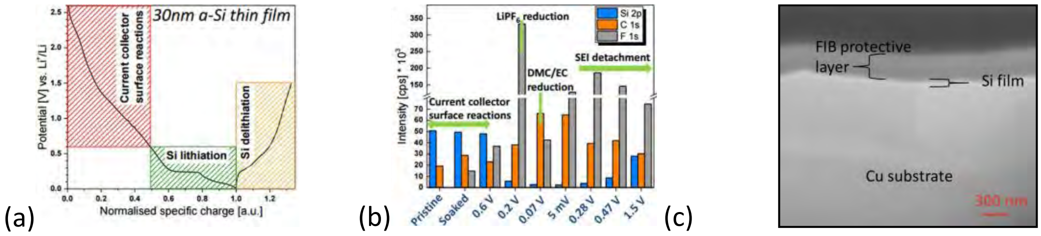

Figure 1 (a) First galvanostatic cycle of a 30nm a-Si film cycled at C-rate; (b) Evolution of the absolute intensities of different XPS core level peaks on a-Si electrodes cycled at different potential steps; (c) FIB-SEM on as deposited a-Si thin film on Cu substrate

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Direct Electrochemical synthesis of 3D-nanostructured titania anodes for high power Lithium Ion Batteries

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The rate capability of conventional electrodes in Lithium Ion Batteries (LIB) is usually limited by the low rate of the charge transfer reactions and long diffusion pathways. It could be shown that individual active material particles can withstand remarkably higher current densities in comparison with the conventional porous composite electrodes, enabling fast lithiation and delithiation reactions [1,2]. With respect to the electrochemical performance of the electrode, it is favorable to combine the advantages of individual particles (high surface, short diffusion length, high rate capability) and conventional electrodes (good manageability, high capacity). A promising approach is the synthesis of active material nanostructures in macroscopic dimensions by the application of electrochemical methods.

An auspicious material system of high impact is titanium dioxide, acting as anode material in LIBs. Armstrong et al. showed the excellent electrochemical performance of TiO_2 nanowires and nanotubes [3]. Nanotube arrays can be fabricated straightforward by anodic oxidation of titanium foils in fluoride containing electrolytes [4]. Moreover, the morphology of the nanostructures (e.g. pore diameter, wall thickness) and the thickness of the oxide layer are tunable by the variation of the experimental parameters. This includes the composition of the electrolyte, the process temperature as well as the electrochemical procedure.

In this work, the authors present the electrochemical synthesis of TiO_2 nanotube arrays by anodic oxidation. The influence of the anodization parameters, e.g. of the anodization voltage, the duration of the process, and the effect of voltage modulations, on the morphology of the nanostructures is shown. In that way TiO_2 nanotube arrays with a thickness of up to 10 µm and pore radii of down to 50 nm are prepared.

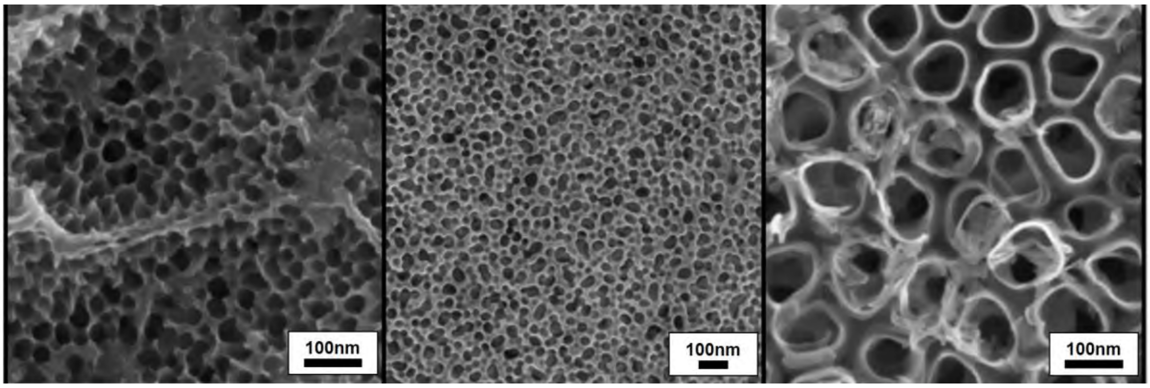

Fig.1: TiO_2 3D-structures with different morphologies, prepared by anodic oxidation.

Moreover, the suitability of the TiO_2 nanostructures as anode in LIBs is evaluated by half-cell tests of the anodically prepared specimen. A correlation between the morphology and the anode performance ought to be found.

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The Lithium-Ion Capacitor, an Internally Hybridized System Combining Advantages of Electrochemical Capacitors and Lithium-Ion Batteries

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The two main electrochemical systems which may be applied to store energy are lithium-ion batteries (LIBs) and electrochemical capacitors (ECs, called also supercapacitors). LIBs store the energy through redox reactions; for these reasons, they are characterized by a high energy density, moderate cycle life and power. In ECs, the energy is stored through electrostatic forces using high surface area carbon electrodes; owing to the surface charge storage, ECs display high power and long cycle life, yet their energy density is relatively low [1]. Consequently, ECs are perfectly adapted for applications requiring to harvesting energy in small amount during short time, for example during breaking of vehicles. Hence, enhancing the specific energy of ECs in order to broaden the spectrum of their applications is an important driver both for researchers and industry players.

In this context, internal hybridization appears as a key for opening a path to more versatile devices which can at the same time deliver high power and high energy, while being able to display a high cycle life. The best example is the lithium-ion capacitor (LIC) which implements an EDL positive electrode made from porous carbon and a LIB faradaic negative electrode made from graphite or hard carbon, while using a lithium salt ($LiPF_6$) generally dissolved in ethylene carbonate:dimethyl carbonate (EC:DMC) mixture [2]. Since lithium must be intercalated in the graphite/carbon negative electrode, the first concept of LIC included an auxiliary metallic lithium electrode which was used for pre-lithiation, hence complicating the cell design and being potentially the cause of safety issues as thermal runaway. Therefore, pre-lithiation has been proposed directly from the electrolyte [3], but it leads to a decrease of concentration and conductivity, which might have a negative impact on the LIC power. A better strategy to lithiate the negative electrode consists in irreversible lithium de-intercalation from a sacrificial lithiated material incorporated together with activated carbon in the positive electrode [4]; using lithiated oxides with low band gap, such as Li_5ReO_6, enables extracting lithium ions at potential around 4.2 V vs. ref. Li/Li^+ and to avoid detrimental electrochemical oxidation of the electrolyte [5].

After introducing the LIC and the various construction strategies, the presentation will be focused on designing new sacrificial materials with low lithium extraction potential while reducing their amount in the positive electrode. We will show examples of renewable materials enabling lithium irreversible extraction ca. 3.3 V vs. Li/Li^+ with a capacity of ca. 350 mAh/g; the resulting LIC cells demonstrate an excellent cycle life in the potential range from 2.2 ~ 4.0 V. The dead mass in the positive electrode could be also dramatically reduced by selecting materials which liberate gases simultaneously to lithium deinsertion. In the latter case, after prelithiation, the positive electrode contains only activated carbon, which leads the resulting LIC to display one order of magnitude higher energy density than a traditional EDLC based on the same total mass of electrode materials.

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Synthesis and Characterization of D-Glucose Derived Nanospheric Hard Carbon Negative Electrodes for Lithium- and Sodium-Ion Batteries

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Lithium- and sodium-ion batteries have been studied extensively for electric vehicle and smart grid applications. However, limited availability and high cost of Li is an increasing constraint when these batteries are deployed and applied on a large scale. Sodium-ion batteries are considered as promising alternative devices to lithium-ion energy storage systems, since sodium and sodium salts are abundant and inexpensive compounds. There are a few fundamental differences between the two elements: the atom is three times heavier than the lithium atom and Na^+ has a larger ionic radius than Li^+. The electrochemical standard potential of Na/Na^+ is 0.34 V higher than that of Li/Li^+ and gravimetric and volumetric energy density based on metallic Na is inevitably much lower than that of metallic Li when they are used as negative electrodes in Li-ion or Na-ion batteries.

In this presentation the **g**lucose **d**erived **h**ard **c**arbon (GDHC) electrode material (Fig. 1a) was prepared in two steps. The hydrothermal carbonization of 2 M D-(+)-glucose solution in H_2O was carried out in a high pressure reactor at 180 °C for 24 hours. Thereafter, the carbonaceous material was collected and washed with Milli-Q^+ water, dried overnight in a vacuum oven at 120 °C and 50 mbar, and then pyrolysed in a quartz stationary bed reactor at 1100 °C under Ar flow. Final treatment of the carbon material was the reduction of surface functional groups with H_2 at 800 °C [1].

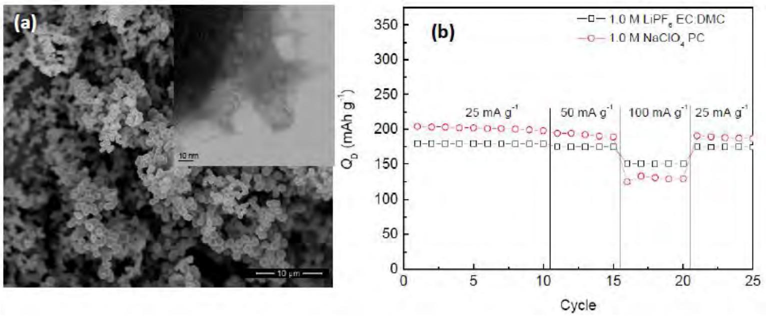

Fig. 1. SEM (a) and TEM (inset) images of the synthesized GDHC powder. Galvanostatic discharge profiles (b) calculated at different current densities for Li- and Na- based systems.

The electrochemical data show that the hydrothermal carbonization and pyrolysis are effective methods for synthesis of GDHC materials for Li- and Na-ion battery electrodes from organic precursors applicable in 1M $LiPF_6$ (EC:DMC) or $NaClO_4$ propylene carbonate electrolyte, respectively. The cycling performance of the GDHC electrode material was investigated using galvanostatic charging/discharging method at current densities ranging from 25 mA g^{-1} to 100 mA g^{-1}. Galvanostatic discharge measurements demonstrated that the specific capacity is somewhat higher than 200 mAh g^{-1} and 160 mAh g^{-1} (at 25 mA g^{-1}) for the Na- and Li-ion battery negative electrode, respectively (2nd discharge cycle) (Fig. 1b). After 200th cycle a specific capacity of 160 mAh g^{-1} (at 50 mA g^{-1}) for the Na-ion battery negative electrode was calculated [2]. Moderate decrease in specific capacity was observed at higher charging/discharging currents, explained by the limited mass transfer step rate of Na/Na^+ or Li/Li^+ into the porous structure of GDHC. The high irreversible capacity and low coulombic efficiency of the first cycle can be explained by the formation of the solid electrolyte interphase (SEI) and by the irreversible reduction of oxygen containing functional groups at GDHC surface. However, it should be noted that D-glucose derived carbons are under intensive development generating novel designs with improved electrochemical characteristics.

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Bi-functional Air electrodes for a Zn-Air accumulator for the storage of renewable energy

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The Zn/Air system has attracted scientists for many years. So far only the primary battery has been developed and applied. The goal of the current project "ZAS – Zinc Air Secondary batteries based on an innovative nanotechnology for efficient energy storage"**-** ID: 646186 are to develop a Zn/Air accumulator for the storage of renewable energy. The current work describes our achievements in the development of the bi-functional air electrode.

The electrochemical oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are studied both in a half-cell and in full cell configurations to investigate the charge/discharge characteristics. Both the GDL and AL layers of the electrodes were optimized. Electrodes were made in different sizes (1, 10, 25 cm^2) to acquire insights in view of cell design up scale. Preliminary studies of GDLs with different carbon blacks and different ratios between the PTFE and carbon blacks, have shown that the most stable GDL is produced from Vulkan XC-72 teflonized with 60 % PTFE – TV-60. The innovation as regards the GDL is in the way it is prepared using high energy mixing which assures an equal dispersion and intimate contact between the carbon black and Teflon particles.

With this GDL an optimization of the AL has been performed with respect to both the thickness (amount of catalytic mass – catalyst + PTFE) and the ratio between the catalyst and the binding agent (PTFE). The catalysts used are: (i) a mixture of Ag (Ferro AG, Ag 311), Co_3O_4 and PTFE and (ii) only Ag (Ferro AG, Ag 311). A study of the following parameters was completed: (i) the catalyst amount, (ii) pressure during production; (iii) thickness of the electrodes; (iv) PTFE amount. The Volt-Ampere characteristics and the charge/discharge tests show that the most suitable catalyst with respect to the stability of the GDE is a mix of Ag and Co_3O_4. The GDE with the above structure reaches 600 cycles without a decrease in performance.

Keywords: Zn – Air stationary accumulator, GDL, electrochemical cell design

Properties and performance of a novel lithium-doped state of polyaniline as positive active material and conducting additive for lithium-ion batteries

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The incorporation of organic materials as active materials in lithium-ion batteries is attractive due to their high theoretical capacity, the great diversity of molecular structures available, and the sustainability of the required resources [1]. In this field the use of conducting polymers allows to overcome some of the drawbacks of organic molecules, such as their low conductivity, which leads to poor rate performance, and their high solubility in traditional, carbonate-based electrolytes. The conducting polymer polyaniline (PANI) is known to be a robust and non expensive positive active material and it even had been incorporated as such in early commercial lithium-ion batteries [2]. The reversible specific capacity of PANI in positive electrodes has always been assumed to be around 145 mAh/g (related to mass of undoped PANI) corresponding to 0.5 electron per aniline unit in the polymer chain. The low stability of the higher oxidation states of PANI in organic lithium-based electrolytes has so far made unfeasible to approach the theoretical capacity of 1 electron per aniline unit (290 mAh/g) [3].

We report here the discovery and synthesis of a novel conducting lithium-doped form of PANI with reversible redox chemistry at high redox potential which allows achieving simultaneously unprecedented capacity, and stability in a non-aqueous lithium battery [4]. Thanks to combination of UV-Vis-NIR spectroelectrochemistry, XPS, FTIR and EQCM characterization a unified description of the chemical and electrochemical behaviour was achieved highlighting facile charge delocalization of the doped states and reversibility of the redox processes. This new form of PANI behaves as a high capacity organic active material (230 mAh/g) which enables the preparation of thick composite electrodes with a low amount of carbon additives (5 wt.%) and high energy density (460 Wh/kg). The rate capability and stability of the material was found to be remarkable in comparison with any other organic materials, for example at 1C rate, 400 cycles can be achieved without significant capacity loss keeping a coulombic efficiency greater than 99%.

In addition we could take advantage of the solution processing of organic materials to easily prepare composite materials; depositing thin coatings of conducting lithium-doped PANI on an active material ($LiFePO_4$) or on an expanded mesoporous carbon [5] significantly improved the power performance of these materials in organic based lithium electrolytes. In contrast to traditional carbon-based conducting additives, this conducting polymer adds its own specific capacity to the mixture, increasing the energy density of the electrodes.

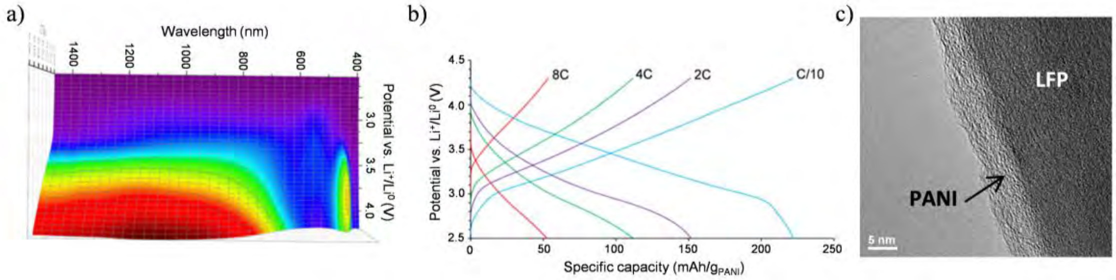

Figure 1: a): UV-Vis-NIR spectroelectrochemistry. b) charge-discharge plots of the new lithium-doped PANI. c) TEM image of a composite material prepared by coating PANI on $LiFePO_4$ (LFP).

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The Black Sea and Hydrogen Energy

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This work is a review of our studies in IEES on Black Sea environmental problem. The Black Sea is a unique system containing H_2S (C_{H2S}=5-10 mg.l^{-1}) in about 90 % of its waters where life does not exist. Only on the top of the Sea there is an aerobic layer of 120 – 180 m.

The aim of our research during the years is the development of an economically feasible electrochemical methods for using/cleaning the H_2S contained in Black Sea waters.

Several electrochemical methods have been proposed and studied. They are based on the low thermodynamic potential of hydrogen sulphide splitting: $H_2S = H_2 + 1/2S$ - Eo=0.17 V. The idea is to use sea water from the depths of the Black Sea, which contains hydrogen sulphide, in the electrolytic stage of Solar-Wind-Hydrogen Energy Systems (SWHES) in order to produce hydrogen and sulphur. The methods proposed and studied are:

(i) Electrolysis of H_2S contained in the waters of Black Sea for hydrogen and sulfur production is investigated conceptually. A multistage process is considered which involves extraction of seawater, adsorption of H2S, electrochemical production of hydrogen and polysulfides;
(ii) Development of H_2S/O_2 (air) fuel cell;
(iii) Simultaneous electrochemical purification of hydrogen sulphide and sulfur dioxide, which is based on affinity of the pair H_2S and SO_2.

The reactions of H_2S oxidation to sulfur and polysulphides have been studied. Low HS^- concentrations and the presence of NaCl, similar to the conditions found in the depths of the Black Sea have been investigated. The electrochemical conditions for the oxidation of sulfide HS^- directly to sulfite and sulfate on the electrode (anode) catalysts have been found. Different anode catalysts for HS^- oxidation have been tested: graphite, cobalt phthalocyanine and perovskite ($La_{1,3}Sr_{0.7}NiO_4$). No catalytic poisoning has been observed by the oxidation products (sulfite and/or sulfate).

Reduction of SO_2 has been studied in the same conditions (C_{HS-}=8 mg.l^{-1}; C_{NaCl}=18 g.l^{-1}).

The natural wind conditions for use of wind turbines on Bulgarian coast of Black Sea have been evaluated.

Some considerations are included regarding the economic and environmental aspects of the above processes.

Keywords: Hydrogen production, hydrogen sulfide.

Understanding the role of Li_2O_2 particle size on Li-O_2 battery charge process

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Li-air batteries have attracted significant attention due to their high theoretical capacity. However, there are several challenges associated to their use such as round trip efficiency. These challenges are mainly due to very high charge overpotential, and need to be overcome before the use of Li-air batteries in practical applications. Despite numerous works on their discharge mechanism and improvement, there is insufficient effort in exploring the charge process. In particular, the reason for two step or sloped charge potential plateau observed experimentally is still unclear. The shape of the charge profile has been affiliated to several mechanisms such as the formation of lithium-carbonates impeding the charge process, and the formation of amorphous and crystalline phases having different kinetics.

We have developed a comprehensive multiscale model describing the charge process in Li-O_2 batteries.[1] This 1D continuum model solves the transport of soluble species along the electrode thickness and considers a number of elementary reaction kinetics as illustrated in Figure 1. With our model, we could show that the two potential plateau of the charge profile results from the polydispersity of Li_2O_2 particle sizes. This suggests that the charge profile will depend strongly on the discharge process.

In this talk, I will present the main outcomes of the model along with corresponding experimental data reported in literature. Moreover, I will show the mechanism we propose for the charge process. The dependence of the charge profile on the size of the discharge products and its relation to the discharge history will be highlighted.

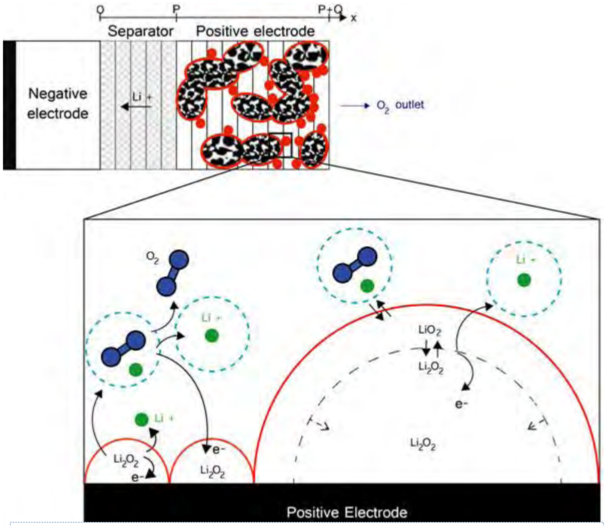

Figure 1. Schematic(s) of the charge mechanisms used in our model for thin-film (small hemi-spheres) and large Li_2O_2 large particles (large hemi-spheres). Reprinted with permission from ref.1

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Materials and nanostructures in electrochemical energy conversion: functionality understood at the atomic level

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In this study, we coat the pore walls of an anodic nanoporous template with atomic layer deposition (ALD) to obtain structured electrode surfaces that provide the experimentalist with a well-defined, tunable geometry. Indeed, the platform consists of a hexagonally ordered array of metallic or oxidic nanotubes of cylindrical shape[1] (Figure *a*). The diameter of the tubes can be defined between 20 and 300 nm, and their length between 0.3 and 300 µm, approximately. We utilize them as a model system in which the electrode's specific surface area can be increased and its effect on the electrocatalytic current characterized systematically. Their morphology, chemical composition and crystal structure are characterized by electron microscopies, X-ray diffraction and X-ray photoelectron spectroscopy. These nanostructured electrodes are further functionalized by either metallic nanoparticles (Pd, Pt) or molecular catalytic complexes based on transition-metal compounds (Co, Fe, Ni) in order to enhance the electrocatalytic turnover. Several reactions of great societal interest such as water (photo)electrochemical splitting are considered and their electrocatalytic performances systematically evaluated[2]. In particular, the steady-state galvanic current densities are recorded and redox properties are determined by cyclic voltammetry (Figure *b*). These results highlight a strategy for optimizing electrochemical energy transformation devices which could be generalized: the geometric tuning of catalytically active, abundant and cost-effective material systems towards mass production of dihydrogen.

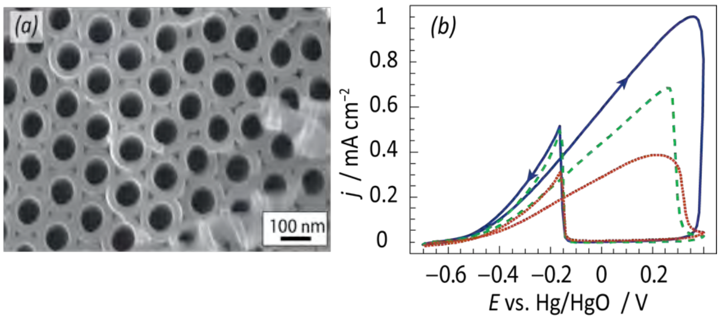

Figure : (a) SEM micrograph of an array of TiO_2 nanotubes. (b) Current densities recorded by cyclic voltammetry for different shapes of catalytic systems.

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Electrophoretic Deposition of $LiFePO_4$ on Carbon Fibres for Structural Battery Applications

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In order to meet the growing demand for electric vehicles (EVs), the overall efficiency of battery systems must be improved. The batteries used in these vehicles are often very heavy, which limits the range of EVs. Large batteries are required as the specific energy of lithium-ion systems is relatively low (orders of magnitude lower than that of the liquid fuels used in internal combustion engines).

There are different ways of improving the overall efficiency of the system. One is to simply look for new battery chemistries with higher specific energy. Another is making the vehicle itself as light as possible. A third way is introducing a structural battery, a material that simultaneously holds a mechanical load and stores electrical energy. This could be placed in a load-bearing part of the structure, lowering the total system weight and increasing efficiency.

There are three key components in a structural battery, the negative electrode, solid electrolyte, and positive electrode. The first two have been under investigation in detail in our group at KTH [1-3]. The negative electrode is based on lithium intercalating carbon fibres, the solid electrolyte is a lithium-ion conducting polymer. One possible way of implementing a positive electrode is under investigation in this work.

A novel electrophoretic deposition method is used to coat individual carbon fibers with lithium iron phosphate ($LiFePO_4$) as active cathodic material, polyvinylidene fluoride (PVDF) as a binder and carbon black as a conductive additive. The carbon fibres are used as current collectors, eliminating the need for metallic ones, which is beneficial for specific energy of the battery. The carbon fibres also provide the mechanical integrity of the system. Embedding the coated carbon fibres (the positive electrode) and raw carbon fibres (the negative electrode) in a solid polymer electrolyte acting as both separator and electrolyte, would result in a structural battery similar to a conventional carbon fibre composite material, with the added energy storage functionality.

This study focuses on optimizing the electrophoretic deposition method, and investigating the electrochemical properties of the resulting electrodes.

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In situ Synchrotron XRD of Silicon Nanowires on 3D Carbon Substrates for Li-Ion- and Li-Sulfur-Batteries

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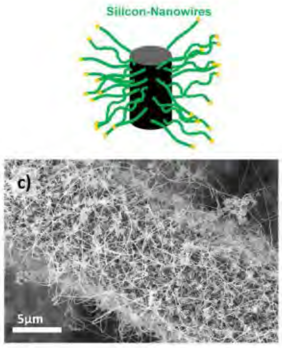
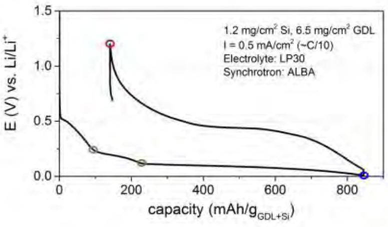
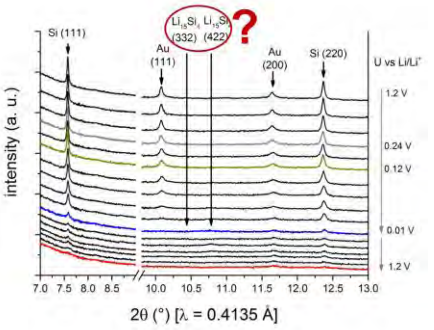
Silicon is one of the most promising negative electrode materials for Lithium-Ion- and post Lithium-Ion batteries. Moreover, silicon materials are already partially implemented in commercialized Lithium-Ion batteries (LIB). Among various structures, silicon nanowires (Si-NW) turned out to be a highly efficient material-design due to the absence of pulverization during volume change, continued electrical contact to the current collector and the superior stress compensation.

In this work, Si-NW deposited on free-standing gas-diffusion-layers (GDL) were implemented in two rechargeable lithium-battery systems. The free-standing Si-NW@GDL material offers reversible areal capacities of up to 9 mAh/cm^2 at a total anode mass just as low as 9 mg/cm^2 representing an attractive candidate as high-performance anode. Pre-lithiated Si-NW were successfully employed in high-energy density Li-S full cells with highly extended lifetime compared to conventional Li-S batteries cycled vs. Li/Li$^+$.[1] Nevertheless, we still find considerable degradation of Si-NW, in particular dependent of the chosen electrolyte system such as ethers for Li-S and carbonates for LIB systems. In order to understand these degradation phenomena, we carried out *in situ* synchrotron XRD measurements to identify phase changes during cycling and *post mortem* XPS to obtain a better understanding of the surficial mechanisms. Galvanostatic cell tests were conducted under test conditions typically used in real systems while recording diffraction patterns on modified coin cells at synchrotron facilities near Barcelona (ALBA) and in Hamburg (DESY). A custom-made cell set-up allows to record high-quality patterns of eight cells in parallel within the beamline hutch ensuring the production of reproducible high-quality data.[2] We investigated conventional carbonate- (LP30) and ether-based electrolyte systems with and w/o additives such as FEC/VC. Furthermore, for the first time we could analyze a Si-Li-S (SLS) full-cell by *in situ* synchrotron XRD.

Among various findings, we observed that at moderate C-rates ranging from C/5 to C/15 the silicon is not fully utilized. New phases such as LiOH were observed evolving over the period of cycling which depend on the carbonate- or ether-based electrolyte system. Similar characteristics in dependency of the electrolyte were found in our previous work dealing with silicon nanoparticles within porous carbon scaffolds.[3][4] Summarizing, this study provides valuable insights in tailoring nanostructured silicon anodes for LIB and post LIB.







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First-Principles Study on the Electric-double layer Capacitance of Water-MXene interfaces

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First reported in 2011, MXenes ($M_{n+1}X_nT_x$) are a new, large family of layered materials synthesized from MAX ($M_{n+1}A_nX_n$) phases by simple chemical treatments and ultrasonication [1]. More than 60 compounds are known to host MAX phases. Moreover, MXenes has large degrees of freedom of surface termination by O, F, OH, and Cl which changes its properties such as electron conductivity and the work function. Due to their enormous variations, MXenes have attracted great attention as promising candidates as anode materials for next-generation secondary batteries. Wang and colleagues reported, for instance, a prototype of Na-ion full cell using Ti_2CT_x MXene as an anode [2]. Unfortunately, the specific capacitance of MXenes supercapacitors is lower than that of active-carbon ones. Theoretical investigation of the electric-double layer (EDL) at electrode interfaces is necessary to improve the capacitance of MXene secondary batteries.

First-principles molecular dynamics (FPMD) simulation based on the density functional theory (DFT) is performed to obtain a potential profile V(z) and a charge distribution q(z) induced by the ions at water-Ti_2CT_x (T=O, F) interfaces. Effective screening medium (ESM) method is imposed to correct the electrostatic interaction between supercells along surface normal direction [3].

Potential profiles V(z) of both Ti_2CO_2 and Ti_2CF_2 decrease about 1.0 eV steeply in a region of only 3 Å from a Ti layer, which is the same profile at the platinum interfaces [4]. On the other hand, induced charge distribution q(z) depends on the species of surface termination. Induced electrons are introduced at Ti layers in the case of O surface termination. However, Ti_2CF_2 is not capable to store electrons at Ti layers because it is mono-valence anions. It indicates that effective surface-position of MXenes depends on the surface terminations.

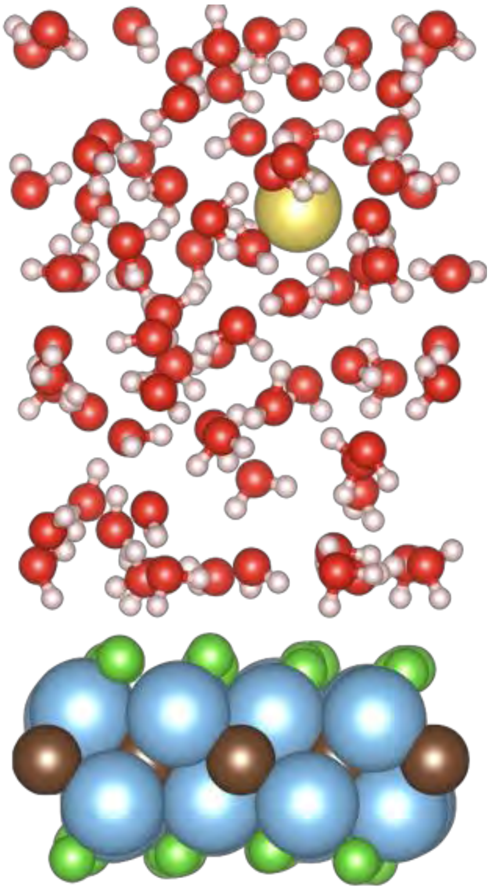

Fig. 1 Simulation model of water-MXene (Ti_2CF_2) interface. Blue, green and brown sphere represent Ti, F, and C, respectively.

From V(z) and q(z), the EDL capacitance is estimated and it is revealed that small induced charge leads the low EDL capacitance at MXene interfaces. This is because interface polarization due to strong interaction between water and Ti_2CT_x induces net charge. The surface net charge hinders the introduction of ion-induced charges.

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Activity and Stability of Carbide- and Oxide-based Electrocatalysts for the H_2/O_2 Evolution Reactions in Acid and Alkaline Electrolytes

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A clean way to produce hydrogen fuel is by water electrolysis, in a process that splits water through the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER). In the cathode, HER takes place with low overpotential values when platinum is used as electrocatalysts, but OER takes place by a more complex mechanism, resulting in a slow kinetics and occurring involving high overpotentials. In this work, investigations of the HER and the OER in acid and/or alkaline electrolytes were carried out in several catalysts, comprising: (1) transition metal-modified molybdenum carbides (TM-Mo_2C) for the HER, where TM = Fe, Co, Ni and Cu. (2) Iridium oxide nanoparticles, prepared by an hydrothermal method and calcinated at different temperatures, for the OER in acidic media. (3) Nickel hydroxides, precipitated in aqueous and ethanolic solvents, for the OER in alkaline electrolyte and (4) gold electrodes for the OER in alkaline media, focusing on the effect of the cations: K^+, Na^+ and Li^+ and on the presence of iron impurities in the reaction kinetics.

TM-Mo_2C catalysts were prepared by a temperature programmed reduction method in both an inert and a reductive atmosphere. Iridium oxide catalysts were synthesized by a hydrothermal method using a Teflon® bottle autoclave. After this step, the precipitate was submitted to heat treatments between 100 to 500 °C, in air atmosphere, for 1 h giving rise to nanoparticles with different crystallinity degree. Nickel hydroxides were precipitated in aqueous and ethanolic solvents, using ammonium hydroxide with a pH controlled method (pH = 9.8). Physicochemical characterization of the catalysts involved several techniques, including X-ray diffraction, energy dispersive X-ray spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and Raman spectroscopy. Cyclic voltammetry and steady state polarization experiments were conducted using thin layer electrodes to characterize the catalyst electrochemical surface properties and the activity and durability of the catalysts.

Important findings of these investigations may be summarized as: (1) high activities toward the HER were observed for all TM-Mo_2C catalysts in acid media, although there is a decrease in the HER activity upon metal doping, with an activity trend of α-Mo_2C > Fe-Mo_2C > Co-Mo_2C > Ni-Mo_2C > Cu-Mo_2C. *In situ* near-edge X-ray adsorption analysis reveals a positive charge of the TM in the materials in the electrochemical environment, possibly at the origin of the deleterious effect of Fe, Co, Ni and Cu. Nevertheless, TM-Mo_2C are more stable (lower catalyst dissolution) in acid media than α-Mo_2C. In contrast, all transition metals exert a promoting effect on the HER activity of α-Mo_2C in alkaline media, following an inverted tendency to the one found in acid media: α-Mo_2C < Fe-Mo_2C < Co-Mo_2C < Ni-Mo_2C. (2) The performance of the IrO_x catalysts toward the OER in acid media decreases with the increase of the calcination temperature, while the opposite tendency is observed regarding the materials' stability. Identical location transmission electron microscopy analyses showed that the low stability of non-calcinated IrO_x is due to degradation of the electrode thin layer structure, besides eventual occurrence some iridium oxide dissolution. (3) In the case of nickel hydroxides, an important effect of the type of the solvent in which they were precipitated was found, measuring higher and lower overpotentials for the OER in alkaline media (+50 and -100 mV relative to the one for IrO_x) for those hydroxides precipitated in ethanol and water, respectively. (4) The activity of OER on gold electrodes in alkaline electrolytes of different cations follows the order K^+ > Na^+ > Li^+, while iron impurities shift the overpotential to lower values in all cases, ~500 mV.

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A transient 2D PEMFC model to investigate cell performance and degradation

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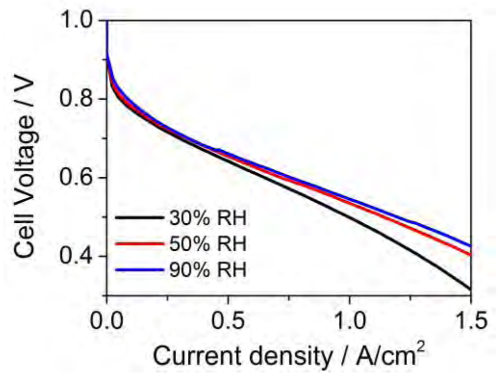
Polymer electrolyte membrane fuel cells (PEMFCs) are environmentally friendly alternatives to conventional energy conversion systems. However, performance degradation still poses a major challenge for this technology. A better understanding of the underlying mechanisms is crucial in order to be able to predict cell performance and durability. Detailed physical models allow identifying and investigating these mechanisms and represent important tools for optimization of cell performance and reduction of degradation.

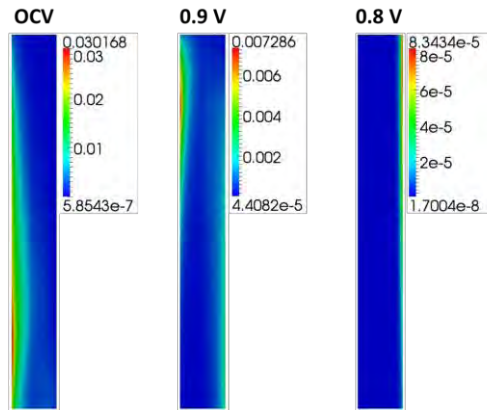
Here, we present a transient, two-dimensional single cell model for PEMFCs implemented in our in-house code NEOPARD-FC, which is based on the open-source framework DuMux [1]. The model is non-isothermal and includes electrochemistry, two-phase multi-component transport in the porous layers as well as water and gas permeation through the membrane.

Simulations of polarization curves and impedance spectra under various operating conditions are performed to validate the model. The validated model provides important insights on the local conditions within the cell which are often not accessible in experiments. The occurrence of heterogeneities of temperature, species concentrations, etc. is discussed. In particular, we focus on the water management which plays an important role for cell performance.

The cell model also provides the basis to study degradation phenomena since the local degradation rates depend on the local conditions within the cell. Simulations of membrane degradation by coupling the cell model with a detailed chemical membrane degradation model are presented. The degradation model incorporates the formation and decomposition of hydrogen peroxide, iron ion redox cycle, radical formation and degradation via “unzipping” and “side chain scission” mechanism.



a) Simulated polarization curves at various relative humidity



b) Simulated rate of local SO3- loss / mol m^{-3} s^{-1} in the membrane for various cell voltages

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Development of Novel Catalysts for Polymer Electrolyte Membrane Fuel Cells

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Microporous-mesoporous carbon powders synthesized from binary and ternary carbides by high-temperature chlorination method have been tested as supports for Pt- ,Pt-Ru, Pt-Ir , Pt-Ce, and d-metal - nitrogen nanoparticles activated catalysts for oxygen electroreduction and hydrogen and methanol oxidation [1-11].The physical characteristics of catalysts have been established using XRD, FIB-TOF-SIMS, XPS, FIB-SEM, HRTEM, Raman and in situ FTIR methods. The porous hierarchical structure has been tested using nitrogen, Ar and CO_2 gas adsorption analysis methods combined with small angle neutron scattering studies [5]. Influence of pore shape on the gas and water adsorption characteristics has been established. Cyclic voltammetry, rotating disk, chronoamperometry and electrochemical impedance studies of various Pt-metal activated and nonactivated carbonelectrodes in 0.1 M $HClO_4$, 0.05 M H_2SO_4 and 0.1 KOH aqueous solutions demonstrated huge role of the microporous-mesoporous hierarchical structure on the oxygen electroreduction and hydrogen as well as methanol oxidation characteristics.

For comparison, Vulcan XC72 carbon based systems have been tested under similar electrochemical conditions. More pronounced catalytic activity of binary and ternary carbide derived carbon powders based catalysts has been demonstrated, e.g. noticeably higher cyclability within wider potential region than that for Vulcan based catalysts.

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Aluminum dissolution preventing additive for LiTFSI based liquid electrolytes in lithium ion battery application

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Commercially available lithium ion batteries consist of graphitic carbon as negative electrode, lithium transition metal oxide as positive electrode and $LiPF_6$ as conducting salt dissolved in mixture of organic carbonates as liquid electrolyte. The limited thermal and chemical stability of $LiPF_6$ and formation of highly toxic fluorinated compounds in the cell such as mono- and di-fluoro phosphates are curious safety issues for large-scale applications and electric vehicles.[1] Due to this fact, a lot of research has been conducted in recent years to replace $LiPF_6$ with a more inert lithium salt having higher thermal and chemical stability, wide electrochemical stability window and high ionic conductivity. The conducting salt lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), first introduced by Armand and Moursli in 1985, is one of the most promising candidates.[2] However, LiTFSI is known for not being able to form a passivation layer on the surface of the Al current collector, in order to prevent Al dissolution at anodic potentials above 3.5 V vs Li/Li^+.[3] Taking into account the aforementioned facts, in the frame of this work, a new lithium salt has been synthesized and investigated as additive in LiTFSI-based electrolytes to suppress the Al current collector dissolution (Figure 1). Lithium (2-trifluoromethyl-4,5-dicyano-imidazolate) (Li-TDI) was introduced by Niedzicki *et. al.* as a new lithium salt for 4V application in lithium ion systems.[4] The authors could show that the salt could suppress the anodic dissolution of aluminum disk working electrode. A new lithium salt is introduces in this work (BF_3-TDI) which demonstrates higher oxidative stability and also better protection of aluminum current collector. Li-TDI was reacted with $Et_2O.BF_3$ to functionalize both nitrogen groups of imidazolium ring in Li-TDI.

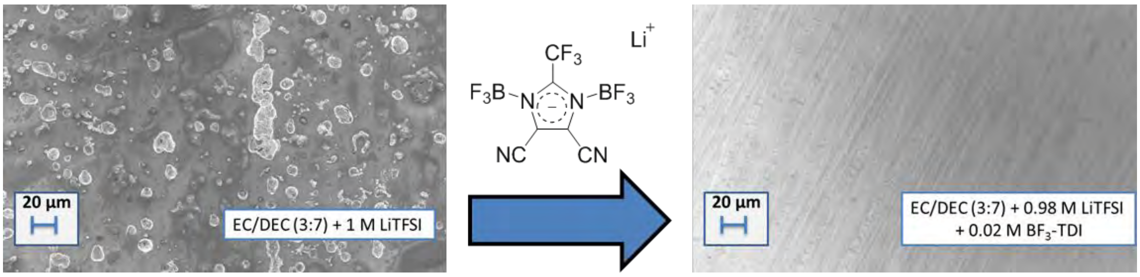

Figure 1: New synthesized lithium salt as Al current collector protection additive; SEM pictures of electrolyte formulation using LiTFSI salt (a) without additive and (b) with 2 mol% additive

The electrochemical investigation of new salt-based electrolyte formulation in a three electrode Swagelok® half-cell setup, using Al disks as working electrode and lithium metal as counter and reference electrode, shows positive effect of new synthesized additive in protection of Al electrode (Fig. 1). Linear sweep voltammetry measurement could prove the improvement of oxidative stability of the salt. Furthermore, galvanostatic cycling measurements in NMC/Li half-cell and graphite/NMC full cell setups, revel reversible cycling of the investigated electrolyte formulation. In addition, XPS measurements have been performed to investigate the surface of aged NMC electrodes after galvanostatic cycling.

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New manganese silicate material with cycling stability as positive electrode for lithium-ion batteries

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Lithium manganese silicate Li_2MnSiO_4 is theoretically one of the most interesting polyanionic material for lithium-ion batteries positive electrode. Its theoretical capacity reaches 333mAh/g thanks to the possible exchange of two lithium ions per formula unit which happens below the organic electrolyte degradation voltage. Indeed, the first lithium ion is calculated to be exchanged at 4.1V vs Li^+/Li and the second one at 4.4V [1]. The high energy density combined with the thermal stability of the Si-O bond make Li_2MnSiO_4 in theory one of the best choice to equip the next generation of electrified transportation [2].

1st studied in 2006 by Dominko et al. [3], lithium manganese silicate still shows severe limitations. Both its ionic and electronic conductivities are low [4] and Li_2MnSiO_4 structure cannot accommodate large Li^+ extraction without amorphization. Thus, it leads to high polarization and capacity fading during cycling, impeding its practical interest. Despite this trend, manganese-based silicate polyanions are essentially interesting because of their high abundance, low cost and environmental friendliness.

Here we propose an unreported manganese silicate material that we recently patented. This new material, usable as a positive electrode for lithium ion batteries, showed remarkable cycling stability. Ex-situ X-Ray Diffraction showed that the structure was maintained during cycling, demonstrating that the material can accommodate reversible extraction of Li^+ ions. To limit particle growth careful attention was paid on the synthesis route. Primary particles of 50 nanometers were obtained by a sol-gel process (Figure 1). Rate capabilities of the material, studied by galvanostatic cycling, will also be presented. Deeper characterization by X-Ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy-Selected Area Electron Diffraction (TEM-SAED) and Differential Scanning Calorimetry (DSC) will be shown to assess the redox process, structure and thermal stability of this material.

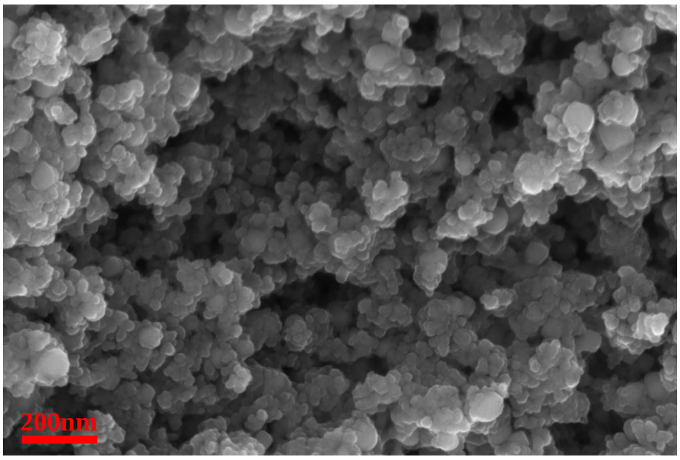

Figure 1: Scanning Electron Microscopy (SEM) picture of new manganese silicate material synthesized by sol-gel process.

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Performance limitations in anion-exchange membrane fuel cells

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Anion-exchange membrane fuel cells (AEMFCs) still need further development of the polymer electrolyte with regard to stability, ion-conductivity, and water management [1]. As the field progresses, it is also important to obtain a better understanding of the electrode processes and limitations in the alkaline membrane system. Previous studies [1, 2] on Pt/C catalysts show that the electrodes kinetics are different in AEMFC compared to PEMFC, as water is consumed at the cathode and produced at the anode:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad \text{(Cathode)}$$

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \qquad \text{(Anode)}$$

The studies indicate that both electrodes have performance limitations in AEMFC and the anode kinetics are slower compared to the cathode. However, these studies have been performed at current densities at which both reaction kinetics and mass transport may limit the performance. In addition the influence of water becomes significant for the same current interval. Water produced at the anode may cause flooding, while the cathode may dry out, limiting the supply of reactant water. This study aims to investigate the Pt/C electrode limitations in the kinetic region of an operating AEMFC. This is achieved by varying electrode thickness (and loading), relative humidity and gas compositions. I-V curves, CVs, and EIS are measured on single cell in-house made electrodes [3], using platinum catalyst (Tanaka), commercial membranes (Tokuyama).

A comparison of different loadings on anode and cathode are shown in Fig 1. The graph to the left shows that in the kinetic region, at low currents, the cathode reaction is limiting. However, as seen in the right figure, low loading at the anode decreases the performance significantly at higher current densities. Decreasing the relative humidity also shows a significant drop in performance around 200 mA/cm^2, which indicates that the performance loss for the low loading anode is related to the water balance. The influences of lower partial pressure of hydrogen and oxygen respectively have also been studied to further clarify the electrodes limiting mechanisms.

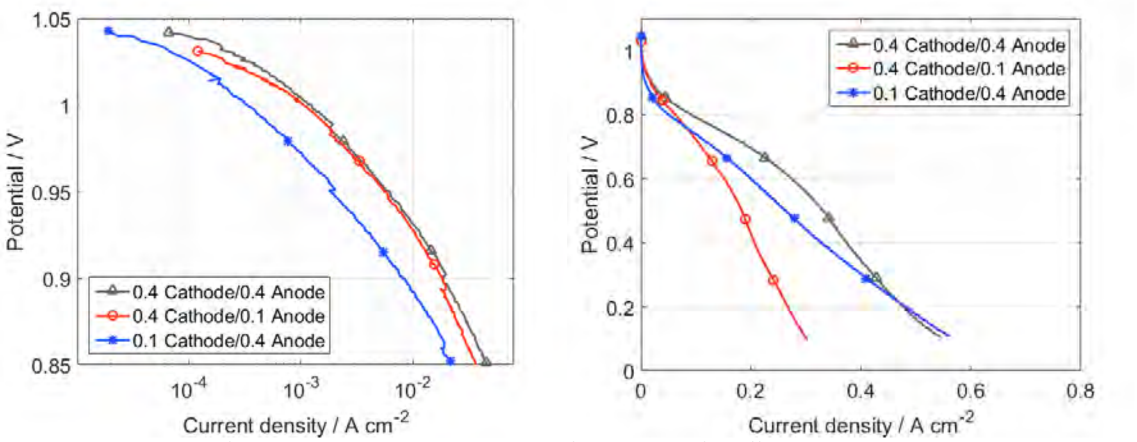

Figure 1 - Enlargement of kinetic region on logarithmic scale (left), I-V curves for different electrode loadings (right). Loading in mgPt/cm^2, curves recorded with O_2 / H_2, IR-correction, scan rate 1 mV/s, OCP - 0.1 V, 95% R.H. and 50°C.

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Going Nano For A Better Understanding Of The First Charge Working Mechanism Of Li_2S-based Li-ion Batteries: An *Operando* XAS/XES Coupled With XRD Analysis

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With their high theoretical energy density (~2600 $Wh.kg^{-1}$), lithium/sulfur (Li/S) batteries are highly promising, but these systems are still poorly understood due to the complex mechanisms/equilibria involved. Replacing S_8 by Li_2S as the active material allows the use of safer negative electrodes, like silicon, instead of lithium metal. S_8 and Li_2S have different conductivity and solubility properties, resulting in a profoundly changed activation process during the first cycle. Particularly, during the first charge a high polarization and a lack of reproducibility between tests are observed [1] (Figure 1a). Differences observed between raw Li_2S material (micron-sized) and that electrochemically produced in a battery (nano-sized) may indicate that the electrochemical process depends on the particle size [2].

Then the major focus of the presented work is to deepen the understanding of the Li_2S material charge mechanism, and more precisely to characterize the effect of the initial Li_2S particle size both on the mechanism and the electrode preparation process. To do so, Li_2S nanoparticles were synthetized according to two ways: a liquid path synthesis [3] and a dissolution in ethanol, allowing Li_2S nanoparticles/carbon composites to be made [4]. Preliminary chemical and electrochemical tests show that starting with Li_2S nanoparticles could effectively suppress the high initial polarization (Figure 1b) but also influence the electrode slurry preparation. Indeed, it has been shown that classical formulation process - a slurry composed of Polyvinylidone Fluoride polymer dissolved in N-methyle-2-pyrrolidone - cannot be used with Li_2S nanoparticles. This reveals a complete different Li_2S material behavior regarding polymers and organic solvents when going at the nanometric scale. Then the coupling between two operando characterizations such as X-Ray Diffraction (XRD) and X-Ray Absorption and Emission Spectroscopy (XAS/XES) have been carried out in order to interpret the poorly understood first charge. The results allow to explain the electrochemical behaviors and particularly the polarization differences observed during the first charge between micrometric and nanometric Li_2S-based electrodes.

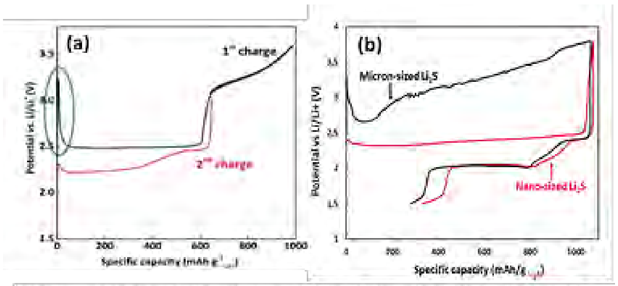

Figure 1: *(a) Typical voltage profiles of two first charges of a Li_2S-based cell* [1] *and (b) comparison of voltage profiles between micro and nano-sized Li_2S particles-based cell.*

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Advanced Electrochemical Impedance Spectroscopy for the Aging Study of Commercial Li Ion Batteries

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Electrochemical impedance spectroscopy is the most promising non-destructive method for lithium ion battery diagnosis and materials characterization due to its simple instrumental requirements and powerful output. However, it is not easy to obtain reliable impedance data from the battery system because of its complexity. Many artefacts can be induced by the experimental procedures and the cell design.

In this work, EIS is performed by using the in-house developed multisine technique: Odd Random Phase EIS (ORP-EIS) [1]. Comparing with classical EIS measurements, ORP-EIS has the advantage that additional information can be quantitatively obtained: the level of disturbing noise, the level of the non-linear distortions and the level of the non-stationary behavior. Based on this information, the data quality can be directly evaluated. Additionally, the modeling procedure can be also benefit from this method. By comparing the residual values between experiment and model with the noise levels, the model is also statistically evaluated (see Fig.1). Many efforts have been put in optimizing the experimental protocol for the compact “sandwich” cell design. The conclusion agrees with Levi [2]: the impedance of individual battery electrodes should be measured in symmetric 2-electrodes cells.

In this work, a comprehensive aging study of $Li_4Ti_5O_{12}$ /$Li(NiCoAl)O_2$ (LTO/NCA) lithium ion batteries is carried out with a set of commercial pouch cells (5 Ah). It includes both cycling aging and calendar aging with varied aging conditions. These aged batteries are post-mortem analyzed by different techniques. Multiple ORP-EIS experiments are performed with different state-of-charge (SOC) levels for both anode and cathode materials. By fitting with the equivalent circuit model, the charge-transfer resistance R_{ct} which is corresponding to the kinetic parameter is identified. The R_{ct} of LTO shows subtle differences but NCA shows significant variation with different SOC levels due to the complex microstructure changes. By comparing with aged electrodes, the changes of the kinetic parameter can be quantified regarding to the different aging condition.

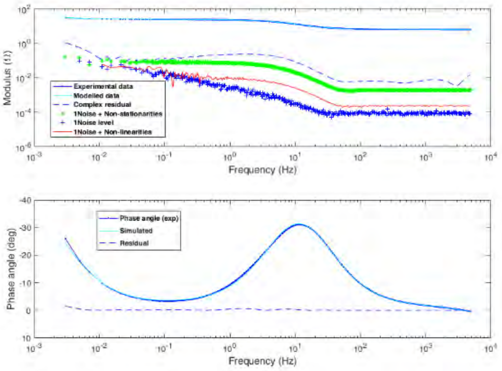

Fig.1. Bode plot of a fitted ORP-EIS spectra. The sample is a non-aged NCA electrode at 40% SOC level. An observable non-stationarity (green line) is dominate the noise signal of spectra but still about two order of magnitude lower than real signal. The fitting residual (dot line) almost overlaps the non-stationary level. Therefore, both the experimental and fitting results are acceptable

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Numerical modelling of CO poisoning induced sustained oscillations in the anode potential of a PEM fuel cell

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A dynamic 1-D model for the simulation of the oscillatory behaviour in the potential of the anode of a PEM fuel cell under constant current conditions and CO impurities in the H_2 inlet is proposed. The model is built upon electrostatic, chemical/kinetic and thermodynamic principles underlying the operation of a fuel cell, thus no empirical variables are introduced. Instead, only variables with physical meaning are fitted. The model is capable of capturing the phenomenon of the oscillatory behaviour while giving an insight into the effect of the composition and the electrical potential on the interconnected kinetics between the HOR and CO-electrooxidation.

Three electrochemical steps are used for the HOR: Tafel non-potential dependent dissociative adsorption of Hydrogen atoms, Heyrovsky potential dependent adsorption-oxidation and Volmer oxidation. As proposed by Zhang [1], three steps are also provided for the CO-electrooxidation: CO adsorption, potential dependent H_2O adsorption-oxidation and irreversible CO electrooxidation.

Following the work of Franco et al. [2], two regions of the electrochemical double layer are modelled. In this work, an explicit solution of the governing differential equations for the diffuse layer is developed for the electrostatic potential and protonic concentration:

$$d\left(\frac{d\phi}{dx}\right)^2 = -\frac{2\,F}{\epsilon_{cd}}\left(C_{H^+}\big|_{ref}\, e^{-\frac{F}{RT}(\phi-\phi_{ref})} - C_{SO_3^-}\big|_{ref}\right)d\phi$$

$$\left(\frac{d\phi}{dx}\right)^2 - \left(\frac{d\phi}{dx}\Big|_{ref}\right)^2 = -\frac{2\,F}{\epsilon_{cd}} C_{H^+}\big|_{ref}\left(\frac{RT}{F}\left[e^{-\frac{F}{RT}(\phi-\phi_{ref})} - - e^{-\frac{F}{RT}(\phi_0-\phi_{ref})}\right] + \frac{C_{SO_3^-}\big|_{ref}}{C_{H^+}\big|_{ref}}[\phi-\phi_0]\right)$$

As for the compact layer, several modifications have been made to the model proposed by Franco et al. to account for the presence of different species of dipole molecules on the surface of the electrode adsorbed molecules.

The model was capable of capturing the shape of the electric potential, as depicted in Figure 1. In agreement with previous works by Zhang [1], Mota and Kadyk [3-4], two different time characteristics for the dynamics of the system were found (Figure 2).

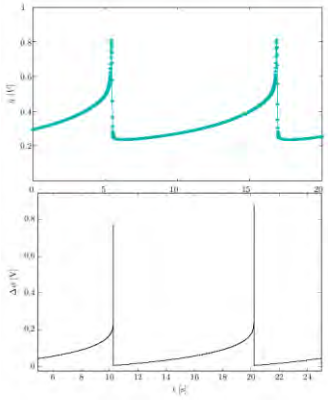

Figure 1

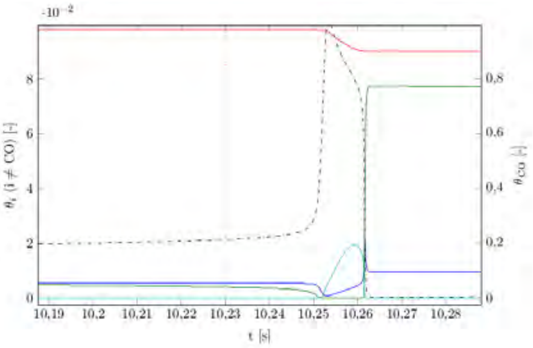

Figure 2

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Fast Top-up Charging of Lithium-ion Batteries
- A comparative ageing study

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Fast-charging of lithium-ion batteries has gained increasing attention as a means of alleviating charge anxiety associated with long charging time in electric vehicles. Normally, lithium-ion batteries are fast-charged at high current rate followed by a charge trickling phase for full charging. However, the charge trickling phase is inefficient taking disproportionately long time with marginal charge return making it non- preferable for public fast-charging stations. Hence, according to the charging station owners recommendation[1] and frequent users preference, batteries are fast top-up charged to about 80% capacity skipping the last charge trickling phase. Partially charging to about 80% capacity means that there will be a combined effect of the higher charging rate and lower state of charge range that may affect the battery differently necessitating in-depth investigation.

In order to study the effect of charging condition on the battery life, cycle ageing of commercially available 18650 NMC/graphite cells in three different charging conditions have been performed; i) charging at 0.5C to 4.2V followed by a constant voltage phase at 4.2V until the current drops to 0.1C (standard CCCV charge) ii) charging at 0.5C until 4.2V without a follow-up constant voltage phase (standard CC charge) iii) charging at 1.5C until 4.2V without a follow-up constant voltage phase (Fast charge). In all the cases the discharge was done at 1C rate with 5 minutes rest time between charge and discharge. In order to track the performance of the cells with ageing, 1C and C/24 discharge capacities were measured after each 200 cycles of ageing. Full cell voltage fitting model using half-cell data was developed to identify and quantify different ageing mechanisms non-destructively. Further post-mortem electrochemical and SEM/EDX analysis has been performed in order to confirm the conclusions from the non-destructive analysis and identify additional more specific ageing mechanisms.

As can be seen from Figure a, the rate of ageing in the fast top-up charging case is lower than the other two cases. Additionally, the ageing mechanism analysis shows that the dominant mechanisms for capacity loss are cyclable lithium-loss and impedance rise. Furthermore, significant active mass loss of positive electrode has been observed, while that of the negative is insignificant. Electrochemical impedance spectroscopy tests done on symmetric cells indicate that the positive electrode contributes dominantly to the total cell impedance and its rise with ageing. The SEM micrographs in Figure b-c show that the graphite particles of the cycle aged cell are roughened and covered with a surface film. EDX analysis shows the presence of small amount of manganese on the graphite particles due to the cycling. Particle cracking is seen on the SEM micrographs of positive electrode. In general, the dominant ageing mechanisms are similar in the cells cycled in the different cases showing that the different cycling profiles only affect the rate of ageing. Detailed results and discussion will be presented during the conference.

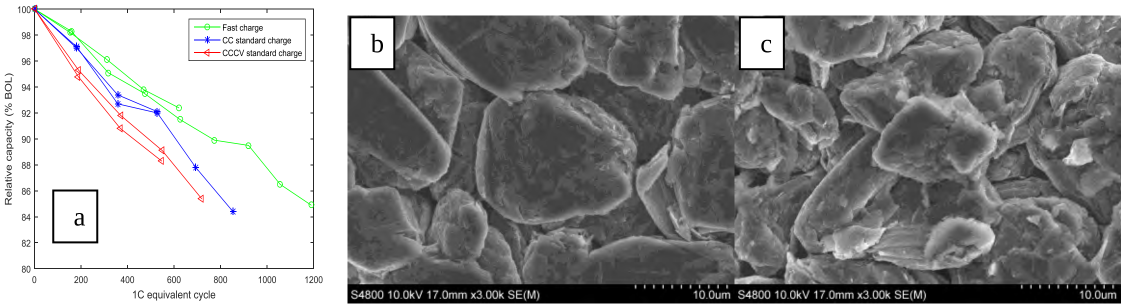

Fig a) 1C discharge capacity as function of 1C equivalent cycle number and SEM micrograph of b) calander aged c) cycle aged at CC standard

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Optimized mesoporous carbon supports for Pt-Ru catalyst. Synthesis and characterization.

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An assorted variety of carbon materials have been employed as support for catalyst fuel cells [1]. Among those, mesoporous carbons (MC) with different pore sizes and distribution have been evaluated. Mesoporisity in the order of 5 nm has been related to optimal catalytic activity for methanol oxidation due to formation of particles with an adequate size and good distribution across the support [2]. In a previous work, MC obtained by a soft template method was employed as support for PtRu showing a 25% increase of the methanol oxidation current and an 8 % higher conversion efficiency to CO_2, determined by differential electrochemical mass spectroscopy (DEMS), compared to the PtRu catalyst supported over commercial carbon Vulcan [3].

With this motivation, a new optimized route of synthesis employing soft template (ST) and hard template (HT) is proposed. Different MC were prepared from a resorcinol formaldehyde resin employing two types of commercial SiO_2, Aerosil® (d=12 nm) and Sipernat® (d= 50 µm), used as hard template (HT). After carbonization of the resin the HT was removed with concentrated NaOH @ 60ºC for 24 h. PtRu catalysts were prepared by the impregnation-reduction method, supported on the MCs [3]. CO stripping, CV, and chronoamperometry were performed in a three electrodes cell. DEMS experiments were carried out to monitor the reaction products for methanol oxidation on both, PtRu/MC and PtRu/C. Fuel cell characterization of the PtRu/MC catalysts and PtRu/C were performed on a single MEA cell having 5 cm^2 active area with 1 M methanol used as anode fuel and dry O_2 on the cathode [4]. The synthesized MC with higher amount of pores in the 5 nm size (Sipernat) presents an improved performance when used in the fuel cell as catalyst support, as previously indicated [2, 3].

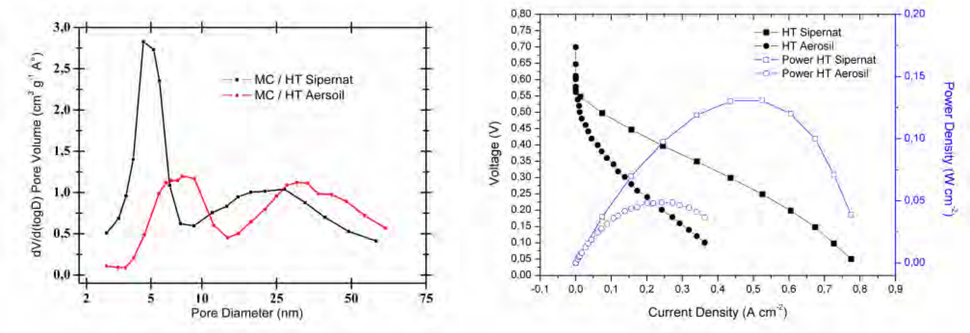

Figure 1: A) Pore width distribution MCs synthetized with different HTs. B) Polarization and power curves for PtRu supported on MC prepared with the different HT in 1 M methanol and dry O_2 (200 sccm) at 80 ºC.

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Inelastic X-ray scattering spectroscopy of Li stage intercalation in graphite

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The high-energy consumption in our day-to-day life can be balanced by harvesting power from pollution-free renewable energy sources. However, the latter requires from adequate energy carriers, which allow proper storage and distribution of energy. In this regard, the lithium ion battery is currently considered as an effective energy storage device and is involved in much active research in the electrochemical community. Li-intercalated graphite (LIG) is of particular interest both as the best studied intercalation compound but also due to its relevance for present day rechargeable battery technology.

In the present work we investigate near edge fine structure at the Li and C K-edge in electrochemically prepared LIG in stages I and II by means of inelastic X-ray scattering spectroscopy. An inelastic X-ray scattering (IXS) experiment with high energy resolution provides information about electronic excitations by measuring the double differential scattering cross section as a function of the energy and momentum transfer. The present work applies IXS spectroscopy in the regimes of scattering from core electrons to investigate electron excitation dynamic in LIG in stages I and II. In the former regime, collective and single particle like excitations of valence electrons can be investigated. In the latter, IXS gives the possibility of measuring absorption edges in the soft X-ray or VUV energy range, but with the advantages of using hard X-rays. Making use of the momentum transfer dependence of the IXS cross section, excitation channels other than dipolar can be investigated when core electrons are excited to empty states. This is a unique property of a spectroscopic technique based on a scattering process. We also present first-principles calculations results obtained for both stages to support the analysis obtained for the experimental results. Density functional theory calculations were performed using the Quantum Espresso package with Van der Waals interactions (DFT-D). Ultrasoft pseudopotentials were employed with the GGA approximation for exchange and correlation in the PBE functional.

The theoretical results are in close accordance with the experimental measurements allowing studying the electronic density characteristics of the materials [Figure 1]. For the first time stage II samples were measured permitting to define the physical disturbance of the unoccupied states of carbon atoms upon lithium insertion.

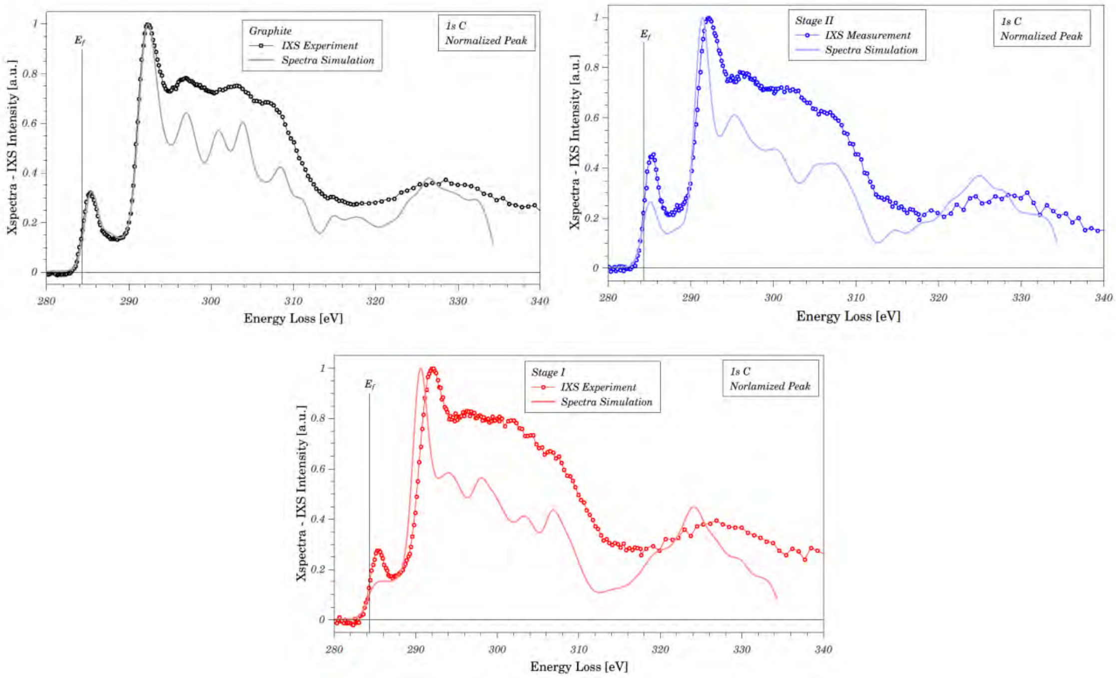

Figure 1 – Experimental IXS measurements (points) and DFT calculation (line) of Graphite (black), Stage II (blue) and Stage I (red) intercalated Lithium.

Influence of Ultrathin Carbon Coatings on Silicon Nanowires to Capacity and Cycling Stability in Li-Ion Batteries.

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Si nanowires (SiNWs) have been selected as one of the most promising nanomaterials to replace conventional anodes, such as graphite in high capacity Li-ion (LIB)[1] or elemental Li in Li-S batteries[2]. In this work, SiNWs were modified by an adjustable highly conductive, nano-crystalline carbon layer covering the whole nanowire network, with the aim to improve the cycling stability and reduce degradation of the anode. The SiNWs have been densely and conformally grown *via* the VLS mechanism[3] directly onto 3D carbon current collector. This composite anode architecture enables high Si loadings of up to 2 mg /cm^2 required to target high capacity energy storage applications.[2] Further on, a conductive pyrolytic carbon layer with a tunable thickness between 5 and 80 nm was deposited.[4] The anodes consisting of SiNWs with and without carbon coating, respectively, were integrated into half-cells *vs.* metallic Li and full-cells with NCM cathode with the electrolyte LP30 and FEC additive. The cells show high cycling stability of at least 650 cycles (half-cell, 1st cycle 0.4-1.5 mAh/cm^2 at 1C) and 450 cycles (full-cell, 1st cycle 2 mAh/cm^2 [t_{carbon} = 10 nm] at 1C) without full degradation. Detailed electrochemical investigations and *post-mortem* analyses reveal new insights on the surface structure to improve battery lifetime.

The main difference between SiNW without and with carbon coating is shown on the effect on the long-term stability and the degradation processes. As for previous battery setups based on pure graphite anodes, for example, electrolytes were optimized with respect to their reactivity towards carbon surfaces. The carbon coating may affect the formation of the solid electrolyte interphase (SEI) and thus act as a protection layer on SiNWs. Moreover, the high electric conductivity of the pyrolytic carbon layers ensures a continuous electrical contact of SiNWs during cycling (Figure 1). For this composite anode it is proven that the SiNW electrode only negligibly contributes to the degradation of the half-cells. Cell degradation originates from the consumption of electrolyte at the Li surface of the counter electrode, when applying high current rates (up to 5C). In the case of full-cells, the carbon coating improves the long term stability by ensuring a continuous electrical contact with the active material. For this reason, an optimal layer thickness for the carbon covering was realized where the competitive processes of electrical and Li ion conductivity can co-exist and are balanced to reach high charging/discharging rates > 1C.

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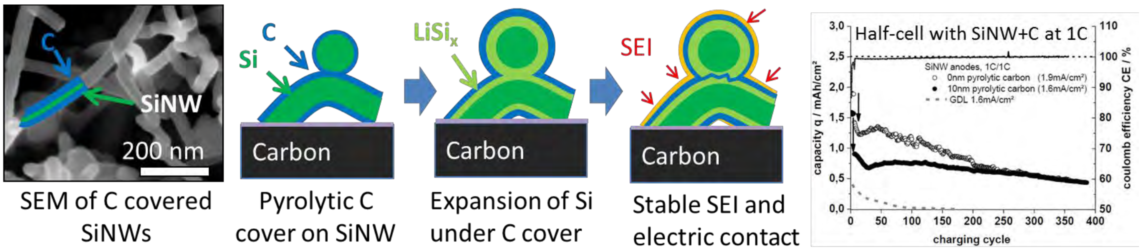

SEM of C covered SiNWs

Pyrolytic C cover on SiNW

Expansion of Si under C cover

Stable SEI and electric contact

Figure 1: SiNWs covered with conductive pyrolytic carbon to improve stability and cycling behavior of SiNW/C anodes in high capacity LIB.

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Perovskite Proton Conductors for Energy Conversion and Storage at Intermediate Temperatures

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Fuel cells and electrolysis cells are expected to be key technologies for transportation and stationary applications with high energy conversion efficiency and ability to balance the energy flow, enabling large scale deployment of renewables. However, due to the sluggish kinetics on the electrodes at low temperatures and high degradation rate of the systems at high temperatures, the realization of the existing low-temperature and high-temperature fuel cells and electrolysis cells is inhibited by high component cost and poor durability in service.

A proton-conducting membrane fuel and electrolysis cell technology has been developed recently. The electrochemical cells can be operated at intermediate temperatures to overcome the kinetic and degradation challenges facing the low and high temperature cells, and be easily integrated with renewable systems. The technology promises low capital cost and high system efficiency at high energy conversion rate.

In this presentation, we will discuss the thermodynamic and transport properties of perovskite proton conductors and their applications in hydrogen fuel cells and water electrolysis cells at intermediate temperatures. Results will be discussed and compared with other type of fuel cells and electrolysis cells. Applying perovskite protons conductors as electrolytes in other electrochemical manufacturing will be also address.

Composite Polyvinyl Alcohol – Polybenzimidazole Membranes for Alkaline Water Electrolysis and Ethanol Fuel Cell

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The current tendency of alkaline energy conversion systems is the development of suitable materials which improve their performance, being one of the most important issues to optimize the membrane as electrolyte [1], [2]. We propose and assess an innovative composite polyvinyl alcohol (PVA) – polybenzimidazole, as anionic membrane applied to both, zero gap alkaline electrolyzers and alkaline ethanol fuel cells. The challenge was to combine PVA either with poly [2-2'-(m-fenylene)-5-5' bibenzimidazole] (PBI) or poly (2,5-benzimidazole) (ABPBI), to complement those non-conductive polymers, with alcohol groups that facilitate the conduction of the OH$^-$ ions through the membrane. We evaluate PVA-PBI and PVA-ABPBI membranes with compositions varying between 2:1 and 8:1, resulting 4:1 the best ones. PVA was also crosslinked inside the copolymer with glutaraldehyde (GA) with the aim to enhance the structural properties of the membranes. Chemical stability in KOH environment, thermal stability, water and KOH sorption, and conductivity of linear (L-PVA-PBI, L-PVA-ABPBI) and crosslinked (C-PVA-PBI, C-PVA-ABPBI) membranes alkali doped were analyzed.

In short-term electrolysis tests circulating 2.3M KOH solution at 50 °C (Figure 1), the C-PVA-ABPBI (0.5 vol. % GA) membrane duple the performance of the commercial porous Zirfon$^{®}$ diaphragm, attaining current densities of 300 mA·cm^{-2} at 2.0 V. Increasing the temperature to 70 °C this last membrane performance achieved 360 mA·cm^{-2} at 1.9V, being a promising result for the future uses.

Polarization curves in ethanol fuel cell were measured at 90ºC and 0.5 atm O$_2$ backpressure (Figure 2). The PVA:PBI 4:1 membrane showed the best performance, reaching 70mW/cm^2, thus improving the performance of simple PBI membrane by 43%. The result is important to realize the compromise present between the higher conductivity of the high PVA-content membranes and the better mechanical properties of the high PBI-content membranes, been the PVA:PBI 4:1 membrane the optimal combination. This result, and the complete characterization performed, will be interesting for the future development and application of this type of membranes.

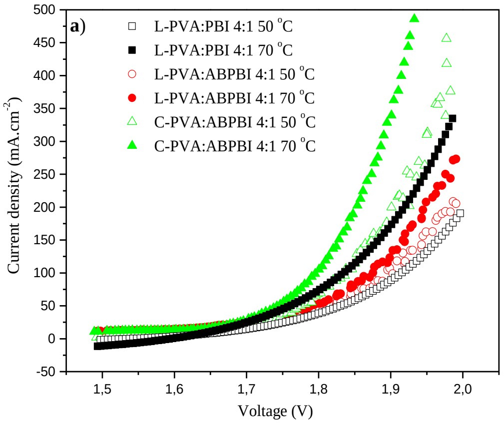

Figure 1: Short term in alkaline electrolysis test

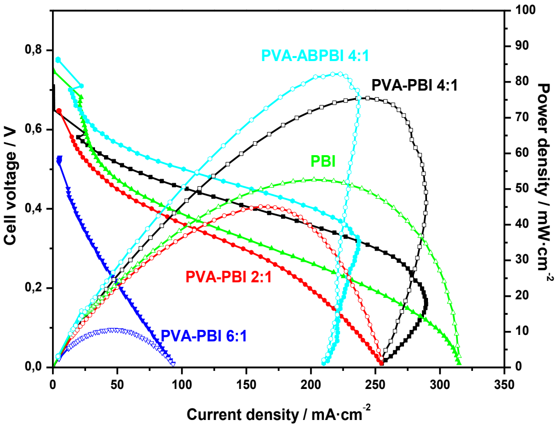

Figure 2 Polarization curves in ethanol fuel cell

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Study of formal potential of pyrolyzed catalysts as reactivity index for oxygen reduction reaction in basic media.

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MN4 complexes, as metallophthalocyanines and metalloporphyrins, are well known catalysts for the electroreduction of O_2 (ORR) and have been extensively investigated in order to achieve a better understanding of the fundamentals of ORR process at modified electrodes and with the final scope of designing MN4 catalysts to replace Pt in fuel cells. However, heat-treated M-N-C catalysts are more active and stable than intact MN4 complexes for ORR [1]. In previous studies, we have established that the formal redox potential is a good reactivity descriptor for the electrocatalytic activity of surface-confined MN4 complexes (MN4 complexes) toward the reduction of molecular oxygen [2] and this is also valid for pyrolyzed MN4 catalysts [1(iii)]. This work explores the relation of the formal potential of M-N-C (M: Co, Fe) pyrolyzed catalysts with their catalytic activity for the ORR. Different MN4 (Co, Mn and Fe porphyrins) complexes were adsorbed on carbon Vulcan and then pyrolyzed at different temperatures (600, 800 and 1000 ºC). The formal potential of M-N-C catalysts was determined by square wave voltammetry and related to the catalytic activity of the pyrolyzed catalysts expressed as $(\log i)_{E=cte}$. The results showed how the pyrolysis process increases the catalytic activity towards ORR of all heat-treated MN4 complexes. However, this catalytic increase is dependent of the precursors ratio (MN4/Carbon), the amount of nitrogen in MN4 precursor and temperature treatment under nitrogen. The increase in activity also depends how different the original structure is compared to the final structure upon pyrolysis. The pyrolyzed (M-N-C) and un-pyrolyzed (MN4) catalysts followed a unified trend where the activity increases when their formal potential is shifted to more positive values. This lineal dependence implies that the formal potential of the pyrolyzed and un-pyrolyzed catalysts acts as reactivity index to predict the activity toward oxygen reduction reaction.

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Silicon as negative electrode material – what have we learnt through interface studies

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Silicon in a graphite matrix is expected to increase the overall specific capacity of a Li-ion battery. The cycling stability is, however, a problem. In an attempt to understand reactions leading to capacity fade we have performed an extensive research program at the Ångström Advanced Battery Centre (ÅABC) at Uppsala University in studying the silicon/electrolyte interfaces [1,2,3], the role of binders [4] and different coating material which has led to the development of free standing flexible electrodes [5,6]. We have used both hard kinetic energy photoelectron spectroscopy and ambient pressure photoelectron spectroscopy to study the interfaces. Our attempts have been to address the negative electrode and the challenge of the large volume expansion experienced when alloying lithium with silicon. We show of our more promising results.

The lithium salt is one important parameter for better cycling of a silicon electrode. Salts that do not generate HF during cycling are vital for a more stable cycling, or $LiPF_6$ where the electrolyte contains a HF-scavenger or an additive which prevents HF etching are another route to take. It is important to prevent etching of the silicon oxide layer which always is present on silicon particles.

We have also worked with methods to prevent HF etching by protecting the silicon particle from direct contact with the electrolyte. We then attached silicon nanocrystals to grapheme layers with a sol gel process which was then freeze dried with PVA before heat treatment with a combustion process. This gave the free-standing electrode a cycling stability vs. lithium for more than 1400 cycles but also a stable cycling performance in a full cell where the cathode was $LiFePO_4$ (also made as a free-standing electrode). The results will be discussed based on detailed electrochemical analysis, in-situ technique and post-mortem morphological characterizations. We confirmed and quantitatively analyzed the contributions from traditional alloying/de-alloying mechanisms and non-diffusion controlled pseudocapcitive behavior for high rate Li^+ storage.

Acknowledgements

All my students and post docs who have worked and are still working on silicon electrodes are acknowledged for their contributions: Bertrand Philippe, Fabian Jeschull, Fredrik Lindgren, Yue Ma, Chao Xu. The funding from the SiLiCoat project and the Swedish Energy Agency as well as the Swedish Research Council are highly appreciated.

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Influence of Mo-site doping on the electrochemical properties of $Sr_2MgMo_{0.9}A_{0.1}O_{6-\delta}$ (A = Co and Mn)

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Solid oxide fuel cells (SOFCs) are electrochemical devices that directly convert chemical into electrical energy with high efficiency. One of the main characteristics of these devices is its fuel flexibility, promoted by the high operating temperature (T> 800ºC). However, there is a compromise between good electro-catalytic properties of non-precious metal electrodes and degradation issues produced by the high operating temperature. As temperature decreases, one major concern, from the point of view of anode materials, is its degradation due to SH_2 impurity of H_2-fuel produced by hydrocarbons reforming.

One promising material as SOFCs-anode is the double perovskite Sr_2MgMoO_6 (SMMO) [1], which exhibits high electrocatalytic performance for H_2-oxidation, sulphur tolerance and thermal stability, but poor electrical conductivity. The oxygen vacancies concentration and cation valence determine the physical and electrochemical properties of these oxides [3]. Therefore, it is expected that the partial substitution of Mo^{+6}/Mo^{+5} by A-cations (A = Co and Mn) with lower oxidation state will impact not only in the oxygen content, but also on the structural and electrochemical properties of the double perovskite $Sr_2MgMo_{0.9}A_{0.1}O_{6-\delta}$ (SMMA; A = Co and Mn). XRD patterns revealed that SMMCo, similarly to the undoped SMMO compound [4], crystalize with triclinic structure, while SMMMn adopts a tetragonal structure. Microstructural variations, due to increasing synthesis temperatures, between SMMA compounds were observed by using transmission (TEM) and scanning (SEM) electron microscopy. X-ray photoelectron spectroscopic analysis (XPS), combined with O-content determination by thermogravimetry, were used to study the oxidation state and to evaluate changes in the SMMO surface due to the partial substitution of Mo by transition metals (Co and Mn). Electrochemical impedance spectroscopy (EIS) measurements under reducing conditions (10%H_2-Ar) allowed to see the influence of the cation substitution on the H_2-oxidation area specific resistance (ASR).

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Reactivity predictors for oxygen reduction reaction (ORR) on substituted Cu(I) 1,10-phenanthroline-modified electrodes.

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In previous works, we have established that the $M^{+n}/M^{+(n-1)}$ formal redox potential is a good reactivity index for the electrocatalytic activity of surface-confined MN4 complexes (metal phthalocyanines, metal porphyrins) and also, that the redox potential of the catalyst can be "tuned" by the electron-withdrawing or electron-donor power of the substituents on the ligand [1]. In this work we present two new correlations between the Cu(II)/(I) formal potential ($E^{o\prime}_{cat}$) of several substituted copper(I) bis-1,10-phenanthroline derivatives, and their catalytic activities for oxygen reduction reaction (ORR). The first correlation corresponds to the *electronic series*, where the increase of formal potential, and hence their catalytic activity, is related to the electronic nature of the substituent. However, in the second one, named the *steric series*, the change on the formal potential is related to the steric effect induced by the 2,9 substituents, which hinder the Cu(I) to Cu(II) tetrahedral/planar conformational transition, favoring the stabilization of the tetrahedral coordination geometry of Cu(I) center. The results show that 2,9-substituted complexes favor a mixed mechanism with more hydrogen peroxide formation than the complexes without substituents in these positions.

In order to explain their electro-catalytic activity for ORR, theoretical studies under DFT methodology (DFT) were carried out. The theoretical calculation, using the donor-acceptor approach explained by the intermolecular hardness ($\Delta\varepsilon_{D-A}$) [2], allow us to demonstrate the *electronic series* tendency (see Figure 1). Nevertheless, the *steric series* requires other studies related with the structural effect. This effect can be explained in terms of a potential energy surface constructed in function of the degree of flattening of these compounds, compared to that of the electronic series. Finally, the RRO mechanism for some representative compounds of both series was also studied, demonstrating a concerted mechanism which implies the adduct formation and the first electron-transfer in a single step, keeping the Cu(I) oxidation state.

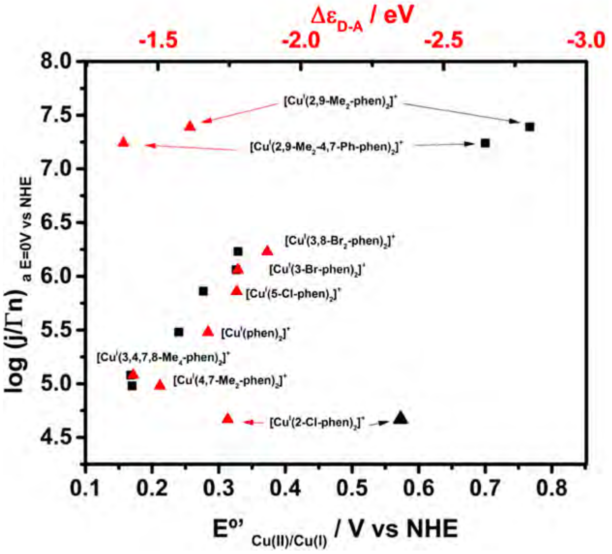

Figure 1. Linear correlations for ORR activities, expressed as $(\log j)_E$, corrected by surface coverage and electrons transferred, on modified glassy carbon electrodes in 0.1M $NaClO_4$ and 0.04M of acetic acid/sodium acetate buffer, pH 5.2, versus (black) the formal potential of the catalyst ($E^{o\prime}_{cat}$), and (red) the calculated intramolecular hardness ($\Delta\varepsilon_{D-A}$), between HOMO of Cu(I) complexes and SOMO of molecular oxygen.

Acknowledgements: The authors are grateful for the support of FONDECYT projects 1161117 and 1140199.

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Methods for Determining the "Ultimate" Lithium Insertion/Extraction Kinetics.

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Arguably, electric and hybrid electric vehicles are at the frontiers of lithium batteries development. As a comparably new market it is distinctly different from mass produced microelectronics, not only in the energy per battery unit but also in the power performance requirements. Especially the required charging rates during deceleration and emergency charging, as well as, the discharge rates during startup from standstill are exciting challenges. Consequently new chemistry and new material morphologies like nanowires, shape controlled nanoparticle and size/shape controlled meso-scale agglomerates are being developed at an impressive rate.

The standard methodology to characterize the rate performance of these new materials is to fabricate composite electrodes that combine the electroactive materials with a conductive carbon/polymer binder matrix and electrolyte. The electron and electrolyte transfer paths thus established to the active material are therefore highly complex. This brings about an important question inherent to the composite electrode, *i.e.* is the electrochemical performance limited by the active material *or* by the transport of electrons and/or ions in the electrolyte filled electrode structure?

We have in responds to this type of question developed a simple analysis technique based on classical chronopotentiometry and composite electrodes, as well as, a series of solution based analytical techniques that allow for the study of the redox reaction kinetics *without* the use of composite electrodes. These include both *in situ* and *ex situ* detection schemes, as well as, several different redox systems appropriate for different positive electrode materials. A major advantage of our solution based approach is that the reaction uniformity throughout the sample provides new kinetic insight, which can help to distinguish between possible reaction mechanisms, thus providing better fundamental understanding of both new and existing redox chemistries.

Properties of Lithium Battery Particles From Electrochemical Micro-Pipets Measurements

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Lithium ion batteries are a commercially successful method for portable electrical energy, demonstrated by their use in portable electronics and the recent application as an alternative automotive power source to the internal combustion engine.[1] However, for lithium ion batteries to be a competitive alternative to fossil fuels in the automotive industry, electrode materials with improved capacity and charge/discharge rates are required. As new anode and cathode materials are developed[2] they are typically screened for advantageous properties by assembly into a working battery. This involves the fabrication of a film from a mixture of conductive material (*e.g.* carbon), a binder (*e.g.* polyvinylidene fluoride), and the active material of interest. A film is cast onto a conductive material to form the active electrode, before assembly within a coin cell. How the film is cast, the ratio of the individual components of the film, the drying procedure for the film and the final assembly of the coin cell can significantly alter the performance of the battery.[3,4] In order to avoid misleading information about the effectiveness of a novel active material many coin cells are required to validate findings.

Here we present micro-pipet measurements[5,6] which demonstrate the suitability of the technique for probing lithium ion battery materials. Specifically, we probed dispersions of active materials to determine the oxidation and reduction potentials, and the charge capacity of the material. Data obtained on candidate materials by the micro-pipet method was compared to coin cell measurements, to critically assess this technique for characterization of active battery materials.

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Synthesis of $LiMg_{0.05}Mn_{1.95}O_4$ cathode using lithium compounds with high magnesium content from natural brines

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In present work, Mg-doped $LiMg_{0.05}Mn_{1.95}O_4$ (LMO-Mg) powders were successfully prepared by a simple ultrasound-assisted sol–gel (UASG) method using lithium compounds with high magnesium content from natural brines. The structure, morphology and electrochemical properties of the products have been investigated in detail. The results were compared with those of the pure $LiMn_2O_4$ (LMO) spinel.

Cycling tests were conducted in 2032 type-coin cells, which were cycled between 3V and 4.2V at a constant current C/3 for 100 cycles. All experiments were operated at room temperature. The cycling performance was analyzed using a tool based in MATLAB software.

Figure 1, shows the X-ray diffraction patterns of LMO-Mg and LMO, both patterns reveal that the materials are crystalline and that the Mg-doping does not alter the crystal structure.

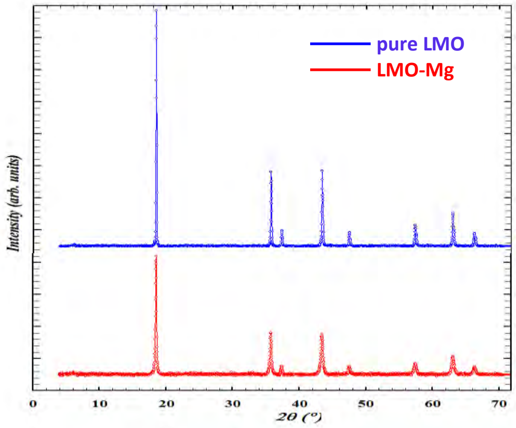

Figure 1. X-ray diffraction patterns of LMO-Mg and LMO.

Figure 2a, shows the profiles of charge and discharge of LMO-Mg for 100 cycles and Figure 2b, shows graphic of discharge capacity with cycle number for LMO-Mg and LMO, respectively. The performance of the discharge capacity variation for LMO-Mg show a more stable behaviour with the cycle number, compared with pure LMO.

After 100 cycles the capacity retention of the initial discharge capacities, 102.12 and 101.95 mAh g^{-1}, were 94.92 and 89.46% for LMO-Mg and LMO, respectively (Table 1). The results of capacity retention showed and excellent cycling performance and stability for LMO-Mg synthesized by ultrasound-assisted sol–gel (UASG) method.

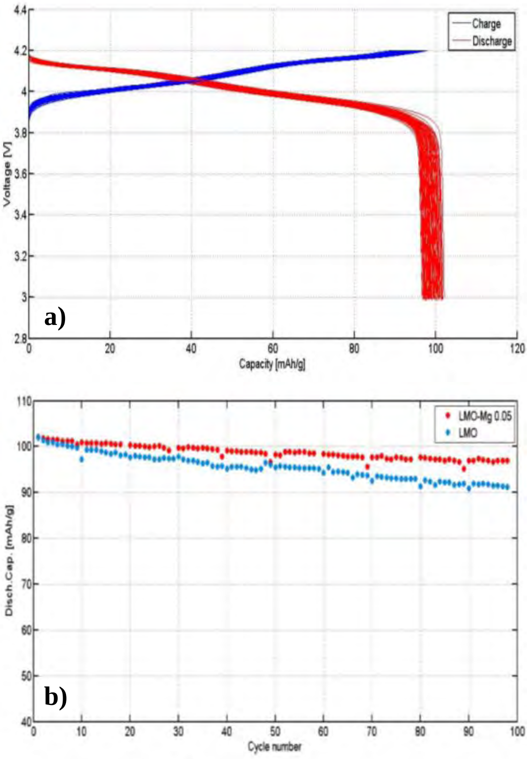

Figure 2. a) Variation of the charge and discharge curves of LMO-Mg with the cycle number from 3 V to 4.2 V for 100 cycles, a) 2D and b) 3D graphics; **b)** Variation of discharge capacity with cycle number LMO-Mg and LMO.

Cathode active material	**LMO-Mg**	**LMO**
Initial capacity (mAh g^{-1})	102.12	101.95
Final capacity (mAh g^{-1})	96.94	91.21
Capacity retention %	94.92	89.46
Capacity fade %	5.08	10.54

Coulombic efficiency %	99.45	97.95

Table 1. Results obtained from cycling test of LMO-Mg and LMO.

Novel permselective membranes for lithium-sulfur batteries

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The escalating demand for energy due to fluctuation in the oil prices and global warming has prompted researchers to find alternative energy resources around the world. Fuel cells, supercapacitors, and lithium batteries are identified as strong contenders to fulfill the future energy requirements. The unique properties, such as high single cell voltage, energy density, no-memory effect, and long cycle life have qualified lithium-ion batteries as the ultimate power source for portable electronic gadgets such as laptop computers and mobile phones. However the state-of-the-art lithium-ion batteries cannot meet out the demands from transport sectors.

Lithium-sulfur batteries, characterized by high theoretical capacity, low cost and natural abundance of the active element, have attracted increasing attention as one of the most promising system to meet the market requirements. Despite these unique properties, the challenges such as low electronic conductivity of sulfur, formation and subsequent shuttling of polysulfides, and poor interfacial properties of lithium metal anode hamper Li-S system from commercialization. In order to conquer these challenges, several strategies have been adopted. Coating of separators with suitable ion selective materials is considered as more effective than modifying the cathode materials. Herein we introduce a 1, 3, 5 benzene tricarboxylate-manganese (Mn-BTC) metal organic framework (MOF) covered polyolefin separator which acts as permselective in a Li-S cell g. The Li-S cell with coated membrane exhibited higher discharge capacity and Coulombic efficiency than the one with uncoated. The diffusion of polysulfides is successfully blocked by the coated separator due to the repulsive ionic forces provided by the COO^- that is present in the periphery of Mn-BTC MOF. In addition, multi-walled carbon nanotubes (MWCNT) and magnesium aluminate ($MgAl_2O_4$) were coated on either side of commercially available Celgard 2320 membrane by doctor blade method to prepare a tri-layer (TLM) membrane. Each layer of the TLM functions for a specific purpose: the MWCNT provides electronic conductivity while the pores of Celgard 2320 facilitate for lithium-ion transport and $MgAl_2O_4$ supresses the shuttling of polysulfides due to the electrostatic attractive force. The TLM exhibited superior thermal stability and ionic conductivity than the uncoated Celgard 2320 membrane. The Li-S cell with TLM offered higher discharge capacity than the one with uncoated membrane.

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High Performing Composite Cathode Comprising Graphene and Magnesium Aluminate for Li-S Batteries

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These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated. Technological advancements in rechargeable batteries are being driven by the humongous need to power portable electronic devices and hybrid electric vehicle applications. The lithium-ion battery which is widely used to power electronic gadgets (with a specific capacity of ~250 mA h g^{-1} and an energy density of ~800 Wh kg^{-1}) is insufficient to meet out the requirements from transport sector and for power grid applications. Lithium-sulfur batteries stand as a promising alternative owing to their low cost, and abundance of sulfur active element. By assuming complete reduction of sulfur to form Li_2S, the theoretical specific capacity and energy density of Li-S battery has been calculated as 1675 Ah kg^{-1} and 2600 Wh kg^{-1}, respectively which is almost five-fold higher than that of conventional lithium-ion batteries. However, the challenges such as low electronic conductivity of sulfur, formation and subsequent shuttling of polysulfides, and poor interfacial properties of lithium metal anode hamper Li-S system from commercialization. In order to circumvent these issues, numerous attempts have been made such as developing electrode materials via composite sulfur cathodes by encapsulating sulfur in carbonaceous matrices, conducting polymers etc.,

Here herein we introduce a novel ternary composite electrode composed of sulfur, graphene, and magnesium aluminate ($MgAl_2O_4$). Synergistically, each component functions for a specific purpose: the added graphene sheets facilitate for fast electron transfer while $MgAl_2O_4$ provides strong binding sites for trapping polysulfide intermediates. The sulfur active material which resides in this ternary mixture involves in the electrochemical reactions and delivers energy. With this unique architecture the Li-S cell delivered a specific discharge capacity of 1394, 800, 492 and 117 mAh g^{-1} at 0.1, 1, 2 and 5C-rate respectively on its first cycle. The charge-discharge characteristics are found to be better than earlier reports with metal-organic frame work as additive.

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Synthesis and mechanical characterization of nanocomposite membranes with Halloysite Nanotubes and phosphotungstic acid for Electrochemical Hydrogen Compression System (EHCS)

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Abstract

One of the most important problem in an Electrochemical Hydrogen Compression System (EHCS) is the membrane, due generated pressure in the catholic chamber where the hydrogen is reduced at high pressure. For this reason, we are working in the synthesis and characterization of membranes based on SPEEK and compared with standard Nafion®. It has demonstrated that incorporation of halloysite nanotubes (HNT) improvement mechanical properties in the membranes, likewise, this membrane need it improve its proton conductivity for this motive we add the phosphotungstic acid (PWA).

In this investigation, we work in the synthesis of composite membranes baseline Sulfonated poly (ether ether ketone) with different sulfonation degree (SD). In addition these membranes were characterized mechanically for tensile test and it was observed the membrane with SD = 0.7 has the better tensile strength (TS = 29 MPa) in comparison with other SD. However it observed this SD increase the water uptake resulting in a deformation of the membrane. The incorporation of HNT proportion mechanical stability and PWA improvement proton conductivity. The membranes synthetized present excellent properties to be used in an EHC due to high mechanical stability and its proton conductivity compared with Nafion.

Nanostructured Ni/(Ce,Gd)$O_{2-\delta}$ Anodes For Intermediate-Temperature Solid-Oxide Fuel Cells (IT-SOFC)

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The development of intermediate temperature solid Oxide Fuel Cells (IT-SOFC) as high efficient energy conversion systems requires the optimization of its components: cathode, anode and electrolyte.

Composite materials formed by NiO and $Ce_{1-x}Gd_xO_{2-x/2}$ (GDC) were widely studied for the preparation of efficient IT-SOFC anodes [1] while perovskite materials such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-d}$ (LSCF) were recognized as excellent cathodes [2].

The electrocatalytic activity of Ni-CGO cermet anodes towards different fuels is strongly affected by their preparation conditions, which determine the microstructure and morphology of these materials, although the correlation between the electrochemical performance and the materials characteristics are not fully understood [3]. In previous works we investigated samples prepared by a new method, which produces a powder with a very homogeneous NiO distribution with smaller particle sizes and narrower distribution than the commercial cermet [4]. The study of the oxidation state and coordination of Ce and Ni in these cermets, simulating in-situ conditions, was performed using synchrotron Dispersive X-ray Absorption Spectroscopy (DXAS) technique. Nanometric sized particles showed faster and higher reduction extents than micrometric particles of the same composition [5]. In this work, we present a study of the performance of these anodes sintered at different temperatures, in order to obtain different characteristic grain sizes and microstructures, under diluted hydrogen and methane atmospheres. The cell power of Ni-CGO/CGO/LSCF cells configuration is measured in a home-made equipment. The structural and morphological characteristics are analyzed by X-Ray Diffraction and Transmission and Scanning Electron Microscopy, respectively. The correlation between the electrochemical behavior, electronic properties and microstructural characteristics will be discussed.

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Fluorination surface treatment to mitigate carbon corrosion and improve the durability of Pt electrocatalysts in Proton-exchange Membrane Fuel Cells.

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One of the principal issues in proton-exchange membrane fuel cells (PEMFC) is the electrochemical degradation of the high surface area carbon supporting the Pt-based electrocatalyst. This electrochemical oxidation of carbon into CO_2 is promoted by Pt, specially proceeds in the harsh condition of the PEMFC cathode (acidic environment, O_2 atmosphere.), and results in irreversible performances loss.

In this contribution, controlled fluorination of several carbon supports is studied as a surface treatment to improve their resistance to corrosion. Pt-nanoparticles were deposited by the polyol method on each support. The catalytic activity of these Pt/C electrocatalysts towards the oxygen reduction reaction (ORR) was determined, and their durability probed from accelerated stress tests (AST) conducted at T = 80°C in a four-electrode cell, both in load cycle (0.6-1.0 V) and start-up/shutdown (1.0-1.5 V) protocols. XRD, TEM and Raman spectroscopy were used, before and after AST, to characterize the materials degradations.

The results show the interest of the fluorination. Firstly, the fluorination treatment does neither affect the dispersion of the Pt nanoparticles on the carbon supports, nor their ORR activity.

Secondly, from the electrochemical and physical characterizations, an increase in the corrosion resistance is observed for the fluorinated carbons compared with the bare carbons. An optimal fluorination rate was demonstrated for the most resistant (graphitized) carbon support (CBs).

Fig. 1. a), b), e) and f) TEM images on the fresh and after 15k cycles (load protocol) of the carbon black support (CBe) and of the fluorinated CBe carbon (F-CBe~~) with~~ , F/C (at) = 0.24), respectively. c) and g) corresponding particle size distribution before and after AST. d) and h) Pt/C activity toward the ORR on the fresh and after AST, 5 mV/s at 168 rad/s in oxygen-saturated 0.1 M $HClO_4$ aqueous solution.

Study of electroplated Ni-Mo and Ni-Mo-P coated stainless steel as bipolar plates in PEM fuel cell

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The bipolar plates (BPPs) are important components in PEM fuel cells, as they serve as current collectors, distribute the reactants uniformly through flow field channels, facilitate water and thermal management through the stack, and separate individual cells in the stack [1]. The development of cost effective BPPs with acceptable performance and durability is a key challenge for PEMFCs.

In a recent study [1] we characterized electroplated Ni-Mo and Ni-Mo-P coatings on stainless steel BPPs by means of SEM/EDX, AFM, XRD, water droplet angle measurements and corrosion tests, and evaluated the internal contact resistance (ICR) *ex-situ*. This investigation aims to evaluate the performance and the internal contact resistance (ICR) of the coatings by electrochemical measurements performed *in-situ*. Parameters such as cell temperature, current density and operation time in a fuel cell are studied and post analysis of the surface morphology and the effluent water are carried out by using SEM/EDX and inductively coupled plasma mass spectrometry (ICP-MS), respectively.

Figure 1a shows the performance of the electroplated BPP after 45 h of galvanostatic operation at 0.143 A cm^{-2}. All coatings show better performance than the bare stainless steel BPP. In line with the *ex-situ* measurements [1], best performance was obtained for Ni-Mo(100) coating (electroplated at 100 mA cm^{-2}). The phosphorous element was introduced in order to improve the anti-corrosion properties of the coating [1], but no enhancement in performance was registered by the addition. Instead, concentration polarization was revealed for the Ni-Mo-P(100), while the Ni-Mo-P(30) showed the highest cell resistance at all measured current densities. Figure 1b clearly shows that the ICR of the bare 316L is very unstable, especially at high current densities, in accordance with the results presented by Ihonen et al. [2] and Oyarce et al. [3]. The ICR is significantly decreased and much more stable for the Ni-Mo(100) coated BPP and meets the DOE requirement.

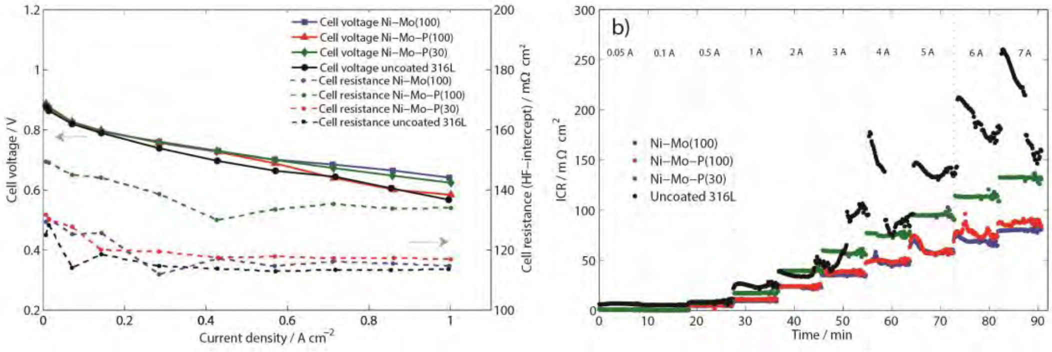

Figure 1. a) Steady state polarization curves of the bare as well as Ni-Mo(100), Ni-Mo-P(100) and Ni-Mo-P(30) coated 316L BPPs, after 45 h of operation. b) ICR of each sample at different current densities. (Conditions: T=80^{O}C, clamping pressure=8 bar, RH=90%, flow rate 60 ml min^{-1}).

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Measurement of Oxygen and Hydrogen Solubilities in Electrolytes for Lithium-ion Batteries

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Lithium-ion batteries (LIB) are well established as one of the best system for energy storage devices. In this technology, classical electrolytes are composed of mixed alkyls carbonates with some safety concerns. During the standard utilization of the battery, gases are inherently generated due to undesirable side reactions. Their accumulation induces a rise of the internal pressure, leading to swelling and potential safety risk. Additionally the pressure buildup can affect the capacity fade and overall cycle life. Various solubility of gases (CO_2 and CH_4) in alkyls carbonates studies have been reported[1,2] but to date no work has been done for O_2 and H_2 solubility even though they are the most importantly produced gases in LIB.
In this study, we present the solubility evaluated by an isochoric saturation technique and expressed as Henry's constant K_H, for O_2 and H_2 in pure alkyl carbonates solvents as well as their mixtures containing 1M LiX (X = PF_6 or TFSI) as a function of temperature. The measured solubility are compared to those reported previously for CO_2 and CH_4 and their evolutions are discussed according to the thermodynamic properties like the standard Gibbs free energy, enthalpy and entropy of the dissolution:

$$K_H \equiv \lim_{x_2 \to 0} \frac{f_2(p,T,x_2)}{x_2} \cong \frac{\phi_2(p_{eq},T_{eq})p_{eq}}{x_2} \; ; \quad \Delta_{solv}G = RT \ln\left(\frac{K_H}{p^0}\right); \quad \Delta_{solv}H = -RT^2 \frac{\partial}{\partial T}\left[\ln\left(\frac{K_H}{p^0}\right)\right]; \quad \Delta_{solv}S = -RT \frac{\partial}{\partial T}\left[\ln\left(\frac{K_H}{p^0}\right)\right] - R\ln\left(\frac{K_H}{p^0}\right)$$

From results, it appears that the solubility of O_2 varies quasi-constantly with temperature with no lithium salt and increases in presence of $LiPF_6$. On the contrary, in presence of LiTFSI, O_2 solubility decreases drastically as the temperature rises.

- At T < 273K, O_2 solubility increases according to the following order: LiTFSI < no salt < $LiPF_6$.
- At T = 303K, all three mixtures present a similar solubility.
- At T > 333K, the tendency of O_2 solubility is inverted: $LiPF_6$ < no salt < LiTFSI.

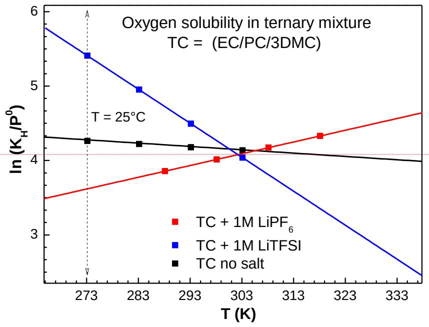

Figure 1 : *O_2 solubility as a function of temperature in TC, TC + 1M $LiPF_6$ and TC + 1M LiTFSI, expressed as Henry's constant K_H*

Table1*: Thermodynamic parameters for H_2 solubility in TC, TC + 1M $LiPF_6$ and TC + 1M LiTFSI at 293K*

AX 1 mol.L^{-1}	T(K)	$\Delta_{diss}H$ (kJ.mol^{-1})	$\Delta_{diss}G$ (kJ.mol^{-1})	$\Delta_{diss}S$ (JK^{-1}.mol^{-1})	$\Delta_{mix}H$ (kJ.mol^{-1})
no salt	293	6.80	1072	-13.35	7.70
$LiPF_6$	293	-0.71	10.90	-39.61	0.19
LiTFSI	293	-0.64	10.98	-39.62	0

The obtained solubility trends and thermodynamic values (Table 1) can been explained by the chemical interactions of the participating chemical species (solute: Li^+, PF_6^-, $TFSI^-$ and O_2) and (solvents: PC, EC and DMC). In general, entropy variation of dissolution informs on the solvents' molecules interaction around the gas or salt, while standard enthalpy governs the intermolecular interactions between the solute and solvents. The results indicate that the new organization induced by oxygen or hydrogen molecule introduced as solute 2 in concurrence with LiX as solute 1, is directly in relation with the cross-interactions (solvent-gas-ions) especially in the case of $TFSI^-$ anion.

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Development of SiO_2 based Composite Anode Material for Li-ion Batteries

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Lithium-ion batteries (LIBs) play a crucial role in fulfilling increasing demands on portable energy storage systems. Nevertheless, improvements are still necessary since storage capability of commercially available LIB system is still insufficient. Graphite is one of the commercially successful anode materials with low cost and good cycle performance, but its low theoretical specific capacity (~ 372 mAh g^{-1}) cannot meet the demands of the energy market [1]. Therefore, recently research in exploring alternative high-capacity LIB anodes has predominantly focused on Li-alloying anodes [1]. Silica (SiO_2) is under consideration as a potential next-generation anode material for LIB due to its high energy density, cost effectiveness and abundance on the Earth's crust. It was also found that it is capable of storing Li-ions with a theoretical specific capacity of 1965 mAh g^{-1} [2]. The cyclic dimensional variations of silica during charging and discharging processes is known to result in pulverization of active-material particles and cracking of the electrode structure by leading to fast capacity fading and poor cycle life [3]. This is a considerable barrier to the practical application of silica anodes. There are several approaches existed to eliminate this problem. Firstly, nanostructuring of silica is regarded as an effective strategy to relieve mechanical stress of the electrode [4]. Secondly, combining silica with buffer media like carbon, not only increasing the electronic conductivity but also hampering the pulverization of electrode material [4]. In this work, novel three-dimensional SiO_2/Carbon nanotube/graphene hybrid material is presented as a novel anode material for LIBs. Moreover, two various nanocomposites with multi-walled carbon nanotubes (MWNTs) as well as single-walled carbon nanotubes (SWNTs) were successfully developed for further investigations. The unique hybrid 3D structure of this composite was obtained by chemical free method. The strain in electrode can be effectively alleviated due to the nanostructed features of silica spheres. The volume change during lithium ion insertion/extraction process was buffered as well due to conductive carbon layer leading to enhanced cycle stability and rate performance. The physical and electrochemical characterizations of ternary composites SiO_2/MWNT/G and SiO_2/SWNT/G with various weight ratio were performed. Electrochemical properties of the obtained composite anode material were studied in coin-type cells (CR2032). Galvanostatic charge/discharge measurements were conducted between 0.01 and 3.0 V versus Li^{+}Li/ by multichannel Neware battery testing system. The further details of this work will be presented at the conference.

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Acknowledgements

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Impregnation Study of Graphite Electrode by Vinylene Carbonate Doped Ionic Liquid Electrolyte

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Lithium-ion batteries have rapidly become the most common power source for mobile applications, as portable electronic devices, power tools due to their high energy density and good cycling stability. However, the current lithium-ion technology has an inherent safety problem arising from the use of readily volatile and highly flammable organic carbonates as electrolyte solvents.[1,2] A solution to increase the battery safety could be the replacement of the conventional solvents with ionic liquid, due to their thermal and electrochemical stability, flame retardant performance and high ionic conductivity.[3,4]

Recently, we have tested the harmless and low-cost full cell configuration based on the electrochemical couple Cgr//$LiFePO_4$ (LFP) using an electrolyte composed of a mixture of (1-hexyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide) ($[C_1C_6Im][NTf_2]$) with $LiNTf_2$ ($1 mol.L^{-1}$) and vinylene carbonate (VC) (5 % vol.), referred as to IL*. VC was indispensable to perform the lithium intercalation and de-intercalation in Cgr based electrochemical cell.[5] As a consequence, an understanding study combining Electrochemical Impedance Spectroscopy (EIS) and X-ray photoemission spectroscopy (XPS) was conducted for pointing out the role of VC on the electrolyte wettability and surface impregnation in Cgr electrode.

The wetting time of Cgr electrode was determined through EIS experiments performed at 333K in three electrode Swagelok cells using Cgr as working (WE), Li foil or stainless steel (ss) as counter (CE) and Li ribbon as reference (RE) electrode. Once the cell assembled and placed in the oven, the measurements at the Open Cell Voltage (OCV) were launched immediately and repeated at different impregnation times. The evolution of the Nyquist plot with time and its modelling by equivalent electrical circuits have evidenced a period of 2 to 4 h long enough to stabilise the graphite/IL* interface by an efficient impregnation at 333 K. Moreover, independently on the nature of the counter electrode, the Nyquist plots are consistent with a capacitor behaviour of Cgr close to OCV.

In parallel, the XPS spectra of core levels C 1s, N 1s, O 1s, F 1s, S 2p and Li 1s of $C_1C_6ImNTf_2$, $C_1C_6ImNTf_2$/ $LiNTf_2$ ($1 mol.L^{-1}$) and $C_1C_6ImNTf_2$/ $LiNTf_2$ ($1 mol.L^{-1}$) /VC (5% vol.) on a glass fiber support and a pristine Cgr electrode were performed for studying the chemical composition of the graphite electrode surface after 12h of wetting. XPS results, especially the qualitative and quantitative analyses of C 1s, N 1s and S 2p core peak have shown a change in the surface dipole and a better impregnation of the IL based electrolyte when the VC is present. Additionally, the Cgr dipole change and the better impregnation of IL based electrolyte induce a change in the electrical series resistance and double layer capacitance deduced from EIS measurements.

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Structural characterization and growth study of Au-Ru branched nanoparticles for oxygen evolution catalysis

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Electrochemical water splitting is a critical reaction for the storage and conversion of renewable energy sources such as hydrogen production, rechargeable metal-air batteries and fuel cells. The cell is limited by the anodic oxygen evolution reaction (OER), which typically requires high overpotentials to drive the reaction. The major drawback to designing an efficient OER catalyst is the inherent tradeoff between high activity at low overpotentials and stablity over multiple uses.[1] Currently, Ru is the best catalyst metal for OER due to its low onset potential □1.3 V and high mass activity, achieving □100 mA mg^{-1} at 1.48 V, in acid electrolytes.[2,3] The critical limitation to Ru nanocatalysts is their complete loss of activity over <5 cycles, due to the formation and dissolution of unstable $Ru^{n>4+}$ species at high potentials.[1,2]

To achieve a commercially viable OER electrode, intense research efforts have focused on improved catalyst design by alloying or changing the crystal structure to develop stable nanomaterials with high mass activities.[2] Nanoparticle catalysts with controlled morphologies and surface structures show high electrochemical activity due to their high surface areas and active faces. Synthesizing a nanocatalyst with structural features that address both activity and stability separately offers a way to overcome this issue. To form advanced, next generation, Ru OER catalysts that can outperform spherical and faceted nanoparticles in terms of activity and stability, nanostructures that are needed are (i) three-dimensional (3D) that have (ii) exposed facets in (iii) the nanoscale size range.

This work will present the synthesis of Au-Ru branched nanoparticles that are three-dimensional and faceted in the nanoscale size range. State-of-the-art microscopy techniques were used to characterize the nanoparticle structure, including Transmission Electron Microscopy (TEM), Scanning TEM (STEM), Energy Dispersive X-ray Spectroscopy (EDX) and tomography reconstructions. Time-resolved TEM imaging of intermediate nanoparticles will be presented, which elucidates a new growth mechanism for three-dimensional and faceted nanoparticles. This presentation will discuss the synthesis and growth of Au-Ru core-branched nanostructures and the importance of morphology control on the catalytic performance.

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3D Ru-Au branched nanoparticles for OER with enhanced activity and stability

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The development of new approaches for energy from renewable resources storage and conversion such as metal air-batteries and fuel cells have been attracting increasing attention. In both cases, the cell operation is limited by the sluggish oxygen evolution reaction (OER) happening at the cathode of the metal-air battery during charging and at the anode of the fuel cell. This is because it is thermodynamically and kinetically unfavorable to remove the four electrons from the water to form the oxygen-oxygen bond [1], resulting in high overpotentials for the reaction to occur.

Because of that, many efforts have been done to develop catalysts for the OER to decrease the reaction overpotential. To date, Ru is the best catalyst in terms of activity in aqueous electrolytes, providing high current densities at relatively low overpotentials [2]. However, it suffers from low stability, especially when nanostructures are employed to increase the surface area, limiting its use in practical devices [3].

In order to increase the catalyst stability without compromising the activity, many efforts have been done to improve the catalyst performance by alloying or changing the crystal structure to develop stable nanomaterials [4, 5]. In this work, we have synthesized and characterized 3D Au-Ru branched nanoparticles with well-faceted, uniform branches, which show enhanced activity and stability for the OER electrocatalysis. The nanoparticles deposited over a carbon substrate and in an acid electrolyte have shown improved activity and stability, being the 3D structure crucial for the increased activity, while the low index faceting provided a stability two orders of magnitude higher than the Ru nanoparticles. The development of the Au-Ru branched nanoparticles provide a new design criteria for the development of the next generation of nanoparticles catalysts.

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From the sustainable extraction of lithium to advanced lithium air batteries: An electrochemical approach

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Lithium has attracted interest in recent years due to its application in batteries for portable devices, electrical vehicles, and renewable electrification, pharmaceuticals, nuclear fuels, ceramics, etc. LiCl and Li_2CO_3 , are obtained from Li-containing Li-Al silicate (spodumene) or from Li-rich brines from high altitude salt lakes such as the Salar de Atacama (Chile), Salar de Uyuni (Bolivia), and Salar del Hombre Muerto or Olaroz (Argentina). Lithium ion batteries allowed mobile electronics while advanced lithium-air batteries have high energy density to compete with fossil fuels in electric vehicles.

In this presentation we will discuss experimental studies on two systems:

a) Electrochemical extraction of lithium using a battery type reactor with intercalation of lithium ions into λ-MnO_2 and chloride ions into polypyrrole electrode from natural brine from Olaroz salar (Jujuy, Argentina) and LiCl recovery from $LiMn_2O_4$/ polypyrrole at less of 1 V overall cell.

and,

b) Studies on lithium air battery cathodes in non aqueous lithium electrolyte. The ideal non-aqueous Li air battery comprises a Li metal anode that dissolves in a non aqueous electrolyte and the resulting Li^+ ions react with O_2 products to form insoluble lithium peroxide Li_2O_2 at a porous carbon cathode during discharge. However, real batteries exhibit high charge over potential and capacity fading after few cycles due to side reactions of the highly reactive oxygen reduction reaction (ORR) intermediates such as LiO_2 and $L_{i2}O_2$ that degrade most solvents and electrolytes.

We have employed a variety of electrochemical and spectroscopic techniques to study in detail the interfacial processes during lithium intercalation/deintercalation in $Li_{1-x}Mn_2O_4$ and formation of insoluble and poorly conductive Li_2O_2 upon ORR and detection of side-products such as Li_2CO_3, LiF, etc.
Among the electrochemical techniques we have employed cyclic voltammetry (CV), rotating ring disc electrode (RRDE), and quartz crystal microbalance under electrochemical control (EC-EQCM). These studies were complemented with atomic force microscopy, (AFM), FTIR and X-Ray photoelectron spectroscopy on different surfaces, namely gold, glassy carbon, and HOPG for the study of the ORR. A purpose built electrochemical cell and manipulators system was part or the spectrometer without exposure of the samples to the air.

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Cathode material for Li-Ion batteries prepared by screen printing for Smart Textile applications

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The presented study is focused on the development of cathode for thin and flexible screen printed secondary lithium based accumulators. An ink formulation was developed for the screen printing technique, which enabled mass production of accumulator's cathode for Smart Label and Smart Textile applications. The screen printed cathode was compared with an electrode prepared by the bar coating technique using an ink formulation based on the standard approach of ink composition. Obtained $LiFePO_4$ or $LiNi_{0.5}Mn_{1.5}O_4$ cathode layers were characterized by scanning electron microscopy (SEM), energy-dispersive Xray spectroscopy (EDS) and galvanostatic charge/discharge measurements at different loads. The discharge capacity, capacity retention and stability at a high C rate of the $LiFePO_4$ cathode were improved when Super P and PVDF were replaced by conductive polymers PEDOT:PSS. The achieved capacity during cycling at various C rates was approximately the same at the beginning and at the end, and it was about 151 mAh/g for cycling under 1C. The obtained results of this novelty electrode layer exceed the parameters of several electrode layers based on $LiFePO_4$ published in literature in terms of capacity, cycling stability and overcomes them in terms of simplicity/industrial process ability of cathode layer fabrication and electrode material preparation.

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Development of Lithium ion Battery Components in Bolivia: Towards Renewable Energy Applications

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Bolivia is the country with the largest lithium reserves in the form of brines [1]. This natural resource is a key component in the development of electrode materials for lithium ion batteries such as cathodes, anodes and electrolytes. Many research works are been carried on by the University and the government owned company in order to develop the Bolivian lithium ion batteries industry. This is a summary of these works.

The synthesis and characterization of hybrid $LiFePO_4$-CP (PANi, PPY, PT) was carried on through the use of commercial LiFePo4 material dispersed in water and further polymerization of aniline on the surface of the $LiFePO_4$ particles by self-assembling process [2]. SEM and XRD characterization techniques were used to study the morphology and crystallinity of the obtained material.

A comparison study between LiFePO4 materials of different particle sizes was carried on [3]. The particle size was controlled through the synthesis process in order to enhance the material's electrochemical properties. Three particle sizes were obtained and characterized by SEM and XRD techniques, finally a discharge rate capability retention study was performed. Preliminary results shown an increase of capacity retention as the particle size become smaller.

Solid electrolyte materials based on $LiTi_2P_3O_{12}$ NaSICon ionic conductor structure were synthetized within a lithium boron silicate matrix ($Li_xSi_{1-x}B_xO_2$ /$LiTi_2P_3O_{12}$) by solid state reaction technique [4]. XRD patterns analysis were used to determine the phase formation in function of the stoichiometry and temperature.

An accelerated ageing study of commercial 18650 cylindrical NMC lithium ion cells is been carried out. Lifetime prediction of batteries under particular off-grid PV system charge and discharge profiles will be evaluated. Various SOC ranges are covered regarding incomplete charging, variable charging rate, deep discharge, calendar ageing at high and low SOC among others [5]. Those profiles represent the battery behavior for a typical user from remote and disperse locations in rural regions. The experiment will last at least 6 months, during which, capacity fading and impedance increase will be monitored on each cell. Furthermore, a *post-mortem* evaluation will allow us to find the possible reasons of materials degradation.

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O_2 Selective Membrane Based on a Dextrin-Nanosponge in Polymer Matrix for Li–air Cells Actually Working in Ambient Air

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Global warming and reduction of fossil-fuel supplies demand the pursuit of renewable energy sources and sustainable storage technologies. The rechargeable Li-air battery, coupling the light Li metal with the inexhaustible source of O_2 of the surrounding air, represents an exciting opportunity. However, for many practical applications such as EV, air is the only viable option to supply the battery. In this context, moisture and gases other than O_2 may cause side reactions and corrosion of the Li anode. We report a facile strategy to fabricate a highly effective O_2 selective membrane based on highly hydrophobic fluorinated polymer and cyclodextrins. Several other major issues are responsible for the limited actual capacity and cycle ability. In principal, the high recharge potentials needed to decompose the insulating Li_2O_2 and the parasitic products formed from the electrolyte decomposition during cell discharge result in important energy losses. Palladium nanoparticles, due to the strength of O_2 binding on the Pd surface, have very high intrinsic ORR activities in non-aqueous electrolytes. The use of carbon nanofibers (CNFs) as a support assures high surface area and high pores volume compared to other carbon-based materials. Pd doped mesoporous CNFs produced by electrospinning were used at the cathode of the Li-air pouch cell. Galvanostatic cycling tests in a potential/time controlled mode showed an outstanding cycling life superior to 1500h with more than 150 cycles.

Solvent and electrolyte instability during Oxygen Reduction Reaction in Li-O_2 battery cathodes.

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The importance of lithium metal and lithium salts has rapidly increased due to its multiple applications in diverse fields. Particularly, lithium is the key component in a number of electrochemical devices for energy storage and conversion; some of them constitute nowadays a mature technology (the well-known lithium-ion batteries) whereas some others are still under development (which is the case of Li-O_2 high energy density batteries for electric vehicles). As for the latter, during the discharge reaction (ORR) the O_2 from the air is reduced to form lithium peroxide at the cathode, and the reverse reaction (OER) takes place during charging in the ideal Li-O_2 battery:

$$2Li_{(s)} + O_{2(g)} \leftrightarrow Li_2O_{2(s)}$$

It is precisely in the reversibility of this reaction where the success of the device relies, as the occurrence of "parasitic" reactions results in a loss of charge and a greater over potential of recharge, in case the products of these reactions are deposited on the surface of the electrode. Therefore, one of the major obstacles to overcome is the choice of a suitable solvent/electrolyte pair, as it must exhibit complete stability against the highly reactive species generated during the discharge process. In this context, the stability towards the species arising from ORR and further OER of different solvent/electrolyte pairs (combinations of DMSO or acetonitrile with $LiPF_6$ or $LiBF_4$) has been tested. For this purpose, a vast number of different techniques have been used in order to study these systems from different and complementary points of view: the electrode surface, the liquid phase and even the gas phase, leading us to the conclusion that all solvent/electrolyte pairs tested were unstable at some extent.

As for the understanding of the surface chemistry taking place at the electrode-electrolyte interface, X-ray and UV-ray photoelectron spectroscopies (XPS and UPS, respectively) have been performed. These experiments were carried out in an electrochemical cell coupled to an ultra high vacuum line (UHV) equipped with a transfer system built in our laboratory that allows easy, rapid and controlled transfer of the sample between the UHV environment and the ambient pressure (Argon) liquid electrochemical environment. This transfer system serves the purpose to perform ex-situ electron spectroscopic measurements on samples that are initially clean in UHV and are not exposed to the laboratory atmosphere before or after electrochemical measurements, ensuring optimal clean conditions for the experiments. Surface studies were also complemented with atomic force microscopy (AFM) imaging. The electrolyte solution was monitored using IR spectroscopy, while the composition of the gas mixture released during ORR and OER was examined with differential electrochemical mass spectroscopy (DEMS).

All these results will be presented as pieces of the same puzzle that, when put together, give the whole picture for a deep understanding on the unfeasibility of the solvents and electrolytes tested to be used in a future Li-O_2 battery.

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Adhesion Control Mediated by Organic Molecules at Metal/Non-metal Interface

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It is important to control interfacial properties between metal and non-metallic substrates such as polymer and ceramics to obtain high performance of semiconductor chips and electronic/electric devices as well as energy conversion systems. Various attempts have been engaged to get intimate adhesion between heterogeneous interfaces through depositing metallic layer on non-metallic substrate followed by pressing both substrates at high temperature and high pressure conditions. In any methodology, the main issue is to form stronger metallic layers on the non-metallic layers to make electric pathway of devices withstand at more stringent conditions.

For this purpose, we formed an organic molecule layer, (3-Aminopropyl)triethoxysilane, on the surface of silicon wafer dissolved in the organic solvents, toluene, at moderate temperature in the humidity controlled chamber. Then it was catalyzed with Pd/TiO_2 nuclei and sintered, which resulted in more robust adherence between metal and silicon wafer substrate. Then, we chemically and electrochemically deposited nickel and copper layers on it, and measured the mechanical and electrical characteristics between two parallel layers. Now, this technique is also applied other materials such as glass, silicon wafer, silicon nitride layer and polyimide film.

Traceable chemical analyses of new liquid and solid battery components by X-ray spectrometry in UHV environment

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The development of new battery materials aims the optimization of key parameters such as energy density, cycle life and safety. The complete understanding of the functionality of battery components requires the correlation with underlying physical and chemical properties. The determination of these properties is the challenge for most analytical methods due to a lack of reference materials, thus calling for alternate traceability chains and complementary techniques. For this purpose, PTB implemented physically traceable methods based on X-ray spectrometry.

The decomposition of the electrolyte solution, the degradation of the active material and the deposition of impurities are among the main aspects that worsen the performance of the battery so that the elemental composition and the species of the single components need to be studied. With reference-free X-ray fluorescence spectrometry we can determine the mass deposition of elements and with X-ray absorption spectrometry (XAS) we get access to the oxidation state of single elements.

In view of variety of battery components with respect to composition and state of aggregation, dedicated equipment for each material type is favorable. To investigate fluid systems such as electrolyte solutions we designed in collaboration with TU Berlin a fluid cell with a 150 nm thin silicon nitride entrance window that enables soft X-ray investigations to probe even light elements such as fluorine. Battery components which are sensitive to air or humidity have to be handled in argon filled cells. All our experiments are performed in a UHV chamber to ensure highest soft X-ray transmittance. For further steps, and in collaboration with TU Berlin, an in-situ and in-operando cell is under construction. With that and the combination of simultaneous Galvanostatic Cycling with Potential Limitation (GCPL) and XAS measurement capabilities we can get access to the link between material properties and battery behavior (functionality).

Lithium Sulfur (Li-S) batteries are promising candidates for improved high capacity batteries, with up to 5 times higher capacity than conventional lithium ion batteries (LIBs). But the cycling stability of currently developed Li-S cathode materials is limited due to undesired side reactions and occurring polysulfides. With sulfur K-edge near absorption spectrometry (NEXAFS) for the cathode done under protective argon atmosphere we can identify the polysulfide for different SOC and SOH of a battery.

NCM based LIBs are well working systems and under steady development. Some degradation processes of the cathode results in the deposition of manganese at the separator and the graphite anode. With reference-free XRF technique we can quantify the mass deposition of manganese on the anode and the separator. With additional manganese K-edge and L-edge NEXAFS we also can conclude to the present species of manganese.

For improving the conducting properties and the stability of the electrolyte, ionic liquids (ILs) are used for new LIBs more and more frequently. With the fluid cell and performing fluorine K-edge NEXAFS technique we can investigate the different behavior of the anions FSI^- (bis(fluoromethylsulfonyl)imide) and $TFSI^-$ (bis(trifluoromethylsulfonyl)imide) from the ILs in the presence of lithium hexafluorophosphate.

The knowledge about the elemental distribution and the related chemical species will support the directed development of advanced battery materials.

3D graphene-functionalized silicon anode for lithium ion battery with excellent cycle stability and rate capability

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In recent decades, lithium ion batteries (LIBs) have been considered as the most effective and practical technology products for portable electronic devices because of their flexibility, high energy density and long lifespan. An increasing trend of renewable energy, rapid development of electronics, and improved electrode materials for LIBs have inspired researchers to develop high performance LIBs to meet the increasing demand for higher energy load and better cycle performance. Great effort has been dedicated to the fabrication of various materials for LIBs electrodes. Graphite, as a traditional anode material, still plays a prominent role in the LIB commodity because of its high lithiation-dilithiation reversibility and low voltage window. Unfortunately, the capacity is limited to 372 mAh g^{-1}. To search for materials with higher lithium storage capacity, a great number of investigations on metal oxides (or sulfides), Sn, P, and Si have been carried out in recent decades. Among these materials, silicon can make alloy with lithium in the form of $Li_{22}Si_5$ to deliver a highest theoretical gravimetric capacity of ~4200 mAh g^{-1}, and thus is considered to be one of the most promising anode materials for next generation LIB. It is worth mentioning that its quite low delithiation potential and high lithium storage capacity can provide a high working voltage and energy density, which enable promising potential application in electric vehicles. However, those advantages are seriously offset by a great challenge of large volume expansion during lithiation process and the resultant breakage of bulk silicon particles and solid electrolyte interface (SEI), which causes a serious damage to the electrode structure and thus gives rise to a fast decay of the specific capacity. In this work, novel 3D graphene-functionalized silicon will be demonstrated by chemical vapor deposition for a LIB anode, which can overcome the common silicon issue in Si anode The elastic feature of graphene has excellent function to self-adaptively buffer the volume variation during charge-discharge process. In particular, different from traditional graphene or carbon shells (core-shell and yolk-shell), the 3D graphene networks provide much improved unique functions with excellent long-cycle stability and rate capability.

Behavior of Water in Polymer Electrolyte Membranes Investigated by Nuclear Magnetic Resonance Spectroscopy

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Understanding on the mechanism of ion transport in electrochemical systems[1,2] and the signaling in biological systems.[3,4] can be enhanced through probing the behavior of chemical species confined in the nano-meter scale spaces. Our Overhauser dynamic nuclear polarization (ODNP) nuclear magnetic resonance (NMR) data[5] indicate that water close to the hydrophobic inner walls of the channels move faster than those surrounded by water in the middle of the hydrophilic channel. In addition, the ^{1}H magic angle spinning (MAS) NMR spectra of the Nafion membranes thermally degraded with the replacement of SO_3H groups to H show that the water exposed to more hydrophobic environment moves faster. This result is in agreement with the ODNP results described above. The MAS NMR data additionally indicate that the chemical shift of channel water is influenced not only by the number of water per SO_3H group but also by the degree of hydrophobicity where the water is placed.

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Anion Exchange Membrane Fuel Cells: State-of-the-Art

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The Alkaline Anion Exchange Membrane Fuel Cells (AEM-FCs) have recently received increasing attention since in principle, they allow for the use of non-precious metal catalysts, which dramatically reduces the cost per kW of power. Until recently the main barrier in the development of AEM-FCs was the availability of highly conductive AEMs [1]. Latest improvements done in this front are impressive, and some of the new developed AEMs already reached anion conductivities close to those of Nafion for acidic PEM-FCs. In the past four years an increasing number of research studies has been published showing cell performance results from AEM-FC tests. First results are very promising. However, in spite of the advances in AEM development, performance of AEM-FCs is still far from reaching its limits.

Due to present challenges to develop suitable electrocatalysts for the sluggish hydrogen oxidation reaction (HOR), most of the AEM-FC tests found in the literature are still based on Pt as anode electrocatalyst. Recent work has proved for the first time that highly active HOR not-Pt electrocatalysts can indeed be developed for AEM-FCs [2-3]. Another remaining challenge in this technology is the chemical stability of the AEMs [1, 4-5]. Recent breakthroughs in development of ex-situ techniques that provide the true alkaline stability of anion conducting polymers, simulating in-situ environment of an AEM-FC in operation is now leading to design of better functional polymers [6]. This will assure rapid success in development of highly stable AEMs [6].

In this talk a review of the performance results published in the AEM-FC field will be presented. Latest research activities on anion conducting polymers and electrocatalysts for AEM-FC technology will be also discussed.

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Modelling of the Electrochemical Impedance of Oxygen Ion Conductors

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Oxygen ion conductors, like yttrium stabilized zirconia (YSZ) or doped ceria, are currently the most suitable electrolytes for solid oxide fuel cells due to their mechanical and chemical stability and compatibility with the employed electrode materials [1]. Their electrical conductivity is strongly influenced by dopant concentration, temperature, atmosphere and microstructure of the material. While theory and experiments generally agree on the influence of the first three parameters, the influence of the microstructure remains a hot topic. Nanocrystalline samples could display superior conductivity through enhanced grain boundary diffusion or through the effects of space charge overlap. However, accepted theories all predict a lower conductivity for nanocrystalline materials [2], [3] – a point of view that is backed up by many experimental studies [1] but opposed by some [4], [5].

Experimentally, it is possible to separate the bulk and grain boundary conductivities using Electrochemical Impedance Spectroscopy (EIS), but the interpretation of the obtained impedance spectra is not straightforward. The current approach is to interpret the measurement data using the dilute solution model with the Mott-Schottky approximation. However, we know from measurements and atomistic simulations that these assumptions are simply not accurate at realistic doping percentages [6]. This implies that currently, EIS can only provide a qualitative comparison of these materials but not a quantitative assessment of the underlying physical processes.

To remedy these problems, we propose a model that formally describes the atomistic processes on a continuum scale, based on the Cahn-Hilliard description of solid electrolytes [7]. We use this model to calculate impedance spectra and we show how atomistic parameters such as interaction energies and diffusion barriers influence these spectra.

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Development of a Thermally Coupled Hydrogen Storage and Fuel Cell System

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A thermally coupled hydrogen storage and fuel cell system, where the heat produced during the H_2/air PEM fuel cell operation is used to enhance the release of hydrogen from a metal hydride container, is presented. The design involves a vertical arrangement of the hydrogen storage device and the use of the fuel cell exhaust air as the heat transfer fluid instead of water-circulating loops that are used in most of the reported thermally coupled system, which require additional energy for water pumps, electrovalves and control systems. The hydrogen storage device contains a hydride-forming AB_5-type metal alloy ($MmNi_{4.7}Al_{0.3}$, where Mm stands for "mischmetal", a mix of rare earths). The metal alloy absorbs hydrogen forming AB_5H_6 hydride, which has an equilibrium pressure that makes it suitable for both feeding a H_2/air PEM fuel cell and being charged directly from a low pressure water electrolyzer without the need of additional compression.

The metal hydride container is made of 304L stainless steel and has a cylindrical shape. It is provided with aluminum extended surfaces to enhance heat exchange with the surrounding medium. These surfaces consist of internal disk-shaped metal foil and external axial fins.

A H_2/air PEM fuel cell stack (FCgen®-1020ACS fuel cell stack, Ballard Power Systems Inc.) is used. The coolant and oxidant requirements are met with a fan that moves air through the stack. The air is used to cool the stack as well as to provide oxidant for the fuel cell reaction. No external humidification of the air is required. It is designed in a dead-end configuration using dry hydrogen, with no external humidification required.

For the experiments, the metal hydride container was connected to the fuel cell stack by a hydrogen-calibrated digital mass flow controller and the hydrogen pressure was measured using a pressure transducer. Two types of measurements were made. In the first case, the metal hydride container was immersed in air at 20 °C, without thermal interaction with the fuel cell, while in the second case there is a thermal interaction between them by the use of a cone positioned at the outlet of the cell, which directs the fuel cell exhaust hot air to the container exchange fins.

The hydrogen storage device exhibits a good performance to recover hydrogen from the metal hydride decomposition at the design working conditions, i.e., it is capable of delivering 70 L of hydrogen at 0.5 L min^{-1} and 20 °C, which allows a power supply of 50 W for 140 min from the H_2/air fuel cell. Discharges at a higher hydrogen flow rate, namely 2 L min^{-1}, with the container immersed in air at 20 °C, diminishes the hydrogen recovery in approximately 35 %. When the heat generated at the fuel cell is used to increase the container temperature, hydrogen recovery is 100 %, which allows the fuel cell operation at 150 W for 35 min at a high flow rate of 2 L min^{-1}. Therefore, the thermal coupling of the hydrogen storage device and the fuel cell stack substantially improves hydrogen recovery from the metal hydride at high flow rates by favoring the heat transfer through the metal hydride container external wall, which diminishes thermal gradients in the metal hydride bed and leads to a lower decrease of the hydrogen dynamic pressure. Thus, the total hydrogen stored as metal hydride may be used.

Comprehensive understanding of aqueous polymers as effective binders for silicon nanoparticles-based anodes for lithium-ion batteries

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Since the capacity of conventional graphite anode is low for large-scale applications, there has been a great interest to develop new and better materials with higher capacity and lower lithiation potential. At present, silicon is potentially the best replacement because of its elevated theoretical capacity (3590 mAh g^{-1}) and widespread abundance in the Earth's crust. However, the practical application in lithium ion batteries (LIB) suffers from poor cycling performance, due to poor conductivity of bulk Si and structural deterioration resulting from the large volume changes during the alloying/dealloying process with Li ions. Amongst the various strategies for solving the rapid capacity fading, the binder nature and formulation has been recently acknowledged due to its role in the mechanical stability and inter-particle contact between the different phases of the slurries [1,2].

In the present work, we study the performance and properties of SiNPs-based anodes prepared with aqueous polymeric binders in various conditions. Specifically, we conduct a comparative electrochemical performance analysis of slurries prepared with sodium alginate (ALG), poly(acrylic acid) (PAA) and sodium carboxymethylcellulose (CMC) at different pHs (2.50 and 10.00), relative to the standard PVDF binder. Also, the effect of the polymers backbone functional groups and viscosity properties was also investigated. The slurries were made by ball milling a mixture of 40:45:15 wt% of SiNPs:superP carbon:binder and adding the proper solvent.

We found that slurries made with aqueous binders exhibited higher specific capacities and better cycling stability than the conventional PVDF, as the latter can only establish weak van der Waals interactions with the anode constituents. Furthermore, the comparison of cyclic voltammetry profiles and charge-discharge curves revealed that acid pH conditions are preferred to alkaline ones, as both cyclability and electrochemical response towards lithium alloying is greater in the case of acidic pHs. A direct correlation can be made with the viscosity of the polymers solutions as a function of its identity and pH.

SEM images revealed that the laminate morphology and coverage at the electrode are homogeneous and relatively independent of the binder identity and pH. Nevertheless, changes in the degree of segregation between the SiNPs and the superP carbon are observed. This suggests that the cyclability and capacity differences are related to the different abilities of the binders to mix and distribute the SiNPs with the conductive carbon. IR spectroscopic and rheological measurements were made to correlate the electrochemical performance with the interactions between the polymers and SiNPs.

Aqueous polymer binders resulted in an environment-friendly, inexpensive and efficient alternative for Si-based anode preparation relative to conventional PVdF/*N*-Methyl-2-pyrrolidone system. We showed that the performance of SiNP-based anodes for LIBs strongly depend on the polymer binder and its preparation conditions. As the binder is meant to help reduce the level of pulverization of SiNPs and keep contact with the surrounding conducting material, the key of the differences observed rely on the interactions of the polymer chains and the SiNPs surfaces and its mechanical properties.

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$PYR_{14}TFSI$ Ionic Liquid for Li-air Battery

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The rechargeable Li–air battery exhibits a very large theoretical energy density that can compete with fossil fuels for electric vehicle applications with an extended mileage range. The non-aqueous Li–air battery introduced in 1996 by Abraham consists of a lithium metal anode that dissolves in a non aqueous electrolyte and the resulting Li^+ ions react with oxygen to form insoluble lithium peroxide Li_2O_2 at a porous carbon cathode during discharge[1].

A stable electrolyte still remains one of the biggest challenges to resolve for improving a durability of the battery. While the majority of research effort has focused on organic solvents (initially alkyl carbonates, and later ethers, acetonitrile and dimethyl sulfoxide), there has been also some interest in the use of ionic liquids as electrolyte for the Li-oxygen system. However more fundamental studies on oxygen electroreduction reaction (ORR) in this media, as well as stability studies in the presence of reactive oxygen reduced species are needed.

In ionic liquid N-butyl-N-methyl pyrrolidinium bis(trifluoromethane-sulfonyl) amide ($PYR_{14}TFSI$), in the absence of protons and metal ions, reversible formation of O_2/O_2^- couple is observed, an analogous behavior as in the solutions of tetralkylammonium salts in organic solvents[2]. We used Rotating Ring Disc Electrode in order to detect superoxide formation in ionic liquid and its dependence on increased lithium ion concentration, and we have detected the presence of superoxide anion up to concentration of 25 mmol of Li^+. The implications on the mechanism of ORR in the presence of Li^+ ion will be discussed.

In order to investigate the $PYR_{14}TFSI$-based electrolyte stability under conditions relevant to the Li–air cell operation, in situ infrared spectroscopy experiments were performed simultaneously with electrochemical experiments and complemented by differential electrochemical mass spectrometry (DEMS). While DEMS detects electrolyte decomposition products in the gas phase, in-situ SNIFTIRS allows detection of the decomposition products in the solvent phase, adjacent to the electrode surface.

Ionic liquid anion was found to be stable, while the cation PYR_{14}^+ was found to decompose in studied conditions. In oxygen saturated bis(trifluoromethane)sulfonimide lithium (LiTFSI) salt containing $PYR_{14}TFSI$ electrolyte carbon dioxide and water were formed at potential 4.3 V either with or without previous oxygen electro-reduction reaction. However in deoxygenated LiTFSI contacting ionic liquid no formation of CO_2 or water was observed, suggesting oxygen presence to be crucial in carbon dioxide production[3].

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Nanoscale distribution of sulfonic acid groups determines structure and binding of water in Nafion membranes

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Water in proton exchange membranes (PEMs) to a large extent determines the performance of PEM fuel cells because it affects both proton transport and catalytic efficiency. Thus, probing the molecular properties, such spatial arrangement and chemical interactions, of water in PEM materials provides a physico-chemical basis for an improved understanding of PEM device performance. In this work, we make us of the ms temporal and molecular chemical resolution of advanced nonlinear Raman spectroscopy to correlate nanoscale chemical constitution with water properties of Nafion PEMs [1,2].

We quantify chemical interactions between water and Nafion in two chemically equivalent, yet morphologically distinct - extruded and dispersion-cast - Nafion membranes with coherent anti-Stokes Raman scattering spectroscopy. Surprisingly, we find a reduced sulfonic acid head group density in water channels of extruded membranes compared to dispersion-cast ones. These differences result in distinct water-Nafion interactions such that a disproportionally large amount of weakly hydrogen-bound water molecules exists in extruded membranes with lower sulfonic acid density. Interestingly, these membranes also exhibit larger proton conductivity and larger water mobility compared to cast membranes. Our results suggest that future studies comparing fuel cell membrane performance should include parameters that capture the impact of nanoscale channel architecture on macroscopic physical chemistry to accurately evaluate the physics of water and proton transport.

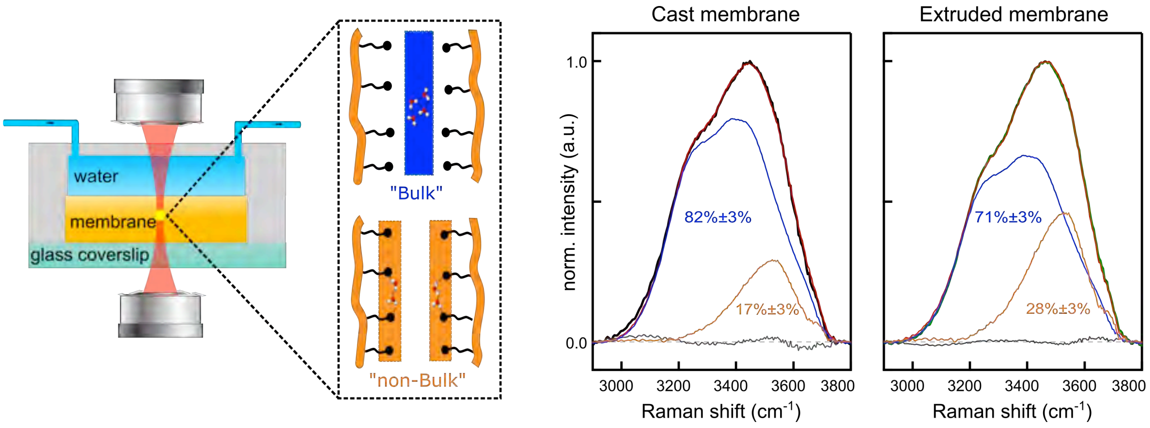

Figure 1. Left: Schematic of CARS experimental setup to probe water in Nafion PEMs. Right: Least-squares fitting result of CARS spectra from two differently processed membranes resolve two types of water species inside the Nafion channels, bulk water (blue) and weakly hydrogen-bound non-bulk water (orange). The extruded Nafion contains a larger relative amount of non-bulk water compared to cast Nafion.

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Electrodeposition of Co_3O_4 thin films for their application in the Oxygen Evolution Reaction

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Co_3O_4 films were obtained by thermal treatment of metallic cobalt electrodeposited on fluorine tin oxide (FTO) substrate from acid and alkaline solutions containing glycine. The Co_3O_4 crystals grew into fine grains under acidic conditions while spheres where obtained with a diameter of 90-200 nm under alkaline conditions. GDS technique was used to determinate the thickness of the films which was ~0.15 µm for all films. XPS analysis showed that Co^{3+}/Co^{2+} ratio of the Co_3O_4 decreases from 1 to 0.6 when glycinate complexes are used as precursors for electrodeposition. Oxygen vacancies increase in crystal structure of Co_3O_4 as the pH of the electrolytic solution increased. Flat band potential of Co_3O_4 films was found to be ~0.18 V (vs SCE) from the Mott-Schottky plot analysis. The electrocatalytic activity of the films for the oxygen evolution reaction (OER) was significantly better compared to commercial Co_3O_4 in 1 M NaOH solution. The Co_3O_4 films obtained in alkaline conditions exhibited a better electrochemical performance with an on-set potential of 0.45 V (vs SCE) achieving a current density of j = 1 mA cm^{-2} at an overpotential of 327 mV while commercial Co_3O_4 reached this value at 447 mV. The highest electrocatalytic activity of Co_3O_4 films obtained at pH 7, 10 and 13, is attributed to the great quantity of Co^{2+} ions formed on the surface of the Co_3O_4 spinel under these conditions, which promote the electroactivity toward the OER.

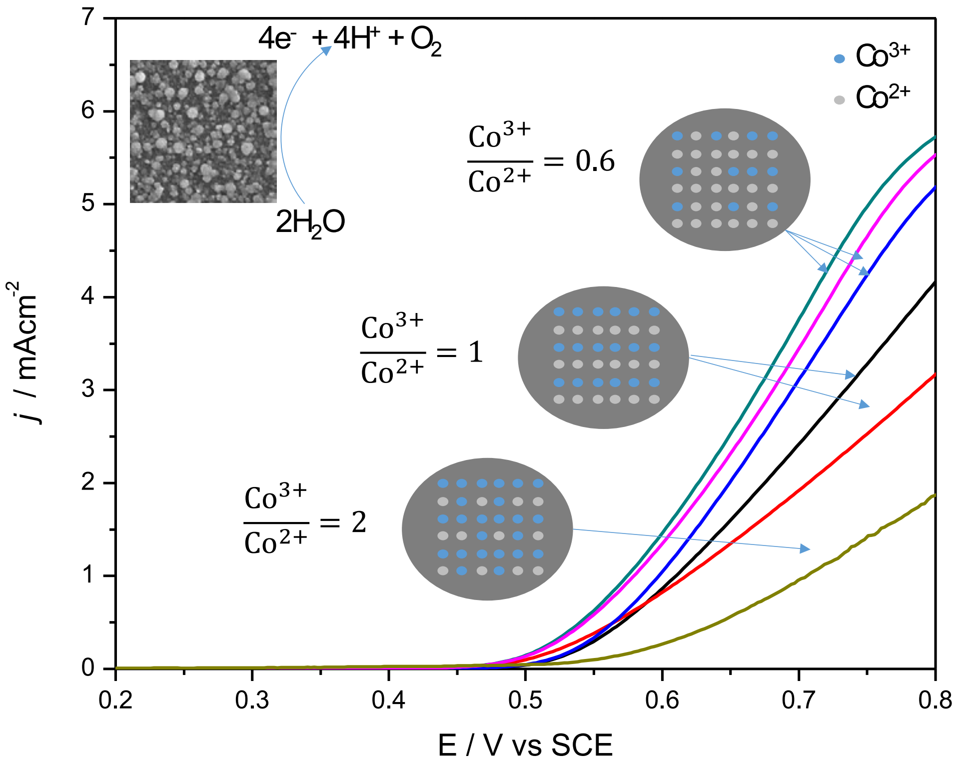

Figure 1.- Polarization curves of Co_3O_4 electrodes in 1 M NaOH at 2 mVs^{-1} without electrode rotation.

Oxygen Reduction Reaction in DMSO Lithium Containing Electrolyte

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Sustainable energy storage devices are required for clean electric vehicles and renewable electrification. Rechargeable lithium-air battery could be the solution for these applications due to its high theoretical energy density. [1]

Lithium-air battery was accidentally introduced by Abraham in 1996. It consists of a metal lithium anode immersed in a non-aqueous electrolyte, and a porous carbon cathode where oxygen reduction reaction (ORR) takes place. [2]

In recent years high donor number solvents such as Dimethyl sulfoxide (DMSO) were proposed due to their capacity to solvate lithium ions and peroxide, a product formed during ORR. Its advantages with respect to other non-aqueous solvents lie on the ORR or OER intermediates and products stabilization and reverse reaction facility. [3]

ORR products and by-products are mainly LiO_2 that could dismutate into Li_2O_2 or could be further reduced by a second electron transfer step to yield Li_2O_2. Therefore lithium peroxide can be formed by two mechanisms, solution phase or surface phase pathways.

Lithium oxygen battery capacity can be enhanced by adding traces of water or redox mediators that shuttle electrons to from the insoluble insulating surface Li_2O_2. The latter can facilitate the OER by oxidation of products and side products formed during the ORR. Extensive studies with 0.1 M $LiPF_6$ in DMSO have proved consistent with those mechanisms.

Rotating ring disc electrode transient experiments have shown two processes, one can be attributed to lithium superoxide formation and the second one to the dismutation in solution mechanism. This chemical mechanism was followed by a simple experiment. Stable superoxide anion was produced by applying 2.2 V in a lithium-free DMSO. Upon addition of 0.1 M $LiPF_6$ to the solution lithium peroxide was formed as revealed by the mass increase with the electrochemical quartz crystal microbalance (EQCM) and atomic force microscopy (AFM).

The ORR products pathway depends on the solvent properties, lithium salt and cathode material as well as current density or potential applied. Lithium superoxide and lithium peroxide formation depend on the lithium concentration and also on the water content. By using EQCM and Differential Electrochemical Mass Spectroscopy (DEMS) it was possible to show that in 5 mM $LiPF_6$ in DMSO insoluble non conducting surface Li_2O_2 is formed by a second electron transfer pathway or LiO_2 disproportionation. Also solvent co-deposition during the ORR has been detected by EQCM. [4]

To recover a clean electrode surface it is imperative to apply high a potential close to 4.5 V. However, at 4.2 V DMSO electrochemically decomposes to form dimethyl sulfone producing CO_2 and consuming H_2O in accordance with Aurbach mechanism. This has been seen by Subtractively Normalized Interfacial Fourier Transform IR Spectroscopy (SNIFTIRS). To avoid this problem, the use of redox mediator it is needed. Tetrathiafulvalene can be used to facilitate the OER by removing all the products and by-products formed during the ORR. Indeed, iron (II) phthalocyanine can also be employed to enhance battery capacity by increasing lithium peroxide deposits on the electrode surface or removing those ORR products. [5,6]

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Effect of Solvent in Electrochemical Environment - Theoretical Studies

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The solvent is the most abundant species and play an important role near the electrochemical interface. In theoretical investigations especially those in which density functional theory calculations are used the solvent is not treated in an appropriate way and modeling of the solvent needs to be improved. Our studies are accomplished by a combination of molecular dynamics simulations (Figure 1), density functional theory, and the theory of electrocatalysis developed by Santos and Schmickler (see ref. [1] and references therein). To model the solvent we use the LAMMPS code [2] and from the simulation we obtain the potential of mean force (pmf) used to calculate the solvent reorganization energy as a function of the distance to the surface. We have applied this methodology in several cases such as metal deposition [3], adsorption of OH on platinum [4], and oxygen reduction reaction [5].

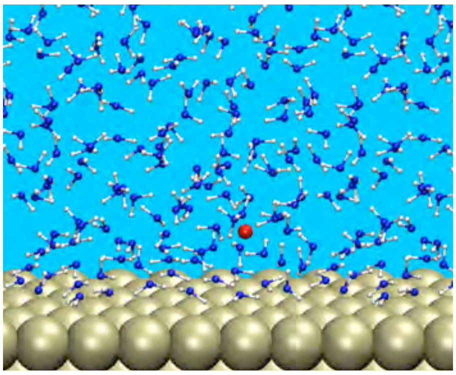

Figure 1: Snapshot of an ion solvated by water molecules approaching the surface.

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rGO Wrapped Activated Microporous Carbon from β-Cyclodextrin Nanosponges for Li/S Batteries

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Future of portables devices, electric vehicles and smart grids demands long life and high energy density batteries. Li/S batteries – a post Li ion technology – provide a sound answer to such requests, as they offer high theoretical capacity (1675 Ah kg^{-1}) and high energy density (2500 Wh kg^{-1}). The development of Li/S system faces several challenges such as low degree of sulfur utilization, gradual capacity fading, poor rate capability and lower Coulombic efficiency mainly due to low conductivity of S (5 × 10^{-30} S cm^{-1}) and Li_2S, solubility of intermediate polysulfides, shuttling of polysulfides and lack of morphology restoration. One of the promising strategy is to encage S in conductive matrices to reduce polysulfides solubility while increasing the cathode electronic conductivity. A sustainable solution is proposed here to produce conductive carbon matrices from bio-based materials. Microporous carbons are manufactured by carbonizing β -cyclodextrin nanosponges and/or pea maltodextrin. Sulfur is incorporated via solvent impregnation and thermal diffusion. Then, the as prepared carbon-sulfur composite is wrapped with reduced graphene oxide (rGO). The obtained cathode material showed an initial discharge capacity of 1130 Ah Kg^{-1} at C/10, maintaining its capacity to 626 Ah Kg^{-1} at C/5 with capacity loss of 0.016% per cycle for more than 100 cycles. In another cell configuration, the same cathode material showed initial discharge capacity of 1130 AhKg^{-1}, but maintained its capacity to 825 AhKg^{-1} at C/5 for more than 100 cycles without nominal decline in capacity.

An ab Initio Calculation of the Effect of Halogen Dopants on Li_2O_2

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Rechargeable lithium-air batteries are promising devices for a new form of energy storage with theoretical energy densities approximately one order of magnitude greater than today's lithium-ion batteries [1]. However, despite this potential, Li-air technology remains at an early stage of development with many performance limitations yet to be addressed, including low capacity and high overpotentials needed for recharging. One of the main reasons of these limitations is the insulating nature of lithium peroxide Li_2O_2. Recent experiments have shown that adding lithium chloride LiCl to the electrolyte improves the electrical conductivity of the Li_2O_2 [2], but the mechanism responsible for this effect is still unclear. Here we perform first-principles calculations to study the effect of several halogen substitutional defects. We calculate the corresponding formation energies, the effect of the strain caused by the defects and analyze the microscopic electronic properties. We conclude that the halogen impurities are electron dopants to the system. The extra charge localizes at an oxygen dimer neighbor to the impurity (see Figure 1), forming small polarons that stretch the O-O bonds. The effect of these polarons in the conductivity is discussed in terms of the thermally activated migration of such diffusive polarons.

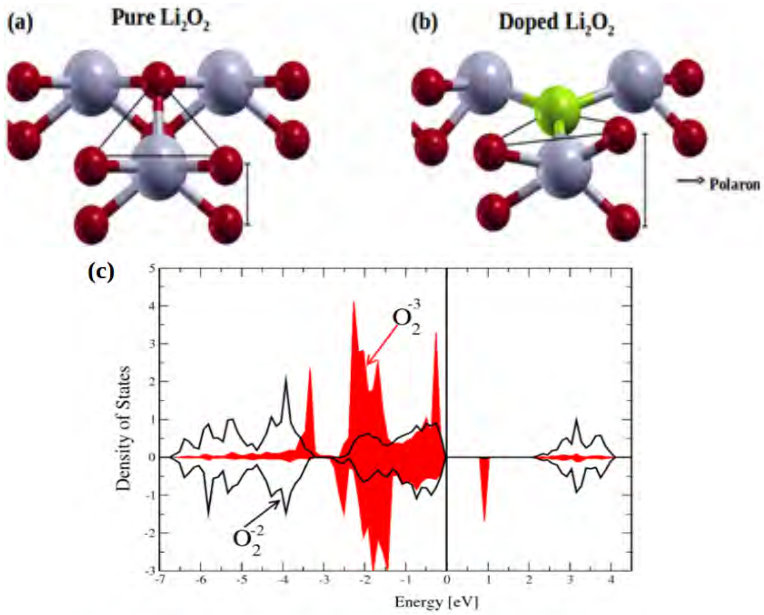

Figure 1. (a) structure of a pure of Li_2O_2. (b) electron polaron stretch the oxygen bond in one oxygen dimer close to the Cl dopant. (c) contrast between the total electronic density of states (DOS) projected on the dimer oxygen p-states for stoichiometric Li_2O_2 (black line) and the doped oxygen dimer ones (red shaded area). Spin up (top) and spin down (bottom). The Fermi level is set to zero.

Keywords: Lithium-air batteries, lithium peroxide, first-principles calculations**,** defects, polarons.

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Dual lithium uptake anode materials: crystalline Fe_3O_4 nanoparticles supported over graphitic matrices for lithium-ion batteries

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In order to fulfill the rapidly growing demand for lithium-ion batteries (LIB) with higher energy density and long cycle life, transition-metal oxides have been investigated as promising high-capacity anodes [1]. Among them, magnetite (Fe_3O_4) is a low cost, environmentally friendly metal oxide that can undertake a reversible conversion reaction which results in a theoretical capacity of 924 mA hg^{-1}, a value which is almost 3 times higher than the industry-standard graphite [2]. The complete utilization of the electroactive metal centers can be challenging for a densely structured material such as Fe_3O_4, because it does not have well-defined layers or tunnels for facile Li^+ insertion. Therefore, the use of nano-sized Fe_3O_4-conductive support hybrids is almost mandatory. This also favors the complete utilization of the material for the conversion reaction, as Fe_3O_4 is an electric insulator.

In this work, we report the use of several graphitic samples (G), with different particle sizes and characteristics, used as substrates for the co-precipitation of Fe_3O_4 nanoparticles (NPs) to obtain Fe_3O_4-G hybrids. The synthesized hybrids were characterized in terms of the carbon support, and further utilized as anode materials for the development of LIBs. The cyclability and charge-discharge profiles were compared taking advantage of the lithiation capacity that both Fe_3O_4 NPs and graphite have.

The graphite samples employed as substrates (G1, G2 and G3) were of 2, 17 and 410 μm lateral size, respectively. In the hybrids, Fe_3O_4 NPs (~12 nm) are mainly located at the edges of the structures, as determined by SEM images and Raman analysis. Hysteresis loops measured with a vibrating sample magnetometer showed that the Fe_3O_4 wt% of each sample was 9% (Fe_3O_4-G1), 16% (Fe_3O_4-G2) and 18% (Fe_3O_4-G3).

Fe_3O_4-G samples exhibit two different regions when cycling them between 3.000 and 0.010 V. The first one (around 0.700 V) corresponds to the lithiation of Fe_3O_4 NPs and the formation of Li_2O and metallic Fe. The second one (around 0.100 V) arises from the intercalation of Li ions in the graphitic planes. Therefore, both constituents play a synergistic role in the lithium uptake. The rapid capacity fading of Fe_3O_4 anode without any carbon support demonstrated that the presence of graphite is essential for a stable performance. The advantage of using these materials is that they are an inexpensive and highly efficient alternative for immobilizing Fe_3O_4 NPs, as other extensively used carbon nanostructures such as carbon nanotubes or graphene cannot act as active substrates for lithium storage.

Fe_3O_4-G1 and G2 based anodes retain their specific capacity after cycling the battery several times, while Fe_3O_4-G3 loses its capacity up to half of the initial one in the first cycles. This shows that the graphite particle size plays a major role in the performance of the LIB by modulating the connectivity of the active Fe_3O_4 zones.

In conclusion, Fe_3O_4-G hybrid materials were synthesized, producing Fe_3O_4 NPs which are uniformly dispersed over the carbon surfaces. The Fe_3O_4-G hybrids with different particle sizes were employed for the development of anodes for LIB. A synergistic effect between the magnetite lithiation conversion reaction and the graphite lithium intercalation was observed. We also determined that Fe_3O_4 loading and the carbon particle size determine the LIB cyclability.

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Synthesis and Electrochemical Properties of Nickel Oxide as Anodes for Lithium Ion Batteries

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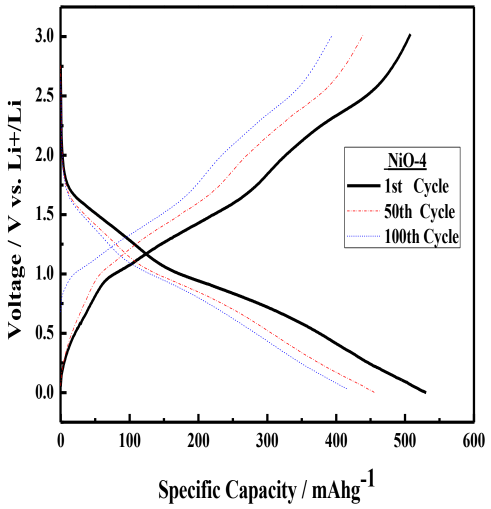
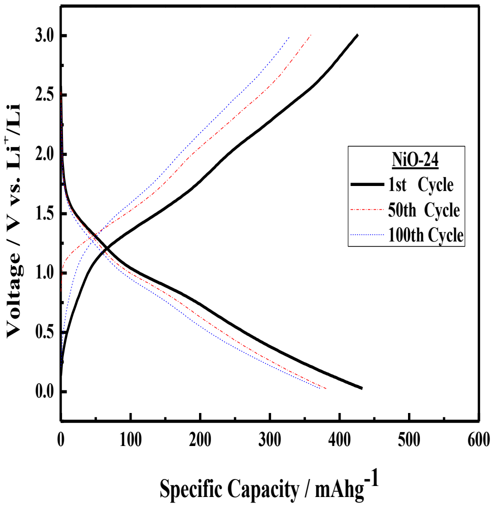
Transition-metal oxides (MO, where M is Fe, Ni, Co and Cu) have been studied since these materials were proposed by Tarascon and co-workers [1-6]. These oxides can offer higher capacities (600-1000 mAh g^{-1}) than graphite material (372 mAh g^{-1}). Particularly, NiO has a high theoretical capacity value (718 mA h g^{-1} for $2Li^+$per NiO) and presents many advantages: natural abundance, low cost and environmental friendliness.

In this contribution we present the preparation and characterization of nickel oxide as anode materials in lithium-ion batteries. Two processes are involved in the synthetic method, in the first step the nickel hydroxide was obtained by hydrothermal synthesis (4h, 180°C) and then the precipitated was washed with distilled water to remove the residual species. The second step consists of material calcinations in air at 300ºC, for 4 (NiO-4h) and 24(NiO-24h) hours.

The structural characteristics and electrochemical properties of the obtained nickel oxides are subsequently investigated employing optical and electrochemical techniques, such as: FTIR, SEM, charge-discharge cycles, galvanostatic discharge at different currents, cyclic voltammetry and electrochemical impedance spectroscopy.

The anode materials (NiO-4h and NiO-24h) were synthesized via a facile two-step route and exhibit a satisfactory specific capacity, cyclability and rate capability. These results indicate that the studied electrodes could be suitable as anodes in lithium ion batteries applications.





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Synthesis of Highly Active Iridium Catalysts for Anodes of Proton Exchange Membrane Electrolyzers

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The anode catalyst is one of the key parts for sustainable hydrogen production via proton exchange membrane (PEM) electrolysis [1]. An optimized synthesis of the oxygen evolution reaction (OER) catalysts may lead to a cost efficient production, promoting the commercialization of new catalyst materials. This work compares the electrochemical characteristics of iridium nanoparticles synthetized in different purities of ethanol (EtOH) and deionized (DI) water as solvents based on our previously reported synthesis route [2]. The use of cetyltrimethyl ammonium bromide (CTAB) as a surfactant is discussed as well. In general, low ethanol purity or water as synthesis media, as well as the absence of surfactant, are detrimental factors for the electrocatalytic properties of the materials. Adding $NaBH_4$ in excess improves the purity of the catalyst (Ir-nano 99.8-P) enhancing the OER activity up to 100 A/g_{Ir} at 1.51 V *vs.* RHE, Figure 1. Small changes in the Tafel slope are observed, which affects the analysis of the specific exchange current, and therefore any interpretation of these parameters can be misleading. The active sites from the Ir^{III}/Ir^{IV} oxidation peak do not correlate exactly with the OER activities, while the capacitive current provides more meaningful information.

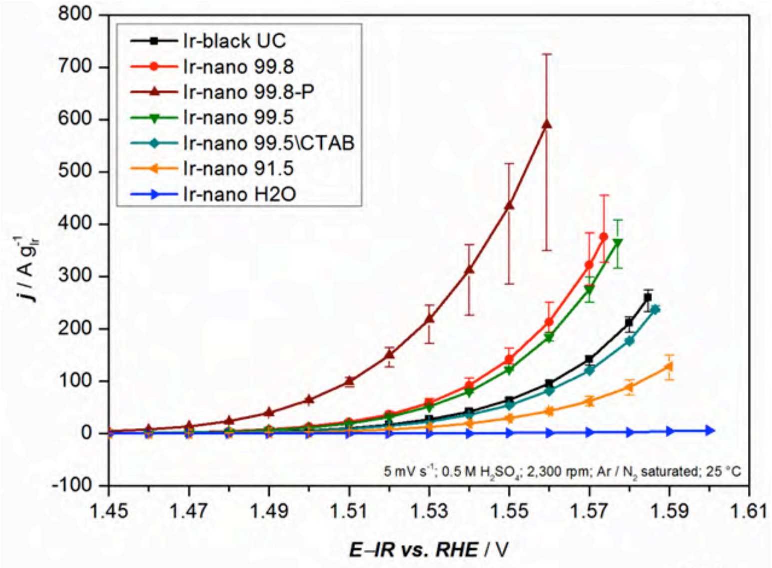

Fig. 1. Oxygen evolution eeaction (OER) characteristics for Ir-black UC; Ir-nano 99.8-P (EtOH 99.8%); Ir-nano 99.8 (EtOH 99.8%); Ir-nano 99.5 (EtOH 99.5%); Ir-nano 99.5\CTAB (EtOH 99.5%, without CTAB); Ir-nano 91.5 (EtOH 91.5%); and Ir-nano H_2O (in DI water). The scanning rate, temperature and rotation speed are 5 mV s^{-1}, 25°C, and 2300 rpm, respectively. The measurements were performed in 0.5 M H_2SO_4 and Ar-saturated solution.

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Metal Organic Frameworks as Catalyst Precursors for Oxygen Reduction in Fuel Cells

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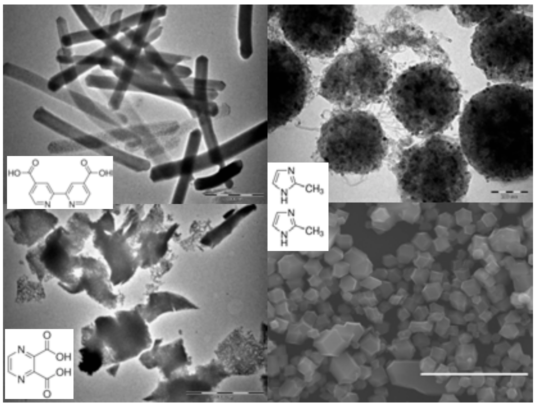
Metal Organic Frameworks (MOFs) are porous coordination compounds formed by bridging organic ligands which produce extended structures, crystalline in most cases. Proton exchange membrane fuel cells could be an alternative to thermal engines that consume fossil fuels. Materials obtained from Co coordination compounds could replace Pt catalysts employed for the O_2 reduction. [1-3]
Cobalt Metal Organic Frameworks (MOFs) were synthetized with the following ligands: 2-methylimidazole, nicotinate, pyrazinecarboxylate, 2,3-pyrazinedicarboxylate and 2,2-bipyridine-4,4-dicarboxylate. The obtained powders were characterized by TGA and XRD. Samples were submitted to thermal treatment at 700 ^{o}C or 900 ^{o}C under inert atmosphere. During this procedure, ligands produce a carbonaceous matrix and Co^{2+} ions are reduced to metallic nanoparticles. Finally, an acid leaching (0.5 M H_2SO_4) eliminated partially these particles, leaving open nanopores accessible to solvent. The catalysts thus prepared were characterized trough Raman, XPS and EDX spectroscopies. Electron microscopies (TEM & SEM) showed several morphologies as sponges, rods, polyhedron, spheres, etc, depending of ligand employed, (see figure, scale 10 μm) and pore sizes between 20-100 nm. The catalytic activity towards Oxygen Reduction Reaction (ORR) was studied through linear sweep voltammetry on a rotating ring disc electrode (RRDE) in acidic medium (0.5 M H_2SO_4). When pyrazinedicarboxylate ligand was employed (700 ^{o}C), the following electrokinetic parameters were obtained: E_{eq} = 0.90 V vs NHE (1.0 V for Pt), j_o = 10 μA cm^{-2}, Tafel slope = 80 mV dec^{-1}, 10 % yield in H_2O_2. The electrochemical results are interpreted in terms of the Nitrogen content (XPS), surface area (BET) and pore sizes. These results will help to design new Pt free catalysts. Fuel cells are being assembled to assess the performance of selected pyrolized MOF as cathode catalyst. Membrane electrode assemblies are being prepared employing commercial Pt 20% w/w over Vulcan carbon as anode catalyst and Nafion 212 as membrane. Initial test are providing similar results to our previous report [3]



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Lithium air batteries: can this be the future for electric vehicles?

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Worldwide, national energy policies are at present based on fossil fuels, with subsequent concerns about CO_2-related warming. Thereby, efforts are devoted to promote an efficient use of renewable energy sources and a sustainable transportation where internal combustion engines are replaced by electric engine partially (hybrid electric vehicles, HEV, plug-in hybrid electric vehicle PHEV) or totally (electric vehicles, EV). This in turns requires high efficiency, energy storage/conversion systems, like batteries. Lithium ion batteries are actually the main used energy source for electric vehicle. The power capability far exceeds that of lithium batteries but, unfortunately, their energy density is too low.

Rechargeable Li-air batteries provide theoretical capacities which are ten times higher than that of current Li-ion batteries, which could enable the driving range of an electric vehicle to be comparable to that of gasoline vehicles. These high energy densities in Li-O_2 batteries result from the atypical battery architecture which consists of an air (O_2) cathode and a pure lithium metal anode. However, hurdles to their widespread use abound with issues at the cathode (relating to electrocatalysis and cathode decomposition), lithium metal anode (high reactivity towards moisture) and due to electrolyte decomposition. All these factors make Li-air batteries far from the market. The cyclability of such system, in particular in the use with atmospheric air, is very low.

This presentation focuses on the use of cathodic electrode with catalysts and suitable binders to enhance efficiency. Moreover a suitable membrane was studied in order to make possible the use of air instead on pure oxygen.

Mesoporous carbon nanofibres [1] doped with palladium nanoparticles (Pd CNFs) are synthesized by electrospinning and used as electro-catalysts at the oxygen cathode of Li–O2 batteries. The surface area of the nanocomposite CNFs is greatly increased with the incorporation of the metal NPs up to 600 m2 g−1 and the presence of the metal promotes graphitization of the carbon. The so obtained Li–O2 battery shows a very low voltage gap of 0.48 V vs. Li+/Li between the terminal discharge and charge voltages, as the recharge occurs at a potential underneath 4.0 V vs. Li+/Li for about 90 cycles at the ccapacity of 200 mAh g−1.

Some binders undergo a decomposition reaction due to superoxide ion attack generated during the discharge process. These unwanted reactions affect the performance of the battery. The galvanostatic response obtained from a cathode under an unstable binder such as PVDF is also reported and its performance is compared with a cathode where Nafion was used.

Moreover the membrane made possible to reach more than 150 cycles [2]. The electrochemical results here reported are one of the first reported for a long cycling cell working in atmospheric air.

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Transport of lithium ions and oxygen in cathodes of lithium-air batteries

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It has been recognized that the level of dissociation of the lithium salt used in a lithium-air battery (LAB) plays a significant role in the oxygen reduction reaction (ORR) [1]. Moreover, the conductivity of the lithium electrolyte and the diffusivity of oxygen determine the overpotentials during charge/discharge of LABs [2]. Thus, it is of relevance to have tools for predicting the values of these transport coefficients, along with the speciation of lithium salts, in solvents used in LABs, particularly in glymes (glycol ethers). These solvents seem to be good candidates for non-aqueous LAB, in view of their good stability under the electrochemical conditions of the cathodic processes.

The estimation of ionic conductivity and diffusion coefficients is commonly performed by resorting to simple hydrodynamic models, which lead to the well-known Stokes-Einstein relationship (SER) for the diffusion coefficients and the Walden rule (WR) for the ionic conductivity. In both cases the hydrodynamic model predict that $\lambda\eta$ and $D\eta/T$ (where λ is the ionic molar conductivity, D is the diffusion coefficient, η is the solvent viscosity, and T is the temperature) are constants that only depend on the hydrodynamic radii of the species that are transported by concentration or potential gradients.

A comprehensive analysis of the literature data indicates that SER underestimate the diffusion coefficient of oxygen in all the solvents of interest for LABs by a factor as large as 5. This is not unexpected in view that SER assumes that the size of the diffusing molecule is much higher that the size of the solvent molecules. We concluded that semiempirical equations that take into account the diffusion-viscosity decoupling, or free volume concepts applicable to the diffusion of small solutes in molecular solvents, describe much better the behavior of oxygen diffusivity with solvent fluidity.

We also performed a detailed analysis of the electrical conductivity of lithium trifluoromethanesulfonate (LiTf: lithium triflate) and lithium bistrifluoromethanesulfonimidate (LiTFSI) in DME and diglyme, over a wide range of concentrations, including the concentrated region where the formation of triplets and quadruplets ions predominates. The maximum specific conductivities of these salts in the studied glymes are of the order of several mS.cm^{-1}, which is appropriate for non-aqueous LABs.

Precise measurements of the ionic conductivity of lithium salts in the dilute and moderate concentration regime allowed us to obtain reliable values of ion pairs and triplet ions formation constants, improving the speciation analysis of lithium salts in glymes, previously reported [3]. It is interesting to note that the infinite dilution conductivity of Li^+ ions in aprotic solvents of different molecular sizes obeys WR. We have analyzed this fact in terms of ionic mobility models and we propose that dielectric friction, instead of viscous friction, determines the mobility of Li^+ ions in these solvents.

Finally, we report preliminary results for the partition and diffusion of Li^+ ions in monolithic mesoporous carbon embedded with glymes, in order to reproduce conditions similar to those at the LAB´s cathodes. Tortuosity and confinement effects are discussed in relation to the pore sizes distribution of the carbon and the bulk transport properties of the electrolytes.

Keywords: Lithium-air batteries, Li^+ conductivity, Oxygen diffusion, Glymes, Ionic association.

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Synthesis and characterization of mesoporous carbon electrodes for lithium-air batteries

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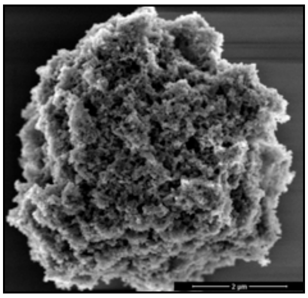
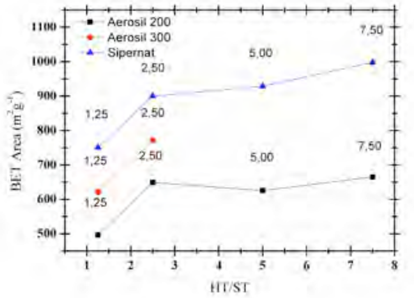
Li-air batteries (LAB) are called to be the next generation of lithium batteries because of its super-high specific energy density of 11,140 Wh.kg^{-1} rivaling that of gasoline [1]. Modeling studies of pore size at air cathode has demonstrated that pores smaller than a critical size does not contribute to the discharge of the battery. The discharge capacity gradually increases when the mean pore size of the electrode ranges between 10 and 50 nm, while capacity decreases when the mean pore size increases to 100 nm [2]. With the motivation of preparing optimal air carbon electrodes, a new simple route of synthesis combining soft template (ST) and hard template (HT) was applied to obtain tailored mesoporous carbons (MC) from carbonization of resorcinol-formaldehyde (RF). [3,4] The hollow HT silica spheres (Aerosil or Sipernat) are surrounded and filled by the resin. After carbonization at 1000 ºC for two hours, and removal of the HT with concentrated NaOH aqueous solution, the porous carbon is obtained.

By adjusting the HT/ST proportion different MCs are obtained. Pore distribution and surface area was determined on the various carbons obtained. BET specific surface area of the MC synthesized with Aerosil varied between 494 m^{2}g^{-1} and 665 m^{2}g^{-1} and total pore volume from 0.89 cm^{3}g^{-1} to 1.40 cm^{3}g^{-1}. Meanwhile BET specific surface area of MC synthesized with Sipernat varied between 662 m^{2}g^{-1} and 998 m^{2}g^{-1} and its pore volume from 0.75 cm^{3}g^{-1} to 1.70 cm^{3}g^{-1}. Besides these materials shows a distribution of pores mainly focused in two regions 5-10 nm and 20-60 nm, these are called to the most suitable ranges of pores to increase discharge capacitance of air cathodes [2].



Left: SEM image of a MC obtained with Aerosil 200 as HT.



Right: BET surface area increases with increasing HT/ST ratio.

Monolithic MCs, prepared using Sipernat as HT, were studied in relation to the partition and diffusivity of lithium salts in the pores. Cell assemblies with *Swagelok*® hardware were prepared to test carbon air cathode with non-aqueous and hybrid electrolytes as proposed by Beattie *et al*. [5].

Prelithiated hard carbons have demonstrated to be a suitable material for (Li-ion)-O_2 [6]. In order to test if the prepared MCs have characteristic of hard carbons, we have characterized them by XRD and FTIR and preliminary results of reversible lithiation are discussed.

Keywords: Lithium batteries, carbon cathodes, specific area, pore size, lithiation.

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High Durability Composite Fuel Cell Membranes

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Fuel cell membrane design undergone a number of important design iterations over the past 15 years or so, such that the general standard of a homogeneous membrane of thickness 225 μm prepared by extrusion has been replaced by a highly heterogeneous membrane system comprising a reinforcing component, radical scavenger and/or hydrogen peroxide decomposition catalyst and in which the architecture of the membrane, of thickness down to one tenth or one twentieth of that of Nafion-117, is designed at the nano- to micro-metric length scales, the latter facilitated by the use of solution casting processes. Within this heterogeneous membrane, the chemical and mechanical reinforcing components, the nature of the ionomer or functionalised polymer, as well as the membrane thickness and any gradient of composition across it represent the design parameters for an engineered fuel cell membrane. Despite the strides forward that have been made, further improving fuel cell membrane durability under operation remains a crucial issue.

Our research over recent years has underlined the critical advantage of the presence of ionic interactions between the components of a composite fuel cell membrane, in particular between the reinforcement material providing mechanical strength and the perfluorosulfonic acid (or sulfonic acid functionalised polyaromatic polymer) that provides the proton transport properties. We will describe the development, characterisation and application in both a fuel cell and PEM water electrolyser of membranes comprising nanofibre reinforcements of basic polymers, and will briefly discuss how the architectures developed in such membranes lend themselves to further improvements in membrane robustness.

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An overview of the reactivity indexes of MN_4 and MN_2 molecular catalysts for the reduction of O_2

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Non precious molecular metal catalysts, especially MN4 macrocyclic metal complexes have been studied for many authors with the purpose of replacing Pt-containing catalysts in the oxygen cathode of fuel cells. In the particular case of Li –air batteries catalysts are also required to promote the 4-e reduction of O_2 as in the full cell reaction, i.e. $O_2 + 4Li$ to $\rightarrow 2Li_2O$ which involves the splitting of the O-O bond. This is the ultimate chemistry for releasing the most energy from O_2 and for constructing a super-high-energy-density Li-air battery. Up to know most authors have identified Li_2O_2 as the discharge product (involving the 2-e reduction of O_2). This limits the specific energy of the Li-air battery to 3500 Wh kg^{-1}, which is 67% of the theoretical value [1]. MN4 metal complexes like Co-phthalocyanines have been proposed as catalysts for the O_2 cathode [1]

In this work the most important reactivity indexes or descriptors for the activity of MN4 molecular catalysts will discussed and compared with the reactivity descriptors of pure metals.

For many years, the M(III)/(II) redox potential of the catalyst has been proposed as a very predictive reactivity index for O_2 reduction (ORR) for metal phthalocyanines, metalloporphyrins and macrocyclic complexes in general [2] and only rather recently [3] it has been proposed for pyrolyzed MNx catalysts [3,4]. In general a more M(III)/(II) redox potential increases the ORR activity. Recently, it has been shown that a direct linear correlation does exists between the M(III)/(II) redox potential of the catalysts and the M-O_2 binding energy, where the binding energy is a classical activity predictor for pure metals and metal alloys. For intact MN4 metal complexes the redox potential can be shifted to positive values by placing electron-withdrawing groups on the ligand. Pyrolysis also cause a shift of the redox potential in the positive direction which increases dramatically the catalytic activity. For Cu phenanthholines, the active species is tetrahedric Cu(I). The Cu(II)/(I) can be shifted by electron-withdrawing groups on the ligand and also by bulky groups that hinder the Cu(II)(planar) → Cu(I)(tetrahedral) transition shifting the redox potential positively and again increasing the ORR activity.

Ackowledgements
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A Quantitative Tool to Predict the Phase Composition of Lithium-Sulfur Batteries

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Lithium-sulfur batteries are one of the most promising candidates for the next generation electrical energy storage. They are made of cheap and abundant elements and they have a theoretical specific energy of ca. 2600 W h kg^{-1}, which is much higher than that of lithium-ion batteries. However, the development of lithium-sulfur batteries is hampered by their complicated reaction mechanism. In order to reach their full potential, lithium-sulfur batteries should achieve the complete reduction of solid sulfur into solid Li_2S, and this reaction occurs via a multistep reaction pathway involving a range of soluble polysulfides. In order to achieve a high specific energy, the battery should run with the minimum amount of electrolyte required, and this corresponds to a situation where all polysulfide species should reach saturation. The corresponding equilibrium voltage profile during change and discharge will be given by the saturation concentration of polysulfides (Nernst equation) and the capacity will depend on the efficiency in the conversion from solid sulfur to liquid polysulfide and to Li_2S. and the reverse reactions. Here we report the first phase diagram of system S-Li_2S-electrolyte, and we demonstrate that the phase diagram is a practical tool to predict the equilibrium polysulphide concentration at any composition, the formation of solid phases, and to develop a quantitative understanding of the effect of solvent on battery performance.[1]

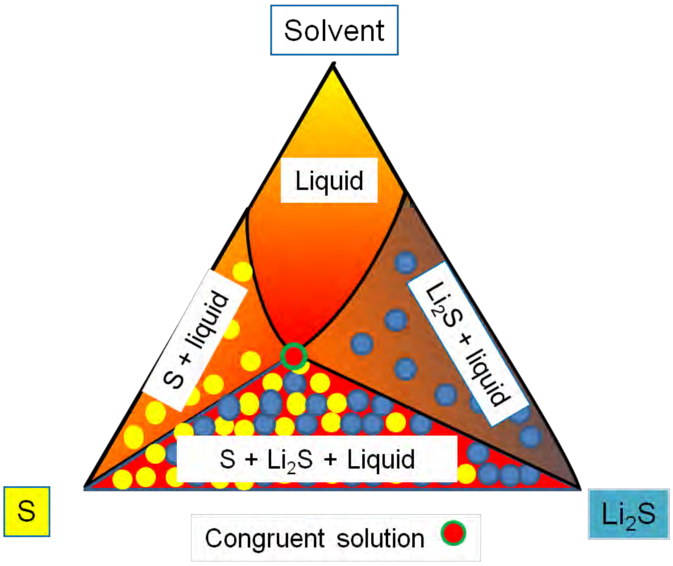

Figure 1. Suggested ternary phase diagram of a S-Li_2S-electrolyte system.

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Polyoxometalate-assisted Synthesis of Polydopamine Composite as Anode Material for Binder-free High-performance Lithium Ion Batteries

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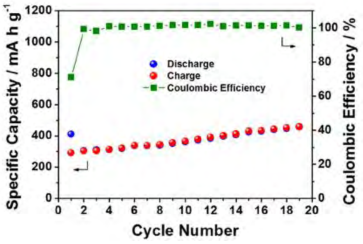
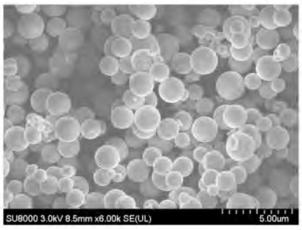
Polydopamine (PDA) is a kind of natural melanin-like material and can usually be self-polymerized in alkaline media. PDA has attracted tremendous attention owing to its multifunctional groups (amino and catechol groups), hydrophilicity and biocompatibility for a widespread applications in energy, biomedical science, water treatment, sensor and so on.[1] PDA is always used as a fantastic carbon source for energy storage and conversion, because it gives nitrogen (N)-doped graphite-like carbon in high yield and exhibits high electrical conductivity, and good electrochemical and mechanical properties.[2] However, the direct use of PDA in energy storage and conversion as an electrode material is seldom reported. Herein, we utilize a one-step process to prepare PDA microspheres in the presence of polyoxometalate (POM) in acid condition. The obtained PDA/POM composite can be employed as both redox-active electrode and binder material for rechargeable lithium ion batteries. The initial discharge and charge capacities of the PDA/POM electrode are 1299 and 552 mA h g^{-1} at a current density of 20 mA g^{-1}. The capacity remains 411 mA h g^{-1} at a current density of 100 mA g^{-1} and presents a gradual increase in capacity as the cycle number increases.





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Anion Exchangeable Polybenzimidazole Ionomers for Solid Alkaline Fuel Cells

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Solid alkaline fuel cells (SAFCs) use anion exchangeable polymers for electrolyte membranes. Compared to fuel cells using proton exchangeable polymers the direction of ion movement is opposite which is from cathode to anode. The hydroxyl ion movement mitigates overpotential for oxygen reduction reaction as well as water flooding at cathode. In addition, they overcome the disadvantages of alkaline fuel cells such as formation of carbonate precipitates, leakage of liquid KOH electrolyte, system complexity and so on by using solid electrolytes. The solid electrolytes were prepared by quaternized polymers having a function to exchange anions. Among recent reported works for anion exchangeable polymers, KOH doped PBI membranes exhibited good ionic conductivity, acceptable mechanical strength, high thermal stability, and low methanol permeability, which make it interesting as electrolyte in alkaline fuel cell and water electrolyzers. Since membrane-electrode assemblies should be prepared for solid alkaline fuel cells, the development of ionomer binder solutions is also highly required. However, few researches on ionomer binder solutions for preparation of electrodes of MEAs were carried out. In this study, new anion conducting polymer were synthesized using quaternized polymers as ionomer binder. The quaternized polybenzimidazoles (QPBIs) having quaternized intermediate 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC) in the main-chain and/or in the side group were synthesized for use as anion conducting ionomer binder for SAFCs. In addition, the QPBIs were crosslinked with crosslinker to improve the mechanical strength and chemical stability. The quaternized polymers were investigated in terms of ionic conductivity, IEC, FT-IR, NMR etc. The thermal stability, mechanical properties, hydroxide conductivity and membrane stability were also investigated. In addition, the performance of membrane-electrode assemblies with the content of the ionomer developed were carried out.

ACKNOWLEDGEMENT

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Preferentially oriented platinum nanoparticles modified by electrochemical hydrogen evolution.

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Platinum nanoparticles have been widely used in electrocatalysis for fuel cell technology, oil reforming catalysts and organic electrosynthesis electrodes. Most of the academic work has been conducted on single crystal surfaces since they ensure a defined surface atomic arrangement allowing conclusions about electrocatalytic selectivity [1]. Nevertheless, single crystals are ideal surfaces which cannot be employed for electrooxidation reactions since the large anodic potentials exceed the values of surface order stability. Thus, the preparation of a select crystalline orientation (*e.g.* (100) and (111)) of a high surface-to-volume ratio for catalytic improvements and selectivity is imperative.

Nanoparticles were prepared by three methods for comparison and testing. Firstly, the *water-in-oil* method with sodium borohydride as reducing agent [2]. Secondly, the *colloidal* method [3] with polyacrylate and an aged solutions of K_2PtCl_4 and H_2PtCl_6. $6H_2O$. Thirdly, asymmetric square wave potential programs for Pt(II) or Pt(IV) ions generation and further reduction [4]. The latter was conducted either by bubbling hydrogen for different times and/or electrogenerating hydrogen under potential control to produce (111), (100) or (110)-oriented platinum nanoparticles [5]. A final extreme cathodization yields underpotential deposited OH_{ads} species as a pre-monolayer with the interfacial increase of pH. Besides, low coordinated (111) stepped planes on platinum leads to a much lower onset potential for OH_{ads} species formation [6]. The (111)-oriented platinum exhibits a net contribution arising from the (111) lattice planes (by (222) planes). Besides, a lower influence of (220) and (311) reflections than polyoriented surfaces confirms that cathodization yields an increase in stepping sites towards [111] directions.

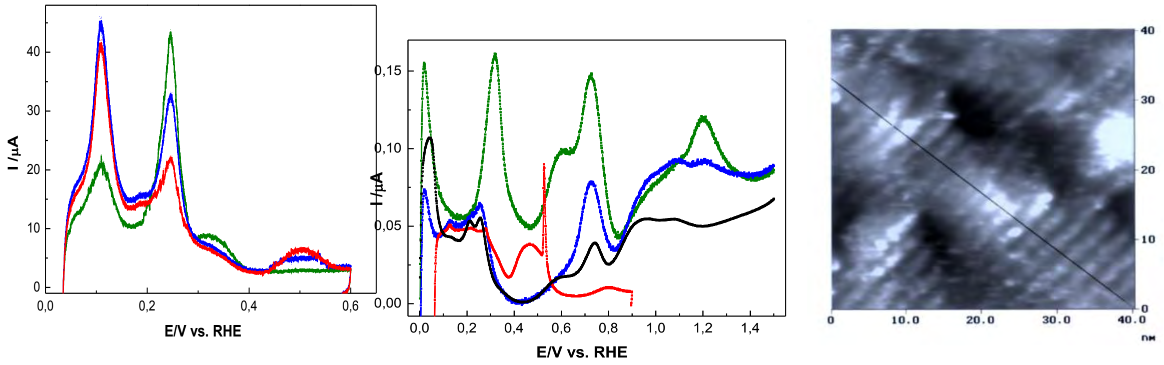

Figure 1.- *(left)* Anodic voltammetric profiles for (111)-oriented (red lines), (110)-oriented (blue lines) and (100)-oriented (green lines) platinum nanoparticles supported on polyoriented platinum run at 50 mV/s between 0.03 and 0.60 V in 0.5 M sulfuric acid.

(center) idem for Pt(111) single crystals (red lines) swept up to 0.90 V, cathodically treated (-2 V for 1 min ; 5 min) Pt(111) single crystal (black ; blue lines) and cathodically treated (-2 V for 5 min) (111)-oriented platinum nanoparticles (green lines) swept up to 1.50 V supported on polyoriented platinum at 50 mV/s in 0.5 M sulfuric acid.

(right) Topographic images for *ex situ* STM of cathodically treated (111)-oriented nanoparticles.

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Electrochemical research efforts on lithium batteries, catalysis and nano-structures

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An overview of the electrochemistry research being conducted at the Universiy of Rhode Island will be presented. The first area of research includes the investigation of electrolytes and interfaces in lithium ion batteries. The research focusses on how modification of of the electrolyte formulation alters the electode interface formation and structure and how these changes effect the cycling performance of lithium ion batteries. The second area of research includes bioanalytical and biophysical chemistry investigations using nanofluidics for single-molecule sensing and manipulation. Nanopore (short nanochannel) sensors are fabricated, chemically tuned, and used to characterize molecular properties and intermolecular interactions, with signature applications in biomedicine. The third area is the nanoelectrochemistry for the energy applications. Newly developed nanoscale scanning electrochemical microscopy (SECM) is employed to quantitatively study the electrochemical activity of single nanostructures and their collective behaviors as catalysts or electrode material in the electrocatalytic reaction involved in the fuel cells or the microbial fuel cells, thereby providing quantitative guidelines for the improvements of the their performance.

Recent advances in the application of scanning electrochemical microscopy for studying the hydrogen electrode reaction mechanism

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The hydrogen electrode reaction (HER) proceeds through a mechanism involving the Volmer (V), Heyrovsky (H), and Tafel (T) steps, and one adsorbed intermediate (H_{ad}), so it can proceed via two parallel and independent routes (for instance, VT and VH routes). The study of this mechanism requires high mass-transport rates to visualize the contributions of all the elementary steps to the global reaction rate over a large-enough potential range before the reaction becomes fully limited by the mass transport of reactant [1]. Precisely, scanning electrochemical microscopy (SECM) is a technique that allows to establish very high mass-transport rates by approaching a microelectrode tip toward another surface (substrate) down to sub-micrometer distances, defining a pseudo thin-layer cell (TLC) between these two electrodes. On that sense, even though the HER was previously studied by SECM in the feedback mode, theoretical formalisms with very simplified kinetic models were employed to process the data, which impeded to obtain complete mechanistic information.

This work describes an approach that allows to use the full capacity of SECM to analyze the HER reaction mechanism, which can be applied to the study of the HER cathodic branch (the hydrogen evolution reaction - *her*), and of the HER anodic branch (the hydrogen oxidation reaction - *hor*). The method proposes to analyze the complete experimental dependence of the normalized tip current (I_T) on the substrate or tip potential (E_S or E_T, respectively) and on the normalized tip-substrate distance (L) by modeling it through a TLC, according to eq. (1): $I_T(E,L) = I_{TLC}(E,L)\varphi(L) + \rho(E,L)$ (1)

This equation involves the TLC current (I_{TLC}) which must be solved either for the *her* or for the *hor* operating through the VHT mechanism [2], and correction factors (φ and ρ) caused by the additional contributions to the SECM response. For example, Fig. 1 shows the correlations with eq. (1) (lines) of SECM results (symbols) of the HER on Pt electrodes with different configurations. Thus, Fig. 1a shows the SECM analysis of the *her* on a Pt microelectrode tip under very high mass transport rates, and Figs. 1b and 1c show the SECM analysis of the *hor* on Pt films deposited on glassy carbon (GC), and on Pt nanoparticle (NP) ensembles deposited on HOPG, respectively. Each of these sets of experimental results was correlated with eq. (1) using the corresponding expressions of I_{TLC}, φ and ρ for each configuration, which allowed to determine the complete set of kinetic parameters involved in the VHT mechanism.

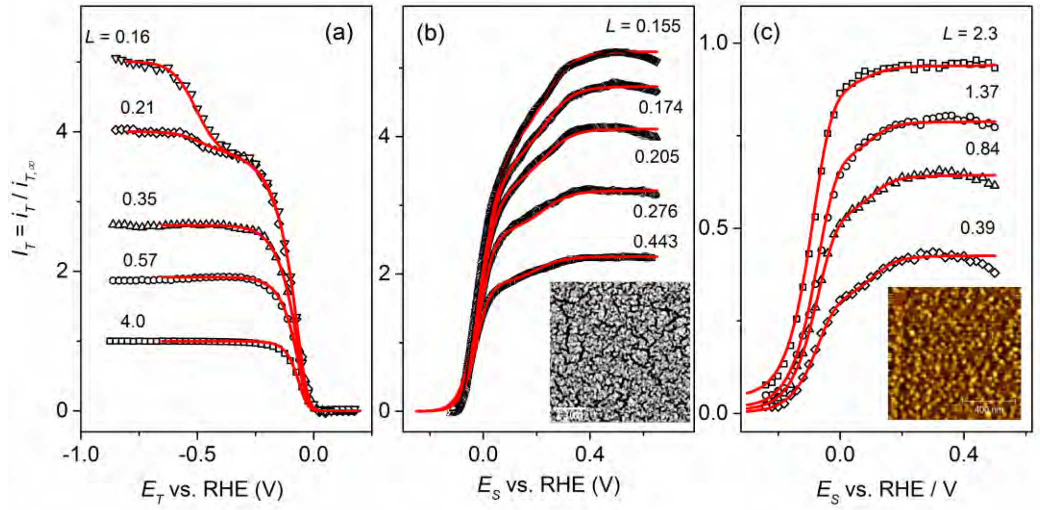

Figure 1. SECM analysis of the *her* on a Pt tip (a), and of the *hor* on a GC-supported Pt film shown in the SEM micrograph (b), and on a HOPG-supported Pt-NP ensemble shown in the AFM image (c).

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Structural and mechanical properties of $La_2NiO_{4+\delta}$ synthesized by sonochemical method

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La_2NiO_4-based oxides show high mixed conductivity and oxygen storage capacity due to the capability of interstitial oxygen formation and have attracted great attention as promising components for the energy conversion and storage devices such as fuel cells, batteries and membrane reactors [1]. Structural stability and mechanical integrity is an important issue for practical membrane application. Typically stresses can be induced by thermal and chemical gradients as well as differences in thermal expansion compared to sealing and housing materials. Hence the structural and mechanical properties of the material will be crucial for the mechanical reliability of the entire assembly and are in addition necessary for the analysis and modeling of deformation and stress states [2].

Low frequency ultrasound assisted synthesis technique was used to synthesize La_2NiO_4 nanostructures. The stoichiometric proportions of La and Ni nitrate precursors were dissolved in distilled water. 20% NaOH solution was added drop-wise to the precursor solution under vigorous stirring along with the ultrasonic irradiation. The ultrasonic irradiation was continued for 1h. The subsequent filtrations of the obtained materials were performed. The filtered residues were re-dispersed and washed with distilled water until the washed solutions reached neutral pH. The obtained materials were dried and calcined at 900 ºC for 5 hours. The powder characteristics such as crystal structure, particle size and morphology are analyzed by X-ray diffraction (XRD) and High resolution transmission electron microscopy (HRTEM). The TEM and XRD studies revealed the uniform equi-axial shape of the obtained nanostructures with the existence of La_2NiO_4 with Tetragonal structure and La_2O_3 as a secondary phase which disappeared in XRD pattern of sintered samples (Fig. 1).

The calcined powders are uni-axially pressed (105 MPa) to fabricate discs sintered at 1400 °C for 5 hours. The elastic behavior, microhardness and fracture toughness of prepared nanostructures are investigated by impulse excitation (IET) and indentation techniques, respectively.

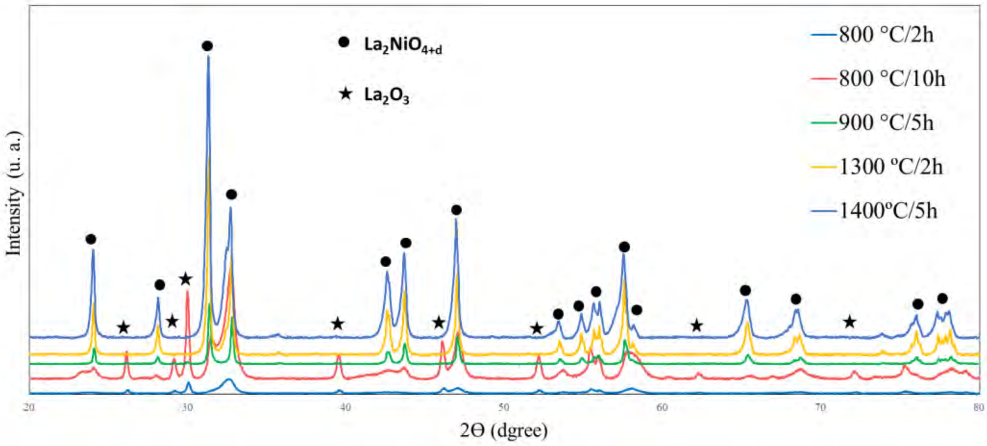

Fig. 1: XRD patterns of calcined nanopowders and discs sintered at different temperatures and times.

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Study of doped-Phosphate Polyanion electrode and bismuth-phosphate glassy electrolyte. Lithium ion solid state batteries.

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Our World demands new alternatives of sources of energy. New ways of production and storage have led the scientific and technological community to develop innovative devices that must be environmentally clean and safe. Those methods have to provide an efficient performance and a renewable use in order to allow a sustainable development. Considering this scenario, Lithium Ion Batteries play a leading role today.

Our main goal has been to improve not only the electrolyte ionic conductivity but also to reach a material suitable for electrodes that fits -as good as it can- the interface between both; one of the most important issues to overcome in order to obtain a new generation of all-solid state batteries.

In the light of these requirements, we will refer to several materials based on Phosphate Polyanion of general formula: $Li_3V_{2-x}Nb_x(PO_4)_3/C$ *and* $Li_3V_{2-x}Cu_x(PO_4)_3/C$ $(0 \leq x \leq 0.3)$; modified by *extra carbon sources* as Carbon Black and Carbon Nano-Fibers and with different *oxides* (TiO_2, MoO_3, WO_3, etc), in order to obtain well-crystallized pure-phase materials with their electronic conduction reinforced. We will develop their structural features through different techniques as micro Raman Spectroscopy, FTIR, Scanning Electronic Microscopy, DSC, DRX, etc. Additionally, we will discuss the results of a comprehensive electrical study, mostly by Impedance Spectroscopy, in order to reveal the electrical behavior of individual materials (including the microscopic fundamental interpretation of the charge carrier mechanisms involved) and their electrical behavior in the electrode/electrolyte interaction in order to show the phenomenon of the charge transport at the interface between them [1].

Furthermore, a new modified lithium-bismuth-phosphate glass has been obtained by the use of environmentally friendly components which are low cost and which can be eventually recycled.

In this work, we report some modifications in phosphate-bismuthate glass which allow huge improvements in their electrical properties because of the changes in the 3D structure making them exceptional candidates for being solid electrolytes in solid lithium ion batteries. Structural and electrical characterization is made by *XRD, DTA, XRF, FTIR,* Density and Impedance measurements.
Frequency-dependent electrical data will be discussed in the framework of the electric modulus representation. Structural properties studied by X-ray diffraction, density and FTIR will be correlated to the electrical behavior of the glass [2].

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New Electroactive Polymer Binders for Li-battery Si-anodes

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In the field of the advanced lithium batteries, a lot of attention has been directed toward the development of new materials increasing the energy and the power density, to obtain high performance batteries. One way to improve the energy density is to use alternative negative electrodes that can reach higher capacities than the carbonaceous materials commonly used (i.e. 372 $mAhg^{-1}$)[1,2]. Silicon can be the most interesting alternative, as it is abundant, non-toxic and exhibits a very high storage capacity (i.e. 3578 $mAhg^{-1}$ for $Li_{15}Si_4$)[3]. But the main inconvenience of Silicon is its large volume changes during alloying and de-alloying with lithium (~313 % volume expansion after lithiation)[4], which results in a lost of capacity upon cycling due to pulverization of the Silicon Nanoparticles (SiNPs), growth of the Solid Electrolyte Interphase (SEI) or broke of electrical contacts (among SiNPs, conductive matrix and current collector)[5,6].

Typically, a polymer binder is used to confine the SiNPs and bring the Silicon back after each cycle to its original state. Several binders was investigated in order to improve the cyclability of the SiNPs, from the carboxymethyl cellulose (CMC)[7] in the early years, to a very recent pyrene-based conductive binder[8], but some progress still need to be made for reaching a commercial application.

The aim of this work is to synthesize new functional polymer binders containing electroactive groups. The molecules studied show interesting properties due to their ability to reversibly take up lithium and electrons, increasing the overall capacity, but also for having specific behaviors when used as polymers. Two kinds of polymers have been investigating here, one based on a shape shifting molecule, the other one on a π–π staking compound.

The shape shifting molecules should induce a shrinking of the polymer during the expansion of the SiNPs, reducing the stress and strain on and in the particles, which can lead to an improvement of the Si-anodes cyclability. The behaviors expected for the other compound are its conductivity and self-healing capability, assured by the π–π staking property of the polymer.

By using electrochemical tests from half-cell batteries and structural characterizations, this research will show the feasibility of new kinds of electroactive polymer binders for Silicon anodes.

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Grafting of Nitrophenyl Group on Carbon Surface by Diazonium Chemistry to Suppress Irreversible Reactions

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Introduction

The spinel-structured LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) is a promising positive electrode for lithium-ion batteries (LIBs). However, since the working voltage (~4.7 V *vs*. Li/Li$^+$) is higher than the electrochemical window of common electrolytes (~4.3 V), electrolyte decomposes during cycling. Moreover, the cell constituents including conductive carbon, which is added to increase the electrode conductivity, are unstable against oxidative decomposition. The electrochemical oxidation (corrosion) of conductive carbon causes a decrease of Coulombic efficiency because it is an irreversible reaction. In this work, as a way to suppress the oxidation of conductive carbon, a strong electron withdrawing group (nitrophenyl) is grafted on the carbon surface by using diazonium chemistry.

Experimental

A nitrophenyl group was attached on a conductive carbon (Super-P) by diazonium chemistry in an acidic medium. A composite LNMO electrode was prepared along with Super-P and PVdF binder. The 2032-type coin cells were assembled with the LNMO electrode and Li counter electrode. The used electrolyte was LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC). The cyclic voltammetry (CV) and galvanostatic charge/discharge cycling was performed at 60^{o}C. The X-ray photoelectron spectroscopy (XPS) was used to analyze the surface of the modified Super-P.

Results and Discussion

The XPS data show that the nitrophenyl group is successfully grafted on the carbon surface. The modified Super-P shows a smaller oxidation current at 4.5 – 6.0 V (Li/Li$^+$) compared to the unmodified one (Fig. 1a). Due to the suppression of irreversible reaction (carbon oxidation) by nitrophenyl grafting, the Coulombic efficiency of Li/LNMO cell is higher when the modified Super-P is used as the conductive carbon (Fig. 1b).

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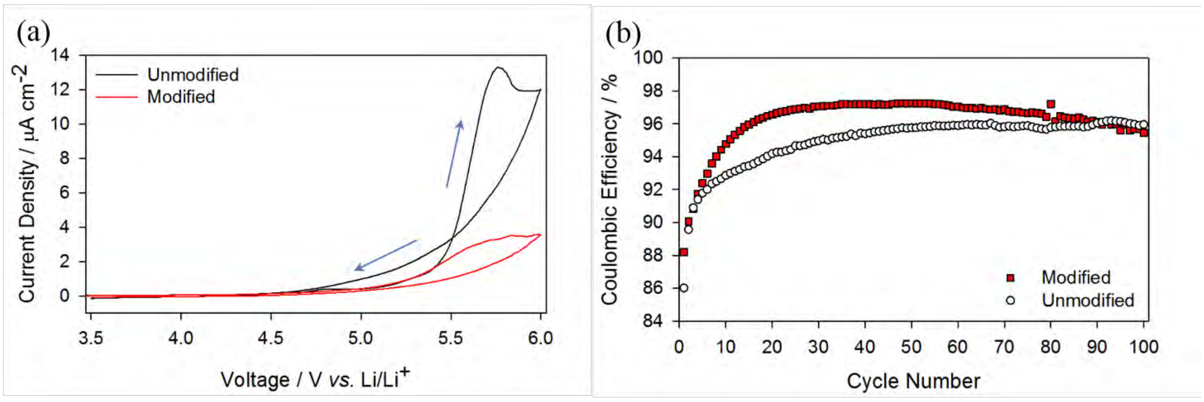

Fig 1. (a) Cyclic voltammetry of Super-P electrodes and (b) Coulombic efficiency of LNMO electrodes

A carbon-coated mixed olivine Li($Co_{1/3}Fe_{1/3}Mn_{1/3}$)PO_4 material as positive electrode in lithium cells

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Polyanion-type electrode materials are one of the great success in the field of electrochemistry: within this family, LiFePO4 (LFP) is a now mature material exploited as cathode material in lithium-ion cells. Recently the attention of the scientific community is focusing the advantage of the substitution in the LFP olivine lattice of Fe with Mn, Co or Ni. In fact the Mn^{3+}/Mn^{2+} and Co^{3+}/Co^{2+} couples show increasing redox potentials, thus opening the door to improvements in the energy performances [2]. The mixed $LiCo_{1/3}Fe_{1/3}Mn_{1/3}PO_4$ (LCFMP) stoichiometry is one of the most promising one. Compared to LFP in lithium cells (LIC) the LCFMP cathodes shows a similar practical specific capacity (120 $mAhg^{-1}$) and an higher working potential (4.2 V vs. Li to be compared to 3.5 V vs Li of LFP). In our laboratories developed an original synthetic route by exploiting a solvothermal treatment followed by an high temperature pyrolysis with sucrose. Our characterization suggests that the LCFMP material consisted in an single phase (see figure 1a for the X-ray diffraction pattern, XRD) crystallized in an olivine lattice similar to LFP (space group 62 Pnma with cell parameters a=10.332Å, b=6.014 Å, c=4.720Å) with an homogeneous round-shaped particle morphology of approximately 50-150 nm in diameter (see figure 1b). Moreover the LCFMP material is free from any contamination from pyrophosphates or Li_3PO_4 as highlighted by FTIR.

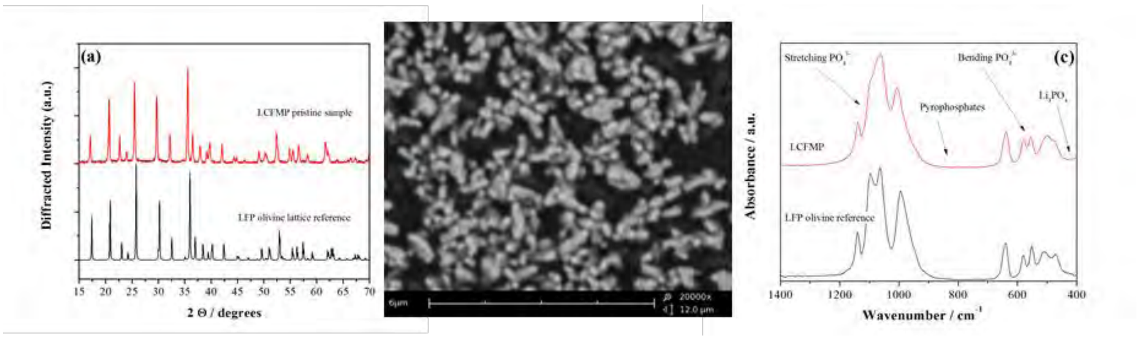

Figure 1. (a) XRD pattern of the LCFMP sample, (b) SEM micrograph and (c) FTIR spectra compared to the reference LFP phase.

The LCFMP electrodes are able to supply a specific capacity in galvanostatic tests on LICs that exceeds 165 $mAhg^{-1}$ in the first charge (corresponding to a almost full de-lithiation, being the maximum theoretical capacity 167 $mAhg^{-1}$) and 110 $mAhg^{-1}$ in the first discharge (corresponding to 67% of reversible lithium incorporation). The capacity retention at cycle 20 is approximately >90% in discharge compared to cycle 1.

Graphite Encapsulation Of Silicon Particles Using Different Metals As Template For Negative Electrode In Lithium-Ion Batteries

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At present it is important to develop higher energy density materials to replace graphite at the negative electrode of lithium-ion batteries, in order to meet today's energy needs. Silicon is a promising candidate given its high theoretical energy density of 3579 mAhg^{-1}. Nonetheless, the commercial use of silicon is limited due to several issues associated with its use, such as the pulverization of the silicon particles caused by the volume expansion when it is lithiated, the high irreversible capacity, and isolation of the particles caused by the formation of the solid electrolyte interphase (SEI) due to the decomposition of the electrolyte at the surface of the Si particles.

The purpose of this work is to overcome these issues in order to obtain a better electrochemical performance of the negative electrode. This study is focused on obtaining a hybrid silicon-graphite material in the form of a yolk-shell[1][2]. This could be achieved by using a metal oxide coating on silicon particles as a template for a uniform graphite layer deposition. The metal oxides were carefully selected and TiO_2 or Al_2O_3 seem to be the best options. The elaboration of a high quality graphite layer will thus ensure a lower irreversible capacity loss.

Metal oxide coating of silicon particles was done by atomic layer deposition in the case of Al_2O_3, and by sol-gel method in the case of TiO_2. Graphite growth was performed by a standard pyrolysis method in the gas phase under argon atmosphere using an organic solvent as source of carbon. The metal oxides were then etched away in order to create void space in between the silicon and graphite. The void can accommodate the expansion of the Si particles upon lithiation and the graphite coating can provide improved conductivity, also leading to the formation of a more stable SEI. In this way, the main issues that silicon faces can be prevented.

The structure surface morphology of the samples were characterised by SEM, XRD and Raman spectroscopy and the electrochemical performance was studied by galvanostatic charge-discharge cycling.

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Importance of the binder on the electro-activity of lithium titanate as negative materials in LIBs using ionic liquids as electrolyte.

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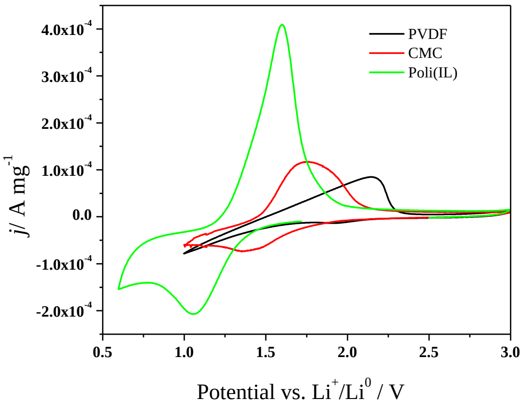
The use of renewable energy and efficient storage systems are topics of current interest. LIBs have the advantage of lower weight, higher energy density, and faster charge and discharge rates, compared to other similar technologies. The lithium titanate $Li_4Ti_5O_{12}$ (LTO) is currently one of the best candidates for anode materials of safer LIB for many reasons: the lithium insertion process takes place at a higher potential than graphite, thereby minimizing the decomposition of the solvent employed and consequently avoiding the formation of a solid electrolyte interface. In addition, LTO is a "zero-strain" material with only a 0.2% of change in unit cell volume when Li^+ ions are intercalated or de-intercalated and has a prolonged lifetime in charge/discharge cycling [1]. LIBs are also the most promising option for the next generation of the hybrid electric vehicles. For this purpose, extensive studies focused on increasing their safety. Indeed, current systems are not safe enough as they use flammable organic carbonate electrolytes, which can cause cracks, ignition, or explosion when cells are exposed to high temperatures or short-circuited. To increase the safety and stability of LIBs, the development of more suitable electrolytes is ongoing subject. Electrolytes derived from ionic liquids (IL) have gained a lot of attention due to their thermal and electrochemical stability, flame retardant performance and negligible vapor pressure [2]. In this work, LTO was synthesized by a solid-state method, and tested as negative electrode using two different kinds of electrolytes: ethylene carbonate (EC) and dimethyl-carbonate (DMC) solvent mixture (1:1 by mass) and N-n-butyl-N-methylpiperidinium (BMP) using $(CF_3SO_2)2N^-$ (TFSI) as anion containing 1 M of LiTFSI as lithium salt. From the results obtained, we found that the response of LTO using IL as electrolyte depend of the nature of the binder employed. Therefore, we have studied three different kind of binder, in the first place polyvinylidene fluoride (PVDF) using N-methy-2-pirrolydinone as solvent, then carboxymethylcelulose (CMC) dispersed in water and finally it was synthesized a poli(ionic liquid), which is a polymer containing one or more ionic group from ILs associated with its monomeric unit [3]. The figure insert, shows the cyclic voltammetry (CV) for this negative material using the same electrolyte (BMPTFSI) comparing each binder employed described before. It is possible to notice that the CV response for the electrode using poli(ionic liquid) as binder, is better and the charge involved is bigger than the others binders tested. This behavior it can be explained because this poli(ionic liquid) it is a ionic conductor, prepared with a 5% of the lithium salt (LiTFSI), which has a better interaction with the IL of the electrolyte; therefore allow a favorable lithium ion diffusion.



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Insertion / Extraction of Magnesium Ion into the Sb, Sn and Bi Modified Au Electrode

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Magnesium based secondary batteries have been regarded as a viable alternative compared to the immensely popular Li-ion systems owing to its high volumetric capacity. One of the largest challenges is the selection of Mg anode material since the insertion/extraction processes are kinetically slow.

Recently, antimony (Sb), tin (Sn) and bismuth (Bi) have been suggested as insertion materials, which could be used as an anode material in rechareable Mg batteries because magnesium can form intermetallics with these materials with a high energy density[1,2]. We electrodeposited Sb, Sn and Bi on polycrystalline Au using cyclic voltammetry and electrochemical quartz microbalance (eQMB). Au(111) has been used as a substrate for STM study of Sb, Sn and Bi UPD and OPD. The cyclic voltammogram for Mg^{2+} ion insertion/de-insertion from MACC/tetraglyme electrolyte[3,4] into/from such a modified electrode shows a positive shift of the onset potential of Mg deposition compared to that at bare Au electrode. The number of moles of deposited anode materials and inserted Mg verify the stoichiometry of Mg_3Sb_2, Mg_2Sn and Mg_3Bi_2 alloy formation. The apparent diffusion coefficients of Mg-insertion into a modified anode materials have been estimated from the chronoamperommetry and cyclic voltammetery at different sweep rate measurements.

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Phenomenological Modelling of GDL in LT_PEMFC

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In this paper, we introduce a 1D model of an elemental portion of the Gas Diffusion Layer (GDL) in Low Temperature Proton Exchange Membrane Fuel Cells (LT_PEMFC), taking into account the following phenomena: inert gases concentration gradients, water condensation and evaporation, convective flows and diffusive flows in gas phase, liquid water flow across GDL, liquid water hold-up, and mass transference across membrane-GDL interphase. Integral balances are proposed for finite volumes in which the GDL thickness is divided. Gas streams leaving a finite volume section must be saturated when a liquid water stream leaves the same section. In cases in which there is no leaving liquid stream, leaving gases may be saturated or undersaturated. Local water hold-up depends upon local liquid water flow rate. Boundary conditions for GDL are related to gas flow rate and gas composition in the chamber, electrochemical reaction rate at the Catalytic Layer, and water flow across GDL-membrane at this interphase. The solution to the equation system is analyzed and the number of elements is adjusted to obtain errors lower than 0.5% in numerical results. Changes in boundary condition values dramatically affect gas composition profiles and water condensation/evaporation processes through the GDL. Either convective or diffusive flows dominate the transport of reactants from the chamber to the membrane, depending on the parameters of those boundary conditions. Furthermore, for some conditions, water hold-up and both flows, diffusive and convective, are non-linear along GDL thickness. Other parameters that greatly influence concentration and flow profiles are identified by sensitivity analysis. A list ranking these parameters according to their relative Lagrange multiplier values is presented, void fraction, tortuosity, and Bruggeman coefficient being among the most important. Lagrange multiplier can be obtained for different optimizing objective functions, i.e.: maximizing reaction rate or minimizing partial pressure drop of reactant. Each objective reveals a different ranking list of the model parameters. Void fraction, tortuosity, Bruggeman exponent, and net water mass transfer across the membrane interphase are always at the top of these lists. Transport rates of reactants from the chamber to the Catalytic Layer are limited by effective diffusion which depends on the void fraction available for gas phase, which, in turn, depends on water hold-up. The greater the reaction rate, the greater the water hold-up in GDL. The model here developed allows computing the maximum transport rate for a given set of model parameters. This value imposes an upper bound on current density. Besides indentifying the importance of theses parameters, water management schemes could be developed on the basis of the model predictions in order to avoid GDL flooding or membrane drying processes. Based on this work, a phenomenological model for a whole LT_PEMFC will be presented in future works.

Definition of Operational Regimes for PEMFC through Dimensionless Numbers

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Through the present work a dimensionless number relating, the diffusive flux, the convective flow, and reaction rate for reactants (H_2/O_2/H_2O) in Proton Exchange Membrane Fuel Cells (PEMFC) is defined. It allows determining the operational regime for PEMFCs previous to any simulation of the entire system. This number is defined as the ratio maximum reaction rates to maximum diffusion rates. The data needed for its calculus are, geometric dimensions, physical properties of the electrode, feeding conditions, and operational conditions. The maximum reaction rate is computed assuming no diffusion limitation in the Gas Diffusion Layer (GDL). Thus, no variation in composition of the reactants through GDL is obtained. The maximum current density is achieved when output potential of the cell attain zero. This calculus includes the solution of a simple algebraic system of equations containing the electrochemical relationships of the PEMFC. The maximum diffusion rate is computed when depletion of the reactants at membrane-GDL interphase is achieved. The dimensionless number obtained has been checked by means of the solution of the whole PEMFC model, showing a significant agreement. Maximum reaction rates and maximum diffusion rates can be computed for different cells arrangements and different utilization factors of reactants giving raise to the definition of inlet and outlet numbers. Some study cases are presented showing changes of the limiting regime along the cell length according to the dimensionless number calculated at both cell ends.

Performance of catalysts coated Nafion as membrane electrode assembly using at hydrogen oxygen polymer electrolyte fuel cell.

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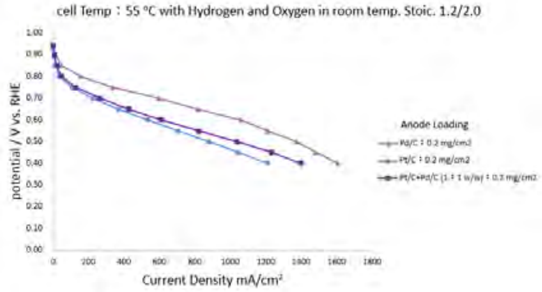
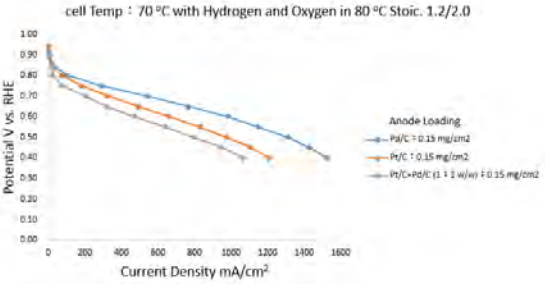
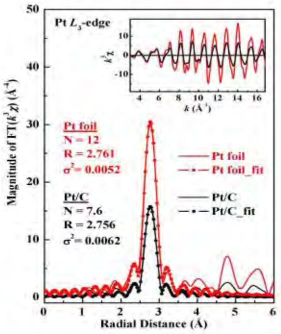
Abstract

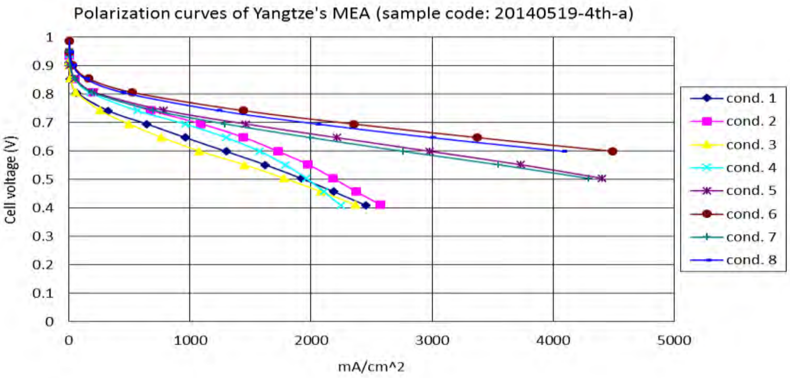
Polymer electrolyte fuel cell (PEFC) is an electrochemical reactor that produces electric power by reacting fuel of hydrogen and oxygen in air. There is no pollution produced from a fuel cell if hydrogen is employed as the fuel. Therefore, a fuel cell is considered as a zero emission device and is a source of green power. A membrane electrode assembly (MEA) with catalysts coated Nafion membrane (CCM) is the key component of a fuel cell. The building up of optimal ionic pathway and electric pathway with porosities for transport of reactants and water management on catalysts layers are beneficial to develop MEAs with high performance[4].

There are several factors needed in fabricating the CCM processes and the micro-pores and macro-pores structures of catalysts layer are determined by the coating ink compositions of binders with hydrophobic and hydrophilic components. The processing of CCM provided by Yangtze Energy Technologies, are supervised by authors team with reproducible uniformity. The catalysts used in this study are carbon supported platinum, carbon supported palladium and carbon supported platinum and palladium mixtures. The catalysts from vendors and the catalysts on Nafion after fabricated by technology of Yangtze Company had been check by using synchrotron light source with XANES and EXAFS results[2,3] to double check the local structure of metal clusters on carbon. The various testing and operation conditions[1] are also an approach to investigate the performances of a fabricated CCM used as MEA in a single cell.









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Lithium Titanate Synthesized by Sol-Gel Method: Influence of the Final Calcination Temperature in the Lithium-Ion Storage

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Nowadays, it is recognized by the scientific community that lithium titanate compounds ($Li_4Ti_5O_{12}$ or LTO) is the anode material in the technology of lithium-ion batteries (LIBs) following close to graphite in the perspectives of low-cost commercial applications to provide electric energy for use in transportation, stationary systems and smart grids. Among its electrochemical characteristics, the LTO material shows no volume changes during the charge-discharge cycle [1] and an outstanding cycling performance, together with an extremely constant operation voltage.

Taking into account the high potential value at which the Li^+ ions insertion-desinsertion occurrs into the LTO material (1.55 V vs Li/Li^+) two opposite aspects about this material arise. On one side, it is avoided the reduction of the electrolyte on the anode surface and the consequent formation of the SEI layer, but on the other, a lower voltage cell compared to the usual graphite anode result. One adequate strategy is to use LTO anodes together with a convenient cathode material, such as lithium-nickel-manganese oxide, lithium-cobalt phosphate or lithium-cobalt-manganese oxide, in order to obtain a high voltage cell of about 3.2-3.5 V. Thus, would be possible to obtain a safer cell without giving up a high voltage. Hence, LTO-based anode materials can offer an important advantage in safety issues, and it can be used to develop extremely safe power lithium-ion batteries for electric vehicles applications.

The specific capacity and cycling performance of the lithium titanate materials are greatly affected by the used synthesis procedure and the eventual post treatments applied. The most used methodologies to synthesize LTO include solid-state (or ceramic), hydrothermal (solvothermal also), and sol–gel synthesis, but spray pyrolysis and solution-combustion methods are also applied at lesser extent. While solid-state reaction method is largely performed because it is simple and easy, the very high temperatures (800-100ºC) and calcination times (about 24 hs) required convert this expensive method in energy, and produce particles in the micrometer range, in spite of the highly crystalline LTO materials produced. Conversely, sol-gel methodology with a final calcination stage at moderately high temperatures (up to 800ºC) and lower times (up to 12 hs) produce smaller particles and with a narrow size distribution. This methodoloy requires lower power consumption but the use of less affordable precursors.

In the present work, we use a different method than the solid-state reaction previously used [2] in order to obtain a LTO material with a more adequate control of particle size and crystallinity properties.

A sol-gel synthesis at different final temperatures was performed to analyze the effect in crystallinity and particle size and its relationship with the specific capacity to Li^+ storage in the host matrix. The obtained LTO materials were structural and morphologically characterized using XRD and SEM techniques. To study the effect of the thermal treatment on materials storage capacity, galvanostatic cycling, cyclic voltammetry and rate capability experiments were performed.

The experimental results obtained indicate that there is an optimal thermal treatment below which the obtained material has no the crystalline phase neither the crystallinity extent required for the optimal use of the total active mass deposited in the electrode, and above which, particle agglomeration occurrs, reducing the actual exposed area to the electrolyte. In either of these two conditions, a diminution in specific capacity, cyclability and rate capability performance was observed. For LTO materials synthesized by sol-gel method with further calcination stage at 700-800ºC it was obtained a little lower specific capacity than those obtained by us using a solid-state procedure at 950ºC, but its performance in rate capability was markedly higher, with a loss in the specific capacity obtained at 10C no more than 10% of that obtained at 0.5C.

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Improving of Activity and Durability of Pt-M/C Electrocatalysts with Different Structure by Thermal Treatment

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Carbon supported platinum nanoparticles are the basic component of catalytic layers in low-temperature fuel cells. Insufficient corrosive and morphological stability of nanoparticles, as well as of the metal-carbon composite itself during the operation and relatively high cost are the main disadvantages of these materials. An efficient way to overcome these problems and to obtain promising electrocatalysts for oxygen electroreduction (**ORR**) is the synthesis of electrocatalyst containing bimetallic PtM nanoparticles (where M – transition metal, such as Cu, Co, Ni, Cr, etc.) with M-core – Pt-shell structure deposited onto highly developed surface of carbon support [1-2]. For such architecture, the decisive factors determining the catalytic properties of PtM nanoparticles are the thickness, composition and continuity of the shell, particle shape, surface morphology, and the stability of the core-shell structure during operation, the effect of the metals type in the core on the catalytic activity and stability of the shell.

The aim of this work was to study an electrochemical performance and structural stability of PtM/C electrocatalysts with different structure before and after thermal treatment at different temperatures.

Bimetallic PtM/C (M=Ni,Co,Cu) electrocatalysts with a non-uniform distribution of the components in the nanoparticle, namely – higher platinum content in the near-surface layers, were obtained by two methods: simultaneous and sequential chemical reduction of M and Pt compounds in a carbon (Vulcan XC-72, Cabot) suspension based on a two-component water-organic solvent at pH = 10 (excess of NH_3). A part of the resulting PtM/C catalysts were heated at different temperature (200 – 350 °C) for 1 hour in Ar atmosphere. The characterization of PtM/C materials was performed by HRTEM, XRD, CV, LSV and Pt L_3- and M K-edge extended X-ray absorption fine structure (EXAFS).

It was found that in the case of Pt-Cu core-shell nanoparticles at a particular temperature (~ 300 ^{0}C) there was a strong shift of the 111 XRD reflection in the region of large values of 2 theta degree indicating the decrease of the lattice parameter (Fig. 1). Meanwhile, alloy PtCu/C material with similar composition did not show a similar effect (Fig. 1).

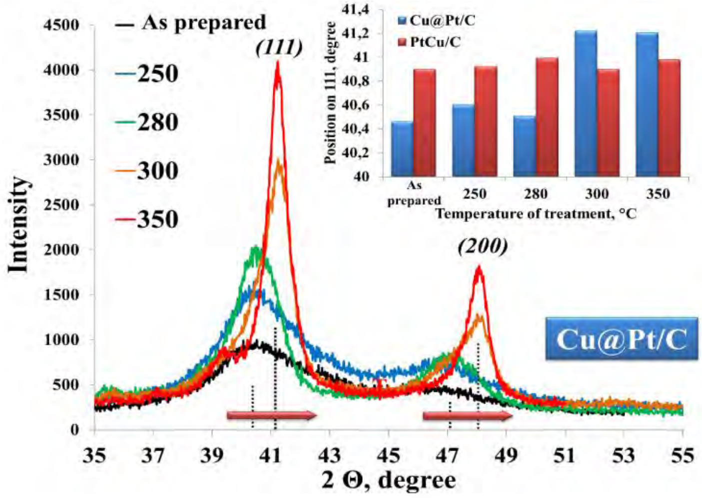

Figure 1. XRD for Cu@Pt/C electrocatalyst before and after thermal treatment at different temperatures.

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Oxygen Reduction Non-Precious Metal Catalyst Synthesis via High Temperature and Pressure Pyrolysis

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Fuel cells indicated themselves as promising highly efficient clean energy converting devices with low emissions. Platinum excessive cost and low abundancy are among the main factors, limiting acidic polymer fuel cell from broad commercialization. Massive effort was made to replace precious metal with inexpensive and widely available alternatives. Recently, non-precious metal catalysts (NPMCs) recommended themselves as encouraging oxygen reduction catalysts for fuel cell cathodes. Heat treated Fe-N/C and Co-N/C type electrocatalysts took the leadership in the NPMC field, as they showed promising stability and impressive activity, almost reaching by performance state of art Pt/C.[1,2]

In this work, we present a simple two-step pyrolysis method for Fe-N/C catalyst synthesis with considerable activity and high turnover frequency rates. First heat treatment step proceeded in a home-made steel autoclave[3] under sufficiently large pressure (approx. 5.0×10^{7} Pa), providing considerable changes in nanostructure of catalytic material. Subsequently, catalyst powder was subjected to high temperature pyrolysis with a direct contact of nitrogen / ammonia flow. A second heat treatment resulted in significant enlargement of pore sizes, as well as increase of the amount of pyridinic-N active sites in a hydrid catalyst, characterized by X-ray photoelectron spectroscopy. Electrocatalytical perfomance was estimated with rotating disc, disc-ring electrodes, as well as in a single-cell laboratory fuel cell.

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When Sulfur Meet RuO_2: Enhancing Polysulfide Redox Reaction for High-Performance Lithium–Sulfur Batteries

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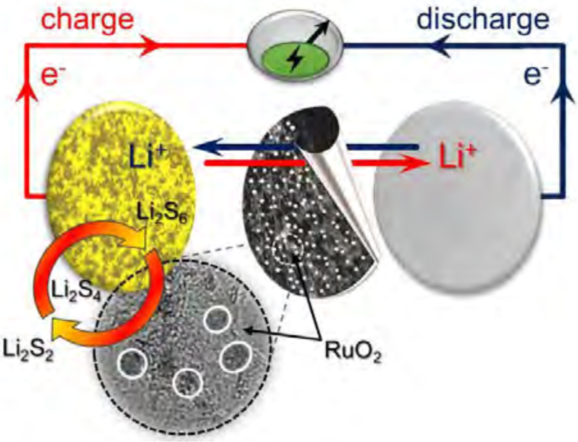
Due to the outstanding high theoretical specific energy density of 2600 Wh/kg, the lithium–sulfur (Li–S) battery is regarded as a promising candidate for post lithium-ion battery systems eligible to meet the forthcoming market requirements. In addition, sulfur has the enormous advantages of being inexpensive, environmentally benign and naturally abundant, making it an ideal candidate for industrial applications. However, its commercialization on large scale is thwarted by fast capacity fading and the poor cycling stability caused by the Achilles' heel of Li–S systems: the polysulfide shuttle. This shuttle phenomenon involves the migration of dissolved polysulfides—intermediates formed through the conversion reaction between Li^+ ions and elemental sulfur during the discharge process of the battery—between the cathode and the anode, inducing the contamination of the lithium anode surface by redeposition of polysulfide discharge products [1, 2].

In order to overcome this issue, we proposed the reconfiguration of the conventional Li–S cell by using a polypropylene-supported ruthenium oxide (RuO_2) nanoparticle/mesoporous carbon hybrid separator which acts as an electrocatalytic and adsorbing polysulfide barrier [2–5]. The RuO_2 nanoparticles-containing separator coating—covering the side of the separator facing the cathode—not only facilitates the electron transport but also enhances the redox reaction of migrating polysulfides by their early adsorption and trapping in the composite-coating and thus retaining the active material in the cathode side to further improve its reutilization [5].

As main result, Li–S cells with a pure sulfur cathode and the RuO_2/mesoporous carbon hybrid separator delivered a high initial discharge capacity (1276 mAh/g at 0.1C) and demonstrated a long-term cycling stability (over 300 cycles) with high Coulombic efficiency (98.2%) and astounding capacity retention (decay rate of 0.022% per cycle, over 200 cycles at 0.5C) [5]. We believe that the implementation of RuO_2 nanoparticles in the design of hybrid separators and also as one of the components in sulfur cathodes promises a new perspective for further improvements in advanced Li–S battery systems.



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Advanced Lithium–Sulfur Batteries with Functional Hybrid Separators

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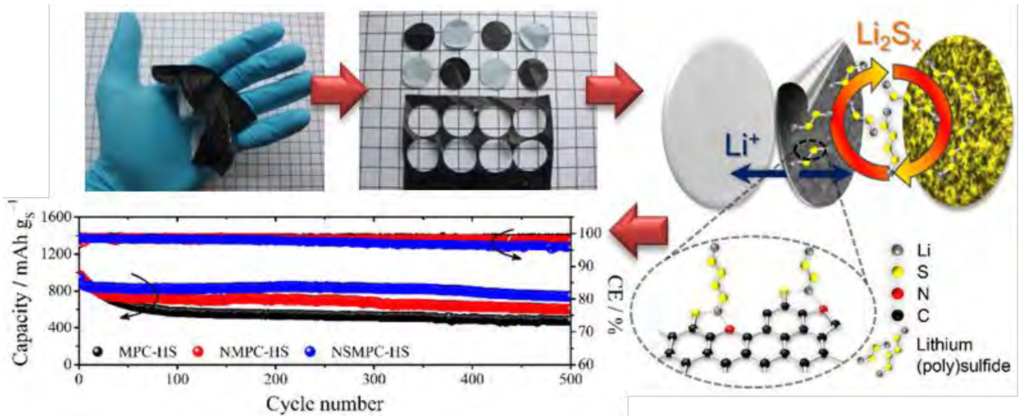
The lithium–sulfur (Li–S) battery is considered one of the most promising candidates for next-generation rechargeable batteries due to its high theoretical energy density of 2.6 kWh kg^{-1}, which is up to 5 times higher compared to state-of-the-art lithium-ion batteries. In addition, sulfur has the enormous advantages of being inexpensive, environmentally benign and naturally abundant. However, its commercialization has been hindered due to the fast capacity fading and the poor cycling stability, mainly caused by the polysulfide shuttle phenomenon [1].

In order to tackle these issues, we focus on the development of functional hybrid separators by a straightforward coating modification of a commercial polypropylene separator (Celgard 2500) with heteroatom-doped mesoporous carbon materials [2–5]. The Li–S cells with a N, S dual-doped mesoporous carbon-coated separator demonstrates a superior high initial capacity of 1267 mAh g^{-1} at 0.2 C and ultralow capacity degradation of 0.041% per cycle for over 500 cycles at 0.5 C [5]. The enhanced electrochemical performance of the Li–S batteries is attributed to the unique features of the N,S codoped mesoporous carbon-coating, which (i) effectively reduces the resistance of the sulfur cathode, (ii) prompts fast electron/lithium ion transport through the carbon network, (iii) successfully sequestrates, stores and maintains available the sulfur active material for further reutilization and (iv) buffers the large volume change during sulfur/Li_2S conversion reaction. Pushing our simple-designed and scalable cathode to a highly increased sulfur loading of 5.4 mg cm^{-2}, the Li–S cell with the functional hybrid separator can deliver a remarkable areal capacity of 5.9 mAh cm^{-2}, which is highly favorable for practical applications [5]. In our poster, the impact of the pore volume of the mesoporous carbons to trap polysulfides intermediates and the effect of the heteroatom doping in the carbon matrix on the electrochemical performance of Li–S batteries will be showed.



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Passive Direct Methanol Fuel Cell Catalysts

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Direct methanol fuel cells (DMFCs), which convert the chemical energy stored in methanol directly and efficiently to electrical energy, have the potential to reduce the dependence on fossil fuels. DMFCs have become increasingly attractive because they are fed at the anode with a liquid fuel with high density energy, easy to handle, store and transport.

In portable applications, passive DMFCs are one of the most prospective power sources. As passive DMFCs require the use of high alcohol concentration to feed the anode, the crossover of methanol causes a considerable loss of fuel cell efficiency, because both the oxygen reduction reaction (ORR) and the methanol oxidation reaction (MOR) occur simultaneously on the cathode.

Pt is the most widely employed cathode catalyst for the ORR, though its catalytic activity towards the oxygen reduction reaction is still insufficient. One approach to solve the alcohol crossover problem in DMFCs consists in the replacement of Pt by a catalyst with high activity for the ORR and low activity for the MOR

Trimetallic PtMN/C cathode catalysts with M and N= Co, Ru or Fe have been obtained by an impregnation procedure using ethylene glycol and $NaBH_4$ as reducing agent. The catalysts, with suitable activity for the oxygen reduction reaction (ORR) and improved tolerance to methanol, have been physically characterized by high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) showing that the catalysts consisted of small particles which are well spread on the carbon support. Pt is mainly found as Pt (0) and the other metals are mostly oxidized.

To study the durability and performance of the synthesized catalysts for ORR and their methanol tolerance over time, the catalysts were subjected to an electrochemical accelerated stress test (AST), consisting in cycling the potential for 25 hours. Polarization curves for ORR with and without methanol were recorded. After the AST the trimetallic PtMRu/C catalysts were able to keep their performance for ORR in the presence of methanol

Development of pore-filled ion-exchange membranes for efficient electrochemical energy storage and conversions

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Ion exchange membranes which consist of polymer backbones attached with fixed charge groups have been widely used in various water treatment processes such as electrodialysis for a desalination of brackish water. Recently, they have also gained increased industrial importance in the applications to electrochemical energy conversion and storage processes such as reverse electrodialysis (RED), fuel cells, redox flow batteries (RFBs) etc. Their intrinsic properties such as electrical resistance and permselectivity are the key parameters dominating the electrochemical energy conversion efficiencies. Especially, in recent years, alkaline direct liquid fuel cells (ADLFCs) employing anion-exchange membranes (AEMs) as a fuel barrier have attracted significant attention as promising alternative energy sources. ADLFCs are allowed to use more abundant anode catalysts which are cheaper than the catalyst used in that using hydrogen fuel. In this work, novel pore-filled anion-exchange membranes (PFAEMs) were successfully fabricated by combining a highly porous PTFE film and cationic polyelectrolytes with structurally stable anion-exchange sites. The results of the membrane characterizations revealed that the optimization in the crosslinking degree and hydrophilicity of membranes should be considered for the successful application of the PFAEMs to ADLFCs. The prepared PFAEMs exhibited excellent electrochemical characteristics and stabilites. Especially, the alkaline stability of the PFAEMs was shown to be superior to that of a commercial membrane because the excellent structural stability of fused ion-exchange sites and the use of a highly stable PTFE substrate. We have also investigated the development of pore-filled cation exchange membranes (PFCEMs) with a high proton conductivity for the applications to various electrochemical energy processes such as RED, PEMFC and RFBs. This work was supported in part by the New & Renewable Energy Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (20153030031720) and the Technology Innovation Program funded by the Korea government (MOTIE) (No. 10047796).

All-Solid-State Li Battery Based on c-$Li_7La_3Zr_2O_{12}$ Solid Electrolyte and Alloy Anode Materials

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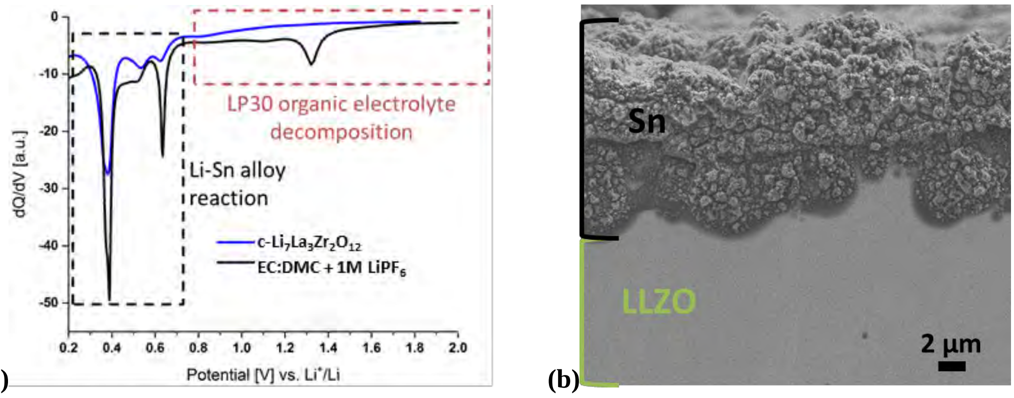
Since the dawn of Li-ion batteries, consumers have always been concerned about the safety of the electronic devices wherein batteries are employed. Recent accidents (Samsung S7 Galaxy Note, Boeing 787 Dreamliner aircraft and Tesla electric cars) have pushed the look for alternatives to liquid electrolytes considered to be the main risk for the low safety of the battery. Solid electrolytes are envisaged as alternative of organic electrolytes since they promise improved safety both at room and elevated temperatures. Among the already discovered inorganic Li-ion conductors, the garnet material with a cubic structure, $Li_7La_3Zr_2O_{12}$ (LLZO), offers both acceptable ionic conductivity at room temperature and stability in contact with Li metal.[1]

Generally, such solid electrolyte is often investigated in half-cells (vs. Li metal) coupled to oxide materials such as $Li_4Ti_5O_{12}$ or $LiCoO_2$ as negative and positive electrode, respectively. Although the solid garnet electrolyte (LLZO) was considered to be stable in the potential range from zero to six volt vs. Li^+/Li, recent studies point out that the stability window could be drastically limited down to 2.9 V.[2]

We investigated the electrochemical performance of alloy-based (Sn, Si) nanoparticles as electrode using a Ta-doped LLZO pellet as solid electrolyte to build all-solid-state Li half-cells. Alloy materials are known to be electrochemically active in the range 0-1.5 V vs. Li^+/Li, thus, within the stability window of LLZO. The electrodes, prepared as a conventional slurry mixture and coated directly on the surface of the electrolyte pellet, show electrochemical activity comparable to the liquid counterpart except the possible absence of a solid electrolyte interphase (SEI) during the first cycle.

For the first time, we discuss the possibility to lithiate/delithiate reversibly alloy-based nanoparticles in combination with the garnet LLZO electrolyte. Such investigation is supported by electrochemical characterization (Figure 1a) coupled with surface and structural characterization (XPS, SEM and XRD) (Figure 1b).



(a) **(b)**

Figure 1. (a) Derivative curve of the first lithiation of nano-Sn material cycled in conventional liquid electrolyte (LP30) and solid electrolyte (LLZO); (b) Cross-section SEM of the pristine Sn/LLZO interface

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Reactors with N+1 bipolar electrodes. Simplified mathematical model.

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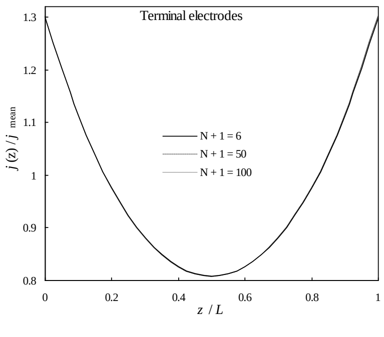
Frequently used technologies in large scale reactors for hydrogen production are electrochemical reactors with bipolar electrodes, which have several advantages over reactors with monopolar electrodes. They are also more energy efficient in industrial plants. However they have a very serious drawback: the inevitable parasitic currents flowing in the bypass duct, affecting their performance, and producing undesirable reaction rates distributions on the electrodes.

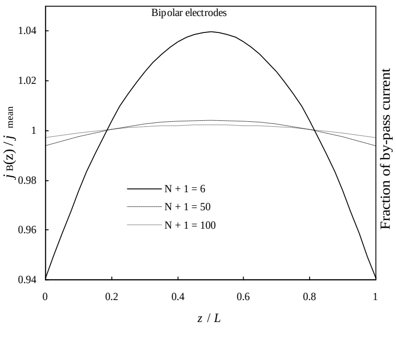
A few years ago, mathematical modelling activities using balance equations of current in a reactor for producing hydrogen with one bipolar electrode, considering a Tafel kinetic on the electrodes, [1] have been developed. Later in [2] a more complex mathematical model was developed, also considering a single bipolar electrode, but using the technique of finite differences to represent the potential distribution in the electrolyte phase. Also, experiments with hydrogen and oxygen evolution to validate the model, in a reactor with electrolyte without movement, have been performed.

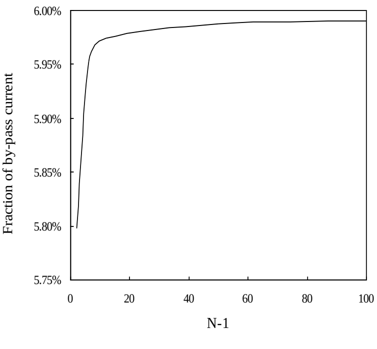
In electrochemical reactors, primary current distribution establishes itself when the influence of overpotential is negligible. Considering primary current distribution [3], the knowledge of reactors with multiple bipolar electrodes, has been increased. On the other hand, a theoretical work, comparing primary and secondary currents distributions in a reactor with only one bipolar electrode, with recessed electrodes [4] was performed. In this work, it has been shown that secondary currents distributions are more pronounced than the primary, for the cases of industrial importance. In addition, it has made a great contribution in the field of industrial design of these units.

In this contribution, a simplified mathematical model, based on [1], considering that the reactor is used for the production of hydrogen and consisting of N-1 bipolar electrodes (where N is the number of reaction compartments), is presented. Tafel and Butler-Volmer kinetics, were taken into account. In the above figures, simulations considering Tafel kinetic are shown. The dimensionless current density distribution on the terminal electrodes does not vary if the number of bipolar electrodes is increased. However distributions in bipolar electrodes become less marked. On the other hand, the fraction of current drained by the bypass ducts increases, but this increase has a limit.

With this work, knowledge of the phenomena produced in reactors having multiple bipolar electrodes, mainly in terms of current distributions on electrodes and parasitic currents, has been increased.







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Silicon thin film anode on porous current collectors for lithium ion batteries

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During the last two decades, a growing number of research works have been devoted to design thin film silicon (Si) anode for future development of lithium ion microbatteries. In spite of its high specific electrical capacity and low discharge potential, silicon thin film still has problems with rapid capacity fading due to the electrical contact loss during lithium ions insertion and extraction processes. On the other hand, thin film mass loading is not enough to design battery with good performance. In this context, the porous current collectors can overcome these problems owing to its high specific area of the porous current collectors, which is capable of keeping a good electrical contact between the current collector and the silicon layer during the electrochemical tests. In addition, the voids in the porous structure will help the active silicon to accommodate the volume change without pulverizing.

Herein, we report on the study of combining best approaches towards obtaining thin films of high stability, such as employing 3D structured substrates and various facile techniques for thin film deposition, oxygen removing, silicon-current collector adhesion enhancement. The preparation of the nano-scale Si thin film anode was carried out on the 3D structured raw, chemically pre-treated and graphite coated Ni foam (NF) substrates by means of the magnetron sputtering system (Kurt J. Lesker company,USA). Chemical vapor deposition (CVD) was employed to deposit carbon atoms on the NF. The technical parameters of the deposition methods will be in the presentation. The cyclic voltammograms of Si thin films on raw and graphite coated NF recorded at scan rate of 0.2 mVs^{-1} are shown in figure 1. As it can be seen that the electrochemical behavior of the second anode differs dramatically. The galvanostatic cycling performance measurement was performed in the range between 0.02-1.2 V at 1C scan rate. The voltage profiles showed good cycling stability of the Si anode on graphite coated NF from the second cycle at around 700 mAh g^{-1}. We supposed that the alloy containing nickel, oxygen and carbon could form during thermal deposition. X-ray diffraction, Raman spectroscopy, focused ion beam microscopy and scanning electron microscopy were used for physical characterization of prepared samples. The structure and morphology features of the obtained samples and further results from the electrochemical characterization will be discussed at the conference.

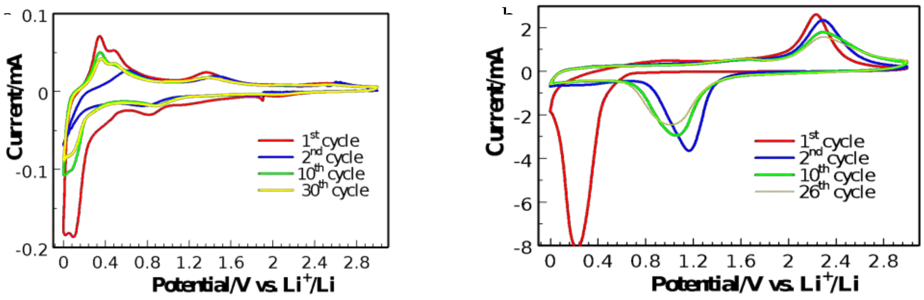

Figure 1. Cycling voltammograms of Si thin film on (a) raw NF and (b) graphite coated NF.

Acknowledgements
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Solar micro-generation and accumulation in Lithium ion batteries. Simplified phenomenological model.

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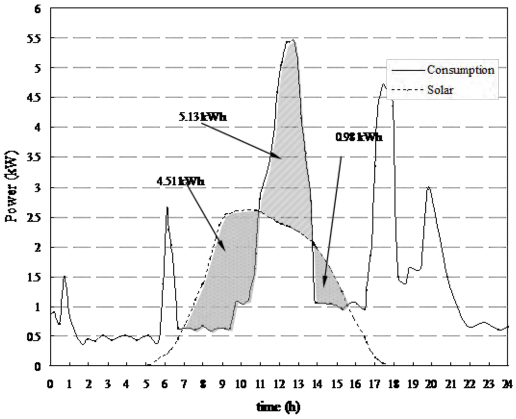
Electricity storage is an important problem of discontinuous sources of energy such as solar and wind. The potential of lithium ions batteries has been extensively tested in small devices, since its creation. This has attracted the attention of several manufacturers in the world to achieve the same performance in electric or hybrid vehicles and in stationary applications such as energy storage houses, public buildings and even neighbourhoods

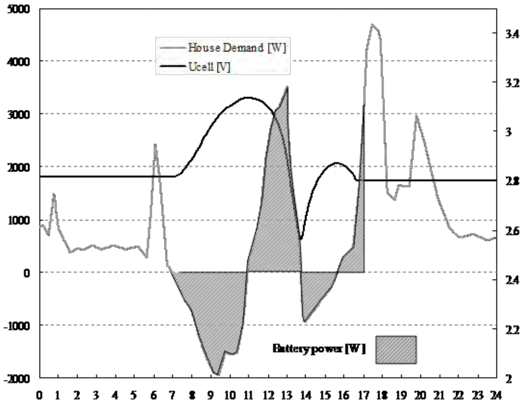
However, the net effect of these systems depends critically on the design of the device power consumption, technological design of the battery, the time pattern of delivery of power, recharge times and capabilities of batteries re-charging systems.

To analyze these interactions and to provide results that can generate applicable technologies in different areas, it is desirable to have mathematical models that integrate the phenomenological description of lithium ion batteries, with computer models of recharging a battery pack as well as mathematical models of power distribution logistics.

Argentina is one of the most important global reserves of lithium mineral. In previous years, a phenomenological simplified, flexible and robust mathematical model to represent all temporary physico-chemical phenomena produced in a battery (voltage cell, potentials, overpotential, reaction rates, concentrations), and can be solved even in a spreadsheet [1], has been developed. More recently, a mathematical model, also simplified and based on [1], but considering that the electrodes of the lithium battery is composed by a particle size distribution [2] has been shown. When considering more than one particle size, temporary responses of all physicochemical properties of the battery, changes drastically. On the other hand, the evaluation of energy use in a typical Canadian household connected to the electricity grid and equipped with a system of microgeneration, comprising: a stiling Motor, coupled to a set of lithium batteries 2kW and 6kWh, [3], was made. The mathematical model used for this study, has no easy solution because of the highly nested differential equations and nonalgebraic boundary conditions.

In this paper, simplified models [1] and [2] are used to perform the energy analysis and to assess the autonomy and performance of battery LiPO4Fe connected to the power grid and a solar panel. Consumption curves and solar panel generation shown above are average curves countries of South America in summer. Based on these curves, the energy necessary for the operation of the home, and the battery size are calculated.





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Metal-glass interactions during the hydrogen oxidation reaction sensed by scanning electrochemical microscopy on Pt microelectrodes

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The hydrogen oxidation reaction (*hor*) proceeds on Pt and other noble metals over potential ranges where atomic hydrogen is electroadsorbed (H_{ad}) from proton or water, either as a reaction intermediate or as an spectator (i.e. the under-potential deposited H_{UPD}). The behaviors of these adsorbed species (adsorption energy, surface mobility, among others) have strong influence on the *hor* reaction rate. Moreover, the coverage of H_{ad} is a key factor that governs the current-potential dependence for the *hor*. Thus, modification of the H_{ad} coverage by cooperative effects from other catalyst components that surround the active material may be an interesting strategy to increase the *hor* current. In particular, oxides are able to adsorb H^+ through their surface acid-base equilibria, and may act as additional H sources for the *hor* when they are in contact with a catalyst. Scanning electrochemical microscopy (SECM) has the capability to sense the adsorption and surface diffusion of H_{ad} on metals [1] and of H^+_{ad} on oxides [2] when operating in the feedback mode using the H^+/H_2 couple as mediator, through a variant usually known as scanning electrochemical induced desorption. The local variation of the mediator concentration underneath the tip causes a potential-dependent gradient of the H_{ad} surface coverage at the substrate over the tip-affected region, which drives the H_{ad} surface diffusion toward this area and the consequent positive feedback of mediator, reaching a steady state. The method was successfully applied to detect H electroadsorption and surface diffusion on Pt and Au [1], and the effects of these processes on the SECM responses. The purpose of this work is to apply this SECM-based method on an heterogeneous material composed by an active metal (i.e. Pt) and an inert and non-conductive source of H_{ad} (i.e. glass) with the goal to sense not only the adsorption/surface diffusion of H_{ad} on these two materials but also to detect the possible transfer of H_{ad} from/to the oxide to/from the metal. This study was carried out on Pt disk microelectrodes sealed in borosilicate glass by setting the SECM configuration shown in Fig. 1, in deareated solutions of 0.02 M $HClO_4$ - 0.1 M $LiClO_4$. Once the tip was located right over the Pt disk by screening the substrate activity, steady-state tip current (I_T) vs. substrate potential (E_S) curves as those shown in Fig. 2 were measured at different tip-substrate distances (L), keeping the tip potential at -0.65 V vs. RHE and sweeping the substrate potential from 0.5 V to -0.25 V vs. RHE. The $I_T(E_S)$ curves present a sharp peak at *ca*. 0.1 V vs. RHE overlapped to the *hor* response. This increment on feedback current is attributed to the diffusion of H^+ adsorbed on glass being transferred to the Pt-disk surface through the Pt/glass interface. At E_S values where H_{ad} is consumed on Pt, a H_{ad} coverage gradient is generated in the Pt/glass interface causing a flux of H_{ad} from the glass surface. According to numerical simulations and to previous works [1], such surface process leads to a peak in the $I_T(E_S)$ dependence, whose intensity increases when L decreases. Such effect was not observed in SECM experiments performed on glass-free Pt disks.

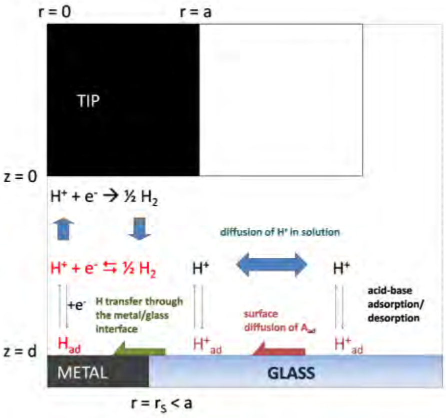

Figure 1. Scheme of the SECM setup to study H adsorption, surface diffusion and transfer through the metal/glass border.

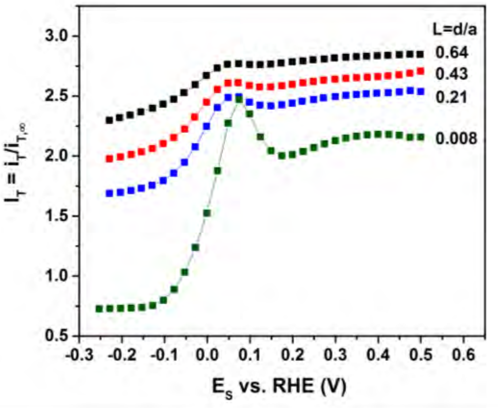

Figure 2. $I_T(E_S,L)$ curves of *hor* over a glass-sealed Pt-disk substrate (r_S = 3 µm, a = 12.5 µm).

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Silicon carbide thin films for lithium ion batteries

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Li-ion batteries (LIBs) have attracted enormous attention as energy storage devices for a wide range of portable electronics due to their high energy density and long lifespan [1-5]. Thin film batteries are the next generation of LIBs since, in comparison with the conventional batteries; they can be utilized in the fabrication of small and light devices with outstanding performance and low cost [6, 7]. Moreover, thin film batteries can achieve significantly high volumetric energy densities due to their thickness (10-15 µm). Today, they are used for diverse range of applications: as solar cells, various type diodes, thin-film transistors (TFTs), small scale sensors, smart cards, drug delivery systems, and other portable electronics [8]. Nanostructuring of thin film electrode materials has increased the energy density of electrochemical capacitors (ECs) for LIBs. For the time being, silicon carbide (SiC) is a promising candidate for Li-ion storage due to its outstanding electrical, mechanical and thermal properties, and extremely thin structure [9,10].

In this study, novel SiC-based alloy electrode with thin film structure was developed as anode material for LIBs. In contrast to conventional anodes, the proposed material illustrates superior characteristics such as high capacity, low cost, electrochemical stability and easy handling. The alloy structure of the electrode can be obtained through substitutional incorporation of C into the Si lattice along with various dopants (positive or negative) by using Chemical Vapor Deposition (CVD) technique. Electrical, chemical and physical properties of the crystalline silica can be effectively controlled by this method.

Herein, we report on the electrochemical performance of SiC alloy based thin film anode material for Li-ion batteries (LIBs), which was fabricated by reduced pressure chemical vapor deposition (RP-CVD) method on the silicon substrate. With the purpose to improve physical and electrochemical properties of the SiC material, phosphorus and boron dopants were incorporation into its structure. The Li-ion insertion and extraction propersties of the SiC thin film anode were investigated by cyclic voltametry (CV) at a scan rate of 0.1 mV s−1 between 0.01 and 3 V. The structural changes that took place long Li-ion migration process were evaluated by using scanning electron microscopy (SEM).

Acknowledgements

We thank Dr. Myronov for his cooperation in the experiments and synthesis of samples. This research was funded under the target program №0115РК03029 "NU-Berkeley strategic initiative in warm-dense matter, advanced materials and energy sources for 2014-2018" from the Ministry of Education and Science of the Republic of Kazakhstan.

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Synthesis, Characterization and Cathodic Behavior of Nanostructured Mixed Oxides $LiNi_xCo_yMn_{2-x-y}O_{4 \pm \delta}$ (x, y = 1/3, 1/4).

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In this work, the effect of the synthesis method and the composition of new mixed oxide complex materials nanostructured based on Li, Ni, Co and Mn synthesized by the sol-gel (SG) and ultrasonic-assisted sol-gel method (SGUS)**[1]** was studied. The compounds $LiNi_xCo_yMn_{2-x-y}O_{4 \pm \delta}$ (x, y = 1/3, 1/4), were studied as insertion cathode materials in lithium ion batteries and the results were compared between the two groups of materials. It was found that the performance of the electrodes depends on the method of synthesis, being the SGUS preparation the most appropriate method.

The materials were characterized by X-rays diffraction (XRD), Rietveld refinement, Optical Emission Spectroscopy (ICP-OES), scanning electron microscopy (SEM) and transmission electron (TEM), surface area (BET), X-ray Photoelectron Spectroscopy (XPS) and Electrochemical Impedance Spectroscopy (EIS).

The results show that the oxides crystallize in the phase spinel (FCC) without impurities. The cell parameters are in accord with the morphological and surface area results. As expected, oxides prepared by the SGUS method show higher surface area and smaller particle size giving rice to a higher lithium diffusion coefficient D_{Li^+}**[2]**. The samples were studied as cathode materials through discharge curves, insertion and discharge capacity versus voltage showing significant differences between the composition and the preparation method. The discharge/charge curves for both oxides give voltage up 4V. The materials show high electrochemical stability. The electrochemical results obtained for both compounds $LiNi_{1/3}Co_{1/3}Mn_{4/3}O_4$ and $LiNi_{1/4}Co_{1/4}Mn_{6/4}O_4$ can be explained on its ionic distributions and its XPS surface composition. The better results were obtained using materials prepared by SUGS method because it shows the higher concentration of Mn^{+4} in the structure, considered as the responsible of the behavior observed**[3,4]**. The Mn concentration values observed allow to prepare electrodes more stable, avoiding the Jahn-Teller effect and favoring the electrochemical process. On the other hand, the electrochemical reactivity is macroscopic attributable to the effect of particle size, and therefore the surface area.

Acknowledgments. This work was supported by CONICYT (Fondecyt grant Nº 1150371).

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Electrosynthesis of Polypyrrole Nanowires

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Using the methodology previously reported for the obtaining of various conducting polymers by electrochemical methods, on a silica template modified Pt electrode, that tunes the growth into its pores confined space [1], in the current work poly(pyrrole) nanowires (PPy-nw), also obtained directly on the electrode surface, were prepared.

The Pt electrode was first modified by potentiostatic deposition of a thin layer of PPy. Upon this Pt|PPy modified electrode a porous silica film was electrodeposited (Pt|PPy|(SiO_2)n) to serve as template for polymeric nanowires preparation. This is achieved following the methodology proposed by Walcarius [2], at a fixed potential of -1.2 V for 4 s. The modification to the previously reported methodology for polythiophene [1] consists just in the pre-coating of a PPy thin film on the bare Pt.

PPy-nw are synthesized by cyclic voltammetry (CV) from 0.01 mol L^{-1} monomer and 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate in acetonitrile, on Pt|PPy|(SiO_2)n. The optimum anodic inversion potential for the monomer oxidation under these conditions is 0.91 V, value which is100 mV less than that required to prepare massive PPy under similar conditions. This would show that the growth confined in silica nanochannels greatly favors the formation of oligomers which give rise to the polymer deposit. Subsequent removal of the template without damaging the nanostructured polymer is also achieved by the method previously reported by us [3]. The modified electrodes are characterized by CV and scanning electron microscopy, SEM. The results are subsequently compared with the response of the PPy modified electrode, prepared under identical working conditions, but template-free.

The voltammetric response of Pt|PPy|PPy-nw electrodes shows a process of *p*-doping/undoping which remains fully reversible, but with 350 times greater charge than that recorded for Pt|PPy massive. Finally, in Fig. 1 can be seen SEM photomicrographs demonstrating obtaining PPy-nw about 30 nm in diameter and 1.8 μm in length, on average.

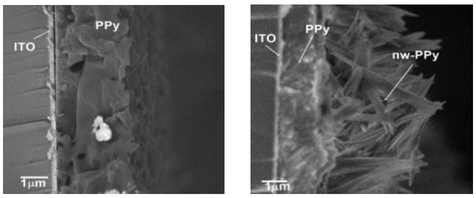

Figure 1. SEM micrographs of electrosynthesized PPy and PPy-nw.

In summary, experimental conditions were optimized for PPy-nw electrosynthesis on platinum electrodes previously modified with a film of the same polymer and subsequently with a porous silica film, to guide polymer growth. It was established thus a method for decreasing the influence of the nature of the electrode substrate. Consequently, the nanowires grow upon its same bulk polymer, affording a "brush-like" nanostructure which, besides adherence, offers the advantages of using as supporting electrode cheaper conductive substrates, *e.g*. stainless steel or other material, and ensuring excellent reproducibility. The validity and usefulness of the proposed methodology using solely electrochemical methods to obtain polymeric nanostructures has been successfully confirmed, with the advantages that structures with this type of morphology present and, further, the deposition of the PPy-nw is accomplished directly on the electrode surface, which has only been carried out so far with metal deposits.

Acknowledgements

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Electrosynthesis and Characterization of Poly(3,4-ethylenedioxythiophene) Nanowires

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Kinetic study of the interface of AlZnSnMg sacrificial anode by electrochemical impedance spectroscopy

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In the last twenty years, significant progress has been made in the development of cathodic protection systems by sacrificial anode for reducing marine corrosion materials. Anodes contain aluminium alloys are extensively used in marine structures as sacrificial anodes for the protection of steel in sea water due to their corrosion resistance and their good mechanical properties **[1-2].**

In this work, an alloy containing Al, Zn, Sn and Mg has been prepared by melting the pure elements (99.99% Heraeus-GMBH) in a furnace under argon atmosphere. The ingot that obtained, are machined into anodes form of 1 cm of height then the samples were mechanically polished to mirror.

The microstructure of the anodes before and after immersion test, were observed by scanning electron microscopy (SEM). The kinetic behavior of the anodes and ordinary steel was performed by impedance measurements after one month of galvanic coupling in 3% NaCl solution. The system response (anode or steel) was examined in a frequency range of 100 KHz to 10 mHz with an amplitude of 10 mV. The values of the electrical parameters were obtained after adjustment of the impedance diagrams with equivalent electrical circuits. The results indicate that the addition of Mg reduces the precipitates at grains boundaries and increase general dissolution.

Keywords: sacrificial anode , EIS, SEM.

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Fabricated α-Bi_2O_3/TiO_2 heterojunction for photocatalytic activity

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In photocatalysis, anatase TiO_2 nanotubes (TiNT) is one of the most investigated materials. However, its large band gap fails to absorb a considerable part of visible light and hence limit their performances in photocatalytic field. Coupling TiNT with appropriate semiconductor could improve the use of solar light and it has been considered as a most efficient way to promote the performance of TiNT [1, 2]. In this context, bismuth oxide (α-Bi_2O_3) is one of an important considered p-type semiconductor. It has drawn increasing consideration for photocatalytic applications in recent years [3, 4].

In the present work, well ordered arrays of TiNT were obtained by anodization at different voltages of Ti foil in a solution containing glycerol and NH_4F α-Bi_2O_3/TiNT was fabricated by electrodeposition process.

A detailed study has been performed to evaluate the morphology and electrochemical characteristics of α-Bi_2O_3/TiO_2 heterojunction prepared in different conditions. Photoelectrochemical characterizations and comparative investigations on the degradation efficiency of methylene blue reveal the improved photoactivity of α-Bi_2O_3/TiNT with respect to the pure TiNT.

Photocatalytic and photoactivity of the junctions was found to be strongly dependent on the geometric characteristics of TiNT.

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Development of theoretical models of bimetallic nanostructures for hydrogen electrocatalysis

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Catalytic processes ocurring in an electrochemical environment are more complex than those investigated in surface science. The chemistry of hydrogen on various surfaces and nanostructures has been explained by several authors [1], due to its fundamental and practical importance.

Accordingly, our work is focused on the design of bimetallic nanostructures as electrocatalysts for the hydrogen reaction. The structures were moldeled as Pt_n-Pd_m, being n and m interger numbers, deposited on a gold surface. We have analyzed various geometric arrangements (2D clusters, wires, etc.) and several chemical compositions (n and m), in orden to assess differences in the reactivity and selectivity thereof [Fig. 1].

In addition, we have studied the adsorption of hydrogen on these systems in different sites of high symmetry, in order to determine the stability, reactivity, adsorption process and, finally, contribute to the design of electrocatalysts.

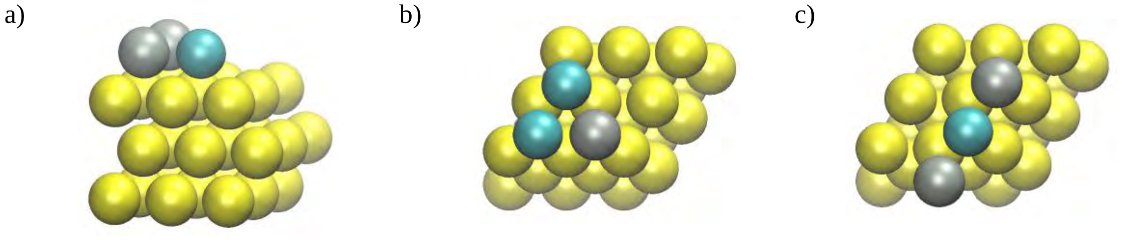

Figure 1. a) Side view of a 2D cluster Pd_2Pt. b) Top view of a 2D cluster $PdPt_2$. c) Top view of a wire Pd_2Pt.

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Design-Considerations regarding Silicon/Graphite and Tin/Graphite Composite Electrodes for Lithium-Ion Battery

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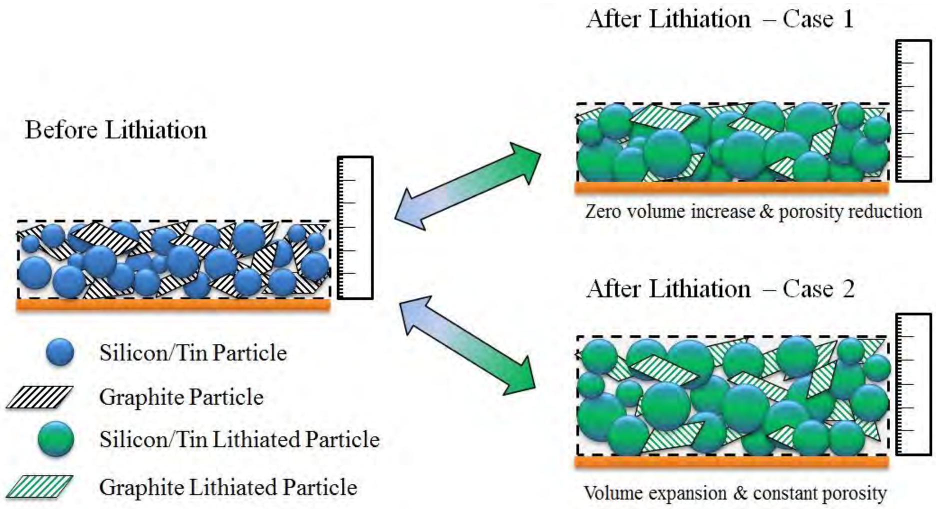

For the study and design of composite electrodes consisting of more than one active material we derive analytical equations for the calculation of specific and volumetric capacity as well as volumetric energy density. The derived equations explicitly take into account the volume changes of the active materials and thus the effect on electrode porosity and electrode dimension.

To demonstrate the applicability of the derived equations we investigate and compare silicon/graphite and tin/graphite composite electrodes as examples with practical relevance. To this end we study several cases assuming theoretical boundaries. By utilizing an expansion factor we demonstrate the dependencies of lithiated electrode porosity, volumetric capacity and expansion tolerance. Results lead to the conclusion that the functional behavior for the volumetric capacity between increasing silicon and tin content is different.

Underpotential Deposition of Sn on Defective Graphene and its Relevance as Active Material for Li-ion Batteries

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The anode of commercial Li-ion batteries is based on graphite. This carbonaceous material has a theoretical specific capacity of 372 mAh/g, and has many favorable characteristics for its use in a massive application such as low cost, easy manipulation and processing, chemical stability and a good reversibility. Nevertheless, the inherent limitations of graphite with respect to its electrical power and specific energy storage capacity are withholding further development of high technology industrial applications for Li-ion batteries. For that reason the search of new materials with well defined characteristics at the nanoscale to be used as anodes is a very active line of research.

Anodes based on Si or Sn are particularly attractive due to their high specific capacity (4200 mAh/g for Si and 998 mAh/g for Sn), low cost and natural abundance. However, for these materials the process of Li insertion corresponds to the formation of an alloy. This lithiation process is accompanied by a change of volume which can be of up to 400 %. This expansion of the material, and the corresponding contraction during the reverse process, produces irreversible damage to the material which reduces dramatically the lifespan of the electrode. Several strategies can be applied to overcome the mechanical failure of the material, such as the incorporation of nanometric clusters of Si/Sn deposited on carbonaceous materials such as graphene.

In a recent computational work of our laboratory it was shown that it is possible to decorate defective graphene layers with Si atoms at an electrochemical potential under the potential for massive deposition of Si.[1] Interestingly, it was also found that the presence of defects not only enhances the interaction of the surface with Si atoms, but it also promotes the lithiation process.

On one hand, in this work we present the results of a similar computational study of Sn clusters on a single graphene layer. A comparative study on the thermodynamics for the adsorption of Sn clusters on pristine and defective graphene layers was performed. The defects evaluated were single and double vacancies, as well as the Stone-Wales defect. The potential of adsorption from the bulk material was determined from first principle calculations. The electrochemical potential of lithiation and charge capacity for the hybrid C-Sn material was also evaluated.

On the other hand, we have also studied the effect of Sn adsorption on the adhesion of two graphene layers. A DFT + van der Waals corrections scheme was employed throughout.

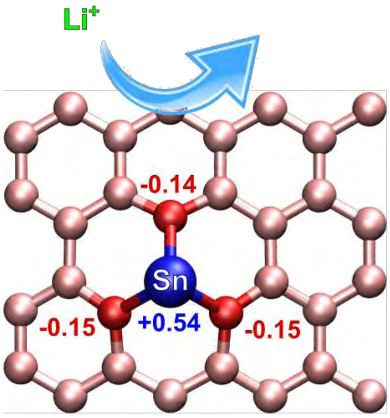

Figure 1: Illustrative representation of the system studied.

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IRRAS study of ethanol electrooxidation in alkaline media

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Direct Alcohol Fuel cells (DAFCs) are a class of Proton Exchange Membrane Fuel Cells (PEMFC) in which alcohol is used directly as fuel. Most studies DAFCs have been performed using methanol as fuel. However, the use of ethanol offers certain advantages mainly related to the fact that ethanol can be obtained from renewable sources is less toxic and it has higher energy density than methanol[1]. Pt based catalysts are the most active ones for the electrooxidation of alcohols. However, the formation of intermediate, partially oxidized, species such as CO_{ad} results in the poisoning of Pt. In order to overcome this issue, PtM where M is an oxophilic metal such as Ru or Sn promotes the oxidation of such intermediate species. Whereas this strategy is suitable to overcome catalyst poisoning during the electrooxidation of alcohols with no C-C bonds, it fails to promote the complete electro-oxidation of ethanol. This is because C-C bonds are difficult to activate at low temperatures. In order to design catalysts with improved performance towards the ethanol oxidation reaction (EOR) further characterization studies are needed to identify the nature of adsorbed species during EOR and the potential window at which such species are stable. One of the most successful approaches for this end is the use of *in operando* spectroscopies, typically IRRAS (infrared reflection absorption spectroscopy). This technique has been widely used for the study of the electrooxidation of alcohols in acid media[2]. Despite the rising interest in alkaline fuel cells due to the faster kinetics for the electrooxidation of alcohols[3], in operando studies during the electrooxidation of ethanol in alkaline electrolyte are scarce. We have studied the EOR using *in operando* IRRAS with Pt/C, PtRu/C and Pt_3Sn/C catalysts. Moreover, we have studied the reaction in both H_2O (Fig. 1) and D_2O (not shown) electrolytes in order to identify properly the intermediate species overcoming the overlapping of vibrational bands of H2O. Spectra (reported as the R/R_0 ratio) were acquired during positive sweep at $1 mVs^{-1}$.

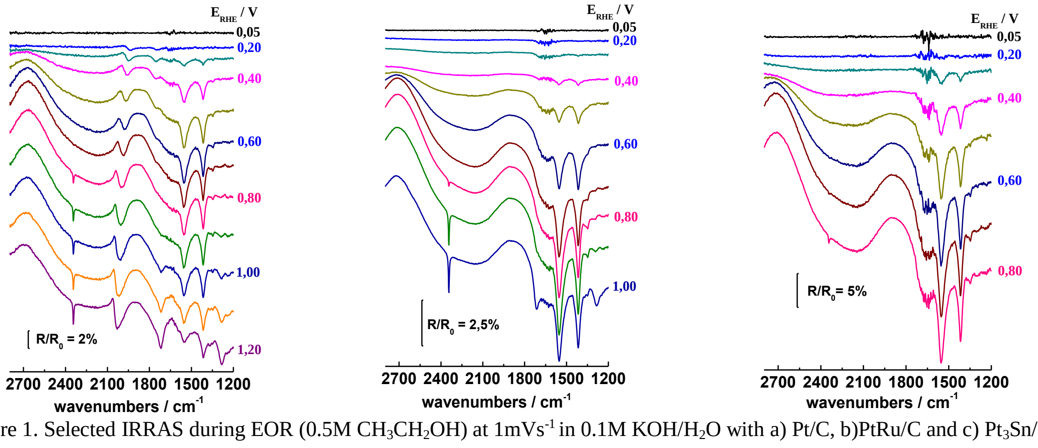

Figure 1. Selected IRRAS during EOR (0.5M CH_3CH_2OH) at $1 mVs^{-1}$ in 0.1M KOH/H_2O with a) Pt/C, b)PtRu/C and c) Pt_3Sn/C.

The spectra shown in Figure 1 demonstrate that the EOR proceeds by different pathways on each catalysts. Thus, at low potentials only Pt/C shows the formation of CO_{ad} (band at 2020 cm^{-1}) indicating the scission of the C-C bond. Acetates (bands at 1410 and 1550 cm^{-1}) are the most abundant species at high potentials. . At high potentials, other characteristic band is recognized, corresponding with ν_{CO} in carbonyl groups (band at 1715 cm^{-1}).

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Study of the Hydrogen Electrode Reaction on Iridium Electrodes Covered by a Hydrous Oxide Film.

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The iridium electrode, unlike the rest of the noble metals, has a great ability to form thick films of hydrous oxides. Moreover, the film obtained exhibits a markedly different behaviour with respect to the other noble metals. The most important characteristics are: (i) oxide layer grows with the increase of the number of applied potentiodynamic cycles, it is amorphous, its stoichiometry is undefined and it is inhomogeneous in depth. (ii) Oxide exhibits highly reversible redox behaviour, being the cathodic peak almost a mirror image of the anodic peak. (iii) Hydrous Ir oxide exhibits electrochromism, originated in the proton flow to or from the oxide layer during the oxidation/reduction process. (iv) The process of adsorption/desorption of underpotentially deposited hydrogen (H_{UPD}) still takes place although the electrode surface is completely covered by the iridium hydrous oxide, and it only disappears when the oxide film reaches significantly high thickness values. On the other hand, it is well known that the inhibition of the H_{UPD} adsorption sites is always accompanied by a decrease in the reaction rate of the hydrogen evolution, although the surface sites involved are different. All these aspects emphasize the role played by the Ir electrode pretreatment on its electrocatalytic activity towards hydrogen electrode reaction (HER). In this context, the objective of the present work is the study of the HER in acid solution on iridium electrodes covered by a hydrous oxide film, with special emphasis in the changes in the oxide structure with the variation of the film thickness.

The iridium electrodes were prepared via sputtering on a glassy carbon substrate in argon atmosphere and annealed in hydrogen atmosphere in order to have an initial surface free of oxide. The development of the oxide layer was carried out throw the application of repetitive cyclic voltammetry and the thickness of the resulting oxide layer was modified varying the time of cycling. All the electrochemical experiments were carried out in a three electrode cell, in solution 0.5 M H_2SO_4. The reference electrode was a hydrogen bubble electrode in the same solution (RHE), and the counterelectrode was a platinum wire of high area, located in a separate compartment in order to avoid contamination. The working electrode was mounted in a Teflon holder and connected to a rotating disc device. The electrodes were electrochemically characterized via cyclic voltammetry under nitrogen atmosphere. The surface morphology of the electrodes was characterized by AFM and EDS spectra were obtained for superficial composition determination. The HER was experimentally studied on the hydrous iridium oxide electrodes. The kinetic response was analysed on electrodes prepared with different oxide layer thicknesses. The results obtained show that thin hydrous oxide layers voltammetrically grown on Ir do not affect significantly the experimental current-overpotential dependence of the hydrogen electrode reaction. The same influence was found on the adsorption of the underpotentially deposited hydrogen H_{UPD}. Nevertheless, once a critical thickness is overcome, both processes are unfavourably influenced. Consequently, taking into account that the inhibition of the adsorption sites of the H_{UPD} affects the behaviour of the reaction intermediate of the hydrogen electrode reaction and therefore the reaction rate, the identification of the source of such inhibition will facilitate the understanding of the kinetics of the reaction on this type of electrodes.

As conclusion of the obtained results, it can be mentioned that: on the basis of the evaluation of the charges involved in the voltammetric peaks corresponding to H_{UPD} electroadsorption, to the couple Ir^{+3} / Ir^{+4} of the hydrous Ir oxide and that of the small anodic peak at 0.65 V, the behaviour of the hydrogen electrode reaction on this type of electrodes could be explained. It was demonstrated that the determining factor that govern the growth of the oxide film is related to the requirement of water as a source of oxygen. Depending on the film thickness, two types of Ir oxides are developed. The inner oxide, almost anhydrous, is an electronic conductor similar to IrO_2. The outer oxide layer is highly hydrated with a gel-like structure. It was found that for the preparation conditions used there is a threshold charge of 720 $\mu C\ cm^{-2}$ below which the inner layer is not formed. On these conditions the hydrogen reaction is verified on the Ir metal. On the other hand, when the oxide charge is higher than 6800 $\mu C\ cm^{-2}$, the reaction takes place on the interphase between the inner and the hydrous oxide layers. Finally, for charges ranging between those values it is verified simultaneously on both surfaces.

Effect of binder on performance of aprotic Li–O_2 cells.

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The Lithium-air cell presents a very high energy density (11428[1] Wh/kg). This value is close to the theoretical density of gasoline, making it very attractive. However, actual efficiency is much lower than the theoretical value mainly due to problems with unwanted reactions generating overpotentials because of decomposition or accumulation of insoluble species on the cathode. To date, the most widely used binder for Li batteries is polyvinylidene fluoride, PVDF. It has recently been reported that this type of binder undergoes a decomposition reaction due to superoxide ion attack generated during the discharge process[2]. These unwanted reactions strongly affect the performance of the battery. On the other hand, it has been found that other binders such as Nafion are more stable[2].

In this work, the galvanostatic response obtained from a cathode under an unstable binder such as PVDF will be studied and their performance is compared with a cathode where Nafion was used.

The cells were galvanostatically discharged by an Arbin BT-2000 battery tester at room temperature. During the tests, pure O_2 was continuously circulated at the cathode (3.0 ml min^{-1}). Li–O_2 cells were tested after 6 h of rest at open circuit potential (OCV). Long time charge/discharge tests were also carried out by potential time controlled steps between 2.25 V and 4.4 V vs. Li^+/Li at a current rate of 0.1 mA cm^{-2}. In this study, 0,5M of $LiClO_4$ /tetraglyme solution was used as electrolyte. The air cathode was prepared as a thin film over carbon paper GDL24BA based current collector. A N-methyl-2-pyrrolidone (NMP) slurry of previously prepared α-MnO_2 or Co_3O_4 was mixed with CSW as electronic conductor and poly-(vinylidenefluoride) PVDF or Nafion as binder in the weight ratio of 10:70:20 respectively, was deposited over GDL using doctor blade technique. In this work the cell is used is ECC-Air electrochemical cell (El-Cell, GmbH).

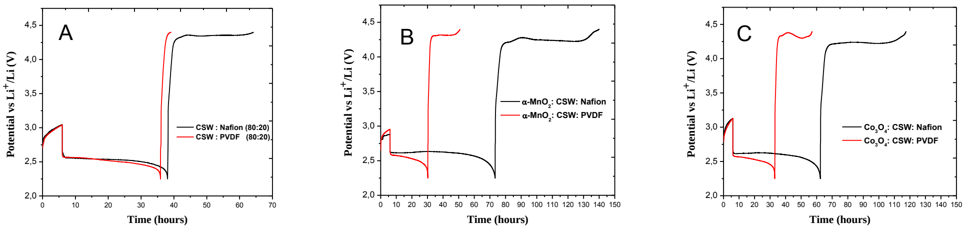

Fig. 1. Comparison of first discharge/charge profile of the cells with Nafion and PVDF as binder in cathode (A) without catalyst and in presence of catalyst (B)α-MnO_2 and (C) Co_3O_4.

Figure 1A compares the 1st complete discharge/charge profiles of the cells assembled with two binders, Nafion and PVDF without catalyst. Both cells exhibited a high discharge capacity, however the cell with PVDF was completely unable to be recharged.

In presence of catalyst (Fig1. b and c), in both cells with PVDF, the discharge is very similar and the recharge is better compared to uncatalyzed cathode but the times still are lower in comparison with cathodes with Nafion as a binder.

Finally, based on these preliminary results, it could be established that the stability of the binder plays a very important role for the performance of Li-O_2 cell.

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Hydrogen electrode reaction: a general description of the equilibrium polarization resistance

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The equilibrium polarization resistance [$R_p=\partial\eta/\partial j)_{\eta=0}$] is an experimental parameter that contains valuable kinetic information and can be evaluated directly and precisely. On metal electrodes the hydrogen electrode reaction (HER) is verified in both, alkaline and acid solutions, through the mechanism of Volmer-Heyrosky-Tafel (VHT). It shows a strong diffusion contribution of the molecular hydrogen in the anodic potential region, which turns to be negligible for cathodic overpotentials lower than -0.15 V, being significant around equilibrium potential. Moreover, R_p is widely used to evaluate the exchange current density (j_o), although it is distorted by the diffusion contribution. Previous studies [1], carried out considering Langmuir adsorption isotherm, demonstrated that the variation of R_p on the limiting difussion current density (j_L) follows the equation,

$$\left.\frac{\partial\eta}{\partial j}\right)_{\eta=0} = R_p(j_L) = R_p^o + \frac{RT}{2F}\frac{f_{aa}}{j_L} \tag{1}$$

where R_p^o is the faradaic equilibrium polarization resistance (free from any mass transfer contribution), which is related to the equilibrium reaction rate of the elementary steps v_i^e(i = V,H,T) [2],

$$R_p^o = \frac{RT}{4F^2}\left[\frac{4v_T^e + v_H^e + v_V^e}{v_T^e v_V^e + v_T^e v_H^e + v_H^e v_V^e}\right] \tag{2}$$

In this context, it is carried out the derivation of a general dependence $R_p(j_L)$, independent of the description of the adsorption process of the reaction intermediate, starting from the following equation of the relationship $j(\eta, j_L)$,

$$j = \frac{v_T^e\left[\left(\frac{1-\theta}{1-\theta^e}\right)^2 S(\theta)^{-2\lambda} - \left(\frac{\theta}{\theta^e}\right)^2 S(\theta)^{2(1-\lambda)}\right] + v_H^e\left[\left(\frac{1-\theta}{1-\theta^e}\right) S(\theta)^{-\lambda} e^{\alpha_H f\eta} - \left(\frac{\theta}{\theta^e}\right) S(\theta)^{(1-\lambda)} e^{-(1-\alpha_H) f\eta}\right]}{\left[\frac{1}{2F} + f_{aa}\frac{v_H^e}{j_L}\left(\frac{1-\theta}{1-\theta^e}\right) S(\theta)^{-\lambda} e^{\alpha_H f\eta} + f_{aa}\frac{v_T^e}{j_L}\left(\frac{1-\theta}{1-\theta^e}\right)^2 S(\theta)^{-2\lambda}\right]} \tag{3}$$

where $S(\theta)$ is a generic expression that characterizes the type of adsorption. For instance, Langmuir: $S(\theta)$ = 1, Frumkin: $S(\theta) = \exp[u(\theta-\theta^e)]$, etc.

Starting from Eq. (3) it was demonstrated that, independently of the $S(\theta)$ equation, the dependence $R_p(j_L)$ given by eqs. (1) and (2) is always valid. Consequently, the dependence of j_o previously derived [2],

$$j_o = \frac{RT}{2F}\frac{\nu_m}{R_p^o} \tag{4}$$

can be extended to any adsorption description. The mean stoichiometric number (ν_m) is given by the following expression [2],

$$\nu_m = \left[\frac{4v_T^e + v_H^e + v_V^e}{2v_T^e + v_H^e + v_V^e}\right] \tag{5}$$

Thus, eqs. (1-5) constitutes a basic tool for the correct kinetic interpretation of the hydrogen electrode reaction.

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Tetrapyrrolic Organic Polymers Cathodes for Lithium Ion Batteries

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Due to the relatively slow intercalation kinetics of Li^+ in most of the inorganic cathode materials in lithium ion batteries (LIB), these conventional cathodes exhibited low rate performance, which is one of the most important challenges for its practical applications. For the development of the next generation of green batteries, it is necessary to develop fast, high energy density and heavy metal-free cathode materials. Several studies have revealed that organic cathode materials (formed by organic molecules and polymers) are promising for (LIB) development and application, because of their high energy and power densities, fast charge-discharge cyclability, structural variety, resource renewability and environmental friendliness [1]. Additionally, the organic materials possesses advantages that are not easily available for inorganic compounds. They are potentially low-cost, because no expensive elements are involved, easily recyclable, and can be specifically designed to achieve the needed characteristic for the devices application. Also, a common procedure for inorganic intercalation compounds production such as high-temperature annealing, is not required for organics materials. These organic compound-based cathode materials for (LIB) mainly include organosulfur compounds, organic carbonyl compounds, conducting polymers, and organic free radical compounds [1]. However, the dissolution of small organic molecules in nonaqueous electrolyte will lead to the fast declining of electrochemical capacity of the organic electrode, which is one of the most problems in practical applications. In this frame, the development of synthetic routes allow the generation of organic compounds with the desired physical properties for application as building blocks of electronic devices. In this context it deserves special consideration the use of organic conducting polymers, which in general are insoluble in most solvents. It is reasonable to expect that the development of organic polymers with adequate electronic properties will introduce a significant advance in the construction and application of devices for energy storage. On the other hand, tetrapyrrolic compounds such as metal phthalocyanines were extendedly studied as electrode material for Li batteries, and iron phthalocyanine demonstrated high energy density (2300Wh kg^{-1} at a rate of 0.3 $mAcm^{-2}$ [2]).

In this work, we shows our preliminary results of the use of electrochemically synthetized tetrapyrrolic organic polymers as cathodes for (LIB). 5,15-bis[4-(*N*,*N*-diphenylamino)phenyl)]-10,20-bis[3-(*N*-ethylcarbazoyl)]porphyrin (PCBZTPA) and Zn(II) 5,15-bis[4-(*N*,*N*-diphenylamino)phenyl)]-10,20-bis[3-(*N*-ethylcarbazoyl)] porphyrin (PCBZTPA-Zn, Fig. 1). Upon oxidation, both carbazol (CBZ) and triphenylamine (TPA) moieties undergo the well-known radical cation dimerizations producing dicarbazol (DCBZ) and tetraphenylbenzidine (TPB) units, which conduct to porphyrin polymer formation (Figure 2). This conducting polymers were tested in a 3 electrodes swagelock cell using metallic lithium as counter and reference electrodes. The materials exhibited moderate charge storage and adequate cyclability exhibited moderate charge storage and adequate cyclability.

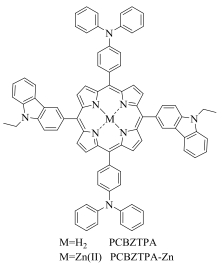

Figure 1

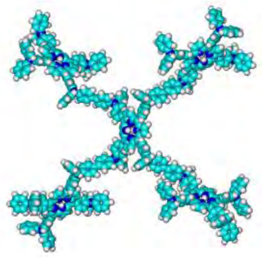

Figure 2

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Study of $BaCe_{0.8}Pr_{0.2}O_{3-\delta}$/$BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ Bilayer Proton Conductor Electrolytes

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Barium cerates and zirconates are interesting materials due to their ability for transporting protons through their crystal lattice. This feature and their stability at high temperatures makes them potential candidates as hydrogen sensors, membranes for hydrogen purification and isotopic exchange (hydrogen, deuterium, tritium -H/D/T-) and as electrolytes for proton conductor solid oxide fuel and electrolyzer cells (PC-SOFC). In previous works, we studied the $BaCe_{0.8}Pr_{0.2}O_{3-\delta}$ (BCP) [1] and $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ (BCZY) [2] oxides. We found that, whereas BCP electrical conductivity is dominated by a mixed (ionic and electronic) conductivity, especially under O_2-containing atmosphere, BCZY behaves as a pure proton conductor electrolyte. On the other hand, BCZY ionic bulk conductivity is one or two order of magnitude higher than for BCP, however its grain boundary conductivity is so low that compromises the use of this material as a proton-conductor membrane. Besides, CO_2 tolerance is also an important issue for these oxides. When they operate under low quality H_2 atmospheres, the same basicity that promotes H_2O incorporation also induces carbonate formation. In this sense, zirconates show much better stability under CO_2 containing atmospheres.

Considering this, we propose a novel approximation: the use of a bilayer electrolyte with the aim to combine the best properties of each material for its use as a complex proton conductor membrane. Therefore, a thin layer (500 nm) of BCZY was deposited by Pulsed Laser Deposition (PLD) on a dense thick BCP electrolyte. The microstructure, composition and crystal structure of the thin layer and the BCP-BCZY interface was studied by grazing angle X-ray diffraction (GA-XRD), and electron scanning (SEM) and transmission (TEM) microscopies. The transport properties were studied by electrochemical impedance spectroscopy (EIS) as a function of temperature (100 to 600 °C) and atmosphere (H_2-containing atmosphere and H_2O or D_2O wet air to analyze the isotopic effect). The EIS response of the bilayer electrolyte was analyzed by comparison with that of the BCP and BCZY single-layer membranes. The three systems (BCP, BCZY and BCP-BCZY) were evaluated in a single chamber furnace by using Pt as current collector. The i-V curves of the membranes, working under atmospheric air and H_2/Ar-mixture, were also evaluated. The EIS responses were analyzed by using an electrical equivalent circuit, where it can be confirmed that the electronic conductivity of the BCP is blocked by the thin (and almost single crystal) BCZY layer.

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Computer Simulations of Lithium Ion Storage in Graphite

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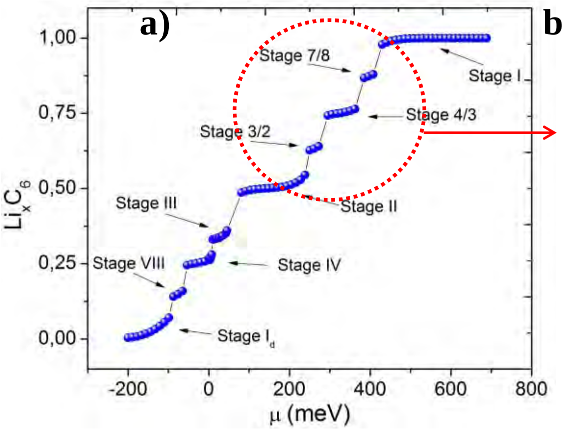
Rechargeable lithium batteries have become of primary importance due to their technological applications in portable electronic devices, and appear as the most promising alternative for transport based on sustainable electricity. Currently, the market of rechargeable batteries is primarily based on Li-ion batteries, whose production is continually increasing. However, to extend their applicability at other fields as electric vehicles, their energy and power density must be improved. In this sense, understand the processes by which Li-ion intercalation take place on graphite, the preferred material for anode in Li-ion batteries, is a fundamental topic to improve the capabilities of this type of batteries.

A typical isotherm curve of Li-ion insertion into graphite, shows different stages $\left(\mathrm{VIII} \rightarrow \mathrm{IV}, \mathrm{IV} \rightarrow \mathrm{III}, \mathrm{III} \rightarrow \mathrm{II}, \text{ and } \mathrm{II} \rightarrow \mathrm{I}\right)$ (Figure 1a). However, there are experimental evidence [1, 2] indicates the existence of intermediate stages, which are usually called "dilute phases". Its interpretation and phenomenology are not yet entirely clear. In this contribution, we show our most recent computational advances in the characterization of such stages during the Li-ion insertion into graphite . We address this theoretical characterization by using a similar parameterization for the Li-ion interactions as Reference [3]. A Grand Canonical Monte Carlo scheme is used to get thermodynamic information such as: adsorption isotherms, differential entropy and energy.



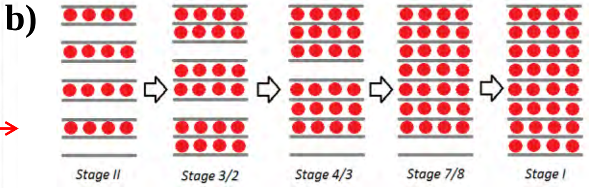


Figure 1: a) adsorption isotherms of Li in graphite (Li-concentration vs. chemical potential). b) Scheme of the intermediate states found between the transition II-I.

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Evaluation of Polybenzimidazole-c-PVBC/OH as Anion Exchange Membrane for Alkaline Conversion Systems

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Development of anion exchange membrane with desirable properties for different alkaline uses is one of the most desirable goals in the alkaline energy conversion systems. Working under alkaline conditions allows many advantages like faster electrode kinetics, lower alcohol crossover and non-noble metal electrocatalysts, compared with acid systems [1]. In this direction, an anion exchange membrane is considered a critical component, which role is transport OH^- ions, be electrical isolating and prevents the mix of the fuel and oxidant flows.

We prepare membranes of polybenzimidazole crosslinked with poly(vinylbenzil chloride) (PVBC) which are quaternized via the PVBC with 1,4-diazabicyclo (2.2.2) octane (DABCO) obtaining fixed positive quaternary ammonium groups that allow an optimal conductivity [2]. We arrange Polybenzimidazole-c-PVBC/OH membranes with compositions varying between 1:1 and 1:4 of PBI:PBVC, resulting 1:3 the membrane witch exhibits optimal conductivity (Figure 1) and mechanical properties. Chemical stability in KOH environment and conductivity were analyzed, for applying these novel membranes to both, zero gap alkaline electrolyzers and alkaline ethanol fuel cells. In this work we evaluate their performance in short-term electrolysis tests circulating 2.3M KOH solution at 50°C and compare their performance with PBI membranes.

In ethanol fuel cell, single cell polarization curves were measured at a fuel flow of EtOH 2M KOH 2M aqueous solution and an oxidant flow of pure O_2 with different backpressures. The temperature range explored was between room temperature and 90ºC and the results showed a peak power density around 70mW/cm^2 (Figure 2). We consider these results very interesting and thus further research in this type of alkaline membranes will be performed.

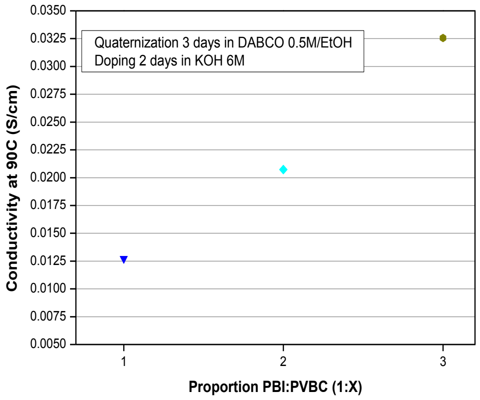

Figure 1

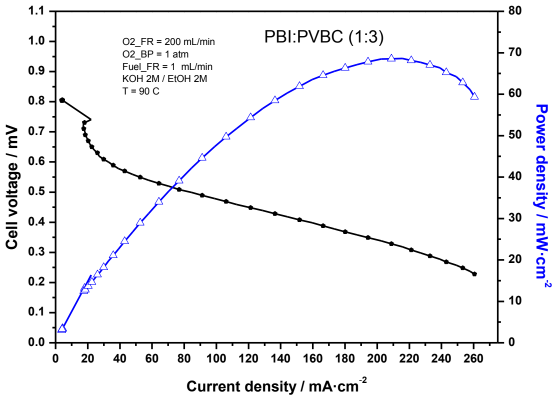

Figure 2

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Study of Fe inclusion in carbon nanotubes and its effect on oxygen adsorption

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Electronic and magnetic effects of Fe inclusion in two types of single walled carbon nanotubes (SWCNT) have been analyzed. (5,5) and (8,0) carbon nanotubes were considered, which are conductive and semiconductive, respectively. Four different Fe geometries were studied: atom, dimer, trimer and an infinite chain. The Fe atom showed a more favorable "hollow" adsorption site than in the center of the nanotube. In addition, the adsorption energy of Fe increases with the chain length, and becomes more favorable for the semiconductor nanotube. In the case of the infinite chain, a "zig-zag" arrangement allowed the minimization of the energy, keeping the Fe-Fe distance as close as possible to that of the trimer. For the case of the (5,5) SWCNT, the spin density distribution showed higher localization around the Fe atom as can be seen in Figure 1.

Finally, the oxygen adsorption on Fe-SWCNT systems was investigated. It was found that in some cases, the adsorption energy was enhanced by the Fe inclusion, and the oxygen dissociation energy was lowered, turning this system attractive for technological applications.

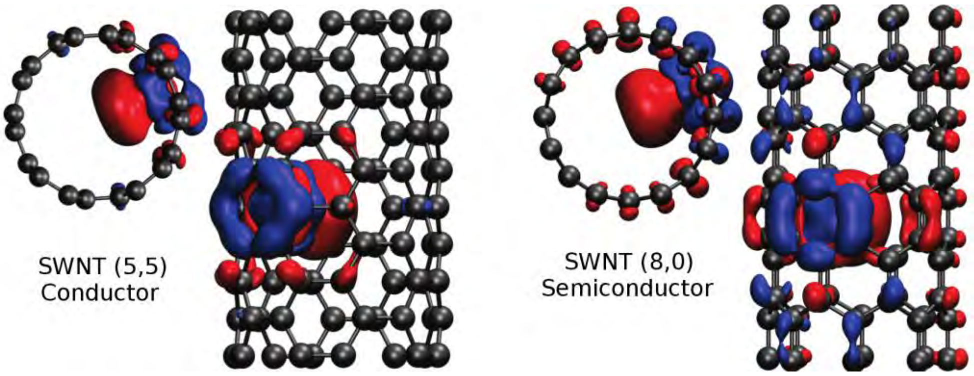

Figure 1: Difference of spin density distribution of a Fe atom in (5,5) and (8,0) SWCNT.

Oxygen reduction reaction on different materials: theoretical studies

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The constant increase in the price of oil, the dwindling in its reserves, growing energy needs as well as problems associated with environmental pollution, among many other factors, have oriented the scientific world to search alternative technologies for the generation of clean energies in order to ensure sustainable development in economic, social and environmental terms. In this sense, one of the crucial points is clarifying the fundamental and mechanistic aspects that determine the electrocatalytic activity of electrode materials used in fuel cells. This information would be essential to achieve a rational development of electrode materials leading to an improvement of the electrocatalytic activity and hence, in the operation of the device. In this framework, theoretical studies based on quantum-chemical calculations were performed to clarify energetic, geometric and electronic effects governing the electrocatalytic activity of different electrode materials for the oxygen reduction reaction (orr). Various metal surfaces as Au(100), Pt(100) and bimetallic systems were studied, and the influence of the electrolyte was analyzed. Our results show that a synergistic effect is detected in Pt-Au juntions, revealing changes in the intermediate behaviour for the orr, mainly by modifications in the electronic structure of each metal.

Identification of the main electrolyte decomposition byproduct in Na-ion batteries through FEC: towards an improvement of safety and lifetime

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Electrolyte is a crucial point for the safety and the lifetime of lithium-ion batteries (LIBs). The electrolyte decomposition must be avoided in order to guarantee LIBs development in the future. It's also the case for post-lithium systems as sodium-ion batteries (NIBs). Today, organic carbonates are the predominant electrolyte base used in the best LIBs and NIBs.

In this study, we determine and quantify the formation of the main byproduct of Na-ion system: ethylene glycol bis-(methyl carbonate) (EGMC);[6,7] utilizing liquid GC/MS (Gas Chromatography/Mass Spectrometry). EGMC resulting from the degradation of the commonly used electrolyte: 1M $NaPF_6$ in EC:DMC (1:1). The effect of an additive, fluoroethylene carbonate (FEC), on electrode passivation and electrolyte decomposition is also investigated. The rate of EGMC formation on bare sodium metal statically immersed in the electrolyte (Figure 1.a) and on cathode materials after cycling in a half-cell configuration (Figure 1.b) have been probed. A well-known positive electrode materials for Na-ion battery was chosen for the study: a fluorophosphate ($Na_3V_2(PO_4)_2F_3$). Moreover, two types of half cell designs were used and compared with different amount of FEC using galvanostatic charge-discharge and cyclic voltammetry methods.

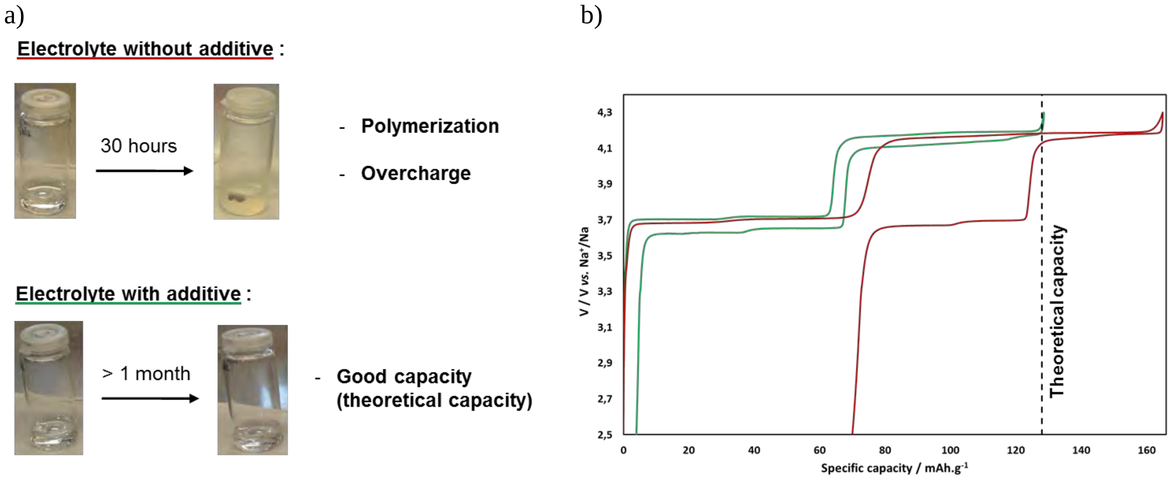

Figure 1: a) kinetics following of bare sodium metal immersed in the electrolyte with or without FEC. b) Galvanostatic curves of the first charge-discharge cycle with or without FEC in half cell system.

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Preparation and Characterization of Nanofibrillated Cellulose Separators for Lithium-Ion Batteries

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A separator is an indispensable part of the Li-ion battery design, which functions as a physical barrier for the electrode as well as an electrolyte reservoir for ionic transport. The properties of the separators directly influence the performance of the batteries. Traditional polyolefin separators employed in Li-ion cells showed low thermal stability and poor wettability toward the electrolyte. To improve either the performance or durability of Li-ion batteries, development of advanced separators is required [1]. Eco-friendly cellulose nano-fiber paper (CNP) derived separators are promising alternatives to synthetic polymer-based separators. Cellulose isolated from vegetable fibers requires intensive mechanical treatment to produce nano-fibrillated cellulose (NFC). Methods for producing NFC were first reported by Herrick [2] and Turbak [3].

In the present work, NFC was produced employing a micro-fluidization process form alfa-cellulose (Sigma C8002) and cellulose isolated form rice husk as a suspension in water (Figure 1). After 10 passes through the Microfluidizer (Microfluidics M-110P), cellulose fibrillates to a high diameter / length aspect ratio. Then, NFC suspensions (1 wt. %) were spread onto a regular surface and dried by circulating heated air in a specially designed oven.

In order to investigate the separator performance, a homemade unit cell device was employed, with stainless steel and mesoporous carbon (MC) / 5% w/w PVDF binder as current collectors and electrodes, respectively. Binder solution was prepared by dissolving PDVF pellets in N-Methyl-2-pyrrolidone (NMP). For electroactive ink preparation, MC and binder were mixed in ultrasonic bath for 30 min in a fixed proportion in which the amount of PVDF was 10% w/w of the final mixture. The ink was sprayed over a Ni foam disc, and heated over night at 110ºC to eliminate NMP solvent.

Ion conductivity performance, electrochemical stability window, discharge capacities and cycling performance of the separator were determined in the assembled cell.

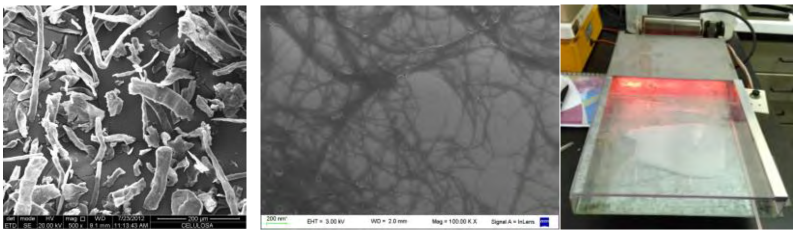

Figure 1: *Sigma C8002 Alpha-cellulose (left), fibrillated NC (middle), casted NFC suspension (right)*

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Synthesis and characterization of hybrid nickel/mesoporous TiO$_2$ catalysts for hydrogen evolution reaction.

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Hydrogen has attracted recent attention as a clean energy vector, which can be used in fuel cells, or in replace of natural gas in the so-called "hydrogen economy". Hydrogen production through water electrolysis is considered to be the cleanest production way for hydrogen economy in the near future.

In this communication, a simple and reproducible method for the synthesis of hybrid nickel/TiO$_2$ electrodes is presented. This method consists in a direct modification of a conventional nickel electrodeposition bath, making the synthesis industrially scalable. The synthesized catalyst was structural and electrochemically characterized, and compared to the conventional electrodeposited nickel. The kinetics of hydrogen evolution reaction (HER) was studied on conventional nickel Watts (Ni-Watts), a nickel/TiO$_2$ hybrid (Ni/TiO$_2$) synthesized using commercial TiO$_2$ particles and a nickel/TiO$_2$ hybrid (Ni/mTiO$_2$) synthesized using a mesoporous TiO$_2$ aerosol synthesized in our laboratory.

The catalysts were synthesized using a conventional Ni Watts electrodeposition bath prepared by dissolution of 25 g of boric acid in water at 50 ºC. 240 g of nickel sulfate and then 25 g of nickel chloride were added to the boric acid solution under constant stirring to obtain 1 L of solution. This Watts electrodeposition bath was used to synthesize a conventional electrodeposited nickel catalyst.

Part of that Ni Watts bath was separated to prepare a modified Ni/TiO$_2$ bath to electrodeposite the Ni/TiO$_2$ and Ni/mTiO$_2$ hybrid catalysts. For that, 0.2 g of the TiO$_2$ powder was added to 65 mL of the Watts bath.

The synthesis of both catalysts was carried out by electrodeposition on a commercial Ni electrode (RC S.A. 99.9 purity), with a circular area of 0.196 cm^2, which is mounted on a rotating disk electrode (RDE) support (Pine Research Inst.; Raleigh, NC). The nickel electrodes were polished with 0.05 μm alumina and cleaned with ethanol and consecutive immersion steps in KOH (1 M), and HCl (10 % w/w) solutions, during 1 minute, in order to clean the surface. Both syntheses of catalysts were carried out in a two electrodes electrochemical cell thermostatized at 50 ºC, using a massive nickel counter electrode with high area. During the process, to ensure the homogeneity of the electrodeposit, the working electrode was maintained with a rotation rate of 1600 rpm. Moreover, the working electrode rotation facilitates the species in the solution (both, Ni ions and TiO$_2$ particles) reach the surface of the electrode.

The electrodes were electrochemically characterized in 1 M KOH by cyclic voltammetry (between 0.1 and -1.5 V vs. SCE), 4 hs chronoamperometry at -1.5 V (vs SCE) and EIS at different potentials.

Changes in the catalytic activity and the formation of superficial nickel hydrides were observed. The Ni/TiO$_2$ catalyst presents a higher catalytic activity towards HER and the presence of TiO$_2$ in the Ni matrix inhibits the nickel hidruration.

It can be seen that the presence of TiO$_2$ in the catalyst matrix significantly increases the catalytic activity of nickel, which is increased even more in the case of the mesoporous TiO$_2$ particles. This may be due to a synergistic electronic effect, and an increase in the electrochemically accessible surface area of the nickel electrode.

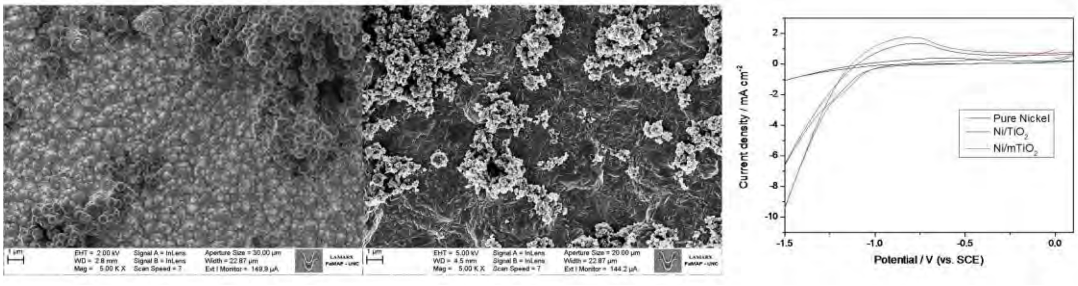

Figure 1: (left) SEM micrographs of Ni/mTiO$_2$ hybrid catalyst, (center) SEM micrographs of Ni/TiO$_2$ hybrid catalyst, (right) comparison of cyclic voltammograms of pure nickel, Ni/TiO$_2$ and Ni/mTiO$_2$.

Synthesis and properties of a hybrid nickel/nitrogenated-GO for hydrogen evolution reaction.

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Hydrogen is considered one of the most promising alternatives as an energy vector for the future. New methods for hydrogen production that do not generate greenhouse gases emission are of great interest, being the water electrolysis in alkaline medium, one of the most interesting. Since the hydrogen evolution reaction (HER) is an heterogeneous reaction, the electronic state of the electrode surface plays a dominant role in determining the reaction kinetics.

Graphene oxide (GO) can be nitrogenated for different chemical methods that have been proposed in the last years [1]. The obtained product (NGO) is a promising material for heterogeneous catalysis, particularly when the flakes are included in the nickel matrix.

In this communication, hybrid nickel/nitrogenated-GO catalysts were synthesized via direct electrodeposition employing a modified nickel Watts bath. The synthesized catalyst was structural and electrochemically characterized, and compared to the conventionally electrodeposited nickel electrode.

The catalytic activity for HER in alkaline solutions of modified nickel electrodes is analyzed using a rotating disk electrode. The catalysts were synthesized using a conventional Ni Watts bath prepared by dissolution of 25 g of boric acid in water at 50 ºC. 240 g of nickel sulfate and then 25 g of nickel chloride were added to the boric acid solution under constant stirring to obtain 1 L of solution. This electrodeposition bath was used to obtain a conventional electrodeposited nickel catalyst on steel samples. Part of that Ni Watts bath was separated to prepare the modified Ni/Graphene bath in order to obtain the electrodeposited Ni-NGO hybrid catalyst. For that, a 0.08 g/L NGO aqueous dispersion was sonicated during 30 minutes in order to disperse the NGO flakes. Then, an aliquot of 10 mL of the NGO dispersion was added to 40 mL of the Watts bath.

The catalysts obtained with the different electrodeposition baths have very different optical properties. While the Ni-Watts electrode is dull gray, the Ni-NGO electrode is black, suggesting the presence of NGO reduced in the matrix of the catalyst, which is homogeneously distributed.

The Raman scattering spectra from the Ni-Watts electrode don't show signals, indicating that nickel is in a metallic state and there is no evidence of nickel hydrides. However, bands at 3581 and 3660 cm^{-1} indicate the nickel hydrides presence in the composite catalyts [2]. Furthermore, the Ni-NGO electrode spectra show the NGO characteristic bands, evidencing the intercalation of graphene in the structure of the nickel electrodeposits.

The catalysts were electrochemically characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). The comparison of cyclic voltammograms without electrode rotation shows that Ni-Watts catalysts have the same values of HER onset potential (OP) and current density (at -1.5 V vs. SCE), before and after chronoamperometric ageing in alkaline solutions. On the other hand, the Ni-NGO catalysts after ageing maintain the OP values (100 mV lower than that observed with electrodeposited Ni-Watts), but there is a diminution of the current density.

It was demonstrated that GO is electrochemically reduced during the catalyst synthesis, increasing the conductivity of flakes. As a consequence, the charge transfer resistance corresponding to pure nickel electrodeposits can be significantly decreased.

It can be seen that both catalysts behave differently in terms of variations of the (dj/dV) slopes when they are characterized by CV (without electrode rotation), and linear sweep voltammetry (at 1600 rpm). These results are due to the catalysts show different dependencies on the diffusional control, indicating that the Ni-NGO catalyst possibly has better performance on systems of flow electrolyzers.

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Design of metal complexes containing thiophene units toward metallopolymers.

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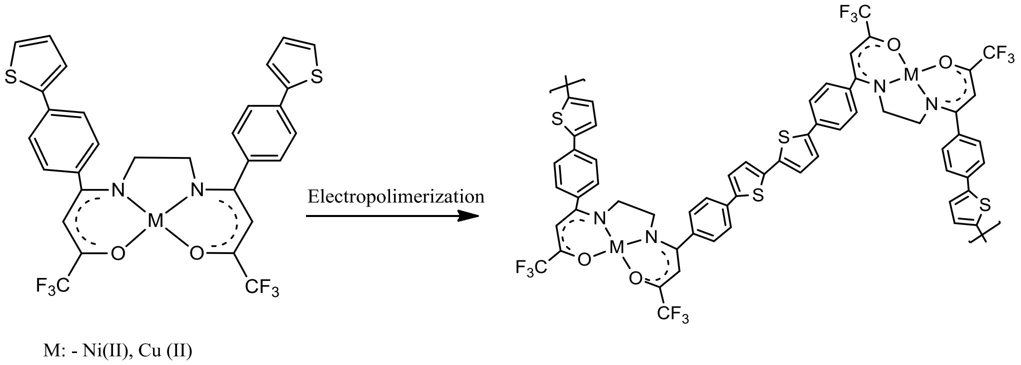
Over the last decade, conducting metallopolymers (CMP) have attracted growing interest and considerable efforts have been directed toward their molecular engineering, because they offer potential applications in the field of emerging technologies.[1,2] This kind of materials offer important opportunities to combine the features of organic polymers, with their abilities to become electric conductors via chemical or electrochemical doping, with magnetic, optical, redox or catalytic properties arising from the presence of transition metals.[3] In this respect, we present here the synthesis, spectroscopic and structural characterization of a new Schiff base ligand and the corresponding square-planar complexes containing appended thiophene moieties (see figure below). The modified electrodes were fabricated through the electropolymerization of the monomers in a 0.1 M of tetrabutylammonium hexafluorophosphate in anhydrous CH_2Cl_2 solution, in the potential range of –1.5 V to 2.5 V vs Fc/Fc^+ couple. The thin film modified electrode response were studied employing 0.1 M of tetrabutylammonium hexafluorophosphate solution in CH_2Cl_2.



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Impregnation strategy to improve Solid Oxide Cells (SOC) cathode materials: Gadolinium doped Ceria on La-Sr cobalt-ferrite

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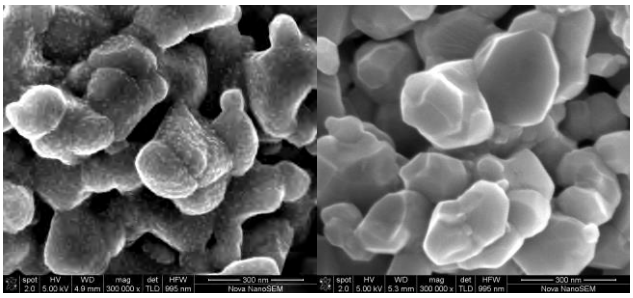
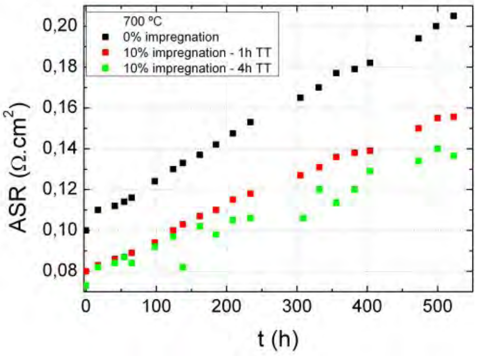
Solid Oxide Cells (SOC's) are ceramic devices which transform chemical energy into electrical energy (in SOFC mode) or viceversa (in SOEC mode) without running out of fuel, as long as fuel or electrical energy is provided. Several fuels can be used in SOFC mode to produce electrical energy, among them methane and hydrogen. In SOEC mode, fuels of high purity can be produced (such as H_2) by means of providing electrical energy. The cells efficiency is mainly limited by the electrochemical processes activation energies, ionic transport, diffusion, microstructure, etc. In the last few years effort has been made towards achieving a lower operation temperature, in the range of 600 ºC to 800 ºC (IT-SOFC), which is why reducing the cells area specific resistance (ASR) at that temperatures is a necessary step. As one of the limiting factor is the cathode overpotentials associated to O2-reduction reaction, different strategies have been essayed with the aim to reduce the ASR. Mixed ionic and electronic conductors, nanostructured materials, composites or surface modified electrodes were some of the strategies employed.

In this work, the surface modification by nanoparticles impregnations was applied. $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) ceramic cathodes impregnated with $Ce_{0.8}Gd_{0.2}O_{3-\delta}$ (GDC) nanoparticles were characterized with electronic scanning (SEM) and transmission (TEM) microscopy. The electrochemical response as a function of temperature, oxygen partial pressure and time was evaluated by electrochemical impedance spectroscopy (EIS). We obtained reproducible and homogeneous impregnations, which generate a better electrochemical performance of the cathodes.



LSCF impregnated with 10% GDC before and after 500 h at 700 ºC.



ASR measurements vs time for a non impregnated cell (black) and for two10% impregnated cells (red and green)

Evaluation and Characterization of Bipolar Plates Printed by 3D Technology for a Fuel Cell

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Fuel cells are devices that allow generate electricity from the chemical energy contained in fuels such as, hydrogen,, methanol or ethanol, among others. Because of their high efficiency, the devices are attractive for three main applications: automotive, stationary, and portable power.

One of the disadvantages for fuel cells mass marketing is the high cost of their components, for example precious metal catalysts, graphite of high purity, membranes of high ionic conductivity, etc.

3D printing has become a very popular tool for the general public as well as for the industry. This technology makes possible to create prototypes and final products in a fast and cheap way.

At present there exists a particular interest in using the 3D printing to produce several components of the fuel cells .

This work deals with the production and operation of gas flow plates (traditionally composed of high purity graphite) built with 3D printing technology. The pieces have been made from different plastic materials (ABS and PLA) which become conductive by the deposit of thin silver layers. The bipolar plates are characterized under the same conditions they will be employed in a fuel cell. Parameters such as mechanical resistance, chemical resistance and electrical conductivity are measured. This approach will allow us to perform and evaluate many experimental fuel cell prototypes in a rapid and cheap mode.

Degradation of Oxygen Reduction Reaction Kinetics at $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ Cathodes Aged at Different Temperatures

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Solid Oxide Fuel Cells (SOFCs) are highly efficient electrochemical devices which convert a wide range of fuels (i.e. hydrogen, methane, carbon monoxide) into electrical energy and heat. This characteristic makes them an extremely attractive solution for the transition period between fossil fuels and hydrogen. Nevertheless, the commercialization of SOFCs is still hindered by their cost and long term degradation. SOFC efficiency and durability is mainly determined by the area specific resistance (ASR) and degradation of the cathode, the electrolyte and the anode. Since the cathode is typically the component with the highest ASR, it is very important to limit its degradation.

This work aims at studying the degradation of the oxygen reduction reaction (ORR) kinetics at $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ (LSCFO) cathodes induced by aging at different temperatures (i.e. 600, 700 and 800 ºC) in air for 50 h. LSCFO oxide powders were prepared by solid state reaction and deposited on $Ce_{1-x}Gd_xO_{2-d}$ electrolytes by spin coating. The studied cathodes have an intermediate microstructure between that of a dense pellet and that of a porous film since they are indeed porous but are mainly composed of particles within the micrometric range (as the dense pellets). This particular microstructure was chosen because our preliminary results [1,2] suggest that it facilitates, under the aging conditions mentioned above, the occurrence of one of the most reported degradation mechanisms of LSCFO cathodes: surface Sr-enrichment. The evolution of the cathode electrochemical properties was continuously monitored by Electrochemical Impedance Spectroscopy (EIS) during the aging treatment while the microstructural changes were characterized by Scanning Electron Microscopy (SEM) before and after the aging treatment. Our EIS analysis, based on the Adler-Lane-Steele model [3], allowed us to analyze separately the evolution of the oxygen ion diffusion and the oxygen surface exchange contributions during the aging treatment without requiring the knowledge of thermodynamic, surface kinetics, transport and microstructural parameters as usual for the ALS model. In addition, the origin of the ORR kinetics degradation and its dependence on the aging temperature were identified.

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Structural Characterization and Theoretical Modelling of LiFe$_{1-x}$Co$_x$PO$_4$ cathodes for Li-ion Batteries

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There is a growing interest in moving towards the generation of clean and renewable energies. This work focuses on the characterization and electrochemical performance of LiFePO$_4$ cathodes, which has crystalline phase "olivine" or "heterosite" with space group Pnma (a= 6.00 Å, b= 10.33 Å and c= 4.69 Å). This series of materials has the advantage of it low cost and the security that it can offer [2]. The nanostructure of this series of materials is of great importance in order to improve the performance due to the enhancement of electric and the Li-ion conduction. The present work will show the synthesis and characterization of LiFePO$_4$, doped with Cobalt, and coated with polyaniline (PANI), obtained by gel/precursor method [3]. For the structural characterization we will present results from conventional X-ray Powder Diffraction, Small Angle X-ray Scattering, Confocal Raman Microscopy, Atomic Force Microscopy, Transmission Electron Microscopy. This complete set of tools will demonstrate the nanometric character of PANI-coated LiFe$_{1-x}$Co$_x$PO$_4$ nanoparticles. In addition, electrochemical characterization we will presented for the series.

Finally, we will present theoretical Density Functional Theory Calculations [4,5], for the simulation of the Li-ion diffusion, and activation energies, in bulk LiFe$_{1-x}$Co$_x$PO$_4$ and LiFe$_{1-x}$Co$_x$PO$_4$/graphite structure. These models will help in understanding of the role of Co doping in this series of composites.

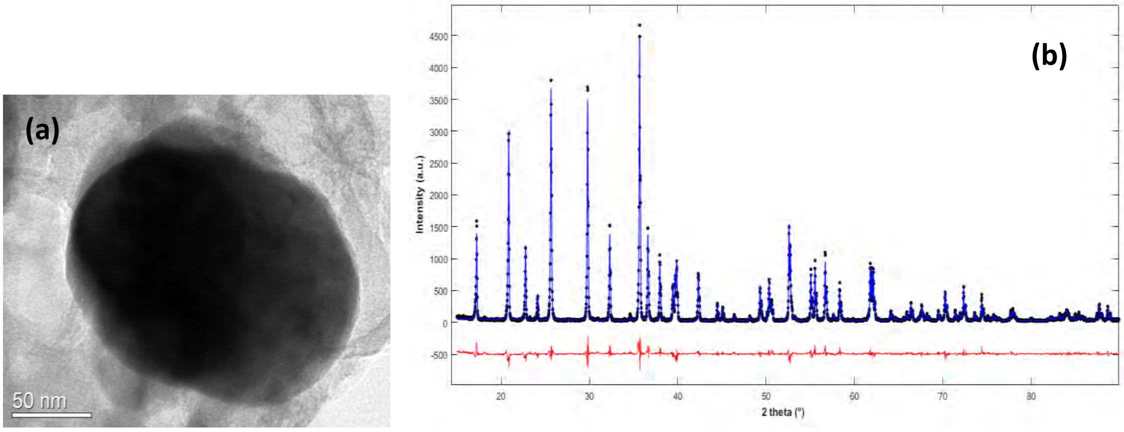

Figure 1. **(a)** TEM image **(b)** Rietveld Profile Fitting for X-ray Powder Diffraction.

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Electrochemical impedance spectroscopy for a IT-SOFC cathode. Experiments and modelling.

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In this work, we characterize the electrochemical behaviour of commercial cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) in the symmetric cell configuration, [cathode/electrolyte/cathode] by electrochemical impedance spectroscopy (EIS). The materials are tested in oxygen containing atmospheres, both concentrated and diluted ones. This study consists of two parts: an experimental stage and a simulation counterpart. In the latter, a model is presented and numerically solved. The advantage of comparing results with a model is that all parameters fitted have a physical meaning.

The overall cathodic reaction is $O_2 + 4e^- \leftrightarrow 2O^{2-}$. While the oxygen ion comes from the SDC (electrolyte), O_2 comes from the gas phase and transforms over the perovskite type cathode material into oxygen ions.

The present model assumes the following steps: 1) O_2 is dissociated into O atoms; 2) atomic O diffuses either across the volume or the surface of the crystallite, through a finite length; 3) atomic O reduces by capturing two electrons from the Ni; 4) the O^{2-} migrates through the diffuse layer which separates the reaction zone from the electrolyte bulk. It is further assumed that at the diffuse layer, chemical and electric forces on the O^{2-} are equilibrated, thus yielding the Boltzmann distribution.

For the reaction, a Butler-Volmer kinetics is employed [1,2], considering two electronic jumps (which is strictly forbidden by Pauli's exclusion principle) in the reaction $O + 2e^- \leftrightarrow O^{2-}$

$$i = i_0 \left\{ \frac{c_O}{c_O^*} e^{-nf\alpha\left(\Delta\phi_{cc} - \Delta\phi_{cc}^{eq}\right)} - e^{f\left[(1-\alpha)n\left(\Delta\phi_{cc} - \Delta\phi_{cc}^{eq}\right) - z\left(\Delta\phi_{cd} - \Delta\phi_{cd}^{eq}\right)\right]} \right\}$$

where $n = 2$, $z = -2$ and $f = F/RT$. The model considers that the electric potential active to the reaction is that of the compact layer, $\Delta\phi_{cc}$ [3]. The drop at the diffuse layer is $\Delta\phi_{cd}$ [1,2]. Superscript *eq* stands for equilibrium conditions at $c_O = c_O^*$ and $c_{O^{2-}} = c_{O^{2-}}^*$, the values at each bulk conditions. The graphical situation is sketched in Figure 1, and a typical response of this system is depicted in Figure 2.

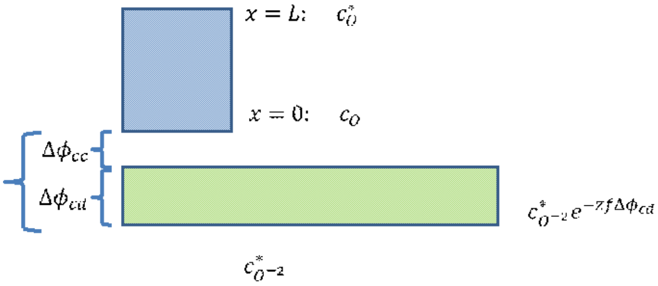

Figure 1

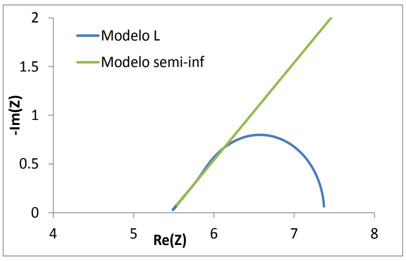

Figure 2

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Design and optimization of in-situ cell for lithium ion batteries X-ray absorption studies.

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The entire comprehension of the processes that occurs during the battery use is indispensable to improve the performance and efficiency of these devices. But some times, these physicochemical processes can not be detected by electrochemical measurements, and in the case of lithium ion batteries, the possibility to make electrochemical experiments in a typical tree electrodes open cells joined to other chemical or physical techniques is quite impossible. Typical impediments to this type of experiment are, for example,, the nature of the electrodes, electrolytes and working conditions of these type of batteries. For this reason we are developing an in-situ lithium ion battery cell system capable to work in typical current/potentials for these kinds of batteries and at the same time allow performing X-Ray absorption experiments.

In the first version of the developed system it is now possible to characterize different anodic and cathodic active materials by X-ray spectroscopy techniques like XANES and EXAF at different working conditions i.e. different states of charge (SOC) or during a potentiodynamic running. Our setup also allow to use the same battery setup in biggest facility like a synchrotron beamline dedicated not only to XAFS but also to other types of techniques (XRD, XRF, etc) working at faster potentiodynamic experiments or higher current conditions.

In this work we present a preliminary study using the in-situ system working in a Rigaku X-ray Absorption equipment (Looper) installed in our institute with different cathodic active materials at different conditions. Figure 1(a) shows a picture of the in-situ cell ensemble (inside of the adapter) ready to work in the X-ray spectrometer and (b) charge-discharge potential profile of the cell. XANES spectra using the cell at different states of charge are shown in the Figure 2 and these states are marked in the discharge curve of the cell working with a homemade $LiMn_2O_4$ cathode.

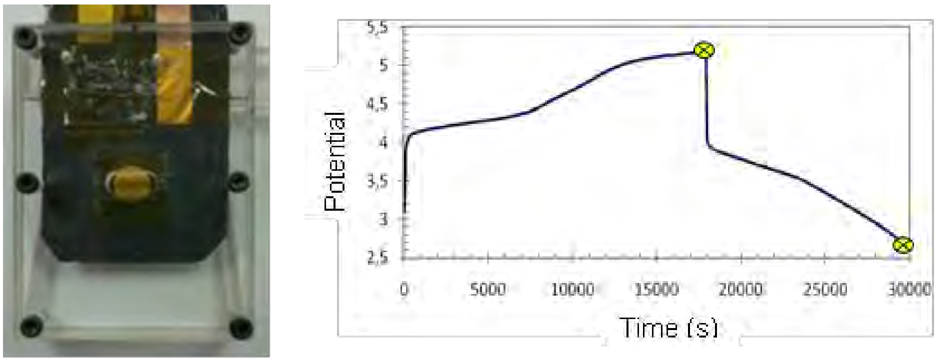

Figure 1.(a) In-situ cell ensemble SOC and (b) charge-discharge potential profile marked at studied SOC.

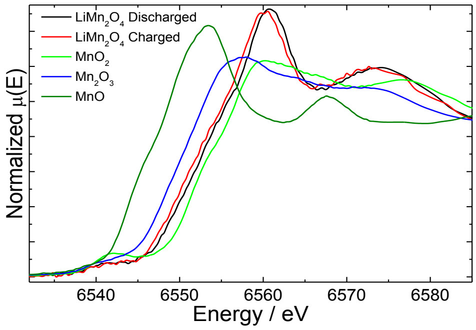

Figure 2. XANES spectra of $LiMn_2O_4$ at different SOC.

Organic-inorganic hybrid multilayered photo-electrochemical cells

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The production of hydrogen from water *via* solar energy conversion has attracted immense attention as a potential solution for addressing energy supply issues. We demonstrated a highly stable and efficient organic-inorganic hybrid photoelectrochemical (H-PEC) cell. Modifying the surface energy and structure of the organic photoactive layer using multi-functional nanomaterials including –OH-modified NiO nanoparticles and reduced graphene oxide (RGO) led to a 2.8-fold enhancement of the water splitting performance in a single junction H-PEC cell. The enhanced performance was attributed to the i) improved water-wettability, ii) enhanced charge extraction property by band-edge alignment, and iii) the catalytic effect of the introduced NiO-OH nanoparticles. In addition, because of the effects of the RGO layer preventing water penetration and photo-corrosion during the oxidation of water, a distinguishable long-term stability was achieved from the H-PEC cell with an RGO capping layer. The best performance was obtained from the organic-inorganic hybrid multi-junction PEC cells consisting of the WO_3 photo-anode (activated under UV irradiation) and the H-PEC cell (activated under visible light irradiation). The H-PEC cell with a WO_3 photo-anode exhibited significantly enhanced stability and performance by a factor of 11.6 higher than photocurrent of the single H-PEC cell

$ZrCr_{1-x}NiMo_x$: Microsegregated Phases Study

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It was demonstrated that the electrocatalytic performance of Zr-based alloys are based on the presence of Zr_8Ni_{21}, Zr_7Ni_{10}, Zr_9Ni_{11} and ZrNi as secondary phases [1-3]. The term “synergetic effect” employed by Nei *et al.* [4] is used to describe the discharge capacity enhancements or high-rate dischargeability (HRD) positively contributing to the overall performance of the AB_2 phase in the presence of Zr_xNi_y. Understanding these secondary phases behavior is crucial for future improvement of AB_2MH alloys. We observed in a previous work that partial replacement of chromium by molybdenum (in the studied amounts) promotes the segregation of Zr_xNi_y phase and new Laves phases such as $ZrMo_2$ and $ZrCr_2$ [5]. The present study is focused on the microsegregated phases after molybdenum incorporation and its effect on electrocatalytic performance. We will try to discriminate the effects of Mo and secondary phases on the performance of AB_2 alloys. We synthesized three alloys replacing chromium by molybdenum ($ZrCr_{1-x}NiMo_x$): AB_2M0 (Mo 0% w/w), AB_2M1 (Mo 13 % w/w) and AB_2M2 (Mo 25% w/w). The electrodes were characterized by X-ray diffraction at the National Synchrotron Light Laboratory (LNLS) in Campinas. Rietveld refinement was used to characterize the structure of the observed phases. From this results, Zr_7Ni_{10}, Zr_9Ni_{11} secondary phases as well as $ZrCr_2$ and $ZrMo_2$ alloys were prepared. We conducted all the electrochemical experiments using a PGZ 301 Voltalab® potentiostat-galvanostat device. We performed charge/discharge curves, self discharge experiments and linear sweep voltammetry was conducted on each surface for SOC 100% starting from E_{OCP} in order to calculate Tafel slope for hydrogen evolution reaction (HER) which is the first step in hydriding mechanism. As far as secondary phases are concerned, Zr_7Ni_{10} has the largest capacity. However, its activation takes approximately 50 cycles. On the other hand, $ZrMo_2$ phase activates at the first cycle and later decrease as a result of KOH reactivity. $ZrCr_2$ depicts almost zero discharge capacity because this phase has very low equilibrium pressure and thus a very high equilibrium potential. Therefore it could not reach hydrogenation and will not be totally dehydrided after experimental conditions. For the first 40 hours, the capacity degradation for AB2M0 is faster than AB2M1 and AB2M2 ones. In this period, the capacity decay of non molybdenum containing alloy is averagely three times faster than AB2M1 and AB2M2 ones. The capacity drop becomes very slow after 130 hours. Molybdenum containing alloys depicted similar decay profiles and nearly the same capacity retention after 160 hours. It is worthwhile noticing that the capacity decay profiles for both secondary phases are similar. After 80 hs capacity retention is nearly 70 %. The presence of molybdenum produces a positive effect for hydriding processes (see table 1) and self discharge behaviour. There is a trade-off in the amounts of secondary phase and Laves phases in order to improve the kinetic and thermodynamic performance. From polarization curves we conclude that secondary phases change *rds* mechanism for HER and improve its kinetic. AB2M1 depicts the better behaviour for HER and hydriding mechanism.

Table 1- Discharge capacity for 1, 3, 10, 30, 50 cycles for studied alloys

	C_{dis}(1)	C_{dis} (3)	C_{dis} (10)	C_{dis} (30)	C_{dis} (50)
$ZrCr_2$	3	7	8	7	7
$ZrMo_2$	245	35	X	X	X
Zr_9Ni_{11}	4	7	32	80	118
Zr_7Ni_{10}	3	6	36	111	157
AB_2M0	2	31	120	181	214
AB_2M1	4	50	221	270	282
AB_2M2	11	40	82	183	177

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Titanium effect in electrochemical hydrogen storage in $Zr_{1-x}Ti_xCr_{0.7}NiMo_{0.3}$ alloy.

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The partial replacement of zirconium by titanium was studied for AB_2-type alloys, which are commonly used as the negative electrode in Ni-MH batteries. We observed in a previous work that partial replacement of chromium by molybdenum depicts a positive effects in the behaviour of NiMH batteries, improving hydride reaction performance [1]. Three different alloys were studied: $Zr_{0.5}Ti_{0.5}Cr_{0.7}NiMo_{0.3}$, $Zr_{0.3}Ti_{0.7}Cr_{0.7}NiMo_{0.3}$ and $Zr_{0.7}Ti_{0.3}Cr_{0.7}NiMo_{0.3}$. They were synthesized by arc melting method, under high purity argon. As well as electrochemical testing, the surface alloy microstructures were examined, both after and before activation, by means of a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) microanalysis. Characterization by X-ray powder diffraction was also performed for each alloy. The electrochemical characterization was performed by cyclic voltammetry, charge/discharge cycling, studying the discharge capacity, the activation (number of charge-discharge cycles needed to reach the maximum capacity) and reversibility of the charge-discharge process, based on the difference between the potential at the end of the charge and the middle of the discharge. Besides we study the electrochemical performance at different current discharges, specially taking into account high rate discharges. DRX characterization evidenced the presence of Laves phases and secondary phases Zr_7Ni_{10} and Zr_9Ni_{11} as well as TiNi. From these results we synthesized and electrochemical characterized TiNi alloy which depicted the highest discharge capacity at the fourth cycle. The presence of titanium in the alloy improves activation although the alloy with slower Ti concentration studied depicts the highest discharge capacities. This fact could be associated with its highest Laves phases/secondary phases ratio. On the other hand, the increase of titanium in the formula brings slower over potentials during charge-discharge cycles. We can conclude that Ti has a positive effect in activation processes and kinetic behaviour. Microstructural further investigation is needed in order to elucidate the effect of Ti in microsegregation of secondary phases and its effect on thermodynamic and kinetic performance.

	C_{dis} (mAh/g)	ΔE (V)	A_C
$Zr_{0.7}Ti_{0.3}Cr_{0.7}NiMo_{0.3}$	213.4	-0.175	40
$Zr_{0.5}Ti_{0.5}Cr_{0.7}NiMo_{0.3}$	171.6	-0.137	24
$Zr_{0.3}Ti_{0.7}Cr_{0.7}NiMo_{0.3}$	183.2	-0.111	7
TiNi	106.3	- 0.197	4
Zr_7Ni_{10}	159.9	-0.213	52
Zr_9Ni_{11}	129.3	-0.206	54

Table 1. Experimental measurements. C_{dis} is the discharge capacity and A_c activation cycle number

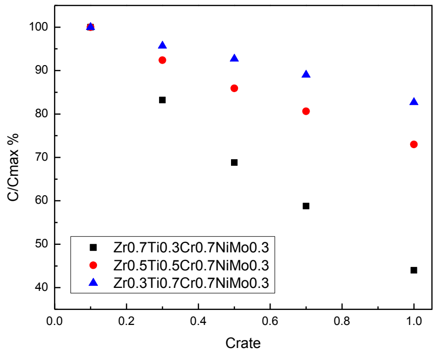

Figure 2. High rate discharge (HRD) curves expressed as a percentage of maximum capacity.

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Electrochemical and gaseous hydrogen storage in $LaNi_{5-x-y-z}Al_xCo_yMo_z$.

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MH alloy can absorb hydrogen in two different environments: through an electrochemical charging process in alkaline solution or gaseous absorption in a dry container. Since the electrochemical environment is more complicated for hydrogen absorption compared to the gaseous phase, the pressure-concentration-temperature (PCT) measurement is commonly used to study the thermodynamics of gaseous phase hydrogen absorption of an MH alloy [1]. The information obtained from PCT (hydrogen storage capacity, hysteresis and heat of hydride formation) are all essential for the design of MH alloys used for gaseous hydrogen storage and electrochemical applications. Current investigations about hydrogen storage alloys used in NiMH batteries are focused on improving the composition of the material, in order to obtain a higher discharge capacity, a fast activation, great high rate discharge and cycling resistance.The partial replacement of nickel by aluminum, molybdenum and cobalt was studied for AB_5-type alloys, which are commonly used as the negative electrode in NiMH batteries. Six different alloys were studied: $LaNi_5$, $LaNi_{4,7}Al_{0,3}$, $LaNi_{4,7}Co_{0,3}$, $LaNi_{4,7}Mo_{0,3}$, $LaNi_{4,4}Al_{0,3}Co_{0,3}$ and $LaNi_{4,1}Al_{0,3}Co_{0,3}Mo_{0,3}$. They were synthesized by arc melting method, under high purity argon. As well as electrochemical testing, the surface alloy microstructures were examined, both after and before activation, by means of a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) microanalysis. Characterization by X-ray powder diffraction was also performed for each alloy. The electrochemical characterization was performed by using charge/discharge curves. In order to study thermodynamical (ΔH and ΔS) parameters, PCT curves were carried out in a Sievert's type equipment at 25°C, 45°C and 60°C. Substitution of Ni by Al improves the thermodynamic performance, giving a higher discharge capacity. Meanwhile, the presence of Co helps with the cycling resistance, providing a longer lifetime for the alloy. A lower over potential during the charge-discharge process is obtained with the substitution by Co and Mo. In the three situations, the activation process was not affected, and a fast activation was obtained, reaching the highest capacities during the first cycles. In gaseosus absorption, the highest absorption capacity was found for $LaNi_5$ alloy, whereas the partial substitution of Ni only affects equilibrium pressure and the alloy's thermodynamical parameters.

	C_{dis} (mAh/g)	% C_{lc}/ C_{max}	ΔE (V)	A_C
$LaNi_5$	221.4	38.1%	-0.091	1
$LaNi_{4,7}Mo_{0,3}$	175.6	58.8%	-0.043	1
$LaNi_{4,7}Al_{0,3}$	188.9	75.2%	-0.071	1
$LaNi_{4,4}Al_{0,3}Mo_{0,3}$	260.9	73.1%	-0.052	3
$LaNi_{4,7}Co_{0,3}$	84.9	48.8%	-0.032	1
$LaNi_{4,1}Al_{0,3}Co_{0,3}Mo_{0,3}$	274.2	84.0%	-0.044	3

Table 1. Experimental measurements. C_{dis} is the discharge capacity and A_c activation cycle number

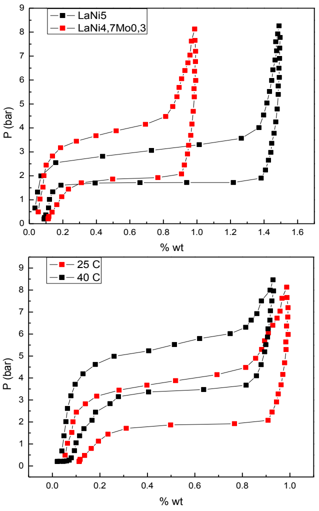

Figure 1. a) *PCT* curves for two different AB_5 alloys at 25 °C
b) *PCT* curves for $LaNi_{4,7}Mo_{0,3}$ at two different temperatures

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Density Functional Theory Study of Structural and Electronic Properties of Hydrogenated $ZrCr_2$ and $ZrMo_2$ Phases

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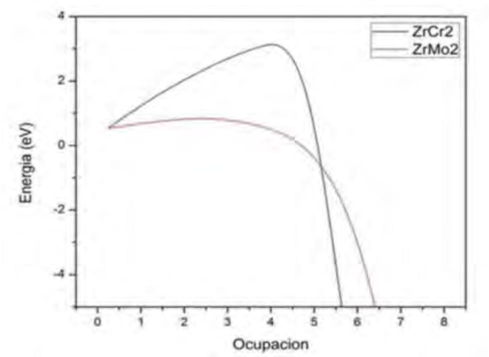
AB_2 alloys employed as the negative electrode in these batteries are multi-element and multi-phase materials.We had previously demonstrated that the electrocatalytic performance of $ZrCr_{1-x}NiMo_x$ alloys are strongly dependant on structural microsegregated phases [1]. X-ray diffraction characterization at the National Synchrotron Light Laboratory (LNLS) in Campinas revealed the existence of $ZrCr_2$ and $ZrMo_2$ as Laves phases in molybdenum containing alloys. Density Functional Theory (DFT) calculations [2,3] were performed for the study of structural and electronic properties of hydrogenated $ZrCr_2$ and $ZrMo_2$ phases employing the projector-augmented wave (PAW) method [4,5] as implemented in the Vienna ab initio simulation package VASP [6]. An energy cutoff of 500 eV was used to expand the Kohn-Sham orbitals into plane wave basis sets. In addition, the semicore states of Cr, Mo and Zr have been explicitly treated as valence states throughout this work. In all of the calculations reported here, GGA-PBE exchange-correclation functional [7,8] is selected. A Monkhorst-Pack *k*-point mesh [9] equivalent to 4x4x4 was taken for the full (reducible) Brillouin Zone, allowing the convergence of total energy and forces.We started from the reported crystal structures of ZrMo2 and ZrCr2 in its hexagonal crystal system. Then, dimensions and ions positions, were allowed to optimize, until residual forces and stress tensor components were positioned down to 0.01 eV/Å and 5 kbar respectively. We consecutively added hydrogen to these structures determining the corresponding formation energy from the reaction: $ZrM_2+n/2H_2 \rightarrow ZrM_2H_n$ (M=Cr y Mo), using $E_{form} = -(E(ZrM_2H_n) - (n/2*E(H_2)) - E(ZrM_2))$. The results indicate that there is an optimum load for every phase, which is higher in the case of $ZrCr_2$ and lower in the $ZrMo_2$. Additionally, the formation energy becomes unfavorable nearly to a Hydrogen atom occupation of 5, for both samples. This is a demonstration that the thermodynamics of the Hydrogen storage is better for $ZrCr_2$ in comparison to $ZrMo_2$. Strong thermodynamic stability should negative affected discharge capacity of this alloy.



Figue1.- Formation Energy as a function of the Hydrogen occupation for both phases: $ZrCr_2$ and e $ZrMo_2$

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Nanostructured Sodium Titanate for Sodium-ion Batteries

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The price of pure lithium carbonate as the most crucial precursor for active electrode materials for lithium-ion batteries got far beyond its previous historical maximum at the beginning of the year 2016. The price increase is credited to the expectations of massive increase in the production of Li-ion batteries for EV. Sodium-ion batteries are very promising complementary power sources to the lithium-ion batteries because they utilize the same principles and technology. At the cost of lower energy density they can potentially offer solid energy storage system without the need of rarer elements – mostly lithium. Sodium is abundant element, it occupies 2.6 % of the Earth's crust and which is extremely easy to obtain.
The general sodium-ion battery working principle, components and chemistry are common with lithium-ion battery. This work is focused on the synthesis and electrochemical characterization of sodium titanium oxides with different sodium content like $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ and its mixtures. The purity and crystallographic composition of the samples were examined by XRD and the morphology was observed by SEM (Fig1). Electrochemical behavior was studied by cyclic voltammetry (Fig.2) and galvanostatic cycling.

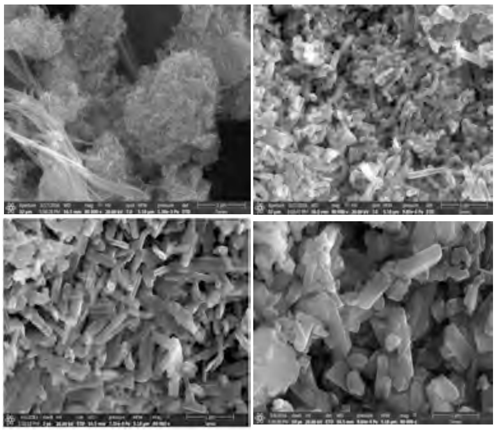

Fig.1 SEM of titanate nanorods

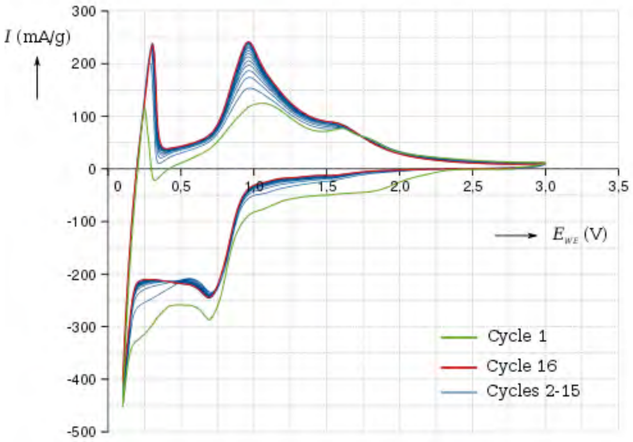

Fig. 2 CV on mixed titanate electrode performed by 2mV/s

The products of hydrothermal synthesis with further calcination were sodium titanate nanorods in general, where particle size and mainly particle diameter was strongly influenced by the calcination temperature. The phase composition, on the other hand, was strongly influenced mainly by precursor ratio. $Na_2Ti_3O_7$:$Na_2Ti_6O_{13}$ with different ratios was obtained together with pure monophasic $Na_2Ti_6O_{13}$. The CV experiments show very good cycling stability (peak currents rise during cycling) and galvanostatic charge/discharge cycling reveal discharge capacity of 90 mAh/g in the first cycle.

Acknowledgments

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Development and characterization of graphene-based electrodes for microbial electrolysis cells

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Microbial electrolysis cells (MEC) are biocatalyzed electrolysis reactors employed in the production of hydrogen. These systems are based on the ability of certain *electrogenic* microorganisms, such as bacteria of the genus Geobacter, that are capable of extracellular electron transfer while oxidizing organic compounds. This mechanism can be used to transfer electrons to an electrode in an electrochemical cell, where they can be used for the production of value added products. Currently, MEC represent a promising technology to turn the organic pollutants dissolved in wastewaters in a renewable source of energy. Bioelectrochemical wastewater treatment can capture the chemical energy present in various effluents and transform it into storable energy, such as H_2. However, the development of this technology has been hampered mainly by the low rate of charge transfer to the electrodes. For this reason, various materials like graphene, that could overcome this limitation, have arisen great interest in the area.

The objective of this work was to develop graphene-based electrodes that promote the establishment of biofilms of electrogenic bacteria and increment the performance of MEC. Graphene was obtained from the reduction of graphite oxide with ascorbic acid and further prepared as a hydrogel. The hydrogel was prepared on different meshworks, such as carbon cloth or 304 stainless steel mesh. The resulting modified electrodes were used as anodes in MECs. The MECs consisted of sterile anaerobic single-chamber cells with three electrodes, where a platinum wire was used as counter electrode and a Ag/AgCl electrode was used as reference electrode. The cells were filled with 200 ml of culture media, flushed continuously with N_2:CO_2 and cultured at 30ºC during operation. The working electrode was poised at a constant potential (+240 mV vs Ag/AgCl) and the current intensity was recorded. After 24 h, in order to initiate bacterial growth on the electrodes, the MECs were inoculated with stationary-phase cultures of *Geobacter sulfurreducens* that had been grown with sodium fumarate as the electron acceptor (20% inoculum). Sodium acetate was provided as the electron donor, and no electron acceptors other than the electrode were present. The current intensity was monitored during 10 days. The results were compared against a pristine mesh of comparable size without graphene, and also against a solid graphite rod. Controls in the absence of bacteria were also performed. The electrodes were characterized, before and after bacteria inoculation, by cyclic voltammetry, Raman spectroscopy and electron microscopy techniques.

Cyclic voltammetry showed that graphene-based electrodes have larger surface area than the control electrodes. After inoculation, a significant increase in current intensity was observed when graphene-based electrodes were employed, indicating that the bacteria were able to adhere to the electrode surface and replicate. Furthermore, this increase was faster than for the respective pristine mesh and the graphite rod electrodes. The maximal current intensity was reached earlier with graphene-based electrodes and it was five folds than the control electrodes. No significant changes in current intensities were observed in any of the cells operated without bacteria. Bacterial biofilms were established in the graphene-based electrodes and the graphite rod, as observed by SEM. Their thickness was similar for each electrode (approx. 20 µm), but the architecture was different. In the graphene-carbon cloth and the graphite rod electrodes, the biofilms formed heterogeneous pillar structures. When the electrode consisted of graphene over stainless steel mesh, *G. sulfurreducens* formed a thick homogenous layer of cells evenly distributed, with minimal pillar structures. Finally, electrochemical experiments and Raman spectra of graphene indicated that graphene has been further reduced by the bacterial biofilm during the MEC operation.

In conclusion, the graphene-based electrodes proved to be suitable to develop dense and conductive biofilms and to produce high currents. Currently, we are improving the design of the electrode in order to allow longer operation times. Moreover, we are investigating how the different biofilm architectures observed affect the electrochemical response of the MEC, and whether the better performance of the graphene-based electrodes is due to the wider surface area, an enhanced bacterial anchorage and/or a better electron transfer on the cell-electrode interface.

Electrochemical and Fuel Cell Evaluation of PtIr/C Electrocatalysts

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Considering the world economy, there is great interest in obtaining new energy sources that combine high efficiency with reduction of environmental impacts [1, 2]. In this sense, there is a great interest in the use of renewable fuels and more efficient power sources such as direct alcohol fuel cells (DAFC) [3].

Ethanol has been considered one of the most promising candidates for DAFC, because it could be produced in a large scale from renewable sources, which will not change the natural balance of carbon dioxide in the atmosphere in contrast to the use of fossil fuels; moreover, it is less toxic than other liquid combustible [4, 5]. However, the high efficiency of the ethanol oxidation reaction (EOR) is still a significant goal because the cleavage of C–C bonds for the complete oxidation of ethanol to CO_2, which requires the use of more active and selective anode catalysts [5].

Platinum or palladium are generally used as electrocatalysts for the ethanol oxidation in acidic or alkaline media environment; however, the formation of intermediates that poison Pt/C or Pd/C anodes, reducing the fuel cell performance is an inconvenience [6]. An alternative to overcame this problem is the addition of co-catalysts to Pt or Pd electrocatalysts [6–7]. It is reported that the incorporation of Ir or IrO_2 on Pt (PtIr or $PtIrO_2$) has also improved the catalytic activity and stability towards ethanol electro-oxidation in acid media [7]. Which was attributed to the OH groups that are more easily adsorbed on both metallic Ir or IrO_2 at lower potentials, assisting the oxidation of adsorbed intermediates [7].

Therefore, this work describes the use of PtIr/C electrocatalysts, prepared in different Pt:Ir atomic ratios (90:10; 80:20; 70:30; 50:50), for the ethanol oxidation reaction in alkaline media. PtIr/C electrocatalysts prepared by borohydride reduction process were characterized by X-ray diffraction, transmission electron microscopy, and cyclic voltammetry. The X-ray diffraction measurements showed peaks characteristic of Pt face centered cubic (fcc) and suggested the PtIr alloy formation; furthermore, peaks of IrO_2 were not observed; nevertheless, the presence of Ir oxides in small amounts and amorphous forms cannot be discarded). The transmission electron microscopy showed the average particle diameter between 4.0 and 6.0 nm for all compositions prepared. The catalytic activity for ethanol electrooxidation in alkaline medium at room temperature (cyclic voltammetry and chronoamperometry) were conducted at a scan rate of 10 mV s^{-1} in 1 mol L^{-1} KOH aqueous solution in the presence and absence of 1 mol L^{-1} ethanol. The amperometric curves (I–T) were recorded in the same electrolyte containing ethanol at −0.35 V for 1,800 s. The results showed that PtIr/C (70:30) and PtIr (90:10) exhibited higher performance toward ethanol oxidation than the other electrocatalysts. The introduction of Ir leads to an increase in the electro-activity of the binary electrocatalysts (PtIr) compared to pure Pt. This effect was explained by the activation of interfacial water molecules at lower potentials than in the case of pure Pt, due to the presence of preferential sites for OH_{ads} adsorption. The presence of OH_{ads} species, necessary for the complete oxidation of poisoning intermediates adsorbed, associated with the electronic modification of Pt might be the possible reason for the enhanced activity. Experiments using the direct ethanol alkaline fuel cell took place in a single cell with an area of 5 cm^2. The temperature was set to 75 °C for the fuel cell and 85 °C for the oxygen humidifier. All electrodes used contained 1 mg of Pt per cm^2 in the anode and in the cathode, except for Ir/C which contained 1 mg of Ir per cm^2. In all experiments, Pt/C BASF was used in the cathode. PtIr/C (90:10) was the best electrocatalyst, the maximum power density using PtIr/C (90:10) was 2.5 times higher than on Pt/C and Ir/C as virtually inactive for ethanol oxidation. The best result obtained using PtIr/C may be associated to the electronic effect between Pt and Ir that could decrease the poisoning on catalyst surface and also by the occurrence of bifunctional mechanism.

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Shedding Light on the Entropy Change Found for the Li-ion Storage in Graphite

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It is well known that intercalation materials are widely used as anodes or cathodes in electrochemical cells to store energy. Materials of intercalation such as lithium cobalt oxide (LiCoO2), lithium iron phosphate (LiFePO4), lithium titanate oxide (LTO), graphite, are commonly found in electrodes of commercially lithium-ion cells. Particularly, graphite is the most common material found in anodes of commercial lithium-ions cell. These materials allow a fast ion insertion and extraction of them and therefore, high power densities cells can be obtained. However, Li-ion insertion and extraction generates heat into the cell. This heat can produce high temperature excursions of the cell and a premature aging of it. It has been demonstrated that a great portion of the heat which is generated into the intercalation materials comes from the intercalation entropy during discharge [1,2].

In the present work we use a simplified lattice-gas model with different energy levels associated to stages or phases of the lithium/graphite compound to study the intercalation entropy of this compound. Our calculations are made within the canonical ensemble where the partition function is given by:

where labels the degeneracy of the energy level, the number of inserted ions and indicates the total number of sites where the ions may be inserted. A Bragg-Williams approximation is used for the energy levels , where is an interaction parameters, is the number of neighbors in each of the lattices, are the occupancies of the layers, and the factor is to account for the double summation in the average interaction. The intercalation entropy and all the thermodynamic properties of the system can be obtained from once it is known. Figure 1 shows the intercalation entropy from for a two energy level system as a function of the lithium concentration (x). For x ≈ 0.5 the curve shows a step which correspond to the experimental step of the transition from stage II to stage I [2].

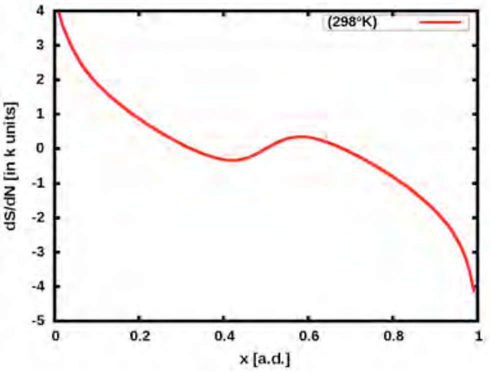

Figure 1: Intercalation entropy vs. lithium concentration

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New ecofriendly low-cost binders for Li-ion anodes.

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In the commercial Li-ion batteries production, the electrodes active materials slurries are prepared using polyvinylidene fluoride (PVdF) as binder, thanks to its good adhesion properties and electrochemical stability [1]. Unfortunately there are some disadvantages related to the use of PVdF: most important the requirement of toxic and environmentally unfriendly solvents, such as N-methyl-pyrrolidone (NMP) and, secondly, the high costs [2]. On these premises it seemed straightforward to investigate the suitability of some water-soluble, inexpensive and eco-friendly binder (Gelatin, Sodium Alginate, Tragacanth Gum, Vinyl Glue, Chitosan) as an alternative to the well-known PVDF/NMP couple [3], in negative electrodes graphite slurries. All the electrodes, assembled with the different binders under study, were firstly electrochemically characterized and, in a second time, the rheological properties of these materials were also investigated to better understand their industrial scale-up feasibility with a particular focus on possible future applications. In addition, the results have been compared to the also commonly used carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) binder combination.

Some of this water-soluble binders, besides good electrochemical performances, showed a high adhesion to the current collector and a good electrochemical stability under the experimental conditions employed, which makes them interesting for the next generation of Li-ion Batteries.

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Development of Oxide Modified Nanostructured Carbon Materials for using as Electrocatalyst Supports in Hydrogen/Oxygen Fuel Cell Electrodes

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The polymer electrolyte membrane fuel cell (PEMFC) is a promising technology for efficient energy conversion. However, both durability and cost of the membrane are still obstacles for its commercialization. In this regard, the current research is focused on the development of new supports and coverings to improve the life time of the catalytic layer, the self-humidification of the membrane-electrode assembly (MEA) and the electronic properties of the active layer [1-3]. In this work, the results of the performance of three different nanostructured support materials for platinum electrocatalysts used in PEMFC are presented. These materials were: i) nanoporous composite with SiO_2-C composition, ii) mesoporous carbon with non-crystalline subgraphitic structure (MPC), and iii) tin and silicon binary oxide modified MPC. The SiO_2-C composite was synthetized by using a sol-gel technique with a phenolic resin and alcoholic solution of TEOS as precursors. The product obtained is a composite material with two different crosslinked frameworks, one of amorphous SiO_2 and the other of a carbonaceous subgraphitic structure, as determined by XRD. The MPC is obtained through dissolution of the SiO_2 network by using HF treatment. Finally, the MPC is covered with a binary tin and silicon oxide by a method similar to that used to obtain the composite, using $SnCl_4$ and TEOS as precursors. The polycrystalline Pt catalysts were deposited on the supports by means of the urea-polyol method, by using ethylene glycol as solvent and urea as precipitant agent. The amounts of H_2PtCl_6 and support material were adjusted to obtain powders with 20 wt. % Pt. The characterization of the supports and catalysts were made by using XRD, TEM, SEM and voltammetry techniques. The PEMFC performance was evaluated by means of making different MEA with synthetized materials, where the Pt load was adjusted to 0.1 mg/cm^2 .The geometric area of the electrodes was 9 cm^2. The catalyst stability was evaluated by a potentiostatic technique, where a potential of 1.2 V was applied to the cathode respect to the anode during 320 h. The cathode was fed with N_2 and the anode with H_2. The SEM images of the composite and MPC show characteristic spongiform structures. The TEM images of binary oxide modified MPC show that the oxide is deposited as a thin layer on the carbon substrate. The average particle size determined by TEM for all the materials is 5.3 ± 0.6 nm. The decrease in electrochemically active area was determined by in-situ voltammetry before and after the stability test. Decreases in active area of 63 % for the MPC supported catalyst, 58 % for the SiO_2-C composite supported catalyst and 51 % for the binary oxide modified MPC supported catalyst, were found. The results show that oxide layer modification improves the long time stability of the catalyst, whereas binary tin and silicon oxide modified MPC exhibits the best performance, making it a suitable substitute for the Vulcan XC-72 support.

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The Development of a 3D Anode for Zn/$LiFePO_4$ Aqueous Battery

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Recently, our group has developed a novel combination of electrodes (Zn/$LiFePO_4$) for aqueous rechargeable Li-ion batteries (ARLB), which operates at 1.2 V and has a capacity of 92 mAh g^{-1} after 400 cycles [1]. The system is very safe due to aqueous electrolyte, is easy to prepare, and has long cycling life. Despite that, it has low cycling life at high C-rates and the volumetric energy density requires improvement. Therefore, this work was focused on the development of a three-dimensional (3D) Zn anode for Zn/LFP system to address important objectives such as (i) facilitating long range electronic conductivity, (ii) managing uniform current distribution, and (iii) increase of confined void space to increase effective surface area. The morphological structure of the anode material is shown on the SEM image below (Figure 1).

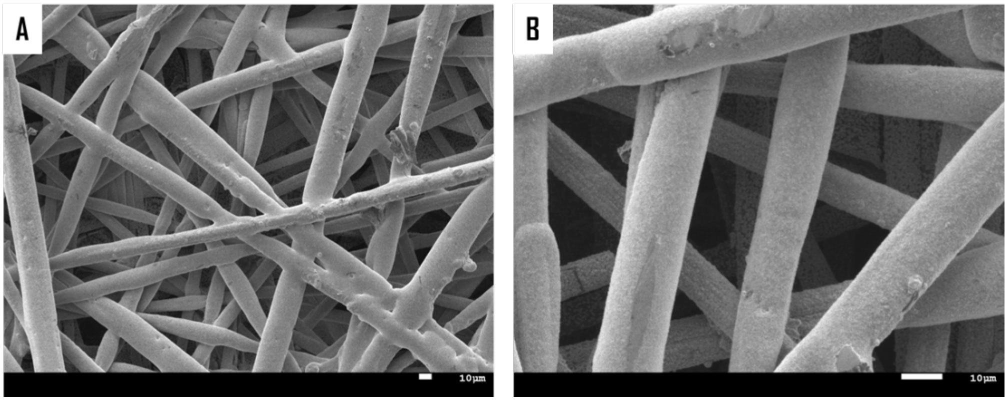

Figure 1. SEM images of 3D Zn anode material at (a) x300 and (b) x1000 zooming.

The anode material was prepared by anodic electroplating of metallic Zn onto 3D current collector, which was then tested in a full cell configuration in Swagelok type cells. As a result, the battery with 3D anode had 148 mAh g^{-1} initial capacity at 0.5 C with 80% retention after 80 cycles. Further, the batteries will be improved by volume reduction and development of full 3D structure.

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Acknowledgements

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Electrochemical and spectroscopic studies of carbon-based porous electrodes for lithium-sulfur batteries

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It has been reported that Li-S batteries, with Li metal as anode and S as cathode, would have a much higher specific energy compared to lithium-ion batteries available today [1, 2]. Furthermore, the great abundance and low cost of sulfur explain why these batteries are considered as promising energy storage systems although they are still at a research and development stage.

The energy gain when comparing Li-ion batteries with Li-S batteries is evident. This is because the discharge product at the cathode can store much more lithium and therefore more charge per unit mass with respect to discharge products in Li-ion batteries. In addition, the Li metal anode accumulates much more charge than intercalated graphite (C_6Li).

Although many significant progresses have been achieved in the field of Li-S batteries, its further development is still limited by several issues. Major challenges to attack are:

- Li metal anodes are chemically and morphologically unstable because of the drastic changes in volume provoking the growth of dendrites [3];
- Recharge with low efficiency and slow kinetics due to insulating nature of sulfur and other reaction products such as Li_2S;
- Capacity decays in successive cycles by formation of polysulfide intermediates which give rise to unwanted mechanisms known as shuttle mechanisms [4].

In the current research project, we have planned the synthesis of new materials that will be tested as possible cathode materials. For our target materials the size and distribution of pores (micro, meso and nanopores) can be varied while keeping the same chemistry and the most of the other material properties. The materials will be characterized to have structures with porosities and surface chemistry well defined.

In this work, a number of porous electrodes were synthesized by hard template method using melamine. We explore the use of melamine for several reasons; the first is the low solubility of melamine in the polymerization media, which makes possible its use as a hard template. Moreover, melamine has been reported as a Nitrogen precursor, able to modify the phenolic resin (resorcinol-formaldehyde) adding N-containing groups. Last, but not least, the porous carbon is obtained in a single step from low-cost commercial precursors.

Here we report the synthesis, impedance spectroscopy (EI) analysis and electrochemical/microscopic characterization of the base electrodes.

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Efficiency of Semi-transparent Organic Photovoltaics Based on Semi-transparent Electrode

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Semi-transparent and/or transparent electrode/substrate is crucial component to fabricate flexible power conversion device such as organic photovoltaics. Organic photovoltaics have intensively studied in recent years due to their advantages such as cost effectiveness and possibility of applications in flexible and transparent devices. In spite of these attractive aspects, the OPV still have a draw-back of their low power conversion efficiency and stability issue. One of the ideal device structures of organic photovoltaic, to solve these problems, is the inverted structured single and tandem organic photovoltaics which have greatest potential for achieving an improvement of device performances. Beside the device structure, various nanomaterials such as doped metal oxide interlayer, nanowire, plasmonic metal nanoparticles, carbon based materials (graphene, CNT, fullerene), and etc. are introduced, which show simultaneous enhancement of the efficiency and stability of organic photovoltaics. In recent, semi-transparent organic photovoltaics are also proposed to achieve the high performance and stability, which exhibited better stability compared to the non-transparent organic photovoltaics cell with conventional Ag top electrode. For this reason, we developed semi-transparent and/or transparent electrodes through wet process such as electroplating, chemical plating and spin coating techniques. We will summarize several technical points related to efficiency and stability of organic photovoltaics fabricated semi-transparent electrode/substrate.

Surface modification of $LiCoO_2$ cathode material by β-alumina

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Lithium ion batteries (LIBs) have become the dominant power sources for portable electronic devices. Most recently, the fast development of hybrid electric vehicles (HEVs), electrical vehicles (EVs) and energy storage apparatus set higher and higher demand on their energy sources. To meet the requirements of higher capacity and longer cycle life for LIBs, many researchers are focusing on the development of the cathodes working at higher potentials, including traditional electrode materials.

$LiCoO_2$ is the most widely used cathode material in commercially available Li-ion batteries, due to its high-energy density and good cycle life performance. However, some research groups reported poor cycling performance above 4.2 V, which is attributed to structural instability and/or irreversible phase transition from a hexagonal phase to a monoclinic phase with accompanying volume change of □2.6% along *c*-axis [1]. This volume change causes the accumulation of stress and propagation of microfractures in positive electrode, resulting in fast capacity decay with cycling. Oxides including LiCoO2, can only tolerate elastic strain of □0.1% before fracture [2]. In addition, the cathode surface easily reacts with acidic electrolyte. This implies that dissolution of the transition metals in the cathode and formation of an unwanted layer could have occurred at the interface between the cathode and the electrolyte, which in turn could disturb the movement of lithium ions and electrons during cycling [3].

In order to improve the electrochemical properties of the cathode material, researchers have attempted to modify the cathode surface by using stable materials. Experiments have shown that oxide coating layers like Al_2O_3, ZrO_2, MgO, et al, can improve the structural stability and thus the cycling performance [4]. The coated cathode exhibits an enhanced rate capability, thermal stability, and cyclic performance. However, the coating effect is highly dependent on the material and shape of the coating layer. Therefore, the identification of a suitable coating layer is a key factor in obtaining a highly improved cathode material by using the coating process. In this work, a β-alumina coated lithium cobalt oxide [$LiCoO_2$] thin film was characterized. $LiCoO_2$ cathode material synthesized by a solution combustion synthesis (SCS) was modified by different contents of β-alumina via sol-gel method. The structure and morphology of pristine and β-alumina-coated $LiCoO_2$ were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The effects of β-alumina on the electrochemical behaviors of $LiCoO_2$ were studied by charge/discharge curves, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

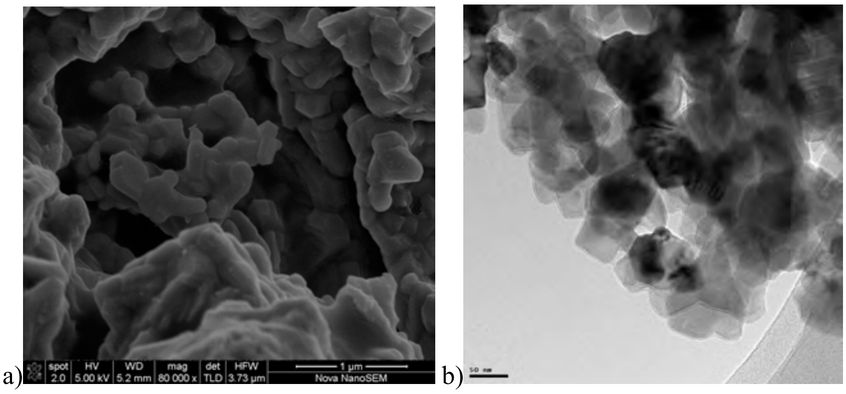

Fig. 1. a) SEM image of β -alumina -coated $LiCoO_2$, b) TEM image of β -alumina

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N-doped Carbon Electrocatalysts Treated by Fe: Surface Properties and Electrocatalytic Activity

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Pt and Pt alloys loaded on carbon support suffer from high cost and low durability of the noble metal electrocatalyst in fuel cell. Recently, non-Pt based heteroatom-doped carbon catalysts, due to their high stability, excellent electrocatalytic performance, and economic viability over costly Pt-based catalysts are being pioneered as a suitable alternative.

Although the heteroatom-doped porous carbon materials have evolved as one of best possible solutions, the probable synergy of heteroatom doping and textural properties has not been well investigated yet in details. Active species, electrical conductivity, porous structure and surface area are the key factors affecting overall electrocatalytic activity of carbon-based electrocatalysts [3]. In this work, we report Fe-treated N-doped ordered mesoporous carbons (Fe/N-OMC) as oxygen reduction reaction (ORR) catalysts through pyrolysis of iron phthalocyanine (FePc)-infiltrated SBA-15 silica. Excellent ORR activity with a nearly four-electron transfer process is observed for the Fe/N-OMC prepared with FePc in both alkaline and acidic media. Interestingly, it is found that although Fe is necessary for the preparation of highly active N-doped carbon catalyst, its presence may be not necessary for N-doped porous carbon to be active in the ORR in either alkaline or acidic media. The ORR activity is discussed in terms of heteroatom content, surface area, porous structure, and conductivity of the carbon.

Characterization and comparison between different binders applied to Sn-based anodes for lithium ion batteries

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The development of new electrodes for lithium ion batteries is a challenge to overcome in order to increase the batteries capacity and allow the introduction of new sustainable technologies. Sn has been proposed as replacement for the commercially used graphite, given that the theoretical capacity of the former (998 $mAhg^{-1}$) exceeds the capacity of the latter (372 $mAhg^{-1}$). Nevertheless, before Sn can be successfully used in commercial applications, there are issues that must be addressed. In particular, it has an important volume change (260%) upon lithiation and delithiation, and this process leads to cracking and pulverization of the electrode. Recently, several strategies have been proposed to contain the expansion of Sn without any loss in capacity using new binders and additives.

In this work, we study the effect of different types of aqueous polymeric binders in the preparation and performance of Sn-based anodes. Using a Sn/C nanostructured active material, we compare the anodes made with sodium alginate (ALG), sodium carboxymethylcellulose (CMC) at different pHs, and Collagen from common jelly, relative to the standard PVDF binder. Electrochemical cells were assembled in a dry box under argon atmosphere, using lithium foil as counter electrode and reference. The as-prepared electrodes were characterized by charge-discharge galvanostatic cycling to determine the capacity of the electrodes over several cycles. We completed the physicochemical characterization of the electrodes using voltammetry, high current discharge tests and SEM microscopy.

We found that the electrodes obtained have higher capacities than commercially used graphite. By using more elastic polymers as binders, we observe the differences in cyclability without significant loses in capacity or electrical contact. The higher elasticity of the aqueous binders allows better accommodation of the active material upon volume change during lithiation and delithiation.

Efficient Co_3O_4 electrocatalyst for the Oxygen Evolution Reaction (OER): Role of Co-Glycine complexes

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Co_3O_4 films were obtained by thermal treatment of metallic cobalt electrodeposited on fluorine tin oxide (FTO) from three different electrolytic solutions containing different Co^{2+} complexes: $CoCl^+$, $CoGly_2$ and $CoGly_3^-$. The identification of the three different complexes was carried out by Uv-Vis spectroscopy. $CoCl^+$ showed a broad band between 400-600 nm with a highest absorption at ~510 nm. $CoGly_2$ and $CoGly_3^-$ complexes shifted the highest absorption peak to ~490 nm and a second band was showed at ~370 nm. Electrodeposition from $CoCl^+$ complex produces a flat Co_3O_4 coating, while a small sphere morphology was obtained from complexes $CoGly_2$ and $CoGly_3^-$. Electroactive surface area, obtained from impedance measurements, was 2.11, 4.12 and 4.01 cm^2 for Co_3O_4 electrodes synthetized from $CoCl^+$, $CoGly_2$ and $CoGly_3^-$ complexes, respectively. The electrocatalytic activity of films for the oxygen evolution reaction (OER) was measured in 1 M NaOH solution. Co_3O_4 film obtained from $CoGly_3^-$ complex showed the highest activity, achieving a current density of $j = 1$ mA cm^{-2} at an overpotential of 327 mV. The highest activity of Co_3O_4 is attributed to the fact that Glycine complexes allow the obtaining of a small grain sphere-like morphology of Co_3O_4 which increase the electroactive surface area of the electrodes.

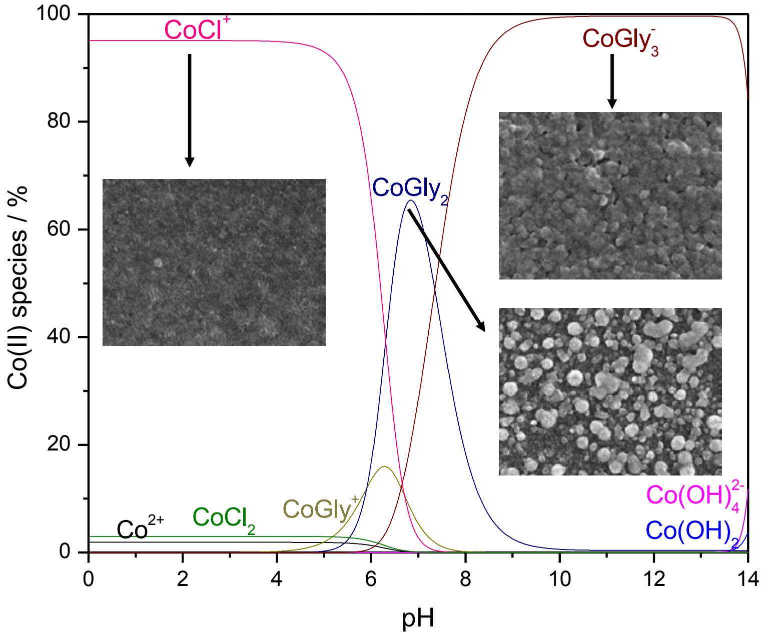

Figure 1.- Distribution species diagram for Co complexes. Morphologies of Co_3O_4 films obtained from different complex precursor are shown in the insets.

Nanostructure study of a sulfoneted semi-interpenetrating polymer network electrolyte membrane composed of DGEBA/DDS and PEI

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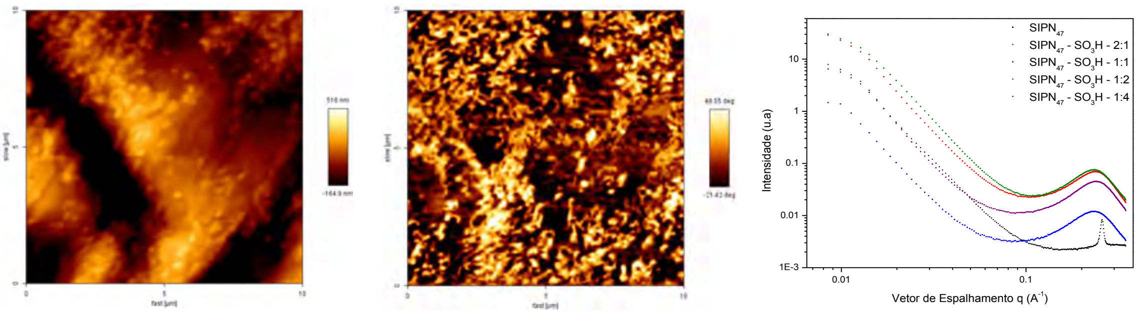
The increasingly high energy demand generated by the increase of the world population and consumption of fuels based on non-renewable sources has stimulated, in recent decades, the development of alternatives with less environmental impact and are based on renewable sources. Among these, the fuel cells (FC) have extremely promising possibilities. For the development of FC with market viability, it is necessary to obtain materials with optimized properties, among which the proton conducting membranes. In this work, it were developed semi-interpenetrating polymer membranes (SIPN) based on diglycidyl ether of bisphenol-A (DGEBA) and polyethyleneimine (PEI), aiming their application in PEMFC. It was employed the ratio1:1 DGEBA:crosslinking agent (4,4'-diaminodiphenylsulfone, DDS) (w/w) and PEI in mass ratios of 33, 38, 41, 44, 47 and 50%. From the purified SIPN, the membranes were obtained by casting and after submitted to a sulfonation reaction using a method previously described [1]. $SIPN_xSO_3H$ membranes were obtained using different sulfonation degrees (ratio between the sulfonating agent and the aromatic groups) of 1:4; 1:2; 1:1 and 2:1. The membranes' nanostructure was studied by AFM and SAXS. The ohmic resistance was measured using an AUTOLAB PGSTAT30/FRA from 10 mHz to 1 MHz at different temperatures from 20 to 80 ^{o}C. Before each electrochemical measurement, the membrane sample was fully hydrated by immersion in de-ionized water for 24 h. Figure 1 shows, illustratively, AFM images of a $SIPN_{47}$-SO_3H membrane and SAXS profiles. The maximum of conductivity obtained was 10^{-2} $\Omega^{-1}.cm^{-1}$. The AFM study identified ordinate hydrophobic/hydrophilic nanodomains, which might determine the membrane properties, specially the proton conductivity. Both, the AFM images and the SAX analyzes, allowed characterizing a hydrophobic/hydrophilic phase morphology dispersed in the bulk for this SIPN system.



(a) **(b)** **(c)**

Figure 1: AFM images (10x10µm) of the $SIPN_{47}$ SO_3H membrane (2:1 ratio of styrene:sulfonating group) (a) topographic micrograph, (b) phase contrast micrograph and (c) SAXS profiles of $SIPN_{47}$ SO_3H membranes

Acknowledges

Authors would like to thank FAPERJ, CNPq and CNPq/PIBIC.

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Influence of the crosslinking agent on the properties of SIPN proton conductive membranes based on DGEBA/PEI

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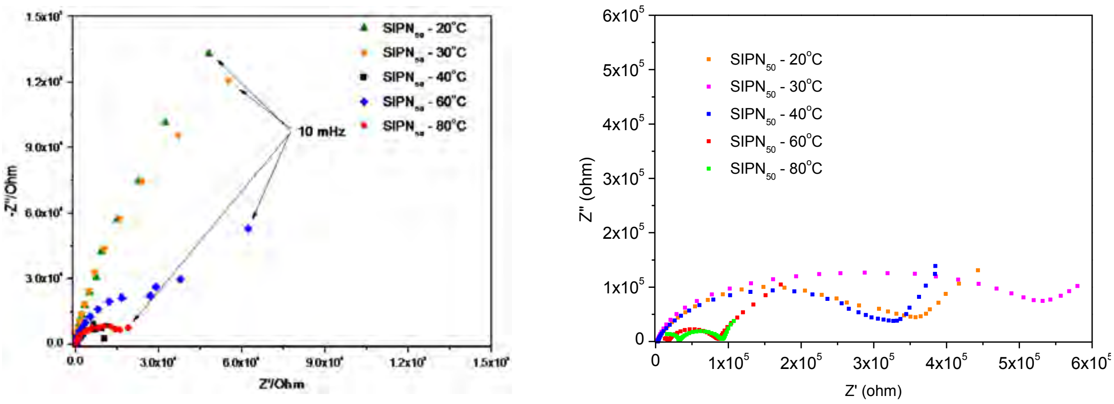
The development of new membranes in order to replace Nafion®, with greater thermal stability, chemical, electrochemical, and high conductivity is one of the keys to reducing the manufacturing costs of PEMFC [1]. In this work, two different semi-interpenetrating polymeric membranes (SIPN) systems were formed by the reaction of diglycidyl ether of bisphenol A (DGEBA) with two curing agents: (A) 4,4'-diaminodiphenyl-sulphone (DDS) and (B) Triethylenetetramine (TETA), both using Polietilenoimina (PEI) as a linear polymer. With the different crosslinking agents, it could be possible to control the free volume of SIPN, which might result in the modulation of nanometric structures along the membrane, influencing its properties. It were employed the ratio1:1 DGEBA/crosslinking agent (w/w) and PEI in mass ratios of 33, 38, 41, 44, 47 and 50% (w/w). Membranes with these compositions ($SIPN_x$) were obtained by casting. All samples were doped in H_3PO_4 20% aqueous solutions during 24 h and dryed for proton conductivity determinations by electrochemical impedance spectroscopy (EIS), using Nyquist representation. System (A) showed, for high PEI composition (50%), in the high frequency region, a semicircle associated with the ion transport resistance and, in the low frequency region, a straight line associated with the electrode/electrolyte interface capacitive effects. System (B), on the other hand, showed two semicircles, which indicate different diffusion mechanisms of proton. The conductivity values were 10^{-2} to 10^{-1} and 10^{-7} to 10^{-4} $\Omega.cm^{-1}$, for (A) and (B), respectively, from 20 to 80 °C. It was verified a linear increasing conductivity alongside temperature by Arrhenius plots for all membranes obtained from (B). By the thermal analyses, DSC and TG, differences in the nano and microstructures were inferred between both systems.



Electrochemical impedance spectrum at different temperatures of the $SIPN_{50}$/20% H_3PO_4 membranes obtained from the SIPN systems (A) and (B)

Acknowledges

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Electrochemical reactor modeling and simulation for electrochemical extraction process of lithium chloride from brine

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The current industrial lithium extraction method from salt lakes, the evaporitic method, is simple but relatively inefficient. With the current technology, approximately 0.5 million liters of water are evaporated and lost per ton of extracted Li_2CO_3. Moreover, the evaporitic method is rather slow, taking 1-2 years to evaporate water by solar radiation and wind. The Electrochemistry group at INQUIMAE has developed an electrochemical method for extracting lithium from brine; patented by CONICET, which is fast, efficient in laboratory tests, has low environmental impact, and low energy consumption.

The method comprises the use of an electrochemical reactor with electrodes which are highly selective for lithium. Lithium ions are inserted in the crystal structure of a battery-type lithium insertion electrode (e.g., λ-MnO_2) functioning as a cathode in an extraction step in which the electrolyte is a brine or other aqueous solution containing lithium. The inserted lithium ions are then extracted from the crystal structure of $LiMn_2O_4$ in an extraction or concentration step in which the battery-type lithium insertion electrode functions as the anode and the electrolyte is a diluted aqueous solution [1]. The counter electrode is a chloride reversible electrode that comprises an electrically conductive polymer: polypyrrole. These is depicted in figure 1.

The electrochemical processes at the cathode [1]:

$$x\mathrm{Li}^+\text{ (brine)} \;+\; \mathrm{Mn_2}^{IV}\mathrm{O_4}\text{ (cathode)} \;+\; xe^-\text{ (cathode)} \underset{\text{Li release}}{\overset{\text{Li insertion}}{\rightleftharpoons}} \mathrm{Li}_x\mathrm{Mn}_{2-x}{}^{IV}\mathrm{Mn}_{1-x}{}^{III}\mathrm{O_4}$$

At the anode [1]:

$$x\mathrm{Cl}^-\text{ (brine)} \;+\; x\mathrm{PP}^o\text{ (anode)} \underset{\text{Li release}}{\overset{\text{Li insertion}}{\rightleftharpoons}} x[\mathrm{PP}^+\mathrm{Cl}^-] \;+\; xe^-\text{ (anode)}$$

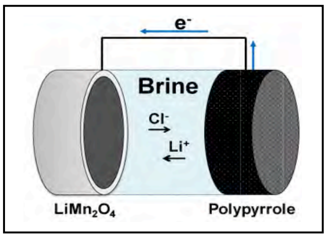

Figure 1. From reference [2].

Our work, consist on the development of the conceptual and detail engineering of this electrochemical extraction method. Here we are going to present the results of the mathematical modeling of a laboratory-scale electrochemical reactor, using COMSOL® software for simulation.

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Energetic and phonon dispersion of lithium silicates formed in-operando reduction of SiO_2 with Li in lithium ion battery. A theoretical and experimental study.

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Most of materials used for lithium-ion battery are based in anodes with silicon as active material due that the theoretical capacity of silicon is about of 3800 $mAhg^{-1}$ which is significantly grater than graphite (372 $mAhg^{-1}$) [1]. As well know the silicon expand the volume 380 % in the formation of $Li_{22}Si_5$ alloy and it change of volume produce the pulverization of the electrode. A possible solution is coated silicon with carbon so as palliate the expansion of silicon [2]. However, the reduction of silica to silicon is a process highly activated and expensive. An alternative it could be use SiO_2 coated with carbon due that the silicon is formed in-operando, and the theoretical capacity can be calculated trough the following reaction (considering Li_4SiO_4 and Li_2O as majoritary products) [2]:

$8Li^+ + 8e^- + 3\ SiO_2$ -----> $2Li_2O + Li_4SiO_4 + 2Si$ (1) Theoretical Capacity= 950 $mAhg^{-1}$

$5Si + 22\ Li^+ + 22ye^-$ --------> $Li_{22}Si_5$

The high capacity involved in the reaction 1 can be concern a good alternative to get stable and high power anodes with low coast and facile preparation. Moreover, silica is one of most abundant component in the Earth's crust and constitutes almost clays.

Even though in the recent years was increase the studies of SiO_2 (nanoparticles, meso and micrporous, among others) applied to lithium ion battery in the bibliography practically there is no information about the free energies of formations of different lithium silicates. We use the free energy calculation to obtain the complete thermochemical energy and to study how the vibrational entropy of Li^+ in different products of reactions affect at the free energy.

In this work we used Quantum Espresso software with phonon implementation to get the internal and vibrational energy to obtain the free Helmholtz's energy of formation of several silicates from the lithiation of silica. On the other hand, this results are compared with charge/discharge and rate capability performance of mesoporous coated SiO_2/C.

We found a high exothermic energies in the irreversible reactions and theses energies are strongly dependent of the type of lithium silicate formed. On the other hand, the vibrational analysis allowed the study of the Li^+ entropy in the lattice of different lithium silicates and how affect in the energetic of the reactions.

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Computational studies of polysulfides interaction with graphene oxide structures

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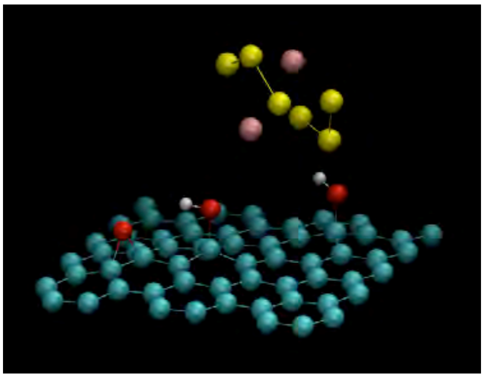
Lithium−sulfur present great attention nowadays due to its high specific capacity and energy density. The great energy storage is accomplished through the phase transformation chemistry based on elemental sulfur. The use of sulfur also present the great advantages such as being environmental friendly, great natural abundance, low cost and wide operating temperature range.

Nevertheless the usage of sulfur present the disadvantages of being insulating, also, the anode and the cathode suffers from volume changes during cycling and the polysulfides intermediates that are generated diffuse between cathode and anode causing side reactions conducting to low Coulombic efficiency, self-discharge and fast fading capacity.

In order to solve this last issue, the utilization of permselective membranes present as a great result for the retention of polysulfides. In this sense, graphene oxide membranes show a great promise blocking the polysufide transportation. Here we present ab initio density functional studies of the interaction of graphene oxide with long-chain polysulfides as a possible membrane to prevent the shuttle mechanism. The computational studies were carried on with SIESTA.

We made different studies with different levels of graphene oxidation and taking into consideration altered oxygen functionalities. We mainly study long chain polysulfides (Li_2S_6 and Li_2S_8) and its interaction with the different graphene oxide structures. We performed optimization geometries of those systems and performed Mulliken population analysis, pseudo charge densities and density of states (DOS) studies. The next figure illustrates the unit cell considered for one of this systems: graphene oxide interacting with Li_2S_6 polysulfide.



Study of the Electrochemical Behavior of Different Carbon Materials as Anodes for Lithium Ion Batteries

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The lithium ion battery was first commercialized by the Sony Corporation in 1991, and its development becomes critical for their improvement in a variety of applications ranging from hybrid electric vehicles to consumer electronics [1]. Most lithium ion commercial batteries use $LiCoO_2$, $LiNiO_2$ or $LiFePO_4$ as cathode material, organic solvent as the electrolyte and carbon composites as anode materials [1-2]. The electrochemical reactions involve Li mass transfer and charge transfer processes.

So far, a number of studies have been performed for providing a high performance carbonaceous material as anodes of Li-ion batteries [3]. In this study, from the many available carbonaceous materials we have selected some of them to be prepared as anodes material and to study their electrochemical behavior The carbon electrodes were fabricated by coating a slurry mix on a copper current collector, then dried and pressed. The slurry mix was prepared by mixing 80 wt% of the active material powder such as: carbonaceous commercial graphite (Anedra) and graphene (Graphenano), and 10 wt% conductive additive powder (Super C carbon) with the binder solution of n-methylpyrrolidone and 10 wt% poly-vinylidene fluoride (PVDF). These anode materials were characterized employing scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and electrochemical techniques as: cyclic voltammetry, charge-discharge cycles, galvanostatic discharge at different currents and electrochemical impedance spectroscopy. The analysis of all results, allowed us to improve the understanding of their physical, chemical and physic-chemical parameters.

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Electrochemical Characterization of Carbon/Sulfur as Lithium-Sulfur Battery Cathodes

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Nowadays, rechargeable batteries with high energy density are required for our society, due to the needs of cleaner and more efficient energy systems and, with the objective of supplying the increasing technological demands. Commercial lithium batteries are systems based on intercalation compounds that are able to delivering specific energies, about 150-200 WhKg^{-1}, one-third of their theoretical energy (≈ 600 Wh kg^{-1}). The reversible capacity for these intercalation compounds results difficult to be increased. Consequently, the need to explore new cathodes formed by lighter materials and involving electrochemical reactions of more than one electron becomes very important. An element as sulfur would be satisfying these conditions (with a theoretical capacity of 1675 mAhg^{-1} and a specific energy of 2600 WhKg^{-1}) [1,2]. The lithium-sulfur battery has been investigated by different groups in past decades; however, there are serious drawbacks, which have not yet been overcome and limit the practical development of this system [3]. Moreover, sulfur is much more abundant, inexpensive, and non-toxic compared to the transition-metal oxide cathodes.

We present, in this study, the preparation of composites with carbon and sulfur materials in a single fabrication process: using S_2C as the solvent. The characterization of the prepared material was performed using optical techniques (X-ray diffraction, scanning electron microscopy and transmission) and its electrochemical performance in lithium-sulfur batteries was studied using electrochemical techniques such as: charge-discharge cycles, galvanostatic discharges to different currents and cyclic voltammetry. The prepared composite materials delivered higher capacities during the first cycles (≈800 mAhg^{-1}) and then they were stabilized at values around 60% of the initial capacity. Furthermore, carbon electrochemical response was not observed; these results indicate that its main function is to act effectively as an electron-conducting material and support of the matrix.

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Sensitivity analysis of water management in cathode side PEMFC varying structural and operational parameters by computational simulation

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Membrane humidification is an important factor affecting PEM fuel cell performance. In this way flow channels plays an important role among the components of a fuel cell, because they perform various essential functions that enable the system to improve water management. In most cases operational conditions have a strong contribution over the water production[1].

Several studies describe the advantages and disadvantages for different kinds of bipolar plates and flow channels configurations, being parallel, serpentine and interdigitated geometries the most habitually studied [2-4]. It is well known that not all the operations variables have the same impact over performance of the PEMFC [5]. Most of this studies mainly consider the field flow and the reactant distribution as the result [6], giving less importance to the water generation and distribution.

Water management is of vital importance to achieve maximum performance and durability from PEMFCs [1] for this reason in this work a sensitivity analysis was performed to consider the production and distribution of water in the cathode as function of several parameters. The operational parameters simulated were back pressure, cathode inlet velocities, cathode inlet water mass fraction and the structural parameters were gas diffusion layer porosity, gas diffusion layer thickness, porous electrode thickness, height, width and shape of the distribution channels (collectors) as over the the main channels and operations. The numerical model for the cathodes (Flow channel, gas diffusion layer and catalyst layer) was developed and analyzed by using the COMSOL® software package, air flow simulations were carried out, obtaining water and current density distribution as a results.

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Carbonaceous Separators Modified to Improve the Cyclability of Lithium Sulfur Batteries

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Within electrochemical batteries, lithium-containing batteries are being used in various electronic devices such as electric cars, hybrid motors, laptops, cell phones, etc. Due to the diversity of materials that can be used as electrodes[1-4] the spectrum of applications of these devices is in constant increase. However, current commercial batteries still present operational problems that limit their application, for example the low capacity. This is why new materials constantly come up that try to overcome such problems.[5,6] Lithium–sulfur batteries are especially promising electrochemical systems because of their high theoretical capacity of 1672 mAh/g and energy density of 2600 Wh/kg. The high energy density is due to the phase transitions undergone by sulfur which allows capturing more lithium ions than the transition metal based materials currently used. In a charge/discharge cycle two plateaus can be seen: one at 2.3 V vs. Li/Li^+ which corresponds to reduction from S_8 solid to Li_2S_4 and the other at 1.9 V vs. Li/Li^+ which corresponds to reduction of Li_2S_4 to yield Li_2S with the corresponding formation of intermediate products. The active material is sulfur, which is economical, abundant, and non toxic.[7-10] Nevertheless this material has several problems that need solution. Some of these problems are: Li_2S and S_8 are insulating, so it is necessary to cover them with some conductive material; the material has a change of volume of 80% between lithiated and delithiated phase; polysulfides formed as intermediates are very soluble in the electrolyte, causing a loss of active material; shuttle effects takes place, where the efficiency of the lithium anode can be lowered due the passivation with insoluble sulfides; metallic lithium is used as anode, generating degradation of the electrolyte; degradation of electrolyte by the polysulfides.

One of the strategies used to improve the cyclability of the material, avoiding shuttle effects, is the modification of the separator with some materials like TiO_2[11], or carboneaus materials[12], etc., that trap the polysulfides avoiding diffusion and suppressing the shuttle effect.

In this work we study the cyclability of S/C composites as cathodic materials. We used modified separators with different quantities of hard carbon oxidized prepared in the laboratory. Two kinds of separators were used: Celgard and ceramic impregnated separators. It can be seen than when modified separators are used, the retention of the initial capacity with the number of cycles is improved whith respect to the separator without modification. We also studied the effect of the quantity and the oxidation degree of hard carbon in the separator on the cyclability of the system. All samples were characterized physically and electrochemically using techniques as Scanning Electron Microscopy, Energy-dispersive X-ray spectroscopy, Cyclic voltammetric, Galvanostatic charging/discharging test, etc.

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NMR study of SEI formation and structural changes in silicon anodes of lithium-ion batteries

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One of the main problems to be resolved when we are linking together the renewable energy sources with the electric distribution systems, is the delivery potency variation through time. Therefore, a successful strategy is to complement the renewable sources with batteries that, once charged, are able to deliver a constant potency to the net. Nowadays, the most promising products are those of the electrochemical kind, like the recharged lithium-ion batteries.

In this work we used the Nuclear Magnetic Resonance technique (NMR) to study the structural changes that occur in the silicon-graphite anodes, during the electrochemical charge-discharge cycles, of a lithium-ion battery.

The NMR technique is useful to study of the anode during the charge-discharge process. The NMR spectra depends on the lithium nuclei local environment [5,6], allowing to obtain information about the state of charge of a battery. The lithium nuclei (^{7}Li and ^{6}Li) are used as probes due to the fact that the Li$^+$ ions are directly involved in the electrochemical processes occurring in a lithium-ion battery. This method allows to determine which is the species removed during the charge process and how the local structure changes over the extended charge cycle [7].

The active material of the electrodes studied where silicon nanoparticles [3] and silicon nanotubes (SBA-15) [8].

The static ^{7}Li 1D NMR spectra were obtained with a Bruker Avance II 300 spectrometer (B$_0$=7.05 T) operating at 116.64 MHz for ^{7}Li.The experimental results show differences in the NMR spectra depending on the electrode state of charge. In this way, it is possible to identify the lithium charge (because of the) through spectrum changes, as it is observed in Figure 1.

Figure 1. NMR spectra for silicon anodes, with SBA15-graphite as active material, after 25 cycles. The spectra show differences according to the battery state of charge. a) Discharged anode. The broad peak of 6950 Hz width and the narrow peak of 964 Hz width are is attributed to the SEI and the electrolyte, respectively. b) Spectrum for the charged anode. The peaks have the same meaning as in the case of the discharged anode but the broad one has a bigger intensity due to the adsorbed lithium ions.

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High-voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ for lithium-ion batteries: synthesis improvement using different thermal treatment

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Nowadays, technology advances have reached such a development level where the use of different kinds of renewable energies (wind, solar, geothermal, etc) is a reality on continuous growth. This requires solving the problem of proper storage of the energy, usually generated as electricity. In that sense, lithium-ion batteries have become a worldwide recognized useful technology.

One relevant issue for industrial processes is making batteries lighter and with high power densities. That is an essential feature required for electrical vehicles. The challenge consists on working to improve the power density of active materials for cathodes such as $LiNi_{0.5}Mn_{1.5}O_4$. This has been tested as a high-voltage cathode with discharge potential plateau of approximately 4.7 V versus lithium.[1, 2, 3]

This work presents the synthesis and characterization of $LiNi_{0.5}Mn_{1.5}O_4$ materials using the solid-state method,[4] by mixing stoichiometric proportions of NiO, $MnCO_3$ and Li_2CO_3 with different thermal treatments in an oxygen atmosphere: 1) First period of 8 hours at 350ºC and second period of 22 hs at 850ºC, 2) First period of 6 hours at 600ºC and second period of 16 hs at 850ºC, 3) First period of 6 hours at 600ºC and second period of 22 hs at 850ºC

The materials have been tested electrochemically by charge-discharge cycling, cyclic voltammetry (CV), rate capability and electrochemical impedance spectroscopy (EIS). The samples have shown a discharge capacity at C/10 of 1) 136.4 mA.h/g, 2) 116.5 mA.h/g, 3) 135.8mA.h/g.

The samples obtained are being characterized by X-Ray Photoelectron Spectroscopy (XPS) and the results are going to be used in order to improve the synthesis. XPS measurements have been helpful to optimize the synthesis process and design better active materials.[5] In these materials, the interest is set on regions corresponding to Li1s, Ni2p, Mn2p y O1s. This technique allows the differentiation of specific signals from every element at the corresponding oxidation state. That makes possible to identify and quantify species, in order to evaluate the progress of the synthesis reaction.

Acknowledgments

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Synthesis and characterization of $LiFePO_4$ prepared by high temperature thermal decomposition of organometallic precursors

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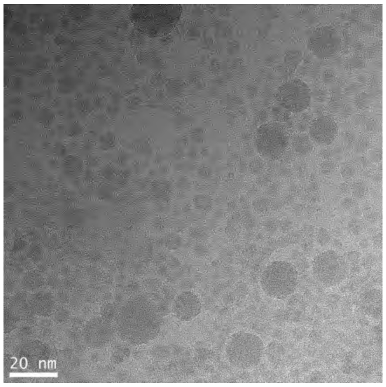
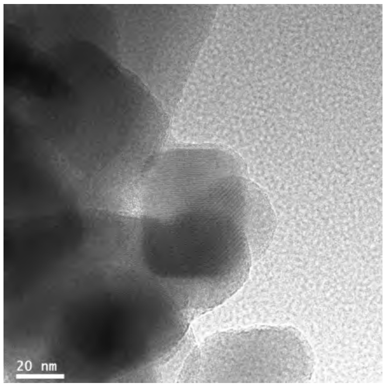
Among the materials for lithium ion battery cathode, lithium iron phosphate ($LiFePO_4$) is one of most studied cathodes due to its properties such as low toxicity, low material cost, flat voltage profile, long cycle ability and high safety compared to other cathode materials [1]. The poor electronic conductivity ($<10^{-9}$ s/cm) and the slow kinetics of lithium-ion diffusion coefficient (10^{-14} to 10^{-16} cm^2/s) are the main disadvantages of lithium iron phosphate [2]. One strategy to improve the electronic conductivity of $LiFePO_4$ cathodes is so-called carbon coating, where the surface of the material is coated with conductor carbon. On the other hand, the use of nanoparticles may have considerable kinetic advantages because of the reduction of the diffusion pathway length of Li^+ in the electrode materials.

The high-temperature decomposition of organometallic precursors is a synthesis procedure that is widely used to produce highly crystalline nanoparticles [3], with complete control of the morphology and composition of the material. From the view of point of materials for lithium batteries this kind of synthesis is attractive because the product resultant of it is immersed in an organic medium, which could be a source of carbon for the conducting layer.

In this work we present the results of the synthesis of $LiFePO_4$ by high-temperature thermal decomposition of organometallic precursors and their characterization. Acetylacetonates of respective metals were used as reactants in oleic acid and oleylamine as solvents. In order to obtain different morphologies and sizes of the particles, synthesis temperature and concentration of the reaction medium were modified. Then, part of the synthetized particles with the organic medium was annealed to obtain the carbon conducting layer and the other fraction was washed to remove the organic medium for comparison. The samples were characterized by XRD, TEM (HRTEM), electron diffraction, FTIR, DLS, DTA-TGA and charge-discharge cycles for the electrochemical characterization.





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FeOOH/graphene oxide composite as anode for lithium ion battery

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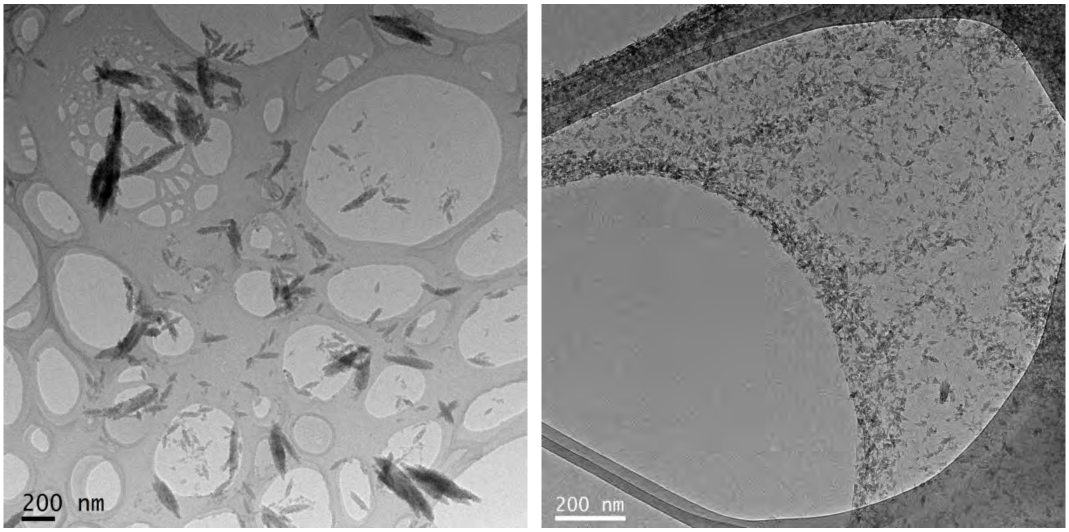
The development of new electrode materials for lithium-ion battery is a field very active due to the growing performances required to the batteries. Composite materials have gained relevance due to the possibilities of improvements in the material properties and its synthesis in a more efficient way. Also, they offer a wide morphology control, aspect that is relevant for battery charge-discharge kinetic.

Iron compounds as oxides and oxyhydroxides (FeOOH), are widely studied for its applications in areas such as environmental, industrial, geology, biology and medicine [1]. Also, FeOOH has been recently reported as a high capacity anode for lithium battery [2]. The synthesis of this material is interesting due to the simplicity of it and because small changes in the synthesis variables enables to obtain different morphologies and size in the material. On the other hand, graphene oxide (GO) has a number of applications because of its high reactivity due to the presence of oxygen containing functional groups on its surfaces.

In this work, we present the synthesis of unsupported FeOOH and supported FeOOH/GO compounds, obtained from iron(III) chloride and iron(III) nitrate, as sources of iron, at different reaction times and at 80°C. The samples were characterized by X-ray diffraction, HRTEM, electron diffraction and electrochemical measurements. Our results shows that the use of GO allows to control the particle size as can be clearly seen in figure 1. The obtained compounds depends on the iron source used being β-FeOOH for iron chloride and ferrihydrite for iron nitrate. We also found the conversion of ferrihydrite to hematite for long reaction times. We also present the results of electrochemical characterization for the supported and unsupported materials.



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Oxygen reduction reaction at MWCNT-modified nanoscale Iron (II) tetrasulfophthalocyanine: Remarkable performance over Platinum and tolerance to methanol in alkaline medium

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In fuel cell technology, especially the alkaline fuel cell (AFC), oxygen reduction reaction (ORR) with non-noble metal-based catalysts has remained a field of intense research activities**.** ORR, which is a cathodic process, provides maximum energy only when the oxygen molecule is completely reduced to water via the 4-electron rather than the 2-electron pathway.

There has been a desperate search in the fuel cell community for low-cost and efficient non-noble metal catalysts to replace Pt catalyst. M-N4 macrocyles, notably the iron phthalocyanine (FePc) complexes, have been demonstrated as efficient catalyst for ORR, first by Jasinki[1] and then by other workers.[2–4]

In this study, we report the synthesis of an organo-soluble nanostructured FeTSPc (nanoFeTSPc) by incorporation of long-chain alkane of the CTAB via coordinate covalency .To explore the impact of surface functional groups on MWCNT support, this organo-soluble nanostructured nanoFeTSPc was subsequently integrated on sulfonate-functionalised (*s*-MWCNT) and carboxyl/hydroxyl-functionalised MWCNTs (*o*-MWCNT) to enhance their dispersibility in aqueous media.

The nanoFeTSPc loading on MWCNT was 9% of the total weight. This is one of the lowest loading of any MPc catalyst on carbon support ever reported in the literature for ORR. We also clearly demonstrated that the as-prepared nanoFeTSPc-*o*-MWCNT exhibits a 4-electron ORR pathway and extraordinary tolerance to possible methanol crossover

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Modeling, Parameterization, and Identification of Rechargeable Lithium-Ion Batteries

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In this paper, following electrochemical arguments, we show that Lithium-Ion rechargeable battery can be modeled as a cascade of a linear dynamic system with a static nonlinearity. The linear dynamic system is related to the transport of the reacting substances in the active material, governed by Fick's laws. It is described by two parameters and the structure of the diffusional process (S), used to model the active Qmax) and the other is a positive constant (α) related to the diffusion coefficient and maximum concentration of reactants. The static nonlinearity is the electromotive force (EMF) which depends on the electrochemical reactions at the electrode interfaces governed by a Butler-Volmer type equation. Consequently, it is possible to write the potential at the battery terminals (E) as a function of both the EMF and the internal resistance (r). The scheme is shown in the Figure 1, where the input is the charge/discharge battery current (I).

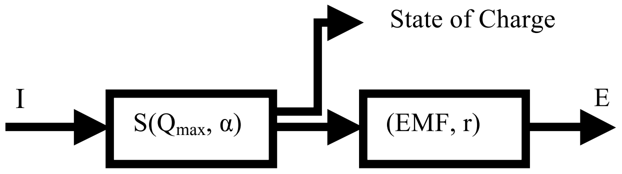
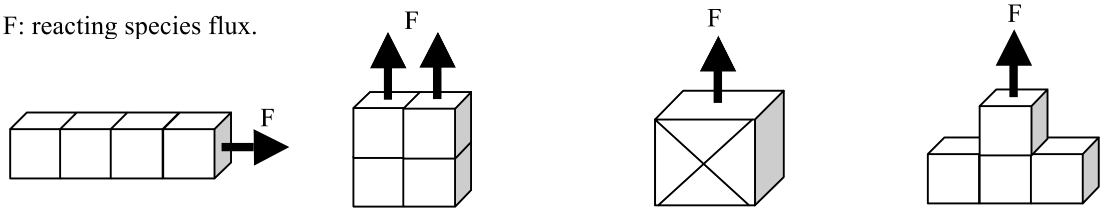


Figure 1: Current-Potential schematic battery model.

Qmax, α, r), the EMF and S.

We show that with these parameters is sufficient to completely describe the dynamic response of the Qmax, r) and the EMF can be obtained with great precision using a periodic squared pulse train of current. However, it is not the case for the parameter α, nor for the structure S. Thus, we present an identification procedure to obtain both. It consists on using an optimization method to find the parameter value α together with a proposed structure S that minimizes a relative cost function (J). The cost function is given by the norm of the difference between the experimental and model potentials using several I/E experiments. From various structures, in the Figure 2 are shown those who have the lowest relative costs. The costs J showed in the Figures are scaled by the lower cost between them. The reacting species of each elementary volume can diffuse between neighbors and flow with the electrolyte as shown with arrows in the Figure 2.

We conclude that the proposed model those best matches the experimental data are with structures S3 and S4. They are the most probable candidates for model the dynamic response of the rechargeable lithium-ion batteries used.



S_1: (α_1 =1.59;J=4) S_2: (α_2 =2.56;J=1.28) S_3: (α_3 =6.81;J=1) S_4: (α_4 =15.7;J=1)

Figure 2: Several schematic diagram of structures S, optimal parameter α, and relative cost J obtained.

Thermal behavior investigation of a LiFePO4 battery cell determined by optimum power management of fuel cell electric vehicles.

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The optimization and design of electric vehicles' powertrain systems can greatly benefit from mathematical models which include auxiliary management and control strategies of the energy fluxes as the use of a virtual platforms limits the expensive and time-consuming experimental activity.

In this work, the authors focus on the battery's current request of a small non plug-in hybrid Fuel Cell Electric Vehicle (FCEV), determined by the optimum power management, which is achieved with an instantaneous power distribution for each one of the sources (FC and Battery), such that the hydrogen consumption is reduced to its minimum and the battery's state of charge at the end of the cycle is the same as the beginning. In the vehicle studied, the fuel cells are the primary source of energy and the battery pack is used for energy storage and as an auxiliary source.

The power management is optimized using a quasi-Newton method using the vehicle model coupled with a fuel cell dynamic model that takes into account the main electrochemical, fluid-dynamic and thermal phenomena to predict the power output [1] and an empirical quasi-static model of the battery stack that takes into account the temperature. This process was done over three driving cycles that represents varied situations: the NYCC which represents a real life city driving cycle, the FTP UDDS which represents an intercity environment, and the HWFET which is a highway driving cycle.

Finally, given the importance of heat management in batteries in order to ensure safe operation and optimum performance, the battery's load profiles were simulated using a validated thermally coupled electrochemical model of $LiFePO_4$ pouch cell [2] to ensure a reasonable SOC at the end of the cycle and to predict the temperature increase in the battery due to the driving cycle.

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Synthesis and characterization of $LiFePO_4$/C composites cathode for lithium – ion batteries

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Lithium iron phosphate ($LiFePO_4$) is a promising candidate for the use as cathode material in lithium-ion batteries, especially the batteries for electrical energy storage involved in transportation such as hybrid electric vehicles or pure electric vehicles. Despite its high theoretical specific capacity (170 mAh/g) and long cycling lifetime, the high-rate performance of the raw $LiFePO_4$ is restricted by its poor electronic conductivity (10^{-9} S/cm) [1] as well as low lithium ion diffusion rate [2-4]. Many different approaches involving surface coating have been tried to improve the capacity and rate performance of $LiFePO_4$ as cathode for batteries. Increasing the conductivity by coating the $LiFePO_4$ surface with carbon [5] or conducting polymers, [6] has been two of the most popular. In addition to coating, the control of surface microstructure constitutes another general approach towards faster electrode reaction for batteries. These structures could be easily and effectively coated with a thin and uniform carbon layer for increased conductivity, as it is well established for simpler microstructures.

In this work, preparation, physical and electrochemical characterizations of LiFePO4 and LiFePO4/C as cathodes, for lithium-ion batteries, are presented.

XRD measurements confirmed production of pure and highly crystalline LiFePO4 cathode material. The morphological characterization of the materials revealed that the carbon is distributed uniformly in the $LiFePO_4$ particles. Electrochemical measurements confirmed increasing the intra-particle conductivity by carbon. The electrochemical tests exhibited that the electrodes with LiFePO4/C composite show better capacity than the bare LiFePO4 electrodes. This fact could be attributed to the enhanced electrical contacts by carbon.

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Solution Combustion Synthesis of $LiFePO_4$/C by using Li_2CO_3 as precursor

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Olivine $LiFePO_4$ (LFP) is a promising cathode candidate for high power lithium-ion batteries due to its excellent thermal stability, while Fe is inexpensive and environmentally benign [1]. The solution combustion synthesis method takes advantage of the highly exothermic nature of a reaction to complete combustion process within a short span of just 150-180 seconds with flame temperatures reaching as high as 1500ºC. It is a fast and easy to scale up [2] process that uses relatively simple equipment, allowing controlling composition, structure, homogeneity and stoichiometry of the products [3]. The use of Li_2CO_3 over other Li-precursors has advantages like the lower cost and the lower environment impact since its production requires less steps of industrial processing.

In this work, $LiFePO_4$/C was synthesized by the glycine-assisted combustion method and making use of Li_2CO_3 as Lithium precursor. It is shown that combination of Li_2CO_3 and the synthesis method would be commercially advantageous in mass production, despite a reduction in electrochemical discharge capacity. We also analyze the effect of post-synthesis annealing between 700 and 850 ºC for 6h under Ar atmosphere. Results of powder X-ray diffraction confirmed the formation of the olivine $LiFePO_4$ as the main phase, while other minor impurities also appear depending on the temperature treatment. Lattice parameters show the growth of crystallite size with increasing treatment temperature, which is in accordance with results of discharge capacity, rate capability and linear sweep cyclic voltammetry of electrochemical tests. HRTEM images confirmed the one step carbon-coating of $LiFePO_4$ particles during combustion synthesis and its morphology. Gas adsorption, laser diffraction and SEM measuring of particles were also compared to determine the chemical Li^+ diffusion coefficient into $LiFePO_4$/C.

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