Program of the

# 18th Topical Meeting of the International Society of Electrochemistry

## Oxygen Electrocatalysis in Chemical Energy Conversion and Storage Technologies

8 – 11 March 2016
Gwangju, South Korea

*Organized by:*
Division 3 Electrochemical Energy Conversion and Storage
Division 7 Physical Electrochemistry
ISE Region South Korea

# Sponsors

Ertl center

American Elements

Korean Electrochemical Society

Gwangju Convention & Visitors Bureau

Korea Tourism Organization

ACS Applied Materials & Interfaces

# Exhibitors

PINE Research

IVIUM Technologies

WonATech

Metrohm

DropSens

Bio-Logic

FC International

CM Corporation

International Society of Electrochemistry
Chemin du Closelet 2
1006 Lausanne
Switzerland

Printed in South Korea

# Table of Contents

# Organizing Committee

**Naoko Fujiwara**, *Osaka, Japan*
**Timo Jacob**, *Ulm, Germany*
**Frédéric Jaouen**, *Montpellier, France*
**Jaeyoung Lee**, *Gwangju, South Korea (Chair)*
**Bongjin Simon Mun**, *Gwangju, South Korea (Co-Chair)*
**Yongsug Tak**, *Incheon, South Korea*
**Hiroyuki Uchida**, *Kofu, Japan*

# Tuesday 8 March 2016, Afternoon

## Room 112

17:50 to 18:30

*Chaired by: Jaeyoung Lee*

**Hasuck Kim** *(Department of Energy Systems Engineering, DGIST, Daegu, Korea)*, Sungyul Bong, Sangaraju Shamugam

Will $H_2$ be an Option for the Future Energy after Fossil Fuels?

18:30 - 20:30

**Welcome Reception**

Gwangju Institute of Science and Technology, Restaurant Area

# Wednesday 9 March 2016, Morning

## Session 1

Room 112

*Chaired by: Bongjin Simon Mun*

### 09:00 to 09:40 Keynote

**Robert Schlögl** *(Fritz-Haber-Institut der MPG, Berlin, Germany)*

On the surface chemistry of OER electrodes

### 09:40 to 10:20 Keynote

**Nenad M. Markovic** *(Materials Science Division, Argonne National Laboratory, Lemont, USA)*

Electrochemical interfaces, electrocatalysis and green energy

### 10:20 to 10:50

Coffee Break

*Chaired by: Dangsheng Su*

### 10:50 to 11:20 Invited

**Wolfgang Schuhmann** *(Analytical Chemistry, Center for Electrochemical Sciences, Ruhr-Universität Bochum, Bochum, Germany)*, Corina Andronescu, Stefan Barwe, Karina Elumeeva, Bharathi Konkena, Justus Masa

Activity vs. stability. Design of electrocatalysts for the oxygen evolution reaction and oxygen reduction reaction in alkaline media

### 11:20 to 11:40

**Colleen Jackson** *(Department of Chemical Engineering, University of Cape Town, Cape Town, South Africa),* Denis Kramer, Pieter Levecque, Graham Smith

Carbides as a catalyst support materials for the oxygen reduction reaction

### 11:40 to 12:00

**Yuta Nabae** *(Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Japan)*, Muthukrishnan Azhagumuthu, Yoshihisa Harada, Hideharu Niwa, Takeo Ohsaka, Masaharu Oshima, JiaJia Wu

Quasi-Four-Electron Reduction of Oxygen over Fe/N/C Non-Precious-Metal Cathode Catalysts Prepared from Polyimide Fine Particles

12:00 to 12:30 Invited

**Zongping Shao** *(College of Energy, Nanjing Tech University, Nan Jing, China)*, Yubo Chen, Xiaomin Xu, Jie Yu, Wei Zhou, Yinlong Zhu

Boosting oxygen reduction reaction activity of palladium by stabilizing its unusual oxidation states in perovskite

---

## Session 2

Room 101

*Chaired by: Olaf Magnussen*

10:50 to 11:20 Invited

**Sang Hoon Joo** *(School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea)*

Design of Highly Active and Durable Nanostructured Carbon-Based Oxygen Reduction Electrocatalysts

11:20 to 11:40

**Yilin Deng** *(Department of Chemistry, National University of Singapore, Singapore, Singapore)*, Yonghua Du, Albertus D. Handoko, Shibo Xi, Boon Siang Yeo

*In Situ* Raman Spectroscopy of Copper and Copper Oxides Surfaces during Electrochemical Oxygen Evolution Reaction: First Identification of CuIII Oxides as Catalytic Active Species

11:40 to 12:00

**Juchan Yang** *(Energy Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea)*, Hyun-Kon Song

Corrosion-Resistive Islands-by-Islands Composite of Platinum Catalyst Supported by Carbon Nano-Onion for Oxygen Reduction Reaction

12:00 to 12:30 Invited

**K. Andreas Friedrich** *(Electrochemical Energy Technology, German Aerospace Center, Stuttgart, Germany)*, Norbert Wagner, Dennis Wittmaier

Bifunctional Oxygen Electrocatalysis in Alkaline Media: Addressing the Challenge of high Activity, Durability and Cost Effectiveness

# Wednesday 9 March 2016, Afternoon

## Session 1

Room 112

*Chaired by: Jinwoo Lee*

14:00 to 14:30 Invited

**Plamen Atanassov** *(Center for Micro-Engineered Materials, The University of New Mexico, Albuquerque, New Mexico, USA)*, Kateryna Artyushkova, Alexey Serov

Chemistry of the Active Sites in Transition Metal-Nitrogen-Carbon Electrocatalysts for Oxygen Reduction Reaction

14:30 to 14:50

**Mariangela Longhi** *(Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy)*, Stefania Marzorati, Francesco Nobili, Marco Renzi

Sugar-Based Catalysts For Oxygen Reduction Reaction

14:50 to 15:10

**Shun Sakamoto** *(Graduate School of Engineering, Iwate University, Morioka, Japan)*, Yoshihiro Kadoma, Miyuki Kojima, Akari Matsutomo, Tatsuya Takeguchi, Koich Ui

Influence of Mesopore Volume of Carbon Materials on Electrochemical Performance for Lithium-air Secondary Battery

15:10 to 15:30

**Travis E. Jones** *(Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany)*, Rosa Arrigo, Michael Hävecker, Axel Knop-Gericke, Verena Pfeifer, Robert Schlögl, Eugen Stotz, Juan J. Velasco-Vélez

Monitor oxygen-evolving iridium surfaces *in situ* by XPS & NEXAFS

15:30 to 16:00 Invited

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

Nanoscale Analysis of Fuel Cell Electrodes before and after Operation by Material-Sensitive and Conductive Atomic Force Microscopy

16:00 to 16:30 Coffee Break

*Chaired by: Karl Mayhofer*

16:30 to 16:50

**Yun Jeong Hwang** *(Clean Energy Research Center, Korea Institute of Science and Technology, Seoul, Korea),* Michael Jee, Cheonghee Kim, Byoung Koun Min

Silver Nanoparticles Electrocatalysts for $CO_2$ Reduction

16:50 to 17:10

**Rémi Costa** *(Institute of Engineering Thermodynamics, German Aerospace Center, Stuttgart, Germany)*, Vitaliy Yurkiv

Understanding electro-catalysis in Solid Oxide Cells (SOCs) for designing electrodes

17:10 to 17:30

**Cyriac Massue** *(Inorganic Chemistry, Fritz-Haber-Insitute of the Max-Planck-Society, Berlin, Germany)*, Sebastien Cap, Verena Pfeifer, Robert Schlögl

The Role of Amorphous Ir-oxohydroxides for the Oxygen Evolution Reaction

17:30 to 17:50

**Laetitia Dubau** *(LEPMI, CNRS, Saint-Martin d'Hérés, France)*, Tristan Asset, Raphaël Chattot, Frédéric Maillard, Jaysen Nelayah

Controlling the Activity for the Oxygen Reduction Reaction and the Stability of Hollow PtNi/C Nanoparticles *via* Synthesis Conditions and Post-treatments

17:50 to 18:10

**Juan J. Velasco-Vélez** *(Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Mülheim, Germany)*, Rosa Arrigo, Cheng-Hao Chuang, Michael Hävecker, Axel Knop-Gericke, Verena Pfeifer, Miquel Salmeron, Robert Schlögl, Eugen Stotz, Robert Weatherup, Gisela Weinberg

Soft X-ray photoelectron spectroscopy at electrified solid-liquid interfaces

18:10 to 18:30

**Sungeun Yang** *(Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea)*, Jiwhan Kim, Hyunjoo Lee

Single-Atom Platinum Supported on Titanium Nitride as a Catalyst for Selective Electrochemical Reactions

## Session 2

Room 101

*Chaired by: Jong-Sung Yu*

14:00 to 14:30 Invited

**Hansung Kim** *(Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul, Korea)*, Woong Hee Lee

Novel method for improving carbon corrosion resistance for polymer electrolyte membrane fuel cells using water electrolysis catalyst

14:30 to 14:50

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

Nanosized OER Catalysts with Superior Activity for Anodes of PEM Electrolysis Produced by a Cost-Effective Procedure

14:50 to 15:10

**Joey Ocon** *(Chemical Engineering, University of the Philippines Diliman, Quezon City, Philippines)*, Graniel Harne Abrenica, Beomgyun Jeong, Jaeyoung Lee, Dongyoon Shin

Non-noble oxygen reduction reaction catalysts based on activated iron-containing electrospun carbon nanofiber in semiconductor-air batteries

15:10 to 15:30

**Hyunah Kim** *(Materials Science and Engineering, Seoul National University, Seoul, Korea)*, Kisuk Kang, Ki Tae Nam, Jimin Park

Pyrophosphate based Materials as a New Oxygen Evolution Catalyst

15:30 to 16:00 Invited

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

What Types of Defects Enhance the Activity of Platinum for the Oxygen Reduction Reaction?

16:00 to 16:30

Coffee Break

*Chaired by: Pei Kang Shen*

16:30 to 16:50

**Serhiy Cherevko** *(Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH, Dusseldorf, Germany)*, Simon Geiger, Olga Kasian, Gareth P. Keeley, Nadiia Kulyk, Karl J. J. Mayrhofer, George Polymeros

Platinum Dissolution as one of the main Fuel Cell Electrocatalyst Degradation Mechanisms

16:50 to 17:10

**Tatsuya Shinagawa** *(KAUST Catalysis Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia)*, Kazuhiro Takanabe

Impact of Electrolyte Identity on the Electrocatalytic Conversion of Dissolved Gases in Buffered Solutions

17:10 to 17:30

**Kuang-Hsu Wu** *(Catalysis Division, Shenyang National Laboratory, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China),* Ian Gentle, Dang-Sheng Su, Da-Wei Wang

Origin of the Synergistic Effect in Metal Oxide/Carbon Hybrid Electrocatalysts and the Oxygen Reduction Reaction Mechanism

17:30 to 17:50

**Hyung-Suk Oh** *(Department of Chemistry, Technical University Berlin, Berlin, Germany)*, Hong Nhan Nong, Tobias Reier, Peter Strasser, Detre Teschner

Carbon-Free $IrO_x$ Electrocatalysts Supported on Sb-doped $SnO_2$ for the Oxygen Evolution Reaction in Acid PEM Water Electrolyzers

17:50 to 18:10

**Jinheung Kim** *(Department of Chemistry and Nano Science, Ewha Woman's University, Seoul, Korea)*, Soojin Kim

Electrochemical Regeneration of a Nicotinamide Cofactor Using a Cyclopentadienyl-rhodium Complex on Functionalized ITO Electrodes

18:10 to 18:30

**Hye Jin Lee** *(Department of Chemistry, Kyungpook National University, Daegu, Korea)*

Electrochemical Reduction of $CO_2$ using an Interface between Water and Propylene Carbonate Electrolyte Solutions

# Thursday 10 March 2016, Morning

## Session 1

Room 112

*Chaired by: Sang Hoon Joo*

### 09:00 to 09:20

**Daniel Bick** *(Institut für Werkstoffe der Elektrotechnik 2, RWTH Aachen, Aachen, Germany)*, Jan Griesche, Felix Gunkel, Andreas Kindsmüller, Ilia Valov, Rainer Waser

Lifetime and Degradation of Perovskite Electrocatalysts for Oxygen Evolution Reaction in Alkaline Media

### 09:20 to 09:40

**Daniel Kimmich** *(Department of Chemistry, Carl von Ossietzky University Oldenburg, Oldenburg, Germany)*, Carsten Dosche, Dereje Hailu Taffa, Michael Wark, Gunther Wittstock

Photoelectrochemical screening of water splitting catalysts

### 09:40 to 10:00

**Taisei Sekiguchi** *(Graduate School of Engineering, Iwate University, Morioka, Japan)*, Yoshihiro Kadoma, Miyuki Kojima, Tatsuya Takeguchi, Koichi Ui
Effect of Cobalt-doped to Hollandite-type Manganese Oxides Nanoparticles on ORR and OER Activities

### 10:00 to 10:20

**Vladimir Guterman** *(Chemistry Faculty, Southern Federal University, Rostov-on-Don, Russia)*, Anastasiya Alekseenko, Sergey Belenov, Natalya Tabachkova, Vadim Volochaev

Supported Pt-containing Catalysts: Durability Against Activity

### 10:20 to 10:50

Coffee Break

*Chaired by: Woonsup Shin*

10:50 to 11:20 Invited

**Seong Ihl Woo** *(Department of Chemical and Biomolecular Enginering, EEWS, Korea Advanced Institue of Science and Technology, Daejeon, Korea),* Min Wook Chung, Jaekang Koh, Seung Yong Lee, Sung Hyeon Park

Morphological and Dimensional Effect of the Carbon on High Performing Oxygen Reduction Reaction Catalysts in Acidic Media

11:20 to 11:40

**Juergen Kahr** *(Mobility Department, AIT Austrian Institute of Technology, Vienna, Austria)*, Iliyan Popov, Tadios Tesfu-Zeru, Atanaska Trifonova

Bifunctional Catalysts in Li-Air Batteries for Automotive Applications

11:40 to 12:00

**Vivek J. Padmanabhan** *(Department of Chemistry, University of Liverpool, Liverpool, United Kingdom*), Laurence J. Hardwick, Richard J. Nichols

*In Situ* Surface Enhanced Infrared Spectroscopy Studies of Interfacial Processes Relevant to Nonaqueous Lithium-Oxygen Batteries

12:00 to 12:30 Invited

**Jong-Sung Yu** *(Department of Energy Systems Engineering, DGIST, Daegu, Korea)*, Fatemeh Razmjooei, Kiran Pal Singh, Min Young Song, Dea-Soo Yang

Non-Pt Carbon Electrocatalyst: Surface Properties and Electrocatalytic Activity

---

## Session 2

Room 101

*Chaired by: Artur Braun*

09:00 to 09:20

**Nils Baumann** *(Applied Electrochemistry, Fraunhofer Institute for Chemical Technology ICT, Pfinztal, Germany)*, Carsten Cremers, Florina Jung

Ni-Foam Anode GDEs for PEM-Water Electrolysis

09:20 to 09:40

**Lin Gan** *(Division of Energy and Envrionment, Graduate School at Shenzhen, Tsinghua University, Shenzhen, China)*, Hongda Du, Weiyan Liu

Trends in the Activity of Iron-Based Spinel Oxide Nanoparticles for Oxygen Evolution Electrocatalysis

09:40 to 10:00

**Christian Durante** *(Chemical Sciences, University of Padova, Padova, Italy)*, Armando Gennaro, Gaetano Granozzi, Valentina Perazzolo, Luca Picelli, Gian Andrea Rizzi

Synergistically Enhanced Performances of Pt Nanoparticles on Doped Mesoporous Carbon for Oxygen Reduction Reaction

10:00 to 10:20

**Yongjun Feng** *(State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, China)*, Dianqing Li, Pinggui Tang, Ran Tian

Highly Active Bifunctional Electrocatalysts Derived from Layered Double Hydroxides for Oxygen Reduction and Oxygen Evolution

10:20 to 10:50

Coffee Break

*Chaired by: F. Calle-Vallejo*

10:50 to 11:20 Invited

**Karl Mayrhofer** *(Helmholtz Institut Erlangen-Nürnberg (IEK 11), FZ Jülich, Erlangen, Germany)*, Serhiy Cherevko, Chang-Hyuck Choi, Olga Kasian

Is there an inverse relationship between activity and stability for OER and ORR catalysts?

11:20 to 11:40

**Youngmi Yi** *(Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Muelheim an der Ruhr, Germany)*, Sylvia Becker, Saskia Buller, Marina Prenzel, Robert Schlögl

Active and stable sites on carbon materials for oxygen electrocatalysis

11:40 to 12:00

**Daniel Schröder** *(Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Gießen, Germany)*, Conrad L. Bender, André Hilger, Jürgen Janek, Ingo Manke, Markus Osenberg

*In-Operando* Tomography of Na/$O_2$ Batteries: Visualizing the Growth of $NaO_2$-Particles at Various Current Densities

12:00 to 12:30 Invited

**Hyungjun Kim** *(Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon, Korea)*, Yoonhoo Ha, Hyung-Kyu Lim, Hyeyoung Shin

Design principles of electrochemical catalysts for $CO_2$ conversion

# Thursday 10 March 2016, Afternoon

## Session 1

Room 112

*Chaired by: Renate Hiesgen*

### 14:00 to 14:30 Invited

**Olaf Magnussen** *(Institute of Experimental and Applied Physics, Kiel University, Kiel, Germany)*, Philippe Allongue, Francesco Carla, Jacub Drnec, David Harrington, Fouad Maroun, Björn Rahn, Finn Reikowski, Martin Runge, Jochim Stettner

Operando X-ray Scattering Studies of Pt and Co Oxidation

### 14:30 to 14:50

**Da-Wei Wang** *(Chemical Engineering, University of New South Wales, Sydney, Australia)*

Reduction-induced surface amorphization enhances oxygen evolution activity in $Co_3O_4$

### 14:50 to 15:10

**Jakub Drnec** *(Experimental Division, European Synchrotron Radiation Facility, Grenoble, France)*, Francesco Carla, Roberto Felici, David A. Harrington, Olaf Magnussen, Björn Rahn, Finn Reikowski, Martin Ruge, Jochim Stettner

*In-Situ* x-Ray Diffraction Study of Pt(111) Oxidation during Oxygen Reduction Reaction

### 15:10 to 15:30

**Jiye Kim** *(Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Choonsoo Kim, Seonghwan Kim, Jeyong Yoon

Highly Efficient Chlorine Production Using a $RuO_2$/Blue $TiO_2$ Nanotube Array Hybrid Electrode

### 15:30 to 16:00 Invited

**Jinwoo Lee** *(Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea)*

Porous Structure Based High Performance Oxygen Electrocatalysts for Low Temperature Fuel Cells

### 16:00 to 16:30 Coffee Break

*Chaired by: Hye Jin Lee*

16:30 to 17:10 Keynote

**Hubert Girault** *(LEPA, EPFL, Sion, Switzerland)*, Véronique Amstutz, Jonnathan Hidalgo, Astrid Olaya, Pekka Peljo, Lucie Rivier, Heron Vrubel

Oxygen electrocatalysis at soft interfaces. Indirect water electrolysis using a vanadium/cerium redox flow battery

17:10 to 17:50 Keynote

**Dang-Sheng Su** *(Shenyang National Laboratory, Institute of Metal Research, Shenyang, China)*, K.-H. We

On the Activity Origin in Metal-Free Nitrogen-Doped Carbons for Oxygen Reduction Reaction and Their Mechanisms

17:50 to 18:30 Keynote

**Hideo Daimon** *(Science and Engineering, Doshisha University, Kyotanabe, Japan)*

Development of Highly Active Pt Core-Shell Catalyst for PEFCs

**Conference Dinner**, *Student Union bldg. 2, 1st floor*

---

## Session 2

Room 101

*Chaired by: Jinheung Kim*

14:00 to 14:30 Invited

**Zhi Liu** *(Division of Condensed Matter Physics and Photon Science, ShanghaiTech University, Shanghai, China)*

Probing Solid-Liquid Interface Using APXPS

14:30 to 14:50

**Tania Rodenas** *(Heterogene Reaktionen, MPI für Chemische Energiekonversion, Muelheim an der Ruhr, Germany)*, Sylvia Becker, Saskia Buller, Robert Schlögl, Youngmi Yi

Design and synthesis of Cobalt-MOF nanocrystals and graphitic carbon nanomaterials for electrochemical energy conversion

14:50 to 15:10

**Justus Masa** *(Analytical Chemistry and Center for Electrochemical Sciences, Ruhr-University Bochum, Bochum, Germany)*, Martin Muhler, Wolfgang Schuhmann, Ilya Sinev, Philipp Weide, Wei Xia

Electrocatalytic water oxidation using cobalt and nickel boride

15:10 to 15:30

**Dongyoon Shin** *(School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea)*, Xianghua An, Myounghoon Choun, Jaeyoung Lee

Effect of Transition Metal Induced Pore Structure on Oxygen Reduction Reaction of Electrospun Fibrous Carbon

15:30 to 16:00 Invited

**Pei Kang Shen** *(School of Physics and Engineering, Sun Yat-sen University, Guangzhou, China)*, Shuiping Luo

Nanoframe structured catalysts towards oxygen reduction reaction: A strategy to balance the activity and durability of the catalysts

16:00 to 16:30

Coffee Break

**Conference Dinner**, *Student Union bldg. 2, 1st floor*

# Friday 11 March 2016, Morning

## Session 1

Room 112

*Chaired by: Andreas Friedrich*

### 09:00 to 09:40 Keynote

**Piotr Zelenay** *(Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, USA)*, Hoon T. Chung, Edward F. Holby, Ulises Martinez, Geraldine M. Purdy, Xi Yin

Precious Metal-Free Electrocatalysts for Fuel Cell Applications: In Pursuit of Performance and Understanding

### 09:40 to 10:20 Keynote

**Yung-Eun Sung** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Dong Young Chung

Electrocatalyst design from nanoscale to macroscale for fuel cells

### 10:20 to 11:50

Coffee Break

*Chaired by: Wolfgang Schuhmann*

### 10:50 to 11:20 Invited

**Woonsup Shin** *(Department of Chemistry, Sogang University, Seoul, Korea)*, Mijung Park

Dental Amalgam as an Electrode Material for the Electrochemical Reduction of Carbon Dioxide to Formate

### 11:20 to 11:40

**Hyacinthe Randriamahazaka** *(ITODYS, CNRS UMR 7086, Univ. Paris Diderot, Sorbonne Paris Cité, Paris, France)*, Jalal Ghilane

Scanning Electrochemical Microscopy Interrogation of Electrodeposited Nanostructured Nickel Oxide for Oxygen Evolution Reaction

11:40 to 12:00

**Yuya Tada** (*Graduate School of Engineering, Iwate University, Morioka, Japan)*, Yoshihiro Kadoma, Miyuki Kojima, Akari Matsutomo, Tatsuya Takeguchi, Koichi Ui

Synthesis of Platinum Carbon Composite Catalyst by Ethanol Reduction Method and Its Electrochemical Properties

12:00 to 12:30 Invited

**Tatsumi Ishihara** *(International Institute for Carbon Neutral Energy Research, Kyushu University, Fukuoka, Japan)*, Shintaro Ida, Atsushi Inoishi, Hack Ho Kim

Reversible Type Solid Oxide Fuel Cells and Applied for Energy Storage

---

## Session 2

Room 101

*Chaired by: Hubert Girault*

10:50 to 11:20 Invited

**Peter Strasser** *(Department of Chemistry, Technical University Berlin, Berlin, Germany)*

Water splitting on Ir oxide-based electrocatalysts: From single crystals to core shell particles

11:20 to 11:40

**Kaido Tammeveski** *(Institute of Chemistry, University of Tartu, Tartu, Estonia)*, Urmas Joost, Arunachala Kannan, Ivar Kruusenberg, Sander Ratso, Protima Rauwel, Rando Saar, Ave Sarapuu

Iron, cobalt-containing nitrogen-doped carbon nanotubes for oxygen reduction reaction

11:40 to 12:00

**Gerda Seiffarth** *(Technische Chemie, Martin-Luther-Universität, Halle (Saale), Germany)*, Michael Bron, Mathias Kühhirt, Matthias Steimecke, Till Walther

$Ni_xCo_yFe_2O_4$ on carbon supports as bifunctional electrocatalysts – an active material for both oxygen evolution and oxygen reduction reaction

12:00 to 12:30 Invited

**Artur Braun** *(High Performance Ceramics, Empa, Duebendorf, Switzerland)*, Debajeet K. Bora, Florent Boudoire, Edwin C. Constable, Michael Graetzel, Jinghua Guo, Yelin Hu

Water oxidation with holes: What we learn from operando studies

# Poster Presentations

*Chaired by: Hyungjun Kim and Jaeyoung Lee*

All posters will be on display on
Wednesday from 10:00 to 20:00

# Poster Presentations

## s1-001

**Prabhakarn Arunachalam** *(Department of Chemsitry, Science College, Riyadh, Saudi Arabia)*, Almayouf Abdullah, T. Weller Mark, Al Ghanem Mohamed

Stronitum iron oxychoride as electrocatalyst for oxygen evolution reaction in alkaline solution

## s1-002

**Junhwan Baek** *(Department of Chemical Engineering, Inha University, Incheon, Korea)*, Mingyu Kim, Yongsug Tak

Fabrication of Pt-Co Alloy for Polymer Electrolyte Membrane Fuel Cell Cathode by Sequential Pulse Electrodeposition Method

## s1-003

**Stefan Barwe** *(Analytical Chemistry, Center for Electrochemical Sciences, Ruhr-Universität Bochum, Bochum, Germany)*, Corina Andronescu, Jordi Arbiol, Aziz Genç, Stefan Klink, Justus Masa, Wolfgang Schuhmann, Edgar Ventosa

MnxCoyOz Nanocubes Embedded in a Polybenzoxazine-derived Nitrogen-Doped Graphite-type Carbon Matrix as New Catalyst for the Oxygen Evolution Reaction

## s1-004

**Debajeet K, Bora** *(High Performance Ceramics, Empa, Duebendorf, Switzerland),* Artur Braun, Miguel Modestino, Christophe Moser

Ni electrocataylsts functionalized membrane electrode assembly for hydrogen generation

## s1-005

**Artur Braun** *(High Performance Ceramics, Empa, Duebendorf, Switzerland)*, Debajeet K. Bora, Edwin C. Constable, Giuseppino Fortunato, Catherine E. Housecroft, Niamh S. Murray, Rita Toth, Roche M. Walliser

Self-assembled Ru-Co based molecular POM WOC

## s1-006

**Marina Bukhtiyarova** *(Heterogeneous Reactions, Max Planck Institue for Chemical Energy Conversion, Muelheim a.d. Ruhr, Germany)*, Robert Schlögl

Chemical Energy Storage by Methanol Synthesis at Dynamic Change of Reaction Conditions

s1-007

**Saskia Buller** *(Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany)*, Marius Heise-Podleska, Robert Schlögl

Systematic Studies of Binder Free Non-Noble Electrocatalytic Disc Materials

s1-008

**Federico Calle-Vallejo** *(Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, Leiden, Netherlands)*, Aliaksandr S. Bandarenka, David Loffreda, Philippe Sautet

What Types of Defects Enhance the Activity of Platinum for the Oxygen Reduction Reaction?

s1-009

**Yanxia Chen** *(Department of Chemical Physics, University of Science and Technology of China, Hefei, China)*

New insights on the electrocatalysis of oxygen reduction reaction

s1-010

**Ho Sum Samson Cheng** *(Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China)*, Chi Yuen Chung

A Novel Solid-State Li-air Battery using Inorganic Garnet-Type Electrolyte

s1s1-011

**Serhiy Cherevko** *(Electrocatalysis, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany)*, Simon Geiger, Olga Kasian, Karl J. J. Mayrhofer

Activity and Stability of Thermally Treated Iridium Hydrous Oxides for the Oxygen Evolution Reaction

s1-012

**Chang Hyuck Choi** *(Department of Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany)*, Karl J. J. Mayrhofer

Oxygen Reduction by Single-Atom Pt: Selective Production of $H_2O_2$ instead of $H_2O$

s1-013

**SangWon Choi** *(Department of Chemical Engineering, Inha University, Incheon, Korea)*, Boyoon Shin, Yongsug Tak

Electrochemical Behaviors of Aluminum Anode in Ionic Liquid Electrolyte for Al-ion Battery

s1-014

**Juhyuk Choi** *(Department of Chemical and Biomolecular Engineering, KAIST, Daejeon, Korea)*, Hyunjoo Lee, Jinkyu Lim, Chi-Woo Roh

Stability Enhancement of Octahedral PtNi Nanoparticles for the Oxygen Reduction Reaction by Bromine Treatment

s1-015

**Myounghoon Choun** *(School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea)*, Jaeyoung Lee, Dongyoon Shin

Polydimethylsiloxane Treated Cathode Catalyst Layer to Prolong Hydrogen Fuel Cell Lifetime

s1-016

**Dong Young Chung** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Yung-Eun Sung

Ordered intermetallic nanoparticles as highly active and durable electrocatalyst for oxygen reduction reaction

s1-017

**James Digol** *(Department of Chemical Engineering, University of the Philippines - Diliman, Quezon City, Philippines)*, Jaeyoung Lee, Joey Ocon

$CoMn_2O_4$ Anchored on N-doped 3D Hierarchical Porous Carbon Derived from Biomass as an Oxygen Reduction Reaction Catalyst for Zinc-Air Batteries

s1-018

**Joanna Dolinska** *(Department of Electrode Processes, Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland)*, Arunraj Chidambaram, Marcin Holdynski, Wojciech Lisowski, Marcin Opallo, Liza Rassaei

Electrocatalytic Oxidation of Water on Copper Nanoparticles Modified Electrodes

s1-019

**Miao-Syuan Fan** *(Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan)*, Kuo-Chuan Ho, Chia-Liang Sun, Yu-Hao Tseng

Fiber-like Reduced Graphene Oxide Nanoribbons as an Electrocatalytic Material for Dye-Sensitized Solar Cells

s1-020

**Naoko Fujiwara** *(Research Institute of Electrochemical Energy, Advanced Industrial Science and Technology (AIST), Ikeda, Japan)*, Hajime Arai, Tsutomu Ioroi, Tsukasa Nagai, Zempachi Ogumi

Reversible Air Electrodes Based on Perovskite Oxide and Sb-doped $SnO_2$ in Zinc-Air Secondary Batteries

s1-021

**Karl Adrian Gandionco** *(Department of Chemical Engineering, University of the Philippines Diliman, Quezon City, Philippines)*, Jaeyoung Lee, Joey Ocon

Electrocatalytic Reduction of Carbon Dioxide ($CO_2$) into Cn Organic Molecules on Nanostructured Copper-Gold Electrodes

s1-022

**Jing Gao Gao** *(Department of Applied Chemistry, Zhejiang University of Technology, hangzhou, China),* Wei Yang Yang

Preparation of WC/MMT nanocomposite and its electrocatalytic activity for methanol oxidation

s1-023

**Sang Wook Han** *(Department of Chemistry, Sungkyunkwan University, Suwon, Korea),* Dae Han Kim, Soong Yeon Kim, Il Hee Kim, Young Dok Kim, Eun Ji Park, Ki Jung Park

Low Temperature CO Oxidation Catalyzed by $NiO/Al_2O_3$

s1-024

**Jaejin Han** *(Department of Chemistry and Chemical Engineering, Inha University, Incheon, Korea)*, Jinsub Choi, Moon-su Kim

Application of Dimensionally Stable Anode for Vanadium Redox Flow Battery

s1-025

**Feng Han** *(Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany)*, Rémi Costa, Robert Semerad, Patric Szabo

Processing and Electrochemical Performance of Metal Foam Supported Solid Oxide Fuel Cells with Nanostructured Anode and Thin-film Electrolyte

s1-026

**Sujik Hong** *(School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, GIST, Gwangju, Korea)*, Seunghwa Lee, Jaeyoung Lee

Morphological Effect on Product Selectivity of Electrochemical Reduction of $CO_2$ on Cu Catalyst

s1-027

**Akimitsu Ishihara** *(Institute of Advanced Sciences, Yokohama Natioanl University, Yokohama, Japan)*, Makoto Hamazaki, Yuji Kohno, Koichi Matsuzawa, Shigenori Mitsushima, Ken-ichiro Ota

Durability of Titanium-Niobium Oxides Mixed with $Ti_4O_7$ as Non-Precious- and Carbon-Free Cathodes for PEFCs in $H_2SO_4$ at 80 ºC

s1-028

**Inyoung Jang** *(Department of Energy Engineering, Hanyang University, Seoul, Korea)*, Chanho Kim, Sungmin Kim, Ungyu Paik, Heesung Yoon

Fabrication of Thin Films on Anode Support with Surface Modification for High Efficient IT-SOFC by Dip-coating Method

s1-029

**Hansaem Jang** *(School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea)*, Jaeyoung Lee, Youngeun Park

Fuel Heterogeneity in Solid Oxide Carbon Fuel Cells: Carbon Disproportionation and its Reverse Reaction

s1-030

**Jaehoon Jeong** *(School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea)*, Xianghua An, Jaeyoung Lee, Dongyoon Shin

Unravelling the Effect of Improved Mesoporous Structure in Fibrous Carbon for Oxygen Evolution Reaction

s1-031

**Vinayak Kale** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Taeghwan Hyeon, Ki Tae Nam, Uk Sim

Heteroatom doped graphitic Carbon Nitride Nanostructures as Efficient Catalyst for Oxygen Evolution Reaction

s1-032

**Jin Soo Kang** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Dong Young Chung, Jin Kim, Myeong Jae Lee, Yung-Eun Sung

Electrochemical Synthesis of Nanostructured Transition Metal Carbides for Hydrogen Evolution Reaction

s1-033

**Jin Soo Kang** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Dong Young Chung, Heejong Shin, Yoonjun Son, Yung-Eun Sung

Room-Temperature Synthesis of Nanostructured Transition Metal Nitride Electrocatalysts for Oxygen Evolution Reaction

s1-034

**Parisa (Fatemeh) Karimi** *(Department of Chemical Engineering, Queens University, Kingston, Canada)*, Aimy Bazylak, Brant Peppley

Studying the Impact of Several Supporting Materials on the Structure and Catalyst Activity of Ruthenium Oxide Nanoparticles for the Oxygen Evolution Reaction in PEM Water Electrolysis

s1-035

**Balwinder Kaur** *(Department of Chemistry, Indian Institute of Technology Ropar, Ropar, India)*, Rajendra Srivastava

Synthesis of $CeO_2$ Decorated Nanocrystalline Zeolite Based Nanocomposite Material and Its Application in the Electrocatalytic Oxidation of Methanol

s1-036

**Il Hee Kim** *(Department of Chemistry, Sungkyunkwan University, Suwon, Korea)*, Sang Wook Han, Dae Han Kim, Soong Yeon Kim, Young Dok Kim, Ki Jung Park, Eun Ji Park

Low Temperature CO Oxidation Catalyzed by $NiO/SiO_2$ Prepared by Atomic Layer Deposition

s1-037

**Sung-Wook Kim** *(Nuclear Fuel Cycle Process Development Group, Korea Atomic Energy Research Institute, Daejeon, Korea)*

Noble Metal Anodes for Electrolytic Reduction in Pyroprocessing

s1-038

**Nam-In Kim** *(Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, Korea),* Sung Ryul Choi, Jun-Young Park, In-Seop So

Carbon Nanotube-supported Metal Oxide catalysts for Bifunctional Oxygen Electrode Catalysts

s1-039

**Ho Young Kim** *(School of Energy and Chemical Engineering, Ulsan National Institute of Science and Techonolgy (UNIST), Ulsan, Korea)*, Sang Hoon Joo, Young Jin Sa, Sung Dae Yim

Self-Supported Pt-Ni Mesostructures as Ultrastable Oxygen Reduction Reaction Electrocatalysts in Proton Exchange Membrane Fuel Cell

s1-040

**Sungmin Kim** *(Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST)*, Daejeon, Korea)

*Metal Valency* Change during Oxygen Reduction Reaction at Fe-$N_4$ Catalyst

s1-041

**Minho Kim** *(Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon, Korea)*, Chang Hyuck Choi, Minkee Choi, Hyungjun Kim

Kinetic Selectivity of Oxygen Reduction Reaction on a Single-Atom Catalyst: Application of Marcus Theory to Proton-Coupled Electron Transfer

s1-042

**Sang Hoon Kim** *(Center for Materials Architecturing, Korea Institute of Science and Technology, Seoul, Korea)*, Jiyoung Byun, Yunjeong Choe, Thi May Do

Magnetite coated metallic support as one-body catalyst for Electro-Fenton reactions

s1-043

**Hyungjin Kim** *(Department of Advanced Chemicals and Engineering, Chonnam National University, Gwangju, Korea)*

A study on effects of oxidation time of carbon felt electrode on chemical and electrochemical properties for all vanadium redox flow battery

s1-044

**Yong-Tae Kim** *(SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Korea)*, Yong Ho Kim, Jaeyoung Lee

Engineering of Supramolecular Protein Assembly for Elucidation of High-Performance Oxygen Reduction Reaction

s1-045

**Chanho Kim** *(Department of Energy Engineering, Hanyang University, Seoul, Korea)*, Inyoung Jang, Sungmin Kim, Ungyu Paik, Heesung Yoon

Cost effective IT-SOFC by adopting surface-doped ceria for anode support layer

s1-046

**Seoni Kim** *(Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Jiye Kim, Seonghwan Kim, Jaehan Lee, Jeyong Yoon

Electrocatalysis-integrated Strategy for Lithium Recovery from Industrial Wastewater

s1-047

**Ju Seong Kim** *(Materials Science and Engineering, Seoul National University, Seoul, Korea)*, Eun-suk Jeong, Kisuk Kang, Hyunah Kim, Inchul Park

Amorphous Cobalt Silicate Hydroxide Electrocatalyst for Water Oxidation

s1-048

**Mi-Ju Kim** (*School of Chemical & Biological Engineering, Seoul National University, Seoul, Korea)*, Yun Sik Kang, Yung-Eun Sung

Controlling of Specific Adsorption in Oxygen Reduction Reaction by Modification of Platinum-Based Nanocatalysts

s1-049

**Seonggyu Lee** *(Chemical Engineering, POSTECH, Pohang, Korea)*, Jinwoo Lee

Effects of Pore Size and Doping-Site Position of Metal-Free Oxygen Reduction Catalysts in the Membrane Electrode Assemblies for Alkaline Fuel Cells

s1-050

**Seunghwa Lee** *(School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea)*, Jaeyoung Lee

Electrocatalytic Conversion of $CO_2$ to Multi-Carbon Fuels on a Chloride-Induced $Cu_2O$-Cu Catalyst

s1-051

**Sang Ha Lee** *(School of Chemical Engineering, Sungkyunkwan University, Suwon, Korea)*, Misuk Cho, Won Bin Kim, Soochan Kim, Youngkwan Lee

Fabrication of porous iridium oxide/graphene film using pyrolysis for oxygen evolution catalysis

s1-052

**Hae-Min Lee** *(Institute of NT. IT Fusion Technology, Ajou University, Suwon, Korea)*, Hwang Bo Jung, Chang-Koo Kim

Environmentally benign synthesis of graphene based binary metal oxides for electrochemical capacitors

s1-053

**Myeong Jae Lee** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Dong Young Chung, Jin Soo Kang, Yun Sik Kang, Kug-Seung Lee, Yung-Eun Sung

Effects of hydrous metal oxide blended catalyst for efficient CO management in polymer electrolyte membrane fuel cell

s1-054

**Hae-Min Lee** *(Institute of NT. IT Fusion Technology, Ajou University, Suwon, Korea)*, Hwang Bo Jung, Chang-Koo Kim

A facile synthesis and electrochemical analysis of vanadium nitride for electrochemical capacitors

s1-055

**Seonggeun Lee** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*

Effect of Crystal Structure of $TiO_2$ Nanotube Array on Capacitive and Oxidant-generating Properties Formed by Electrochemical Self-doping

s1-056

**Guohua Li** *(Applied Chemistry, Zhejiang University of Technology, Hangzhou, China)*

Preparation of Tungsten Carbide with Different Morphologies and Their Electrochemical Properties

s1-057

**Hyung-Kyu Lim** *(Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon, Korea)*, Hyungjun Kim

Mechanistic Role of Ionic-liquid/water Mixture in Enhanced Electrochemical $CO_2$ Reduction

s1-058

**Ying Liu** *(Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China)*, Chiyuen Chung

Ag-$CeO_2$ Composites as Electrocatalysts for Lithium-Air Batteries

s1-059

**Sawanta Mali** *(School of Advanced Chemical Engineering, Chonnam National University, Gwangju, Korea)*, Chang Kook Hong, Hyungjin Kim

Secondary hydrothermally processed engineered $TiO_2$ nanostructures for efficient perovskite solar cells: Role of nanorod length, precursor solution concentration and etching time

s1-060

**Justus Masa** *(Analytical Chemistry and Center for Electrochemical Sciences, Ruhr-University Bochum, Bochum, Germany)*, Wolfgang Schuhmann, Daniela Wintrich

Rotating-ring disk electrodes: Effect of the choice of the redox mediator on the Ring collection efficiency; Case of adsorption of $CN^-$ anions on platinum

s1-061

**Cyriac Massue** *(Inorganic Chemistry, Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany)*, Sebastien Cap, Verena Pfeifer, Robert Schlögl

Characterization of amorphous Ir-oxohydroxides for the Oxygen Evolution Reaction

s1-062

**Nozomi Matsuhashi** *(Graduate School of Engineering, Iwate University, Morioka, Japan)*, Koichi Ui, Yoshihiro Kadoma, Miyuki Kojima, Akari Matsutomo, Tatsuya Takeguchi

Effects of Pore Volume on Discharge Reaction of Carbon Electrodes for Lithium-air Secondary Battery

s1-063

**Ibrahim Mohamed** *(Bionanosystem Engineering, Chonbuk National University, Jeonju, Korea)*, M. Shaheer Akhtar, Nasser A. M. Barakat

Enhancement of the Photovoltaic Performance of Dye Sensitized Solar Cell using $TiO_2/SnO_2$ Nanofibers as a Photoanode

s1-064

**Hend Mohamed** *(Bionanosystem Engineering, Chonbuck National University, Jeonju, Korea)*, Nasser A. M. Barakat, M. Obaid

Feature performance of activated carbon charcoal as anode material on power generation in single air cathode MFC using food waste water

s1-065

**Yeongdong Mun** *(Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea)*, Min Jeong Kim, Jinwoo Lee, Young-Eun Sung

Soft-template approach to One-pot synthesis of Mesoporous Fe/N/C for Non-precious metal catalyst of Oxygen reduction

s1-066

**Bongjin Mun** *(Physics and Photon Science, GIST, Gwangju, Korea)*

Surface stability of Pt skin-layer in $Pt_3Ni(111)$ under oxidation environment

s1-067

**Sebastian Neugebauer** *(Heterogeneous Catalysis, Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany)*, Sebastien Cap, Robert Schlögl, Ioannis Spanos, Youngmi Yi

Standardized Measurements for Oxygen Evolution Reaction-Rotating Disk Electrode Measurements and Beyond

s1-068

**Jonas Ohms** *(Institut für Anorganische und Analytische Chemie, Albert Ludwigs Universität Freiburg, Freiburg, Germany)*, Philipp Hillebrand, Philipp Kurz

Behaviour of Birnessite Coated Electrodes Operated as Water Oxidation Anodes

s1-069

**Marcin Opallo** *(Department of Electrode Processes, Institute of Physical Chemistry PAS, Warszawa, Poland)*, Wojciech Adamiak, Saustin Dongmo, Hubert Girault, Justyna Jedraszko, Wojciech Nogala, Gunther Wittstock

Electrocatalytic $O_2$ reduction at Room Temperature Ionic Liquid|Water Interface

s1-070

**Ebru Ozer** *(Department of Chemistry, Technische Universität, Berlin, Germany)*, Tobias Reier, Camillo Spöri, Peter Strasser

Ir (111)/(110) and Ru (0001) single crystals as model catalysts for the oxygen evolution reaction: Oxide formation and electrocatalytic activity

s1-071

**Dong-Won Park** *(Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany)*, Natalia A. Cañas, K. Andreas Friedrich, Norbert Wagner

Novel solvent-free direct coating process for battery electrodes and their electrochemical performance

s1-072

**Ji Eun Park** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Yong-Hun Cho, Sung-jun Kim, Yung-Eun Sung

Application of Graphene Foam on Flow Field of Bipolar Plates in Polymer Electrolyte Membrane Fuel Cells

s1-073

**Han-Saem Park** *(Department of Energy Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea)*, Hyun-Kon Song

Ruthenium oxide nanoparticles embedded in carbon matrix as a durable bifunctional catalyst for Zn-air batteries

s1-074

**Fatemeh Razmjooei** *(Dept. of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, Korea)*, Kiran Pal Singh, Jong-Sung Yu

A New Class Electroactive Fe and P-Functionalized Graphene for Oxygen Reduction

s1-075

**Oonhee Rhee** *(Department of Chemical Engineering, Inha University, Incheon, Korea)*, Jinsub Choi, Minkyeong Jeong, Gibaek Lee

Self-organized anodic titanium oxide microcones for Li-ion battery application

s1-076

**Ahmed S. Yasin** *(Bionanosystem Engineering, Chonbuk National Universiy, Jeonju, Korea)*

Photo-assisted& electro-oxidation of organic pollutants using Zirconium Doped Titanium Dioxide Nanofibers

s1-077

**Young Jin Sa** *(Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea)*, Jae Yeong Cheon, Sang Hoon Joo, Youngsik Kim, Jinwoo Woo

Highly Active and Durable Bifunctional Oxygen ElectrocatalystsBased on Graphitic Nanoshell/Mesoporous Carbon Hybrids for Rechargeable Aqueous Na-Air Batteries

s1-078

**Gunther G. Scherer** *(Electrochemistry Laboratory, TUM CREATE, Singapore, Singapore)*, Tam Nguyen Duy, Zhichuan J. Xu

A Facile Synthesis of Size-Controllable $IrO_2$ and $RuO_2$ Nanoparticles for Oxygen Evolution Reaction

s1-079

**Gerda Seiffarth** *(Technische Chemie, Martin-Luther-Universität, Halle (Saale), Germany)*, Michael Bron, Matthias Steimecke

Raman-coupled scanning electrochemical microscopy - investigation of oxygen evolution at NiFe thin film electrodes

s1-080

**Bora Seo** *(Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea),* Hu Young Jeong, Sang Hoon Joo, Young Jin Sa, Jinwoo Woo

Size-Dependent Activity Trends in Combination with In Situ X-ray Absorption Spectroscopy Reveal Insights into Cobalt Oxide Catalyzed Bifunctional Oxygen Electrocatalysis

s1-081

**Silver Sepp** *(Institute of Physical Chemistry, University of Tartu, Tartu, Estonia)*, Heisi Kurig, Enn Lust, Jaak Nerut, Indrek Tallo, Kersti Vaarmets

Activity and Stability of Hierarchical Microporous-Mesoporous Carbon Supported Pt-Catalysts in PEMFC Application

s1-082

**Joongpyo Shim** *(Department of Nano & Chemical Engineering, Kunsan National University, Gunsan, Korea)*, Kareen Lopez, Gyungse Park, Ho-Jung Sun

Electrochemical Characterization of Ag deposited on $La_{1-x}Sr_xCoO_3$ for ORR and OER in an Alkaline Solution

s1-083

**Mun-Sik Shin** *(Department of Environmental Engineering, Sangmyung University, Cheonan, Korea)*, Moon-Sung Kang, Hyoung-Juhn Kim, Jin-Soo Park

Anion-conducting ionomer binders for solid alkaline fuel cells

s1-084

**Hyeyoung Shin** *(Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea)*, Hyungjun Kim

Computational strategies for designing and discovering $CO_2$ electro-conversion catalysts.

s1-085

**SeungMin Shin** *(Sungkyunkwan Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan, Suwon, Korea)*, Yong-Tae Kim, Yong Ho Kim

Fabrication of Novel Catalyst Assembly by Engineering Mussel Adhesive Proteins Mimics for Associating Carbon Nanotube

s1-086

**Dongyoon Shin** *(School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea)*, Xianghua An, Myounghoon Choun, Jaeyoung Lee

Unravelling the Electrocatalytic Activity of Oxygen Evolution Reaction on the Charged Carbon Species by Incoporated Metal

s1-087

**Heejong Shin** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Dong Young Chung, Yung-Eun Sung, Ji Mun Yoo

Scaffold-like Titanium Nitride Nanotube with a Highly Conductive Porous Architecture as a Nanoparticle Catalyst Support

s1-088

**Kirapal Singh** *(Energy Systems Engineering, Daegu Gyeongbuk Institute of Science & Technology (DGIST), Daegu, Korea)*, Min Young Song, Jong-Sung Yu

Iodine-Treated Heteroatom-Doped Carbon: Conductivity Driven Electro-catalytic Activity

s1-089

**Min-ah Song** *(ElchemFaraday R&D Lab, Elchemtech Co., Ltd., Seoul, Korea)*

Preparation and Evaluation of Ir-Pt/Nafion117/Pt MEA by Electroless deposition method

s1-090

**Kersti Vaarmets** *(Institute of Chemistry, University of Tartu, Tartu, Estonia),* Enn Lust, Jaak Nerut, Silver Sepp

Time Stability Tests for Pt Nanoclusters Modified Carbide Derived Carbons Catalysts in 0.5 M $H_2SO_4$ Solution

s1-091

**Kuang-Hsu Wu** *(Catalysis Division, Shenyang National Laboratory, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China)*, Dang-Sheng Su, Da-Wei Wang

Extending Analytical Methods for the ORR Evaluation Based On the Electrokinetics On a Rotating Ring-Disk Electrode

s1-092

**Jingjing Xiao** *(Department of Chemistry, Fudan University, Shanghai, China),* Hubert Girault, Lei Liao, Baohong Liu, Yujie Liu, Huiying Xu

Mesoporous Graphene as a Synergistic Electrocatalyst Matrix for High-Performance Hydrogen Evolution and Oxygen Reduction Reaction

s1-093

**Jingjing Xiao** *(Department of Chemistry, Fudan University, Shanghai, China),* Lei Liao, Baohong Liu, Yi Tang, Qingbin Wu

N-graphene-NbOx Hybrid Nanosheets with Sandwich-Like Structure as Electrocatalyst for Oxygen Reduction Reaction

s1-094

**Junyuan Xu** *(Shenyang National Laboratory, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China)*, Dang-Sheng Su

Electrocatalytic reduction of carbon dioxide enhanced by surface nitrogen atoms of doped nanocarbon

s1-095

**Fengchun Yang** *(College of Chemistry & Material Science, Northwest University, Xian, China)*, Xin Zhang, Hanzhi Zhang

Separation of Single-walled Carbon Nanotubes and Their Electrochemical Behaviors Study

s1-096

**Youngmi Yi** *(Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Muelheim an der Ruhr, Germany)*, Sylvia Becker, Mark Greiner, Robert Schlögl, Gisela Weinberg

Electrochemical degradation of glassy carbon under the condition for oxygen evolution in acidic vs. alkaline media

s1-097

**Ji Mun Yoo** *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Dong Young Chung, Heejong Shin, Yung-Eun Sung

ZIF Encapsulation: Simple Route for Synthesis of PtCo Intermetallic Nanoparticles for Highly Durable Oxygen Reduction Reaction Catalyst

s1-098

**Jihyun Yu** *(School of Chemical and Biological Engineering, Seoul National University, Seoul , Korea)*, Junil Kang, Taeyoung Kim, Jeyong Yoon

Major redox reaction and its control in long-term capacitive deionization

s1-099

**Kangjong Kim** *(Department of Chemistry, Kunsan National University, Gunsan, Korea)* Ho-Jung Sun, Joongpyo Shim, Gyungse Park

Synthesis of Co-containing metal-organic frameworks and their application to cathode materials in Zn-air batteries

s1-100

**Anja Talke** *(Fuel Cells, Daimler AG, Kirchheim Teck, Germany)* Ulrich Misz, Gerhard Konrad, Angelika Heinzel

Impact of air contaminants on automotive fuel cells under realistic operating conditions – dynamic drive cycle

s1-101

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

Cationic Pore-filled Polyelectrolyte Membranes for Electrochemical Energy Conversion Processes

s1-102

**Sam Yoon** *(Mechanical Engineering, Korea University, Seoul, Korea)* Hyun Yoon, Min-woo Kim, Hong Seok Jo

Enhanced photoelectrochemical solar water splitting using a platinum-decorated CIGS/CdS/ZnO photocathode

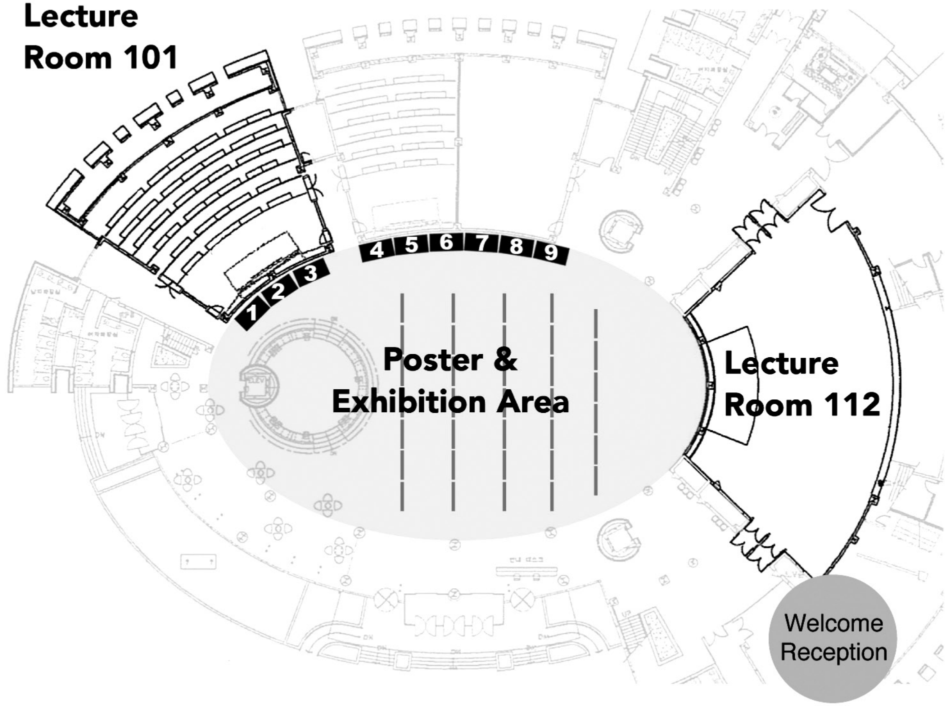
s1-103

**Sam Yoon** *(Mechanical Engineering, Korea University, Seoul, Korea)* Hyun Yoon, Min-woo Kim, Mukund Mali, Tae Yoon Ohm

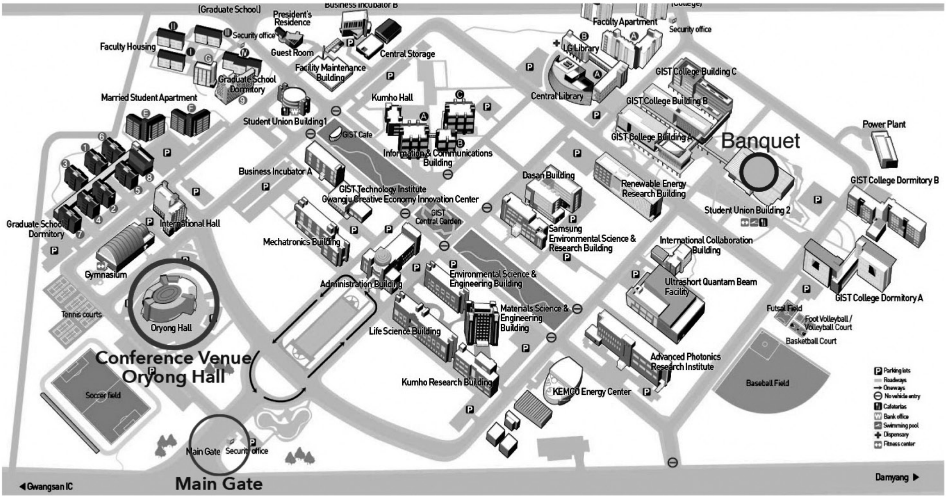
Nano-textured Pillars of Electrosprayed Bismuth Vanadate for Efficient Photoelectrochemical Water Splitting

# Index

# Floor plan



# Campus Map



# Electrocatalyst design from nanoscale to macroscale for fuel cells

Yung-Eun Sung*, Dong Young Chung

*Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 151-742, Korea*
*School of Chemical & Biological Engineering, Seoul National University, Seoul 151-742, Korea*
*ysung@snu.ac.kr*

Due to being highly efficient and environmentally friendly, fuel cells are one of the most promising energy conversion devices. However, the sluggish kinetics of the oxygen reduction reaction and poor long-term stability are still big hurdles. One of the important strategies to improve both activity and durability is nanoscale architecturing. Developments that have been achieved by tailoring the activity of catalyst through alloying and core-shell at the nanoscale level was suggested. However, the atom-level design of the nanoparticle structure is still challenging. Here, we will discuss the synthesis highly durable and active alloy and core-shell nanoparticles and evaluation of electrochemical performance. Another approaches to obtain high performance and stability are optimizing electrode structure. To utilize nanostructure on real application, catalyst design based on the membrane electrode assembly (MEA) is highly important. Applying support-less metal systems with very thin electrode structure such as inverse-opal structure and 1-d nano-architecture alloy catalyst will be discuss in terms of high activity and long-term stability. Finally, non-noble electrocatalyst for oxygen reduction reaction electrocatalyst will be discussed based on the electrochemical analysis and materials design.

# Development of Highly Active Pt Core-Shell Catalyst for PEFCs

Hideo Daimon[1], Shunya Higuchi[1], Yuki Matsui[1], Kota Mizoue[1], Kosuke Okuno[1],
Naoya Aoki[2], Hideo Inoue[2], Takayuki Doi[1], and Minoru Inaba[1]
*[1]Doshisha University, Kyoto, 610-0321 Japan [2]Ishifuku Metal Industry, Saitama, 340-0002 Japan*
*E-mail: rs-dh21@mail.doshisha.ac.jp*

Cost reduction of PEFCs is crucial for real commercialization of fuel cell vehicles. PEFCs employ expensive Pt catalyst and a high Pt loading is required in cathode due to sluggish kinetics of oxygen reduction reaction (ORR). Thus, enhancement of the ORR activity is a key for the Pt usage reduction. Carbon supported Pd core-Pt shell catalyst (Pt/Pd/C) is a promising alternative to a conventional carbon supported Pt catalyst (Pt/C) because of high Pt utilization and enhancement of the ORR activity [1]. We developed a modified Cu under potential deposition (Cu-UPD)/Pt replacement process for mass-production of the Pt/Pd/C catalyst [2]. However, the Pd core dissolves under the PEFC cathode condition owing to its lower redox potential relative to that of the Pt [3]. Recently, we found that the ORR mass activity of the Pt/Pd/C catalyst was enhanced with an accelerated durability test (ADT) [2]. The ADT thickened the Pt shell and induced a compressive strain in the Pt shell associated with the Pd core dissolution. In order to further enhance the ORR mass activity of the Pt/Pd/C catalyst, we explored potential cycling protocol using a glassy carbon (GC) electrode and developed a Cu-$O_2$ treatment for mass-production of highly active Pt/Pd/C catalyst.

Pt/Pd/C catalyst was prepared with a modified Cu-UPD/Pt replacement process [2]. A carbon supported Pd core (Pd/C, 4.2 nm, 30 wt.%, Ishifuku Metal Industry) was ultrasonically dispersed in 50 mM $H_2SO_4$ containing 10 mM $CuSO_4$ and stirred with co-existence of a metallic Cu sheet at 5ºC under Ar atmosphere. After 5 h's stirring, the Cu sheet was removed and $K_2PtCl_4$ was added to replace the Cu shell with the Pt shell, by which the Pt/Pd/C catalyst was obtained. The Pt/Pd/C catalyst was characterized by TG, XRF, XRD, TEM, STEM-EDX, CV and XAFS. ORR activity of the Pt/Pd/C catalyst was evaluated with RDE technique in $O_2$ saturated 0.1 M $HClO_4$ at 25ºC. ADT was performed using a rectangular wave potential cycling (0.6 V (3 s)-1.0 V (3 s) *vs*. RHE) in Ar saturated 0.1 M $HClO_4$ at 80ºC for 10,000 cycles.

Electro-chemical surface area (ECSA) and ORR activity of the Pt/Pd/C catalyst are summarized in Table 1 together with a carbon supported Pt catalyst (Pt/C, 2.8 nm, 46 wt.%, TKK). The ORR mass activity of the Pt/Pd/C catalyst was enhanced with the ADT and the enhancement arose from increase of the ORR specific activity. Thus, much higher ORR mass activity can be obtained if the ECSA decay is mitigated. We found that a new potential cycling protocol (rectangular wave potential cycling of 0.4 V (300 s)-1.0 V (300 s) *vs*. RHE, High Activation Protocol: HAP) mitigates the ECSA decay (Table 1).

In order to scale-up the HAP on the GC electrode, we developed a Cu-$O_2$ treatment where equilibrium potentials of Cu/$Cu^{2+}$ (ca. 0.3 V) and ORR (ca. 1.0 V) are used. The Pt/Pd/C catalyst (100 mg) was dispersed in 2 M $H_2SO_4$ containing 0.1 M $CuSO_4$. Then, the Cu sheet was immersed into the solution and stirred for 300 s under Ar atmosphere. Next, the Cu sheet was removed and the $O_2$ was introduced for 300 s with stirring. In the Cu-$O_2$ treatment, ca. 0.3 V is applied to the catalyst when the catalyst contacts with the Cu sheet and ca. 1.0 V is applied to the catalyst when the $O_2$ is introduced.

Change in the electrochemical properties of the Pt/Pd/C catalysts after the HAP (30 cycles) and the Cu-$O_2$ treatment (30 cycles) is summarized in Table 1. All properties after the Cu-$O_2$ treatment are almost equivalent to those of the HAP, indicating that the Cu-$O_2$ treatment mimics the HAP on the GC electrode and is suitable for mass-production of highly active Pt/Pd/C catalyst.

**Table 1 ECSA and ORR activity of Pt/C and Pt/Pd/C catalysts**

| Catalyst | ECSA ($m^2$/g) | Specific activity (μA/$cm^2$) | Mass activity (A/g-Pt) |
|---|---|---|---|
| Pt/Pd/C, As prepared | 133 | 235 | 312 |
| Pt/Pd/C, After ADT | 37 | 1172 | 434 |
| Pt/Pd/C, After HAP | 75 | 813 | 610 |
| Pt/Pd/C, After Cu-$O_2$ | 67 | 913 | 612 |
| Pt/C, As received | 75 | 340 | 255 |
| Pt/C, After ADT | 25 | 568 | 142 |

This work was supported by New Energy and Industrial Technology Development Organization (NEDO), Japan.

[1] J. Zhang *et al*., *J. Phys. Chem. B*, **108**, 10955 (2004).
[2] M. Inaba and H. Daimon, *J. Jpn. Petrol. Inst*., **58**(2), 55 (2015).
[3] K. Sasaki *et al*., *Angew. Chem. Int. Ed*., **49**, 8602 (2010).

# Precious Metal-Free Electrocatalysts for Fuel Cell Applications: In Pursuit of Performance and Understanding

Piotr Zelenay, Edward F. Holby, Hoon T. Chung, Ulises Martinez, Geraldine M. Purdy, Xi Yin
*Materials Physics and Applications Division*
*Los Alamos National Laboratory*
*Los Alamos, New Mexico 87545, USA*
*zelenay@lanl.gov*

Precious metal-free catalysts for oxygen reduction reaction (ORR) have received significant attention as a possible replacement of catalyst formulations primarily based to date on platinum and platinum alloys. The main drivers of that research have been the reduction of cost and, possibly, also performance enhancement of polymer electrolyte fuel cells (PEFCs), especially those under development for higher power applications, including automotive propulsion. Major performance progress has been accomplished by using high-temperature synthesis of precious metal-free ORR catalysts, pursued by a number of research groups in North America, Europe, and Asia. Through those efforts a possible replacement of Pt and Pt-alloys in the PEFC cathode with earth-abundant elements, such as Fe, Co, Mn, N, and C, has by now become a realistic possibility, contingent upon meeting stringent requirements set forth by the fuel cell industry (by now mostly fulfilled by precious metal catalysts). In addition to meeting high electrocatalytic activity, successful precious metal-free catalysts must exhibit good long-term stability, which is a major challenge in the strongly acidic environment of proton-conducting polymers. Today's precious metal-free catalysts seem to be especially vulnerable at high cathode potentials reached, for however brief periods of time, during the fuel cell stack startup and shutdown. In turn, low ORR activity results in thick electrodes, limiting performance at high power. It can also lead to high cost of fuel cell stack components, potentially outweighing the low cost of the catalyst itself. In that context, a better understanding of the origin of ORR activity of precious metal-free catalysts is imperative for the successful development of viable catalysts for fuel cell applications.

Most recently, improvements in performance and performance durability of precious metal-free catalysts have been pursued *via* the use of highly porous carbon matrices, maximization of the density of sites perceived as imparting catalytic activity (*e.g.*, N-coordinated transition metal atoms), implementation of highly graphitic nanostructures to assure better long-term stability, and the use of other than iron transition metals to minimize peroxide generation within the catalyst phase.

One approach to achieving controlled functionality of precious metal-free ORR catalysts has involved graphene- and graphene-oxide-based model systems, combined with advanced theory, modeling and simulation. In this approach, successful incorporation of nitrogen heteroatoms into the graphitic structures of the starting precursors has been obtained either by high-temperature processing using chemical methods or by low-temperature physical techniques. The density functional theory (DFT) and *ab initio* molecular dynamics has been also used to characterize the structural properties and activity of possible active sites. That part of research has focused on the active-site molecular configuration, surface accessibility, sensitivity to N and Fe chemical potentials, response to an aqueous environment, and adsorption of ORR intermediates. Structurally, particular attention has been paid to the clustering tendencies of different N-coordinated structures.

# Electrochemical interfaces, electrocatalysis and green energy

**Nenad M. Markovic,**
**Materials Science Division, Argonne National Laboratory, USA**

In recent years, improvements in the fundamental understanding of electrochemical interfaces and their role in electrocatalytic processes have started to revolutionize the development of alternative energy systems for clean energy production, storage and conversion. In this presentation, we describe how a synergistic interaction between fundamental science and technological progress has resulted in both the development of greatly enhanced understanding of electrocatalytic systems and the development of materials that can efficiently transform chemical energy into electricity, and synthesize chemicals that can be stored and reused in energy conversion systems. We begin by discussing the oxygen electrochemistry in aqueous-based environments, focusing on the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) on well-characterized metals, metal/metal-oxides and complex oxide materials. Then, by addressing functional links between activity and stability of electrode materials we define the landscape of parameters that control the efficiency of the water energy cycle that incorporates a complex bond making and bond breaking events between hydrogen, oxygen and water molecules. We also propose key descriptors that are controlling reactivity of electrochemical interfaces during the ORR and OER in fuel cells and elecytrolyzers.

In the second part, we argue that in many respects the subject of dioxygen electrochemistry in organic solvents is much less advanced than the corresponding understanding of interfaces in aqueous systems. This is due to the long-standing difficulty associated with developing *in situ* methods that are capable of characterizing interfaces at atomic-/molecular levels in organic solvents. One prime example is Li-$O_2$ electrochemistry that has been studied on ill-defined, polycrystalline and/or high surface area cathode materials in organic solvents containing trace levels of water and other impurities that, even in ppm levels, can dominate interfacial properties. Not surprisingly, then, it has been very difficult to reproduce many claims of high re-chargeability and reversibility of the Li-$O_2$ battery systems. This intrinsic disparity in understanding water-based and organic-based solvents, however, has a tendency to mask the inherently close ties that may exist between interfacial phenomena in aqueous and organic environments. In this lecture, we build a bridge between dioxygen electrochemistry in alkaline and ether-based environments in order to yield unique insights into the synergetic nature of double layer interactions and provide an integrated, stepwise link between inherently multicomponent electrochemical interfaces and the role of various components that control dioxygen electrochemistry in Li-$O_2$ systems. We conclude that understanding the complexity (simplicity) of electrochemical interfaces would open new avenues for design and deployment of alternative energy systems.

# Oxygen electrocatalysis at soft interfaces
# Indirect water electrolysis using a Vanadium/Cerium Redox flow Battery

Hubert H. Girault, V. Amstutz, J. Hidalgo, A. Olaya, P. Peljo, L. Rivier, H. Vrubel
*Laboratoire d'Electrochimie Physique et Analytique*
*Rue de l'Industrie 17, 1951 Sion*
*Hubert.Girault@epfl.ch*

This keynote lecture will include two different parts.

The first part will review our work at a polarized liquid interfaces both to reduce water and to photo-oxidise water.
For oxygen reduction, we shall discuss first oxygen reduction using molecular catalysts such as porphyrins self assembled as dimers (1) to drive a four electron oxygen reduction and using gold nanoparticles catalysts assembled as a gold film act as an electrocatalysts for oxygen reduction by decamethylferrocene.
Then, we shall discuss how the self-assembly of organic molecules such as tetrathiafulvalene can be used to reduce water (2) and we shall further discuss how self-assembly could be used for water photo-oxidation.
We shall also discuss water oxidation on $IrO_2$ nanoparticles in mixed solvent systems (3).

The second part of the lecture will present our pilot plant for making hydrogen on demand using a Vanadium/Cerium redox flow battery. The concept here is to chemically discharge the battery by reacting on a floating electrocatalyst a solution of Vanadium (II) in sulfuric acid (4). We shall present data using a 10kW/50 kWh battery able to produce a kilo of hydrogen a day at high pressures.
The second aspect of the chemical discharge is the reduction of a solution of Ce(IV) in sulfuric acid on a floating electrocatalyst to produce oxygen but more importantly to produce protons to balance the system.
The principle of electrocatalysis on a electrically floating supported catalysts will be discussed.

1. A.J. Olaya, D. Schaming, P.-F. Brevet, H. Nagatani, T. Zimmermann, J.Vanicek, H.J. Xue, C.P. Gros, J.M. Barbe and H.H. Girault, J. Am. Chem. Soc., 138 (2012) 498, A.J. Olaya, D. Schaming, P.-F. Brevet, H. Nagatani, H.J. Xu, M. Meyer and H.H. Girault, Angew. Chem., 51 (2012) 6447
2. A.J. Olaya, P.Y. Ge, J.F. Gonthier, P. Pechy, C. Corminboeuf and H.H. Girault, J. Am. Chem. Soc., 133 (2011) 12115
3. J.C. Hidalgo-Acosta, M.A. Méndez, M.D. Scanlon, H. Vrubel, V. Amstutz, W. Adamiak, M. Opallo and H.H. Girault, Chem. Sci., 6 (2015) 1761-1769
4. V. Amstutz, K.E. Toghill, F. Powlesland, H. Vrubel, C. Comninellis, X. Hu and H.H. Girault Energy Eng. Sci., 7 (2014) 2350-2358

# On the Activity Origin in Metal-Free Nitrogen-Doped Carbons for Oxygen Reduction Reaction and Their Mechanisms

K.-H. Wu[1,2], D. S. Su[1,*]
[1] *Shenyang National Laboratory, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, Liaoning, 110016 China;* [2] *School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, QLD 4072, Australia;* [3] *School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia.*

[*] *e-mail: dssu@imr.ac.cn*

## Abstract

The origin of oxygen reduction reaction activity in metal-free N-doped carbons has been a stimulating, yet unsolved issue for the rational design of cost-effective electrocatalysts for fuel cells and metal–air batteries. At present, there are several inconsistent opinions on the materials chemistry and the mechanism of the oxygen reduction reaction (ORR) performed on this type of materials. This presentation provides a brief overview of the current understanding of ORR processes and the history of electrocatalyst development. With special attention, this work focuses on the major contentions of the current opinions towards metal-free N-doped carbon chemistry and the arguments for the probable ORR mechanisms. By clarifying the fundamental aspects of each opinion, a converging consensus on N-doped carbon electrocatalysts can be established and thus facilitate the substantial development of large-capacity energy devices.

In the first part, the history of the electrocatalyst development and how the research converges into the class of metal-free N-doped carbons are described for a brief background. Along the path, we will discuss in order the significant contentions in three major aspects: (1) the activity of metal impurities, (2) the configuration of active nitrogen functional groups and (3) the involvement of physical and chemical structures of the carbon framework. All of these questions have been under serious debates. Beyond that, a summary of the converging general consensuses derived from the debates about the activity origin in N-doped carbons are provided. Furthermore, the general understanding of the ORR mechanism, considering only on N-doped carbons, are reviewed on the aspects of preferential $O_2$ adsorption and the reaction pathway through either associative or dissociative mechanism, based on modern computational methods and classical chemical reactivity perspective. Finally, some potential future directions are put forward as to motivate the research towards further fundamental understanding of the ORR.

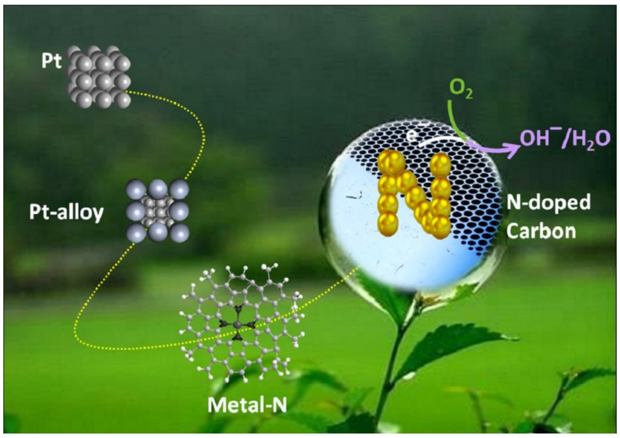


Fig. 1. A general scheme about the evolution of ORR electrocatalysts.[1]

## Reference

[1] K.-H. Wu, D.-W. Wang, D.-S. Su, I. R. Gentle, *ChemSusChem* **2015**, *8*, 2772-2788.

# On the surface chemistry of OER electrodes

Robert Schlögl
*Fritz-haber-institut der MPG, Faradayweg 4-6 D 14195 Berlin, Germany*
*www.fhi-berlin.mpg.de*

Water splitting is a crucial element in any sustainable energy system with larger amounts of primary renewable electricity generation. This historic process suffers from fundamental and technological shortcomings with respect to the requirements of a world-scale application with volatile energy input.

The oxygen evolution reaction is a critical issue as we have few well-working electrode systems and see extensive over-potentials in oxygen evolution. Multiple attempt are made to better the situation and many publication report success albeit little of that success transforms into tangible technology. Issues of testing the performance are here of relevance as much as a still fundamental lack of understanding the underlying elementary processes.

This presentation addresses the intricacy generated by the convolution of the performance of several interfaces involved. It further addresses our findings in the chemical dynamics[1-4] of the electrolyte-electrode interface generated by the reaction products of OER and by the components of the electrolyte. These findings create a gap between the theoretical models and the experimental observations hindering a concise deconvolution of the overall performance into elementary reactions.

[1] R. Arrigo, M. Hävecker, M.E. Schuster, C. Ranjan, E. Stotz, A. Knop-Gericke, R. Schlögl, In Situ Study of the Gas-Phase Electrolysis of Water on Platinum by NAP-XPS, Angew. Chem. Int. Ed. 52 (2013) 11660-11664.
[2] Y.T. Law, S. Zafeiratos, S.G. Neophytides, A. Orfanidi, D. Costa, T. Dintzer, R. Arrigo, A. Knop-Gericke, R. Schlögl, E.R. Savinova, *In situ* investigation of dissociation and migration phenomena at the Pt/electrolyte interface of an electrochemical cell, Chem. Sci. 6 (2015) 5635-5642.
[3] T. Reier, Z. Pawolek, S. Cherevko, M. Bruns, T. Jones, D. Teschner, S. Selve, A. Bergmann, H.N. Nong, R. Schlögl, K.J.J. Mayrhofer, P. Strasser, Molecular Insight in Structure and Activity of Highly Efficient, Low-Ir Ir–Ni Oxide Catalysts for Electrochemical Water Splitting (OER), J. Am. Chem. Soc. ASAP (2015).
[4] J. Velasco Velés, V. Pfeifer, M. Hävecker, R.S. Weatherup, R. Arrigo, C.-H. Chuang, E. Stotz, G. Weinberg, M. Salmeron, R. Schlögl, A. Knop-Gericke, Photoelectron spectroscopy at the graphene-liquid interface reveals the electronic structure of an electrodeposited cobalt/graphene electrocatalyst, Angew. Chem. Int. Ed. (2015).

# Novel method for improving carbon corrosion resistance for polymer electrolyte membrane fuel cells using water electrolysis catalyst

Woong Hee Lee, Hansung Kim*
*Dept. of Chemical and Biomolecular Engineering , Yonsei University, Rep. of Korea*
*134 Shinchon-Dong, Seodaemun-gu, 120-749*
*Seoul, Korea*
*e-mail: elchem@yonsei.ac..kr*

The issue of electrochemical carbon corrosion has received much attention because it is considered to be one of the critical determinants of the lifetime of polymer electrolyte membrane fuel cells (PEMFCs). According to the mechanism of electrochemical carbon corrosion, carbon reacts with water and produces $CO_2$ which is the main product of carbon corrosion

In the present study, we adopted a new strategy for tackling the carbon corrosion problem especially occurring at the cathode. Unlike previous approaches, in which corrosion-resistant materials were developed, this method was designed to remove water from the catalyst layer of a PEMFC. In our previous study, the presence of water was found to be indispensable for electrochemical carbon corrosion [1]. No electrochemical carbon corrosion occurred under dry conditions, even at a high oxidative overpotential. Based on this result, the addition of water electrolysis catalyst to the catalyst layer of the cathode was proposed as a method of removing water. Water electrolysis catalyst promotes oxygen evolution, which is the anodic reaction during water electrolysis. The presence of water electrolysis catalysts in the cathode catalyst layer of PEMFC was hypothesized to decompose water molecules around the carbon supports if the potential was increased under carbon corrosion conditions. As a result, electrochemical carbon corrosion was expected to be suppressed. Moreover, we attempted to decrease the amount of water electrolysis catalysts used while preserving the resistance to electrochemical carbon corrosion. The effects of water electrolysis catalyst content on carbon corrosion was investigated and optimized. The water electrolysis catalyst content was decreased further by improving OER catalytic activity, which is achieved by shape control of Ir nanoparticles.

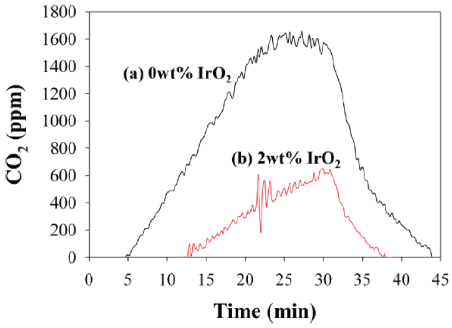


**Fig. 1** Comparison of $CO_2$ mass spectra for the MEAs (a) without $IrO_2$ and (b) with 2 wt % $IrO_2$ in the cathode catalyst layer of the PEMFC. Corrosion tests were performed at 1.6 $V_{NHE}$ with a humidifier temperature of 70 °C.

Figure 1 shows a mass spectrogram indicating $CO_2$ production during the corrosion test in the presence and absence of $IrO_2$ in the catalyst layer. The MEA without $IrO_2$ displayed $CO_2$ evolution 5 min after the start of the corrosion test. The concentration of CO2 increased to 1600 ppm and then decreased after the corrosion test was terminated. In contrast, the MEA containing $IrO_2$ began to release $CO_2$ 12 min after the start of the corrosion test and showed considerably less $CO_2$ generation. The total amount of CO2 generated (248 μL) was less than that generated by the MEA without $IrO_2$ (1018 μL) by a factor of 4.1. This observation indicated that electrochemical carbon corrosion was substantially inhibited by the addition of $IrO_2$.

[1] K. H Lim, H Oh, S. Jang, Y. Ko, H. Kim, H. Kim, Effect of operating conditions on carbon corrosion in polymer electrolyte membrane fuel cells J Power Sources 193 (2009) 575.

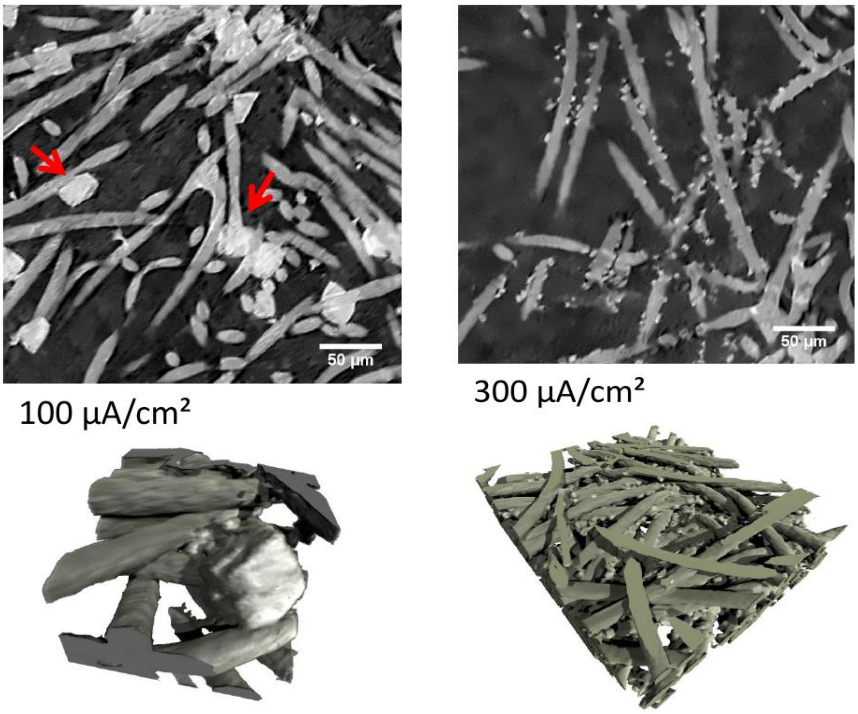
# In-Operando Tomography of Na/$O_2$ Batteries: Visualizing the Growth of $NaO_2$-Particles at Various Current Densities

Daniel Schröder[a,*], Conrad L. Bender[a], André Hilger[b], Markus Osenberg[b], Ingo Manke[b], Jürgen Janek[a]
[a] *Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, 35392 Gießen, Germany,* [b] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany,* * *daniel.schroeder@phys.chemie.uni-giessen.de*

Amongst other next-generation battery types, Na/$O_2$ batteries are very appealing for future energy storage applications. Despite continuous progress [1], fundamental challenges for improved Na/$O_2$ batteries prevail: understanding the oxygen electrode reaction and the formation of reaction products in detail. Both processes are essential to further enhance the performance and cycle life of Na/$O_2$ batteries [2].

Recent studies have shown that in-operando X-ray tomography is highly suitable to gain detailed understanding of the underlying processes during battery discharge [3,4]. In this work, we apply ex-situ and in-operando synchrotron X-ray tomography on an in-house Na/$O_2$ battery set-up with the aim to elucidate the spatial distribution of the reaction product $NaO_2$ in the battery cathode. Batteries were discharged at 100, 200 and 300 µA/cm², respectively, to visualize the impact of current density on the reaction product deposition inside the gas diffusion electrode. Furthermore we aim to visualize dendrite formation in the anode of the batteries investigated. Fig. 1 shows examples of the results obtained: we observe that large 20-µm-sized cubical particles of $NaO_2$ are formed at lowest current density, whereas smaller 5-µm-sized particles form at high current density operation.

Our analysis yields a comprehensive insight into the formation of $NaO_2$ and helps to understand limitations inside the cathode and anode. From this results, we gain further understanding of the underlying processes and derive limitations for Na/$O_2$ battery operation, which in the end might help to improve their performance and cycle life.



100 µA/cm²

300 µA/cm²

Fig. 1: X-ray tomography of two cathodes, extracted from discharged Na/$O_2$ cells.

**References:**

[1] C. L. Bender, P. Hartman, M. Vracár, P. Adelhelm, J. Janek, Adv. Energy Mater. 1301863 (2014).
[2] Ortiz-Vitoriano et al., Journal of Physical Chemistry Letters 6(13) (2015), 2636–2643.
[3] D. Schröder, T. Arlt, I. Manke, U. Krewer, Electrochem. Comm. 40 (2014) 88–91.

# Is there an inverse relationship between activity and stability for OER and ORR catalysts?

S. Cherevko, S. Geiger, N. Hodnik, G. Keeley, C. Choi, C. Baldizzone, J. Grote, O. Kasian, A. Zeradjanin, K.J.J. Mayrhofer
*Department of Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung, Max-Planck-Strasse 1, 40237 Düsseldorf, Germany*
mayrhofer@mpie.de
*Forschungszentrum Jülich, "Helmholtz-Institut Erlangen-Nürnberg" (IEK11), Nägelsbachstrasse 49b, 91052 Erlangen, Germany*

The oxygen reduction and the oxygen evolution reaction are essential for continuous electrochemical flow reactors for efficient conversion of electrical energy into chemicals and vice versa, i.e. fuel cells and electrolyzers. The electrocatalyst materials, which constitute the core of electrochemical energy conversion devices, however are still a bottleneck for their efficiency. While the optimization of kinetics of electrocatalysts has been widely explored, the highly important stability of the materials has only recently gained more attention. In this presentation I will discuss different types of degradation processes on various material classes considered for OER and ORR. Based on studies utilizing IL-TEM for structural characterization as well as SFC/ICP-MS for time-resolved, online dissolution determination, I will compare activity data with stability under various conditions. Finally I will try to answer the question if catalyst activity and stability is necessarily connected, or if this general believe is over-simplified and they are de-coupled from each other.

*1. Katsounaros, I.; Cherevko, S.; Zeradjanin, A.R.; Mayrhofer, K.J.J.; Oxygen Electrochemistry as a Cornerstone for Sustainable Energy Conversion; Angewandte Chemie – International Edition 2014, 53, 102 – 121.*
*2. Topalov, A.A.; Cherevko, S.; Zeradjanin, A.R.; Meier, J.C.; Katsounaros, I.; Mayrhofer, K.J.J.; Towards a comprehensive understanding of platinum dissolution in acidic media; Chemical Science, 2014, 5, 631-638.*
*3. Cherevko, S.; Topalov, A.A.; Zeradjanin, A.R.; Katsounaros, I.; Mayrhofer, K.J.J.; Gold dissolution: towards understanding of noble metal corrosion; RSC Advances 2013, 3, 16516-16527.*
*4. Reier, T.; Pawolek, Z.; Cherevko, S.; Bruns, M.; Jones, T.; Teschner, D.; Selve, S.; Bergmann, A.; Nong, H.N.; Schlögl, R.; Mayrhofer, K.J.J.; Strasser, P.; Molecular insight in structure and activity of highly efficient, low-Ir Ir-Ni oxide catalysts for electrochemical water splitting (OER), J. Am. Chem. Soc., 2015.*
*5. Choi, C.H.; Baldizzone, C.; Grote, J.; Schuppert, A.K.; Jaouen, F.; Mayrhofer, K.J.J.; Stability of Fe-N-C Catalysts in Acidic Medium Studied by Operando Spectroscopy; Angew. Chem. Int. Ed., 2015.*
*6. Schuppert, A.K.; Savan, A.; Ludwig, A.; Mayrhofer, K.J.J.; Potential-resolved dissolution of Pt-Cu: A thin-film material library study; Electrochimica Acta 2014, 144, 332 – 340.*
*7. Meier, J.C.; Galeano, C.; Katsounaros, I.; Witte, J.; Bongard, H.J.; Topalov, A.A.; Baldizzone, C.; Mezzavilla, S.; Schüth, F.; Mayrhofer, K.J.J.; Design criteria for stable Pt/C fuel cell catalysts; Beilstein J. Nanotechnology 2014, 5, 44 – 67.*

# Operando X-ray Scattering Studies of Pt and Co Oxidation

O. M. Magnussen[1], M.Ruge[1], F. Reikowski[1], B. Rahn[1], J. Stettner[1], D.A. Harrington[2], F. Maroun[3], P. Allongue[3], J. Drnec[4], F. Carlà[4], R. Felici[4]
[1] *Institute of Experimental and Applied Physics, Kiel University*
*Olshausenstr. 40, 24118 Kiel, Germany*
[2] *Department of Chemistry, University of Victoria*
*Box 3065, Victoria, BC, Canada, V8W 3V6*
[3] *Physique de la Matière Condensée, Ecole Polytechnique*
*CNRS, 91128 Palaiseau, France*
[4] *Experimental Division, ESRF*
*71 Avenue des Martyrs, 38000 Grenoble, France*
*magnussen@physik.uni-kiel.de*

Understanding of oxygen evolution and reduction reactions and the electrochemical formation and reduction of oxide layers on metal electrode surfaces are two closely related topics. On metal electrodes, these reactions often occur on oxide covered surfaces and the oxide has a pronounced influence on the surface reactivity. Even on noble metal electrodes ultrathin oxide layers are present in the positive potential regime relevant for OER. More recently, transition metal oxides themselves are getting much attention as earth-abundant catalyst materials. Furthermore, oxide formation/reduction processes are of great importance for the stability of electrocatalysts. Nevertheless, only a limited body of data on these processes and on the electrode structure under OER and ORR conditions exists. As will be shown here for the case of Pt and Co, surface X-ray diffraction (SXRD) methods using synchrotron radiation provide a powerful tool for *in situ* studies of structural changes of metal electrodes during oxidation/reduction reactions on the atomic or nanometer scale.

The electrochemical formation and reduction of surface oxides on Pt surfaces is an extensively studied process and is known to involve place exchange between metal and oxygen atoms, leading to surface roughening upon potential cycling. In this work detailed SXRD data and parallel single crystal voltammetry were obtained on Pt(111) electrodes in oxygen-free and oxygen-containing perchloric acid solution. These measurements allowed direct quantitative study of the place exchange during Pt oxidation and subsequent reduction. Place exchange initially is fully reversible up to a threshold coverage of exchanged Pt surface atoms, above which the formation of nanoscale Pt mounds is observed in oxidation/reduction cycles. The temporal evolution of the lateral mound size was measured by *in situ* grazing incidence small angle x-ray scattering as a function of cycle number and potential, revealing a characteristic saturation behavior.

Iron-group oxides, in particular Co oxides, are recently receiving increasing interest as Pt-free catalysts for OER reaction in light-driven water splitting. For further development of these materials deeper insight into the structure of these electrocatalytic materials as well as into suitable preparation procedures is highly desirable. The latter is also required for clarifying more complex, synergetic effects, such as the strong increase in the OER activity of Co oxide on Au surfaces as compared to the bare oxide. Motivated by this, the electrochemical oxidation of thin epitaxial Co(001) films, formed by electrodeposition on Au(111) and consisting of nanoscale crystallites, was studied by *in situ* SXRD in alkaline solution. In the potential regime of Co hydroxide formation a rapid reduction of the amount of hcp Co is observed, while the characteristic height of the Co crystallites decreases only slightly. On longer times scales, growth of 3D crystals of $Co(OH)_2$ as well as irreversible Co dissolution into the electrolyte occurs. On the basis of the structural observations oxidation of the Co film is proposed to proceed via fast formation of an ultrathin passivating layer, followed by nucleation and growth of 3D hydroxide crystals at the grain boundaries in the Co deposit.

# Platinum Dissolution as one of the main Fuel Cell Electrocatalyst Degradation Mechanisms

Serhiy Cherevko, Gareth P. Keeley, Simon Geiger, George Polymeros, Olga Kasian, Nadiia Kulyk, Karl J.J. Mayrhofer
*Department of Interface Chemistry and Surface Engineering, Max-Planck Institut für Eisenforschung*
*Max-Planck-Str. 1, 40237, Düsseldorf , Germany*
cherevko@mpie.de

The instability of electrocatalysts is one of the major obstacles to the commercialization and widespread application, *e.g.* in the automotive industry, of low-temperature fuel cells. Together with carbon corrosion, platinum dissolution is one of the primary degradation mechanisms in carbon-supported platinum (Pt/C) anode and cathode electrocatalysts in proton exchange membrane fuel cells (PEMFCs). The other mechanisms such as Ostwald ripening, particle detachment, and particle agglomeration are secondary degradation mechanisms as they are typically triggered by either platinum dissolution or carbon corrosion or both [1]. Despite intensive research in the last decade, not only does the complex interplay between primary and secondary mechanisms in real PEMFCs remain unclear, but even "simple" platinum dissolution is still poorly understood.

Instability of platinum oxygen reduction reaction (ORR) catalysts in the corrosive acidic environment at the cathode of a PEMFC arises from the thermodynamic tendency of platinum to ionize. The resulting ions either move in electrolyte as a soluble complex or remain on the electrode as a practically insoluble oxide. Hence, dissolution of platinum at equilibrium can be in principle estimated. A typical example would be dissolution at open circuit potential (OCV). During operation, however, equilibrium conditions are rarely met – dissolution is dictated by kinetics. This is especially true for short potential spikes to highly anodic potentials, typical in PEMFCs during start-up and shut-down.

In this work we discuss the complexity of platinum dissolution in relation to the application of Pt-based catalysts in PEMFCs. The discussion is based on data obtained in our group over the last several years using an electrochemical scanning flow cell (SFC) inductively coupled plasma mass spectrometer (ICP-MS) based setup and numerous literature reports, especially on the equilibrium platinum dissolution [2-6]. Besides the data on platinum bulk stability, new results on high-surface-area model Pt/C electrocatalysts dissolution and an effect of catalyst loading and mass-transfer on platinum stability will be communicated [2, 7]. Special attention will be given to the dissolution of Pt/C at elevated temperatures. Experimental data will be used in the discussion of the mechanisms of equilibrium and non-equilibrium (both happening during platinum oxidation and platinum oxide reduction) platinum dissolution. In the end, a unified picture of platinum dissolution in the operational range of fuel cells will be presented and mitigating strategies for suppression of platinum dissolution will be discussed.

**References:**

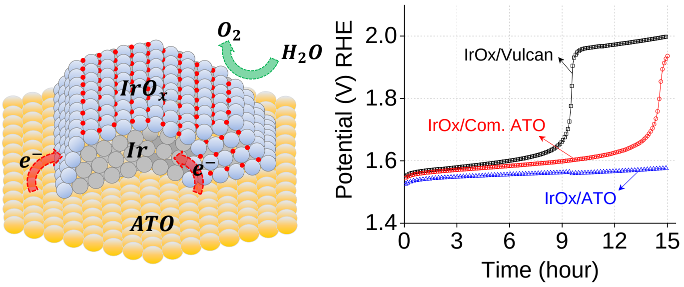
[1] I. Katsounaros, S. Cherevko, A.R. Zeradjanin, K.J.J. Mayrhofer, Angew. Chem. Int. Ed., 53 (2014) 102-121.
[2] S. Cherevko, G.P. Keeley, S. Geiger, A.R. Zeradjanin, N. Hodnik, N. Kulyk, K.J.J. Mayrhofer, ChemElectroChem, 2 (2015) 1471-1478.
[3] S. Cherevko, A.R. Zeradjanin, G.P. Keeley, K.J.J. Mayrhofer, J. Electrochem. Soc., 161 (2014) H822-H830.
[4] S. Cherevko, A.A. Topalov, A.R. Zeradjanin, G.P. Keeley, K.J.J. Mayrhofer, Electrocatalysis, 5 (2014) 235-240.
[5] X. Wang, R. Kumar, D.J. Myers, Electrochem. Solid-State Lett., 9 (2006) A225-A227.
[6] P.J. Ferreira, G.J. la O', Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, H.A. Gasteiger, J. Electrochem. Soc., 152 (2005) A2256-A2271.
[7] G.P. Keeley, S. Cherevko, K.J.J. Mayrhofer, ChemElectroChem, (2015) DOI:10.1002/celc.201500425.

# Carbon-Free $IrO_x$ Electrocatalysts Supported on Sb-doped $SnO_2$ for the Oxygen Evolution Reaction in acid PEM water electrolyzers

Hyug-Suk Oh[1], Hong Nhan Nong[1], Tobias Reier[1], Detre Teschner[2] and Peter Strasser[1]*
[1]*Department of Chemistry, Technical University Berlin, Berlin, Germany*
[2] *Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Plank-Gesellschaft, Berlin, Germany*
*hyung-suk.oh@tu-berlin.de*

The polymer electrolyte membrane water electrolyzer (PEMWE) technology has received much attention to produce pure hydrogen, because it has high operating current density, energy efficiency, easy operation, compactness and greater operating safety.[1, 2] However, a key limitation of PEMWE is the high cost and high loading of the anodic electrocatalyst for the oxygen evolution reaction (OER). This catalyst is generally incorporates metal oxides of very scarce and expensive precious metal, such as $IrO_2$ and $RuO_2$.[3-5] This is why, as the number of the produced PEMWEs units increases, it will become critically important to significantly reduce the amount of these precious metals per PEMWE unit. To solve this issue, we used the antimony doped tin oxide (ATO) as high surface area support, which stabilizes the initial catalyst surface area, and hence the mass based activity of the catalysts.[6] In additional, the nanostructured iridium nanodendrites (Ir-ND) supported on ATO as efficient and stable water splitting catalysts for PEM electrolyzers. The active Ir-ND structures exhibited superior structural and morphological properties, such as particle size and surface area compared to commercial state-of-art Ir catalysts. Supported on tailored corrosion-stable conductive oxides, the Ir-ND catalysts exhibited a more than 2-fold larger kinetic water splitting activity compared with supported Ir nanoparticles, while showing excellent durability under galvanostatic mode of 1 mA cm$^{-2}$ in a period of 15 hour.[7] In order to propose the role of metal-oxide support in PEM electrolyzers, the electronic structure of ATO supported $IrO_x$ catalyst was also studied using X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS).

***Keywords**: Water Splitting, PEM water electrolyzer, Hydrogen, Oxygen evolution reaction (OER), Stability*



## References

1. J. Nieminen, I. Dincer and G. Naterer, *International Journal of Hydrogen Energy*, 2010, **35**, 10842-10850.
2. S. A. Grigoriev, V. I. Porembskiy, S. V. Korobtsev, V. N. Fateev, F. Auprêtre and P. Millet, *International Journal of Hydrogen Energy*, 2011, **36**, 2721-2728.
3. T. Reier, M. Oezaslan and P. Strasser, *ACS Catalysis*, 2012, **2**, 1765-1772.
4. E. Antolini, *ACS Catalysis*, 2014, **4**, 1426-1440.
5. Y. Lee, J. Suntivich, K. J. May, E. E. Perry and Y. Shao-Horn, *The Journal of Physical Chemistry Letters*, 2012, **3**, 399-404.
6. H.-S. Oh, H. N. Nong and P. Strasser, *Advanced Functional Materials*, 2015, **25**, 1074-1081.
7. H.-S. Oh, H. N. Nong, T. Reier, M. Gliech and P. Strasser, *Chemical Science*, 2015, **6**, 3321-3328.

# Scanning Electrochemical Microscopy Interrogation of Electrodeposited Nanostructured Nickel Oxide for Oxygen Evolution Reaction

Hyacinthe Randriamahazaka, Jalal Ghilane

*Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS*
*15 rue Jean-Antoine de Baïf, 75202 Paris Cedex 13, France*
*hyacinthe.randria@univ-paris-diderot.fr*

The increased interest in direct conversion of solar energy into storable fuels has led to intensified research efforts with respect to artificial photosynthesis. The water oxidation half-reaction has often been identified as a bottleneck in artificial photosynthetic devices, and much research has been focused in the development of inexpensive and efficient electrocatalysts from abundant elements. Then, recent research efforts have been concentrated on the development and understanding of oxygen evolution reaction (OER) electrocatalysts. However, the application of such catalysts under the conditions of the OER faces severe challenges related to the activity, the stability, and the abundance of the materials used.

Herein, we investigate the electrochemical properties of nanostructured nickel oxide surfaces with respect to OER. These nanostructured surfaces are prepared by means of electrodeposition. Electrodeposition is attractive because this technique enables us to selectively synthesize materials onto conductive substrates. Moreover, its possible control of morphology by tuning applied current densities or potential appears applicable to the synthesis of nanostructured materials. Scanning electron microscopy (SEM) and X-ray photoelectron spectrometry (XPS) are used to characterize the surface. We find that the applied potential and the duration of the electrodeposition control the morphology of the electrode interface (Figure 1). The electrocatalytic properties of nanostructured nickel oxide surfaces are studied. We show that the nanostructured nickel oxide electrodeposited on carbon ultramicroelectrode is able to sustain a current density of 140 mA/cm$^2$ at 0.7 V. Furthermore, we use scanning electrochemical microscopy (SECM) in the substrate generation/tip collection (SG/TC) to follow the electrocatalytical activity. The nanostructured nickel oxide surfaces displayed good electrocatalytic activity and durability for OER in alkaline media.

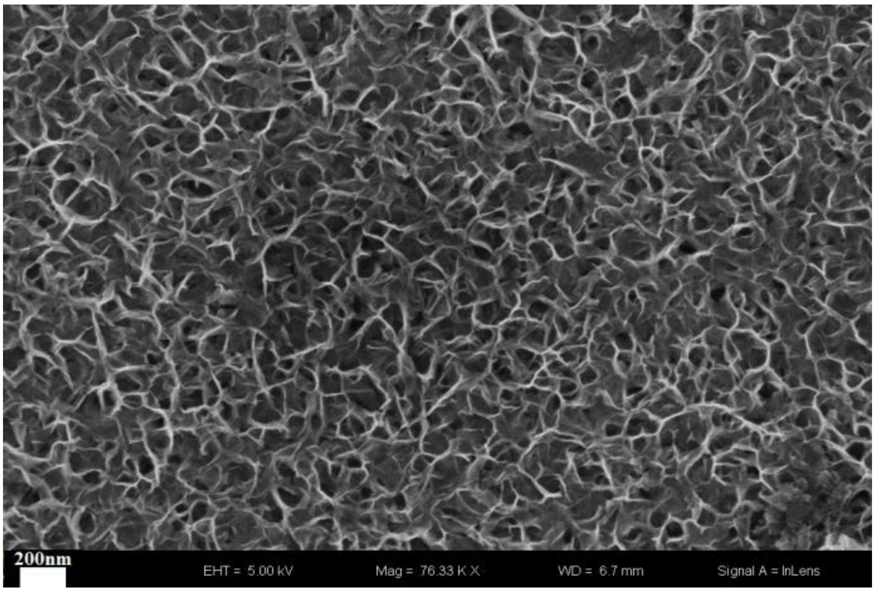


Figure 1: SEM image of the electrodeposited nickel oxide onto ITO substrate.
Deposition potential $E$ = 0.9 V during 7000 s.

# Origin of the Synergistic Effect in Metal Oxide/Carbon Hybrid Electrocatalysts and the Oxygen Reduction Reaction Mechanism

Kuang-Hsu (Tim) Wu,[1,3] Da-Wei Wang,[2] Ian R. Gentle,[3] Dang-Sheng Su[1*]
*[1] Shenyang National Laboratory, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, Liaoning, 110016 China; [2] School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, QLD 4072, Australia; [3] School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia.*

*e-mail: dssu@imr.ac.cn*

## Abstract

The oxygen reduction reaction (ORR) is an important but sluggish cathode reaction in fuel cells and metal-air batteries. So far, precious metals still represent state-of-the-art electrocatalysts to efficiently drive the ORR, despite of their very high cost.[1] Non-precious metal-based and metal-free materials therefore attracted good attention in recent years. In particular, metal oxide/carbon hybrid electrocatalysts have been of special focus for the synergistically promoted ORR activity from the covalently bridged structure.[2] It has been suggested that the ORR appears to be a direct four-electron (4e) ORR, presumably through a dissociative mechanism and the covalent connection may have promoted the electron transport across the hybrid interface.[3] However, there is a lack of understanding of the ORR mechanism and the structural correlation of the synergistic effect with the covalent interface. New mechanistic insight into the structure and functional role of the covalently bound interface is required to unravel the origin of the high activity observed in the hybrid electrocatalysts.

In this presentation, we provide evidence to stepwise ORR mechanism in which the hybrid components work together to deliver an apparent 4e-ORR and the covalently bridged interface further facilitates the ORR by lowering the primary reaction overpotential. Through advanced spectroscopy techniques, the structure of the covalently bound interface is also resolved. To exploit the idea further, a single-site metal oxide cluster on an oxidized carbon nanotube (OCNT) support, as a mimic to the hybrid interface, is also investigated and thoroughly characterized. Our results suggest that not only the primary reaction is synergistically promoted, but also the secondary peroxide electro-reduction is facilitated by the covalent linkage.

## References

[1] L. Yang, Y. Zhao, S. Chen, Q. Wu, X. Wang, Z. Hu, *Chin J Catal* **2013**, *34*, 1986-1991.
[2] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nat Mater* **2011**, *10*, 780-786.
[3] Y. Liang, H. Wang, J. Zhou, Y. Li, J. Wang, T. Regier, H. Dai, *J Am Chem Soc* **2012**, *134*, 3517-3523.

# Non-noble oxygen reduction reaction catalysts based on activated iron-containing electrospun carbon nanofiber in semiconductor-air batteries

Joey D. Ocon[1,2,*], Dongyoon Shin[1], Beomgyun Jeong[2], Graniel Harne A. Abrenica[1]
Jaeyoung Lee[2,3,*]
[1]*Laboratory of Electrochemical Engineering (LEE), Department of Chemical Engineering*
*University of the Philippines Diliman, Quezon City 1101, Philippines*
[2]*Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea*
[3]*Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies, Gwangju Institute of Science and Technology, Gwangju, 500-712, South Korea*
*jdocon@up.edu.ph*

Semiconductor-air batteries are metal-air batteries that use semiconductor anodes such as silicon (Si) and germanium (Ge) as multi-electron high-energy capacity anodes [1]. Combining the above results with our recently reported Fe-CNF catalysts, which show comparable activity with platinum on carbon (Pt/C) [2-3], we describe here the oxygen reduction reaction (ORR) performance of two types of activated Fe-N-CNF electrocatalysts in gelled alkaline electrolyte-based semiconductor-air cells. Consistent with the ORR catalysts' performance in linear sweep voltammetry (LSV), ball-milled Fe-N-CNFs and water activated Fe-N-CNFs exhibited excellent ORR performances as air cathodes in actual semiconductor-air cells. The present study demonstrates that non-noble based ORR catalysts (e.g. Fe-triad element-based) could indeed successfully replace conventional yet expensive Pt-based catalysts in semiconductor-air cells.

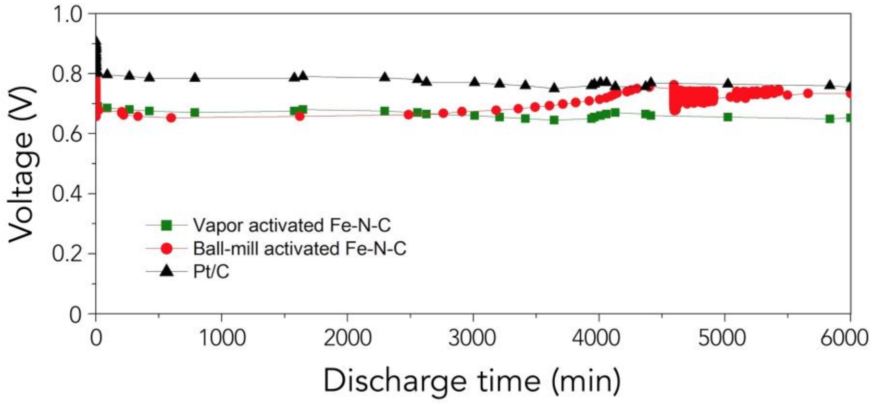


*Figure 1. Long-term discharge profile of Ge-air cells operated using Fe-N-CNF electrocatalysts in the cathode in comparison with Pt/C.*

## References

[1] (a) J. D. Ocon, J. W. Kim, S. Uhm, B. S. Mun, J. Lee, *Phys. Chem. Chem. Phys.*, **15** (2013) 6333-6338. (b) J. D. Ocon, J. W. Kim, G. H. Abrenica, J. K. Lee, J. Lee, *Phys. Chem. Chem. Phys.*, **16** (2014) 22487-22494 (c) J. D. Ocon, G. H. Abrenica, J. Lee, submitted. (d) D.-W. Park, S. Kim, J. D. Ocon, G. H. A. Abrenica, J. K. Lee, J. Lee, ACS Appl. Mater. Interfaces, **7**, (2015) 3126-3132.
[2] B. Jeong, D. Shin, H. Jeon, J. D. Ocon, B. S. Mun, J. Baik, H.-J. Shin, J. Lee, *ChemSusChem*, **7** (2014) 1289-1294.
[3] B. Jeong, D. Shin, M. Choun, S. Maurya, J. Baik, B. S. Mun, S.-H. Moon, D. Su, J. Lee, submitted.

# Quasi-Four-Electron Reduction of Oxygen over Fe/N/C Non-Precious-Metal Cathode Catalysts Prepared from Polyimide Fine Particles

Yuta Nabae[1], Hideharu Niwa[2,3], Yoshihisa Harada[2,3], Masaharu Oshima[3], Muthukrishnan Azhagumuthu[4], JiaJia Wu[4], Takeo Ohsaka[4]
*[1] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 S8-26 Ookayama, Meguro-ku, Tokyo 152-8552, Japan.*
*[2] Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan.*
*[3] Synchrotron Radiation Research Organization, The University of Tokyo, SPring-8, 1-1-1, Koto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan.*
*[4] Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama, Kanagawa 226-8502, Japan.*
*nabae.y.aa@m.titech.ac.jp*

The development of a non-precious metal (NPM) fuel cell catalyst is extremely important to achieve globalization of polymer electrolyte fuel cells. Our research group has been developing Fe/N/C NPM catalyst prepared from polyimide fine particles, which exhibits quite high fuel cell performance[1]. The objective of this study is understanding the reaction scheme and active sites of the oxygen reduction reaction (ORR) over such active NPM catalysts.

The reaction scheme over the Fe/N/C catalyst was studied by rotating ring-disk electrode voltammetry[2]. By carefully investigating the effect of catalyst loading on the reaction selectivity (Figure 1), the 2 + 2 electron reduction pathway that produce $H_2O_2$ as an intermediate was suggested (Scheme 1). Fe-free N/C catalyst was also studied and found to be quite active for the first 2 electron reduction to $H_2O_2$. To understand of the effect of the Fe species, the N/C catalyst was modified with very small amount of Fe and electrochemically and spectroscopically studied[3]. Figure 2 shows the cyclic voltammogram (CV) of the N/C catalyst before and after the Fe decoration. The onset potential for ORR positively shifted. This Fe decorated catalyst was characterized by extended X-ray absorption fine structure (EXAFS) and the Fourier transform spectra are shown in Figure 4. The peak at 1.5 Å can be assigned to a Fe-N bond. This results suggest that Fe-$N_x$ sites increase the onset potential of the N/C catalyst by enhancing $k_3$ and/or $k_1$ in the ORR.

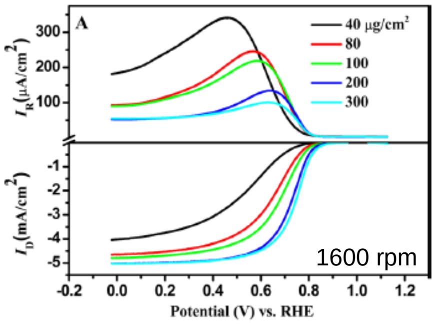
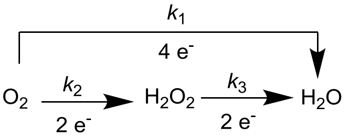


Figure 1. RRDE voltammetry with various loading of Fe/N/C catalyst in $O_2$ saturated 0.5 M $H_2SO_4$.



Scheme 1. Reaction scheme of ORR.

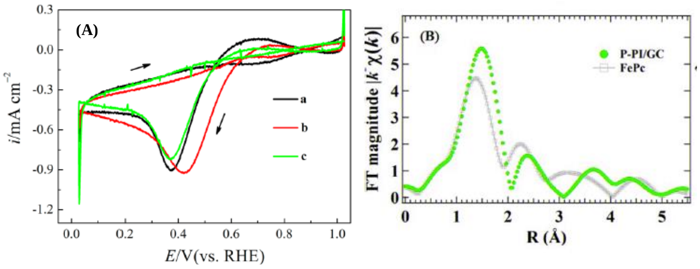


Figure 2. (A) CVs in $O_2$ saturated 0.5 M $H_2SO_4$ with the N/C catalyst (a) before the treatment, (b) after the electrochemical treatment with 0.1 M $FeSO_4$ and (c) after the electrochemical treatment without $FeSO_4$. Scan rate: 50 mV s$^{-1}$. (B) FT EXAFS spectra of the sample (b) and Fe phthalcyanine.

References
1) Nabae, Y. et al. *J. Mater. Chem. A* **2014**, *2*, 11561.
2) Azhagumuthu, M. et al. *ACS Catal*. **2015**, *5*, 5194.
3) Wu, J. et al. *Langmuir* **2015**, *31*, 5529

Acknowledgement: This study was financially supported by NEDO.

# What Types of Defects Enhance the Activity of Platinum for the Oxygen Reduction Reaction?

Federico Calle-Vallejo[1], David Loffreda, Philippe Sautet, Aliaksandr S. Bandarenka

*[1]Leiden Institute of Chemistry, Leiden University*
*Einsteinweg 55, 2333 CC Leiden, The Netherlands*
*f.calle.vallejo@chem.leidenuniv.nl*

The surfaces of heterogeneous catalysts are normally composed of a wide variety of sites. Typically, low-index surfaces coexist with more open facets and various types of defects. All those sites contribute differently to the overall catalytic activity. In order to achieve maximal catalytic activities, materials design techniques should identify the most active sites and suitable synthesis procedures must increase their surface abundance. The challenge lies in the elucidation of the active sites for a given reaction.

In particular, the role of defects on the oxygen reduction reaction (ORR) catalyzed by platinum is puzzling. On the one hand, it is known that stepped Pt(111) electrodes are more active than the pristine ones [1]. On the other hand, the activity of convex Pt nanoparticles, in which steps are abundant, is never as high as that of Pt(111) [2]. The question is then why do steps enhance the activity of extended surfaces and decrease that of nanoparticles?

I will show that “coordination-activity plots” [3] can help solve this puzzle capitalizing on the relationship between the geometric structure of Pt catalysts and their ORR activity. Such relationship is captured for all types of sites on nanoparticles of different sizes and shapes and extended surfaces by generalized coordination numbers [4, 5]. Optimal Pt sites for the ORR are located at more coordinated environments than those of Pt(111), a condition fulfilled by defects on extended surfaces but not on nanoparticles.

## References

[1] A. Hitotsuyanagi, M. Nakamura, N. Hoshi, Electrochimica Acta, 82 (2012) 512-516.
[2] F.J. Perez-Alonso, D.N. McCarthy, A. Nierhoff, P. Hernandez-Fernandez, C. Strebel, I.E.L. Stephens, J.H. Nielsen, I. Chorkendorff, Angewandte Chemie International Edition, 51 (2012) 4641-4643.
[3] F. Calle-Vallejo, J. Tymoczko, V. Colic, Q.H. Vu, M.D. Pohl, K. Morgenstern, D. Loffreda, P. Sautet, W. Schuhmann, A.S. Bandarenka, Science, 350 (2015) 185-189.
[4] F. Calle-Vallejo, J.I. Martínez, J.M. García-Lastra, P. Sautet, D. Loffreda, Angewandte Chemie International Edition, 53 (2014) 8316-8319.
[5] F. Calle-Vallejo, P. Sautet, D. Loffreda, The Journal of Physical Chemistry Letters, 5 (2014) 3120-3124.

# Porous Structure Based High Performance Oxygen Electrocatalysts for Low Temperature Fuel Cells

Jinwoo Lee
*Department of Chemical Engineering, Pohang University of Science & Technology*
77 Cheongamro, Nam-gu, Pohang, Kyungbuk, Republic of Korea
*Jinwoo03@postech.ac.kr*

In this presentation, a simple and scalable method to produce ordered-intermetallic FePt nanotubes by electrospinning will be presented. When tested at cathode catalysts, under the US Department of Energy's reference condition, the activity of face-centered-tetragonal (fct) FePt NTs surpasses that of commercial Pt/C. In an accelerated degradation test at 1.4 V for 3h, the degradation activity rate of fct-FePt NTs is only 10%, whereas that of commercial Pt/C catalysts is 65%. This approach would provide simple route to support-free intermetallic nanotube structure with superior kinetic activity and higher durability than those of commercial Pt/C catalyst. We will also present the effect of the pore size and doping site position on the single-cell performance of metal-free catalysts using wee-defined ordered mesoporous carbon systems. Well-defined large pore sized mesoporous carbons were synthesized by simple self-assembly of block copolymers with carbon and silicate precursors. The single-cell tests prove that control of pore size and doping-site positon directly affects the cell performance by changing the mass-transport properties and utilizing the doping sites in the catalyst layer. NPOMC with precisely controlled doping sites to be near the large mesopores exhibited a remarkable on-set potential and achieved 70% of the maximum power density of Pt/C.

# Boosting oxygen reduction reaction activity of palladium by stabilizing its unusual oxidation states in perovskite

Zongping Shao, Yinlong Zhu, Wei Zhou, Yubo Chen, Jie Yu, Xiaomin Xu
*State Key Laboratory of Materials-Oriented Chemical Engineering, College of Energy, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009 (P.R. China), E-mail:* shaozp@njtech.edu.cn

The high cost, scarcity and poor stability of metallic platinum (Pt) as an oxygen reduction reaction (ORR) catalyst in fuel cells and metal-air batteries have limited the commercialization of these attractive clean-energy technologies [1]. Thus, developing alternative electrocatalysts that are economical and achieve maximized efficiency of stably catalyzing ORR is of prime importance in the societal pursuit of sustainable energy. Metallic palladium (Pd) is an alternative electrocatalyst that is less expensive than Pt; however, its current performance remains insufficient [2]. Here we report for the first time that the ORR activity of the different oxidation states of Pd increased in the following order: $Pd^0 < Pd^{2+} <$ perovskite-type ionic (Pi) $Pd^{3/4+}$. Especially, the intrinsic activity on Pd active site of (Pi) $Pd^{3/4+}$ is ~ 84-fold higher than that of $Pd^0$ (Fig. 1). By doping the Pd element as a cation into the perovskite oxide lattice to form $LaFe_{0.95}Pd_{0.05}O_{3-\delta}$ and $LaFe_{0.9}Pd_{0.1}O_{3-\delta}$, unusual oxidation states of 3/4+ for Pd are stabilized, and the catalysts exhibit superior mass activity, durability and tolerance to methanol compared with the benchmark commercial Pt/C catalyst.

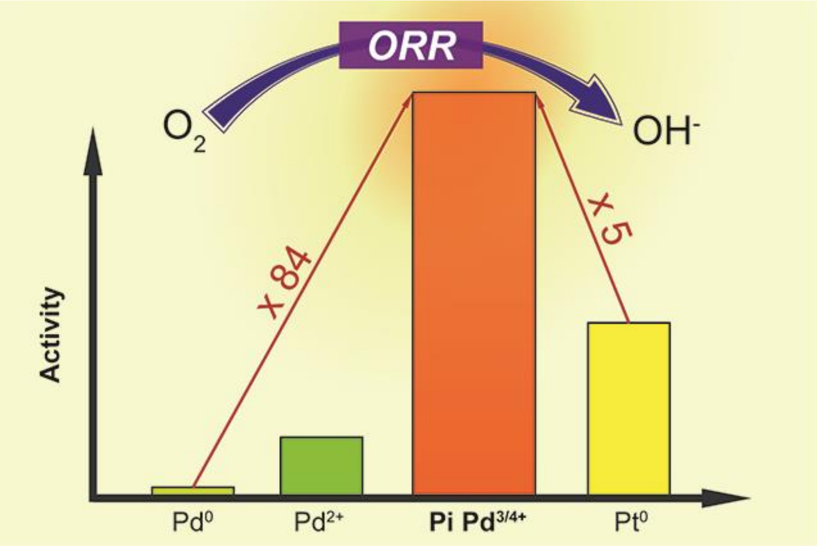


Fig.1 Comparison of the ORR activity of different oxidation states of Pd and Pt

References:
[1] Debe, M. K. Nature 2012, 486, 43-51.
[2] Antolini, E. Energy Environ. Sci. 2009, 2, 915-931.

# In-Situ x-Ray Diffraction Study of Pt(111) Oxidation during Oxygen Reduction Reaction

**J. Drnec[1*], M. Ruge[2], F. Reikowski[2], B. Rahn[2], F. Carlà[1], R. Felici[1], J. Stettner[2], O.M. Magnussen [2] and D. A. Harrington[3]**
*[1] ESRF, Grenoble, 38000 (France)*
*[2] University of Kiel, Kiel, 24118 (Germany)*
*[3] University of Victoria, Victoria BC, V8P 5C2 (Canada)*
*** drnec@esrf.fr**

ORR is one of the most studied electrochemical reactions due to its tremendous fundamental and practical importance. Oxygen is a common, readily accessible oxidizing agent and, therefore, the Pt ORR cathode is part of many energy conversion devices, e.g. fuel cells. Unfortunately, the slow kinetics of ORR negatively affects the performance and is currently one of the main bottleneck in large scale fuel cell commercialization. It has been suggested that this is partly caused by the presence of surface Pt oxides, which slow the reaction rate and trap reaction intermediates on the surface. The oxide formation and dissolution is also known to cause dissolution of Pt catalyst, which further degrades the performance.

Even though the electrochemical formation of surface oxides on platinum surface has been extensively studied in the past, there are still many questions unanswered, mainly regarding the detailed structure of the oxide and its growth mechanism [1 and references therein]. Most of the studies were performed in the absence of $O_2$, the fuel cell oxidant, and therefore they are less relevant to the fuel cell operation as gaseous $O_2$ can modify the oxidation potentials and mechanism. Given the above, further fundamental understanding of the Pt oxidation mechanism and its atomistic picture is clearly needed in order to determine the role of surface oxides in ORR and its effect on the fuel cell performance. Here we show the results of an in-situ surface X-ray diffraction (SXRD) study of electrochemical oxide formation on Pt(111) and how it is influenced by the presence of $O_2$ during ORR.

The place exchange process associated with the initial stages of oxidation is followed dynamically by parallel SXRD and electrochemical measurements during cyclic voltammetry (CV) and potential step experiments in the presence and absence of oxygen. Detailed analysis at two potentials shows that the structural changes are consistent with a place exchange process between Pt and O atoms, in which the exchanged Pt atoms are located directly above their original positions in the Pt(111) lattice. The surface restructuring initiates with the CV peak at 1.02 V vs RHE, even though repeated cycling to 1.15 V leads to no changes in the CV. Adding $O_2$ to the electrolyte does not have any significant effect on the oxidation behavior, in contrast to some literature reports, and the $O_2$ -accelerated Pt dissolution is not caused by the negative shift in the oxidation potential. Furthermore, the ORR current decreases before oxidation, implying that the presence of the surface oxide is not the limiting factor in the ORR and the high ORR overpotential is solely due to the slow ORR mechanism on an unreconstructed surface.

## References

# Highly Active Bifunctional Electrocatalysts Derived from Layered Double Hydroxides for Oxygen Reduction and Oxygen Evolution

Ran Tian, Dianqing Li, Pinggui Tang, Yongjun Feng*
*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology*
*No. 15 Beisanhuan East Road, Beijing 100029, China*
*E-mail: yjfeng@mail.buct.edu.cn*

Fuel cells (FCs) as one of alternatives to traditional fossil enery have attracted increasing interest. In the FCs technologies, both of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) play the key roles[1]. Till now, however, the high price and the instability of the electrocatalysts for the two reactions (e.g., Pt-based, Ir-based materials) in the operation environment have seriously limited the commercialization of fuel cells. Therefore, it is of great interest and importance to explore one kind of non-precious metal electrocatalyst with low cost and high performance for both of the ORR and the OER[1].

Layered double hydroxides (LDHs), as one kind of anionic clays with a general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}\cdot mH_2O]$, has been widely used as various kinds of catalysts, the precursor of the catalysts, absorption materials, and functional additives for polymers because of adjustable compositions ($M^{II}$ and $M^{III}$) in the host sheet, exchangeable interlayer anions ($A^{n-}$) in the interlayer region, and tuneable charge density ($M^{II}/M^{III}$ ratio)[2-4]. Recently, some non-precious metal electrocatalysts derived from the LDHs have shown promising performance for the ORR and the OER in alkaline medium[5,6]. It is possible to develop bifunctional electrocatalysts with high performance based on the absorption and the intercalation properties of LDHs.

Here, we successfully prepared CoPcTs/$Ni_2Fe$-$CO_3$ LDH precursor by adsorbing sulfonated phthalocyanine cobalt (CoPcTs) on the surface of LDH and CoPcTs-$Ni_2Fe$-LDH precursor by intercalating CoPcTs into LDH interlayer spacing and then obtained the bifunctional electrocatalysts by calcining the two precursors under inert atmosphere. Also, we furthermore investigated the ORR and the OER electrocatalytic performance of the obtained electrocatalysts as a function of the amount of CoPcTs, the annealing temperature, and dispersion of active centers. Some interesting and promising results have been obtained, for example, the catalyst from CoPcTs/$Ni_2Fe$-$CO_3$ LDH at 700 °C for 3 h shows the highest ORR activity when the absorption amount of CoPcTs was 120 mg/g and the one displays the best OER activity when the absorption amount is 40 mg/g. Also the catalysts obtained from the intercalated LDH have shown excellent bifunctional activity, higher selectivity, and longer durability due to the synergistic effect between CoPcTs guest and $Ni_2Fe$ host sheet and the confinement effect of the LDH interlayer spacing. Undoubtedly, the LDH materials are one kind of potential and available precursors for highly effective bifunctional electrocatalysts for the ORR and the OER in alkaline media.

[1] S. Park, Y.Y. Shao, J. Liu, Y. Wang, *Energy Environ. Sci.*, **2012**, 5, 9331-9334.
[2] F. Cavani, F. Trifirò and A. Vaccari, *Catal. Today*, **1991**, 11, 173-301.
[3] J.T. Feng, Y.F. He, Y.N. Liu, Y.Y. Du, D.Q. Li, *Chem. Soc. Rev.*, **2015**, 44, 5291-5319.
[4] G.L. Fan, F. Li, D.G. Evans, X. Duan, *Chem. Soc. Rev.*, **2014**, 43, 7040-7066.
[5] D. Wang, X. Chen, D. G. Evans and W. Yang, *Nanoscale*, **2013**, 5, 5312-5315.
[6] W. Huang, H.H. Zhong, D.Q. Li, P.G. Tang and Y.J. Feng, *Electrochim. Acta*, **2015**, 173, 575-580.

# Impact of Electrolyte Identity on the Electrocatalytic Conversion of Dissolved Gases in Buffered Solutions

Tatsuya Shinagawa, Kazuhiro Takanabe
*Division of Physical Sciences and Engineering, KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology (KAUST)*
*4700, KAUST, Thuwal, 23955-6900, Saudi Arabia*
*kazuhiro.takanabe@kaust.edu.sa*

Effective energy conversion is crucial in developing a sustainable society. Chemical energy can be converted into electricity in the fuel cells system with high efficiency, where hydrogen is oxidized at the anode (hydrogen oxidation reaction; HOR), and oxygen is reduced at the cathode (oxygen reduction reaction; ORR). Recently, greater attentions have been given to electrochemistry at near-neutral pH levels using buffered solutions, owing to its advantages over extreme pH: a safe and abundant environment and more choices of available materials. Although the electrolyte itself plays crucial roles in such circumstances, there have been little studies reported regarding electrolyte influences on the ORR/HOR.

Herein, our comprehensive electrochemical study on the ORR and HOR is presented.[1] A platinum rotating disk electrode was employed as a working electrode in all the measurements. Unless otherwise specified, sodium phosphate solutions were used as electrolytes (0.2 mol $L^{-1}$ – 4.2 mol $L^{-1}$ at pH 5). Our controlled electrochemical study revealed that current densities for both the ORR and HOR logarithmically decreased with increased electrolyte concentration. Detailed kinetic analysis on the ORR disclosed that the Tafel slope became larger than 120 mV $dec^{-1}$ in denser electrolytes ($\geq$150 mV $dec^{-1}$). Such large Tafel slope suggests that the oxygen adsorption on the active sites determines the rate, implying that the concentrated solute inhibits the access of the reactant to the active sites.

We then separately evaluated the sodium phosphate solution properties of the gas solubility, the kinematic viscosity and the diffusion coefficient. The electrolyte properties were found to be drastically altered with the concentration: the gas solubility decreased, the kinematic viscosity of the solution increased and the diffusion coefficient of the dissolved gases decreased with increasing solute concentration. Simulated limiting diffusion currents using these parameters well reproduced measured currents (Figure 1a), suggesting that the mass transport parameters associated with the electrolyte property solely determine the overall electrochemical performance. Our study was then further extended to a variety of electrolytes: in various concentrations of cations ($Li^+$, $K^+$, $Na^+$) and anions ($H_2PO_4^-$, $HPO_4^{2-}$, $PO_4^{3-}$ and $HCO_3^-$). Even in such electrolyte solutions, the altered properties were found to determine majorly the mass transport phenomena (Figure 1b). These alterations of the electrolyte properties are universally applicable to other aqueous gas-related electrochemical reactions because the currents can be purely determined by mass transport of the dissolved gases. This fundamental yet greatly significant aspect of “effect of ions” on the electrocatalytic reactions have to be well taken into consideration for better understanding and advancing of electrochemical energy conversion.

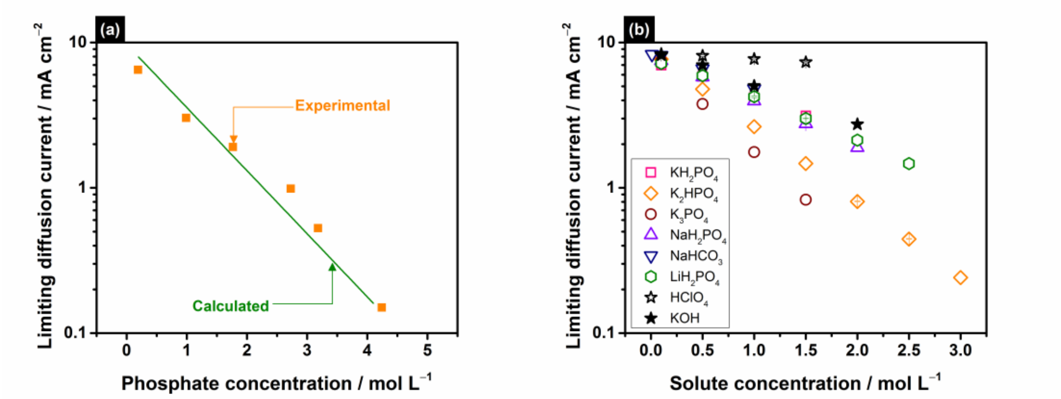


**Figure 1.** (a) Calculated and experimentally measured ORR in sodium phosphate solution (at pH 5) and (b) ORR diffusion limiting currents in various electrolyte solutions as a function of solute concentration.

## References

[1] T. Shinagawa and K. Takanabe, *J. Power Sources*, **2015**, *287*, 465-471.

# Water splitting on Ir oxide-based electrocatalysts: From single crystals to core shell particles

Peter Strasser

*The Electrochemical Energy, Catalysis, and Materials Science Laboratory*
*Department of Chemistry, Chemical Engineering Division, Technical University Berlin, Germany*
pstrasser@tu-berlin.de

Nanoscale catalytic materials are key components of dark electrolytic and photoelectrochemical devices for storing and converting solar energy. Their successful development and optimization requires insight into the relations between atomic-scale structure of the catalytic interface and its catalytic activity and stability.

In this talk, I will highlight some of our recent work on the design and understanding of electrocatalytic Ir oxide based catalyst materials [1-13] and their liquid-solid interfaces. I will outline the preparation, characterization, and catalytic performance of Ir oxide model catalysts as well as nanostructured core-shell particles for water splitting and discuss fundamental aspects of their structure-activity relationships.

1. Reier, T.; Pawolek, Z.; Cherevko, S.; Bruns, M.; Jones, T.; Teschner, D.; Selve, S.; Bergmann, A.; Nong, H. N.; Schlögl, R.; Mayrhofer, K. J. J.; Strasser, P., Molecular insight in structure and activity of highly efficient, low- Ir Ir-Ni oxide catalysts for electrochemical water splitting (OER). *J. Am. Chem. Soc.* 2015, DOI: 10.1021/jacs.5b07788.
2. Oh, H.-S.; Nong, H. N.; Strasser, P., Preparation of Mesoporous Sb-, F-, and In-Doped SnO2 Bulk Powder with High Surface Area for Use as Catalyst Supports in Electrolytic Cells. *Adv. Funct. Mater.* 2015, 25, 1074-1081.
3. Nong, H. N.; Oh, H. S.; Reier, T.; Willinger, E.; Willinger, M. G.; Petkov, V.; Teschner, D.; Strasser, P., Oxide-Supported IrNiOx Core-Shell Particles as Efficient, Cost-Effective, and Stable Catalysts for Electrochemical Water Splitting. *Angew. Chem.* 2015, 54, 2975-2979.
4. Nong, H. N.; Gan, L.; Willinger, E.; Teschner, D.; Strasser, P., IrOx core-shell nanocatalysts for cost- and energy-efficient electrochemical water splitting. *Chem. Sci.* 2014, 5, 2955-2963.
5. Oh, H.-S.; Nong, H. N.; Reier, T.; Gliech, M.; Strasser, P., Oxide-supported Ir nanodendrites with high activity and durability for the oxygen evolution reaction in acid PEM water electrolyzers. *Chem. Sci.* 2015, online DOI: 10.1039/C5SC00518C.
6. Cherevko, S.; Reier, T.; Zeradjanin, A. R.; Pawolek, Z.; Strasser, P.; J.J.Mayrhofer, K., Stability of nanostructured iridium oxide electrocatalysts during oxygen evolution reaction in acidic environment. *Electrochem. Commun.* 2014, 48, 81-85.
7. Reier, T.; Teschner, D.; Lunkenbein, T.; Bergmann, A.; Selve, S.; Kraehnert, R.; Schlogl, R.; Strasser, P., Electrocatalytic Oxygen Evolution on Iridium Oxide: Uncovering Catalyst-Substrate Interactions and Active Iridium Oxide Species. *J. Electrochem. Soc.* 2014, 161, F876-F882.
8. Johnson, B.; Girgdies, F.; Weinberg, G.; Rosenthal, D.; Knop-Gericke, A.; Schlögl, R.; Reier, T.; Strasser, P., Suitability of Simplified (Ir,Ti)Ox Films for Characterization during Electrocatalytic Oxygen Evolution Reaction. *J. Phys. Chem. C* 2013, 117, 25443-25450.
9. Reier, T.; Oezaslan, M.; Strasser, P., Electrocatalytic Oxygen Evolution Reaction (OER) on Ru, Ir, and Pt Catalysts: A Comparative Study of Nanoparticles and Bulk Materials. *ACS Catal.* 2012, 2, 1765-1772.
10. Ortel, E.; Reier, T.; Strasser, P.; Kraehnert, R., Mesoporous IrO2 Films Templated by PEO-PB-PEO Block-Copolymers: Self-Assembly, Crystallization Behavior, and Electrocatalytic Performance. *Chem. Mat.* 2011, 23, 3201-3209.
11. Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P., The Mechanism of Water Oxidation: From Electrolysis via Homogeneous to Biological Catalysis. *ChemCatChem* 2010, 2, 724-761.
12. Forgie, R.; Bugosh, G.; Neyerlin, K. C.; Liu, Z.; Strasser, P., Bimetallic Ru Electrocatalysts for the OER and Electrolytic Water Splitting in Acidic Media. *Electrochem. Solid-State Lett.* 2010, 13, B36.
13. Neyerlin, K. C.; Bugosh, G.; Forgie, R.; Liu, Z.; Strasser, P., Combinatorial Study of High-Surface-Area Binary and Ternary Electrocatalysts for the Oxygen Evolution Reaction. *J. Electrochem. Soc.* 2009, 156, B363-B369.

# Silver Nanoparticles Electrocatalysts for $CO_2$ Reduction

Electrochemical $CO_2$ conversion is a favorable approach to generate clean energy fuels for the future because it can be coupled with a renewable energy source such as solar energy. However, development of selective and efficient electrocatalyts for $CO_2$ reduction in an aqueous electrolyte is challenging because i) it typically requires high overpotential to overcome its unstable intermediate species, ii) its poor solubility in water easily limits its mass transfer, and iii) hydrogen evolution reaction is a significant competitive reaction. Therefore, it is important to develop a catalyst having low overpoential for $CO_2$ reduction and suppressing hydrogen generation reaction. Au, Ag, and Cu are popular catalysts for $CO_2$ electro-reduction because of their appropriate binding affinities with CO intermediates. Especially, Ag is a promising material to have high CO production selectivity over 80 % with bulk foil and to be relatively cost effective compared to Au. Here, we present our recent efforts to develop efficient $CO_2$ electrocatalysts based on monodispersed Ag nanoparticles. We found that 5 nm size Ag nanoparticles on the carbon support showed the lowest overpotential and highest CO particle current efficiency over hydrogen generation with more stable durability, all of which were enhanced activities compared to polycrystalline Ag foil as well. The improved $CO_2$ reduction activity with Ag nanoparticles on the carbon support is attributed to the interaction between silver surface and the anchoring agents. We suggest that the subtle changes of the Ag nanoparticle surface induced by the p block elements such as sulfur and oxygen are considered to cause significant improvement in $CO_2$ reduction activity.

# Highly efficient chlorine production using a $RuO_2$/Blue $TiO_2$ nanotube array hybrid electrode

Jiye Kim, Choonsoo Kim, Seonghwan Kim, Jeyong Yoon†
*School of Chemical and Biological Engineering, College of Engineering, Institute of Chemical Process,*
*Asian Insititute for Energy, Environment & Sustainability (AIEES), Seoul National University*
*Gwanak-ro 1, Gwanak-gu, Seoul, Republic of Korea*
*imkjy5@snu.ac.kr, jeyong@snu.ac.kr†*

Chlorine production is one of the largest processes of electrochemistry. Especially, anode material is the significant factor for the electrochemical chlorine generation process. Dimensionally Stable Anode (DSA), which is typical anode material for the electro-chlorination, has been studied for decades to increase the chlorine generation efficiency and to reduce the electrode cost. Although DSA has high efficiency for chlorine generation, it has limitations in the electrode cost. One of the reasons for the high cost is that DSA is usually based on the precious metals, such as Ruthenium and Iridium.

$TiO_2$ also has been intensively studied to use for the anode material because of its feasibility and low cost. Especially, $TiO_2$ nanotube array has been used in numerous applications because of its ordered structure and large surface area. However, $TiO_2$ is hard to use as an electrode because the nonconductive oxide film is generated on the surface and acts as an insulator. As one of the efforts to use $TiO_2$ as an electrode, Blue-$TiO_2$ nanotube array (Blue TNT) was developed recently. Blue TNT is fabricated with cathodic polarization of $TiO_2$ nanotube to convert $Ti^{4+}$ to $Ti^{3+}$. It highly increases the conductivity of $TiO_2$ and provides the possibility of using $TiO_2$ as anode material. Moreover, significant amount of chlorine is generated on the Blue TNT which is comparable with DSA electrode.

There are two different pathways to generate the chlorine according to the electrode materials. On the DSA electrode, chloride ions are directly oxidized to chlorine. Meanwhile, Blue TNT electrode has large overpotential for the direct chlorine generation. Hydroxyl radical is firstly generated with water splitting and reacts with chloride ion to generate the chlorine in indirect way.

In this research, $RuO_2$ was coated on the Blue TNT and the chlorine generation efficiency was illustrated along with the direct and indirect chlorine generation pathway. When the $RuO_2$ was coated on the Blue TNT, chlorine was generated in both direct and indirect way from the $RuO_2$ and Blue TNT. And chlorine production was increased compared to the Blue TNT and DSA electrode.

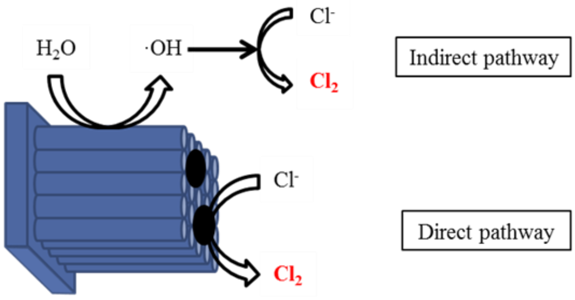


**Figure 1** Scheme of chlorine evolution in Blue TNT-$RuO_2$ electrode

## References

Kim, C., Kim, S., Choi, J., Lee, J., Kang, J. S., Sung, Y. E., Lee, J., Choi, W., Yoon, J. (2014) Blue $TiO_2$ Nanotube Array as an Oxidant Generating Novel Anode Material Fabricated by Simple Cathodic Polarization. *Electrochim. Acta*, **141**, 113 -119.

# Reduction-induced surface amorphization enhances oxygen evolution activity in $Co_3O_4$

Da-Wei Wang,[a] Xue Leng, [b] Qingcong Zeng,[b] Kuang-Hsu Wu,[c] Ian R. Gentle[b]
[a]*School of Chemical Engineering, University of New South Wales, Sydney, Australia*
[b]*School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Australia*
[c]*Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China*
*da-wei.wang@unsw.edu.au*

The increasing public concern about global climate change and energy crisis demands more efficient sustainable technologies for renewable carbon-neutral energy. Oxygen evolution reaction (OER) plays a pivotal role in a number of energy conversion and storage processes and devices, such as water-splitting and rechargeable metal-air batteries. First-row transition metal oxides, such as spinel oxides and perovskites, have received increasing interest for their great potentials as alternative low-cost OER electrocatalysts. Among them, spinel oxide $Co_3O_4$ has shown good activity and stability in OER. In this work, we report the surface amorphization of $Co_3O_4$ crystals caused by thermal $H_2$ reduction and stabilization in air. We demonstrate the largely improved OER activity which is facilitated by the newish amorphous surfaces. The crystal structure and the surface properties of the modified $Co_3O_4$ crystals were studied by using XRD, X-ray photoelectron spectroscopy and transmission electron microscopy. The results suggested that the mixed hydrated cobalt hydroxide/carbonate species in the surficial amorphous layer are essential to the performance improvement.

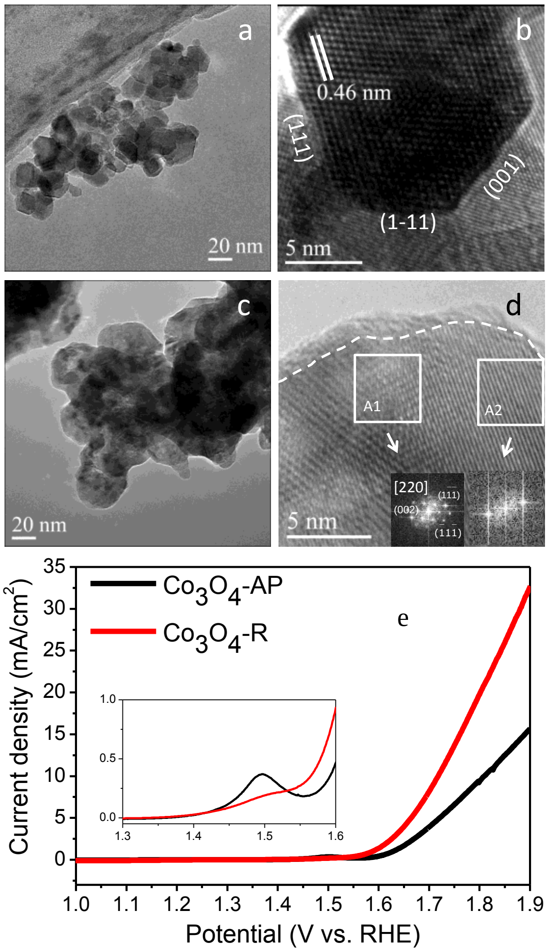


**Figure 1.** TEM images of starting $Co_3O_4$ (a, b) and $Co_3O_4$ with amorphous surface layers (c, d). Insets in (d) are FFT from ~15 nm × ~15 nm areas labelled by squares A1 and A2, respectively. (e) Electrochemical performance tested in 0.1 M KOH. Linear sweep voltammograms collected on a rotating ring-disk electrode with a rotating speed of 1600 rpm.

# Design of Highly Active and Durable Nanostructured Carbon-Based Oxygen Reduction Electrocatalysts

Sang Hoon Joo
*School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST)*
*Ulsan 689-798, Republic of Korea*
*shjoo@unist.ac.kr*

The development of highly active, durable, and low-cost oxygen reduction reaction (ORR) catalysts is central to making polymer electrolyte fuel cell and Li-air battery technologies commercially viable. In this regards, tremendous recent efforts have been devoted to replacing expensive, scarce Pt-based electrocatalysts with non-precious metal or metal-free materials for the ORR. In this presentation, we show our recent efforts toward new electrocatalysts for the ORR based on nanoporous/nanostructured carbons including mesoporous carbon, carbon nanotubes (CNTs), and graphene [1-6]. We present transition metal and nitrogen co-doped ordered mesoporous porphyrinic carbons (M-OMPC) with high surface areas and tunable pore structures, which were prepared by nanocasting mesoporous silica templates [1]. A family of M-OMPC catalysts generally showed very high ORR activity in an acidic medium. Particularly, the most active FeCo-OMPC represented one of the best performances among the non-precious metal catalysts (NPMCs). The characterizsation by EXAFS and high-resolution TEM revealed the molecular face-to-face porphyrin-like active site structure in the FeCo-OMPC catalyst. We further demonstrate that the nanocasting with Ni and Fe macrocyclic compounds generate graphitic shell embedded mesoporous carbon (GNS/MC) structure, which exhibits very high activity and durability for both oxygen evolution and reduction reactions in an alkaline medium [2]. We also show highly active, durable CNT-based core-sheath structure catalysts [4,5]. CNTs wrapped with ionic liquid-driven, heteroatom-doped carbon (CNT/HDC) structure showed an excellent ORR activity in an alkaline solution, which is one of the best performances among the metal-free, heteroatom-doped nanocarbon catalysts [4]. The CNT/HDC also showed high current and power densities when employed as cathode catalysts in alkaline fuel cell. In addition, CNTs with metallomacrocycle-driven sheath layer exhibited very high ORR activity in both alkaline and acidic medium, and demonstrated excellent performance in both anion and proton exchange membrane fuel cells [5].

[1] J. Y. Cheon et al., *Scientific Reports* 3, 2715 (2013).
[2] J. Y. Cheon et al., *Adv. Energy Mater.* Revised (2015).
[3] J. Y. Cheon et al., *J. Am. Chem. Soc.* 136, 8875 (2014).
[4] Y. J. Sa et al., *Angew. Chem. Int. Ed.* 53, 4102 (2014).
[5] J. Y. Cheon et al., Manuscript in preparation (2015).
[6] J. Han et al., *Angew. Chem. Int. Ed.* 54, 12622 (2015).

# Ni$_x$Co$_y$Fe$_2$O$_4$ on carbon supports as bifunctional electrocatalysts – an active material for both oxygen evolution and oxygen reduction reaction

G. Seiffarth[a], M. Steimecke[a], M. Kühhirt[a], T. Walther[b], M. Bron[a]
[a]*Martin-Luther-Universität Halle-Wittenberg,*
*Von-Danckelmann-Platz 4, 06120 Halle (Saale),*
[b]*Martin-Luther-Universität Halle-Wittenberg,*
*Kurt-Mothes-Straße 2, 06120 Halle (Saale),*
*gerda.seiffarth@chemie.uni-halle.de*

Abstract:

Electrocatalysts, which are active for both, the oxygen evolution (OER) and the oxygen reduction reaction (ORR) in alkaline media, have actually a high importance in energy conversion systems. Promising materials are spinels [1]. A study of bifunctional catalysts by both rotating disk electrode measurements for ORR respectively linear sweep measurements for OER and scanning electrochemical microscopy (SECM) were done to compare the important electrochemical parameters such as onset potential and number of transferred electrons for both methods. For SECM measurements the redox competition mode, which is a pulsed method, where additionally information about selectivity of an electrocatalyst can be obtained, is used [2]. Here, a Ni$_{0.9}$Co$_{0.1}$Fe$_2$O$_4$ mixed oxide, which is a of a precursor of a spinel (sp) and which is synthesized using a polyol mediated synthesis route, is embedded in nitrogen doped carbon nanotubes (N-CNT) or Baytubes® (BT) and tested for OER and ORR. The tested material, which consists of N-CNT/BT known as a well (electrical) conducting material [3], has an enhanced activity for both reactions in comparison to the raw material sp. To evaporate the included palmitic acid, which may reduce the activity by blocking the active sites, a pyrolysis (py) is performed on the mixture. The received results are shown in Table 1 and Figure 1.

Table 1: Comparison of potentials with different current densities for different catalysts and calculated potential difference ($\Delta E_{1(5)} = E_{OER,1(5)} - E_{ORR}$).

| catalyst | $E_{ORR}$ / V -1 mA cm$^{-2}$ | $E_{OER,1}$ / V 1 mA cm$^{-2}$ | $E_{OER,5}$ / V 5 mA cm$^{-2}$ | $\Delta E_1$ / V | $\Delta E_5$ / V |
|---|---|---|---|---|---|
| **sp** | -0,595 | 0,685 | - | 1,280 | - |
| **N-CNT** | -0,144 | 0,684 | - | 0,828 | - |
| **sp/N-CNT** | -0,184 | 0,661 | 0,742 | 0,845 | 0,926 |
| **sp/N-CNT-py** | -0,136 | 0,664 | 0,732 | 0,800 | 0,868 |
| **sp/BT** | -0,343 | 0,669 | - | 1,012 | |
| **sp/BT-py** | -0,255 | 0,700 | - | 1,087 | |

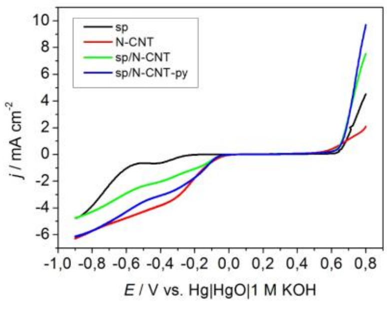


Figure 1: ORR and OER polarization curves of catalysts sp, N-CNT, sp/N-CNT and sp/N-CNT-py

Literature:

[1] Y. Liu, D. C. Higgins, J. Wu, M. Fowler, Z. Chen, *Electrochem. Commun.* **2013**, *34*, 125–129.

[2] A. Dobrzeniecka, A. Zeradjanin, J. Masa, A. Puschhof, J. Stroka, P. J. Kulesza, W. Schuhmann, *Electrocatalysis* **2013**, *202*, 55–62.

[3] T. C. Nagaiah, S. Kundu, M. Bron, M. Muhler, W. Schuhmann, *Electrochem. Commun.* **2010**, *12*, 338–341.

# Effect of Cobalt-doped to Hollandite-type Manganese Oxides Nanoparticles on ORR and OER Activities

Yoshihiro Kadoma[*], Taisei Sekiguchi[*,**], Miyuki Kojima[*,**], Koichi Ui[*], and Tatsuya Takeguchi[*,**]
[*]*Department of Frontier Materials and Function Engineering, Graduate School of Engineering*
*Iwate University 4-3-5 Ueda, Morioka, Iwate, 020-8551, Japan*
[**]*CREST, JST, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan*
*takeguch@iwate-u.ac.jp*

**Introduction** The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) activities of metal oxides have been investigated to develop effectively for renewable energy technologies including fuel cells and metal-air secondary battery. Manganese dioxides have been studied as the ORR and OER catalysts from the resourceful and economical standpoints. Manganese oxides have many structural forms, such as $\alpha$-, $\beta$-, $\gamma$-, $\delta$-, and todorokite-$MnO_2$, which consist of octahedral $MnO_6$ with different connectivity. Among various polymorphs of $MnO_2$, hollandite-type manganese dioxide ($\alpha$-$MnO_2$) has the tetragonal crystal system with a (2 × 2) tunnel structure, which has been known as a catalyst having high ORR and OER activities [1, 2]. In this study, we have synthesized the $\alpha$-$MnO_2$ sample and its Co-doped sample using a solution method and examined their physical properties, ORR, and OER activities.

**Experimental** The $\alpha$-$MnO_2$ sample and the Co-doped $\alpha$-$MnO_2$ sample were prepared using a solution method [3]. The aqueous $MnSO_4$ solution and the $CoSO_4$ aqueous solution were added to a stirred 1 M $K_2S_2O_8$ aqueous solution at 80 °C (molar ratio of Mn to Co Mn : Co = 1 : 0.25 and 1 : 1). After that, the mixed solutions were further stirred at 80 °C for 7 h. The precipitates were filtered, washed with distilled water, and dried in an oven at 80 °C for about 12 h. These samples were characterized by XRD, FE-SEM, and TEM. The ORR and OER activity measurements were carried out by the rotating disk electrode (RDE) method using three-electrode cell. The working electrode was glassy-carbon electrode coated with a thin film catalyst. The reference electrode was a commercial alkaline / mercurous oxide reference electrode and the counter electrode was platinum wire. All measurements were conducted at 10 mV $s^{-1}$ in an $O_2$-saturated 0.1 M KOH solution at room temperature.

**Results and discussion** From the XRD patterns, all strong diffraction peaks of the $\alpha$-$MnO_2$ sample and the Co-doped sample could be indexed to the tetragonal phase (space group: *I4/m*). The Co-doped sample maintained the structure of $\alpha$-$MnO_2$. The crystallite size of Co-doped $\alpha$-$MnO_2$ of 1 : 0.25 (Mn : Co) sample was larger than that of $\alpha$-$MnO_2$ sample. The SEM and TEM observations showed that all samples consisted of needle-like particles having the average width of 10 - 50 nm. The needle-like particles aggregated into the secondary particles with spherical shape. From the ORR measurement, the Pt/C catalyst showed high ORR activity. On the other hand, the onset potential for ORR of the Co-doped $\alpha$-$MnO_2$ was at the higher side than that of $\alpha$-$MnO_2$. Fig.1 shows the OER activities of $\alpha$-$MnO_2$, Co-doped $\alpha$-$MnO_2$ of 1 : 0.25 and 1 : 1 (Mn : Co), and Pt/C catalyst. The Co-doped $\alpha$-$MnO_2$ of 1 : 1 (Mn : Co) shows the highest activity because the on-set potential is at the lowest. The current density is as follows: Co-doped $\alpha$-$MnO_2$ of 1 : 1 (Mn : Co) > Co-doped $\alpha$-$MnO_2$ of 1 : 0.25 (Mn : Co) > $\alpha$-$MnO_2$ > Pt/C catalyst. It is suggested that the Co-doping has an influence on the ORR and OER activities.

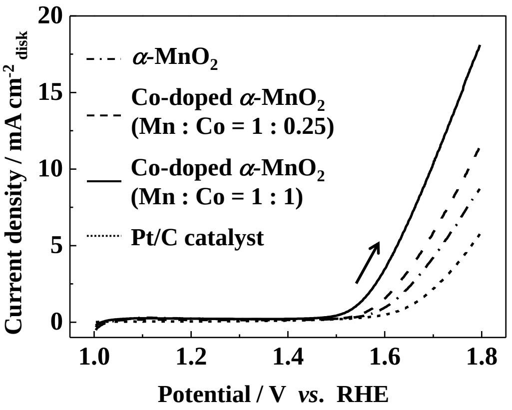


**Fig. 1** OER activies of $\alpha$-$MnO_2$, Co-doped $\alpha$-$MnO_2$ of 1 : 0.25 and 1 : 1 (Mn : Co) in an $O_2$-saturated 0.1 M KOH solution; potential range: 1.0 - 1.8 V *vs.* RHE; scan rate: 10 mV $s^{-1}$; rotation rate: 1600 rpm.

## References

1) Y. L. Cao *et al.*, *J. Electroanal. Chem.*, **557**, 127 (2003).
2) Y. Meng *et al.*, *J. Am. Chem. Soc.*, **136**, 11452 (2014).
3) Y. Kadoma *et al.*, *Solid State Ionics*, **179**, 1710 (2008).

## Acknowledgments

This research was partially supported by CREST, JST.

# Non-Pt Carbon Electrocatalyst: Surface Properties and Electrocatalytic Activity

Dea-Soo Yang, Min Young Song, Kiran Pal Singh, Fatemeh Razmjooei and Jong-Sung Yu

*Department of Energy Systems Engineering, DGIST, Daegu, 42988, Republic of Korea,*
*Fax: (+82)53-785-6409, E-mail: jsyu@dgist.ac.kr*

Oxygen reduction reaction (ORR) takes place usually on Pt or Pt alloys loaded on carbon support in fuel cell, but their large-scale commercial application has been precluded mainly by high cost and low durability of the requisite noble metal electrocatalyst [1]. 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 [2,3]. Heteroatoms such as N, P and S are most common elements doped into carbon framework for electrochemical reactions.

Although the heteroatom-doped porous carbon materials have evolved as one of best possible solutions in this regard, 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 [4.5]. In this work, we report Fe and N-functionalized ordered mesoporous carbons (OMCs) 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 OMC prepared with FePc in both alkaline and acidic media. Interestingly, it is found that although the use of iron is necessary for the preparation of highly active N-doped ORR carbon catalysts, its presence may be not necessary for N-doped OMC to be active in the ORR in either alkaline or acidic media. This remarkable upsurge in activity is mainly attributed to the high increase in electrical conductivity and surface area of the non-Pt doped carbon sample. The ORR activity is discussed in terms of heteroatom content, surface area, porous structure, and conductivity of the carbon [4-7].

References

1. B. Fang, M. S. Kim, J. H. Kim, J. -S. Yu, *Acc. Chem. Res*. 46 (2013) 1397.
2. G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science* 332 (2011) 443.
3. D.-S. Yang, D. Bhattacharjya, S. Inamdar, J. Park, J. -S. Yu, J. *Am. Chem. Soc*. 134 (2012) 16127.
4. D.-S. Yang, S. Chaudhari, K. P. Rajesh, J. -S. Yu, *ChemCatChem* 6 (2014) 1236.
5. D.-S. Yang, D. Bhattacharjya, M. Y. Son, F. Razmjooei, J. Ko, Q.-H. Yang, P J.-S. Yu, *ChemCatChem* 7 (2015) 2882.
6. D.-S. Yang, M. Y. Song, K. P. Singh, J.-S. Yu, *Chem. Commun*. 51 (2015) 2450.
7. K. P. Singh, E. J. Bae, J.-S. Yu, *J. Am. Chem. Soc*. 137 (2015) 3165-3168.

# Carbides as a catalyst support materials for the oxygen reduction reaction

C. Jackson[a*], G.T. Smith[b], A. E. Russell[c], D. Kramer[b] and P.B.J. Levecque[a]

*[a]HySA/Catalysis Centre of Competence, Centre for Catalysis Research, Department of Chemical Engineering, University of Cape Town, Rondebosch, Cape Town, 7700, South Africa*
*[b]Engineering and The Environment, University of Southampton, Highfield Campus, Southampton, Hants, SO17 1BJ, United Kingdom*
*[c]School of Chemistry, University of Southampton, Highfield Campus, Southampton, Hants, SO17 1BJ, United Kingdom*
*[*]colleen.jackson@alumni.uct.ac.za*

Long recognised as key to the reduction of precious metal loading in PEMFC is the use of small catalyst nanoparticles (c.a. 3nm) stabilised by supporting them on high surface area carbon. However PEMFCs using this technology achieve only 50% of the lifetime required by the US DOE's target[1] with the oxidation of carbon supports at the cathode identified as a major lifetime limitation during typical load cycles[2]. Significant emphasis has been placed on increasing the activity of supported cathode catalysts and preventing the loss of catalyst surface area due to support corrosion during automotive use[3,4]. Silicon carbide and boron carbide ($B_4C$) are refractory compounds[5] exhibiting high chemical inertness[6,7] and electrochemical stability[8,9]. We will present our work on these carbides as electrocatalyst support materials for the oxygen reduction reaction (ORR). The in-situ experimental characterisation methods include electrochemical ORR activity and durability testing. Ex-situ advanced surface characterisation techniques X-ray Absorption Near Edge Structures (XANES), Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Photoelectron Spectroscopy (XPS) were used to investigate surface characteristics of the catalysts and provide information into the kinetic activities in comparison to Pt/C. In addition to anticipated enhanced electrochemical stability, we will show evidence that when boron carbide is used as a support material, the intrinsic activity of the supported platinum for the ORR almost doubles.

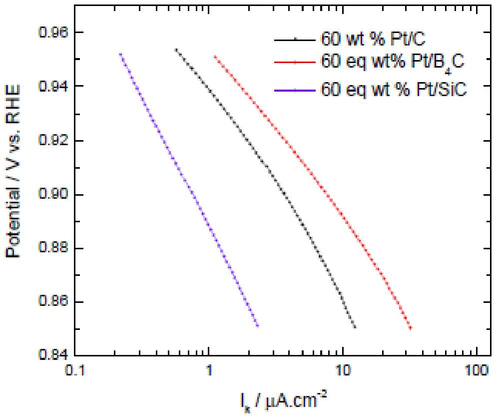


**Figure 1:** Tafel plot for the oxygen reduction reaction activity of Pt supported on carbon (commercial), boron carbide (prepared) and silicon carbide (prepared) showing that the Pt/$B_4C$ catalysts outperformed the catalysts supported on carbon and SiC.

**Table 1:** The specific activities for the oxygen reduction reaction with catalysts supported on carbon versus carbides.

| Catalyst | Specific Activity ($\mu A/cm^2_{Pt}$) |
|---|---|
| 60 wt% Pt/C | 181 |
| 60 eq wt% Pt/$B_4C$ | 334 |
| 60 eq wt% Pt/SiC | 61.2 |

1. Fuel Cell Technical Team Roadmap, 2013, US DOE
2. Antolini, E., and E. R. Gonzalez. Solid State Ionics, 2009, 180.9, 746
3. Reiser, C.A., Bregoli, L., Patterson, T.W., Yi, J.S., Yang, J.D., Perry, M.L. & Jarvi, T.D. 2005. *Electrochemical and Solid-State Letters*. 8(6):A273-A276.
4. Huang, S., Ganesan, P. & Popov, B.N. 2011. Applied Catalysis B: *Environmental*. 102(1–2): 71-77.
5. Antolini, E. & Gonzalez, E.R. 2009. *Solid State Ionics*. 180(9–10): 746-763.
6. Krasotkina, N.I., Yakovleva, V.S., Voronin, N.I. & Shmitt-Fogelevich, S. 1968. Refractories. 9(11-12): 723-726.
7. Samsonov, G.V. 1962. US Atomic Energy Commission, Division of Technical Information.
8. Lv, H., Mu, S., Cheng, N. & Pan, M. 2010.. *Applied Catalysis B: Environmental.* 100(1–2): 190-196.
9. Ding, H. & Hihara, L. 2006. ECS Transactions. 1(4):103-114.

# Synergistically Enhanced Performances of Pt Nanoparticles on Doped Mesoporous Carbon for Oxygen Reduction Reaction

Durante C., Perazzolo V., Picelli L., Rizzi G.A., Granozzi G., Gennaro A.

*Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova*
*e-mail: christian.durante@unipd.it*

Mesoporous carbons (MCs) are highly porous materials, which offer high surface area, chemical inertness and superior electrochemical performance with respect to traditional carbon materials [1]. Hetero-functional groups introduced into a carbon support appear to influence at least three aspects of the catalyst/support system: i) affect the nucleation and growth kinetics during catalyst nanoparticle deposition, ii) increase the support/catalyst chemical binding, which results in enhanced durability and iii) modify catalyst nanoparticle electronic structure, which enhances intrinsic catalytic activity [2]. In this work, nitrogen- or sulphur-doped (N-MC and S-MC) and dual doped MC (S,N-MC) are modified with Pt nanoparticles (Pt@N-MC, Pt@S-MC and Pt@N,S-MC) in order to verify the presence of these three distinct effects. The Pt loading was set to 25% (wt.) in order to compare the catalytic activity with commercial standards of high Pt content. Several Pt salt precursors and deposition conditions were tested in order to obtain the best particle dispersion and dimension. It is found that Pt deposition from $Pt(acac)_2$ affords the best results in terms of NPs dimension and dispersion. TEM analysis suggests the formation of very small NPs (1-3 nm) well dispersed inside and outside the mesopore structure of the carbon support (Fig. 1a), whereas XPS proved a slightly interaction between Pt and nitrogen and/or sulfur [3]

Linear sweep voltammetry was used to characterize electrocatalytic activity of the synthetized materials, and to compare their performances with respect to commercial Pt-supported undoped Vulcan (Tanaka, Pt loading 50 %). All synthetized Pt cathodes exhibit excellent electrocatalytic activity, which is comparable to or even higher than that of the standard material with higher Pt content. Electrochemical stability tests were also be carried out to elucidate the degradation of Pt nanoparticles.

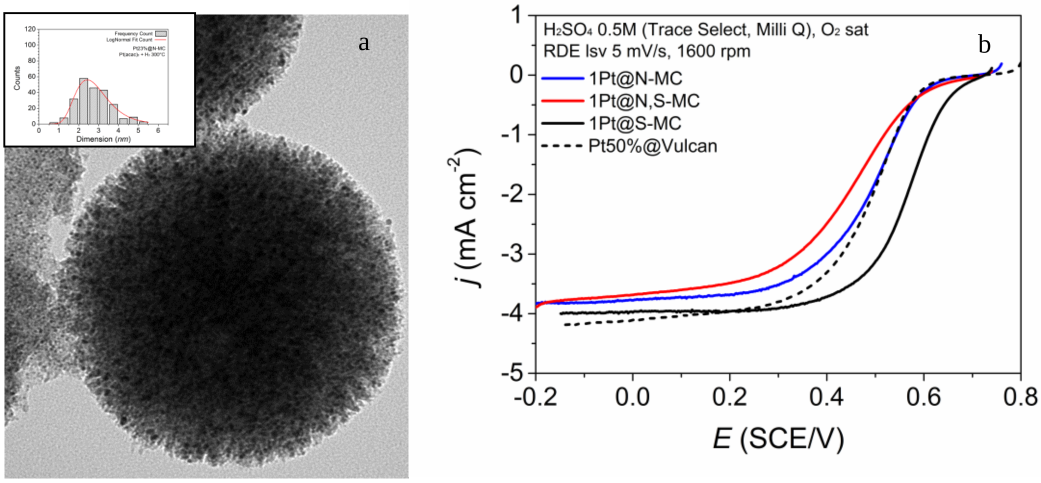


Figure 1: (a) TEM image of Pt@N-MC, (b) RDE LSV in $O_2$-saturated 0.5 M $H_2SO_4$.

We acknowledge financial support from Joint Undertaking (FCH-JU) within the CathCat project under contract No. 303492

[1] V. Perazzolo, C. Durante, R. Pilot, A. Paduano, J. Zheng, G.A. Rizzi, et al., Carbon 95 (2015)
[2] A.S. Bandarenka, M.T.M. Koper, J. Catal. 308 (2013) 11–24.
[3] L. Perini, C. Durante, M. Favaro, V. Perazzolo, S. Agnoli, O. Schneider, et al., ACS Appl. Mater. Interfaces. 7 (2015) 1170–1179.

# *In Situ* Surface Enhanced Infrared Spectroscopy Studies of Interfacial Processes Relevant to Nonaqueous Lithium-Oxygen Batteries

Vivek J. Padmanabhan, Richard J. Nichols and Laurence J. Hardwick
*Department of Chemistry, Stephenson Institute for Renewable Energy, University of Liverpool*
*Liverpool, L69 7ZF, UK*
*jpvivek@liverpool.ac.uk*

The rechargeable nonaqueous lithium-oxygen (Li-$O_2$) battery (also referred to as 'lithium-air' battery) offers enhanced energy storage over other existing battery systems [1]. Though promising, some severe technological problems need to be addressed for the successful development of this system into a commercially viable device. The development of an efficient cathode material and a stable electrolyte that allows reversible electrochemical reduction of oxygen is an area where significant research is necessary. Li-$O_2$ cells generate electrical current when lithium ions react with oxygen at the negatively polarised electrode during discharge, the as formed $Li_xO_2$ reaction products can be converted back to Li and $O_2$ during the charging cycle. The problem is that the discharge products (presumably superoxides and peroxides of lithium) and the metastable intermediates formed are highly reactive, and conventional battery electrolytes easily degrade in their presence. For a greater understanding of the oxygen reduction mechanism and for a direct detection of the intermediates and reaction products formed during the oxygen reduction process, surface sensitive spectroscopy techniques can be utilised. Compared to conventional infrared spectroscopy techniques, electrochemical attenuated total reflection surface enhanced infrared spectroscopy (ATR-SEIRAS) is particularly attractive for these studies because of its superior surface sensitivity [2]. A schematic representation of the ATR-SEIRAS cell used for our studies is shown in Figure 1. The beam of infrared radiation propagating in the internal reflection element (IRE) undergoes total internal reflection at the interface where a thin layer of gold (ca. 20 nm) was deposited. Total internal reflection at the interface between two media of different refractive indices creates an evanescent wave that penetrates into the medium of lower refractive index; here the evanescent wave penetrates several hundreds of nanometres from the surface into the electrolyte. For the nanostructured gold film formed on the IRE, the plasmon absorption band extends well into the infrared region, which gives rise to enhanced electromagnetic fields resulting in an increased IR absorption in the interfacial region formed by the gold film working electrode. This increased surface enhancement at the interfacial region helps to detect the surface bound species selectively while total internal reflection eludes any overwhelming bulk electrolyte signal. As opposed to the commonly used Si IRE, we use a ZnSe prism for our studies as it offers a wider range of infrared throughput extending to the region where lithium superoxides and peroxides can be detected. We will report on the electrochemistry of dioxygen in nonaqueous electrolytes relevant to lithium-oxygen batteries, discussing electrolyte degradation pathways, reaction products and intermediates probed using *in situ* ATR-SEIRAS technique.

1. P.G. Bruce, S. Freunberger, L.J. Hardwick, J.-M. Tarascon, Nature Materials, 2012 11, 19-29.
2. M. Osawa, Topics in Applied Physics, 2001, 81, 163-187.

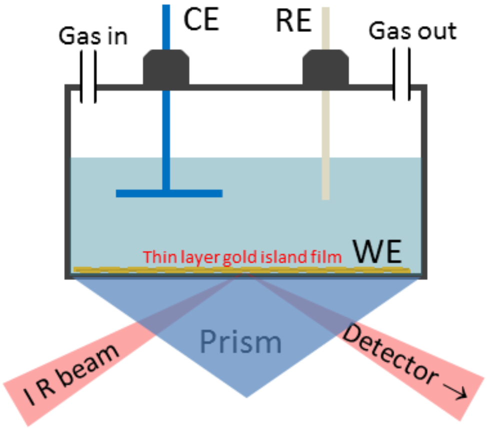


**Figure 1. ATR- SEIRAS Cell**

# Ni-Foam Anode GDEs for PEM-Water Electrolysis

Nils Baumann, Florina Jung, Carsten Cremers
*Fraunhofer Institute for Chemical Technology ICT*
*Joseph-von-Fraunhofer-Strasse 7, 76327 Pfinztal, Germany*
*nils.baumann@ict.fraunhofer.de*

## Introduction

A hydrogen based energy economy with $H_2$ being produced by Polymer Electrolyte Membrane Water Electrolysis (PEM-WE) has very good prospects of increasing in importance, due to technical simplicity, high purity of produced $H_2$ and good adaptability to fast changing loads. Most of the time Membrane Electrode Assemblies (MEAs) are produced by coating the membrane with the catalyst layer. As the membrane has to be dried for coating, it is subjected to thermal and mechanical stress, which could lead to cell failure during operation.[1] Here we manufactured and studied MEAs that were produced by coating modified Ni-foams with anode catalyst layers to produce Gas Diffusion Electrodes (GDEs).

## Results and Discussion

GDEs were manufactured by sanding porous Ni-foam on both sides, followed by slight compression to a thickness of about 250 µm. Sanding leads to an increased surface area for catalyst to be deposited, see Figure 1. Finally Ni-foams were sputter coated with a thin Au layer to increase electronic conductivity. Supported or unsupported $Ir_{0.5}Ru_{0.5}O_2$ catalysts were sprayed on finished GDEs using Hot-Spraying technique with commercial airbrush pistol.

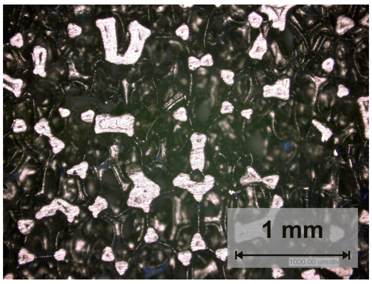


*Figure 1: Digital micrograph of sanded Ni-foam.*

GDEs were tested in single cell configuration using Fumatech F-950 membrane and commercial cathode GDEs (Pt/C on carbon felt) by applying 2.0 V with ultrapure $H_2O$ at both electrodes. Figure 2 shows maximum current density per day - with respect to loading of catalyst - of two single cell tests (measurements were rested during night). Maximum current densities with respect to the geometrical area were 661 mA $cm^{-2}$ (black) and 637 mA $cm^{-2}$ (red). Both GDEs were manufactured at the same time with same catalyst ink. It is hypothesized that the difference in activity arises from a difference in sanded area, i.e. available area for catalyst deposition. This area can be ascertained from micrographs, but has not been done for shown GDEs. Future studies will include measurement of sanded area and correlation to activity.

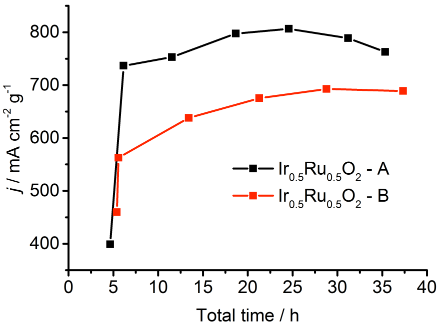


*Figure 2: Current density of two single cell tests. Lines are only given for optical guidance.*

## Conclusion

We have manufactured PEM-WE anode GDEs by sanding Ni-foam and coating it with catalyst. GDEs coated with $Ir_{0.5}Ru_{0.5}O_2$ show high activity of over 600 mA $cm^{-2}$ for at least 40 h. In most studies activity is only given with respect to gravimetrical loading of catalyst. Our results show that for a more accurate comparison of different GDEs the contact area of catalyst to membrane has to be taken into account, as well.

*Acknowledgment: Financial support by the German Federal Ministry of Education and Research (BMBF) under the contract number FKZ 03SF0432A is greatly acknowledged.*

## References

1. Collier, A., et al., *Degradation of polymer electrolyte membranes.* International Journal of Hydrogen Energy, 2006. **31**(13): p. 1838-1854.

# Bifunctional Catalysts in Li-Air Batteries for Automotive Applications

Juergen Kahr, Iliyan Popov, Tadios Tesfu-Zeru, Atanaska Trifonova
*AIT Austrian Institute of Technology, Mobility Department, EDT,*
*Giefinggasse 2, 1210 Vienna*
*juergen.kahr@ait.ac.at*

Great efforts have been taken in the development of hybrid vehicles equipped with both combustion engines and electric powertrains.[1,2] In recent years, fully electric powered cars with rechargeable batteries have received considerable attention. In any case, secondary batteries are a vital part of electric drive technologies and their performance greatly influences the vehicle characters. Lead or Ni-MH batteries have been used conventionally for automotive applications; nevertheless energy storage systems based on Li-Ion battery (LIB) technologies accomplish longer cruising ranges. However, in order to compete with the range of a full gasoline tank batteries with higher energy densities are of paramount importance.[3]

One approach to meet this demands is the Li-Air Battery which attracted much addition in recent years because of their high theoretical energy density compared to Li-Ion batteries.[4,5] The open battery concept using oxygen from surrounding air is promising regarding cost and specific energy. Although the rechargeability of a Li-Air battery was presented for the first time by Abraham and Jiang in 1996,[6] stability issues of electrolyte and electrode materials must be challenged before commercial application.

In order to promote cycle stability careful selection of morphology and composition of oxygen electrode materials is of great importance. Porous carbon widely functions as catalyst support in Li-Air batteries.[7] A catalyst of this kind serves two purposes which are the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during charge. Precious metal catalyst as Pt, Pd and Au have previously been proved as bifunctional catalyst.[8,9] Metal oxide catalyst such as $Co_3O_4$ and $MnO_2$ have also shown to improve cycle stability.[10,11]

We investigated different catalysts for OER and ORR as cathode components for Li-Air batteries in non-aqueous electrolyte systems for electric drive technologies. Here we present candidates as a new class of bifunctional catalyst for Li-Air batteries. In particular pyrolysed heterocycles containing metal centers such as cobalt or manganese were in the focus of our studies. Selected materials were compared with conventional metal or metal oxide catalyst by exploring the anodic and cathodic peak current with the result of good catalytic activities.

The author gratefully acknowledges the Austrian Research Promotion Agency (Project No. 845364) for funding of this research.

(1) M. Zackrisson, L. Avellán and J. Orlenius, J. Clean. Prod., 2010, 18, 15, 1519–1529.
(2) K.G. Høyer, Utilities Policy, 2008.
(3) F. Mizuno, K. Takechi, S .Higashi, T. Shiga, T. Shiotsuki, N. Takazawa, Y. Sakurabayashi, S. Okazaki, I. Nitta, T .Kodamaa, H. Nakamotoa, H. Nishikoori, S. Nakanishi, Y. Kotani and H.Iba, J. Power Sources, 2013, 228, 47-56.
(4) P. Bruce, S. Freunberger, L. Hardwick and J. Tarascon, Nat. Mater., 2012, 11, 19–30.
(5) G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson and W. Wilcke, J. Phys. Chem. Lett., 2010, 1, 2193–2203.
(6) K. M. Abraham and Z. Jiang, J. Electrochem. Soc., 1996, 1, 143, 1.
(7) M.M. O. Thotiyl, S. A. Freunberger, Z. Peng and P. G. Bruce, J. Am. Chem. Soc., 2013, 135, 494–500.
(8) Y.-C. Lu, H. A. Gasteiger and Y. Shao-Horn, J. Am. Chem. Soc., 2011, 133, 19048–19051.
(9) J. R. Harding, Y.-C. Lu, Y. Tsukada and Y. Shao-Horn, Phys. Chem. Chem. Phys., 2012, 14, 10540–10546.
(10) W. Ryu, T. Yoon, S. H. Song, S. Jeon, Y. Park and I. Kim, Nano Lett., 2013, 13, 4190–4197.
(11) A. Debart, A. J. Paterson, J. Bao and P. G. Bruce, Angew. Chem., Int. Ed., 2008, 47, 4521–4524.

# Nanosized OER Catalysts with Superior Activity for Anodes of PEM Electrolysis Produced by a Cost-Effective Procedure

A. S. Gago, P. Lettenmeier, L. Wang, K. A. Friedrich
*Institute of Engineering Thermodynamics*
*German Aerospace Center (DLR)*
*Pfaffenwaldring 38-40, Stuttgart, 70569, Germany Address*
*e-mail address: aldo.gago@dlr.de*

Proton exchange membrane (PEM) water electrolysis represents one of numerous environmentally friendly but at present economically unattractive technologies. Iridium is commonly used as oxygen evolution catalyst (OER) catalyst [1], but is highly priced and one of the rarest elements in the earth crust. Several approaches have been proposed to overcome the challenges associated with the precious metal OER catalyst such as reducing the particle size thus increasing the surface to mass ratio [2], using electroceramic supports [3] or enhancing the phase structure [4]. We present a variety of highly active nanostructured iridium based catalysts for anodes of proton exchange membrane (PEM) electrolysis: $IrO_x$-Ir, IrPt, $IrRuO_x$, IrV, and Ir/$Ti_4O_7$. Clusters of nanosized crystallites, Fig. 1a, are obtained by reducing surfactant stabilized $IrCl_3$ in water free conditions [5]. The catalysts shows up to five-fold higher activity towards OER than commercial Ir-black, Fig 1c. The improved kinetics of the catalysts are reflected in the high performance of the PEM electrolyzer (1 $mg_{Ir}$ $cm^{-2}$), showing an unparalleled low over-potential and so far negligible degradation. Our results demonstrate that this enhancement cannot be only attributed to increased surface area but rather to the ligand effect and low coordinate sites resulting in a high turnover frequency (TOF). The catalysts developed herein set a benchmark and pave a strategy for the development of ultra-low loading catalyst layers for PEM electrolysis.

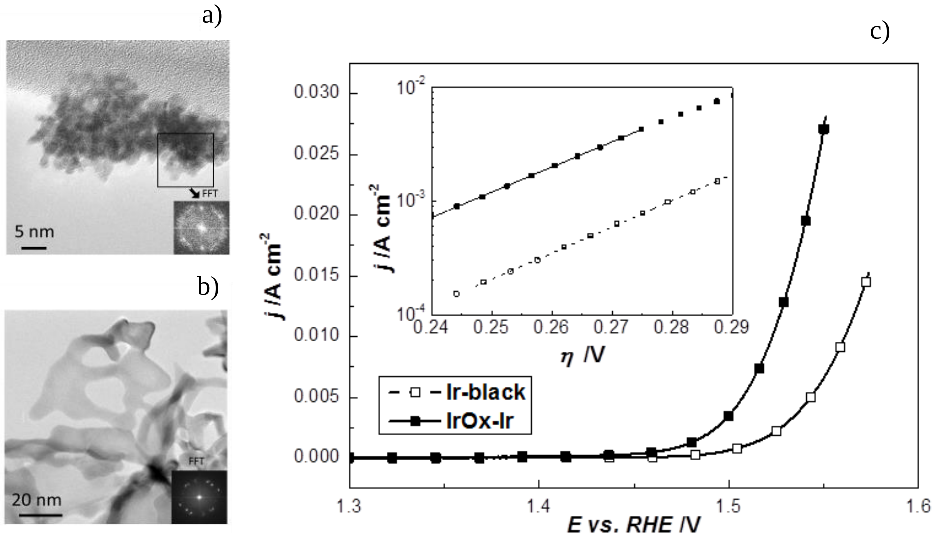


Fig. 1. TEM micrographs and Fourier transform (FFT) of the selected area of (a) $IrO_x$-Ir and (b) Ir-black; (c) current-potential curves of $IrO_x$-Ir and Ir-black with inset showing the Tafel slopes vs. the overpotential at 25 °C and sweep rate of 5 mV $s^{-1}$, rotation speed of 2500 rpm, in Ar-saturated 0.5 M $H_2SO_4$.

## References

[1] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, Int. J. Hydrogen Energy 38 (2013) 4901.
[2] E. a. Paoli, F. Masini, R. Frydendal, D. Deiana, C. Schlaup, M. Malizia, T.W. Hansen, S. Horch, I.E.L. Stephens, I. Chorkendorff, Chem. Sci. 6 (2015) 190.
[3] H.-S. Oh, H.N. Nong, T. Reier, M. Gliech, P. Strasser, Chem. Sci. 00 (2015) 1.
[4] M.S. Smith, Rodney D. L. Prévot, R.D. Fagan, Z. Zhang, P.A. Sedach, M.K.J. Siu, S. Trudel, C.P. Berlinguette, Sci. Express (2015).
[5] P. Lettenmeier, L. Wang, U. Golla-Schindler, P. Gazdzicki, N. Cañas, M. Handl, R. Hiesgen, S.S. Hosseiny, A.S. Gago, A.K. Friedrich, Angew. Chemie (2015) In press.

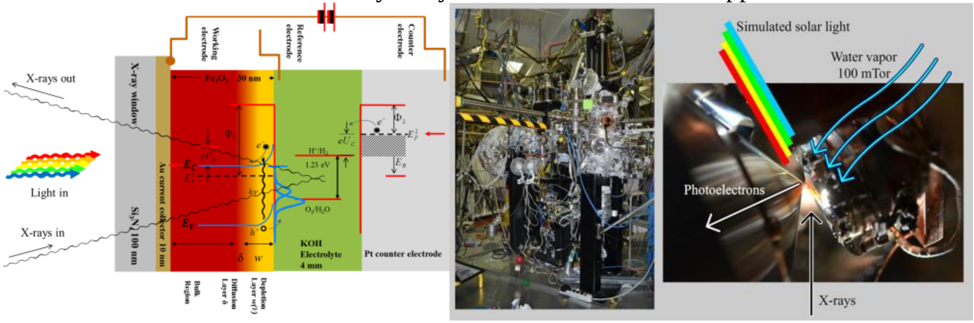
# Water oxidation with holes: What we learn from *operando* studies

Artur Braun[a], Yelin Hu[a,b], Debajeet K. Bora [a], Florent Boudoire [a,c],
Jinghua Guo[d], Michael Grätzel [c], Edwin C. Constable [b]

*[a] Laboratory for High Performance Ceramics, Empa. Swiss Federal Laboratories for Materials Science and Technology, CH - 8600, Dubendorf, Switzerland.*
*[b] Department of Chemistry, University of Basel, CH - 4056 Basel, Switzerland.*
*[c] Laboratory for Photonics and Interfaces, Ecole Polytechnique Federale de Lausanne, CH - 1015 Lausanne, Switzerland*
*[d] Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA 94720, California*

*artur.braun@alumni.ethz.ch*

Photogenerated electron holes are the key players in photoelectrochemical water oxidation. They provide the basis for direct solar fuel production in photoelectrochemical cells. The physics and the chemistry underlying the processes relevant for the water oxidation are probably the most complex known in physical chemistry. Therefore it is not surprising that the science of solar water splitting rests still on some speculative elements. Thanks to considerable progress in synchrotron radiation instrumentation, x-rays and electrons as fundamental probes for chemical and physical processes can now be used in complex electrocatalytic and photoelectrochemical experiments during actual device operation (1). The results of these studies which were impossible until very recently are indeed spectacular. We show (2-5) how we can assess with x-ray based ligand and valence band NEXAFS and AP-XPS spectroscopy the density of hole states in photoelectrodes as a function of electrochemical parameters and at the same time find quantitative information on the surface intermediates formed prior to, during and after water splitting. We are able to resolve the interaction of the photoelectrode with the electrolyte down to the Fe3d and O2p orbitals with bias parameterized energetic and spatial depth resolution, including the charge carrier accumulation layer, the electrode surface and the Helmholtz layer. The x-ray electronic structure data are in full alignment with the charge carrier dynamics probed with electroanalytical methods. Noteworthy is that we could verify and confirm a historically speculated second electron hole, which corresponds to a transition into the charge transfer band, which precedes the water splitting and coincides with the formation of a hydroxyl intermediate. Latter disappears when water oxidation sets on.



## References

(1) D. K. Bora et al. Between Photocatalysis and Photosynthesis: Synchrotron spectroscopy methods on molecules and materials for solar hydrogen generation, J. Electron Spectr. Rel. Phenom. 2013, 190 A, 93-105.
(2) A Braun et al. The electronic, chemical and electrocatalytic processes and intermediates on iron oxide surfaces during photoelectrochemical water splitting, Catal. Today (2015) http://dx.doi.org/10.1016/j.cattod.2015.07.024
(3) A. Braun et al. Direct observation of two electron holes in hematite during photo-electrochemical water splitting, J. Phys. Chem. C 2012, 116 (23) 16870-16875.
(4) A. Braun et al. Iron resonant photoemission spectroscopy on anodized hematite points to electron hole doping during anodization, invited for Special Issue: Electrochemistry and Energy in ChemPhysChem 2012, 13(12), 2937-2944.
(5) D.K. Bora et al. Evolution of an oxygen NEXAFS transition in the upper Hubbard band in α-Fe2O3 upon electrochemical oxidation, J. Phys. Chem. C, 2011, 115 (13), 5619–5625.

# Chemistry of the Active Sites in Transition Metal-Nitrogen-Carbon Electrocatalysts for Oxygen Reduction Reaction

Plamen Atanassov, Kateryna Artyushkova and Alexey Serov
*Center for Micro-Engineered Materials and Department of Chemical & Biological Engineering*
*The University of New Mexico · Advanced Materials Laboratory, 1001 University Blvd. SE, Suite 103*
*Albuquerque, NM 87106, USA*
*plamen.unm.edu*

The makeup and structure of the active site/sites of the non-PGM ORR electrocatalysts, including geometry (coordination) and chemistry (composition and oxidation state) remain contentious even after 50 years of research. There is an emerging agreement that iron and nitrogen functionalities, displayed on the surface if the carbonaceous substrate/support, govern ORR activity. This is often combined with a broadly accepted hypothesis that microporous surface area plays a critical role forming the active site. Candidate structures participating in ORR include multitudes of nitrogen defect motifs in the carbon matrix of different degrees of graphitization, with metal incorporated as metal nano-particles, corresponding (native) oxides and/or as atomically dispersed, oxidized metal species, linked (coordinated) to nitrogen defects in carbonaceous matrix in a variety of possible configurations. The types of nitrogen and iron-nitrogen functionalities that can be present in these materials are displayed in FIG. These consist of in-plane defects such as graphitic nitrogen and Fe-coordinated to three or four nitrogen atoms and a plurality of possible edge sites such as pyridinic, pyrrolic, quaternary and Fe-$N_2$/Fe-$N_x$ sites.

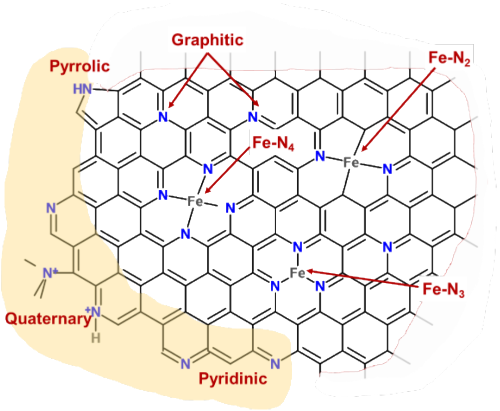


**FIG:** principal schematic of the various in-plane and edge N- and Fe-containing moieties in Transition Metal-Nitrogen-Carbon

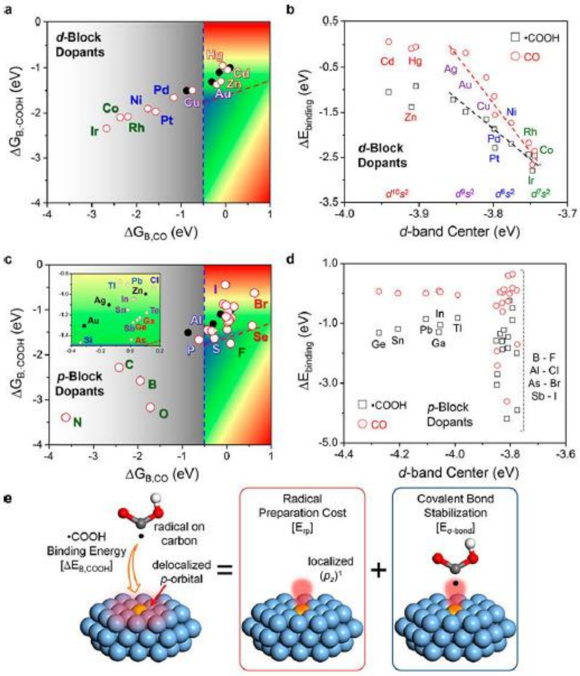
In this study, we have analyzed more than 45 distinct M-N-C electrocatalysts synthesized from three different families of precursors, such as (i) N-containing polymer, (ii) N-chelating macrocycles and (iii) N-containing small organic molecules (amines). Catalysts were evaluated and analyzed structurally using exactly the same protocol for deriving structure-to-property relationships. We have identified possible active sites participating in different ORR pathways: (1) metal-free electrocatalysts support partial reduction of $O_2$ to $H_2O_2$; (2) pyrrolic nitrogen acts as a site for partial $O_2$ reduction to $H_2O_2$; (3) pyridinic nitrogen displays catalytic activity in reducing $H_2O_2$ to $H_2O$; (4) Fe coordinated to N (Fe-$N_x$) serves as an active site for 4$e^-$ direct reduction of $O_2$ to $H_2O$. The ratio of the amount of pyridinic and Fe-$N_x$ to the amount of pyrrolic nitrogen serves as a rational design metrics of M-N-C electrocatalytic activity in oxygen reduction reaction occurring through the preferred 4$e^-$ reduction to $H_2O$.

There are two main hypotheses in the literature: one claiming that nitrogen functionalities on/in carbon-based support are directly responsible for their ORR activity and the second suggesting that nitrogen groups serve as the coordinating environment for metal ions, serving as reactive centers for the ORR. Theoretical calculations have confirmed that incorporation of nitrogen atoms in the carbon matrix enhances its electronic properties, but nitrogen atoms are not catalytically active towards a direct reduction of oxygen. Our mechanistic and structural studies have shown that multiple (yet similar) chemical functionalities most likely co-exists in practical M-N-C catalysts, displaying engagement in various steps of the ORR and thus obscuring the "simple model" of the "most active "*active site*".

# Design principles of electrochemical catalysts for $CO_2$ conversion

Hyungjun Kim, Hyung-Kyu Lim, Hyeyoung Shin, and Yoonhoo Ha
*Graduate School of EEWS, Korea Advanced Institute of Science and Technology*
*291 Daehak-ro, Yuseong-gu, Daejeon 305-701, KOREA*
*linus16@kaist.ac.kr*

To develop a sustainable carbon economy for the present and the future, it is essential to develop a carbon dioxide ($CO_2$) conversion technology to recycle environmentally threatening chemical of $CO_2$ into renewable carbon-based fuels and useful chemical feedstocks. However, there is not yet a solution sufficiently high enough efficiency and stability to demonstrate practical applicability. A key obstacle here is mostly due to the limited performance of the catalysts in terms of activity, stability, etc. To improve and tailor the catalytic properties, it is thus required to understand the operational mechanism of the various possible $CO_2$ reduction pathways and identify the mechanistic role of catalysts. We use first-principles based quantum mechanics (QM) simulations to understand, design, discover, and chemically modify catalytic active sites to improve the performance of the electrochemical $CO_2$ conversion. Based on our theoretical studies, we suggest design principles to realize efficient $CO_2$ electrochemical reduction catalysts. We expect this work to provide useful insights to guide the development of a feasible strategy to overcome the limitations of current technology for electrochemical $CO_2$ conversion.



[1] H.-K. Lim, H. Shin, W. A. Goddard, Y. J. Hwang, B. K. Min, and H. Kim, *J. Am. Chem. Soc.*, 2014, **136**, 11355-11361.

# Corrosion-resistive islands-by-islands composite of platinum catalyst supported by carbon nano-onion for oxygen reduction reaction

Juchan Yang, Hyun-Kon Song
*Department of Energy engineering, Ulsan National Institute of Science and Technology (UNIST)*
*Ulsan, 689-798, Republic of Korea*
*Juchana83@gmail.com*

Platinum supported by carbon (Pt/C) is the most representative catalysts for oxygen reduction reaction (ORR) for fuel cells and metal air batteries. However, the electrocatalytic performances of the composite catalysts are not durable during long-term operation of devices due to (i) loss of active Pt mass caused by carbon corrosion [1] and (ii) Pt particle agglomeration [2]. Since carbon atoms at edges, defects and dislocations are susceptible to oxidation [3], graphitization [4] and surface passivation [3] improve the corrosion resistivity of carbons. Non-carbon materials [5] are alternative to carbon blacks for the same purpose. Mechanisms of Pt agglomeration in low-temperature fuel cells were explained by Ostwald ripening (dissolution and re-deposition) and/or migration along the surface of carbon supports [2]. Ostwald ripening was expected to be dominant at more oxidative potentials (> 0.7 V vs. RHE) while the surface migration was thought to drive the Pt agglomeration at more reductive potentials (< 0.7 V vs. RHE). Nanostructured carbon supports having voids in which catalyst islands are trapped would be useful for suppressing Pt agglomeration.

To address the issues of the conventional carbon supports, here we present carbon nano-onion (CNO), a new class of carbon allotrope, as a support for Pt catalysts. The CNOs are spherical particles composed of concentric shells of $sp^2$-bonded carbon planes surrounding a hollow core. It had the spherical shape with 3 to 5 nm as its diameter consisting of ~5 concentric graphitic layers. There were no significant differences in the characteristics of ORR polarization observed between Pt/CNO and Pt/C (commercial catalyst by Etek; 20 wt. % Pt supported by carbon black) at their initial polarization. However, durability of catalytic oxygen reduction reaction (ORR) was guaranteed by Pt supported by CNO (Pt/CNO) possibly due to (1) the graphite-like concentric layers guaranteeing corrosion resistivity and (2) the *islands-by-islands* configuration of the Pt/CNO composites (c.f. islands-on-a-particle configuration for Pt/C) to isolate each Pt nanoparticle from its neighbors by the same-size CNO particles as well as to suppress Ostwald ripening by highly tortuous void structure. The current at a fixed potential (−0.6 V versus RHE) in alkaline media decayed to 92 % of the initial value after 15000 sec in Pt/CNO, which is higher than 70 % in Pt/C. Electrochemical surface area (ECSA) of Pt/CNO did not significantly change during 5000 times repeated potential scans in acid media. Direct evidences on corrosion-resistivity of CNO and suppressed Pt agglomeration on CNO were presented by thermogravimetric analysis and transmission-electron-microscopic images. Additionally methanol tolerance was improved in the presence of CNO.

[1] a) H. Tang, Z. Qi, M. Ramani, J. F. Elter, J. Power Sources 2006, 158, 1306-1312; b) S. Maass, F. Finsterwalder, G. Frank, R. Hartmann, C. Merten, J. Power Sources 2008, 176, 444-451; c) Y. Shao, J. Wang, R. Kou, M. Engelhard, J. Liu, Y. Wang, Y. Lin, Electrochim. Acta 2009, 54, 3109-3114.
[2] Y. Shao-Horn, W. C. Sheng, S. Chen, P. J. Ferreira, E. F. Holby, D. Morgan, Top. Catal. 2007, 46, 285-305.
[3] P. Atanassova, G. Rice, J.-P. Shen, Y. Sun, M. Dowlapalli, P. Atanassov, in Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, USA, 2007.
[4] H. Yano, T. Akiyama, M. Watanabe, H. Uchida, J. Electroanal. Chem. 2013, 688, 137-142.
[5] Y.-J. Wang, D. P. Wilkinson, J. Zhang, Chem. Rev. 2011, 111, 7625-7651.
[6] J. K. McDonough, Y. Gogotsi, The Electrochemical Society Interface 2013, 22, 61-66.

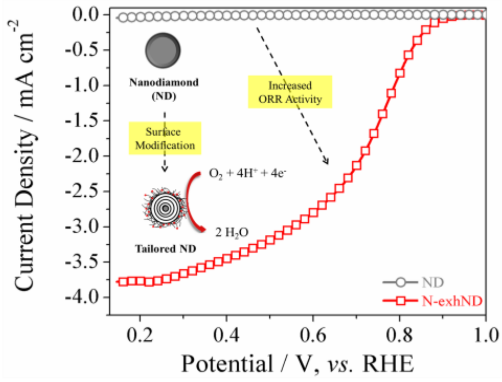
# Morphological and Dimensional Effect of the Carbon on High Performing Oxygen Reduction Reaction Catalysts in Acidic Media

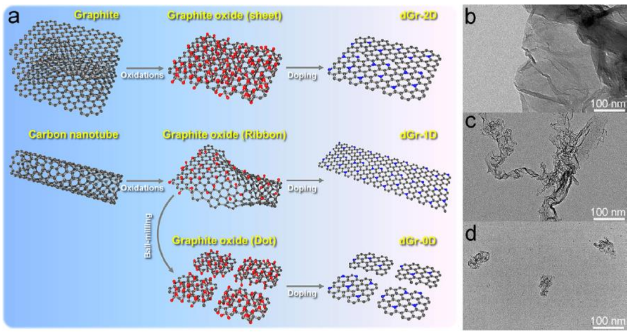
Seong Ihl Woo*[,a,b], Min Wook Chung[b], Jaekang Koh[b], Sung Hyeon Park[a] and Seung Yong Lee[b]

*[a] Graduate School of EEWS, Korea Advanced Institute of Science and Technology, 305-701, Daejeon, Republic of Korea*
*[b] Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 305-701, Daejeon, Republic of Korea*
** Corresponding author email address: siwoo@kaist.ac.kr*

Recently, carbon based catalysts have been extensively studied as a cathode material in Polymer Electrolyte Membrane Fuel Cells (PEMFCs) due to their intrinsic properties such as high surface area and high conductivity. Although various state-of-the-art modification techniques have been applied recently in order to enhance activity of the carbon-based catalysts, the improvement of carbon-based catalysts with competitive performance of oxygen reduction reactions (ORRs) towards Pt-based catalysts still require further exploration where the management of the active sites within the catalyst would be crucial. Moreover, the fundamental understanding for the nature of unexpected low catalytic activity towards ORR of carbon catalyst is still desired which has not yet been fully resolved.

Firstly, a new approach to advance the nature of carbon-based material as ORR catalyst is presented. Our optimized tailored nanodiamond catalyst showed a high current density which is about 54 % to that of Pt/C catalyst at 0.8 V (*vs.* RHE). Moreover, the catalyst retained a 71 % of performance even after harsh operations (0.6 - 1.4 V) of Accelerated Degradation Test (ADT), which was superior to that of Pt/C catalyst (retained 20 %). Through the modification of nanodiamond, the $sp^3$-hybridized diamond structure was deliberately preserved at the core which could retain stability, while the modification of the $sp^2$-hybridized at the surface carbon layers by the construction of defect- and edge-sites enhanced the catalytic activity. Secondly, to understand the fundamental aspects of the catalyst performance in ORR, the dimensionality of carbon catalysts is sequentially tuned from sheets (2D) to ribbons (1D) and to dots (0D), and physical along with electrochemical properties are investigated. In ultraviolet photoelectron spectroscopy (UPS), an increment in electropotential is measured as the dimensionality of the catalysts decreases, of which the result infers the enhanced kinetics of the electron transfer from the graphene catalysts to $O_2$ (electropotential: 0D > 1D > 2D). However, ORR performance does not follow the order of electropotential, and the graphene ribbons showed the best activity among the prepared graphene catalysts (ORR activity: 1D > 0D > 2D). Further electrochemical impedance spectroscopy studies demonstrate that ORR kinetics is primarily determined by charge transfer rates in the fabricated graphene electrodes, which are strongly related to the electrode configurations and thus also to the length–to–width ratios of the graphene catalysts. This study suggests the importance of void channels in the fabricated graphene electrode, which has not previously been considered significantly as a factor for improving ORR activity on the graphene catalysts.





# Single-Atom Platinum Supported on Titanium Nitride as a Catalyst for Selective Electrochemical Reactions

Sungeun Yang, Jiwhan Kim, Hyunjoo Lee*
*Korea Advanced Institute of Science and Technology*
*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea*
*justwalkon@kaist.ac.kr*

Single-atom platinum catalyst is the most efficient means to reduce platinum usage by maximizing catalytic active site per unit mass. Single-atom platinum catalyst was successfully prepared by using incipient wetness impregnation method. Titanium nitride nanoparticle was used as a support material. HAADF-STEM images (Figure 1) and EXAFS analysis revealed the successful preparation of single-atom platinum at platinum content of 0.35 wt%. 0.35 wt% Pt/TiN consists of single atoms, 2 wt% Pt/TiN consists of single-atoms as well as nanoparticles, and 5 wt% Pt/TiN consists of nanoparticles. Geometric effect of single-atom active sites resulted unconventional catalytic properties. When single-atom platinum was used for electrochemical oxygen reduction, hydrogen peroxide was dominantly produced showing selectivity up to 65% (Figure 2). Mass specific activity of 0.35% Pt/TiN at 50 mV overpotential was 78 A $g^{-1}_{Pt}$ which is the highest reported activity for electrochemical hydrogen peroxide production using platinum. Single-atom platinum was stable over 1 h durability test. Formic acid oxidation reaction and methanol oxidation reaction were also tested. Lack of platinum ensemble site in single-atom platinum catalyst controlled reaction pathway of formic acid oxidation reaction toward efficient direct dehydrogenation pathway, while showing negligible activity for methanol oxidation reaction.

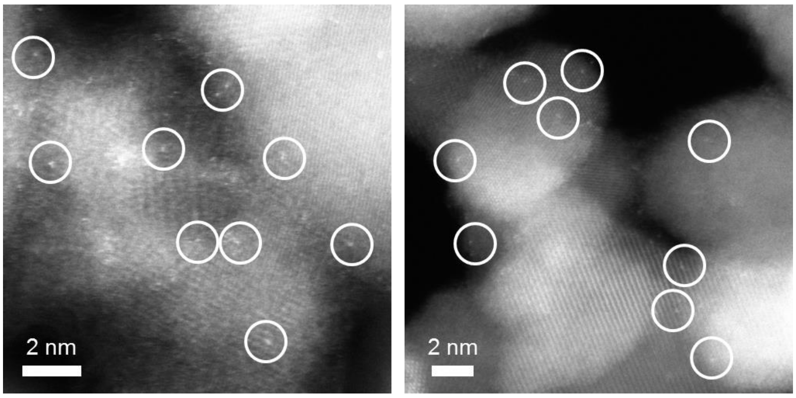


**Figure 1.** HAADF-STEM images of the single-atom Pt catalyst (0.35 wt% Pt/TiN). Some of the single-atom Pt were circled.

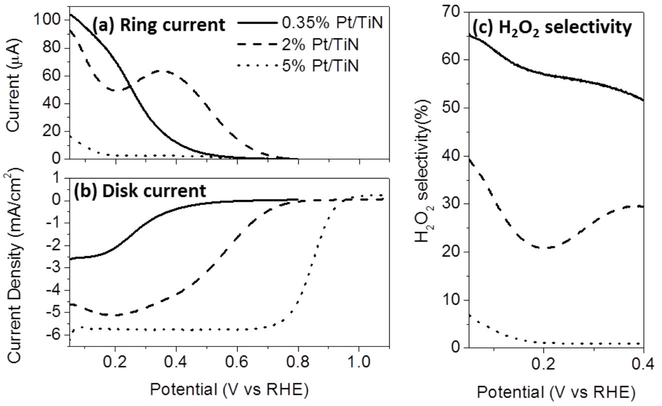
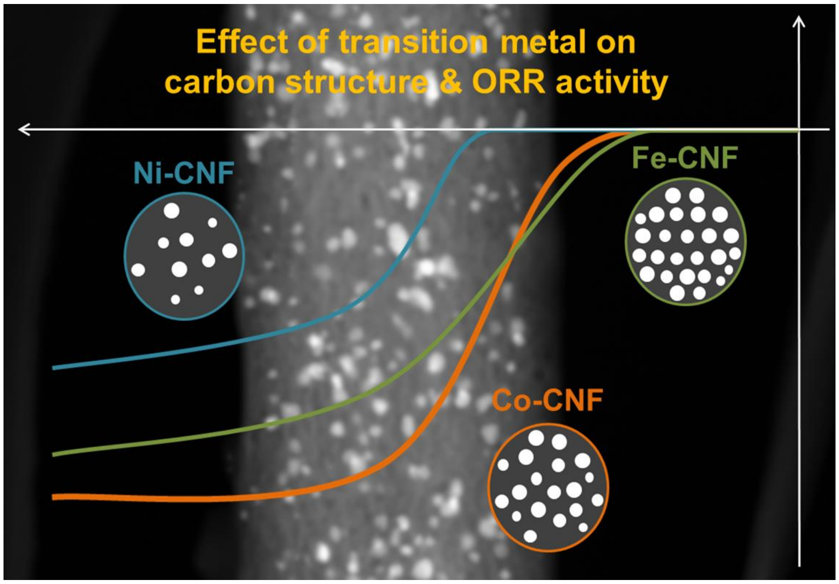


**Figure 2.** (a) Ring currents concurrently obtained during the ORR with a potential maintained at 1.2 V, (b) ORR polarization curves in $O_2$-saturated 0.1 M $HClO_4$, and (c) $H_2O_2$ selectivity calculated from the oxygen reduction current and the $H_2O_2$ oxidation current.

# Effect of Transition Metal Induced Pore Structure on Oxygen Reduction Reaction of Electrospun Fibrous Carbon[1]

Dongyoon Shin[a], Xianghua An[a], Myounghoon Choun[a], Jaeyoung Lee[a,b,*]
[a] *Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea*
[b] *Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies, GIST, Gwangju, 500-712, South Korea*
*jaeyoung@gist.ac.kr, shingoon@gist.ac,kr*

Finding cost-effective alternative electrocatalysts for oxygen reduction reaction (ORR) is considered as one of the most overriding challenges in the development of electrochemical technologies such as fuel cell and metal-air batteries. Although significant progress has been made in developing carbon-based ORR catalysts as cost-effective alternative to platinum, most of alternative electrocatalysts have been synthesized *via* heat treatment in trial and error. Therefore, it is necessary to investigate factors that can affect to electrocatalysts during synthesis process and how the difference in electrocatalysts can influence the ORR activity. In this study, we investigated effect of transition metal on carbon pore structure formation and ORR activity. Based on the detailed physicochemical analysis with electrospun transition metal containing carbon nanofibers (TM-N-CNFs), we reveal that the ORR activity was totally different in various TM-N-CNFs due to difference in pore structure. Moreover, the reason of different carbon structure formation might be catalytic graphitization that generally occurs during heat treatment of mixture of carbon and transition metal at high temperature.[2,3] Such knowledge is important for the understanding of carbon-based ORR catalysts and the knowledge should attribute the rational design of other carbon-based ORR catalysts to improve performance of them as alternative catalysts.



**References**

[1] D. Shin, X. An, M. Choun, J. Lee, *Catalysis Today* **2015**, *In press*.

[2] K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, Wiley, Berkeley, **1988**.

[3] X. An, D. Shin, J. D. Ocon, J. K. Lee, Y. Son, J. Lee, *Chinese Journal of Catalysis* **2014**, *35*, 891–895.

# Supported Pt-containing Catalysts: Durability Against Activity

Guterman V.E.[a], Belenov S.V.[a], Alekseenko A.A.[a], Tabachkova N.Yu.[c],
Volochaev V.A.[a]
[a]*Southern Federal University, Zorge st.,7, Rostov-on-Don, Russia, 344090.*
[b]*National Research Technological Univ. "MISIS", Leninskiy av.,4, Moscow, Russia.*
*e-mail:* gut57@mail.ru, guter@sfedu.ru

Efficiency of platinum-containing catalyst use in the low-temperature Fuel Cells (LTFC) is determined, primarily, by the mass activity and durability. From the general considerations, it is clear that increasing of electrochemically active surface area (ESA) of catalyst should increase its mass-activity and reduce the stability. However, there are a number of factors, which influence on these characteristics, still insufficiently studied. There is no a single answer to the question, what range of ESA values corresponds to the optimal combination of mass activity and stability.

The aim of this work was to investigate the relationship between ORR activity and stability for a wide number of Pt/C and Pt-M/C catalysts, obtained by means of chemical reduction of metal's precursors. Commercial Pt/C materials were also used as the test samples. It was important to study the influence the microstructure of the catalysts on their activity and stability and to assess the relationship of such influence with the composition and structural characteristics of catalysts.

Studies carried out in a laboratory cell. Specific current values (A $g^{-1}$(Pt)) at E = 0.8 V and RDE speed 1000 rpm were used as an index of the of catalyst mass activity in the ORR. Durability of electrocatalysts was evaluated by a change of the ratio $ESA_k/ESA_{max}$ (where k is a number of cycles) in the process of long-term CV cycling (potential range 0.6 V - 1.4 V, $\nu$ = 100 mV $s^{-1}$), to be exact - the ratio $ESA_{1000}$ / $ESA_{max}$.

The presence of a linear antisymbatic relationship between activity and stability of the investigated electrocatalysts has been determined (fig.1). Strong correlation between the values of these parameters is caused by the dependence of each parameter from catalyst microstructure. It would seem that the results of the study demonstrate the impossibility to obtain Pt/C electrocatalyst, which simultaneously display both high mass activity and high stability. However, the values of mass activity and stability for some catalysts were higher than the mean values calculated by the equation of linear correlation (fig.1).

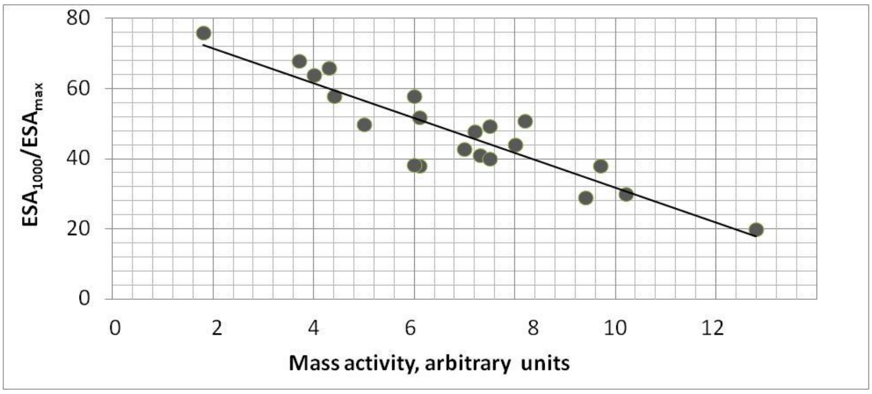


Figure 1. Interrelation of durability and mass-activity in ORR for a number of Pt/C and PtM/C electrocatalysts.

Very interesting results were obtained for some catalysts based on Pt-M nanoparticles with a core-shell structure. Their parameters are not plotted in Fig. 1. ESA of such catalysts is determined not so much by the size of nanoparticles, as by the thickness of the Pt-shell. Perhaps, features of the composition/structure of the electrocatalysts influenced on the significant increase of the ratio of the activity/stability compared with the parameters of the corresponding linear correlation equation. We believe that the approach, connected with the determining the position of marker for each electrocatalyst in a particular area of the correlation diagram, can be used for initial choice of samples, which combine high values of activity and stability.

We are grateful to the RSF (project No 16-19-00023), inspired us to conduct this study.

# Monitor oxygen-evolving iridium surfaces *in situ* by XPS & NEXAFS

T. E. Jones[1], V. Pfeifer[1,3], J. J. Velasco Vélez[1,2], R. Arrigo [1,2], M. Hävecker[1,2], E. Stotz[1],
A. Knop-Gericke[1], R. Schlögl[1,2]

*[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*
*[2] Max-Planck-Institut für Chemische Energiekonversion, Stiftstr. 34-36, 45470 Mülheim a. d. Ruhr, Germany*
*[3] Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany*
*trjones@fhi-berlin.mpg.de*

Iridium oxide based electrodes are promising candidates for electrocatalyzing the oxygen evolution reaction (OER) in acidic media. X-ray photoemission spectroscopy (XPS) and the near-edge X-ray absorption fine structure (NEXAFS) allow us to gain a deeper understanding of the electronic structure of OER-active iridium oxide surface species.

For a fundamental investigation of the electronic structure of iridium oxides and the generation of a reference library, we combined XPS and NEXAFS of benchmark systems with theoretical calculations. We found that the peculiar Ir 4f line shape of rutile-type $IrO_2$ is due to a shake-up satellite 1 eV above the main line. Furthermore, our experiments reveal that a pre-edge feature appears in the O K-edge of catalytically more active X-ray amorphous $IrO_x$, along with additional intensity at higher binding energies in the Ir 4f spectrum when compared to rutile-type $IrO_2$. We identify the former as the emergence of O 2p hole states and the latter as formally $Ir^{III}$ species. These electronic defects in the near-surface region of the anionic and cationic framework are likely critical for the enhanced activity of X-ray amorphous $IrO_x$.

To monitor changes in the electronic structure of oxygen-evolving iridium surfaces, we have developed two types of electrochemical cells, Nafion® and $SiN_x$, that are compatible with the Near-Ambient-Pressure XPS setup at the ISISS beamline at the synchrotron BESSYII/HZB in Berlin, Germany. In both cells, membranes separate the evacuated measurement chamber from a continuous flow of electrolyte. The Nafion® cell[1] uses on a proton exchange membrane while the $SiN_x$ cell[2] employs graphene-covered, perforated $SiN_x$ windows. In the Nafion® cell, sputter-deposited iridium faces the X-rays (see Figure 1). The mud crack type structure of the sputtered films is both water permeable and conductive. The water-based electrolyte diffuses through the Nafion® and the mud cracked iridium film into the measurement chamber thereby delivering the reactant molecules to the surface. An externally connected potentiostat permits the application of potentials to the electrodes and gas evolution is directly monitored by online mass spectrometry. In the SiNx cell, the Ir nanoparticles sputter-deposited on graphene are in direct contact with the electrolyte (see Figure 2). The detection principle of the $SiN_x$-cell is based on the electron transparency of graphene. Both cells enable us to follow the formation of highly defective iridium oxide surface terminations during the OER, and changes therein, as a function of the applied potential. Our reference library serves as the basis for the speciation of the observed iridium oxide modifications.

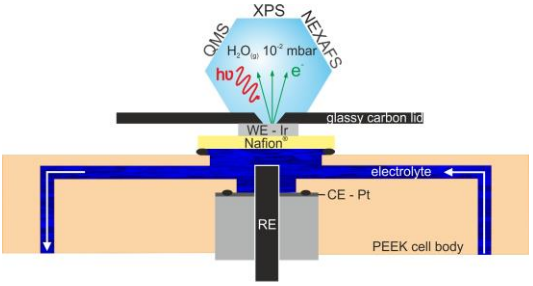


Figure 1: Nafion® cell

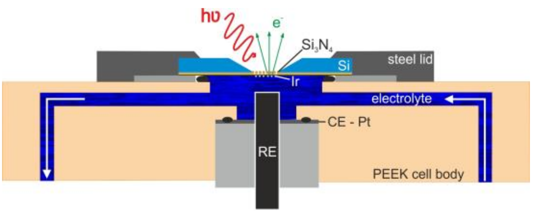


Figure 2: $SiN_x$ cell

(1) Arrigo, R.; Hävecker, M.; Schuster, M. E.; Ranjan, C.; Stotz, E.; Knop-Gericke, A.; Schlögl, R., *Angew. Chem. Int. Ed.* **2013,** *52* (44), 11660 - 11664.
(2) Velasco-Velez, J. J.; Pfeifer, V.; Hävecker, M.; Weatherup, R. S.; Arrigo, R.; Chuang, C.-H.; Stotz, E.; Weinberg, G.; Salmeron, M.; Schlögl, R.; Knop-Gericke, A., *Angew. Chem. Int. Ed.* **2015**, doi:10.1002/anie.201506044.

# Soft X-ray photoelectron spectroscopy at electrified solid-liquid interfaces

J. J. Velasco-Vélez, V. Pfeifer, M. Hävecker, R. Weatherup, R. Arrigo, C.-H. Chuang, E. Stotz, G. Weinberg, M. Salmeron, R. Schlögl, A. Knop-Gericke,
*Max Planck Institute for Chemical Energy Conversion*
*Mülheim 45470 (Germany)*
*velasco@fhi-berlin.mpg.de*

One of the main goals in electrochemistry is the characterization of electrode-electrolyte interfaces under operating conditions, to capture their electronic structure and chemical composition when in contact with the electrolyte and in the presence of applied electrical bias. However, the lack of surface sensitive techniques able to monitor the electronic structure under reaction conditions in aqueous environment hinders the total understanding of such processes. We have overcoming this issue thanks to the development of a new electrochemical setup based in a bi-layer of graphene (BLG) which makes possible electron spectroscopy *in situ*, i.e during electrochemical reactions (see Figure 1a) . Using this approach we investigated the electronic structure of electrochemically grown cobalt on graphene following the underpotential deposition procedure described in figure 1b [1]. Cobalt grown on graphene has demonstrated a remarkable performance for oxygen evolution reaction (OER) [2] even better than of carbon based electrodes functionalized with noble metals such as Pt [3] and Ir [4]. The electronic structure of the electrodeposited Co onto graphene was investigated *in situ* by means of X-ray spectroscopy (XAS and XPS) as figure 1c shows. We found that cobalt anchors on graphene via carbonyl-like species, i.e. $Co(CO)_x$ promoting the reduction from $Co^{3+}$ to $Co^{2+}$ species, which is believed to be the active sites of the catalysts. Based on this approach, we will present in the conference this and other recently results in the frame of the electrochemical energy conversion.

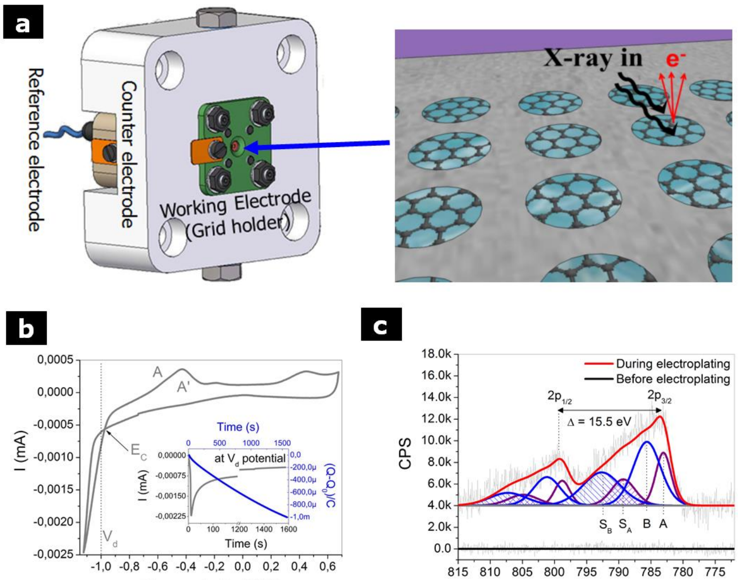


**Figure 1. (a)** Sketch of the liquid flow cell and schematic drawing of the $Si_3N_4$ grid coated by a BLG. **(b)** Cyclic voltammogram and charge transfer curve (inset) at -1 V in 4 mM CoSO4 (overpotential deposition of cobalt) **(c)** Co 2p XPS region before (bottom, black curve) and during the electroplating (top, red curve).

**References:**
[1] J. J. Velasco-Velez et al., *Angewandte International Edition* **2015**, DOI:10.1002/ange.201506044R2
[2] S. Mao et al., *Ener. & Environ. Sci.* **2014**, 7(2), 609-616.
[3] J. Wang, et al., *Ener. & Environ. Sci.* **2013**, 6(3), 926-934.
[4] L. Wu, et al., *JACS* **2015**, 137(22), 7071-7074.

# Synthesis of Platinum Carbon Composite Catalyst by Ethanol Reduction Method and Its Electrochemical Properties

Yoshihiro Kadoma *,**, Yuya Tada *,**, Akari Matsutomo *,**, Miyuki Kojima *,**, Koichi Ui *,
and Tatsuya Takeguchi *,*
* *Department of Frontier Materials and Functional Engineering, Graduate School of Engineering*
**Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan*
** *ALCA-SPRING, JST, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan*
*takeguch@iwate-u.ac.jp*

## Introduction

The lithium-air secondary battery has high capacity and energy density (5200 Wh kg$^{-1}$) 1). It is expected to apply the power supplies of the small and large electronic apparatuses. However, its property and cyclability are poor, since the formation of lithium peroxide ($Li_2O_2$) on the surface electrode prevented oxygen from diffusing in an air electrode. To overcome these problems, the effective $Li_2O_2$ decomposition catalysts are required. Recently, it is reported that the catalyst like the platinum carbon composite catalyst (Pt/C) has an influence on the electrochemical properties of lithium-air secondary battery 2). Therefore, we focused on the Pt/C catalysts. In this study, we have synthesized the Pt/C catalysts using an ethanol reduction method 3) and evaluated the Pt/C catalysts with the various Pt loadings.

## Experimental

The Pt/C catalysts were prepared using an ethanol reduction method 3). $Pt(NO_2)_2(NH_3)_2/HNO_3$ and Ketjen black (ECP600JD, KB) were dispersed in the water containing ethanol solution. $Pt(NO_2)_2(NH_3)_2/HNO_3$ (5, 10, 20, 30, and 40 wt. %) was added into the mixed solution Pt loadings ratio. The mixed solution was filtered after stirring for 12 h. The obtained precursors were dried at 80 °C for 12 h in a nitrogen atmosphere. KB and commercially available Pt/C catalyst (Pt: 46.6 wt. %, TEC10E50E) were used as the catalysts for comparison. The characterizations of catalysts were carried out by XRD, TG analysis, FE-SEM, and TEM. All the catalysts were mixed with a polyvinylidene difluoride binder in the weight ratio of 93:7. The discharge-charge tests to examine the electrochemical properties of the KB and the Pt/C catalysts were performed between 2.0 and 4.5 V at the current densities of 150 $\mu$A cm$^{-2}$.

## Results and discussion

From the XRD patterns and TG analysis, it was confirmed that the Pt/C catalysts (5, 10, 20, 30, and 40 wt. %) were synthesized. The SEM and TEM observations indicated that the Pt particles dispersed on the surface electrode and the prepared Pt/C catalysts showed smaller particle size than TEC10E50E. Fig. 1 shows the first discharge-charge curves of the KB, TEC10E50E, and Pt/C (Pt: 5, 10, 20, 30, and 40 wt. %) catalysts prepared using the ethanol reduction method. The Pt/C (Pt: 10 wt. %) catalyst shows the highest electrochemical properties of all the catalysts. Moreover, it indicates that the overvoltage depends on the Pt loadings of the Pt/C catalysts during discharge process. It was found that the Pt loadimgs of the Pt/C catalysts affected the electrochemical properties of lithium-air secondary battery and the 10 wt. % Pt/C catalyst showed higher electrochemical property than the commercially available Pt/C catalyst.

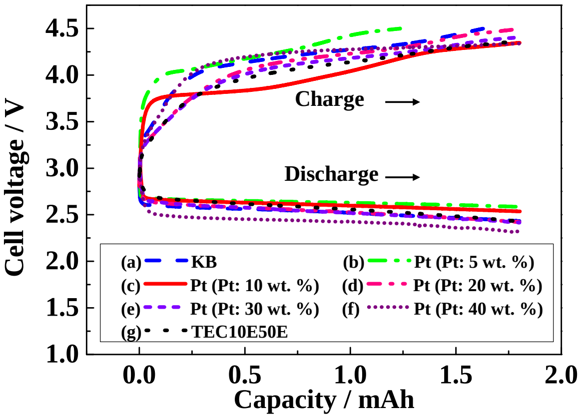


Fig. 1 First discharge-charge curves of the KB, TEC10E50E, and Pt / C (Pt: 5, 10, 20, 30, 40 wt. %) catalysts at 150 $\mu$A cm$^{-2}$; voltage range: 2.0-4.5 V; (a): KB, (b): Pt (5 wt. %), (c): Pt (10 wt. %), (d): Pt (20 wt. %), (e): Pt (30 wt. %), (f): Pt (40 wt. %), and (g): TEC10E50E.

## References

1) T. Ogasawara *et al.*, *J. Am. Chem. Soc.*, **128**, 1390 (2006).
2) L. Jiaxin *et al.*, *ACS Appl. Mater. Interfaces*, **6**, 12479 (2014).
3) J. M. Song *et al.*, *Langmuir*, **22**, 6422 (2016).

## Acknowledgement

This research was partially supported by ALCA-SPRING, JST.

# Controlling the Activity for the Oxygen Reduction Reaction and the Stability of Hollow PtNi/C Nanoparticles via Synthesis Conditions and Post-treatments

Laetitia Dubau[1,2] , Jaysen Nelayah[3], Raphaël Chattot[1,2], Tristan Asset[1,2], Frédéric Maillard[1,2]
*1. Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France*
*2. CNRS, LEPMI, F-38000 Grenoble, France*
*3. Laboratoire Matériaux et Phénomènes Quantiques (MPQ), UMR 7162 CNRS & Université Paris-Diderot, F-75205 Paris Cedex 13, France*

*laetitia.dubau@lepmi.grenoble-inp.fr*

The ever-growing energy demand worldwide and the announced end of the so-called "fossil fuel era" are currently boosting the development of electrochemical energy technologies, such as fuel cells, batteries and supercapacitors. In proton-exchange membrane fuel cells (PEMFC), special effort has been paid to improve the catalytic activity for the oxygen reduction reaction (ORR) of the cathodic material, its stability and to decrease the overall cost.

In this study, hollow PtNi/C nanoparticles were synthesized via a method involving the galvanic replacement of Ni atoms by Pt atoms, and the nanoscale Kirkendall effect. Increasing the Pt:Ni stoichiometry from 1:1 to 1:5 in the initial metal precursor solution resulted into a thinner Pt-rich shell and an increased Pt lattice contraction. The best electrocatalyst achieved 6-fold and 10-fold enhancement in mass and specific activity for the ORR, respectively over standard solid Pt/C nanocrystallites of the same size. This enhancement was ascribed to (i) its opened porous architecture, (ii) its preferential crystallographic orientation ("ensemble effect"), and (iii) the weakened oxygen binding energy induced by the contracted Pt-Pt distance ("strain effect") [1,2]. As it will shown in this contribution, post-treatments in neutral, oxidizing, and reducing atmosphere may be used to control the atomic structure, and thus improve the catalytic activity and the stability of this type of electrocatalysts.

References

1. L. Dubau, M. Lopez-Haro, J. Durst, L. Guétaz, P. Bayle-Guillemaud, M. Chatenet, F. Maillard, *J. Mater. Chem. A*. 2, 18497-18507 (2014).
2. L. Dubau, T. Asset, C. Bonnaud, R. Chattot, V. van Peene, F. Maillard, *ACS Catal.*, 5 (2015) 5333-5341.

Acknowledgements

This work was performed within the framework of the Centre of Excellence of Multifunctional Architectured Materials "CEMAM" n° AN-10-LABX-44-01 funded by the "Investments for the Future" program. The authors acknowledge financial support from University of Grenoble-Alpes through the AGIR program (grant # LL1492017G), and from the French National Research Agency through the HOLLOW project (grant # ANR-14-CE05-0003-01).

# Dental Amalgam as an Electrode Material for the Electrochemical Reduction of Carbon Dioxide to Formate

Woonsup Shin and Mijung Park

*Department of Chemistry, Sogang University, Seoul 121-742, Korea*
*shinws@sogang.ac.kr*

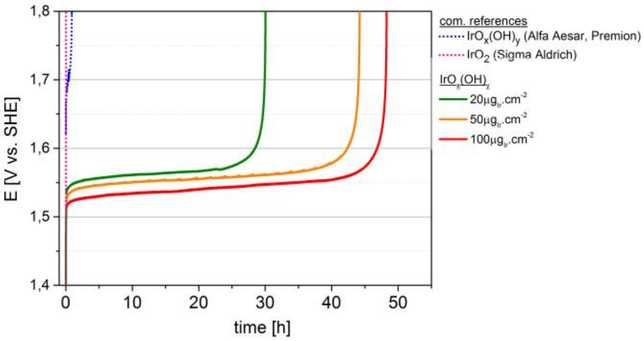
Currently, tin (Sn) is the most actively used electrode material for the conversion of $CO_2$ to formate, but easy corrosion of Sn hinders in the application in a continuous and stable electrolysis of $CO_2$. In case mercury (Hg), although it has been known to the best electrode material for $CO_2$ reduction to formate, mercury has not been used recently because of its toxicity. It is also difficult in handling and constructing the electrochemical system because of its liquid state in room temperature. We tried to avoid the both problem by using dental amalgam which consists of Hg, Sn, Ag, and Cu as an electrode material for $CO_2$ reduction. We succeeded in producing formate with a current efficiency of 80~90% at 50 mA/cm$^2$ for more than a week.

# The role of amorphous Ir-oxohydroxides for the Oxygen Evolution Reaction

C. Massué, V. Pfeifer, S. Cap and R. Schlögl
*Fritz-Haber-Institute of the Max-Planck Society*
Faradayweg 4-6, 14195 Berlin
*cmassue@fhi-berlin.mpg.de*

A successful transition towards renewable energy sources requires efficient energy storage solutions in order to ensure a stable power supply. In this regard, chemical energy storage through hydrogen production has been identified as the most suitable technological solution.[1] Proton exchange membrane (PEM)-based electrolyzer setups for water splitting allow for the production of high-purity hydrogen at high pressures. However, PEM-electrolyzers also require an acidic electrolyte, which impedes the stability of electrocatalysts, especially in the anodic Oxygen Evolution Reaction (OER). Under low pH-conditions, most transition metal oxides such as $Co_3O_4$, $Fe_2O_3$, $MnO_x$ and even $RuO_2$ exhibit severe corrosion rates due to the harsh local chemical conditions imposed by the OER.[2] To the best of the author's knowledge, in acidic electrolyte Ir-based materials are the only stable and active OER-catalysts that can provide a significant lifespan to the anode.[3,4] Due to the elevated costs of Ir, the decrease of electrode loadings and its corrosion stability represent key factors to promote the PEM-based water-splitting as a commercially competitive energy storage solution. P. Strasser et al. recently reported on the prominent role of OER-active amorphous Ir-oxohydroxide-species.[5,6]

In the present contribution, we will report the synthesis of a portfolio of such amorphous Ir-oxohydroxides, using an innovative synthetic route, and present their comprehensive and challenging characterization using several state of the art analytical methods, XRD, Raman, DRIFTS as well as XPS- and NEXAFS- measurements performed at the BESSY II/HZB synchrotron radiation source. The assessment of sample OER-performance was conducted using both linear sweep voltammetry (LSV) for OER-activity and galvanostatic measurements at 10 $mA.cm^{-2}$. For electrode loadings below 100 $\mu g_{Ir}.cm^{-2}$, our best samples clearly outperformed the benchmarks recently reported by McCrory et al. as well as commercial references.[3]



Chronopotentiometric measurement at 10 $mA.cm^{-2}$ for various loadings of synthesized Ir-oxohydroxide in comparison with two commercial references

Thus, Ir-oxohydroxides synthetized in the present work constitute a class of extremely promising candidates for inexpensive and stable OER-electrocatalysis. The understanding of the chemical nature of surface sites present before and during OER should yield critical information for the further optimization of preparation procedures for Ir-based OER-electrocatalysts.

(1) Schlögl, R. *ChemSusChem* **2010**, *3*, 209.
(2) Kötz, R.; Stucki, S.; Scherson, D.; Kolb, D. M. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, *172*, 211.
(3) McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. *J. Am. Chem. Soc.* **2015**, *137*, 4347.
(4) Katsounaros, I.; Cherevko, S.; Zeradjanin, A. R.; Mayrhofer, K. J. J. *Angewandte Chemie International Edition* **2014**, *53*, 102.
(5) Cherevko, S.; Reier, T.; Zeradjanin, A. R.; Pawolek, Z.; Strasser, P.; Mayrhofer, K. J. J. *Electrochemistry Communications* **2014**, *48*, 81.
(6) Reier, T.; Teschner, D.; Lunkenbein, T.; Bergmann, A.; Selve, S.; Kraehnert, R.; Schlögl, R.; Strasser, P. *J. Electrochem. Soc.* **2014**, *161*, F876.

# Influence of Mesopore Volume of Carbon Materials on Electrochemical Performance for Lithium-air Secondary Battery

Tatsuya Takeguchi[*, **], Shun Sakamoto[*, **], Yoshihiro Kadoma[*, **], Akari Matsutomo[*, **],
Miyuki Kojima[*, **], and Koichi Ui[*]
[*] *Department of Frontier Materials and Function Engineering, Graduate School of Engineering,*
*Iwate University, 4-3-5 Ueda, Morioka, Iwate, 020-8551, Japan*
[**] *ALCA-SPRING, JST, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan*
*takeguch@iwate-u.ac.jp*

**Introduction** In recent years, lithium-air secondary battery is expected to be next generation secondary battery due to extremely high theoretical energy density (5200 Wh kg$^{-1}$). However, the reaction product ($Li_2O_2$) deposits on the surface of the electrodes and clogs the porous structure of the air electrodes during discharge process. Therefore, the structure of the air electrode affects the electrochemical performance of lithium-air secondary battery. The influence of the pore structure of carbon materials on the electrochemical characteristics is not clear although the carbon materials are widely studied as air electrodes for lithium-air secondary battery. In this study, we have prepared the carbon electrodes using the carbon materials varying in the mesopore volume and investigated their electrochemical characteristics.

**Experimental** Ketjen black ECP600JD (ECP600JD), Ketjen blak EC300J (EC300J), Vulcan XC-72R (XC-72R), and acetylene black (AB) were used as the carbon materials. The carbon electrodes were prepared by casting the mixture consisting of carbon materials and 10 wt. % polyvinylidene fluoride/*N*-methyl pyrrolidone with the weight ratio of 97 : 3 onto the carbon paper and dried at 80 °C overnight. After drying, the loading amount of the carbon materials on the electrode was about 0.5 mg cm$^{-2}$. The carbon electrodes were transferred into an argon-filled glovebox for the cell assembling. The R2032 coin type cell consisted of the various carbon electrodes (16 mm in diameter), lithium metal foil (16 mm in diameter), 1 mol dm$^{-3}$ $LiCF_3SO_3$ dissolved in tetraethylene glycol dimethyl ether, and glass fiber filter separator (Whatman GF/A). For the electrochemical measurements, the discharge-charge tests and the AC impedance measurements were carried out in a dry air atmosphere at 25 °C.

**Results and Discussion** The SEM results indicated that all carbon materials were spherical particles of around 10-100 nm. From the nitrogen adsorption-desorption isotherms, the order of mesopore volume size was as follows : ECP600JD > EC300J > XC-72R > AB. Fig. 1 shows the first discharge-charge curves of the carbon electrodes. The first discharge plateau voltages of ECP600JD, EC300J, XC-72R, and AB electrodes are 2.69 V, 2.66 V, 2.64 V, and 2.59 V, respectively. From the nitrogen adsorption-desorption isotherms and the discharge-charge curves, the discharge voltage increased with increasing the mesopore volume (mesopore range: 2-50 nm). From the AC impedance measurements, the charge transfer resistance increased with the discharge-charge cycles numbers. After 10 cycles, ECP600JD electrode showed the lowest charge transfer resistance among the carbon electrodes. It was suggested that $Li_2O_2$ deposited on the surface of carbon electrodes and reduced the electronic conductivity of the carbon electrodes during discharge process. Based on these results, it dwas found that the mesopore volume had an influence on the electrochemical characteristics of lithium-air secondary battery.

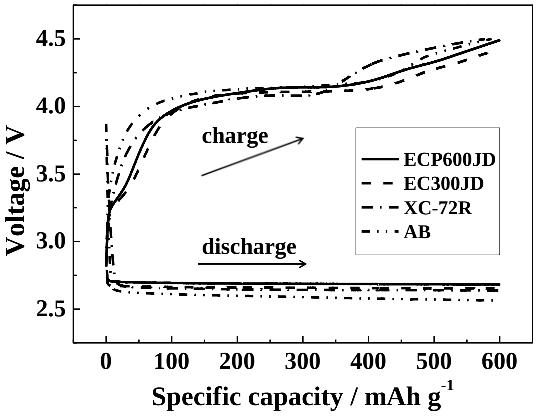


**Fig. 1** First discharge-charge carves of various carbon electrodes at 298 K; voltage range: 2.0-4.5 V, C.D.: 100 mA g$^{-1}$.

**References**

1) J. Xiao *et al.*, *J. Electrochem. Soc.*, **157**, A487-A492 (2010).
2) Y. Li *et al.*, *Carbon*, **64**, 170-177 (2013).
3) L. Wang *et al.*, *J. Power Sources*, **234**, 8-15 (2013).
4) P. Guan *et al.*, *Electrochim. Acta*, **129**, 318-326 (2014).

**Acknowledgments**

This research was partially supported by ALCA-SPRING, JST.

# Reversible Type Solid Oxide Fuel Cells and Applied For Energy Storage

Tatsumi Ishihara,[1,2] Hack Ho Kim[2], Atsushi Inoishi[2] and Shintaro Ida[1,2]
*[1]International Institute for Carbon Neutral Energy Research (WPI-I2CNER)*
*[2]Department of Applied Chemistry, Faculty of Engineering, Kyushu University*
*Motooka, 744, Nishi-ku, Fukuoka 819-0395, Japan*
*ishihara@cstf.kyushu-u.ac.jp*

There are strong demands for large capacity rechargeable battery in order to storage electric power generated from renewable energy like solar cell or wind power generator. For this purpose, NaS batteries are considered as the most promising candidate because of their high theoretical energy density (760Wh kg$^{-1}$), high energy efficiency. However, NaS battery has disadvantage of safety issues because molten Na and S are used. In contrast, Fe is cheap, non-toxic and safety, iron–air rechargeable is expecting as the promising metal-air batter. Up to now, alkaline solution is used for electrolyte for Fe-air battery, however, because of change in the shape of Fe during discharge, cycle stability of Fe-air battery is poor and efficiency of change-discharge is also not high. In this study, solid oxide Fe-air battery was studied by using $LaGaO_3$-based oxide-ion conductor for electrolyte. In the previous study, solid oxide Fe-air have been studied and we demonstrated that the energy density of 420Wh kg$^{-1}_{Fe}$, reasonable charge–discharge properties, and round-trip efficiency of 85% were achieved at operation temperature of 673 K [1]. In this study, effects of oxide mixed with Fe powder for increasing redox property of Fe at low temperature.

An iron powder mixed with various oxide as catalyst was prepared by mixed in an aqueous solution of $Fe(NO_3)_3$ and oxide. After manufacturing, the iron powder was repeatedly reduced and oxidized simulating battery charging and discharge procedure. The powder was exposed to $H_2$ for 5h at 100ml min$^{-1}$ and then to 100ml min$^{-1}$ of $N_2$-3%$H_2O$ for oxidation for 5 h. After redox cycles, it was investigated with respect to microstructural changes using a SEM. A battery test was used a tubular cell. The tubular cell was fabricated using an extruded $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ electrolyte tube. Ni-Fe(9:1)+$Ce_{0.6}Mn_{0.3}Fe_{0.1}O_2$(CMF(10wt%) )was used for anode and $Ba_{0.6}La_{0.4}CoO_3$ was used for cathode. Electrodes ware calcined at 1373K. For charge-discharge measurement, the iron powder was inserted into an alumina tube in the LSGM electrolyte tube, and the LSGM tube was closed with an epoxide resin. After the cell was heated to 673K, 100mlmin$^{-1}$ of 100%$H_2$ gas was supplied to the anode side to reduce the anode electrode and the iron oxide powder.

Although oxidation of pure Fe powder is slow at 673 K, it was drastically increased by mixing with metal or oxide. Among the examined catalyst, it was found that addition of Cr is effective for oxidation of Fe at low temperature, however, oxidation of Fe was not completely occurred. In contrast, mixing with CMF shows large weight change and cycle stability. Therefore, it seems that mixing CMF for Fe is suitable for reversibility of redox of Fe powder. By using Fe with CMF powder, fairly large capacity was exhibited at 673 K and cycle stability is also much increased.

Figure 1 shows the cycle stability of the Fe-air solid state battery operating at 673K. Although the current density is little low (0.1A/cm$^2$), reasonable high efficiency for charge and discharge was observed (>85%) and stable cycle stability was observed up to 30 cycles examined. Therefore, reversible operation of SOFC is realized by using $Ba_{0.6}La_{0.4}CoO_3$ and NiFe/CMF as air and fuel electrode, respectively.

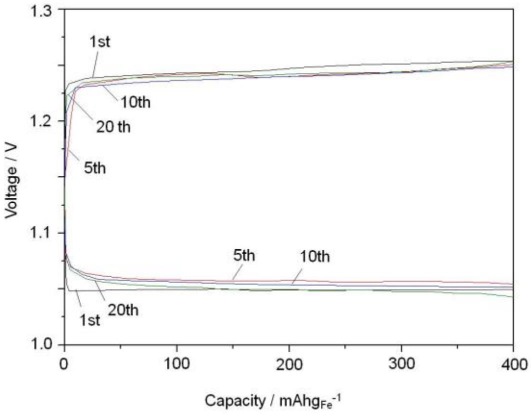


Figure 1 Charge-discharge curves of Fe-air rechargeable battery at 673 K.

Reference
1) A. Inoishi, T. Sakai, Y. W. Ju, S. Ida, T. Ishihara
J. Power Sources, 262, 310-315, (2014)
2) A. Inoishi, T. Sakai, Y.W. Ju, S. Ida, T. Ishihara
Intern. J. Hydrogen Energy, 39(36), 21352-21357, (2014)

# Sugar-Based Catalysts For Oxygen Reduction Reaction.

Stefania Marzorati[a], Marco Renzi[b], Francesco Nobili[b], Mariangela Longhi[a],
[a]*Università degli Studi di Milano, Dipartimento di Chimica*
*Via Golgi 19, 20133 Milano, Italy*
[b]*Università degli Studi di Camerino, Scuola di Science e tecnologie – Sezione Chimica*
*Via S. Agostino 1, 62032 Camerino (MC), Italy*
*mariangela.longhi@unimi.it*

Since a time platinum and platinum-alloys are considered most effective and reliable catalysts for oxygen reduction in PEM fuel cells. In fact, performances of these devices are severely limited by the kinetics of the oxygen reduction reaction (ORR) at the cathode, so that the use of high-cost catalysts, such as Pt, is so far mandatory. Although catalytically optimal, Pt catalysts suffer drawbacks such as formation of poisoning surface Pt-oxides and particle coarsening (by dissolution-reprecipitation, Ostwald ripening), that cause loss of both active surface area and activity. Other problems have economic origin due to the metal natural scarcity and cost. A very interesting research challenge is to find an alternative non-precious, though less catalytically performing, catalyst. Among others, nitrogen-modified carbons doped with non-precious transition metal centres, typically iron, are of interest because of reduced costs of precursors and easiness by which composition and morphology can be modulated by preparation.

In this work we present some results on oxygen reduction reaction by a family of Pt-free catalysts obtained by pyrolysis of guanidine-based nitrogen compounds/sugar mixtures in the presence of a metal salt and a templating agent.

Catalysts were characterized by physical, chemical and electrochemical methods. Results are presented in terms of the influence that precursors nature exerts on oxygen reduction onset potential, presence of defined limiting current and reaction mechanism. They are characterized by a well-defined limiting current, an onset potential approaching Pt ORR starting potential and a number of exchanged electrons $n>3.9$. An attempt of explanation of different electrocatalytic behavior obtained varying the nature of precursor is also done.

# Lifetime and Degradation of Perovskite Electrocatalysts for Oxygen Evolution Reaction in Alkaline Media

*D. S. Bick*[1], *J. D. Griesche*[1], *A.Kindsmüller*[1], *F. Gunkel*[2], *R. Waser*[1,2], *I. Valov*[1,2]

[1] *IWE 2, RWTH-Aachen University, Sommerfeld Str. 24 D-52074 Aachen, Germany*

[2] *Peter Grünberg Institut 7, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

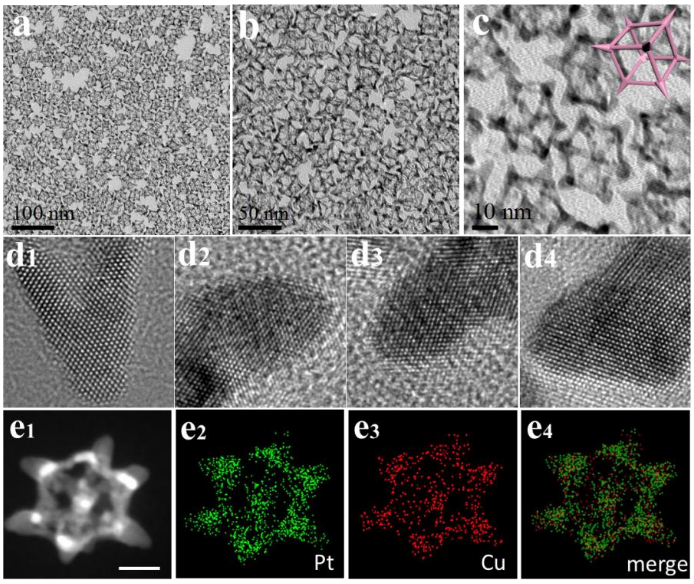
Electrochemical water splitting is the most reliable technology for hydrogen production. Due to the importance of hydrogen to future renewable energy supply, water electrolysis has to be optimized for more efficient hydrogen production. While the hydrogen evolution reaction (HER) is well optimized, the oxygen evolution reaction (OER) is intensively studied because of the potential to increase the reaction rate. As a matter of fact, HER and OER cannot be treated separately in the electrolytic cell, the slower rate of the OER determines the overall reaction rate. More economically reasonable electrocatalysts, especially for the OER have to be identified. Perovskite electrocatalysts count as promising alternatives to mixed Ni/Co/Fe oxides or noble metal containing materials [1]. E.g. BSCF or PBCO (double) perovskites show extraordinary low overpotentials for OER [2,3]. Main issue in using perovskite electrocatalysts for the OER in alkaline electrolyzers is the lack of chemical stability and durability. However, about the mechanisms of degradation very little is known yet [4]. Here, we report the assembly and characterization of different perovskite electrocatalyst thin films and show the dependency of structure and composition on life time and degradation. For lifetime elongation, several prospects regarding doping, surface modification and structural diversification are proposed. Furthermore, the degradation process is analysed with EDX and XPS measurements, supported by structure determination and evaluation of the catalyst interface, to access better understanding of fundamental degradation reactions.

1. L. Trotochaud and S. W. Boettcher. *Precise oxygen evolution catalysts: Status and opportunities*. Scripta Materialia, **74**, 25-32 (2014).
2. A. Grimaud; K. J. May; C. E. Carlton; Y. L. Lee; M. Risch; W. T. Hong; J. Zhou; Y. Shao-Horn. *Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution.* Nat. Commun., **4**, 2439/1-7 (2013)
3. J. Suntivich; K. J. May; H. A. Gasteiger; J. B. Goodenough; Y. Shao-Horn. *A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles.* Science, **334**, 1383-1385 (2011)
4. K. J. May, C. E. Carlton, K. A. Stoerzinger, M. Risch, J. Suntivich, Y. Lee, A. Grimaud, Y. Shao-Horn. *Influence of Oxygen Evolution during Water Oxidation on the Surface of Perovskite Oxide Catalysts.* J. Phys. Chem. Lett., **3**, 3264-3270 (2012)

# Nanoframe structured catalysts towards oxygen reduction reaction: A strategy to balance the activity and durability of the catalysts

Pei Kang Shen*, Shuiping Luo
State Key Laboratory of Optoelectronic Materials and Technologies, School of
Physics and Engineering, Sun Yat-sen University, Guangzhou, PR China
* E-mail: stsspk@mail.sysu.edu.cn

Structure engineering of Platinum-based materials at the atomic level can precisely and effectively tune the size, morphology, facets and composition properties of the electrocatalyst, enabling the synthesis of advanced nanoscale electrocatalysts with low Pt loading, high activity and durability to make PEMFC vehicle commercially viable. Specially, The open-framework nanostructures offer three-dimensionally accessible surfaces and high surface-to-volume ratio, represent a promising and efficient electrocatalysts for oxygen reduction reaction (ORR）[1-2]. Here, we report a facile, one-pot and high yield synthesis of well-defined PtCu octagon-frame nanostructures (OFNs). The novel open nanoarchitecture possess symmetrical foots closed with various high-index facets, and favorable Pt atomic arrangement. In addition, the usage of precious metals can be optimized by tuning the composition of the nanostructure (Pd, Co, and Ni). The PtCu OFNs catalyst exhibits extraordinary activity and durability for the oxygen reduction reaction (ORR). Compared to the state-of-the-art Pt/C catalysts, the PtCu OFNs catalyst achieves a factor of 20-time enhancement in both mass activity and specific activity. On the other hand, the octagon frame nanostructures are well maintained after heat-treatment and accelerated CV cycling, due to the Pt-skin and free-standing nanostructure. In this article, we will discuss the catalyst, its development, and structural and electrochemical characterization using RDE and Cs-corrected TEM. The synthesis mechanistic of the unique nanostructure will be concerned. A mechanistic understanding for the improvement in both activity and durability will also be discussed.



***ACKNOWLEDGEMENT***

This work was supported by the Major International (Regional) Joint Research Project of NNSFC (51210002) and the Guangzhou Auto-mobile Group Project (XW6).

## REFERENCES

[1] Chen C, Kang Y, Huo Z, et al, Science, 2014, 343(6177): 1339-1343.
[2] Stamenkovic V R, Mun B S, Arenz M, et al, Nature Materials, 2007, 6(3): 241-247.

# Pyrophosphate based materials as a new Oxygen Evolution Catalyst

Hyunah Kim[1], Jimin Park[1,2], Ki Tae Nam[1*], Kisuk Kang[1*]

*1. Department of Materials Science and Engineering, Seoul National University (SNU), Gwanak-ro 1, Gwanak-gu, Seoul 151-742, Korea*
*2. Center for Biomaterials, Korea Institute of Science & Technology (KIST), Seoul 136-650, Korea*
*E-mail address: matlgen1@snu.ac.kr, nkitae@snu.ac.kr*

Nowadays global warming and energy crisis has accelerated to develop renewable energy. Splitting water into hydrogen and oxygen molecules is an environmentally-friendly solar-to-energy conversion method which has been studied for more than a half century. However, the oxygen evolution reaction has been regarded as a bottleneck in overall water splitting reaction because of O-O double bond formation and 4 electron-transfer reactions. The noble-metal catalyst such as Pt, IrOx, and RuOx shows remarkable catalytic activity, but their high cost gives limitation for realization of overall water-splitting systems. Therefore, developing cost-effective, abundant, and efficient water splitting catalysts under neutral condition is necessary. In this work, we used $Li_2MnP_2O_7$ and $Li_2CoP_2O_7$, the Li-battery cathode materials for water splitting catalysts for the first time.

Inspired from the $Mn_4CaO_5$ cluster in nature which shows remarkable catalytic performance, previous researches pointed out the importance of Mn(III) in oxygen evolution reaction, but it is hard to know the role of Mn valency itself, because structure of the catalyst always changed significantly as Mn valency changed. We successfully synthesize $Li_2MnP_2O_7$ and obtain $LiMnP_2O_7$, $Li_{1.5}MnP_2O_7$, and $Li_{1.7}MnP_2O_7$ without significant structural change in crystal. We observed that as the averaged oxidation state of Mn in $Li_{2-x}MnP_2O_7$ increases from 2 to 3, the catalytic performance enhanced in the series of $Li_2MnP_2O_7 < Li_{1.7}MnP_2O_7 < Li_{1.5}MnP_2O_7 < LiMnP_2O_7$. Moreover, we compared $Li_2MnP_2O_7$ with $Li_2CoP_2O_7$ to know the influence of transition metals in oxygen evolution reaction. $Li_2CoP_2O_7$ itself exhibited superior catalytic performance compared to $Li_2MnP_2O_7$

In conclusion, we observed the roll of Mn(III) state and the effect of transition metals in water oxidation reaction. We expect that our study provides valuable guidelines for developing an efficient oxygen evolution catalyst under neutral conditions.

**References**

[1] Tamaru, M.; Barpanda, P.; Yamada, Y.; Nishimura, S.-i.; Yamada, A. *J. Mater. Chem.* **2012**, *22*, 24526.
[2] Wizansky, A. R.; Rauch, P. E.; Disalvo, F. J. *J. Solid State Chem.* **1989**, *81*, 203

# Trends in the Activity of Iron-Based Spinel Oxide Nanoparticles for Oxygen Evolution Electrocatalysis

Lin Gan*, Weiyan Liu

*Division of Energy and Environment, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China*
*Email: lgan@sz.tsinghua.edu.cn*

The design of cost-effective and highly active, durable electrocatalysts for the sluggish oxygen evolution reaction in alkaline environment is critical for promoting various energy conversion process such as water splitting and rechargeable metal-air batteries. Owing to their earth-abundance, low cost and well-defined structure, spinel transition metal oxides have attracted considerable interests.[1] While improved OER activities have been demonstrated on several spinel transition metal oxides (such as $NiCo_2O_4$ and electrodeposited Fe-based spinel oxide film), they generally underperformed the best OER catalyst $IrO_2$. Moreover, atomic insights into the surface structure that governs the OER reactivity of spinel metal oxide electrocatalysts, particularly in the nanoparticulate style, have remained unaddressed.

We report here the synthesis, structure and activity trend of monodispersed iron-based spinel oxide ($M_xFe_{3-x}O_4$, M= Mn, Fe, Co, Ni, Cu) nanoparticles (NPs). Emphasis will be placed on the effect of the type of $A^{2+}$ cation of the $AB_2O_4$ spinel structure on the OER activity and its fine-tunings. Our results reveal that the OER activity of the $M_xFe_{3-x}O_4$ spinel oxide NPs follows the trend of Cu<Fe<Mn<Co<Ni substitution, which was ascribed to an over-strongly increased $M^{n+}$-$OH_{ad}$ bonding following the order Ni<Co<Fe<Mn.[2] By tailoring the Ni bulk composition of $Ni_xFe_{3-x}O_4$ nanoparticles, we obtained the highest OER activity on the $NiFe_2O_4$ nanoparticles that significantly outperformed the $IrO_x$ nanoparticle catalysts. To gain atomic insight into the activity trend, we further probed the surface structure and composition by using high-resolution (scanning) transmission electron microscopy combined energy dispersive X-ray mapping and uncover a significant Ni-enrichment on all $Ni_xFe_{3-x}O_4$ nanoparticles, which played important role during the OER electrocatalysts on the spinal $NiFe_2O_4$ NPs. Our results provide an important implications on how to rational design of an efficient spinel 3d-transition metal oxide OER electrocatalysts.

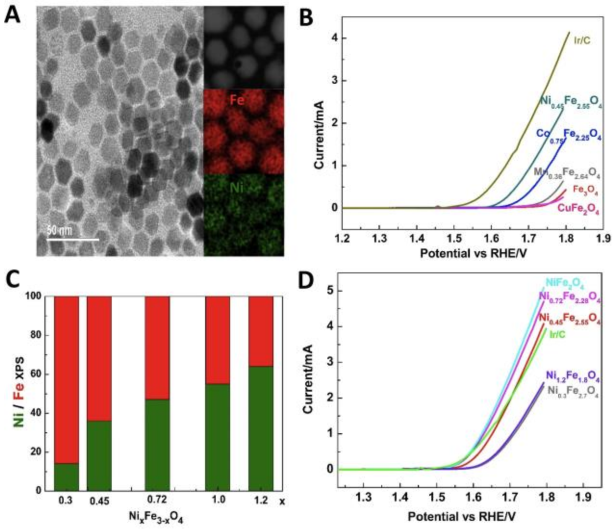


**Figure 1**. Structure, surface composition and OER activities of $M_xFe_{3-x}O4$ spinel oxide NPs. **(A)** TEM image and STEM-EDX elemental mapping of as-prepared $Ni_{0.45}Fe_{2.55}O_4$ NPs. **(B)** OER activity of MxFe3-xO4 spinel oxide NPs (M=Mn, Fe, Co, Ni and Cu), showing the trend in the activity of Cu<Fe<Mn<Co<Ni. **(C-D)** Surface composition (C) and OER activity (D) of NixFe3-xO4 spinel oxide NPs with different Ni bulk compositions.

**References:**

1. Singh, J.P., N.K. Singh, and R.N. Singh, Electrocatalytic activity of metal-substituted $Fe_3O_4$ obtained at low temperature for $O_2$ evolution. International Journal of Hydrogen Energy, 1999, 24: p. 433-439.
2. Subbaraman, R., et al., Trends in activity for the water electrolyser reactions on 3d M(Ni,Co,Fe,Mn) hydr(oxy)oxide catalysts. Nature Materials, 2012,11: 550-557.

# Photoelectrochemical screening of water splitting catalysts

Daniel Kimmich, Carsten Dosche, Dereje Hailu Taffa, Michael Wark, Gunther Wittstock
*Carl von Ossietzky University, Department of Chemistry,*
*D-26111 Oldenburg*
*daniel.kimmich@uni.oldenburg.de*

Due to the forthcoming changes in the energy sector a sustainable way to produce hydrogen is needed. We search for new photocatalysts for the water splitting reaction. Due to the high overpotential at the photoanode, the oxygen evolution reaction (OER) limits the overall efficiency of the cell. Oxides of 3d transition metals are promising semiconductors that can help to overcome this barrier. To date no single material has satisfied simultaneously the different requirements. To find the fittest catalyst from many different elemental compositions, a combination of library preparation and screening has been demonstrated with remarkable success [1,2]. Typically a read-out technique with lateral resolution is used to screen these libraries in array format in which the position encodes the composition.

In the current study material libraries are prepared onto conducting fluorine-doped tin oxide (FTO) by ink-jet printing (IJP). Masks can be used to reduce the (capacitive and parasitic) background currents and enhances the sensitivity [3]. Inks with defined salt concentrations and physical properties (viscosity, surface tension) were developed. We prepared arrays with defined mixing ratios of metal and a good positional accuracy.

The readout of the materials is carried out by using the substrate-collection mode of scanning photo-electrochemical microscopy (SPECM) [4,5,6]. Broadband laser light is coupled into the fiber with an inner core diameter of 105 µm. The optical fiber scans over the surface and the substrate current is plotted as a function of local illumination. Hence the 2D map shows the photocurrent of each coordinate. The photocurrent is correlated to the local photocatalytic activity.

A new bielectrode setup is introduced as new substrate for screening that offers benefits for optical scanning probe techniques. Different electrochemically processed photoanodes were prepared and probed for photocatalytic activity. The new setup excludes the appearance of uncontrolled parasitic photocrurrent by scattering or coupling into the surface. Interestingly, the global response of the photoanodes appears similar but local activity differences are observed. So SPECM is a powerful tool to locate structures that harvest the maximum yield. Those are validated with XPS, Raman- and UV-Vis spectroscopy and SEM measurements as well.

Literature:

[1] V. S. Vidyarthi, M. Hofmann, A. Savan, K. Sliozberg, D. Koenig, R. Beranek, W. Schuhmann, A. Ludwig, *Int. J. Hydrogen Energy* **2011**, *36*, 4724. [2] S. P. Berglund, H. C. Lee, P. D. Nunez, A. J. Bard, C. B. Mullins, *Phys. Chem. Chem. Phys.* **2013**, *15*, 4554. [3] J. Rodriguez-Lopez, M. A. Alpuche-Aviles, A. J. Bard, *Anal. Chem.* **2008,** *80***,** 1813. [4] P. James, N. Casillas, W. H. Smyrl, *J. Electrochem. Soc.* **1996**, *143*, 3853-3865. [5] J. Lee, H. Ye, S. Pan, A. J. Bard, *Anal. Chem.* **2008**, *80*, 7445. [6] C. Bhattacharya, H. C. Lee, A. J. Bard, *J. Phys. Chem. C* **2013**, *117*, 9633.

# Iron, cobalt-containing nitrogen-doped carbon nanotubes for oxygen reduction reaction

Sander Ratso[a], Ivar Kruusenberg[a], Urmas Joost[b], Ave Sarapuu[a], Protima Rauwel[b], Rando Saar[b],
Arunachala M. Kannan[c], Kaido Tammeveski[a]

[a]*Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia*
[b]*Institute of Physics, University of Tartu, Ravila 14c, 50411 Tartu, Estonia*
[c]*Fuel Cell Laboratory, The Polytechnic School, Ira A. Fulton Schools of Engineering,*
*Arizona State University, Mesa, AZ 85212, USA*
*E-mail: kaido.tammeveski@ut.ee*

Modern polymer electrolyte fuel cells are generally hindered mostly by the slow kinetics of the oxygen reduction reaction (ORR) on the cathode of the fuel cell. To improve the efficiency of oxygen reduction, carbon-supported Pt and Pt-alloy catalysts are usually utilised. Unfortunately platinum is sparsely available and very expensive. To replace Pt-based catalysts, carbon nanomaterials, which are durable and highly conductive, have been doped with heteroatoms to increase their ORR activity. Nitrogen doped carbon materials have recently emerged as a viable substitution to the traditional Pt/C catalysts in alkaline conditions, but in acid media their activity is lower and thus more advances are needed to successfully apply them in real fuel cells. An efficient way for this is to include transition metals such as Fe or Co into the catalysts, which further enhances the electrocatalytic activity for ORR, especially in acidic conditions. In this work, a facile method for synthesising transition metal and nitrogen-doped carbon nanocatalysts for ORR is shown. Multi-walled carbon nanotubes (MWCNT) treated in concentrated acid are mixed with dicyandiamide and either a Co or Fe salt and the mixture is pyrolysed at 800 °C for 2 h in inert gas flow. The catalysts' electrocatalytic activity towards the ORR is tested in 0.1 M KOH and 0.5 M $H_2SO_4$ solutions along with the stability and methanol tolerance. Transmission electron microscopy and scanning electron microscopy are used to explore the surface morphology of the materials and X-ray photoelectron spectroscopy and energy-dispersive X-ray spectroscopy are employed to analyse the surface and bulk elemental composition, respectively.

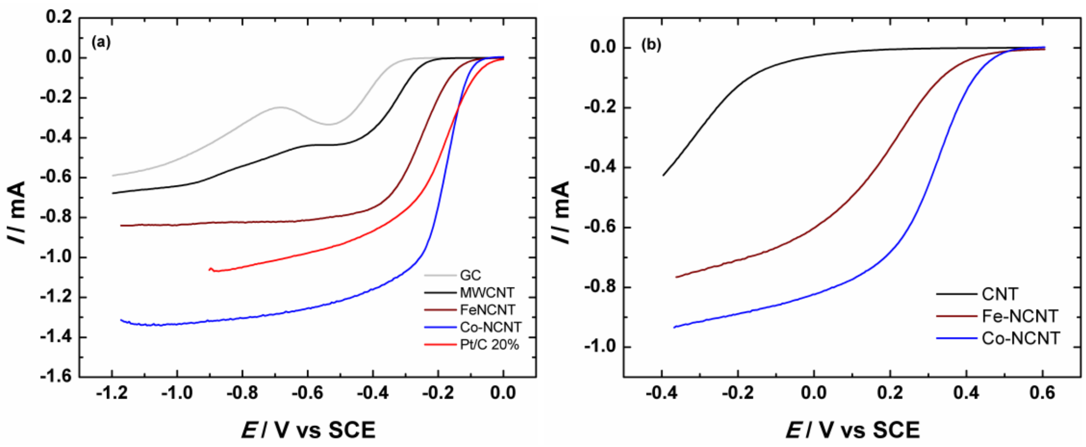


Figure 1. Comparative RDE results of M-NCNT materials in $O_2$–saturated 0.1 M KOH (a) and 0.5 M $H_2SO_4$ (b) at 1900 rpm. $v$ = 10 mV s$^{-1}$.

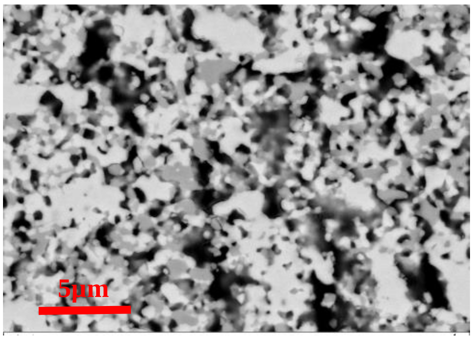
In alkaline conditions, both catalysts showed good activity, especially Co-NCNT, on which the number of electrons transferred per $O_2$ molecule was 4 in the whole range of potentials studied, having a comparable efficiency to that of commercial Pt/C. Fe-NCNT showed somewhat lower activity, but was still active. In acidic conditions, both catalysts showed a good electrocatalytic activity when compared to the undoped CNT material, but the overall ORR activity was still lower than that of commercial Pt/C catalysts. Both catalysts were stable during 1000 potential cycles in alkaline conditions and also tolerant to methanol.

# Understanding electro-catalysis in Solid Oxide Cells (SOCs) for designing electrodes

R. Costa, V. Yurkiv
*German Aerospace Center, Institute of engineering Thermodynamics,*
*Pfaffewaldring 38-40, 70569 Stuttgart, Germany*
*remi.costa@dlr.de*

Beyond the fundamentals of the operation of high temperature Solid Oxide Cells (SOCs), the key performance factors are linked to the functionality of both air and fuel electrodes. Nowadays, the common approach for developing electrodes lies in the investigation of new phases with novel compositions showing improved electro-catalytic performances towards the specific electrochemical processes. Nonetheless, as all functional materials, the final performance of the electrodes stays not only in the intrinsic electro-catalytic performance of the considered phase, but also in the technology implemented for the coating and the resulting microstructure of the electrode. As changing a phase composition may change the mechanism of the electrochemical processes, the implementation of new phases in SOCs and their optimization in terms of performances, requires a deep understanding of the electro-catalytic phenomena to design and manufacture efficient electrodes. Indeed, if historically composite electrode materials made of separate ionic and electronic conductors, for example nickel zirconia cermet as anode, or $La_xSr_{1-x}MnO_{3-\delta}$ (LSM)/zirconia as cathode materials have been widely used as fuel and air electrode respectively in SOCs, materials development over the last 20 years have led to the development of an increased number of Mixed Ionic and Electronic Conductors (MIEC), able to provide better functionality like electronic conductivity in the case of the air electrode or resilience towards events like redox cycles characteristic of practical operation. Shifting from composite materials with single properties for each phase to MIEC has redefined the localization of active sites of the functional electrolyte.

In this paper, we present the results of a combined experimental and electro-kinetic modeling aiming at understanding fundamental physico-chemical and transport processes in SOCs. In the case of $La_xSr_{1-x}TiO_{3-\delta}$ (LST)-$Ce_{1-x}Gd_xO_{2-\alpha}$ (CGO) novel perovskite anodes a detailed multi-step heterogeneous chemical and electrochemical reaction mechanism was established and modeling results were thoroughly compared to electrochemical measurements. It was found that heterogeneous chemistry at LST surface has capacitive behavior that alters the impedance spectra. In addition, surface charge-transfer reaction, which describes partial oxygen ionization, caused impedance feature and is rate-limiting at high temperature. Comparable investigations have been performed on the system $La_xSr_{1-x}Co_{1-y}Fe_yO_{3-\delta}$ (LSCF)-$Ce_{1-x}Gd_xO_{2-\alpha}$ (CGO) as cathode to identify main rate limiting processes (see Fig. 1 Right), which are (*i*) gas conversion (low frequencies), (*ii*) electrochemical oxygen reduction on the LSCF surface (intermediate frequencies) and (*iii*) charge-transfer of double negatively charged oxygen through two-phase boundary between LSCF and CGO (high frequencies). Analyzing the microstructural features governing the models, provides useful indications for optimizing further the electrodes. Moreover this approach would allow the development of operating strategies for increasing cell's lifetime.



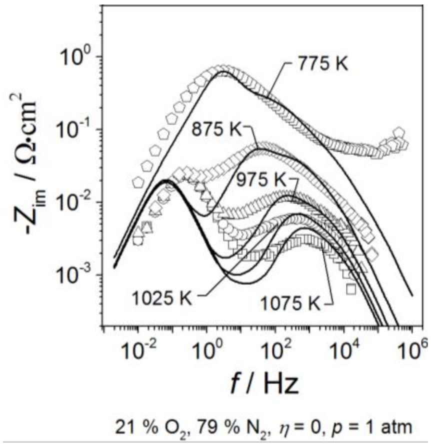


Figure 1. Left – Scanning electron microscopy cross section image (details) of a tested LSCF-GDC cathode; Right – Comparison between experimental (open symbols) and simulated (solid lines) electrochemical impedance spectra for different temperatures.

# Activity vs. stability. Design of electrocatalysts for the oxygen evolution reaction and oxygen reduction reaction in alkaline media

Wolfgang Schuhmann
*Analytical Chemistry - Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum,*
*Universitätsstraße 150, D-44780 Bochum, Germany*
*wolfgang.schuhmann@rub.de*

The design of improved electrocatalysts for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) is of utmost importance for paving the way for the applications of electrolyzers and fuel cells in energy conversion devices. Recently, research was focused mainly on decreasing the overpotential based on the discovery of new classes of materials.

However, a low overpotential is often concomitantly related to limited stability which is hampering the application of the low-overpotential catalysts. For example, despite $RuO_2$ shows a substantially lower overpotential for the OER in acidic solution $IrO_2$ electrodes are used due to their substantially better stability.

In this presentation, emphasis is on specifically developed electrochemical methods to asses the longterm stability of OER, ORR or bifunctional catalysts and the formulation of catalysts preparations to allow a substantially improved adhesion to suitable support materials. Using a variety of examples strategies for stabilizing the electrocatalytic activity of low-overpotential catalysts for OER, ORR in alkaline solution will be described.

# Electrocatalytic water oxidation using cobalt and nickel boride

Justus Masa, Philipp Weide[b], Ilya Sinev[b], Wei Xia[b], Martin Muhler[b], Wolfgang Schuhmann

[a] Analytical Chemistry and Center for Electrochemical Sciences-CES
Ruhr-Universität Bochum, NC04/788, D-44780 Bochum (Germany)
[b] Laboratory of Industrial Chemistry, Faculty of Chemistry and Biochemistry, Ruhr-Universität Bochum, D-44780 Bochum (Germany)
*Justus.masa@rub.de*

The most advanced green means to generate $H_2$ from water is electrolysis, which requires the use of catalysts at both the anode and cathode of the water electrolyzer. However, to date, no catalysts exist which combine cost effectiveness, high performance and long-term durability, which impedes the competitiveness of large scale hydrogen and oxygen production through electrochemical water splitting. In this presentation, we demonstrate that amorphous cobalt boride ($Co_2B$) and nickel boride ($Ni_xB_y$) synthesized by the chemical reduction of $CoCl_2$ and $NiCl_2$, respectively, are exceptionally active for oxygen evolution in alkaline solutions. Most strikingly, ($Co_2B$) annealed at 500 $^oC$, and $Ni_xB_y$ annealed at 300 $^oC$ ($Ni_xB_y$), both evolve oxygen more efficiently than $RuO_2$ and $IrO_2$, achieving a current density of 10 mA $cm^{-2}$ at $\leq 1.61$ $V_{RHE}$ on an inert support (glassy carbon) and $\leq 1.59$ $V_{RHE}$ when impregnated with nitrogen-doped graphene. Furthermore, the catalysts maintained stable performance during electrolysis at 10 mA $cm^{-2}$ for at least 6o h. This performance, to the best of our knowledge, is among the best reported for non-precious metal OER catalysts. We observed using EXAFS that boron induces lattice strain in the crystal structure of the metal which reduces the thermodynamic and kinetic barrier for metal oxyhydroxide formation during oxygen evolution. Additionally, the catalysts exhibits good activity for hydrogen evolution in alkaline electrolytes and can thus be employed at both the anode and cathode of a water splitting device.

# Active and stable sites on carbon materials for oxygen electrocatalysis

Youngmi Yi, Marina Prenzel, Saskia Buller, Sylvia Becker[*], Robert Schlögl
*Max-Planck institute for chemical energy conversion*
*Stiftstreet 34-36, 45470 Mülheim an der Ruhr, Germany*
*youngmi.yi@cec.mpg.de*

A growing interest in cost-effective and metal-free electrocatalysts has stimulated the extensive research on carbon materials for catalysts itself in energy-related technologies, such as fuel cells, water electrolysis and batteries. Oxygen-involving reactions in electrocatalysis, namely oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), have sluggish reaction kinetics due to many intermediates in reaction mechanisms. Thus, these reactions determine the overall efficiency of electrochemical systems. Many research reported the ORR/OER activity of various types of carbon materials, such as carbon nanotube, graphene and mesoporous carbon. Moreover, functionalized carbon with hetero-atom, oxygen or nitrogen etc., shows reasonable ORR/OER activity compared to metal or metal oxide catalysts. Although numerous literatures have introduced an interesting possibility of carbon materials for an alternative catalyst in OER/ORR, the electrocatalytically active sites for oxygen-involving reaction on carbon are still under debate. Furthermore, the electrochemical stability of carbon materials should be considered under an OER/ORR environment, as carbon is oxidized at high anodic potential. In particular, oxygen evolution on carbon electrode is accompanied by carbon oxidation. Therefore, it is important not only for active sites but also for stable sites on carbon surface in OER and ORR.

We systematically approach the OER/ORR performance of carbon materials. First, we focused on the effect of carbon structure. Accordingly, edge plane exposed graphite and basal plane exposed graphite were selected in order to investigate the preferable structure for oxygen evolution and reduction. Moreover, their intrinsic properties were confirmed by analyzing carbon nanotube (CNT), which possesses edge-plane sites on the end and basal-plane site on the wall. Secondly, we examined the influence of functional groups on carbon materials controlled by the plasma treatment with oxygen and nitrogen. By using a low pressure plasma discharge, a controlled bombardment of ions, electrons and radiation is reached. A tailoring of this bombardment allows us to control the incorporation of additional functional groups on the carbon surface. Through this approach on structure and functionality of carbon materials, the aim of this study is to find active and stable sites on carbon surface for oxygen electrocatalysis.

Figure 1 shows the OER/ORR activity of the nanostructured CNT in alkaline media. The overpotential for ORR on CNT shifts to positive potential compared to glassy carbon. While glassy carbon substrate has almost no oxidation current, CNT shows an oxidation activity at high anodic potential for OER. It could be inferred that the carbon structure has a strong influence on OER/ORR activity. Understanding of OER/ORR activity and stability on structured and functionalized carbon could provide a design guideline for further materials and process development of metal-free catalyst.

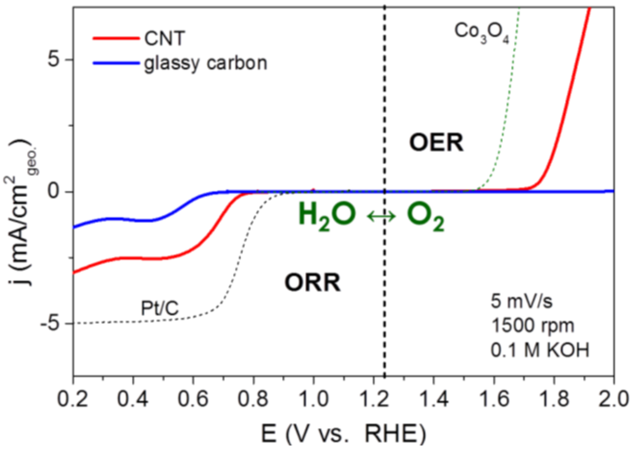


Figure 1. The performance of oxygen electrocatalysis on glassy carbon and carbon nanotube (CNT).

# In Situ Raman Spectroscopy of Copper and Copper Oxides Surfaces during Electrochemical Oxygen Evolution Reaction: First Identification of $Cu^{III}$ Oxides as Catalytic Active Species

Yilin Deng[a], Albertus D. Handoko[a], Yonghua Du[b], Shibo Xi[b] and Boon Siang Yeo[a,c,*]

[a]*Department of Chemistry, Faculty of Science, National University of Singapore, 3 Science Drive 3, Singapore 117543*

[b]*Institute of Chemical and Engineering Sciences, A*STAR, 1 Pesek Road, Jurong Island, Singapore 627833,*

[c]*Solar Energy Research Institute of Singapore, National University of Singapore, 7 Engineering Drive 1, Singapore 117574.*

Deng.nju@gmail.com

Scanning electron microscopy (SEM), X-ray diffraction, cyclic voltammetry (CV), choronoamperometry, in-situ Raman spectroscopy and x-ray absorption near edge structure spectroscopy (XANES) were used to investigate the electrochemical oxygen evolution reaction (OER) on Cu, $Cu_2O$, $Cu(OH)_2$ and CuO catalysts. Aqueous 0.1 M KOH was used as electrolyte. Starting from their rest potentials, all four catalysts were oxidized or converted to CuO and $Cu(OH)_2$ during the slow anodic sweep of cyclic voltammetry and exhibited similar activities for the OER. A Raman peak at 603 $cm^{-1}$ appeared at OER-relevant potentials > 1.62 V vs. RHE on all the four samples. This peak was identified as the marker band of a $Cu^{III}$ oxide, a metastable species whose existence depends on the applied potential. The chemical composition of this oxide is believed to be $CuO_2^-$-like. The four catalysts, in stark contrast, did not oxidize the same way during direct chronoamperometry measurements at 1.7 V vs. RHE. $Cu^{III}$ oxide was observed only on the CuO and $Cu(OH)_2$ electrodes. Interestingly, these two electrodes catalyzed OER ten times more efficiently than the as-prepared Cu and $Cu_2O$ catalysts. By correlating the intensity of the Raman band of $Cu^{III}$ oxide and the extent of the OER activity, we pinpoint $Cu^{III}$ oxide as the active species for electrochemical water oxidation. The formation of $Cu^{III}$ oxides on CuO film was also corroborated by in-situ XANES measurements. The catalytic role of $Cu^{III}$ oxide in OER is proposed and discussed.

# Bifunctional oxygen electrocatalysis in alkaline media: addressing the challenge of high activity, durability and cost effectiveness

K. Andreas Friedrich, Dennis Wittmaier, Norbert Wagner

*Institute of Engineering Thermodynamics, German Aerospace Center*
*Pfaffenwaldring 38-40, 70569 Stuttgart, Germany*
*andreas.friedrich@dlr.de*

Oxygen electrochemistry plays a major role in energy conversion and storage devices, particularly in the field of fuel cells, metal-air batteries and water electrolyzers. Especially metal-air batteries have drawn much attention over the last years due to high theoretical energy densities. The major challenge in metal-air batteries is to design and develop economically feasible, earth-abundant, inexpensive, efficient electrocatalysts for the oxygen evolution reaction (OER) as well as the oxygen reduction reaction (ORR). High overpotentials for ORR and OER are reported especially for lithium-air batteries and precious metal electrocatalysts are commonly used. The choice of an alkaline electrolyte widens significantly the material base and the possibility for cost reduction. This contribution discusses the options available and presents a promising bifunctional catalyst that is presently favored at DLR.

A wide-range of catalysts was screened and many suitable electrocatalysts and combination of catalyst were identified. In particular, $IrO_2$, $Co_3O_4$, $Mn_3O_4$ and $La_{0.6}Ca_{0.4}CoO_3$ are most promising bi-functional catalysts. A promising combination is $Co_3O_4$ - as the most suitable catalyst for OER - and Ag or Ni which are efficient OER catalysts. Ag/$Co_3O_4$ electrodes show high current densities and good long-term stability at reasonable cost and the optimum ratio between the active materials was determined [1-3]. It was shown that the catalyst, electrode thickness, temperature and electrolyte concentration have the highest impact on the current densities, while changing porosity always had a negative impact on the current densities of the investigated electrodes. This contribution discusses the characterization efforts and the investigation of the apparent synergistic effect present in this electrocatalyst mixture.

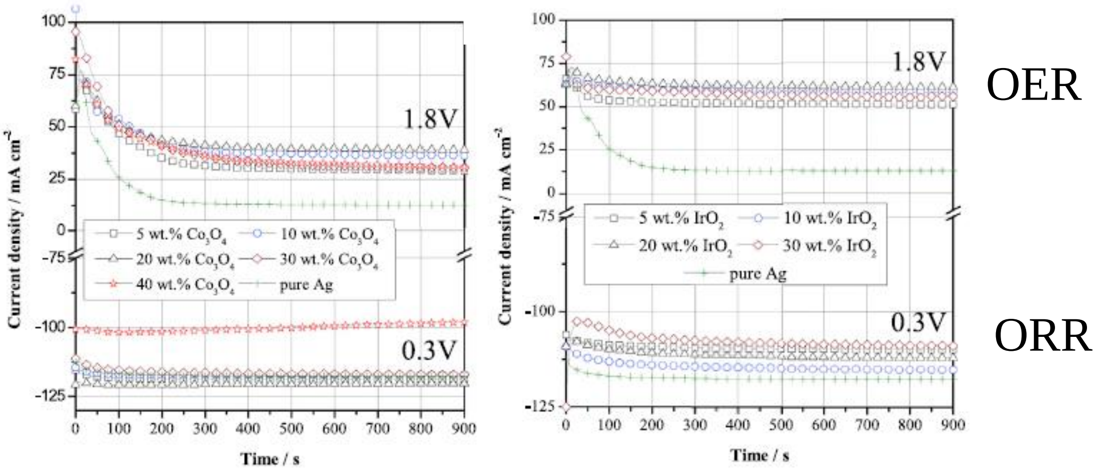


Figure: Chronoamperometric measuremens for $Co_3O_4$/Ag- (left), Ag/$IrO_2$-electrodes (right) potentiostatic curves in 1 M LiOH (aq.) at 25°C.

[1] D. Wittmaier, T. Danner, N. Wagner, K.A. Friedrich, J. Appl. Electrochem. 2014, 44, 73.
[2] H.M.A. Amin, H. Baltruschat, D. Wittmaier, K.A. Friedrich, Electrochim. Acta 2015, 151, 332.
[3] D. Wittmaier, S. Aisenbrey, N. Wagner, K.A. Friedrich, Electrochim. Acta 2014, 149, 355.
[4] D. Wittmaier, Natalia A. Canas, Indro Biswas, K. Andreas Friedrich. Adv. Energy Mater. 2015, doi: 10.1002/aenm.201500763.

# Nanoscale Analysis of Fuel Cell Electrodes before and after Operation by Material-Sensitive and Conductive Atomic Force Microscopy

Renate Hiesgen[a,*], Tobias Morawietz[a], Michael Handl[a], K. Andreas Friedrich[b]
*[a]University of Applied Sciences Esslingen, Kanalstrasse 33, Esslingen 73728, Germany*
*[b] German Aerospace Center, Institute of Technical Thermodynamics, Pfaffenwaldring 38-40, Stuttgart 70569, Germany*
***Author to whom correspondence should be addressed:*
renate.hiesgen@hs-esslingen.de

In this study fuel cell electrodes were investigated as pristine material and after fuel cell operation. A material-sensitive atomic force microscopic (AFM) in tapping mode was combined with current measurements to identify the different components and analyze their distribution and properties, mainly of cross sections of different sulfonated ionomers. Materials include perfluorinated sulfonated ionomer (PFSA) membranes, such as Nafion® and Aquivion® that differ in the lengths of their sulfonated side chains, and also novel non-fluorinated sulfonated multiblock-copolymers.

Electrodes for fuel cells are complex porous compounds with nanosized platinum catalyst particles supported on conducting mesoporous carbons and ionic conducting ionomer and highly influence the performance and longevity of a cell. For example, thick ionomer layers around the Pt-decorated carbon may hinder the diffusion of oxygen to the catalyst and decrease performance. With high-resolution transmission/scanning electron microscopy, the imaging of polymer is difficult due to decomposition by the high-energy electron-beam and analysis at dry conditions causing shrinkage. With material-sensitive and conductive atomic force microscopy the identification of the different components, especially the ionomer phase, can be achieved, especially in combination with measurements of the local current (Fig. 1).

We will present the distribution of carbon, platinum particles, and ionomer layers at cross sections of fuel cell electrodes, dependent on operation time.

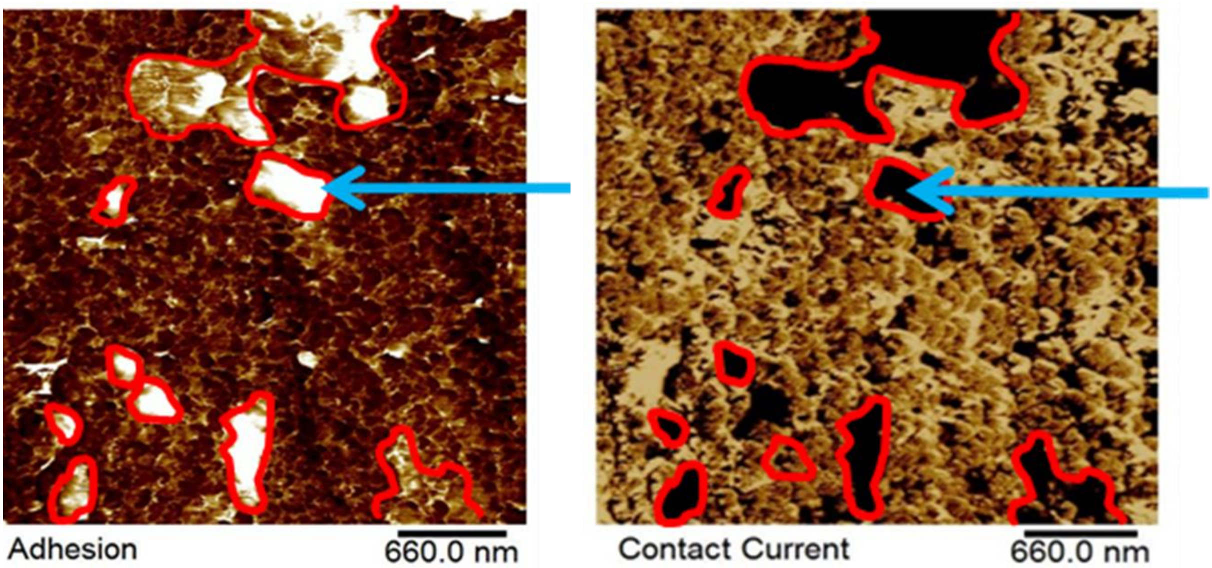


**Figure 1:** AFM adhesion (left) and current (right) mappings of a fuel cell electrode. The ionomer particles are identified by high adhesion and are non-conductive.

# Design and synthesis of Cobalt-MOF nanocrystals and graphitic carbon nanomaterials for electrochemical energy conversion

Tania Rodenas, Youngmi Yi, Saskia Buller, Sylvia Becker, Robert Schlögl
*MPI für Chemische Energiekonversion*
*Stiftstrasse 34-36, D-45470, Mülheim an der Ruhr, Germany*
*tania.rodenas@cec.mpg.de*

Electrocatalysts for oxygen evolution and reduction reactions (OER and ORR, respectively) are key functional components of energy conversion and storage devices [1]. Currently significant research efforts are devoted to the development of alternatives to current electrode materials, which contain large amounts of scarce and expensive noble metals, typically Pt. In particular, electrodes shaped as nanometer and micrometer-thin layers are interesting to be integrated in a wide range of functional devices [2]. Herein we investigate the synthesis of composite materials combining ultrathin graphitic carbons and metal-organic-framework (MOF) nanocrystals and their application as electrocatalysts. The MOF crystals represent a suitable "shuttle" to introduce non-noble transition metal species in the composites. It also offers a means to control their direct chemical environment via judicious choice of the organic linker molecules. A synergism between both components determines the electrocatalytic properties of the resulting composites. Dark-field STEM coupled to EDX elemental mapping confirms the successful incorporation of Co-MOF nanosheet crystals on graphitic sheets, providing evidence for a direct interaction of both components in the composite (Figure 1). In addition, Figure 2 shows the OER performance of Co-MOF/exfoliated graphite composites, alongside reference materials, in alkaline media. Compared to Co3O4, Co-MOF shows higher OER activity and stability. In addition, Co-MOF/exfoliated graphite electrodes exhibit higher oxidation currents during oxygen evolution reaction than pristine Co-MOF. The graphitic nanosheet component enhances the electrochemical properties of Co-MOF and improves OER kinetics.

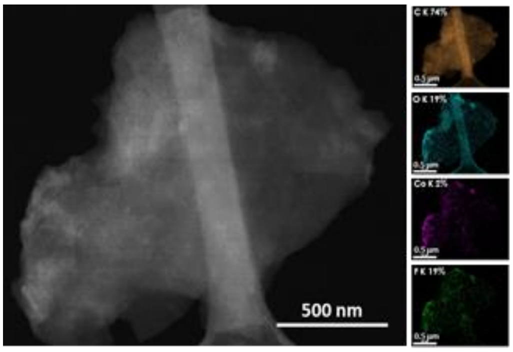


**Fig. 1.** HAADF-STEM micrograph (left) and EDX elemental mappings (right) of Co-MOF/exf-graphite composite with 13.4wt% Co loading.

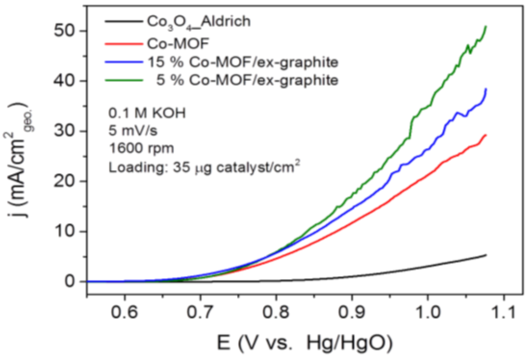


**Fig. 2.** OER-activity (sweep rate of 5 mV·s$^{-1}$) of $Co_3O_4$, Co-MOF, Co-MOF/exf-graphite composites with 5 and 15wt% Co loadings in 0.1 M KOH (1600 rpm).

## References

[1] S. Koohi-Kamali, et al. (2013). Renew. Sust. Energ. Rev., 25, 135.
[2] Q.H. Wang, et al. (2012). Nature Nanotech., 7, 699.

# Probing Solid-Liquid Interface Using APXPS

Zhi Liu
*Division of Condensed Matter Physics and Photon Science, SPST，ShanghaiTech University, China*
*Shanghai Institute of Microsystem and Information Technology, CAS, China*
*E-mail: zliu2@mail.sim.ac.cn*

Multiple new ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this talk, I will present results of in-situ studies on the electrolyte/electrode interface of a working model electrochemical cell.

We believe the successful development of soft and hard X-ray APXPS techniques will provide us and community beyond a powerful in-situ tool to directly study the electrolyte/ electrode interface of many important electrochemical devices.

References

[1] D. E. Starr et.al, Chemical Society reviews 42, 5833-57 (2013).
[2] S. Axnanda et. al, Scientific Reports, 5,9788 (2015)

# Electrochemical Reduction of $CO_2$ using an Interface between Water and Propylene Carbonate Electrolyte Solutions

Hye Jin Lee*
*Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University,*
*80 Daehakro, Buk-gu, Daegu, 702-701, Republic of Korea*
*hyejinlee@knu.ac.kr*

In this poster, an electrochemical reduction of $CO_2$ to produce CO or $HCOO^-$ was described utilizing interfaces between aqueous and organic electrolyte solutions. The aqueous electrolyte composed of perchloric acid or sulfuric acid was served as an anode and also used to supply protons to the organic phase, propylene carbonate (PC) containing 0.1 M tetrabutylammoniumperchlorate ($TBAClO_4$). $TBAClO_4$ was employed as an organic supporting electrolyte to improve the PC phase conductivity. The PC phase served as a cathode where the reduction of $CO_2$ occurred at a gold mesh working electrode (surface area of about 0.5 $cm^2$). The performance in enhancing $CO_2$ reduction efficiency was compared utilizing both the interfaces of perchloric acid/PC-$TBAClO_4$ and sulfuric acid/PC-$TBAClO_4$. Cyclic voltammetry and linear sweep voltammetry were employed to elucidate $CO_2$ reduction at both interfaces under $N_2$ only and in the presence of $CO_2$ in PC-$TBAClO_4$ phase. Chronoamperometry technique was then applied to reduce $CO_2$ continuously purged in the PC phase to generate CO or $HCOO^-$ at an applied potential of -1.8 V (vs Ag/AgCl) for 1 h at room temperature. The concentration of $HCOO^-$ produced in PC followed by transferring to the aqueous via extraction was analyzed using ion chromatography and high performance liquid chromatography. Also the qualitative analysis of CO gas produced in PC phase was performed using gas chromatography-mass spectroscopy.

# Will $H_2$ be an Option for the Future Energy after Fossil Fuels?

Hasuck Kim[1*], Sangaraju Shamugam[1], and Sungyul Bong[2]
[1]Department of Energy Systems Engineering, DGIST, Daegu 42988, Korea
[2]Graduate School of Covergence Science and Technology, Seoul National University,
Suwon 16229, Gyeonggi-Do, Korea
hasuckim@dgist.ac.kr

A series of recent developments such as global warming, weather change, supply of electricity, carbon tax, and Fukushima accident brought us to reconsider seriously about the available energy scheme for the sustainable future. Many agree that the next energy will be hydrogen. There are abundant resources for hydrogen, water, and it burns back to water. However, in order for us to adopt the hydrogen economy, many hurdles have to be overcome, such as generation, storage and transportation, and use of hydrogen..

Statistical analysis of world energy use (1,2) revealed that the portion from nuclear power decreases after the Fukushima incident even though the generation cost is much lower than other methods. It is mainly due to the indirect cost of ricks to human health. This brings the renewable energy sources such as solar panels, wind turbines, geothermal pumpings, and fuel cells. Many of these require a huge capacity of storage devices.

Fuel cells have been receiving a considerable interest as power sources for small electronic appliances, electric vehicles, and to large power stations because they exhibit high energy efficiency and are environmentally benign. Despite these advantages, fuel cells in general need to overcome economic barriers for wide applications. Catalysts are the core material for fuel cell operation and many attempts have been made to find out the most active, efficient and durable formulae in the MEA preparation step.[3] It is focused on the oxygen reduction catalysts because ORR is kinetically sluggish and it requires a large over-potential.

In this respect, various works performed for fuel cell catalysts will be summarized, they are preparation of catalysts such as modified impregnation [4], galvanostatic pulse electrodeposition of Pt-Co on Nafion-bonded carbon layer [5], and ORR catalysts without precious metals. Electrpchemically deposited catalysts showed high utilization of catalyst and thus able to reduce the catalyst loading. Also. nitrogen doped carbon with Fe that exhibited high performance for 4-electron reduction of oxygen will be discussed.

[1] World Key Energy Statistics 2015, IEA (2015).
[2] Statistical Review of World Energy 2015, BP (2015).
[3] Hubert A. Gasteiger, Shyam S. Kocha, Bhaskar Sompalli, Frederick T. Wagner, *Applied Catalysis B: Environmental* **56** (2005) 9.
[4] In Kim, Sungyool Bong, Seunghee Woo Rakesh Kumar Mahajan, Hasuck Kim, *Int. J, Hydrigen Energy*, **36** (2011) 1803.
[5] Seunghee Woo, In Kim, Jae Kwang Lee, Sungyool Bong, Jaeyoung Lee, Hasuck Kim, *Electrochim. Acta,* **56** (2011) 3036.

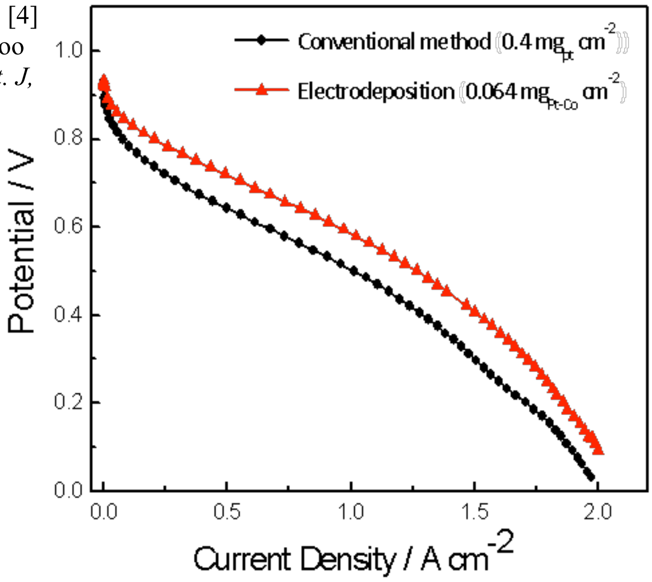


Fig. Comparison of single cell performances of commercial E-Tek catalyst and electrodeposited catalyst.

# Electrochemical Regeneration of a Nicotinamide Cofactor Using a Cyclopentadienyl-rhodium Complex on Functionalized ITO Electrodes

Soojin Kim, Jinheung Kim*

*Department of Chemistry and Nano Science,*
*Ewha Womans University, Seoul, 120-750, Republic of Korea*
jinheung@ewha.ac.kr

An organometallic rhodium complex has been frequently employed as an efficient catalyst for hydride transfer during chemical and electrochemical formation of NADH to selectively reduce $NAD^+$. Several electrochemical NADH regeneration systems have been reported using Rh catalysts to study electron transfer phenomena. Smith et al. reported non-enzymatic electrochemical production of NADH using a Rh catalyst on a glassy carbon electrode (GC). Bulk electrolysis of $NAD^+$ carried out with a Rh catalyst in the absence and presence of platinum nanoparticles (PtNPs) generates enzymatically active 1,4-NADH. PtNPs have also been reported to act as a photosensitizer as well as a catalyst during photocatalytic regeneration of NADH. In those studies, PtNPs were used in a homogeneously dispersed solution. Electron transfer between catalyst and electrode during bulk electrolysis occurs within a short distance from the electrode surface. Understanding a relationship between functional groups on the electrode with fast electron transfer to the metal catalyst is required for an efficient electron transfer reaction between a metal catalyst and an electrode. Functionalized ITO electrodes are used to regenerate NADH using $[Cp^*Rh(bpy)(H_2O)]^{2+}$ (Cp* = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridine) electrochemically in a buffer solution. Amino- and mercapto-functionalized electrodes featured higher activity and stability for electrocatalytic generation of NADH than a bare ITO electrode. Effect of metal nanoparticles was also studied on modified ITO electrodes and the addition of platinum nanoparticles even resulted in improved activity. The electrochemical regeneration was somewhat affected in the presence of dioxygen, but not significantly. In addition, a conversion of carbon dioxide was carried out utilizing the electrochemically generated NADH and formate dehydrogenase to produce formic acid.

# Novel solvent-free direct coating process for battery electrodes and their electrochemical performance

Dong-Won Park[1], Natalia A. Cañas[1], Norbert Wagner[1], and K. Andreas Friedrich[1,2]

[1]*Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany*
[2]*University of Stuttgart, Institute for Thermodynamic and Thermal Engineering, Stuttgart, Germany*
*Correspondence to dong-won.park@dlr.de*

Recent investigations on secondary batteries have focused primarily on material design and synthesis, as a means of improving the performance of the electrodes [1-3]. The electrodes were, however, still fabricated in a conventional manner; i.e., *via* a wet process such as slurry casting. The electrodes prepared using this method typically suffer from several drawbacks such as the use of environmentally hazardous solvents, the electrical/mechanical contact loss, and large volume expansion owing to the use of new active materials. To overcome these drawbacks, several approaches have been adopted to optimize the electrode by using various manufacturing methods such as sputtering, chemical vapor deposition, spray coating, electrochemical etching, chemical bath deposition, etc. [4-9]. However, these methods are complicated and time-/energy-consuming, and are therefore unsuitable for the low-cost, mass production of the electrode material as well as large-area electrodes. Developing a low-cost manufacturing process and high-performance electrode materials is therefore essential to realizing commercially viable mass production. In this work, we report the first-ever battery electrodes fabricated using the dry-spraying method as a novel solvent-free direct coating process. In this process, an electrode component mixture, in powder form, was sprayed on a substrate to form a homogeneous electrode and then isothermally hot-pressed for various times. The electrochemical and physicochemical properties of the dry-sprayed electrode followed by hot-pressing were evaluated in order to understand the correlation between a preparation parameter, morphological characteristic of the electrode, and cell performance. The hot-pressing time had an effect on the binder distribution, which in turn resulted in different electrode morphologies and performance. The dry-sprayed LTO ($Li_4Ti_5O_{12}$) electrode prepared at a hot-pressing time of 60 min had excellent electrical conductivity and $Li^+$ storage capacity, owing to its electron transport structure, which was more suitable than the prepared electrodes at other hot-pressing conditions.

[1] R. Marom, S. F. Amalraj, N. Leifer, D. Jacob, D. Aurbach, J. Mater. Chem., 27 (2011) 9938.
[2] S. Goriparti, E. Miele, F. D. Angelis, E. D. Fabrizio, R. P. Zaccaria, C. Capiglia, J. Power Sources, 257 (2014) 421.
[3] J. W. Kim, J. D. Ocon, D.-W. Park, J. Lee, ChemSusChem, 7 (2014) 1265-1273.
[4] Y. Fan, K. Huang, Q. Zhang, Q. Xiao, X, Wang, X. Chen, J. Mater. Chem. 22 (2012) 20870-20873.
[5] X.H. Liu, J.Y. Huang, Energy Environ. Sci. 4 (2011) 3844-3860.
[6] L.Q. Zhang, X.H. Liu, Y. Liu, S. Huang, T. Zhu, L. Gui, S.X. Mao, Z.Z. Ye, C.M. Wang, J. P. Sullivan, J. Y. Huang, ACS Nano 5 (2011) 4800-4809.
[7] B.M. Bang, H. Kim, J.P. Lee, J. Cho, S. Park, Energy Environ. Sci. 4 (2011) 3395-3399.
[8] B. Liu, X. Wang, H. Chen, Z. Wang, D. Chen, Y.-B. Cheng, C. Zhou, G. Shen, Sci. Rep., 3 (2012) 1622.
[9] D.-W. Park, S. Kim, J. D. Ocon, G. H. A. Abrenica, J. K. Lee, J. Lee, ACS Appl. Mater. Interfaces 23 (2012) 359-366.

# Extending Analytical Methods for the ORR Evaluation Based On the Electrokinetics On a Rotating Ring-Disk Electrode

Kuang-Hsu (Tim) Wu,[1] Da-Wei Wang,[2] Dang-Sheng Su[1*]
[1] *Shenyang National Laboratory, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, Liaoning, 110016 China*
[2] *School of Chemical Engineering, The University of New South Wales, Sydney, NSW2052, Australia*

[*]*e-mail:* dssu@imr.ac.cn

## Abstract

The use of rotating ring-disk electrode (RRDE) has become a general practice for evaluating the oxygen reduction reaction (ORR) performed on electrocatalysts. Typically, this technique comes with simple analytical equations based on the charge/mass balance equations to calculate the average number of electrons transferred ($n_{avg}$, Eq. 1) and the percentage production of peroxide intermediate ($\%HO_2^-$, Eq. 2).[1] However, the underlying mechanistic assumptions of this analysis and the uncertainty involved when considering the chemical decomposition of $HO_2^-$ have not been well elucidated. More importantly, the application of RRDE should be more specialized in providing useful mechanistic information than merely a trivial calculation of $n_{avg}$ and $\%HO_2^-$ as activity indices for the ORR on electrocatalysts.

$$n_{avg} = 4\, j_D / (j_D + j_R/N) \qquad (1)$$

$$\%HO_2^- = 2\, j_R / (N\, j_D + j_R) \qquad (2)$$

In this work, we establish a series of practically useful analytical equations for important ORR parameters as a function of the ratio of disk-to-ring current densities ($j_D/j_R$), based on the fundamental electrokinetic processes on a RRDE from first-principle. Our derivation demonstrates that the conventional analytical equations (Eq. 1 and 2) presume a stepwise ORR scheme as displayed in Figure 1. From this scheme, we provide four complementary activity indices for the ORR, including $n_{avg}$ and $\%HO_2^-$, and two analytical solutions to the reaction current density for $HO_2^-$ generation and reduction reaction. The sensitivity of the activity indices is evaluated and a current density deconvolution method is put forward for a better-resolved Tafel analysis for the ORR. Finally, we obtain the analytical equations for the ORR regarding the chemical $HO_2^-$ decomposition path and discuss the accuracy of direct application of Eq. 1 and 2 when the chemical $HO_2^-$ decomposition is possibly involved.

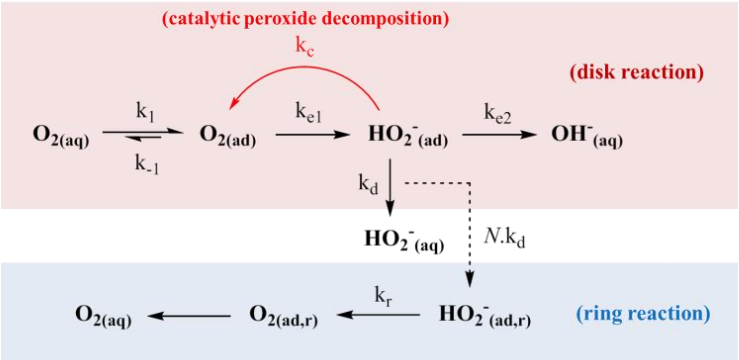


Figure 1. The electrokinetics scheme for the ORR occuring on a RRDE.

## References

[1] O. Antoine, R. Durand, *J Appl Electrochem* **2000**, *30*, 839-844.

# Ag-$CeO_2$ Composites as Electrocatalysts for Lithium-Air Batteries

Ying Liu, C Y Chung
*Department of Physics and Materials Science,*
*City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong, China.*
*E-mail: appchung@cityu.edu.hk*

Lithium-air batteries are generally considered as one of the most promising transformational energy storage technologies due to five times higher energy density compared to traditional Li-ion batteries. The extremely high energy density above 1000 Wh $kg^{-1}$ is ascribed to the Li foil as anode and the unlimited source of oxygen from the air as cathode. However, several problems must be solved before the practical use of Li-air batteries.[1, 2] One of the most important issues for Li-air batteries is the excessive accumulation of discharge products $Li_2O_2$ during charging, leading to high overpotential on charging and discharging. As a result, Li-air batteries can only survive for very limited cycles with low energy efficiency. [3, 4] To overcome these limitations, electrocatalysts have been introduced into Li-air batteries to improve the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics, which can decrease charging overpotential and increase the energy efficiency of Li-air batteries. Herein, we report a facile oxidation-reduction reaction method to prepare Ag-$CeO_2$ nanocomposites as catalysts for Li-air batteries. In a simulated air environment, superior electrochemical performance with high discharge capacity, stable cycling and small charge/discharge polarization voltage is achieved, which is much better than that of the $CeO_2$ or simple mixture of $CeO_2$ and Ag. The enhanced properties can be primarily attributed to the synergy effect between the Ag and the $CeO_2$ resulting from the unique nanostructures possessing plenty of active sites to promote the facile formation and decomposition of $Li_2O_2$.

## References

[1] H. D. Lim, K. Y. Park, H. Song, E. Y. Jang, H. Gwon, J. Kim, Y. H. Kim, M. D. Lima, R. O. Robles, X. Lepró, Adv. Mater. 25 (2013) 1348-1352.
[2] Y. C. Lu, H. A. Gasteiger, Y. Shao-Horn, J. Am. Chem. Soc. 133 (2011) 19048-19051.
[3] Z. Peng, S. A. Freunberger, Y. Chen, P. G. Bruce, Science 337 (2011) 563-566.
[4] B. McCloskey, A. Speidel, R. Scheffler, D. Miller, V. Viswanathan, J. Hummelshøj, J. Nørskov, A. Luntz, J. Phys. Chem. Lett. 3 (2012) 997-1001.

# A Novel Solid-State Li-air Battery using Inorganic Garnet-Type Electrolyte

Samson H.S. Cheng, C.Y. Chung
*Department of Physics and Materials Science, City University of Hong Kong*
*Tat Chee Avenue, Kowloon, Hong Kong SAR*
*shscheng2-c@my.cityu.edu.hk*

Solid state Li-air battery has attracted tremendous attention owing to high safety and no side reaction during discharge[1]. The garnet-type Li ion conductors are regarded most suitable for Li-air batteries as they exhibit Li ion conductivity as high as $1x10^{-3}$ $Scm^{-1}$ and high stability against moisture[2]. In this work, a solid state Li-air battery is constructed with the garnet-type solid electrolyte $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$, CNT/ porous carbon as air electrode and Li metal as anode. The electrochemical performance of this battery was investigated in air atmosphere. The battery output a first discharge and charge capacity of ~7000mAh $g^{-1}_{CNT}$ at a current density of 50mA $g^{-1}$and sustain for more than 40 stable cycles at a fixed capacity of 500mAh $g^{-1}_{CNT}$ at 400mA $g^{-1}$. An electrochemical redox potential of around 3V suggests that the battery is operated by the formation and decomposition of $Li_2O_2$. The morphology and crystal structure of charge and discharge products are further studied by SEM and Raman spectroscopy. Our results suggest that the garnet-type electrolyte has considerable potential for electrolyte in solid state Li-air battery.

## References

1. Liu, Y.; Li, B.; Kitaura, H.; Zhang, X.; Han, M.; He, P.; Zhou, H., Fabrication and Performance of All-Solid-State Li–Air Battery with SWCNTs/LAGP Cathode. *ACS applied materials & interfaces* 2015, *7* (31), 17307-17310.
2. Li, Y.; Han, J.-T.; Wang, C.-A.; Xie, H.; Goodenough, J. B., Optimizing Li+ conductivity in a garnet framework. *Journal of Materials Chemistry* 2012, *22* (30), 15357.

# New insights on the electrocatalysis of oxygen reduction reaction

Yan-Xia Chen
*Hefei National Laboratory for Physical Science at Microscale and Department of Chemical Physics, University of Science and Technology of China,* （*yachen@ustc.edu.cn*）

Oxygen reduction reaction (ORR) is the preferred cathodic reaction for fuel cells. However, the slow kinetics, high over potential and high cost of the noble metal catalyst have been the bottleneck for the commercialization process of PEMFCs. Extensive studies on ORR have been carried out in past deceases, and a lot molecular level information has been gained. However, by now, no agreement is reached about the mechanism and the structure-function relationship for ORR. For example, Feliu et el. Found that ORR activity on Pt [n (111) ×(111)] in acid media decreases with the increase in terrace width,[1] this contradicts with DFT calculations my Norskov et al. [2] Moreover, the rate determining step for ORR is still under debate.[1] In this talk, we will present our recent progress on such issues,[3-10] especially, the result of structural effect for ORR at Pt [n(111)×(111)] single crystal, the temperature effect and the pH effect of ORR and some methodological issues of RDE will be discuss in details.

References:

1. Gomez-Marin, A. M.; Rizo, R.; Feliu, J. M. *Catalysis Science & Technology* 2014, *4*, 1685.

2. J. Norskov, J. Rossmeisl, A. Logadottir and L. Lindqvist, J. Phys. Chem. B, 2004, 108, 17886.

3. L-W. Liao, Y. L. Zheng, J. Wei, Y.-X. Chen, Electrochem. Commun., 2015, 58,73.

4. F. Yang, L-W. Liao, M-F. Li, D. Mei, Y.-X. Chen, Chin. J. Chem. Phy., 2014, 27,479.

5. D. Mei, Z. D. He, Y. L. Zheng, D. C. Jiang, Y.-X. Chen, Phys. Chem. Chem. Phys., 2014,16,13762.

6. Zheng, Y; Mei, D; Chen, Y; Ye, S., Electrochem. Commun., 2014, 39,19.

7. Ming Fang Li, Ling Wen Liao, Dao Fu Yuan, Dong Mei, Yan-Xia Chen，Electrochim. Acta, 2013,110,780.

8. L. W. Liao, M. F. Li, J. Kang, D. Chen, Y. X. Chen and S. Ye, J. Electroanal. Chem. 2013, 688, 207.

9. L. W. Liao, D. Chen, M. F. Li, Y. L. Zheng, J. Kang, Y. X. Chen, SCIENTIA SINICA Chimica, 2013,43,178.

**10.**陈微，廖玲文，何政达，陈艳霞，电化学，2014，20，444。

# Synthesis of $CeO_2$ Decorated Nanocrystalline Zeolite Based Nanocomposite Material and Its Application in the Electrocatalytic Oxidation of Methanol

**Balwinder Kaur** and Rajendra Srivastava
*Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, India*
**Rajendra srivastava:+91-1881-24217; rajendra@iitrpr.ac.in*

***Abstract:*** *Cerium oxide decorated nanocrystalline zeolite based nanocomposite material was synthesized and investigated in the electrochemical oxidation of methanol for their possible application in methanol fuel cell.*

## 1. Introduction

Development of economical anode catalyst for the methanol oxidation with high electrochemical activity and low overpotential is a great challenge for the development of cost effective direct methanol fuel cells.[1] In this poster presentation, synthesis, physico-chemical characterization of $CeO_2$ decorated nanocrystalline zeolite and its application in the electrochemical oxidation of methanol will be discussed.

## 2. Experimental

Nanocrystalline zeolite was hydrothermally synthesized by our own reported procedure.[2] $CeO_2$ decorated nanocrystalline zeolite based nanocomposite materials with different weight ratios were prepared.

## 3. Result and discussion

The results demonstrate that $CeO_2$ decorated nanocrystalline zeolite exhibited significantly high electro-catalytic activity in the electrochemical oxidation of methanol when compared with the individual components $CeO_2$ or nanocrystalline zeolite (Fig. 1).

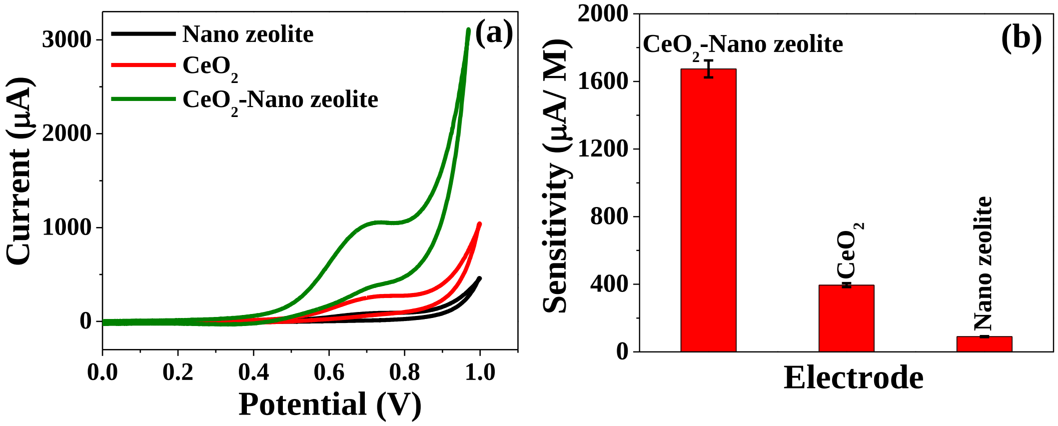


**Fig.1.** Comparison of (a) CV and (b) sensitivity towards methanol oxidation at $CeO_2$ decorated nanocrystalline zeolite, $CeO_2$, and nanocrystalline zeolite modified electrodes investigated in this study.

## 4. Conclusion

The higher oxidation peak current and lower overpotential toward the electrochemical oxidation of methanol indicates that $CeO_2$ decorated nanocrystalline zeolite can act as a promising electrocatalyst for methanol oxidation.

## References

[1] X. Cui, Y. Zhu, Z. Hua, J. Feng, Z. Liu, L. Chen, J. Shi, *Energy Environ. Sci.*, **2015**, *8*, 1261.
[2] B. Kaur, R. Srivastava, B. Satpati, ChemElectroChem, **2015**, 2, 1164.

# What Types of Defects Enhance the Activity of Platinum for the Oxygen Reduction Reaction?

Federico Calle-Vallejo[1], David Loffreda, Philippe Sautet, Aliaksandr S. Bandarenka

*[1]Leiden Institute of Chemistry, Leiden University*
*Einsteinweg 55, 2333 CC Leiden, The Netherlands*
*f.calle.vallejo@chem.leidenuniv.nl*

The surfaces of heterogeneous catalysts are normally composed of a wide variety of sites. Typically, low-index surfaces coexist with more open facets and various types of defects. All those sites contribute differently to the overall catalytic activity. In order to achieve maximal catalytic activities, materials design techniques should identify the most active sites and suitable synthesis procedures must increase their surface abundance. The challenge lies in the elucidation of the active sites for a given reaction.

In particular, the role of defects on the oxygen reduction reaction (ORR) catalyzed by platinum is puzzling. On the one hand, it is known that stepped Pt(111) electrodes are more active than the pristine ones [1]. On the other hand, the activity of convex Pt nanoparticles, in which steps are abundant, is never as high as that of Pt(111) [2]. The question is then why do steps enhance the activity of extended surfaces and decrease that of nanoparticles?

I will show that "coordination-activity plots" [3] can help solve this puzzle capitalizing on the relationship between the geometric structure of Pt catalysts and their ORR activity. Such relationship is captured for all types of sites on nanoparticles of different sizes and shapes and extended surfaces by generalized coordination numbers [4, 5]. Optimal Pt sites for the ORR are located at more coordinated environments than those of Pt(111), a condition fulfilled by defects on extended surfaces but not on nanoparticles.

## References

[1] A. Hitotsuyanagi, M. Nakamura, N. Hoshi, Electrochimica Acta, 82 (2012) 512-516.
[2] F.J. Perez-Alonso, D.N. McCarthy, A. Nierhoff, P. Hernandez-Fernandez, C. Strebel, I.E.L. Stephens, J.H. Nielsen, I. Chorkendorff, Angewandte Chemie International Edition, 51 (2012) 4641-4643.
[3] F. Calle-Vallejo, J. Tymoczko, V. Colic, Q.H. Vu, M.D. Pohl, K. Morgenstern, D. Loffreda, P. Sautet, W. Schuhmann, A.S. Bandarenka, Science, 350 (2015) 185-189.
[4] F. Calle-Vallejo, J.I. Martínez, J.M. García-Lastra, P. Sautet, D. Loffreda, Angewandte Chemie International Edition, 53 (2014) 8316-8319.
[5] F. Calle-Vallejo, P. Sautet, D. Loffreda, The Journal of Physical Chemistry Letters, 5 (2014) 3120-3124.

# Studying the Impact of Several Supporting Materials on the Structure and Catalyst Activity of Ruthenium Oxide Nanoparticles for the Oxygen Evolution Reaction in PEM Water Electrolysis

Parisa (Fatemeh) Karimi[1], Brant Peppley[1], Aimy Bazylak[2]

*[1] Department of Chemical Engineering, Queen's University, 19 Division St., Kingston, Ontario, K7L 3N6, Canada*
*[2] Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario, M5S 3G8, Canada*

Polymer Electrolyte Membrane Water Electrolysis (PEMWE) is an efficient method to produce high purity hydrogen. PEMWE provides several advantages over other water electrolysis methods, such as Solid Oxide Water Electrolysis and Alkaline Water Electrolysis [1]. One of the drawbacks of the PEMWE, however, is the need for precious noble metal catalysts, such as iridium and ruthenium oxides. To reduce the cost, researchers have been trying to increase the active surface area and improve the stability of these precious metal catalysts [2-5]. One way to achieve this goal is by dispersing the precious metals on an inexpensive catalyst support. In this work, several materials including Tantalum Carbide (TaC), Niobium Oxide ($NbO_2$), Niobium Carbide (NbC), Titanium Oxide ($TiO_2$) and Antimony-doped Tin Oxide ($Sb\text{-}SnO_2$) were used as catalyst supports for the ruthenium oxide catalyst. Most of these materials were used for the first time as a support for $RuO_2$-based electrocatalysts for PEMWE. The thermal stability of the support materials were studied using thermogravimetric analysis (TGA) and differential thermal analysis (DSC). The chemical stability of the support materials in an acidic environment were studied by heating a dispersion of the support materials in a mixture of strong acid (such as triflic acid) and hydrogen peroxide. The liquid phase was then analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with the purpose of detecting ions originating from the support materials, which is an indicator of instability/degradation in the acidic environment. The Polyol method was used to synthesize the ruthenium oxide nano particles, and deposit them onto the support surface. The physical morphology of the supported catalysts such as surface area and particle size were measured using nitrogen physisorption and Transmission Electron Microscopy (TEM). Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy (SEM-EDX) analysis was used to measure the noble metal catalyst loading on the support. The electrical conductivity of the compressed catalyst powders were evaluated, and their electrochemical properties were evaluated on a rotating disk electrode using cyclic voltammetry and polarization measurements.

1. A. Marshall, PhD thesis, Department of Material Technology, Norwegian University of Science and Technology (NTNU), (2005).
2. S. Ardizzone and et al., Journal of Electroanalytical Chemistry, **589** (2006) 160–166.
3. E. Mayousse and et al., International Journal of Hydrogen Energy, **36** (2011) 10474-10481.
4. C.P. De Pauli and et al., Journal of Electroanalytical Chemistry, **538** (2002) 145-151.
5. J. Polonsky and et al., International Journal of Hydrogen Energy, **37** (2012) 2173-2181.

# A Facile Synthesis of Size-Controllable $IrO_2$ and $RuO_2$ Nanoparticles for Oxygen Evolution Reaction

**T. D. Nguyen[a,b], G. G. Scherer[d], Z. J. Xu[a,b,c]**
[a]*School of Materials Science and Engineering, Nanyang Technological University, Singapore*
[b]*Energy Research Institute @ Nanyang Technological University, Singapore*
[c]*Solar Fuel Laboratory, School of Material Science and Engineering, Nanyang Technological University, Singapore*
[d]*TUM-CREATE, Singapore*
*guenther.scherer@tum-create.edu.sg*

The efficiency of the water electrolysis process is one of the key technological challenges for a hydrogen fuel economy. This process includes the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. However, the efficiency of the water electrolysis is restricted by the sluggish kinetics of the oxygen evolution reaction (OER). Developing efficient catalysts by novel synthesis methods is highly desired to promote the kinetics of the OER and, therefore, the efficiency of the water electrolysis process. In this report, we present a facile wet-chemical method for synthesizing $IrO_2$ and $RuO_2$ nanoparticles (NPs) for OER. The nanoparticles were synthesized by reducing metal chlorides in ethylene glycol in the presence of polyvinylpyrrolidone, followed by calcination in air at different temperatures. The particle size was controlled by adjusting the annealing temperature. The activities of $IrO_2$ and $RuO_2$ NPs were investigated by cyclic voltammetry (CV) in alkaline (0.1M KOH) electrolyte. As-synthesized $IrO_2$ and $RuO_2$ NPs showed high OER activity. The $IrO_2$ NPs exhibited area specific currents up to 0.76 $\mu A/cm^2_{oxide}$ at 1.48 V (vs. RHE), while the $RuO_2$ NPs achieved values up to 18.71$\mu A/cm^2_{oxide}$. Moreover, $RuO_2$ NPs showed an extremely high mass activity for OER, up to 16.2 $A/g_{oxide}$ at 1.48 V (vs. RHE), which represents the highest value recorded to date.

# Ir (111)/(110) and Ru (0001) single crystals as model catalysts for the oxygen evolution reaction: Oxide formation and electrocatalytic activity

Ebru Özer, Camillo Spöri, Tobias Reier, and Peter Strasser

*The Electrochemical Energy, Catalysis, and Materials Science Group*
*Technische Universität Berlin, Department of Chemistry, Sekr. TC03*
*Straße des 17. Juni 124, 10623 Berlin, Germany*
*ebru.oezer@campus.tu-berlin.de*

Electrochemical splitting of water has been considered to be a very promising technology for a sustainable hydrogen economy. However, the efficiency of water electrolysis is limited by the oxygen evolution reaction (OER) due to kinetics, which results in a large anodic overpotential.[1]

Therefore, the development and optimization of new catalysts for the OER is of great importance in overcoming the challenges in energy conversion.[2]

The influence of different crystal faces such as steps, kinks and edges in defined nanosized catalysts is spotlighted as crucial parameter for understanding surface chemistry. Single crystals are suitable model catalysts to study these morphological effects.

Here, we report a comparative study of the influence of oxidation protocols on the activity of noble metal single crystal surfaces of Iridium (111) and (110) as well as Ruthenium (0001) for the oxygen evolution reaction (OER).

Well-defined and ordered single crystal electrodes were prepared in a modified inductive electrochemical single crystal chamber constructed according to [3] with modifications. The chamber allows controlled annealing and thermal restructuring of the surfaces followed by immediate electrochemical characterization without exposure to ambient conditions while avoiding the cost and complexity of an UHV setup. Prior to each electrocatalytic oxidation the electrode surface quality was characterized by cyclic voltammetry. The clean single crystal surfaces were analyzed towards their electrocatalytic oxygen evolution activities and oxidation behaviour.

Three different oxidation protocols were used revealing a strong activity dependence on the duration and upper potential limit of the electrochemical oxidation. Activities are compared by means of overpotential at a fixed current density and Tafel analysis. The resulting changes of the surface through oxidation were followed using cyclic voltammetry and impedance spectroscopy. Here, important differences between the two faces of iridium in terms of surface morphology of the formed oxide were identified. Thus allowing conclusions for preferable crystal faces in nanoparticle catalysts. On Ru (0001), however, the major effect on activity and morphology was surface roughening by the well known $RuO_4$ dissolution.[4]

[1] Y. Surendranath, M. W. Kanan, D. G. Nocera, *J. Am. Chem. Soc.* 132, 16501 (2010).

[2] M. Carmo, D. L. Fritz, J. Mergel, D. Stolten, *International Journal of Hydrogen Energy* 38, 4901 (2013).

[3] A. S. Bondarenko, I. E. L. Stephens, I. Chorkendorff, *Electrochemistry Communications* 23, 33 (2012).

[4] R. Kötz, S. Stucki, D. Scherson, D.M. Kolb, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 172, 211 (1984).

# Effects of Pore Size and Doping-Site Position of Metal-Free Oxygen Reduction Catalysts in the Membrane Electrode Assemblies for Alkaline Fuel Cells

Seonggyu Lee, Jinwoo Lee*
*Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH)*
*77 Cheongam-Ro,* Nam-gu, *Pohang, Gyeongbuk 790-784, Korea*
*xggyu1@postech.ac.kr*

Alkaline anion exchange membrane fuel cells (AEMFCs) have been garnering attention because oxygen reduction reaction (ORR) is more facile in an alkaline environment and therefore potentially facilitate the use of less expensive catalysts. Recently, metal-free ORR catalysts based on heteroatom doped carbon materials are considered as a promising approach to substitute Pt-based catalysts in AEMFCs. The incorporation of heteroatoms significantly accelerates the reaction compared with that in pure carbon by changing the charge and spin density of carbon. However, most of previous studies are only focused on the kinetic activity of metal-free catalysts using half-cell measurements even though the research on MEAs is greatly important for real AEMFC applications. Here, we report effects of pore size and doping-site position of metal-free catalysts in MEAs using well-defined ordered mesoporous carbon systems for designing a highly active metal-free catalysts in MEA level. As a result, a large pore sized N, P co-doped ordered mesoporous carbon with precisely controlled doping-site position showed a remarkable on-set potential and produced 70 % of the maximum power density obtained using Pt/C in the MEA of AEMFC.

# Electrocatalytic Reduction of Carbon Dioxide ($CO_2$) into $C_n$ Organic Molecules on Nanostructured Copper-Gold Electrodes

Karl Adrian Gandionco[1], Jaeyoung Lee[2], and Joey D. Ocon[1]*
*[1] Laboratory of Electrochemical Engineering (LEE), Department of Chemical Engineering, University of the Philippines Diliman, Quezon City 1101, Philippines*
*[2] Electrochemical Reaction and Technology Laboratory (ERTL), School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea*
**jdocon@up.edu.ph*

The electrochemical reduction of carbon dioxide ($CO_2$) into hydrocarbons is considered as one of the promising solutions to the pressing problems related to energy and climate change. While a number of studies have been made on $CO_2$ electrochemical reduction, most of them are centered on investigating the effect of modifying the catalytic material on the faradaic efficiencies of the process. A study that examines the influence of catalyst preparation methods on the activity and selectivity has not been reported yet. In this work, we synthesized copper-gold electrocatalysts via two solution-based processing techniques, namely co-electrodeposition and co-reduction of metal precursors. In co-electrodeposition, formation of the nanostructured copper-gold alloy is performed by passing current on an electrolyte solution containing copper chloride and gold chloride metal precursors, whereas in co-reduction, nanostructured copper-gold alloy is prepared by heating a solution containing copper acetate and gold acetate in inert atmosphere. The faradaic efficiencies of the electrochemical reduction of $CO_2$ when using the two differently prepared nanostructured copper-gold alloy catalysts are found to be considerably higher as compared to that of copper electrode. Moreover, the co-electrodeposited nanostructured copper-gold alloy catalyst shows significant selectivities for alcohol and formate while the co-reduced type shows significant selectivities for carbon monoxide, formate, and methane. The insights that are obtained through this study can be a guide for the synthesis of a better catalyst for $CO_2$ electrochemical reduction.

# Electrocatalytic $O_2$ reduction at Room Temperature Ionic Liquid|Water Interface

Marcin Opallo[a], Justyna Jedraszko,[a] Wojciech Nogala,[a] Wojciech Adamiak,[a] Saustin Dongmo,[b]
Gunther Wittstock,[b] Hubert H. Girault[c]

*[a]Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland*
*[b]Department of Chemistry, Center of Interface Science, School of Matehmatics and Science, Carl von Ossietzky University of Oldenburg, Germany.*
*[c] Switzerland LEPA, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.*

*mopallo@ichf.edu.pl*

Biphasic systems with room temperature ionic liquid (RTIL)|water interfaces are crucial constituents of an increasing number of physicochemical systems including advanced materials [1,2]. Extraction and phase separation of RTIL and aqueous solution are intensively studied [3,4], whereas the application of RTIL–water systems in synthesis has been limited so far [5,6].

When the aqueous phase containing considerable amount of ionic species is in direct contact with a RTIL, the efficiency and pathway of interfacial processes involving charged reactants depends on the Galvani potential difference across the interface, controlled externally by means of a potentiostat or by the composition and concentration of ions in both phases [7-9]. Polarisation control of the liquid|liquid interface may provide favourable conditions for proton or oxygen reduction [10]. It has been shown that $O_2$ can be reduced at the interface between water and an organic solvent immiscible with water using a strong electron donor such as decamethylferrocene (DMFc) dissolved in the organic phase with $H_2O_2$ as a main product [11,12]. So far, these studies were restricted to interfaces formed by aqueous solutions of acids and salt solutions in nonaqueous polar solvents.

Here, we will demonstrate that this reaction occurs at a RTIL|water interface with DMFc in the RTIL phase [13]:

$$2\ \mathrm{DMFc} + O_2 + 2H^+ \rightarrow 2\ \mathrm{DMFc}^+ + H_2O_2$$

The product was detected by, colorimetric substrate depletion, scanning electrochemical microscopy (SECM) and optical readout with fluorogenic substrate [14]. The experiments with carbon paste electrode with DMFc solution in hydrophobic ionic liquid demonstrated that electron donor can be regenerated electrochemically. This increases the flux of generated hydrogen peroxide.

1. M.V. Fedorov, A.M. Kornyshev, Chem. Rev., 2014, **114**, 2978.
2. M. Opallo, A. Lesniewski, J. Electroanal. Chem., 2011, **656,** 2
3. X. Sun, H. Luo, S. Dai, Chem. Rev., 2012, **112**, 2100.
4. J.H. Zhang, H. Gao, Y.B. Li, Z.Q. Zhou, J. Separation Sci., 2011, **34,** 3178.
5. V. Ladnak, N. Hofmann, N. Brausch, Adv. Synth. & Cat., 2007, **349,** 719.
6. M. Petkovich, K.R. Seddon, Chem. Soc. Rev., 2011, **40**, 1383.
7. Z. Samec, J. Langmaier, T Kakiuchi, Pure Appl. Chem., 2009, **81**, 1473.
8. Y. Wang, T. Kakiuchi, Y. Yasui, M.V. Mirkin, J. Am. Chem. Soc., 2010, **132**, 16945.
9. T. Kakiuchi, Anal. Chem., 2007, **79**, 6442.
10. M. A. Mendez, R. Partovi-Nia, I. Hatay, B. Su, P. Ge, A. Olaya, N. Younan, M. Hojeij and H. H. Girault, Phys. Chem. Chem. Phys., 2010, **12**, 15163.
11. B. Su, R. NiaPartovi, F. Li, M. Hojeij, M. Prudent, C. Corminboeuf, Z. Samec. H.H. Girault, Angew. Chem. Int. Ed., 2008, **47**, 4675.
12. W. Adamiak, J. Jedraszko, O. Krysiak, W. Nogala, J. Hidalgo-Acosta,, H. H. Girault and M. Opallo, J. Phys. Chem. C, 2014, **118**, 23154.
13. J. Jedraszko, W. Nogala, W Adamiak, S. Dongmo, G. Wittstock, H.H. Girault, M. Opallo, Chem. Commun., 2015, **51**, 6851
14. M. Burchardt, G. Wittstock, Langmuir, 2013, **29**, 15090.

# Low Temperature CO Oxidation Catalyzed by NiO/SiO$_2$ Prepared by Atomic Layer Deposition

Il Hee Kim[1], Sang Wook Han[1], Dae Han Kim[1], Ki Jung Park[1], Soong Yeon Kim[1],
Eun Ji Park[1] and Young Dok Kim*[1,2]
[1]*Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*
[2]*Biorefinery Research Group, Korean Research Institute of Chemical Technology, Daejeon 306-600, Korea*
**E-mail:ydkim91@skku.edu*

NiO nanoparticles supported on mesoporous SiO$_2$ were prepared by atomic layer deposition (ALD), and the fabricated samples were annealed at four different temperatures (300, 450, 600, and 750 $^{o}$C). Size of NiO nanoparticles on the surface of annealed samples was smaller than ~ 2 nm up to annealing temperature of 600 $^{o}$C, whereas that of 750 $^{o}$C-annealed sample became bigger as ~ 30 nm due to agglomeration. Among the four samples annealed at different temperatures, 450 $^{o}$C-annealed sample showed the highest catalytic activity for CO oxidation at room temperature. Also the 450 $^{o}$C-annealed catalyst showed the highest resistance toward deactivation, maintaining 60% of the initial catalytic activity for CO oxidation after 680 minutes. Moreover, after additional annealing at 450 $^{o}$C, catalytic activity of the 450 $^{o}$C-annealed catalyst deactivated after CO oxidation experiment was fully recovered. These results suggest that ALD followed by annealing is promising strategy to fabricate highly active and stable catalysts consisting of nanoparticles incorporated in the mesopores of a high-surface area support.

# Low Temperature CO Oxidation Catalyzed by NiO/$Al_2O_3$

Sang Wook Han[1], Dae Han Kim[1], Eun Ji Park[1], Soong Yeon Kim[1], Ki Jung Park[1],
Il Hee Kim[1] and Young Dok Kim*[1,2]

*[1]Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Korea*

*[2]Biorefinery Research Group, Korean Research Institute of Chemical Technology, Daejeon 306-600, Korea*

**E-mail: ydkim91@skku.edu*

We fabricated 50-cycled NiO/mesoporous $Al_2O_3$ using atomic layer deposition (ALD) which can form homogeneous film on complex surfaces such as porous materials. Chemical composition, state and physical properties of the 50-cycled NiO/$Al_2O_3$ were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES), X-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The 50-cycled NiO/$Al_2O_3$ was pre-annealed at various temperatures under dry air condition for 2 h before the CO oxidation experiment at 30 ºC. All of the samples showed high catalytic activity for CO oxidation at low temperature and they also showed an enhanced resistance towards poisoning during CO oxidation as the pre-annealing temperature increased. It implies that ALD-prepared NiO/$Al_2O_3$ could be one of the promising catalysts for low temperature CO oxidation.

# $CoMn_2O_4$ Anchored on N-doped 3D Hierarchical Porous Carbon Derived from Biomass as an Oxygen Reduction Reaction Catalyst for Zinc-Air Batteries

James L. Digol[1], Jaeyoung Lee[2], and Joey D. Ocon[1]*
[1] *Laboratory of Electrochemical Engineering (LEE), Department of Chemical Engineering, University of the Philippines Diliman, Quezon City 1101, Philippines*
[2] *Electrochemical Reaction and Technology Laboratory (ERTL), School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea*
*jdocon@up.edu.ph

The oxygen reduction reaction (ORR) is the main reaction occurring in the cathodes of metal-air batteries and fuel cells, which are promising technologies for clean and efficient energy generation and storage. The reaction is widely known to be sluggish such that an electrocatalyst with superior activity is required to lower the intrinsic overpotential to drive the electrochemical reaction. Despite intensive research efforts, developing an ORR catalyst that is inexpensive, stable, and highly active remains a grand challenge. Herein, we report a novel ORR catalyst for zinc-air battery that consists of spinel-type $CoMn_2O_4$ nanoparticles anchored on N-doped three-dimensional hierarchical porous carbon (N-3DHPC) derived from waste biomass. The catalyst preparation involves carbonization of waste corn cobs with melamine as a promoter followed by a two-step hydrothermal method to bind the $CoMn_2O_4$ nanoparticles onto the carbon substrate. Both $CoMn_2O_4$ and the 3DHPC when used separately as catalysts are known to have low activity but a hybrid of these two enhanced by N-doping of the substrate, has shown a very high activity comparable to 30 wt. % platinum supported on carbon (Pt/C) catalyst. Moreover, a zinc-air battery using the $CoMn_2O_4$/N-3DHPC as a cathode catalyst has also shown a high discharge capacity, excellent rate capability and remained durable under alkaline conditions as compared to the Pt/C catalyst. The catalytic performance is due to the synergic effect of chemical coupling between $CoMn_2O_4$ and N-3DHPC giving rise to an efficient electrolyte penetration and oxygen transport, and increased rate of oxygen electroreduction.

# Secondary hydrothermally processed engineered $TiO_2$ nanostructures for efficient perovskite solar cells: Role of nanorod length, precursor solution concentration and etching time

Sawanta S. Mali, Hyungjin Kim, Chang Kook Hong*
*Polymer Energy Materials Laboratory, School of Applied Chemical Engineering, Chonnam National University, Gwangju, 500-757 (South Korea),E-mail:hongck@chonnam.ac.kr, sawantasolar@gmail.com*

Last few years perovskite solar cells (PSCs) started '*once again*' as a hottest and promising light harvesting materials in the photovoltaic technology scenario. Implementation of 1D hierarchical nanostructures is one of the most promising approaches towards boosting efficiency of PSCs. Here, we have synthesized variety of $TiO_2$ nanostructures from TTIP and TBT precursor with various solution concentration.[1-2] Hollow nanostructures of rutile $TiO_2$ have been synthesized using secondary hydrothermal process. Two typical structures such as $TiO_2$ nanorods and nanoflowers have been subjected to secondary hydrothermal process for realizing perovskite solar cells (PSC). The prepared nanostructures were used in combination with $MAPbI_3$ perovskite which forms sensitized solar cells (Figure 1). The heterostructured perovskite based on hierarchical hollow $TiO_2$ provides enhanced surface area, better contact with perovskite through large area adsorption and effective light penetration which has been confirmed by various experiments including time resolved photoluminescence spectroscopy (TRPL) and solid state impedance spectroscopy (ssIS). Among these structures, the hollow nanoflowers exhibited maximum power conversion efficiency (PCE) of 12.72% with photocurrent density ($J_{SC}$) of 21.05 $mAcm^{-2}$. The major contributions in increased efficiency of the two structures was due to two counts: increased charge generation from the increased surface area of $TiO_2$ obtained by the secondary hydrothermal etching process and better charge separation due to increased contact area with the perovskite.[1-3] Further effect of wetting time of perovskite $MAPbI_3$/(γ-butyrolactone) GBL solution has been studied and our results revealed that 100sec was minimum time required for best penetration. Stability studies of the fabricated solid state devices over a period of 10 days indicated good stability and showed gradual decrease in efficiency. Further we explored the effect of nanorod length and etching time. The fine-tuned etched $TiO_2$ nanorod/nanoflower (345nm thin) sample exhibited $\eta$=14.36%, $V_{OC}$=1.062V, $J_{SC}$=19.175$mAcm^{-2}$ and FF=0.705 with no hysteresis. The results also highlights the important aspects in hysteresis issue and photocurrent stability of etched hollow $TiO_2$ nanostructures.

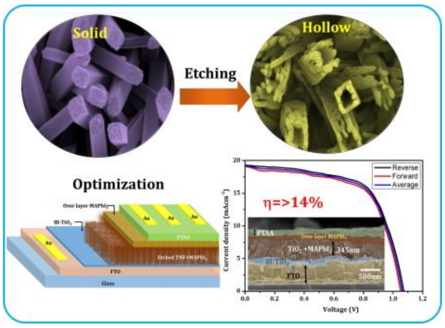


**Figure 1** Schematic representation of transformation of solid nanorods to hollow nanorods for perovskite solar cell and implementation in solid state perovskite solar cells.

## Reference:

[1] S. S. Mali, C. S. Shim, P. S. Patil and C. K. Hong, *Mater. Today*, 2015, 18, 172-173.
[2] S. S. Mali, C. S. Shim, H. K. Park, J. Heo, P. S. Patil and C. K. Hong, *Chem. Mater.*, 2015, 27, 1541–1551.
[3] S.S. Mali, H. J. Kim, C. S. Shim, P. S. Patil, J. H. Kim and C. K. Hong, *Sci. Rep.* 2013, 3, 3004.

# Ordered Intermetallic Nanoparticles as Highly Active and Durable Electrocatalyst for Oxygen Reduction Reaction

Dong Young Chung, Yung-Eun Sung*

*Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 151-742, Republic of Korea*

*School of Chemical & Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea*

*ysung@snu.ac.kr*

Demand on the practical synthetic approach to the high performance electrocatalyst is rapidly increasing for the fuel cell commercialization. However, sluggish kinetics of the oxygen reduction reaction hindered the high performance. Therefore methods to improve the specific activity of catalysts that facilitate the oxygen reduction reaction have been and continue to be a popular area of research. Since electrocatalytic reactions are strongly dependent on the surface structure of catalysts, delicate design of the nanoparticle plays a significant role in a high catalytic activity and the utilization of electrocatalysts. Here we present a synthesis of highly durable and active intermetallic ordered face-centered tetragonal (fct)-PtFe nanoparticles (NPs). First, we will suggest the protection layer coated ordered intermetallic nanoparticles as robust oxygen reduction catalyst. Only few nanometers are obtained by thermal annealing of polydopamine-coated PtFe NPs, and the N-doped carbon shell that is *in situ* formed from dopamine coating could effectively prevent the coalescence of NPs. This carbon shell also protects the NPs from detachment and agglomeration as well as dissolution throughout the harsh fuel cell operating conditions. Second, ordered intermetallic nanoparticles in a carbon cage structure as electrocatalyst for oxygen reduction and alcohol oxidation will be suggested. Ordered intermetallic nanoparticles are easily obtained by spontaneous reduction method and transformed to the fct structure. We suggest that the PtFe ordered intermetallic nanoparticles reside in the rigid carbon network are responsible for high activity and durability.

# Electrocatalytic Conversion of $CO_2$ to Multi-Carbon Fuels on a Chloride-Induced $Cu_2O$-Cu Catalyst

Seunghwa Lee [a], Jaeyoung Lee [a,b]

[a]*Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea.*
[b]*Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies, GIST, Gwangju, 500-712, South Korea.*

*Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea.*
*jaeyoung@gist.ac.kr*

Of late, reducing anthropogenic $CO_2$ is of great interest due to detrimental effect of the accumulated $CO_2$ on environmental ecosystem. In order to reduce the amount of $CO_2$, electrochemical reduction method using metal oxidized composites receives a considerable attention [1-4]. Among a variety of the oxidized materials, herein we show the chloride induced bi-phasic $Cu_2O$-Cu catalyst and its superior $CO_2$ conversion activity and selectivity for production of multi-carbon fuels. Despite of the strong electrolytic condition, the $Cu_2O$ survived with aid of $Cl^-$ more than in $KHCO_3$ electrolyte and catalyzed $CO_2$ conversion toward high multi-carbon fuels (e.g., $C_2H_5OH$, $C_3H_7OH$, and even $C_4H_{10}$) for stably long time period. This remarkable electrocatalysis might be associated with synergistic effect between $Cu_2O$ and $Cl^-$. From this study, it was demonstrated that oxidized Cu species could contribute to the preferential production of multi-carbon fuels, particularly including $C_3H_7OH$, $C_3H_8$ and $C_4H_{10}$. Although the interesting electrocatalytic behavior was observed during limited reaction time when $Cu_2O$ coverage was enough remained, this study opens up a possibility for further critical factor with regard to conversion selectivity of $CO_2$ to the higher-carbon number products.

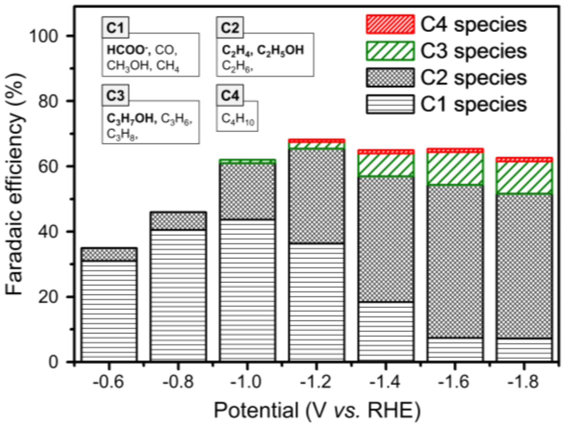


**Figure 1.** Product distribution according to applied cathodic potentials in the range of -0.6 to -1.8 V (*vs.* RHE).

References

[1] D. Kim, S. Lee, J. D. Ocon, B. Jeong, J. K. Lee, J. Lee, Insights into autonomously formed oxygen-evacuated $Cu_2O$ electrode for the selective production of $C_2H_4$ from $CO_2$, Phys. Chem. Chem. Phys., **17** (2015) 824.
[2] S. Lee, J. D. Ocon, Y. Son, J. Lee, Alkaline $CO_2$ Electrolysis toward Selective and Continuous $HCOO^-$ Production over $SnO_2$ Nanocatalysts, J. Phys. Chem. C, **119** (2015) 4884.
[3] S. Lee, D. Kim, J. Lee, Electrocatalytic Production of C3-C4 Compounds by Conversion of $CO_2$ on a Chloride-Induced Bi-Phasic $Cu_2O$-Cu Catalyst, Angew. Chem. Int. Ed., **127** (2015) 1.
[4] Y. Chen, C. W. Li, M. W. Kanan, Aqueous $CO_2$ Reduction at Very Low Overpotential on Oxide-Derived Au Nanoparticles, J. Am. Chem. Soc., **134** (2012) 19969.

# Activity and Stability of Thermally Treated Iridium Hydrous Oxides for the Oxygen Evolution Reaction

Simon Geiger, Olga Kasian, Serhiy Cherevko, Karl J.J. Mayrhofer
*Department of Interface Chemistry and Surface Engineering, Max-Planck Institut für Eisenforschung*
*Max-Planck-Str. 1, 40237, Düsseldorf , Germany*
cherevko@mpie.de

In the future energy concept renewable wind and solar energy will play the dominating role. It is anticipated that due to the intermittent nature of power outcome from the renewable energy sources, there will be an energy surplus which can be efficiently stored. As an example, hydrogen could be successfully produced by proton exchange membrane water electrolysis (PEMWE). Alternatively, causing the greenhouse effect carbon dioxide could be converted to a valuable product in an electrochemical reduction process. As up to now no commercially feasible depolarizing anodic process is suggested, the oxygen evolution reaction (OER) will be the counter reaction for hydrogen evolution as well as $CO_2$ reduction. Nowadays iridium is the main component of the anode catalyst in PEM-electrolysers since it shows the best performance in terms of activity and stability [1]. Due to the high prize and scarcity of iridium, however, the goal for the future is a better utilization or partial to complete replacement of this precious metal. Up to now, however, no alternative to iridium catalyst is in the sight. Hence, current research efforts should be directed towards increase in the surface to mass ratio and specific activity of iridium catalyst. This can be achieved using nanoparticulated, highly porous materials or alloying. Furthermore, tuning of oxide structure, e.g. by varying calcination temperature or introduction and leaching of a less noble metal, should be considered [2-4].

In this study a scanning flow cell (SFC) combined with an inductively coupled mass spectrometer (ICP-MS) is used to obtain synchronized time- and potential- resolved data on the OER-activity and dissolution of different iridium electrodes [4, 5]. The examined materials are iridium (hydrous)-oxides prepared either electrochemically on the surface of model sputtered iridium films and nanoparticulated iridium or chemically using an iridium precursor. Additional thermal treatment of the synthesized materials in the temperature range of 100 – 600 °C is employed to modify structure and composition of the electrodes. The latter is studied by X-ray photoelectron spectroscopy (XPS). The obtained information on the electrochemical activity and stability together with data on the electrodes physicochemical properties and their temperature dependence is used in the discussion of OER mechanism on iridium oxide electrodes.

**References:**

[1] Dmitri Bessarabov, Haijiang Wang, Hui Li, N. Zaho, PEM Electrolysis for Hydrogen Production CRC Press, Boca Ranton, 2015.
[2] M. Bernicke, E. Ortel, T. Reier, A. Bergmann, J. Ferreira de Araujo, P. Strasser, R. Kraehnert, Iridium Oxide Coatings with Templated Porosity as Highly Active Oxygen Evolution Catalysts: Structure-Activity Relationships, ChemSusChem, 8 (2015) 1908-1915.
[3] T. Reier, Z. Pawolek, S. Cherevko, M. Bruns, T. Jones, D. Teschner, S. Selve, A. Bergmann, H.N. Nong, R. Schlögl, K.J.J. Mayrhofer, P. Strasser, Molecular Insight in Structure and Activity of Highly Efficient, Low-Ir Ir-Ni Oxide Catalysts for Electrochemical Water Splitting (OER), J Am Chem Soc, 137 (2015) 13031-13040.
[4] S. Cherevko, T. Reier, A.R. Zeradjanin, Z. Pawolek, P. Strasser, K.J.J. Mayrhofer, Stability of nanostructured iridium oxide electrocatalysts during oxygen evolution reaction in acidic environment, Electrochemistry Communications, 48 (2014) 81-85.
[5] S. Cherevko, S. Geiger, O. Kasian, N. Kulyk, J.-P. Grote, A. Savan, B.R. Shrestha, S. Merzlikin, B. Breitbach, A. Ludwig, K.J.J. Mayrhofer, Oxygen and hydrogen evolution reactions on Ru, RuO2, Ir, and IrO2 thin film electrodes in acidic and alkaline electrolytes: A comparative study on activity and stability, Catalysis Today, (2015) Doi: 10.1016/j.cattod.2015.1008.1014.

# Carbon Nanotube-supported Metal Oxide catalysts for Bifunctional Oxygen Electrode Catalysts

Nam-In Kim, In-Seop So, Sung Ryul Choi and Jun-Young Park
*Department of Nanotechnology and Advanced Materials Engineering, Sejong University*
*209 Neungdong-ro, Gwangjin-gu, Seoul 05006, Korea*
*jyoung@sejong.ac.kr*

Hydrogen has been emphasized as one of clean energy source because of the global climate change and green gas emissions. In addition, hydrogen has high efficiency, high energy density and negligible environmental impact. There are many methods to produce and use the hydrogen, among other things, unitized regenerative fuel cells (URFCs) are an electrochemical device to convert chemical energy of hydrogen fuel to electrical energy (fuel cell mode) as well as produce the hydrogen fuel (electrolysis mode). URFCs have many advantages including longer energy storage and high energy density than Li-ion battery which shows the natural discharge. In spite of these merits, there are some issues which limit the commercialization of the URFCs. One is the use of noble metals as a catalyst to enhance the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) in oxygen electrode. Another is the significant overpotential values due to the slow kinetics of oxygen reaction although noble metals are used for the OER and ORR. As the alternative for these noble metals with the elevated oxygen activity, cobalt-based materials have been studied in many groups. In this study, ABO3-typed metal oxides are investigated to develop the high active, durable and low-cost catalysts for the URFCs. Furthermore, carbon nanotubes are used as a supporting material of metal oxide catalysts to improve the performance of oxygen activity and durability. For the electrochemical analysis, the catalysts are tested by rotating disk electrode system in 0.1 M potassium hydroxide solution as electrolyte with Hg/HgO and Pt wire for reference and counter electrode, respectively. The oxygen evolution activity of the carbon nanotube supported metal oxide catalysts is measured by linear sweep voltammetry (LSV) from 1.2 to 1.7 V at a scan rate of 5 mV s-1 with 1,600 rotating per minute (RPM) and accelerated degradation test is carried out by cyclic voltammetry (CV) from 1.25 to 1.65 V at a scan rate of 200 mV s-1 for 1,500 cycles. The oxygen reduction nature is analyzed by LSV and CV for activity and durability, respectively, of the carbon nanotube supported metal oxide catalysts. The activity is carried out by LSV from 0.2 to 1.2 V at a scan rate of 5 mV s-1 as RPM for 400, 900, 1,600 and 2,500. The durability is investigated by CV from 0.6 to 1.2 V at a scan rate of 200 mV s-1 for 10,000 cycles. For the quantitative comparisons of oxygen activity, the differences in the potentials at 10 mA cm-2 and at -3 mA cm-2 for oxygen evolution and reduction, respectively, are calculated. Physicochemical properties such as crystal structure and morphology are characterized by using various tools such as XRD, FE-SEM and TEM.

Keywords: Unitized regenerative fuel cells; Electrocatalyst; Oxygen evolution reaction; Oxygen reduction reaction; Perovskite oxide; Carbon nanotube.

References
J.A. Turner, Science 305 (2004) 972-974.
S. Park, Y. Shao, J. Liu, Y. Wang, Energy Environ. Sci. 5 (2012) 9331-9344.
K. Miyazaki, K. Kawakita, T. Abe, T. Fukutsuka, K. Kojima, Z. Ogumi, J. Mater. Chem. 21 (2011) 1913-1917.
A. Grimaud, K.J. May, C.E. Carlton, Y.-L. Lee, M. Risch, W.T. Hong, J. Zhou, Y. S.-Horn, Nat. comm. 4 (2013) 25926-25932.
H.W. Park, D.U. Lee, M.G. Park, R. Ahmed, M.H. Seo, L.F. Nazar, Z. Chen, ChemSusChem 8 (2015) 1058-1065.

# Fabrication of porous iridium oxide/graphene film using pyrolysis for oxygen evolution catalysis

Sang Ha Lee, Won Bin Kim, Soochan Kim Misuk Cho, and *Youngkwan Lee

*School of Chemical Engineering,*
*Sungkyunkwan University, Che440-746 Suwon, Korea*
**Correspondance:yklee@skku.edu*

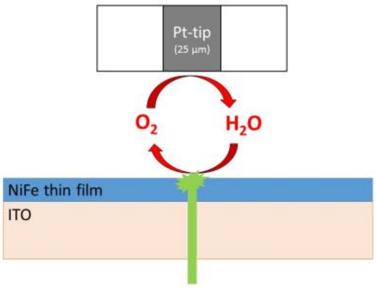
Here we demonstrate a facile method for the preparation of porous iridium oxide/graphene film by using pyrolysis and polystyrene as template. Iridium chloride, graphene, and polystyrene were uniform coated on titanium foil by solution-dipping, and the coated titanium foil was pyrolyzed. During the pyrolysis, porous iridium oxide and graphene composite was obtained, and polystyrene burned away. The morphology of the composite film was controlled by the concentration of polystyrene and iridium chloride and investigated by using scanning electron microscope. The chemical composition and crystal structure of the composite film were also characterized using X-ray photoelectron spectroscopy and X-ray diffraction analysis. The performance of the composite film as oxygen evolution catalysts was characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The porous structure and graphene provide high surface area and efficient ion/electron path. Therefore, the porous iridium oxide/graphene film can be used potentially as oxygen evolution catalyst.

# Raman-coupled scanning electrochemical microscopy – investigation of oxygen evolution at NiFe thin film electrodes

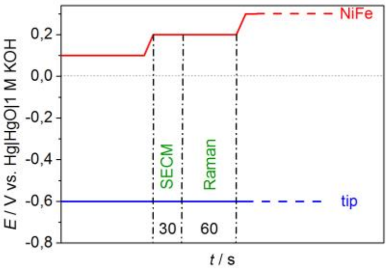
G. Seiffarth, M. Steimecke, M. Bron
*Martin-Luther-Universität Halle-Wittenberg*
*Von-Danckelmann-Platz 4, 06120 Halle (Saale)*
*gerda.seiffarth@chemie.uni-halle.de*

Abstract:

For investigation of the oxygen evolution at NiFe thin film electrodes an advanced approach of electrochemical scanning microscopy is applied. NiFe thin films are promising materials for the oxygen evolution reaction in alkaline media [1, 2]. For examining the evolution of oxygen and determining the onset potential of the respective film electrodeposited on an indium doped tin oxide electrode (ITO), an increasing potential is gradually applied until oxygen evolution is observed. The resulting oxygen is then detected by applying a reductive potential at the ultramicroelectrode (tip, Figure 1) [3]. In addition, spectroscopic information of the film is obtained *insitu* by recording Raman spectra as a function of the applied potential. The combination of electrochemical and spectroscopic properties of NiFe thin films leads to a deeper understanding of the processes during the evolution of oxygen. It was found out, that by increasing the iron content of the thin films an enhanced activity with a higher iron content up to an optimum is observed (Figure 2). Additionally, measurements are also done in an iron free solution to investigate the effect of solved iron traces for the oxygen evolution. Even slightest amounts of iron leads to an enhanced activity. Even slightest amounts lead to a drastically enhanced activity at the Ni films towards oxygen evolution activity and can explain the often described "aging" effects.



a)



b)

Figure 1a: set-up of Raman-coupled scanning electrochemical microscope, b: illustration of applied potentials at NiFe thin film and tip (Pt, 25 µm).

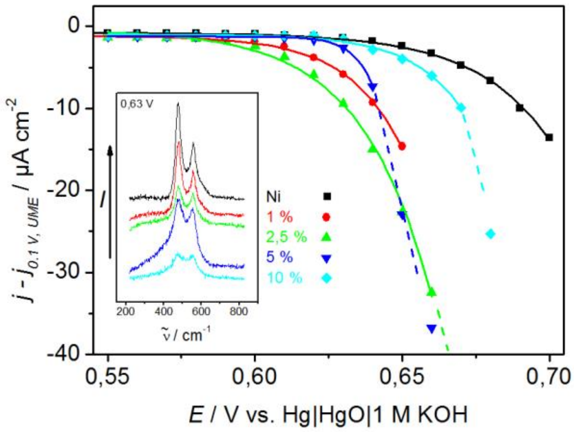


Figure 2: tip current densities (Pt, 25 µm) at different potentials applied to the NiFe thin films with different iron contents and Raman-spectra at 0,63 V vs. Hg|HgO|1 M KOH in 0,1 M KOH solution of the NiFe thin films.

Literature:

[1] S. Klaus, Y. Cai, M. W. Louie, L. Trotochaud, A. T. Bell, *J. Phys. Chem. C* **2015**, *119*, 7243–7254.

[2] L. Trotochaud, S. L. Young, J. K. Ranney, S. W. Boettcher, *J. Am. Chem. Soc.* **2014**, *136*, 6744–6753.

[3] G. A. Snook, N. W. Duffy, A. G. Pandolfo, *J. Electrochem. Soc.* **2008**, *155*, A262.

# Electrocatalytic reduction of carbon dioxide enhanced by surface nitrogen atoms of doped nanocarbon

Junyuan Xu, Dang-Sheng Su*
*Shenyang National Laboratory, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, Liaoning, 110016 China*

**e-mail: dssu@imr.ac.cn*

## Abstract

Recent studies have demonstrated that introduction of nitrogen atoms into nanostructured carbons can give rise to an enhanced activity for the electrocatalytic reduction of carbon dioxide when compared with their pristine analogues.[1, 2] Unfortunately, there is a lack of experimental and/or theoretical studies that can systemically correlate the impact of heteroatom doping in nanocarbons with enhanced electrocatalytic activity. The present work demonstrate the synthesis of surface doped CNT (SNCNT) catalysts with tailored nitrogen contents and varied fractions of pyrrolic, pyridinic and quaternary nitrogen sites. In addition to the material characterization, the activity (Fig. 1a and 1b) was evaluated for electrocatalytic reduction of carbon dioxide with an emphasis on the role of nitrogen site and the reaction mechanism. In combination with the density functional theory (DFT) calculation (Fig. 1d, 1e and 1f), it was proposed that the electrocatalytic reduction of carbon dioxide on the surface of doped nanocarbon catalyst proceeded via an initial rate-determining transfer of one electron to carbon dioxide with the formation of the carbon dioxide radical anion ($CO2^{\bullet-}$). The improved intrinsic activity in the doped nanocarbon catalysts appeared to be the stabilization of the key intermediate $CO2^{\bullet-}$ due to the increase of the work function (Fig. 1c).

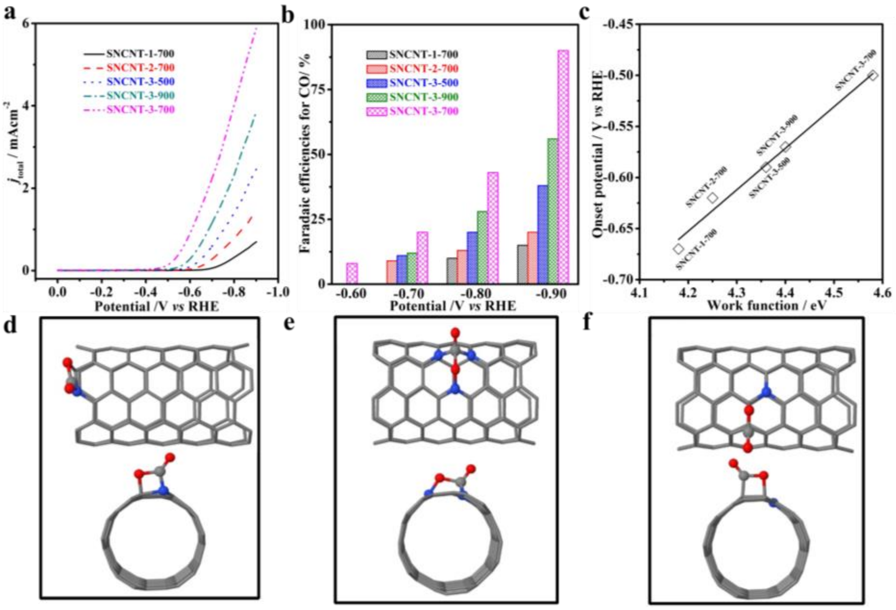


Figure 1. The carbon dioxide electrocatalytic reduction performance on the SNCNT catalysts in 0.5 M $NaHCO_3/CO_2$ at 25 ºC with a scan rate of 2 mV $s^{-1}$; (b) Faradaic efficiencies for the CO production at the applied potentials on the SNCNT catalysts; (c) Correlation of onset potentials of SNCNT catalysts with their work function values; The optimized structures of adsorbed $CO2^{\bullet-}$ on the surface of SNCNT: the pyridinic nitrogen site with only one nitrogen atom (d), the pyridinic nitrogen site with three nitrogen atoms (e) and the quaternary nitrogen site (f). Color code: nitrogen, blue; oxygen, red; carbon, gray.

## References

[1] B. Kumar, M. Asadi et al., *Nat. Commun.* **2013**, *4*, 2819-2826.
[2] S. Zhang, P. Kang, *J. Am. Chem. Soc.* **2014**, *136*, 7845-7848.

# Application of Dimensionally Stable Anode for Vanadium Redox Flow Battery

Jaejin Han, Moon-su Kim, Jinsub Choi*
*Department of Chemistry and Chemical Engineering*
*Center for Design and Applications of Molecular Catalyst*
*Inha University, 100, Inha-ro, Nam-gu, Incheon, 222-12, Korea*
*jinsub@inha.ac.kr**

All-vanadium redox flow battery (VRFB) is a type of redox flow battery which uses vanadium ions as active materials[1]. 2.5mm thickness of graphite is generally used as bipolar plate inside the VRFB to prevent corrosion of current collector. In this research, thick graphite bipolar plate (BP) was substituted by 0.126mm thickness of dimensionally stable anode (DSA) coated with iridium oxide on a Ti substrate, which was anodized to $TiO_2$ with nanotubular structure[2]. It can provide volumetric advantage over the conventional graphite when the VRFB is used as multi-stack. Ir was coated by using spray coating method in order to improve electrochemical properties. In this study, various electrochemical characterization was carried out. Cyclic voltammetry data showed activation of Ir in the positive electrode of VRFB. Additionally, polarization measurements showed Ir-coated BP had low overpotential in the positive electrode of VRFB[3]. In cell test results, VRFB, which used the Ir-coated BP, showed better efficiency than graphite-used VRFB in voltage and overall efficiency.

---

[1] Adam Z. Weber, Matthew M. Mench, Jeremy P. Meyers, Philip N. Ross, Jeffrey T. Gostick, Qinghua Liu, J Appl Electrochem **41** (2011) 1137–1164

[2] Kiyoung Lee, Anca Mazare, and Patrik Schmuki, Chem. Rev. **114** (2014) 9385−9454

[3] W.H. Wang, X.D. Wang, Electrochemica Acta **52** (2007) 6755-6762

# Durability of Titanium-Niobium Oxides Mixed with $Ti_4O_7$ as Non-Precious- and Carbon-Free Cathodes for PEFCs in $H_2SO_4$ at 80 °C

Akimitsu Ishihara[a], Makoto Hamazaki[b], Yuji Kohno[b], Koichi Matsuzawa[b], Shigenori Mitsushima[a,b], and Ken-ichiro Ota[b]
*[a] Institute of Advanced Sciences, Yokohama National University*
*[b] Green Hydrogen Research Center, Yokohama National University*
*79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501 JAPAN*
*a-ishi@ynu.ac.jp*

## Introduction

Development of non-precious metals and carbon-free cathodes as alternative materials of platinum supported carbon catalysts is required for practical application of polymer electrolyte fuel cells (PEFCs). We focused on group 4 and 5 metal oxide-based compounds because their high chemical stabilities in acidic media. In order to achieve both high ORR activity and high durability, we need to develop the oxide-based cathodes without carbon materials. Thus, we prepared the oxide-based catalysts which were composed of niobium-titanium oxides with active sites and titanium oxides with magneli phase of $Ti_4O_7$ as electric conductive[1] ($Ti_xNb_yO_z$+$Ti_4O_7$). In addition, to develop durable cathodes, their durability in acidic media at 80 °C, which is close to the operation temperature of present polymer electrolyte fuel cells, must be evaluated. In this study, we evaluated the durability of the $Ti_xNb_yO_z$+$Ti_4O_7$ in 0.1 mol $dm^{-3}$ $H_2SO_4$ at 80 °C.

## Experimental

$Ti_xNb_yO_z$+$Ti_4O_7$ catalysts were prepared by dry ball-milling with $TiO_2$ and $Nb_2O_5$ powder mixture and reductive heat-treatment in 4% $H_2$/Ar at 1050 °C for 50 h.[1] The powder catalysts were supported about 0.1 mg on the top of the $Ti_4O_7$ rod. In order to evaluate the electrochemical stabilities of the catalysts in 0.1 mol $dm^{-3}$ $H_2SO_4$ at 80 °C, a start-stop cycle test[2] (triangular wave, 1.0 - 1.5 V vs. reversible hydrogen electrode (RHE), $N_2$, a scan rate: 0.5 V $s^{-1}$) and a load cycle test[2] (rectangular wave, 0.6 - 1.0 V vs. RHE, $O_2$, holding time: 3 s) were performed as degradation tests using a 3-electrode cell. An RHE and a GC plate were used as the reference and the counter electrodes, respectively. During the degradation tests, chronoamperometry at 0.7 V under $O_2$ atmosphere was performed to evaluate the catalytic activity of oxygen reduction reaction (ORR). The durability was evaluated by a ratio of $i_{ORR}$ @ 0.7 V during degradation test to that at initial, N-$i_{ORR@0.7V}$.

## Results and discussion

Fig. 1 shows the variation of $N_{iORR@0.7V}$ of the $Ti_xNb_yO_z$+$Ti_4O_7$ during start-stop and load cycle tests. In both tests, the values of the $N_{iORR@0.7V}$ slightly changed during the initial potential cycling up to 5000 cycle. However, these values kept 1 above 5000 up to 20000 cycle, indicating that the $Ti_xNb_yO_z$+$Ti_4O_7$ had superior stability for both start-stop and load cycle tests in 0.1 mol $dm^{-3}$ $H_2SO_4$ at 80 °C. Therefore, we successfully demonstrated that the active sites on the titanium-niobium oxides are highly stable both low and high potential regions at 80 °C. In other words, non-precious metals and carbon-free cathodes based on group 4 and 5 metal oxides have essentially high durability as expected.

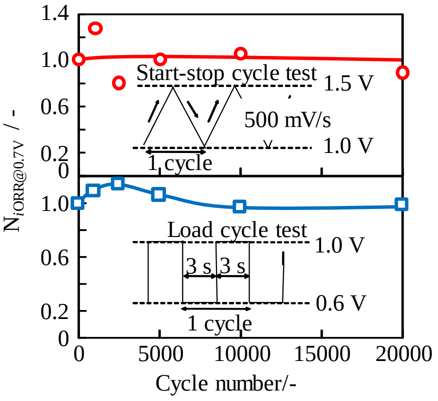


Fig. 1 Variation of $N_{iORR@0.7V}$ of $Ti_xNb_yO_z$+$Ti_4O_7$ during start-stop and load cycle tests in 0.1 M $H_2SO_4$ at 80 °C.

## Acknowledgement

The authors thank for the New Energy and Industrial Technology Development Organization (NEDO) for financial support. The Institute of Advanced Sciences (IAS) in YNU is supported by the MEXT Program for Promoting the Reform of National Universities.

## References

1) M. Hamazaki, A. Ishihara, Yuji Kohno, K. Matsuzawa, S. Mitsushima and K. Ota, *Electrochemistry*, 83, 817-819 (2015).

2) Fuel Cell Commercialization Conference of Japan (FCCJ), Proposals of the development targets, research and development challenges and evaluation methods concerning PEFCs, http://www.fccj.jp/pdf/23_01_kt.pdf

# Oxygen Reduction by Single-Atom Pt: Selective Production of $H_2O_2$ instead of $H_2O$

Chang Hyuck Choi, and Karl J. J. Mayrhofer
*Max-Planck-Institut für Eisenforschung GmbH*
*Max-Planck-Strasse 1, 40237 Düsseldorf, Germany.*
*c.h.choi@mpie.de*

Because maximum atom efficiency as well as distinct chemoselectivity is expected, single-atom catalysis has attracted extensive scientific attention in relation to many chemical reactions.[1] Because single-atom metals are highly unstable and prone to agglomerate due to their maximized surface energy, supports providing strong metal-support interactions (e.g., $CeO_2$, $FeO_x$, and $Al_2O_3$) are indispensable for the preparation of single-atom catalysts.[2-3] Although these catalysts can be used for various thermochemical reactions such as CO oxidation and water-gas shift reaction, they cannot be investigated in electrochemical reactions because the metal oxide supports are insulators or semiconductors having low electron conductivities and furthermore they are unstable under the corrosive electrochemical operating conditions. The most widely used electrocatalyst support, carbon, cannot effectively stabilize single-atom metal species due to the lack of strong metal-support interaction, and single-atom 'electrocataysis' has been extremely difficult to investigate thus far.

Here we succeeded in the unprecedented achievement of preparing a single-atom Pt catalyst stabilized on a carbon-based support and studied its unique electrocatalytic properties in the oxygen reduction reaction (ORR). In this work, we demonstrate that a sulfur-doped zeolite-templated carbon simultaneously exhibiting extra-large sulfur content (17 wt% S) as well as a unique carbon framework structure (i.e., highly curved 3-dimensional networks of graphene nanoribbons) helped to stabilize a relatively high loading of Pt (5 wt%) in the form of single-atom Pt species (Fig. 1). In sharp contrast to cluster-type Pt catalysts, ORR catalysis on the single-atom Pt species selectively followed a 2-electron ORR pathway producing $H_2O_2$ rather than a conventional 4-electron ORR mechanism producing $H_2O$ without significant degradation of the catalyst activity. In addition, the catalyst is also inactive in the consecutive $H_2O_2$ decomposition reactions, and as such holds promise for the production of an important fine chemical, $H_2O_2$, while harvesting electricity in commercial fuel cell systems. Density function theory calculations further revealed that the kinetic control toward the 2-electron ORR is facilitated by substantially increased reorganization energy associated with O-O bond breakage, which elevates the kinetic barrier for the proton-coupled electron transfer (PCET) step of the 4-electron pathway. Thus this approach constitutes a potentially promising route for producing important fine chemical $H_2O_2$, and also offers new opportunities for tuning selectivity of other electrochemical reactions on various metal catalysts.

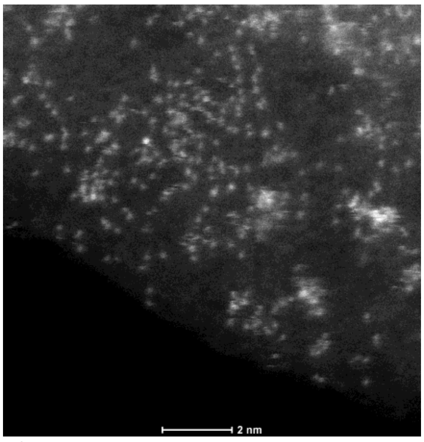


**Figure 1.** Morphology of the synthesized single-atom Pt catalyst stabilized on carbon.

## References

[1] Yang, X. F. *et al.*, Acc. Chem. Res. 46 (2013) 1740-1748.
[2] Qiao, B. *et al.*, Nat. Chem. 3 (2011) 634-641.
[3] Wei, H. *et al.*, *Nat. Commun.* 5 (2014) 5634.

# Separation of Single-walled Carbon Nanotubes and Their Electrochemical Behaviors Study

Fengchun Yang, Xin Zhang, Hanzhi Zhang
*Key Laboratory of Synthetic and Natural Functional Molecule Chemistry (Ministry of Education),*
*College of Chemistry and Material Science, Northwest University, Xi'an 710127, China*
*fyang@nwu.edu.cn*

The as-prepared SWNTs are always a mixture of metallic (m-) and semiconducting (s-) tubes [1], whose different electronic structures [2] make them exhibit distinct electrochemical properties. In this work, we established an effective separation method for SWNTs via a novel binaphthyl based separation agent, and then the separated SWNTs were used for electrochemical study. It is remarkable that the separated m- and s-SWNTs presented very different electrochemical properties, i.e. s-SWNTs was suggested as a promising candidate for supercapacitors application, in contrast to m-SWNTs for electroanalytic application. Furthermore, the electrochemical propertied of s- and m-SWNTs can be interconverted through electron or hole doping. We believe that more exciting discoveries and applications based on m- or s-SWNTs will be revealed in the near future.

References
[1] Ajayan, P. M. *Chem. Rev*. **1999**, 99, 1787-1799.
[2] Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1992**, 60, 2204-2206.

# A New Class Electroactive Fe and P-Functionalized Graphene for Oxygen Reduction

Fatemeh Razmjooei, Kiran Pal Singh, Jong-Sung Yu*
*Department of Energy Systems Engineering, DGIST, Daegu, 711-873, Republic of Korea*
Razmjooei.s@gmail.com

While metal and nitrogen containing carbon, where metal and nitrogen act as the catalytic center, is drawing much attention as an efficient catalyst towards ORR, no combination of metals with other heteroatoms-containing carbon has received the much attention. In this work we have studied a new family of highly efficient, non-precious metal and heteroatom-containing carbon catalyst for oxygen reduction reaction (ORR). A novel iron and phosphorous-containing garphene catalyst was prepared for the first time by a simple pyrolysis of graphene oxide (GO) with phytic acid (PA) and iron (II) chloride ($FeCl_2.4H_2O$) as a catalyst for ORR. Herein we found that PA, used as a P precursor, can act as a porogen to increase the surface area of RGO due to its high amount of acidic functional groups. Fe and P-containing reduced graphene oxide (RGO) catalyst (GPFe) shows excellent ORR activity, which is ~2 times better than that of P-doped RGO in alkaline and showing enhanced activity in acidic medium as well. Introduction of Fe causes remarkable synergistic effects on P-doped reduced graphene oxide by increasing surface area, enhancing P doping level due to the interaction between Fe and P and generating electrochemically active Fe-P species. We found that whereas N-oxides are known to be in-active for ORR in Fe-N system, in present Fe-P system, oxides of Fe and P are found to be beneficial for ORR. On the other hand, the GPFe reveals high ORR activity comparable to that of Pt-based catalyst in terms of onset potential and current density in alkaline medium, and also illustrated reasonable high activity in acidic medium along with much better economic benefit. Furthermore, the excellent long-term stability and methanol tolerance of GPFe catalyst were observed compared to those of commercial Pt/C. This finding shows that current cost-effective novel GPFe is not only promising alternative to costly Pt-based electrocatalysts in fuel cell, but also can open up a rational direction to other new combination of metal and heteroatom-functionalized carbon materials for wide variety of possible applications for Li-ion batteries, Li-air batteries, supercapacitors, and sensors as well as fuel cells. We propose this study will surely provide renewed insights into active sites for ORR in metal and heteroatom-doped carbon system.

# Iodine-Treated Heteroatom-Doped Carbon: Conductivity Driven Electrocatalytic Activity

Kiran Pal Singh, Min Young Song, and Jong-Sung Yu

*Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science & Technology (DGIST), Daegu, 711-873, Republic of Korea*
*kiranpaldude@gmail.com*

A high conductivity and surface area are the most highly desired properties of an electrocatalyst. However, simultaneously obtaining a high conductivity and high surface area has been found to be challenging and one property can only be achieved by sacrificing other. Herein, we report a novel technique to synthesize highly conductive and microporous N and S-doped carbon from polyaniline (PANI) via a simple, template-free hydrothermal method followed by carbonization in the presence of iodine. The iodine treatment removes a large amount of the attached oxygen atoms and other heteroatoms and, as a consequence, increases the carbon content. Thus, the iodine treatment decreases the doping of catalytically active heteroatoms, which is unfavorable for the ORR, but at the same time, significantly increases the electrical conductivity, which is found to be beneficial for catalyzing the oxygen reduction in alkaline condition. In particular, iodine-treated carbonized PANI (CPANI) shows an exceptionally high conductivity i.e., about 3 times that of untreated CPANI. Iodine treatment is also found to enhance the micropore surface area of the PANI during carbonization without using a harmful activating agent or a hard template. An electrocatalytic study indicates that the activity of the iodine-treated sample is considerably higher than that of an untreated sample. This remarkable upsurge in activity is mainly attributed to the large increase in the conductivity and surface area of the iodine-treated sample. The ORR activity is discussed in terms of the heteroatom content, surface area and conductivity of the carbon. This convenient, innovative approach can offer new possibilities for the design of future highly efficient fuel cell electrocatalysts.

# Self-organized anodic titanium oxide microcones for Li-ion battery application

Oonhee Rhee, Gibaek Lee, Minkyeong Jeong, Jinsub Choi*
*Department of Chemical Engineering, Inha University*
*Inha-ro 100 Namgu Incheon, Republic of Korea*
**Corresponding author: jinsub@inha.ac.kr*

Titanium oxides have been studied for various applications such as dye-sensitized solar cells, water splitting electrodes, photocatalysts, gas sensors and electrochemical energy storages because of chemically stability and excellent (photo-) catalytic properties[1-4]. The enlargement of surface area is one of important routes to enhance titanium oxide's physical properties for various applications. Thus, titanium oxides with various morphologies such as nanorods, nanotubes, nanowires and so on have been produced by several research groups[5-7].

In this study, we demonstrate that the self-organization of titanium oxide microcones can be successfully prepared by anodization under specific electrochemical conditions. In detail, the titanium oxide microcones are obtained by anodization at 45-75 V, whereas a barrier type or flower like morphology is synthesized at higher or lower than the optimized voltage. The prepared microcones with a height of more than 8.74 µm and a diameter of 9.1 µm is revealed as $TiO_2$ anatase phase, even though no heat treatment is done. The titanium oxide microcones are applied to anode for Li-ion batteries. Electrochemical studies are performed to evaluate the battery capacity. The charge/discharge capacity of $TiO_2$ microcones is higher than that of $TiO_2$ nanotubes, which is attributed to easy mass-transfer of Li ions in the protruding microcone structure.

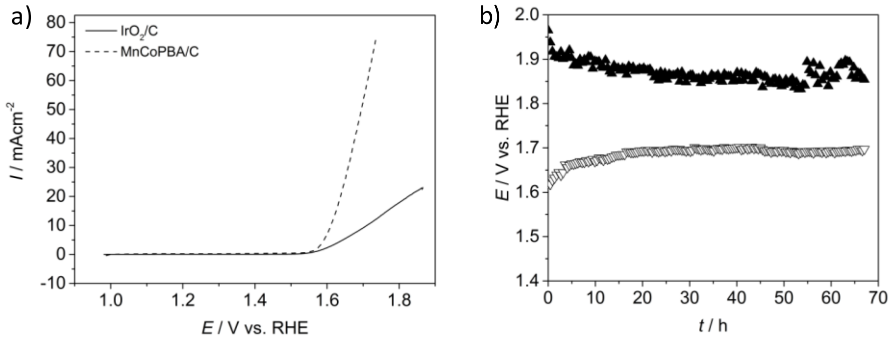
References
[1] D.V. Bavykin, J.M. Friedrich, F.C. Walsh, Adv. Mater. 18 (2006) 2807.
[2] Y. Gim, M. Seong, Y. Choi, J. Choi, Electrochem. Comm. 52 (2015) 37–40
[3] P. Roy, S. Berger, P. Schmuki, Angew, Chem. Int. Ed. 2011, 50, 2904; Angew. Chem. 2011, 123, 956.
[4] B. Lee, S. Nam, J. Choi, Curr. Appl. Phys. 12 (2012) 1580-1585.
[5] A. Ghicov, P. Schmuki, Chem. Commun. (2009) 2791.
[6] J. Jiu, S. Isoda, F. Wang, M. Adachi, J. Phys. Chem. B 110 (2006) 2087-2092
[7] G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, Robert C. Fitzmorris, C. Wang, Jin Z. Zhang, Y. Li, Nano Lett. 11 (2011) 3026–3033

# $Mn_xCo_yO_z$ Nanocubes Embedded in a Polybenzoxazine-derived Nitrogen-Doped Graphite-type Carbon Matrix as New Catalyst for the Oxygen Evolution Reaction

Stefan Barwe[a], Corina Andronescu[b], Justus Masa[a], Edgar Ventosa[a], Stefan Klink[a], Aziz Genç[c], Jordi Arbiol[c,d] and Wolfgang Schuhmann[a]

a) *Analytical Chemistry - Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany*
b) *Advanced Polymer Materials Group, University Politehnica of Bucharest, 1-7 Gh. Polizu street, 011061 Bucharest, Romania*
c) *Catalan Institute of Nanoscience and Nanotechnology (ICN2), The Barcelona Institute of Science and Technology and CSIC. Campus UAB, 08193 Bellaterra, Barcelona, Spain*
d) *Institució Catalana de Recerca i Estudis Avançats, ICREA, 08010 Barcelona, CAT, Spain*
*stefan.barwe@rub.de*

The development of low-cost and non-precious metal catalysts for electrocatalytic water splitting is of major interest in sustainable energy research. The activity towards the electrocatalytic water splitting, especially towards the oxygen evolution reaction, is a key criterion in today's catalyst evaluation. However, the stability of the catalytically active species on electrode surfaces is from at least similar importance for the development of economical oxygen electrodes. Herein, we demonstrate a composite material with both, a good activity against the OER and a good stability during a specially designed test procedure. The composite material is obtained after pyrolysis of a nanocubic Prussian blue analogue (PBA) $K_mMn_x[Co(CN)_6]_y$ x $nH_2O$ precursor embedded in a bisphenol A and aniline based polybenzoxazine (pBO). Several physical characterization methods verified it to be a nitrogen-doped graphite-type carbon matrix doped with $Mn_xCo_yO_z$ nanocubes, in which the transition metals have different conformations. Linear sweep voltammetry (LSV) in oxygen-saturated KOH (0.1 M) at a scan rate of 5 $mVs^{-1}$ and rotation speed of 1600 rpm was employed for activity determination. Carbon-$Mn_xCo_yO_z$ showed high oxygen evolution activity affording a current density of 1 $mAcm^{-2}$ (normalized to the geometric surface area) at 1.55 V, and 10 $mAcm^{-2}$ at 1.61 V (Fig. a)). $IrO_2$, one of the current state of the art OER catalysts, in the same carbon matrix was less active and required 100 mV higher overpotential (1.71 V) to reach 10 $mAcm^{-2}$ (Fig. a)). The Tafel slope of Carbon-$Mn_xCo_yO_z$ determined in the potential region between 1.55 V and 1.63 V was 59 $mVdec^{-1}$ indicating very fast kinetics and a transfer coefficient ($\alpha$) very close 1 ($(2.303RT)/\alpha F$). Stability measurements were conducted with Carbon-$Mn_xCo_yO_z$ modified Ni foam in a custom-built flow-through cell with oxygen-saturated KOH (0.1 M) as the electrolyte. The use of Ni foam as the catalyst support as well as current collector raises the possibility of upscaling the investigated oxygen evolution electrode towards commercial applications. At a constant current density of 10 $mAcm^{-2}$ (with respect to the opening of the cell (ø = 8 mm)), the corresponding potential increased from an initial value of 1.62 V to 1.69 V after 67 hours (Fig. b), white triangles). After the first 19 h, the potential remained constant without any visible change until the end of the measurement, indicating a stable state of the catalyst. In consideration of the fact that Ni foam is itself active for oxygen evolution, the same measurements were performed with pure Ni foam in order not to wrongly attribute the observed performance to the Carbon-$Mn_xCo_yO_z$ catalyst (Fig. b), black triangles). The activity of pure Ni foam increased initially at the beginning of the measurement, obviously due to formation of $NiO_x$/NiOOH, however, it later remained constant at an overpotential 170 mV higher than the Carbon-$Mn_xCo_yO_z$ modified Ni foam electrode. The observed stability can thus safely attributed to the Carbon-$Mn_xCo_yO_z$ catalyst.



# Fiber-like Reduced Graphene Oxide Nanoribbons as an Electrocatalytic Material for Dye-Sensitized Solar Cells

Miao-Syuan Fan[1], Yu-Hao Tseng[1], Chia-Liang Sun[2*], and Kuo-Chuan Ho[1,3**]
*[1] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan*
*[2] Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan 33302, Taiwan*
*[3] Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan*
** Email: sunchialiang@gmail.com; ** Corresponding author: kcho@ntu.edu.tw*

Platinum (Pt) is the most used counter electrode (CE) in the dye-sensitized solar cell (DSSCs), due to its outstanding electrical conductivities and excellent electrocatalytic activity. However, the high cost and energy–consumptive fabrication process of the Pt CE limits its applicability. Several carbon-based materials (graphene, multi-wall carbon nanotube, and carbon black) were extensively researched as the substitutes for the expensive Pt CE. Graphene (Gr) is monolayer graphite and belongs to a two-dimensional (2D) structural material. In the case of graphene nanoribbon (GONR), the electrons can only transfer along one-dimension (1D) direction. It is worth noting that 1D GONR has $sp^2$ hybridized carbon crystal, which favors the electron transport compared to the bare Gr.

In this study, a GONR was deposited on fluorine-doped tin oxide (FTO) substrate by a drop–coating method for use in Pt–free DSSCs. We investigate the effect of annealing temperature on the performance of GONR catalysts. As shown in Fig. 1, when the annealing temperature of GONR is set at 400 °C, hydroxyl group or oxygen atoms in GONR retard the electron transportation. On the other hand, when the annealing temperature is raised up to 600 °C, the surface of GONR can be destroyed easily. The optimized cell efficiency ($\eta$) of 9.05% ($V_{OC}$ of 0.74 V; $J_{SC}$ of 17.14 mA cm$^{-2}$, and *FF* of 0.71) was achieved for the DSSC with the annealing temperature at 500 °C (GONR_500); this is comparable to that of the cell with a Pt CE (7.28%). The surface morphology of the GONR was analyzed by scanning electron microscope (SEM) images (Fig. 2). The SEM image reveals that GONR have porous surface with a fiber-like structure, implying that GONR have large surface area. The catalytic ability and electrochemical properties of the GONR CEs were quantified by cyclic voltammetry (CV) and Tafel curve, both show that the GONR CE exhibits the superior electrocatalytic ability for the reduction of $I_3^-/I^-$. The analysis confirms that the GONR CE is a suitable Pt substitution for the CE in DSSCs.

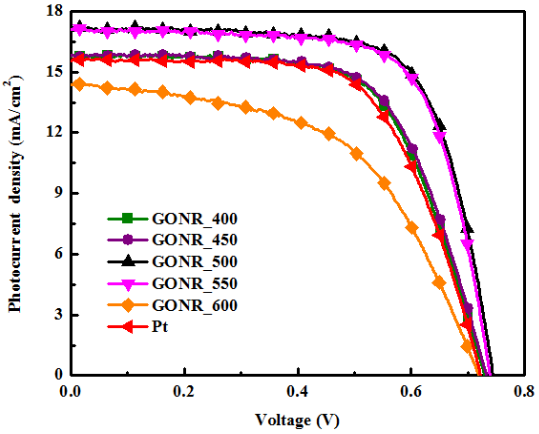


Fig. 1 Photocurrent density–voltage curves of the DSSCs with GONR and Pt CEs, obtained at 100 mWcm$^{-2}$.

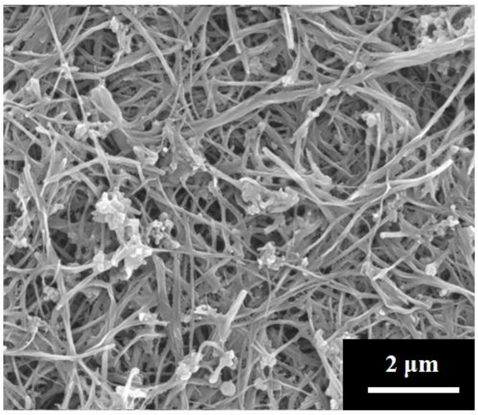


Fig. 2 SEM image for the GONR_500.

# Electrocatalytic Oxidation of Water on Copper Nanoparticles Modified Electrodes

Joanna Dolinska[a], Marcin Holdynski[a], Wojciech Lisowski[a], Arunraj Chidambaram[b],
Liza Rassaei[b], Marcin Opallo[a]

a/Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warszawa, Poland
b/Organic Materials and Interfaces, Department of Chemical Engineering, Delft University of Technology, Delft, Netherlands

*jdolinska@ichf.edu.pl*

Non-noble metal electrocatalysts have recently received much attention due to their specific optical, electronic and mechanical properties, stabilities, and efficiency. Copper is one the most extensively studied material especially for the application in electrocatalysis of carbon dioxide electroreduction [1], ethanol electrooxidation [2] and for water electrooxidation [3]. Quite often this metal is applied as an electrocatalyst in a form of nanoparticles deposited on the non-catalytic electrode surfaces[4].

Here we will report synthesis and electrocatalytic properties of citrate stabilised copper nanoparticles towards water oxidation in alkaline medium. For this purpose three types of electrodes: (i) modified with copper nanoparticles, (ii) modified with copper nanoparticles and mixture with citrate stabilised gold nanoparticles and (iii) copper nanoparticles decorated $MoS_2$ nanopetals were studied. These electrodes were characterized by Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy. The electrochemical water oxidation was then studied by cyclic voltammetry.

Cyclic voltammetry reveals that modification of the electrode results in the decrease of the onset potential for water splitting and an increase of electrochemically active surface. The limitations of electrochemical applications of this material will be also pointed out.

1 K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Energy Environ. Sci.*, 2012, **5**, 7050.

2 G. Karim-Nezhad, B. Z. Dizajdizi and P. S. Dorraji, *Catal. Commun.*, 2011, **12**, 906–909.

3 Z. Chen and T. J. Meyer, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 700–3.

4 Y. Oztekin, M. Tok, E. Bilici, L. Mikoliunaite, Z. Yazicigil, A. Ramanaviciene and A. Ramanavicius, *Electrochim. Acta*, 2012, **76**, 201–207.

# Self-assembled Ru-Co based molecular POM WOC

Artur Braun[a], Rita Tóth[a], Debajeet K. Bora[a], Niamh S. Murray[b], Guiseppino Fortunato[c], Roché M. Walliser[b], Catherine E. Housecroft[b], Edwin C. Constable[b]

*[a] Laboratory for High Performance Ceramics, Empa. Swiss Federal Laboratories for Materials Science and Technology, Uberlandstrasse 129, CH - 8600, Dubendorf, Switzerland.*
*[b] Department of Chemistry, University of Basel, Spitalstrasse 51, CH - 4056 Basel, Switzerland.*
*[c] Protection and Physiology, Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstr. 5, CH - 9014 St. Gallen, Switzerland*
*artur.braun@alumni.ethz.ch*

Water oxygen catalysts (WOC) based on molecular polyoxometalate (POM) WOCs with a tetrametal-oxo cluster in homogeneous and in heterogeneous systems have been presented recently (1). Recently an oxidatively stable, earth-abundant, cobalt-containing polyoxometallate $[Co4(H2O)2(PW9O34)2]^{10-}$ (Co4POM) was presented (2). An even more efficient (vanadate(V)-centered) polyoxometalate $[Co4(H2O)2(VW9O34)2]^{10-}$, which worked as an effective homogeneous WOC when combined with $[Ru(bpy)3]^{3+}$ , was presented (2).

We have now immobilised [Ru(1)3][PF6]2 and Co4POM (Co4POM = K10[Co4(H2O)2(α-PW9O34)2]) on substrates using the Langmuir-Blodgett (LB) self-assembling method (3). We show how monolayers of [Ru(1)3][PF6]2 and Co4POM can be transferred onto electrodes and used as a WOC in an electrochemical water oxidation cell.

We anticipate better charge transfer between the catalyst and the oxidiser, as well as the electrode surface by establishing a close contact between the components in this layer-on-layer structure. We compare the electrocatalytic performance of the highly ordered Langmuir-Blodgett monolayers with layer-by-layer drop-cast (DC) films of the same components.

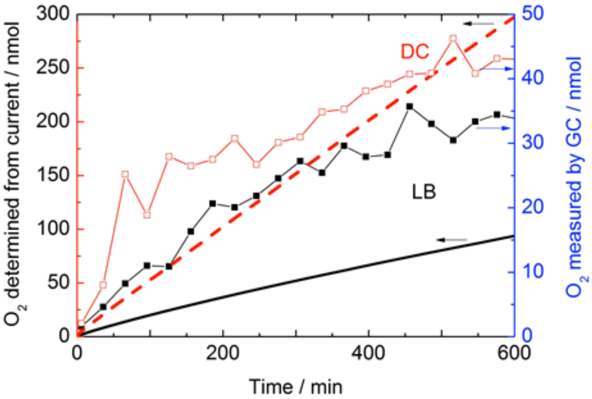


Figure. Comparison of the evolved $O_2$ gas from the LB and DC films measured by gas chromatography (GC) and calculated from the current density data using Faraday's Law. The red open symbols are from the DC films. The black filled symbols are from the LB films. The symbols present measured gas amounts (right abscise). The dashed red line and the solid black line are the integrated current over time divided by four times the Faraday constant from the DC and LB films, respectively (left abscise).

References:

(1) H. Lv, Y. V. Geletii, C. Zhao, J. W. Vickers, G. Zhu, Z. Luo, J. Song, T. Lian, D. G. Musaev and C. L. Hill, Chem. Soc. Rev., 2012, 41, 7572-7589.
(2) Q. Yin, J. M. Tan, C. Besson, Y.V. Geletii, D.G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle and C.L. Hill, Science, 2010, 328, 342, H. Lv, J. Song, Y.V. Geletii, J.W. Vickers, J.M. Sumliner, D.G. Musaev, P. Kögerler, P.F. Zhuk, J. Bacsa, G. Zhu, and C.L. Hill, J. Am. Chem. Soc. 2014, 136, 9268−9271.
(3) N. S. Murray, J. A. Rudd, A.-C. Chamayou, E. C. Constable, C. E. Housecroft, M. Neuburger and J. A. Zampese, RSC Advances, 2014, 4, 11766.

# Ni electrocataylsts functionalized membrane electrode assembly for hydrogen generation

Debajeet K. Bora [1], Miguel Modestino [2], Christophe Moser [2], Artur Braun[1]

[1] *Laboratory for High Performance Ceramics, Empa. Swiss Federal Laboratories for Materials Science and Technology, 8600 – Dübendorf, Switzerland*
[2] *School of Engineering, École Polytechnique Fédéral de Lausanne (EPFL), Station 17, 1015, Lausanne, Switzerland*

Electrocatalytic hydrogen generation is gaining momentum. This is imputable to the growth of both materials and molecular based electrocatalysts with a focal point on low overpotential and comfortability in making device such as membrane electrode assembly. Grounded on this, there are various models of commercial electrolyzers which run on electrocatalysis based water splitting. Their large overpotential decreases the efficiency of the same. Hence the development of catalysts part is really significant in this regard. We have developed Ni catalysts decorated membrane electrode assembly. Our goal is to get cheap and easy fabrication of electrocatalysts MEA with high current density and low overpotential.

Membrane electrode assemblies were fabricated by drop casting Ni catalyst ink on Nafion 117 membrane. During drop casting, Nafion swells when soaked with catalyst ink due to absorption of water molecule inside the membrane. It reassembles back to its original shape once dried at the desired temperature. After the drying process, a small piece of the MEA was cut out in order to check the stability of catalyst particles; mainly the stable adsorption of catalyst particles to the surface of the membrane. Note that the drop casting procedure led to non-uniform coatings and therefore dip coating techniques will need to be implemented for future MEA fabrication. The as-prepared MEA is shown in [Fig. (Right)]. After getting the first sets of MEA, it is further pressed at high temperatures and pressures. The stability of the MEA has been checked by keeping it submerged in double distilled water. The MEA is very stable in the aqueous environment, as carbon black/graphite and catalyst particles remain affixed to the membrane surface. The morphology of the MEA has been studied with scanning electron microscopy using photodiode back scattering, electron mode to distinguish between metallic nickel and organic components. From the result obtained, it is noted that the catalyst particles made a close packing with each other signifying its good particle packing density. The structural properties of the catalysts were studied by X-ray diffraction. The result obtained shows the presence of NiCX phase. A 3D-printed electrochemical cell [Fig. (Left)] is fabricated for testing the first set of MEAs. The MEA with warm pressing temperature and pressure of 120°C and 2 metric ton respectively (MEA 1) shows the best performance with a current density of up to 30 mA/cm2 [Fig. (Centre)].

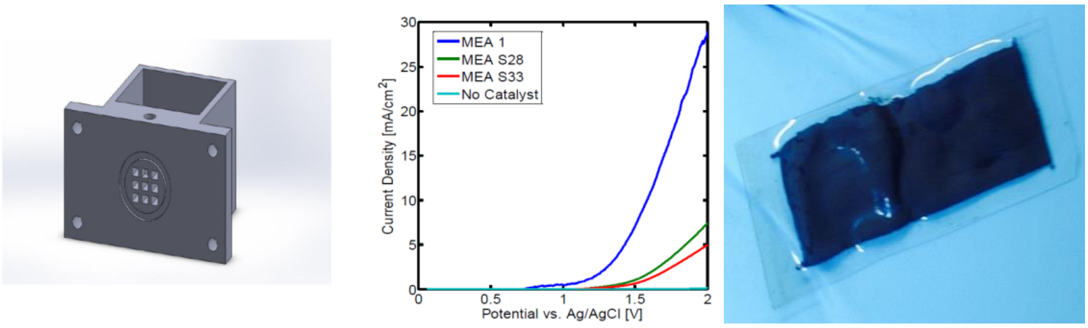


Fig. (left) – A 3D printed electrochemical cell; (center) – electrocatalytic activities of MEA with the help of intentional Ni oxidation to NiO; (right) - Drop casted membrane electrode assembly

# Noble Metal Anodes for Electrolytic Reduction in Pyroprocessing

Sung-Wook Kim, Hyun Woo Kang, Min Ku Jeon, Sang-Kwon Lee, Eun-Young Choi, Wooshin Park,
Sun-Seok Hong, Seung-Chul Oh, and Jin-Mok Hur
*Nuclear Fuel Cycle Process Development Group, Korea Atomic Energy Research Institute*
*111 Daeok-daero 989 Beon-Gil, Yuseong-gu, Daejeon 34057, Republic of Korea*
*swkim818@kaeri.re.kr*

Electrolytic reduction is a key electrochemical technique in pyroprocessing, which is under development for recycling spent fuels. Spent oxide fuels are electrochemically converted to metallic states through the electrolytic reduction (*e.g.*, $UO_2$ (cathode) → U (cathode) + $O_2$ (anode)) in molten salt electrolyte such as $Li_2O$-containing LiCl. During the electrolytic reduction, $O^{2-}$ ions in the electrolyte are oxidized to form $O_2$ gases at the anode surface. In this respect, Pt is the most common anode material in the electrolytic reduction because of its oxidation resistance at high reaction temperature (~650 °C). However, Pt can be damaged during the electrochemical reaction due to formation of $Li_2PtO_3$, anodic dissolution, and Li attack.

Since most metals and their alloys cannot endure this highly oxidizing environment formed by high-temperature $O_2$ gas and strong anodic condition (cell voltage > 2.7 V), it is considered that only several noble metals may be capable of electrochemically reducing oxide fuels in the LiCl-$Li_2O$ molten salt. In this presentation, we will show electrochemical properties of various noble metal anodes for the $O_2$ evolution as potential alternatives of the Pt anode. Their reaction potentials, current densities, and chemical/electrochemical stabilities will be compared to find out the promising candidates. Then, feasibility of the noble metal anodes for electrolytic reduction of $UO_2$ to metallic U will be examined.

# Nano-textured Pillars of Electrosprayed Bismuth Vanadate for Efficient Photoelectrochemical Water Splitting

Hyun Yoon[1], Min-woo Kim[1,2], Mukund G. Mali[1], Tae Yoon Ohm[1], Sam S. Yoon[1,*]

[1]*School of Mechanical Engineering, Korea University, Seoul, 136-713, Republic of Korea*
[2]*Green School, Korea University, Seoul, 136-713, Republic of Korea*
[*]*Sam S. Yoon: skyoon@korea.ac.kr*

We demonstrate, for the first time, electrostatically sprayed bismuth vanadate ($BiVO_4$) thin films for photoelectrochemical water splitting. Characterization of these films by X-ray diffraction, Raman scattering, and high-resolution scanning electron microscopy analyses revealed the formation of nano-textured pillar-like structures of highly photoactive monoclinic scheelite $BiVO_4$. Under optimal spraying conditions, the electrosprayed $BiVO_4$ nanostructured films yielded a photocurrent density of 1.3 mA/cm$^2$ for a light intensity of 100 mW/cm$^2$. The optimal film thickness was ~3 μm, with an optimal post-annealing temperature of 550 °C. The formation of pillar-like structures is attributed to a deposition process where drop convection near the deposition surface is influenced by thermophoretic and diffusive transport along with the convective and electrostatic driving forces that are typical of electrospray processes.

# Enhanced photoelectrochemical solar water splitting using a platinum-decorated CIGS/CdS/ZnO photocathode

Hyun Yoon[1], Min-woo Kim[1,2], Hong Seok Jo [1], Sam S. Yoon[1,*]

[1]*School of Mechanical Engineering, Korea University, Seoul, 136-713, Republic of Korea*
[2]*Green School, Korea University, Seoul, 136-713, Republic of Korea*
[*]*Sam S. Yoon: skyoon@korea.ac.kr*

A $Cu(InGa)Se_2$ film was modified with CdS/ZnO for application to solar water splitting. Platinum was electrodeposited on the ZnO layer as a hydrogen evolution catalyst. The effects of the electroplating time and acidity level of the electrolyte on the photocurrent density were studied. The highest photocurrent density of -32.5 mA/cm$^2$ under 1.5 AM illumination was achieved with an electroplating time of 30 min at a pH of 9. This photocurrent density is higher than those reported in previous studies. The markedly high performance of the CIGS/CdS/ZnO photocathode was rationalized in terms of its type II cascade structure that facilitated efficient charge separation at the interface junction.

# Environmentally benign synthesis of graphene based binary metal oxides for electrochemical capacitors

Hae-Min Lee[1], Hwang Bo Jung[2], and Chang-Koo Kim*[2]

*[1] Institute of NT. IT Fusion Technology,*
*[2] Department of Chemical Engineering and Division of Energy Systems Research,*
*Ajou University, Suwon 443-749, Korea*

**changkoo@ajou.ac.kr*

Electrochemical capacitors (ECs) are attractive energy storage devices because of their high power density, long cycle life, and rapid charging-discharging rates. ECs can be applied in a variety of applications, including consumer electronics, electric vehicles, and medical electronics, military devices, and so on. One of the most promising applications is in electric vehicles (EV) because of their high charge/discharge rates. ECs can be coupled with fuel cells or batteries to deliver the high power needed during acceleration and to recover the energy during braking. However, a major shortcoming of ECs is their low energy density (typically 5-10Wh/kg).

Graphene is an outstanding candidate as an electrode material because of their exceptionally high specific surface area, excellent thermal and electrical conductivity, and good chemical stability. However, graphene sheets usually suffer from agglomeration and re-stacking due to the Van der Waals interactions, which leads to a great loss of effective surface area and, consequently, capacitance than as expected. In order to solve re-stacking problem, graphene-based composites with various metal oxide nanoparticles such as $Ni(OH)_2$, $Mn_3O_4$, and $Co_3O_4$ have been reported. It is reported that compounds of mixed oxide composites, such as Ni-Mn, Ni-Co, and Mn-Co oxides [1-3], have superior capacitive performance to single transition metal oxides. However, synthesis of graphene or graphene based metal oxide nanosheet materials with a facile and environment friendly approach is still a big challenge.

In this work, a direct and environmentally benign method to prepare graphene-based binary metal oxides composites from graphite in water for precluding the re-stacking of GO reduction was developed. The synthesized samples were characterized by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). In addition, the electrochemical analyses were made using cyclic voltammetry, galvanostatic charge-discharge tests, and impedance tests.

[1] K.R. Prasad, N. Miura, J. Electrochem. Commun. 6 (2004) 1004.
[2] P.Y. Chuang, C.C. Hu, J. Mater. Chem. Phys. 92 (2005) 138.
[3] S.G. Hwang, J.E. Hong, G.O. Kim, H.M. Jeong, and K.S. Ryu, ECS Solid State Letters, 2 (2013) M8.

# Electrochemical Synthesis of Nanostructured Transition Metal Carbides for Hydrogen Evolution Reaction

Jin Soo Kang, Jin Kim, Myeong Jae Lee, Dong Young Chung, Yung-Eun Sung*

*Center for Nanoparticle Research, Institute for Basic Science (IBS) and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea.*

**E-mail: ysung@snu.ac.kr*

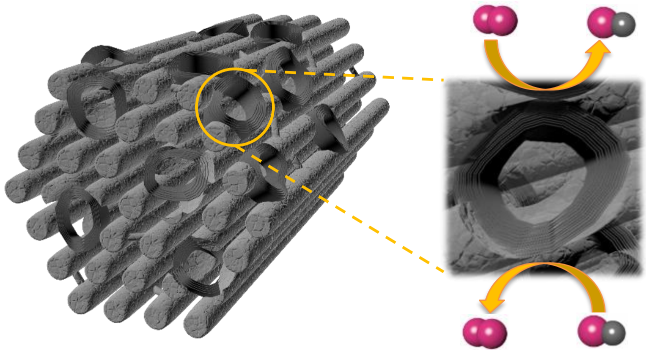
Development of clean and renewable energy sources is one of the most important issues nowadays due to the upcoming depletion of fossil fuels and pollution problems. Among various possible means for the energy production, hydrogen-based fuel cell technologies have feasible properties such as large energy density and environmentally benign exhaust product ($H_2O$), in addition to the abundant water on the earth's surface which may serve as hydrogen source. However, conventional catalysts for electrolytic water dissociation into $H_2$ and $O_2$ are mainly consisted of expensive and rare noble metal (typically Pt). Therefore, low-cost materials including N-/S-doped carbons and transition metal carbides, nitrides, sulfides, and phosphides have been proposed as economic electrocatalysts for hydrogen evolution, though they often suffer from low activity or poor stability. Herein, our recent research works on earth-abundant transition metal carbide materials for efficient hydrogen evolution reactions will be presented. Highly crystalline carbides with tailored nanostructures were prepared by electrochemical corrosion followed by post-treatment, and they were directly applied as cathode ($H_2$ evolving electrode) for electrocatalytic water dissociation. Carbide catalysts exhibited substantial performances, which were confirmed by keen electrochemical measurements, and did not show any sign of activity drop during 3000 cycles of accelerated durability tests. Moreover, general usefulness of the carbide electrodes and their nano-architectures were verified by further applications in photoelectrochemical cells.

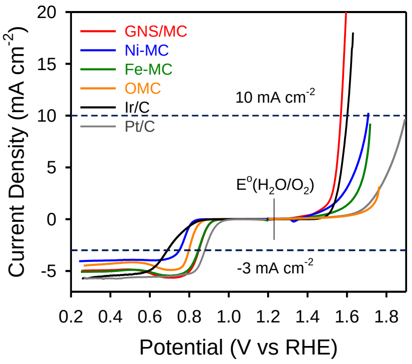
# Highly Active and Durable Bifunctional Oxygen Electrocatalysts Based on Graphitic Nanoshell/Mesoporous Carbon Hybrids for Rechargeable Aqueous Na-Air Batteries

Jae Yeong Cheon, Young Jin Sa, Jinwoo Woo, Youngsik Kim, and Sang Hoon Joo*

*Department of Chemistry, School of Energy and Chemical Engineering*
*Ulsan National Institute of Science and Technology (UNIST)*
*50 UNIST-gil, 44919 Ulsan, Republic of Korea*
** Corresponding Author: E-mail: shjoo@unist.ac.kr*

Efficient and cost-effective bifunctional electrocatalysts for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are of vital importance in energy conversion and storage devices. Despite the recent progress in bifunctional oxygen electrocatalysts, their unbalanced and insufficient OER and ORR activities has continued to pose challenges for the practical application of such energy devices. We here present the design of highly integrated, high-performance, bifunctional oxygen electrocatalysts composed of highly graphitic nanoshells embedded in mesoporous carbon (GNS/MC). The GNS/MC exhibits very high oxygen electrode activity, which is one of the best performances among non-precious metal bifunctional oxygen electrocatalysts, and substantially outperforms Ir- and Pt-based catalysts. Moreover, the GNS/MC shows excellent durability for both OER and ORR. *In situ* X-ray absorption spectroscopy and square wave voltammetry reveal the roles of residual Ni and Fe entities in enhancing OER and ORR activities. Raman spectra indicate highly graphitic, defect-rich nature of the GNS/MC, which can contribute to the enhanced OER activity and to high stability for the OER and ORR. In aqueous Na-air battery tests, the GNS/MC air cathode-based cell exhibits superior performance to Ir/C- and Pt/C-based batteries. Significantly, the GNS/MC-based cell demonstrates the first example of rechargeable aqueous Na-air battery.





# Fabrication of Pt-Co Alloy for Polymer Electrolyte Membrane Fuel Cell Cathode by Sequential Pulse Electrodeposition Method

Junhwan Baek, Mingyu Kim, Yongsug Tak
*Department of Chemical Engineering, Inha University*
*253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea*
*22151650@inha.edu*

Polymer electrolyte membrane fuel cell(PEMFC) is considered to be a reliable power source for transportation vehicles, stationary and potable applications because it is eco-friendly and has low driving temperature and high energy efficiency. Conventional electrodes have been made by spraying Pt/C powder catalyst on carbon sheet. The cathode prepared by conventional method has relatively large inactive electrocatalytic surface area and high reactant gas transfer resistance because of its thick catalyst layer. Recently, studies on fabrication method of thin film cathode in variety of ways are in progress. A cathode prepared by pulse electrodeposition method can solve conventional problems because it has thin catalyst layer and its nanosized Pt particles are concentrated nearby electrode-electrolyte membrane interface. Meanwhile, several Pt-based alloy catalysts with various transition metals have been suggested to enhance the catalytic activity and to reduce the Pt loading amount. Among them, Pt-Co alloy catalyst is known as favorable catalyst because of its high durability and efficiency.

In this study, Pt-Co alloy catalyst for PEMFC cathode is fabricated by sequential pulse electrodeposition method. At first, Pt seeds were predeposited with additive, Polyvinylpyrrolidone, followed by pulse electrodeposition of Pt-Co catalyst layer. Co content was controlled by NaCl concentration in plating bath. Electrochemical characteristics of alloy cathode were analyzed with Cyclic Voltammetry(CV) and surface morphology was observed with scanning electron microscopy(SEM) and Energy-dispersive X-ray spectroscopy(EDX). Cell performances of fabricated membrane electrode assemblies(MEAs) were measured. Electrode prepared by this novel method showed improved electrochemical surface area(ECSA) and cell performance with controlled Pt-Co particle size than former pulse electrodeposition method.

# Reversible Air Electrodes Based on Perovskite Oxide and Sb-doped $SnO_2$ in Zinc-Air Secondary Batteries

Naoko Fujiwara, Tsutomu Ioroi, Tsukasa Nagai, Hajime Arai*, Zempachi Ogumi*
*Research Institute of Electrochemical Energy,*
*National Institute of Advanced Industrial Science and Technology (AIST)*
*1-8-31 Midorigaoka, Ikeda, Osaka 563-8577 Japan*
** Office of Society-Academia Collaboration for Innovation, Kyoto University,*
*Gokasho, Uji, Kyoto 611-0011 Japan*
*n-fujiwara@aist.go.jp*

Reversible air-electrodes with high activity and durability for both oxygen reduction and evolution reactions are required for developing zinc-air secondary batteries. Although carbon black is widely used as a catalyst support, which is mixed with bi-functional catalysts such as perovskite-type oxide, it is potentially oxidizing during the charge step [1]. We have been investigating the potential use of conductive materials alternative to carbon support. In this study, antimony doped tin oxide (ATO) is used as a conductive support to evaluate both activity and durability of air electrodes in zinc-air secondary batteries with perovskite-type oxide catalysts.

The catalyst powder of perovskite-type oxide (LCCMO: $La_{0.6}Ca_{0.4}Co_{0.7}Mn_{0.3}O_3$, 27 $m^2$ $g^{-1}$) mixed with carbon black (CB: Denkablack, 68 $m^2$ $g^{-1}$) or ATO (42 $m^2$ $g^{-1}$) was applied on carbon cloth with PTFE binder to be used as air electrodes in zinc-air batteries. The air electrode with a geometric area of 2 $cm^2$ was mounted in the cell, which was open to the air atmosphere on the air electrode side and contained 0.25 M ZnO + 4 M KOH aqueous solution with a Zn plate on the opposite side. Charge and discharge properties of air electrodes were evaluated at constant current and 25ºC.

The air electrodes of LCCMO+ATO (1:2 w/w, PTFE 5 wt. %) and LCCMO+CB (5:1 w/w, PTFE 10 wt. %) showed favorable charge-discharge performance, after optimizing the composition of the air electrode with ATO and CB support. The air electrode of LCCMO+ATO (1:2 w/w, PTFE 5 wt. %) reached the performance comparable to that of LCCMO+CB (5:1 w/w, PTFE 10 wt. %).

The charge-discharge cycle test was conducted by applying 4 mA $cm^{-2}$, followed by 10 mA $cm^{-2}$ for 1 h at each step. Figure 1 compares charge-discharge cycle performance of zinc-air batteries with two different electrodes. Rapid increase and decrease of the cell voltage were observed for charge and discharge step, respectively after 30 cycles at 4 mA $cm^{-2}$ for LCCMO+CB (5:1 w/w, PTFE 10 wt. %), suggesting that the deterioration of the air electrode with the carbon corrosion in the catalyst layer. On the other hand, the cell voltage for LCCMO+ATO (1:2 w/w, PTFE 5 wt.%) was relatively stable for both charge and discharge step during 100 cycles at 4 mA $cm^{-2}$ and 10 mA $cm^{-2}$. The ATO support shows improved durability toward charge-discharge cycles compared to the carbon support.

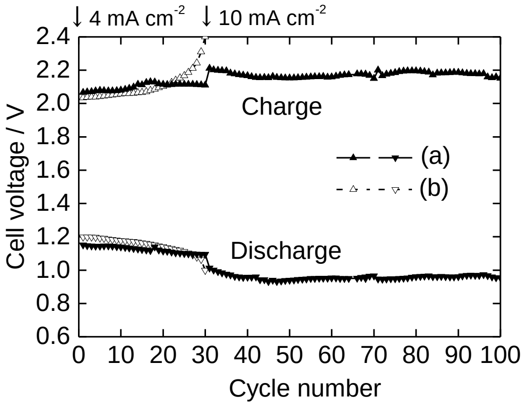


**Fig. 1.** Charge-discharge cycle performance of zinc-air batteries with two different air electrodes at 4 mA $cm^{-2}$ or 10 mA $cm^{-2}$ and at 25ºC. (a) LCCMO+ATO (1:2 w/w, PTFE 5 wt. %) and (b) LCCMO+CB (5:1 w/w, PTFE 10 wt. %).

[1] P. N. Ross and H. Sokol, *J. Electrochem. Soc.*, **131**, 1743 (1984).

**Acknowledgement**
This work was supported by the "Research and Development Initiative for Scientific Innovation of New-Generation Batteries" (RISING) project of the New Energy and Industrial Technology Development Organization (NEDO), Japan.

# Application of Graphene Foam on Flow Field of Bipolar Plates in Polymer Electrolyte Membrane Fuel Cells

Ji Eun Park, Sung-jun Kim, Yong-Hun Cho, Yung-Eun Sung
*Center for Nanoparticle Research, Institute for Basic Science (IBS),*
*School of Chemical & Biological Engineering, Seoul National University,*
*Seoul, 151-742, Korea*
*cathypark7@naver.com*

Graphene foam is three-dimensional graphene-based material which is made by chemical-vapor deposition on nickel foam, following by etching away nickel foam. Various kinds of metal foam have been developed as flow field because high porosity of metal foam distributes uniformly reactants on entire area and removes water inhibiting flooding in flow field. However, metal foam is highly susceptible to corrosion due to acidic operation condition. In this work, we applied graphene foam as flow field by substituting metal for graphene. Graphene foam has advantages such as structure characteristic of foam, hydrophobicity of graphene. Therefore, single cell with graphene foam showed the enhancement of mass transport and increased performance in high current densities. Also oxygen gain and electrochemical impedance spectroscopy were evaluated to investigate the effect of graphene foam on enhanced mass transport and showed the mass transport resistance are decreased.

# Preparation and Evaluation of Ir-Pt/Nafion117/Pt MEA by Electroless deposition method

Min-ah Song
*Elchemfaraday R&D Lab, Elchemtech Co., Ltd.*
*World Meridian Venture Center 2cha 611~616, GASANDONG 426-5, GEUMCHUNGU, SEOUL, KOREA, 153-759*
*masong@elchemtech.com*

Preparing iridium loaded MEA with an existing Impregnation reduction method (I-R method), one of an Electroless deposition method has a few drawbacks, such as low loading amount of iridium, which leads to a low electrochemical efficiency and durability.

In this case study, to overcome this problem, MEA was prepared by modifying an existing I-R method for water electrolysis. The new method involves a repetitive redox reaction of Iridium precursor which forms an iridium on Pt metal layer (Pt/N117/Pt). MEA prepared by the new method contains a higher intensity of iridium, which consequently yields a better performance.

The performances of MEA prepared by I-R method Pt/N117/Pt as well as the one prepared using Pt/N117/Pt MEA with Ir layer on anode Ir-Pt/N117/Pt have been evaluated. Electrochemical characteristics have been analysed by performing a single cell I-V curve and cyclic voltammetry (CV) and for physiochemical characteristic observation, SEM and EDX have been analysed.

As a result, iridium loaded MEA have performed 18.5 % and 15.6 % higher than Pt/N117/Pt MEA at a current density of 0.5 A/cm$^2$ and 1.0 A/cm$^2$ (@ 25 °C) respectively.

# Self-Supported Pt-Ni Mesostructures as Ultrastable Oxygen Reduction Reaction Electrocatalysts in Proton Exchange Membrane Fuel Cell

Ho Young Kim,[1] Young Jin Sa,[1] Sung Dae Yim,[2] and Sang Hoon Joo*,[1]

[1] *Department of Chemistry, School of Energy and Chemical Engineering*
*Ulsan National Institute of Science and Technology (UNIST)*
*50 UNIST-gil, 44919 Ulsan, Republic of Korea*

[2] *Fuel Cell Laboratory, Korea Institute of Energy Research (KIER),*
*152 Gajeong-ro, 34129 Daejeon, Republic of Korea*

** Corresponding author: E-mail: shjoo@unist.ac.kr*

Improving the activity and durability of the cathode catalyst in proton exchange membrane fuel cells (PEMFCs) is of great importance for their commercialization. The most prevalent commercial catalysts are Pt-based nanoparticles, which are finely dispersed on high surface area carbon supports (Pt/C). During the fuel cell operation, considerable activity loss of Pt/C occurs because of corrosion of carbon support material, the dissolution of Pt, and the detachment of Pt nanoparticles from the carbon support. In this work, support-free 3D mesostructured spherical Pt-Ni alloy electrocatalysts (Meso-PtNi) of 100 nm in size were prepared by nanocasting mesoporous silica nanospheres (MSNs). Interestingly, high-temperature annealing at 600 °C afforded the formation of PtNi intermetallic ordered phase while reduction at 300 °C generated disordered Pt-Ni alloy phase. Electrocatalytic activity and stability of Meso-PtNi for the oxygen reduction reaction (ORR) was investigated in 0.1 M $HClO_4$. Meso-PtNi catalysts showed enhanced performance in ORR measurement compared to Pt/C, Pt black, and Meso-Pt. Importantly, Meso-PtNi containing intermetallic phase exhibited better activity than disordered alloy structure. An accelerated degrading test (ADT) was conducted according to the US Department of Energy's protocol. Meso-PtNi showed superior stability as compared to the commercial Pt/C and Pt black catalysts, up to 30,000 potential cycling. Particularly, the Meso-PtNi with intermetallic phase showed a remarkable stability. It was found that Meso-PtNi was activated during the early stage of ADT, and retained its increased ORR activity up to 50,000 cycling. We fabricated membrane electrode assembly based on the intermetallic Meso-PtNi cathode, and achieved the excellent single cell performance in PEMFC.

# Electrochemical Behaviors of Aluminum Anode in Ionic Liquid Electrolyte for Al-ion Battery

Sangwon Choi, Boyoon Shin, Yongsug Tak*
*Department of Chemical Engineering, Inha University, Incheon, 402-751, Korea*
*csw1991@nate.com*

As the environmental issues about exhaustion and the combustion gas of fossil fuel are becoming a global problems, there are many attempts to develop renewable energy systems such as solar cell, fuel cell which can save and use energy efficiently. Li-ion battery has been applied for the storage of energy produced by renewable energy sources for load leveling. However, Li-ion battery has low energy density to apply middle or large-sized energy storage devices and the depletion of lithium resources became an important issue with the rapid increase in demand of lithium and safety issues due to the large reactivity of lithium. Therefore, new secondary battery system with high energy density and safety needs to be developed and aluminum metal is recently suggested to be a new anode material. Aluminum is abundant in earth crest and high energy density with 1.06kWh/kg(Li-ion battery : 0.406kWh/kg). Furthermore, three electrons reaction has a possibility to realize a high capacity – reaction system.

In this work, aluminum-ion battery system was built with aluminum anode and aluminum chloride molten ionic liquid electrolyte, $AlCl_3$ – [EMIm]Cl. Manganese oxide cathode was used as a cathode. Electrochemical behaviors of aluminum anode were investigated with cyclic voltammetry and electrochemical impedance spectroscopy. In order to study the electrochemical stability of Al anode surface in electrolyte, Al surface was modified with electropolishing and selective dissolution of aluminum and the microscopic surface morphology changes was observed with SEM. Additionally, swagelok type of the cell was prepared and the effect of electrolyte composition on charge-discharge behaviors of rechargeable Al-ion battery was investigated.

# Effects of metal hydroxide-composite electrode for efficient CO management in polymer electrolyte membrane fuel cell

Myeong Jae Lee[†,‡], Jin Soo Kang[†,‡], Yun Sik Kang[†,‡], Dong Young Chung[†,‡],
Kug-Seung Lee*[,§], Yung-Eun Sung*[,†,‡]

[†]*Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 151-742, Republic of Korea.*
[‡]*School of Chemical and Biological Engineering, College of Engineering, Seoul National University, Seoul 151-742, Republic of Korea.*
[§]*Beamline Research Division, Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea.*

**E-mail: ysung@snu.ac.kr*

Polymer electrolyte membrane fuel cell (PEMFC) is an electrochemical energy device that converts the chemical energy into electrical energy by chemical reactions occurring at the anode and cathode. In the PEMFCs, CO poisoning of Pt catalysts is one of the most serious problems that hinder the electrocatalytic reactions taking place in the cells. In general, hydrogen reactant which is generally used for fuel cell anode is mostly produced by hydrocarbon reforming, and this process entails critical amounts of CO species. Additionally, oxidation process of alcohols which are also used for fuel of PEMFCs is deteriorated by CO intermediates to a great extent. Here we report bifunctional effect present in the composite of hydrous ruthenium oxide ($RuO_xH_y$) and Pt for effective CO oxidation. In this system, oxidation of CO molecule adsorbed on Pt surface is facilitated by increased coverage of oxygen species on Pt surface and external supply of oxygen species which are confirmed by electrochemical and physicochemical measurements. Moreover, this system is feasible for studying sole bifunctional mechanism in electrochemical condition due to unmodified electronic structure of Pt. Therefore, this work provides a new insight for blended electrode structure and efficient CO removal by bifunctional effect.

# Ruthenium oxide nanoparticles embedded in carbon matrix as a durable bifunctional catalyst for Zn-air batteries

Han-Saem, Park, Hyun-Kon Song*
*Department of Energy Engineering, Ulsan National Institute of Science and Technology (UNIST)*
*Ulsan, 689-798, Korea*
*Hanseam79@unist.ac.kr*

Demands for high energy densities have growingly extended research interests from Li ion batteries to metal air batteries. [1] Zn as a choice for metal in the metal air batteries benefits from low cost, the use of aqueous electrolytes that are environment-friendly and safety. There are various challenges that should be overcome before realizing rechargeable Zn air battery cells, including non-uniform zinc dissolution from anodes, limited solubility of Zn ions in electrolytes and serious overpotential experienced during charge. Developing efficient and stable bifunctional catalysts for air electrodes is one of the most important issues for guaranteeing the efficiency and cyclability of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).[2] Platinum and ruthenium oxide have been known to be the best ORR and OER catalyst, respectively. However, they do not drive efficiently the reaction reverse to what they can do the best on. That is to say, the ORR electroactivity of ruthenium oxide is not as facile as its OER activity.

Secured to achieve high activities of electrocatalysis should be three conditions including facile charge transfer kinetics defined by active sites of catalysts, good accessibility of reactants to the active sites and highly developed electric pathways to them. Coating cathode and/or anode materials with carbon has been widely used as the strategy to improve electric conduction throughout electrodes.[3] Electroactive materials can be easily composited with carbon by reducing carbon precursors in a reductive gas environment at temperatures between higher than the thermal decomposition temperature of the precursors and lower than reduction temperature of the active materials. Therefore, the main concern in making oxide/carbon composites by the thermal method is to prevent the oxides from being reduced. For example, sucrose-coated $Fe_2O_3$ is converted to carbon-coated $Fe_3O_4$ at 500 °C in argon, with a third of iron atoms being reduced from $Fe^{3+}$ to $Fe^{2+}$. [4]

To improve electroactivities of ruthenium oxide for ORR and OER simultaneously, we tuned electric conduction of the catalyst layers by embedding ruthenium oxide nanoparticles in a carbon matrix phase ($RuO_2$@C). $RuO_2$@C was synthesized by annealing micelles consisting of ruthenium ions surrounded by double hydrophilic block copolymers (DHBC) of poly(ethylene oxide)-block-poly(acrylic acid) (PEO-b-PAA) as a template.[5] During the annealing process, hydrous ruthenium oxide cores were crystallized and the shells of PEO-b-PAA were converted to a continuous carbon phase surrounding $RuO_2$. Rejected was the null hypothesis that there is no difference between $RuO_2$ and $RuO_2$@C because both ORR and OER electroactivities were significantly improved by the incorporation of $RuO_2$ into the carbon phase. Durability of $RuO_2$@C in OER conditions was also superior to that of $RuO_2$ and Pt/C. When compared with Pt/C-based cells, Zn air cells based on $RuO_2$@C as the bifunctional air electrodes showed competitively similar ORR overpotentials during discharging and smaller OER overpotentials during charging with better rechargeability for more operational cycles. The difference of working potential between charge and discharge was around 1 V for 40 h over 120 galvanostatic cycles at 20 mA $cm^{-2}$.

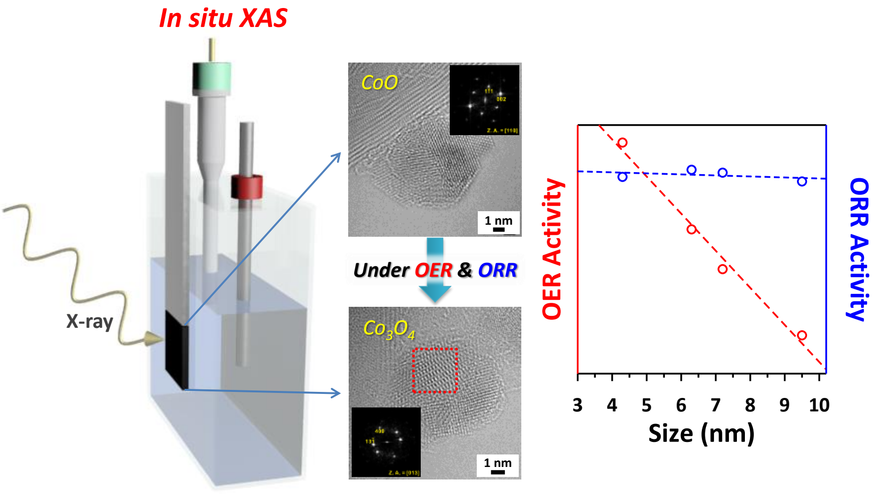
[1] J. Zhang, Z. Zhao, Z. Xia, L. Dai, Nature Nanotechnology 2015, 10, 444.
[2] M. a. Rahman, X. Wang, C. Wen, Journal of the Electrochemical Society 2013, 160, A1759.
[3] H.-S. Park, T.-H. Kim, M.-H. Lee, H.-K. Song, Journal of Materials Chemistry 2012, 22, 20305.
[4] T.-H. Kim, H.-K. Song, Electrochimica Acta 2013, 105, 47.
[5] E. Seo, T. Lee, K. T. Lee, H.-K. Song, B.-S. Kim, Journal of Materials Chemistry 2012, 22, 11598.

# Size-Dependent Activity Trends in Combination with *In Situ* X-ray Absorption Spectroscopy Reveal Insights into Cobalt Oxide Catalyzed Bifunctional Oxygen Electrocatalysis

Bora Seo, Young Jin Sa, Jinwoo Woo, Hu Young Jeong, and Sang Hoon Joo*

*Department of Chemistry, School of Energy and Chemical Engineering, and UNIST Central Research*
*Facilities (UCRF), Ulsan National Institute of Science and Technology (UNIST)*
*50 UNIST-gil, 44919 Ulsan, Republic of Korea*
** Corresponding Author Email: shjoo@unist.ac.kr*

Bifunctional oxygen electrocatalysts play a vital role in important energy conversion and storage devices. Cost-effective, abundant, and active Co-based materials have emerged as promising bifunctional electrocatalysts, for which identifying catalytically active structures under reaction conditions and unraveling the structure–activity relationships are of critical importance. We investigated the size-dependent (3–10 nm) structure and catalytic activity of bifunctional cobalt oxide nanoparticle ($CoO_x$ NP) catalysts for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR). *In situ* X-ray absorption spectroscopy (XAS) revealed that the majority of NPs during OER and ORR was composed of the $Co_3O_4$ phase regardless of their particle sizes. The OER activity increased with decreasing NP size, which correlated to the enhanced oxidation state and larger surface area in smaller NPs, whereas the ORR activity was independent of NP size, revealing the auxiliary role of $CoO_x$ on the $CoO_x$/CNTs for the reduction or disproportionation of peroxide rather than the direct reduction of oxygen. These particle size-dependent catalytic activities in conjunction with the *in situ* XAS results can provide critical insights into the $CoO_x$-catalyzed bifunctional oxygen electrode reactions.



# Kinetic Selectivity of Oxygen Reduction Reaction on a Single-Atom Catalyst: Application of Marcus Theory to Proton-Coupled Electron Transfer

Minho Kim[1], Chang Hyuck Choi[2,3], Minkee Choi[2,*], and Hyungjun Kim[1,*]
[1]*Graduate School of EEWS, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Daejeon 34141, Republic of Korea.*
[2]*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Daejeon 34141, Republic of Korea.*
[3]*Department of Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH Max-Planck-Strasse 1, 40237 Düsseldorf, Germany.*
**Corresponding Author: (H. Kim) linus16@kaist.ac.kr, (M. Choi) mkchoi@kaist.ac.kr.*

Single-atom electrocatalyst is a promising material for its maximized surface area, yet proper support has not been discovered to stabilize dispersed single-atom catalysts as well as to modify the catalytic properties. Here, we report a new sulfur-doped zeolite-templated carbon with the extra-large sulfur content and unique carbon structure (i.e., highly curved 3-dimensional networks of graphene nanoribbons) that can stabilize relatively high loading of Pt in the form of single-atom species. In oxygen reduction reaction (ORR), this single atom catalyst does not follow a conventional 4-electron pathway producing $H_2O$, but selectively produces $H_2O_2$ even over extended times without significant degradation of the catalyst activity. Based on Marcus theory, density functional study illustrates the kinetic control of the oxygen reduction pathways in terms of reorganization energy and activation barrier. This approach constitutes a potentially promising route for producing important fine chemical $H_2O_2$, and also offers new opportunities for tuning selectivity of other electrochemical reactions on various metal catalysts.

# Metal Valency Change during Oxygen Reduction Reaction at Fe-N4 Catalyst

Sungmin Kim[1], Hyungjun Kim[1,*]
*Graduate School of Energy, Water, and Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST)*
*Yuseong-gu, Daejeon 305-701, Korea*
*linus16@kaist.ac.kr.*

Toward the practical use of polymer electrolyte membrane fuel cells (PEMFC), it is important to develop cost-effective and durable oxygen reduction reaction (ORR) catalysts. As such, many researchers are developing nonprecious electrochemical catalysts for ORR to substitute Pt. Among them, metal-porphyrin impregnated carbon catalysts have been demonstrating high ORR catalytic activity with enhanced durability, particularly Fe-porphyrin systems.

For the mechanistic understanding of catalytic activity, many experimental studies have been pursued, and Fe-$N_4$ sites are often discussed as the catalytic active sites for ORR. On top of this, theoretical studies have suggested a sequential proton coupled electron transfers (PCET) to $O_2$ to yield $H_2O$. Considering the characteristic distinction of Fe-$N_4$ active sites where the change of oxidation number is accompanied from that of metallic active sites, however, it should be theoretically and carefully reexamined whether the electron transfer to metal center from the conduction band of electrode must be considered for porphyrin-derived catalysts.

In this study, we used density functional theory calculations to challenge such a question, and thus to provide mechanistic understanding on the source of overpotential. We considered electron transferring step, which called valency change owing to specialty of Fe-$N_4$ active site. By calculating the required electrochemical potentials for the pathways with the valency change considered, and no valency change considered, and by comparing them with experimental potentials, we discuss the ORR mechanism of Fe-porphyrin derived electrochemical catalytic systems.

# Mechanistic Role of Ionic-liquid/water Mixture in Enhanced Electrochemical $CO_2$ Reduction

Hyung-Kyu Lim, Hyungjun Kim*
*Graduate School of EEWS (Energy, Environment, Water and Sustainability)*
*Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Korea*
*zinnia7@kaist.ac.kr*

For the mitigation of global-warming problems and the sustainable development of the inevitable carbon-based economy, carbon dioxide ($CO_2$) conversion technology has been regarded as one of the most important and urgent current scientific issues. Many researchers anticipate the efficient transformation of $CO_2$ from various emission sources into more valuable chemicals and fuels. Among the various ongoing attempts, which are categorized as biochemical, thermochemical, electrochemical, and photo-assisted electrochemical processes, the electrochemical method has certain merits in terms of high reactivity at ambient conditions and good extensibility from small to large-scale processes. Also, the possibility of direct integration with renewable electric sources adds more potential to the electrochemical method as a promising route for $CO_2$ conversion. A number of studies have been performed to improve performance of electrochemical $CO_2$ reduction on various catalyst and electrolyte systems, however it still has many scientific and engineering issues to be elucidated and improved, to achieve commercial-level technology. In 2011, the promising effect of ionic-liquid on the electrochemical $CO_2$ reduction performance have been reported that the mixture electrolyte contains ionic-liquid (18 mol% Emim-$BF_4$) and water lowers the over-potential of $CO_2$ to CO reduction process on silver electrode as only 0.17 V from the equilibrium potential as well as suppress the competitive hydrogen evolution reaction effectively.[1] Further experimental studies have been tried to figure out the mechanism of lowering over-potential with ionic-liquid water mixture electrolyte,[2, 3] but the detailed understanding of complex electrochemical system has not been achieved. In our research, we developed the new grid-based QM/MM (Quantum Mechanics/Molecular Mechanics) methodology which can effectively handle the complex electrostatic interaction between catalyst and mixed electrolyte, and theoretically figured out the main role of ionic-liquid and water mixture electrochemical $CO_2$ reduction system.

[ References ]

[1] B.A. Rosen, A. Salehi-Khojin, M.R. Thorson, W. Zhu, D.T. Whipple, P.J.A. Kenis, R.I. Masel, Ionic Liquid-Mediated Selective Conversion of CO2 to CO at Low Overpotentials, Science, 334 (2011) 643-644.
[2] B.A. Rosen, J.L. Haan, P. Mukherjee, B. Braunschweig, W. Zhu, A. Salehi-Khojin, D.D. Dlott, R.I. Masel, In Situ Spectroscopic Examination of a Low Overpotential Pathway for Carbon Dioxide Conversion to Carbon Monoxide, J Phys Chem C, 116 (2012) 15307-15312.
[3] B.A. Rosen, W. Zhu, G. Kaul, A. Salehi-Khojin, R.I. Masel, Water Enhancement of CO2 Conversion on Silver in 1-Ethyl-3-Methylimidazolium Tetrafluoroborate, J Electrochem Soc, 160 (2013) H138-H141.

# Magnetite coated metallic support as one-body catalyst for Electro-Fenton reactions

Sang Hoon Kim, Thi May Do, Yunjeong Choe, Ji Young Byun

*Center for Materials Architecturing, Korea Institute of Science and Technology, Seoul 136-791, South Korea &*
*Department of Nanomaterials Science and Engineering, University of Science and Technology, Daejeon, 305-350, South Korea*

*kim_sh@kist.re.kr*

In this work, we show that washcoated $Fe_3O_4$ nanoparticles on FeCrAl alloy are highly efficient electrochemical catalyst for electro-Fenton oxidation. We compare their performance to that of conventional stainless steel electrode using methylene blue dye as the target organic pollutant [1]. FeCrAl alloy foam was used as a supporting material for magnetite particle coating. This one-body conducting catalyst was used as the cathode of an electro-Fenton system. Methylene blue dye and phenol were used as model wastewater pollutants. The effect of pH, applied voltage, supporting electrolyte, electrode inner space, and catalyst dosages were investigated and optimized. Our material showed high degradation rate for the molecules in a short time. The pseudo-first-order kinetic study showed that the electro-Fenton system with metal foams with washcoated $Fe_3O_4$ had higher efficiency than that of Fe2+ catalyzed in conventional EF system.

References

1. Thi May Do et al, Research on Chemical intermediates (accepted)

# Computational strategies for designing and discovering $CO_2$ electro-conversion catalysts.

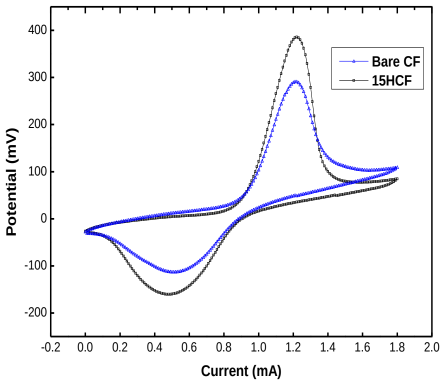
Hyeyoung Shin, Hyungjun Kim*
*Graduate School of Energy, Environment, Water, and Sustainability (EEWS), Korea Advanced Institute of Science and Techn ology (KAIST)*
*Yuseong-gu, Daejeon 305-701, Korea*
*hyshin07@kaist.ac.kr*

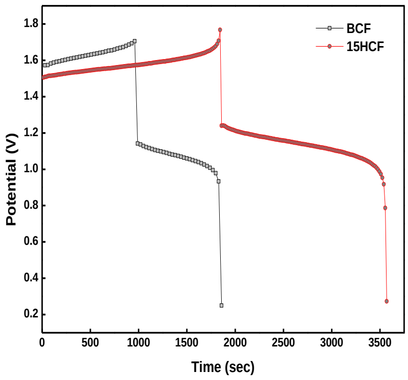
Electrochemical $CO_2$ conversion into fuel is an essential strategy to alleviate global warming which has been a serious issue worldwide. Since the early 1990s, various materials have been extensively investigated for its utilization in $CO_2$ electrolysis. However, it is still required to develop further advanced catalysts in terms of good catalytic activity, selectivity and stability to satisfy commercial requirement. In order to improve the catalytic properties, we need to understand the operational mechanism of the various possible $CO_2$ reduction pathways and identify the mechanistic role of catalysts. Meanwhile, computer-aided theoretical calculations have achieved great success in understanding and facilitating many physical/chemical reactions, thereby accelerating novel material discovery. Herein, we use first-principles based high-throughput computations and propose new efficient catalysts for electrochemical $CO_2$ conversion. This work suggests an approach to design advanced catalysts as well as provides the detailed understanding on the catalytic active center and its each reaction step.

# A study on effects of oxidation time of carbon felt electrode on chemical and electrochemical properties for all vanadium redox flow battery

Hyungjin Kim[1], Chang Kook Hong[*,2]
[1]*Department of Advanced Chemicals and Engineering*
[2]*Department of Chemical Engineering*
*Chonnam National University, Gwangju, 500-757, South Korea*
*Hongck@jnu.ac.kr*

Carbon materials have attracted much attention for electrodes in energy storage system. Among of that, PAN pabsed carbon felt (CF) has been used for electrode in redox flow battery due to its good electrical conductivity and high surface area. In this study, we focused that wettability is depended on degree of oxidation. The oxidation process was used with widely known method. For the oxidation of carbon felts, oxidation time were 1h, 5h, 10h, 15h and 20h, respectively. The prepared samples were characterized by scanning electron microscope and energy dispersive x-ray spectroscopy for analysis surface and functionalities. After that, electrochemical properties were employed with cyclic voltammetry, electrochemical impedance spectroscopy for characterization of redox reaction properties and resistance. The sample with 15h oxidation time showed the highest electrocatalytic reaction with vanadium ions and the peak current reached 440mA. In charge-discharge tests, Oxidized sample for 15h was shown the highest performance for redox flow battery compared to others.





# Engineering of Supramolecular Protein Assembly for Elucidation of High-Performance Oxygen Reduction Reaction

Yong-Tae Kim[1], Jaeyoung Lee[3], Yong Ho Kim[1,2]*

1 – *SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, 440-746, South Korea*
2 – *Department of Chemistry, Sungkyunkwan University, Suwon, South Korea*
3 – *School of Environmental Science and Engineering, Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies (RISE), Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea*

tanatos@skku.edu
yhkim94@skku.edu

There have been so many trials of understanding how to construct nanomaterial-protein superstructures and also a lot of successes have been built up. The stacked principles have been applied for designing the hybrid nanomaterial-protein superstructures can be binding inorganic or DNA or metal ions[1,2]. Additionally, along with the advancement of the computer simulation, protein design has made great progress in the field of protein drug and related bioscience. Recently, our group designed the protein binding the surface of single wall carbon nanotube (SWNT) through the computation approach and also, they showed noble metal alloy nanoparticles (NPs)[3], gold and platinum alloy NPs, directly assembled on the protein-SWNT nanocomposite. Here, we demonstrate that the gold-platinum NPs arrangements and sizes having ORR catalytic ability through manipulating the hybrid structure and multiple mutations with Cysteine residues in a designed protein bundle. It was observed that the size of metal NPs is 2 – 3 nm and easily controlled by varying reduction time and precursor concentration. The position of the alloy NPs depends on the number of thiol group on Cys, and organized in outside of the nanocomposite by changing the number of a functional group that makes differs the alloy NPs density. The altering arrangement, size and density of the alloy NPs result in a significant change on ORR activity of the nanocomposites, and we confirmed the onset potential of the small and well-organized NPs arrangement is as high as the commercial Pt/C. This report suggests that the protein self-assembly structure has a potential to be a an easily modified, highly ordered electrocatalyst and further it is used in a marvelous electrode to other cell, for example, Li ion battery, Li air battery, and Fuel Cell.

[1] Mann, S. *Nature materials* **2009**, *8*, 781.
[2] Song, C.; Blaber, M. G.; Zhao, G.; Zhang, P.; Fry, H. C.; Schatz, G. C.; Rosi, N. L. *Nano letters* **2013**, *13*, 3256.
[3] Grigoryan, G.; Kim, Y. H.; Acharya, R.; Axelrod, K.; Jain, R. M.; Willis, L.; Drndic, M.; Kikkawa, J. M.; DeGrado, W. F. *Science* **2011**, *332*, 1071.

# Fabrication of Novel Catalyst Assembly by Engineering Mussel Adhesive Proteins Mimics for Associating Carbon Nanotube

SeungMin Shin[1], Yong-Tae Kim[1] and Yong Ho Kim[1] *

[1]*Sungkyunkwan Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University*
*Suwon 440-746, South Korea*
*dlsgh@skku.edu*
*yhkim94@skku.edu*

Diverse researches have been focused on fabrication of nanomaterial superstructures mediated by biomolecules such as viral capsid, DNA and proteins. These studies give fresh points of view on generating nano-superstructure using nanoparticles. Superstructure made by self-assembly between biomolecules and nanoparticle has significantly different characteristic from former one mediated on chemical compound. It gives eco-friendly synthetic routes for nanostructure presenting structure-based novel properties. In this paper, we controlled the arrangement of Pt nanoparticles using genetically engineered mussel adhesive protein (MAP) and develop novel superstructure by forming a self-assembled complex between MAP mimic protein and carbon nanotube (CNT). MAP is a bio-molecule which has high affinity with surface of amphiphilic materials and this critical property comes from 3,4-dihydroxy-L-Phenylalanine (DOPA) residues of MAP. Each DOPA gives two hydroxyl groups for bonding with nanoparticle tightly. The MAP-CNT-nanoparticle complex is able to demonstrate the possibility of opening material choice to novel biopolymer for design of catalyst assembly. This novel fabrication with the MAPs can be used in diverse fields of electro-chemical application because of the superior level of conductivity and higher catalytic activity than conventional platinum catalysts. It also presents eco-friendly characteristic toward first step to the invention of new catalyst using natural protein.

[1] Haesin Lee et al, Mussel-Inspired Surface Chemistry for Multifunctional Coatings, *Science*, **318**; 426-430 (2007)

[2] Maryam Moradi et al, Improving the Capacity of Sodium Ion Battery Using a Virus-Templated Nanostructured Composite Cathode, *Nano letter*, **15**, 2917-2921 (2015)

# Polydimethylsiloxane Treated Cathode Catalyst Layer to Prolong Hydrogen Fuel Cell Lifetime

Myounghoon Choun[a], Dongyoon Shin[a], Jaeyoung Lee[a.b]
[a]*Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, South Korea.*
[b]*Ertl Center for Electrochemistry and Catalysis, Research Institute for solar and Sustainable Energies, GIST, Gwangju, 500-712, South Korea.*
*Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea.*
*jaeyoung@gist.ac.kr*, mh.choun@gmail.com

A hydrogen fuel cell vehicle has been attracted as the ZEV due to its various advantages, such as high energy density, low emissions, high efficiency, and silence. However, there has been critical problems such as water flooding and carbon corrosion, which are directly related to its performance and durability, at cathode to commercialize hydrogen fuel cells. Water flooding is attributed to mass transfer limitation blocking pathway of oxygen by water produced from oxygen reduction reaction and supplied with oxygen. Moreover, the excess water can accelerate the carbon corrosion reaction in frequent on/off operation condition. In this study, we prepared polydimethylsiloxane(PDMS) treated cathode, which is hydrophobic, to improve durability in hydrogen fuel cells through effective water discharge. In addition, effect of hydrophobic cathode on durability was investigated via various analyses. We observed that the PDMS treated cathode contributed to limit both mass transfer limitation and carbon corrosion by efficient water withdrawal. Based on our results, we provide the mechanism of performance degradation of normal and PDMS treated cathode and the possibility of PDMS treatment to decline the performance degradation in fuel cells.

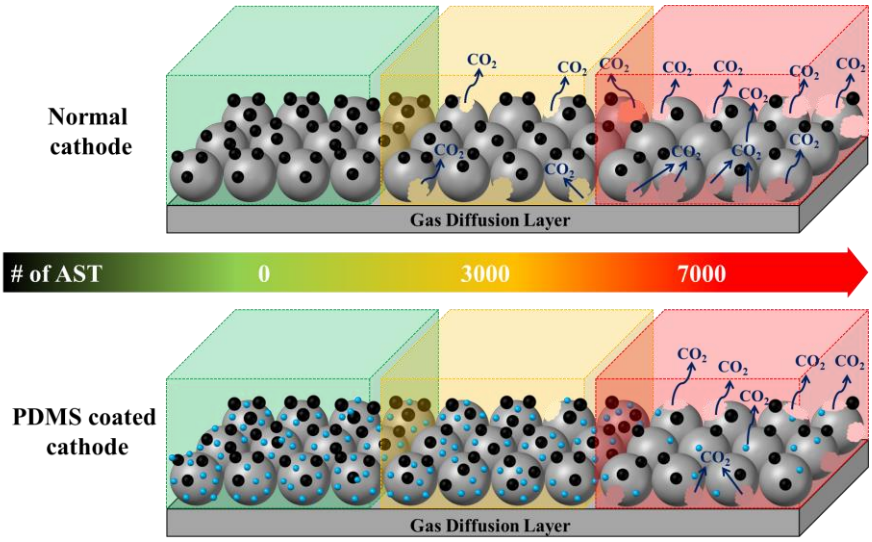


**Figure.** Scheme elucidating how performance is degraded at normal and PDMS treated cathode during AST process. (Black sphere) Pt, (Grey sphere) carbon, and (Blue sphere) PDMS.[1]

## Reference

[1] M. Choun, D Nauryzbayev, D. Shin, J. Lee, Catal. Today, In press

# Major redox reaction and its control in long-term capacitive deionization

Jihyun Yu, Taeyoung Kim, Junil Kang, Jeyong Yoon*
*World Class University (WCU) Program of Chemical Convergence for Energy & Environment (C2E2),*
*School of Chemical and Biological Engineering, College of Engineering, Institute of Chemical Process (ICP), Asian Insititute for Energy, Environment & Sustainability(AIEES)*
*Seoul National University (SNU), Gwanak-gu, Daehak-dong, Seoul 151-742, Republic of Korea*
*jhyu@snu.ac.kr, jeyong@snu.ac.kr**

The capacitive deionization (CDI) is one of desalination technologies for freshwater production. In CDI process, two porous carbon electrodes adsorb ions as forming electrical double layer on the surface by applying potential. Ideally, ion adsorptions are governed by non-faradaic effect below 1.2 V under water electrolysis potential (1.37 V). However, undesirable faradaic reactions occur during operation showing pH changes from 10 to 4.5. The pH at electrode surface is also changed as acidic at anode and basic at cathode. Those redox reactions change the system state and electrochemical properties of electrode. These undesirable phenomenon affects to desalination performance in long-term CDI operation.

Occurrence of anode oxidation was reported by dissolved oxygen in feed water. However the oxidation pathway and the major reaction were not investigated yet. To minimize anode oxidation for sustainable CDI performance, we aimed to determine the major re-dox reaction contributed to electrode and performance degradation among some possible faradaic reactions. Finally, we can delay the anode oxidation and performance degradation in long-term by minimizing the major oxidation reaction as control the sources of the reactant.

Key words: Capacitive deionization, Oxidation, Redox reaction, Long-term control

# Unravelling the Electrocatalytic Activity of Oxygen Evolution Reaction on the Charged Carbon Species by Incoporated Metal

Dongyoon Shin[a], Xianghua An[a], Myounghoon Choun[a], Jaeyoung Lee[a,b,]*
[a] *Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea*
[b] *Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies, GIST, Gwangju, 500-712, South Korea*
*jaeyoung@gist.ac.kr, shingoon@gist.ac,kr*

Highly active, durable, and cost-effective transition metal based electrocatalysts for oxygen evolution reaction (OER) in efficient electrochemical energy conversion and storage processes have been developed in recent years. Moreover, there is a growing interest in nitrogen doped carbon materials as non-metal OER electrocatalysts although the transition metal and their oxide have been considered unique active species in OER electrocatalysts.[1–3] However, its mechanistic origin of active species in non-metal OER electrocatalysts is still undefined. In order to investigate catalytic active site and the function of transition metal, we synthesized transition metal N-C catalysts (TM-N-CNFs) via a facile route of electrospinning and pyrolysis, and the electrospun N-C species (N-CNFs) were prepared by removing the metal with carbon etching and acid metal leaching. Following detailed physico-chemical and electrochemical characterizations, N-CNFs exhibit comparable activity and stability than TM-N-CNFs and 20 wt% Ir on Vulcan carbon black. We revealed that the positively charged carbon species might be mainly responsible for OER activity of non-metal N-C catalysts. This result is important for understanding the non-metal OER catalysts, and it should be attributed to other N-C catalysts with further improved performance.

## References

[1] Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi, K. Hashimoto, *Nat Commun* **2013**, *4*, DOI 10.1038/ncomms3390.
[2] T. Y. Ma, S. Dai, M. Jaroniec, S. Z. Qiao, *Angew. Chem. Int. Ed.* **2014**, *53*, 7281–7285.
[3] J. Zhang, Z. Zhao, Z. Xia, L. Dai, *Nat Nano* **2015**, *10*, 444–452.

# Stability Enhancement of Octahedral PtNi Nanoparticles for the Oxygen Reduction Reaction by Bromine Treatment

Juhyuk Choi, Chi-Woo Roh, Jinkyu Lim and Hyunjoo Lee*
*Korea Advanced Institute of Science and Technology*
*Department of Chemical and Biomolecular Engineering*
*Daejeon 34141, Republic of Korea*
*maring21@kaist.ac.kr*

Proton exchange membrane fuel cell (PEMFC) has been considered to be an eco-friendly power source for automobiles. However, cost reduction is highly necessary for the realization of the commercial fuel cell market. The minimization of Pt usage has been attempted using various strategies [1, 2] because current fuel cells use an excessive amount of Pt as electrode catalysts. The most successful results were reported using shaped PtNi alloy nanoparticles, with PtNi(111) facets [3]. However, these nanoparticles typically suffer from lower activity after long-term use due to the leaching out of the surface Ni during the oxygen reduction reaction (ORR). Leaching out of Ni leads to the disappearance of the activity-enhancing effect caused by deformation of PtNi(111) facet. Here, we report bromine pre-treatment of the octahedral PtNi nanoparticles to significantly enhance their durability. Bromine are adsorbed on the surface Ni more strongly than on the surface Pt, and the surface bromine are found to preserve the surface Ni that induces the ORR activity enhancement. Accelerated durability test (ADT) by repeating 10,000 cycles of cyclic voltammetry between 0.6-1.1 V in ORR condition showed that the half-wave potential decreased by 34 mV for the as-made PtNi octahedral nanoparticles, whereas the half-wave potential decreased by only 7 mV for the Br-treated PtNi nanoparticles. Simple bromine treatment significantly enhanced the long-term stability of the highly active PtNi alloy nano-octahedra.

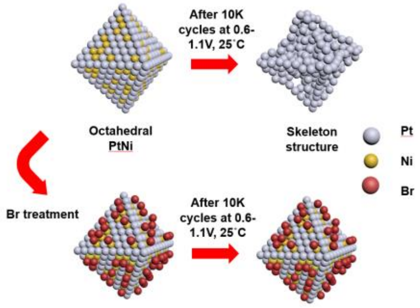


Figure 1. Schematic illustration for Br treatment effect on PtNi(111) facet

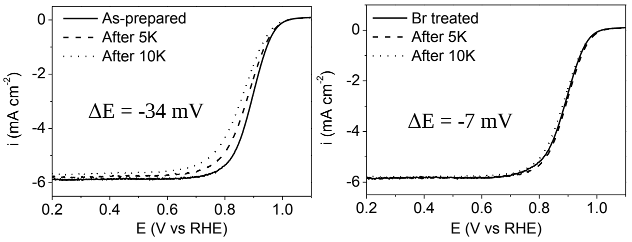


Figure 2. Linear sweep voltammetry (LSV) for the ORR after 5,000 or 10,000 cycles of ADT test.

[1] M. K. Debe, Nature, 486 (2012) 43-51.

[2] N. M. Markovic, T. J. Schmidt, V. Stamenkovic, P. N. Ross, Fuel Cells, 1 (2001) 105-116.

[3] S. Mukerjee, S. Srinivasan, M. P. Soriaga, J. Electrochem. Soc., 142 (1995) 1409-1422.

# Cost effective IT-SOFC by adopting surface-doped ceria for anode support layer

Chanho Kim,[1] Inyoung Jang,[1] Sungmin Kim,[1] Heesung Yoon, [1,]* Ungyu Paik[1,]*
*Department of Energy Engineering, Hanyang University, Seoul, Republic of Korea, 133-791*
**e-mail address: hsyoon64@gmail.com, upaik@hanyang.ac.kr*

Solid oxide fuel cells (SOFC) have taken attention due to high energy conversion efficiency. Gadolinium doped ceria (GDC) is usually adopted for intermediate temperature SOFC (IT-SOFC) due to high oxygen ion conductivity. However, high price of GDC has become a burden to be chosen for material. Particularly for anode support system, although most of catalytic reaction occurred at the interface between anode functional layer (AFL) and GDC electrolyte layer, almost 94% of GDC was used for anode support layer (ASL). In this paper, GDC in ASL was replaced by surface-doped ceria. ASL was fabricated by un-doped ceria and NiO followed by infiltrating Gd-nitrate solution. GDC is formed on ceria surface by decomposition of Gd-nitrate after heat treatment. Energy-dispersive X-ray spectroscopy (EDS) is conducted to confirm dispersion property of gadolinium oxide, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) are also conducted to decide successful doping. By changing the material for ASL with surface-doped ceria, unit cell showed performance on area specific resistance and current-voltage plot as favorable as GDC for ASL. Moreover, highly reduced producing cost could be achieved.

**Paper Size: A4 (21.0 x 29.7 cm)**
**Margins**
Top: 30.0 mm
Bottom: 30.0 mm
Sides: 30.0 mm

# ZIF Encapsulation: Simple Route for Synthesis of PtCo Intermetallic Nanoparticles for Highly Durable Oxygen Reduction Reaction Catalyst

Ji Mun Yoo, Dong Young Chung, Heejong Shin, Yung-Eun Sung
*Center for Nanoparticle Research, Institute for Basic Science*
*School of Chemical and Biological Engineering, Seoul National University*
*Seoul 151-742, Korea*
*ysung@snu.ac.kr*

Polymer electrolyte membrane fuel cell (PEMFC) has been one of the most promising energy conversion devices because of its high efficiency, high power density and zero emission. In spite of many advantages of PEMFC, its actual commercialization has been seriously hindered by high cost and incomplete durability. Especially, Pt nanoparticles supported on carbon have been conventionally employed to improve kinetics of sluggish oxygen reduction reaction (ORR) on cathode, but its high cost and lack of durability remain to be solved. Therefore, the main issue in fuel cell field is to reduce amounts of Pt usage or replace Pt while increasing activity and stability. A number of catalysts have been reported to show high activity by alloying Pt with other metals, especially transition metals like Fe or Co, or synthesizing N-doped carbon materials. Recently, Stamenkovic group reported synthesis of $Pt_3Ni$ nanoframe catalyst whose mass activity is about 35 times higher than Pt/C.[1] Moreover, Huang group reported even more active ORR catalyst with mass activity 60 times higher than Pt/C this year.[2] As a result, it has been shown that it is possible to obtain high enough activity with very low amounts of Pt; however, durability problem still remains because catalysts are exposed to dynamic environment in real operating condition: low pH, high temperature and humidity, and variable potential.

In real operating PEMFC, catalysts are exposed to very low pH where transition metals alloyed with Pt are easily dissolved. Considering variable potential during operation, dissolution of transition metals and decrease of activity can be accelerated. In this point of view, intermetallic catalyst has attracted many researchers because of its high stability in real operating condition. Because of its stoichiometric composition and arranged crystallographic structure, it shows very high resistance to degradation compared with random alloy materials. However, since heat treatment under reductive atmosphere can generate aggregation problem of nanoparticles, many researches employed strategies of coating physical barrier on nanoparticles. Nevertheless, these strategies need additional steps to coat and remove the barrier layer.

Here, we report a new strategy to synthesize intermetallic catalyst with simple process. To make PtCo intermetallic nanoparticles, Pt nanoparticles decorated with polyvinylpyrrolidone (PVP) are encapsulated in zeolitic imidazolate framework-67 (ZIF-67). ZIF-67 can act as both Co supplier and physical barrier between nanoparticles, since ZIF-67 is made up of Co ions and imidazole which turns into N-doped carbon after heat treatment. After one-step heat treatment under $H_2$ atmosphere, synthesized catalysts are characterized with high-resolution transmittance electron microscope, X-ray diffraction pattern, and X-ray photoemission spectroscopy. High catalytic performance and stability of the catalyst are analyzed by rotating disk electrode and single cell test.

Key word: PEMFC, ORR, durability, intermetallic, MOF

---

[1] V.R. Stamenkovic et al. Science, 2014, 343, 1339-1343
[2] Y. Huang et al. Science, 2015, 348, 1230

# Morphological Effect on Product Selectivity of Electrochemical Reduction of $CO_2$ on Cu Catalyst

Sujik Hong [a], Seunghwa Lee [a], Jaeyoung Lee [a,b*]

[a] *Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea.*
[b] *Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies, GIST, Gwangju, 500-712, South Korea.*

*Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea.*
*jaeyoung@gist.ac.kr*

There have been significant studies to reduce concentration of atmospheric carbon dioxide ($CO_2$) due to its contribution to climate change. Among a variety of techniques for reducing $CO_2$ accumulation, electrochemical conversion method attracts great attention as one of the promising techniques. $CO_2$ can be electrochemically converted into a wide spectrum of organic molecules. For example, formic acid (HCOOH) is primarily generated on *sp* group metals (e.g. Sn, Pb and Zn) and *d* group metals (e.g. Ag and Au) catalyze selectively electrochemical reduction of $CO_2$ to CO. In particular, Cu is known as a unique catalyst for electrochemical reduction of $CO_2$ to hydrocarbons such as methane ($CH_4$) and ethylene ($C_2H_4$) [1]. However, the poor controllability of product selectivity hinders further effective utilization of the $CO_2$ electroreduction. Although the product selectivity is strongly dependent on the type of catalyst material, several electrolytic conditions such as electrolyte, pH, $CO_2$ pressure and surface morphology have been also demonstrated as critical factors [2]. Herein, we intensively study a correlation between morphological feature and product selectivity of $CO_2$ electroreduction on Cu catalyst supported by gas diffusion layer (GDL) [3-4]. We observed different product distributions depending on the surface morphology of Cu catalysts that were prepared by electrodeposition controlling experimental conditions such as supporting electrolyte, pH and applied potential [5]. Electrochemical $CO_2$ reduction tests were carried out on a pair of catalysts at various cathodic potentials and subsequently reaction products were analyzed.

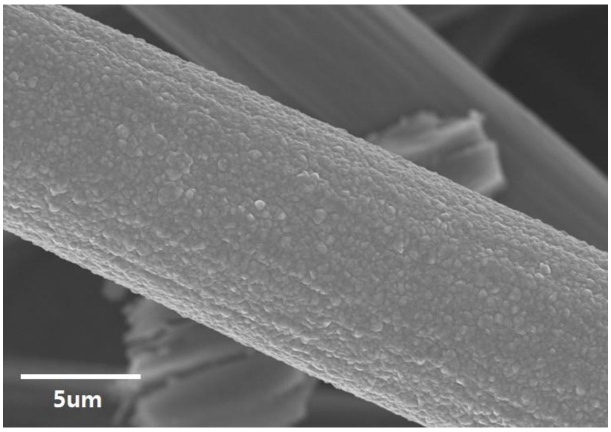


Figure 1. SEM image of as-prepared Cu catalyst electrode

References

[1] J. Lee. *et al.*, *Chem. Asian J.*, 2009, **4**, 1516
[2] Y. Hori, Mod. Aspects Electrochem., 2008, **42**, 89
[3] D. Kim, S. Lee. *et al.*, *Phys. Chem. Chem. Phys.*, 2015, **17**, 824
[4] S. Lee. *et al.*, *Angew. Chem. Int. Ed.*, 2015, **54**, 1
[5] D. Grujicic, B. Pesic, *Electrochimica Acta,* 2002, **47,** 2901

# Systematic Studies of Binder Free Non-Noble Electrocatalytic Disc Materials

Saskia Buller, Marius Heise-Podleska, Robert Schlögl
*Max Planck Institute for Chemical Energy Conversion*
*Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany*
*saskia.buller@cec.mpg.de*

It is well-known that efficient, cheap, abundant, environmentally friendly alternative electrode materials for water splitting are required to overcome a global demand for energy conversion and storage systems. Multi-walled carbon nanotubes (MWCNT) have intrinsically high surface areas and the ability to be chemically/physically modified keeping suitable conductivities. Modification of the MWCNT leads to functional groups that can act as anchor for the deposition of metals. Therefore they are often used as support material for catalytic active species. Promising active candidates are manganese oxides which are able to replace non-abundant noble metals [1].

Hydrothermal carbons (HTC) are likewise potential support materials for catalytic active species, containing definable functional groups due to the bottom-up synthesis process [2]. Oxygen as well as nitrogen containing groups can be implemented by adding different precursor. In comparison to MWCNT the surface areas as well as the conductivities are less well marked. Nevertheless, the big advantage of HTC materials is that mechanically stable disc materials can be obtained, which implies that additional binder for electrocatalytic applications are not needed.

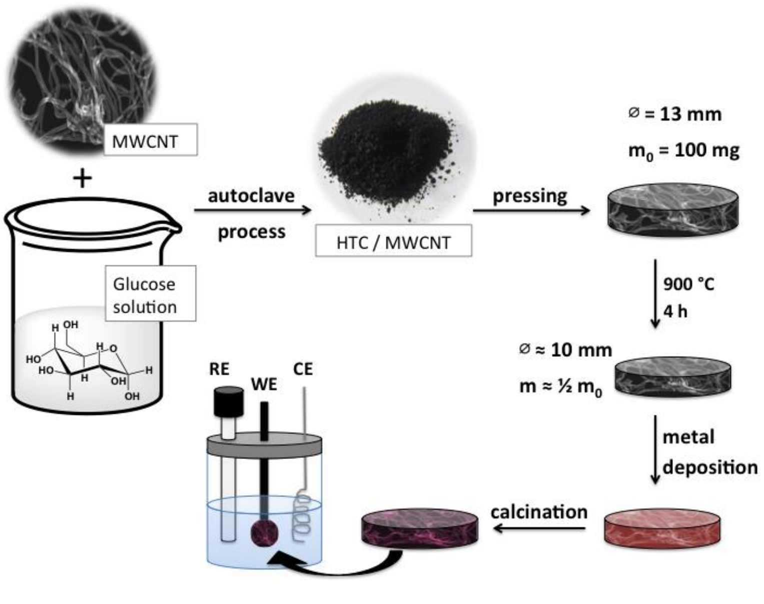
Compounds of MWCNT and HTC combine the beneficial properties of both support materials. Stable disc materials with high aspect ratios, adequate conductivity and homogeneously distributed functional anchoring groups are the consequence.

## Electrode synthesis

Compounds of MWCNT embedded in HTC were synthesized in autoclaves. Different oxygen as well as nitrogen functional groups could be integrated in the HTC structure while adding urea as precursor in the bottom-up approach. Systematic studies of quantitative effects of deposited manganese oxides as well as influence of doping with calcium or cobalt oxides are performed.

## Electrocatalysis

Electrocatalytic tests could be fulfilled with the binder free non-noble disc electrode materials applying appropriate circumstances like in commercial electrolyzers. Long-term stability tests reveal the scope of applicability of the materials.



## References

[1] K. Mette, A. Bergmann, J.-P. Tessonnier, M. Haevecker, L. Yao, T. Ressler, R. Schloegl, P. Strasser, M. Behrens, ChemCatChem, 4 (2012) 851.
[2] S. Reiche, N. Kowalew, R. Schloegl, ChemPhysChem, 16 (2015) 579.

# A facile synthesis and electrochemical analysis of vanadium nitride for electrochemical capacitors

Hae-Min Lee[1], Hwang Bo Jung[2], and Chang-Koo Kim[*2]

*[1] Institute of NT. IT Fusion Technology,*
*[2] Department of Chemical Engineering and Division of Energy Systems Research,*
*Ajou University, Suwon 443-749, Korea*

**changkoo@ajou.ac.kr*

Supercapacitors are generally classified according to their working mechanisms: (i) electric double-layer capacitor (EDLC), with the capacitance attributed to charge accumulation at the electrode-electrolyte interface and (ii) redox capacitor, which has a pseudo-capacitance due to the oxidation-reduction reaction. Various materials have been investigated as an electrode in ESs, including carbon materials, conducting polymers, and transition metal oxides. There is increasing interest in the development of advanced electrode materials having high specific surface areas and conductivity.

Transition metal nitride such as titanium nitride (TiN), molybdenum nitrides (MoN and $Mo_2N$), and vanadium nitride (VN) have received much attention as alternatives to metal oxides in electrochemical supercapacitor applications because of their excellent electrical conductivity and specific capacitance [1-3]. Especially, VN is considered to be a good candidate for electrode materials due to its theoretical capacity (>500F/g), reversible and fast redox Faradic response, and high hydrogen evolution overpotential [4].

Technique for producing vanadium nitride for supercapacitor materials includes sol-gel method and hydrothermal method. Vanadium nitride was usually obtained by calcining a mixture of melamine and vanadium oxide ($V_2O_5$) xerogel at 800 ~ 1000 ℃ under $N_2$ atmosphere in a furnace. However, this method is complicated and inconvenient. A more effective method to prepare vanadium nitride for supercapacitors is chemical precipitation.

In this work, a novel and simple method to prepare vanadium nitride using vanadium chloride precursor and urea was developed. The synthesized samples were characterized by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). In addition, the electrochemical analyses were made using cyclic voltammetry, galvanostatic charge-discharge tests, and impedance tests.

[1] S. Dong, X. Chen, L. Gu, X. Zhou, H. Xu, H. Wang, Z. Liu, P. Han, J. Yao, L. Wang, G. Cui and L. Chen, ACS Appl. Mater. Interfaces, 3(1) (2011) 93.
[2] T.C. Liu, W. G. Pell and B. E. Conway, J. Electrochem. Soc., 145(6) (1998) 1882.
[3] R. L. Porto, R. Frappier, J. B. Ducros, C. Aucher, H. Mosqueda, S. Chenu, B. Chavillon, F. Tessier, F. Chevire and T. Brousse, Electrochim. Acta, 82 (2012) 257
[4] X. Lu, T. Liu, T. Zhai, G. Wang, M. Yu, S. Xie, Y. Ling, C. Liang, Y. Tong, Y. Li, Adv. Energy Mater. 4 (2014) 1300994.

# Synthesis of Co-containing metal-organic frameworks and their application to cathode materials in Zn-air batteries

Kangjong Kim[a], Ho-Jung Sun[c], Joongpyo Shim[b], Gyungse Park[a,]*
*Department of [a]Chemistry, [b]Nano & Chemical Engineering, and [c]Material Science, Kunsan National University*
*#558 Daehangro, Gunsan, Jeonbuk, 54150, Korea*
**parkg@kunsan.ac.kr*

Lithium secondary batteries have shown significantly high performance, but they should overcome several disadvantages for the application to electric vehicles; two of them are safety and cost. Although zinc-air rechargeable batteries (ZARB) have received much attention due to its low cost, high stability, non-explosion and environmental benignity, they have not shown any advantages because their poor cycleability, high solubility of zinc compounds and low rate of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) of air electrode. Platinum has been well known to best catalyst for the ORR, but it has moderate activity for the OER. The catalytic activities of perovskite type materials, such as lanthanum based oxide, and related compounds have also received much attention because of relatively high catalytic activity for the ORR & OER, and low cost synthetic process.

In this study, the materials prepared from Co-containing metal-organic framework (Co-MOF) as a new catalyst were investigated for ORR and OER in alkaline solution. MOF consist of transition metal surrounded by organic molecules. MOF is highly porous material having micro pore in powder. Therefore, it has the possibility for application to electrode materials in batteries and fuel cells.

To prepared Co-MOF, a mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.640 g, 2.2 x $10^{-3}$ mol), 1,4-bdc$H_2$ (0.300 g, 1.8 x $10^{-3}$ mol) and DMF (10 mL) was stirred for 30 min in air at room temperature. The mixture was transferred and sealed in a Teflon reactor (15 mL) and heated at 100 °C for three days. After the mixture cooled to room temperature, purple hexagonal-plate crystals of $[Me_2NH_2]_2[Co_3(1,4\text{-bdc})_4] \cdot 4DMF$ ($Me_2NH_2$ = protonated dimethylamine, 1,4-bdc$H_2$ = 1,4-benzenedicarboxylic acid and DMF = *N*,*N*′-dimethylformamide) were obtained. The Co-MOF powder was heat-treated under $N_2$ atmosphere at different temperatures.

The porous and bifunctional electrodes were prepared using the following process: the Co-MOF powders were mixed with carbon black and Ni powder as the conductive agent and 60% PTFE dispersion as the binder in a solution of isopropyl alcohol. The mass ratio of the catalyst, conductive agent, and PTFE was 20:70:10. The resulting mixture was rolled on glass plate and dried at 60°C for 2h. The obtained sheet was transferred onto a wet-proofed carbon paper by pressing at 10 MPa for 1 min at 350 °C. The bifunctional electrodes were electrochemically characterized for the ORR and OER in an 8M KOH solution using a three-electrode system. The working electrode was cut into a round shape with a cross-sectional area of 1 $cm^2$. The counter and reference electrodes were a Pt mesh and a Zn wire with a diameter of 1 mm, respectively. The cell potential was measured using a linear sweep voltammetry (LSV) method at a scan rate of 1 mV s-1. The scan was conducted between 0.5 and 2.5 V vs. $Zn/Zn^{2+}$.

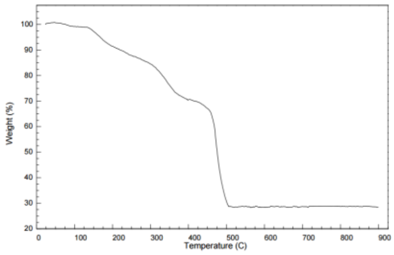


Fig. TGA of Co-MOF under $N_2$ atmosphere

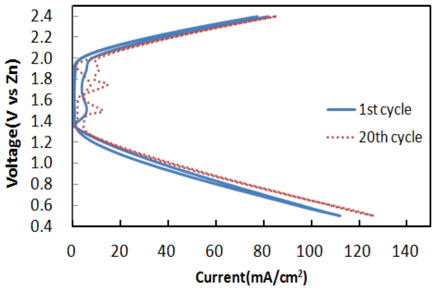


Fig. IV curves of electrode prepared from Co-MOF for ORR and OER in 8M KOH.

References

1. Zhou, H.-C.; Long, J. R.; Yaghi, O. M. Chem. Rev. 2012, 112, 673.
2. Yoon, M.; Shim, J.; Park, G. Bull. Korean Chem. Soc. 2014, Vol. 35, No. 9, 28472.
3. K. Lopez, G. Park, H.-J. Sun, J.-C. An, S. Eom, J. Shim, J. Appl. Electrochem., 45, 313-323 (2015).

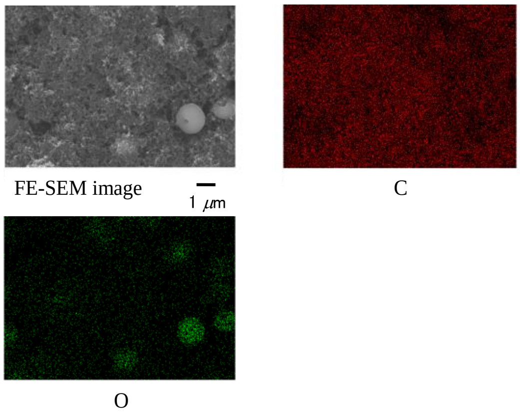
# Effects of Pore Volume on Discharge Reaction of Carbon Electrodes for Lithium-air Secondary Battery

Tatsuya Takeguchi [*, **], Nozomi Matsuhashi [*, **], Yoshihiro Kadoma[*, **], Akari Matsutomo[*, **],
Miyuki Kojima[*, **], and Koichi Ui[*]
[*] *Department of Frontier Materials and Function Engineering, Graduate School of Engineering,*
*Iwate University, 4-3-5 Ueda, Morioka, Iwate, 020-8551, Japan*
[**] *ALCA-SPRING, JST, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan*
*takeguch@iwate-u.ac.jp*

**[Introduction]** Lithium-air battery has attracted much attention as large storage secondary battery due to its high theoretical storage capacity (5200 Wh kg$^{-1}$). However, the reversible capacity is limited because the discharge products cover the oxygen diffusion path in the air electrode. The influence of the pore structure of carbon materials on the electrochemical characteristics is not clear although the carbon materials are widely studied as air electrodes for lithium-air secondary battery. In this study, we have prepared the carbon electrodes using carbon materials with different pore volume, analyzed the discharge products, and investigated the electrochemical characteristics.

**[Experimental]** The carbon materials (ketjen black (KB) and acetylene black (AB)) were mixed with PVdF (carbon : PVdF = 93 : 7). After coating on the carbon paper as a current collector(amount 1 mg, electrode area 2.0 cm$^2$), it was dried at 80 °C for one night in an oven to obtain carbon electrodes. The R2032 coin cell was assembled in an Ar-filled glove box. It consisted of the prepared carbon electrode, lithium foil, 1 mol dm$^{-3}$ $LiCF_3SO_3$/TEGDME, and Whatman glass filter GF/A as the separator. The carbon electrodes were analyzed by FE-SEM, EDX, XRD, and the nitrogen adsorption method. For the electrochemical measurement, the discharge-charge tests were carried out (current value: 100 mA, voltage range: 2.0-4.5 V, measured temperature: 25 °C, and atmosphere: dry air).

**[Results and Discussion]** From discharge-charge tests, the AB electrode showed the voltage shoulder in the first discharge curve. On the other hand, the KB electrode showed the smooth discharge plateau and the good cycle performance compared to the AB electrode. The FE-SEM observations indicated that the spherical products deposited on the surface of the KB and AB electrodes after 6 h discharge. Fig.1 shows the EDX mappings of the KB electrode after the 6 h discharge. The discharge product distribution matched with not the carbon distribution but the oxygen distribution, suggesting the discharge products were oxides. From XRD patterns, the $Li_2O_2$ was generated after the 6 h discharge. Fig. 2 shows the pore size distributions of the KB and AB electrodes before and after 6 h discharge. The pore volume of the KB and AB electrodes decrease after the 6 h discharge. The KB electrode shows the larger pore volume compared to the AB electrode after the 6 h discharge. From these results, it was found that the pore volume of carbon electrode had an influence on the discharge profile.



FE-SEM image

C

O

Fig.1. FE-SEM images and EDX mappings of the KB electrode after the 6 h discharge.

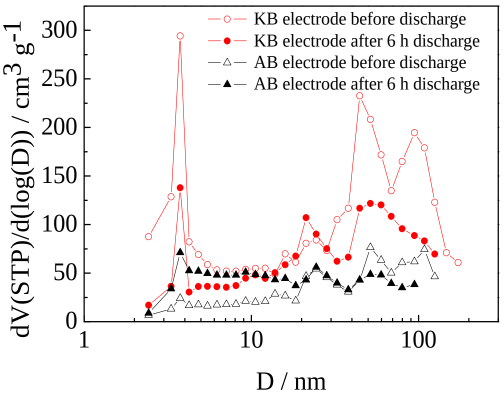


Fig.2. Pore size distributions of the KB and AB electrodes before and after the 6 h discharge.

**[References]**
1) Y. Gao *et al.*, *Int. J. Hydrog. Energy*, **37**, 12725 (2012).
2) T. Cetinkaya *et al.*, J. *Power Sources*, **267**, 140 (2014).

**[Acknowledgments]**
This research was partially supported by ALCA-SPRING, JST.

# Chemical Energy Storage by Methanol Synthesis at Dynamic Change of Reaction Conditions

M.V. Bukhtiyarova, R. Schlögl
*Max Planck Institute for Chemical Energy Conversion*
*45470 Germany, Mülheim a.d. Ruhr, Stiftstr. 34-36*
*Marina.Bukhtiyarova@cec.mpg.de*

## Introduction

Many industrial exhausts contain considerable concentration of carbon dioxide. Conversion of $CO_2$ to methanol by its catalytic hydrogenation is recognized as a process to mitigate atmospheric $CO_2$ level. The required hydrogen can be obtained by water electrolysis. The energy can be provided by suitable energy sources such as sun, wind and hydroelectric. Methanol synthesis can be an efficient way to store this energy [1]. Methanol can be used as a fuel in the engines because of its efficient combustion. Moreover, using methanol as a fuel allows one to reduce emissions of undesirable toxic products [2].

## Experimental/methodology

Methanol synthesis is performed over a commercial $Cu/ZnO/Al_2O_3$ catalyst in a flow type fixed bed reactor. Effects of temperature, pressure and molar ratio of $H_2$:$CO_2$ on catalyst performance are investigated in this study.

## Results and discussion

The first measurements are carried out at pressure of 30 bars, $H_2/CO_2$ = 3:1 and different temperatures. It is shown that $CO_2$ conversion and methanol yield increase with temperature since the reaction rate is higher at higher temperature. However, selectivity to methanol decreases. This fact can be explained by two competitive reactions: methanol synthesis ($CO_2 + 3H_2 = CH_3OH + H_2O$) and reverse water gas shift reaction ($CO_2 + H_2 = CO + H_2O$). These reactions have different thermal effects, high temperature results in higher contribution of the last one.

The catalyst should reveal high stability. The experiments performed at different temperature show the decrease in the methanol production rate in first 40 - 70 hours, after that the catalyst works stable (Fig.1a). The results of stability tests show that the catalyst can operate in the stable way without presence of carbon monoxide in the gas feed. The investigation of the dynamics of the pressure change is done. The time on stream measurements are performed with switch of the pressure between 30 and 50 bars. It is seen that long time is needed for achievement of the steady-state performance of the catalyst. There is continuous decrease in methanol production rate (Fig. 1b).

The effect of $H_2$:$CO_2$ molar ratio on $CO_2$ conversion and $CH_3OH$ yield is investigated. It can be observed that $CO_2$ conversion increases with $H_2/CO_2$ ratio at every specific temperature. The equilibrium of methanol synthesis reaction shifted to the side of the products because of increase of the $H_2/CO_2$ at constant total flow. The stability test is performed at higher ratio than stoichiometric one.

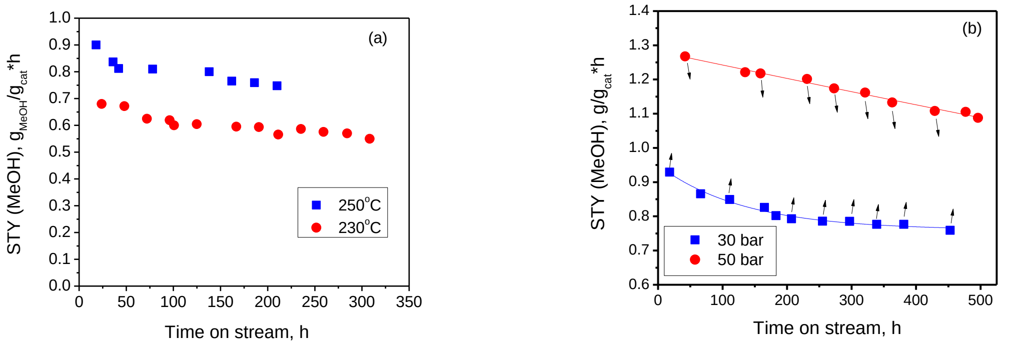


**Figure 1.** Time on stream measurements at $H_2$:$CO_2$ = 3:1 (a) T = 230 and 250°C, P = 30 bars; (b) T = 250°C, P = 30 and 50 bars.

## Reference

[1] G.A. Olah, Angew. Chem. Int. Ed. **2005**, *44* 2636 – 2639
[2] Methanol: the clear alternative for transportation, 2011. Available from http://www.methanol.org

# Scaffold-like Titanium Nitride Nanotube with a Highly Conductive Porous Architecture as a Nanoparticle Catalyst Support

Heejong Shin, Dong Young Chung, Ji Mun Yoo, Yung-Eun Sung*
*Center for Nanoparticle Research, Institute for Basic Science (IBS),*
*School of Chemical and Biological Engineering, Seoul National University*
*Seoul 151-742, Korea*
**E-mail: ysung@snu.ac.kr*

Nanoparticle-based electrocatalysts have been intensively investigated for the fuel cell applications over the last decade. However, the oxidation of carbon catalyst support materials is a big concern for long term stability of the fuel cell. Here we report on the designed synthesis of scaffold-like porous titanium nitride (TiN) nanotube (NT) as a catalyst support for Pt to facilitate the oxygen reduction reaction. Bulk titanium nitride, which is known as an electrically conductive material, is compatible with metals. Although nanoscale catalyst particles and support materials with high surface are generally favored to increase the number of active sites on the catalyst surface, owing to a series of nanoparticle boundaries acting as electron reservoirs and traps. In contrast with TiN nanoparticles, a newly designed scaffold-like porous TiN NT which is analogous to the shape of the one dimensional porous human spine exhibits the high electrical conductivity in spite of having a similar surface area with TiN nanoparticles. The electrical conductivity of TiN NT is 30-fold higher than that of spherical TiN nanoparticles. The electrochemical oxygen reduction measurements between porous TiN NT and TiN nanoparticles after Pt loading clearly exhibit the superiority of TiN NT as a catalyst support. The results from various electrochemical measurements suggest that the electrocatalytic activity per site did not change from a kinetic viewpoint, but the total amount of “utilizing site” in the catalyst layer on the electrode decreased. The Pt/TiN NT composite catalyst exhibited higher activity and stability compared to TiN nanoparticles as well as conventional Pt/C catalysts. The Pt nanoparticle deposited on our ‘Scaffold-like’ TiN nanotubes shows excellent catalytic performance with higher mass activity without any auxiliary carbons. Moreover, we accomplished the accelerated durability test (ADT) for 10,000 cycles without significant activity loss (97 % of its initial electrochemically active surface area (ECSA) remained after ADT test but the standard Pt/C only had 55 % of initial ECSA), demonstrating that this material is highly promising for the practical fuel cell applications. X-ray spectroscopy results verified the strong metal-support interaction between Pt nanoparticles and the TiN NT support. This new approach opens a reliable path for designing new transition metal oxides, nitrides, or carbides as catalyst supports for use in a wide range of energy conversion applications.

# Electrochemical Characterization of Ag deposited on $La_{1-x}Sr_xCoO_3$ for ORR and OER in an Alkaline Solution

Kareen J. Lopez[a], Gyungse Park[b], Ho-Jung Sun[c], Joongpyo Shim[a,*]
*Department of [a]Nano & Chemical Engineering, [b]Chemistry, and [c]Material Science & Engineering,*
*Kunsan National University*
*#558 Daehangro, Gunsan, Jeonbuk, 54150, Korea*
**jpshim@kunsan.ac.kr*

Although zinc-air rechargeable batteries (ZARB) as alternative power source of lithium rechargeable batteries have received much attention due to its low cost, high stability, non-explosion and environmental benignity, they have not shown any advantages because their poor cycleability, high solubility of zinc compounds and low rate of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) of air electrode. Platinum has been well known to best catalyst for the ORR, but it has moderate activity for the OER. The catalytic activities of perovskite type materials, such as lanthanum based oxide, and related compounds have also received much attention because of relatively high catalytic activity for the ORR & OER, and low cost synthetic process.

Lanthanum strontium cobaltite, $La_{1-x}Sr_xCoO_3$, (LSCO) is among the perovskites observed to have high potential as a bifunctional catalyst for ORR and OER. The interesting properties and low-cost production of LSCO makes it a potential substitute for Pt and other noble metal-based catalysts. Silver metal, Ag, a low-cost and abundant, but also considered a noble metal, is regarded as a good replacement for expensive Pt electrocatalysts because of its high catalytic activity. The excellent ORR catalytic activity of Ag catalyst and the bifunctional catalytic activity of LSCO can be a promising hybrid catalyst that can be used for ORR and OER. Ag nanoparticles are chemically deposited on LSCO powder. This study determines the electrocatalytic performance of both Ag metal and LSCP catalyst in an alkaline solution.

The porous and bifunctional electrodes were prepared using the following process: the Ag/LSCO powders were mixed with carbon black and Ni powder as the conductive agent and 60% PTFE dispersion as the binder in a solution of isopropyl alcohol. The mass ratio of the catalyst, conductive agent, and PTFE was 20:70:10. The resulting mixture was rolled on glass plate and dried at 60ºC for 2h. The obtained sheet was transferred onto a wet-proofed carbon paper by pressing at 10 MPa for 1 min at 350 ºC. The bifunctional electrodes were electrochemically characterized for the ORR and OER in an 8M KOH solution using a three-electrode system. The working electrode was cut into a round shape with a cross-sectional area of 1 $cm^2$. The counter and reference electrodes were a Pt mesh and a Zn wire with a diameter of 1 mm, respectively. The cell potential was measured using a linear sweep voltammetry (LSV) method at a scan rate of 1 mV s-1. The scan was conducted between 0.5 and 2.5 V vs. $Zn/Zn^{2+}$.

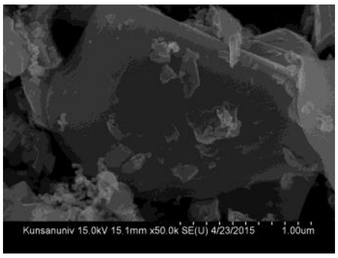


Fig. SEM image of Ag deposited on LSCO powder

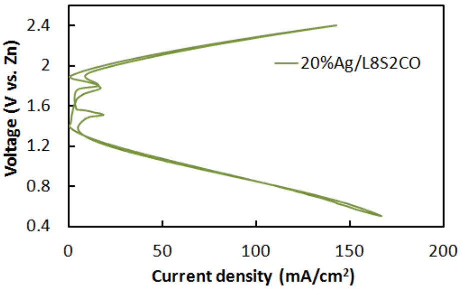


Fig. IV curves of Ag/LSCO electrode for ORR and OER in 8M KOH.

References
1. H.-C. Zhou, J.R. Long, O. M. Yaghi, Chem. Rev. 112, 673 (2012).
2. M. Yoon, J. Shim, G. Park, Bull. Korean Chem. Soc.35, 28472 (2014).
3. K. Lopez, G. Park, H.-J. Sun, J.-C. An, S. Eom, J. Shim, J. Appl. Electrochem., 45, 313-323 (2015).

# Fabrication of Thin Films on Anode Support with Surface Modification for High Efficient IT-SOFC by Dip-coating Method

Inyoung Jang,[1] Chanho Kim,[1] Sungmin Kim,[1] Heesung Yoon, [1,*] Ungyu Paik[1,*]
*Department of Energy Engineering, Hanyang University, Seoul, Republic of Korea, 133-791*
**e-mail address:* hsyoon64@gmail.com, upaik@hanyang.ac.kr

Solid oxide fuel cell (SOFC) is expected to be a major future energy generating system due to its high efficiency and low pollutant emission. A lot of studies to fabricate the thin films in solid oxide fuel cells (SOFC) have been carried out for many years, and the most adequate method for mass production is expected to be a dip-coating method because of their cost-effective and simple procedure. In this paper, dip-coating method was conducted on 10cm x 10cm size of anode support layer (ASL). Furthermore, roughness enhanced layer (AFL-rough layer) was added between anode functional layer (AFL) and electrolyte to increase the number of triple phase boundary for SOFC efficiency. Carbon black particles were used for formation of rough surface between two layers. AFL, AFL-rough layer and electrolyte layer were successfully coated on the only one side of the ASL by just adding a very simple procedure. SEM results confirm that it has pore-free boundary condition between each layer and the thickness of dip coated layer was easily controlled with dipping times(2 ㎛~18 ㎛). Also, it was verified that surface area was increased between AFL and electrolyte because of AFL-rough layer. The performance of SOFC that has AFL-rough layer was compared with SOFC that has flat AFL layer and it shows higher power density then the flat one. Also, the area specific resistance measurement was done to compare the effect of rough surface between AFL and electrolyte layer.

# Electrocatalysis-integrated Strategy for Lithium Recovery from Industrial Wastewater

Seoni Kim, Jiye Kim, Jaehan Lee, Seonghwan Kim, Jeyong Yoon*
*School or Chemical and Biological Engineering, College of Engineering, Institute of Chemical Process,*
*Asian Institute for Energy, Environment & Sustainablility(AIEES), Seoul National University*
*alichino@snu.ac.kr, jeyong@snu.ac.kr*
*Gwanak 1,Gwanak-ro, Gwanak-Gu, Seoul, 151-742, Korea*

The various kinds of industrial wastewater contains not only toxic pollutants, but also various valuable resources. Therefore, the interest in resource recovery including valuable metal ions and essential nutrients from the wastewater has emerged. Especially, the wastewater of a battery recycling plant contains considerable amount of lithium ions, because the battery recycling process is not so effective to lithium ion recovery.

However, we have limited area in the battery recycling plant, so there are some constraints to make efficient process. The process should be simple, fast and applicable in small site. Also, it should be a cost-effective and environmentally benign process. Based on this requirements to recover lithium efficiently from the wastewater, electrochemical system was selected.

On the other hand, this wastewater also contains organic pollutant which need to be decomposed before discharge. Therefore the additional water treatment process should be done after the resource recovery process. These make the process more complex and hard to apply in the real situation.

Herein, we propose an electrocatalysis-integrated lithium recovery system, which can recover lithium and remove organic pollutant together. By this approach, the post-treatment of the wastewater could be more simple, which makes the process more applicable.

# Strontium Transition metal oxyhalide based electro-catalysts for water oxidation in alkaline solution

**Prabhakarn Arunachalam**,[a] Mohammed A Ghanem,[a] Abdullah Al Amayosuf,[a] Mark T Weller[b]

[a]*Department of Chemistry, College of Sciences, King Saud University, Riyadh, Kingdom of Saudi Arabia.*
*parunachalam@KSU.EDU.SA*
[b]*Department of Chemistry, University of Bath, Claverton Down, Bath, UK*

Electrochemical water splitting via alkaline water electrolysis is currently an extremely active research area due to the need for the development of a clean, reliable and sustainable method for large scale production of to produce hydrogen fuel [1-2]. Oxygen evolution reaction (OER) is important reaction in water electrolysis and energy conversion and considerable research efforts have been focused on the development of novel anode materials that has lowest possible overpotential, small Tafel slope, high durability and inexpensive [3]. An effective electrocatalyst with a small Tafel slope and reduced onset potential can enhances the OER and thereby improves the energy conversion process. To date, the most efficient catalysts for the OER are based on $IrO_2$, $RuO_2$ and Pt electrocatalysts but the low abundance and high coast of those metals limits their practical usefulness in application as an as anode for water electrolysis [4]. Perovskites are of great interests for developing noble metal-free alternatives and provide improved activity and advantage over precious metal based catalysts in terms of low price and high durability at high temperature. Among the studied perovskites, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF5582) based perovskites have been highlighted for its bifunctional nature of oxygen reduction reaction (ORR) and OER reactions, even though the structure changes to amorphous during the electrochemical reactions [5]. Considerable research effort has been carried out to develop the efficient bifunctional perovskite based materials. In the present study, we report the OER activities of strontium transition metal oxyhalide based oxyhalides materials in addition to the bifunctional activity of the catalysts for oxygen reduction reaction. The OER activity was studied for various kinds of oxygen sites in transition based oxyhalides, $Sr_4M_3O_8Cl_2$, $Sr_2MO_2Cl_2$, $Sr_2MO_3Br$, and $Pb_4M_3O_8Br$.

All Electrochemical measurements were performed in a one compartment cell, three electrode cells with a 3.0 mm polished diameter Au as working electrode, a platinum wire and saturated calomel as counter and reference electrode respectively. The present catalysts are stable under OER reactions based on the measurements from cyclic voltammetry and OER activity enhanced with the enhancement of ORR activity in the $O_2$ saturated alkaline medium. The electrochemical investigations show that the presence of more oxygen deficient in $Sr_2MO_2Cl_2$ oxide significantly enhances the oxygen evolution at 0.8 V vs SCE more than other perovskite oxides with less oxygen deficient electrocatalysts. The concentration of evolved oxygen was monitored by oxysense measurements and the OER activities of strontium transition metal oxyhalide based catalysts. The catalytic activity of the strontium metal oxyhalide catalyst was investigated for electrochemical water splitting in alkaline solution and found to be the most active, with a lower onset potential and reasonable current density than $Co_3O_4$ and $IrO_2$ catalysts. The water splitting activity of the strontium transition metal oxyhalides was further enhanced by increasing the alkaline solution concentration with holding a superior stability during the long term of electrolysis. This present catalysts hold promise as a non-precious and cost-effective anode material for water electrolysis. This work demonstrates that the oxygen-deficient transition metal oxyhalide is a new class of high performance electrocatalysts for OER in water splitting.

## REFERENCES

[1] P. Häussinger, R. Lohmüller, A. M. Watson, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co., 2011.
[2] J. P. Zheng, P.J. Cygan, T. R. Jow, Journal of the Electrochemical Society, 142 (1995), p. 2699.
[3] G. W. Crabtree, M. S. Dresselhaus, M. V. Buchanan, Phys. Today 57 (2004), p. 39.
[4] Y. Lee, J. Suntivich, K. J. May, E. E. Perry, S. H. Yang, J. Phys. Chem. Lett., 3 (2012), p. 399.
[5] J. Suntivich, H Gasteiger, N Yabuuchi, H Nakanishi, B. Goodenough, Y Shao-Horn, Nat. Chem., 3, (2011), p546.

**ACKNOWLEDGMENTS** This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research center.

# Unravelling the Effect of Improved Mesoporous Structure in Fibrous Carbon for Oxygen Evolution Reaction

Jaehoon Jeong[a], Dongyoon Shin[a], Xianghua An[a], and Jaeyoung Lee[a,b,*]

*[a]Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea.*
*[b]Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies, GIST, Gwangju, 500-712, South Korea.*
*jaeyoung@gist.ac.kr*

Since calls for high efficient, cheap, and renewable energy sources have been mounted as an alternative of petroleum fuel, there are a lot of movements to develop effective energy conversion and storage systems such as water electrolysis and metal-air battery. Even though the water splitting is considered to be a practical and environmentally friendly approach to generate pure hydrogen, it is well known that slow rate of oxygen evolution reaction (OER) highly reduces the performance. Therefore, effective electro-catalyst is essential to trigger faster reaction. Noble metals, such as iridium (Ir) and ruthenium (Ru), have been known as the best electro-catalyst for OER, but these have cost-efficiency and durability problems due to metal dissolution under the oxidative condition during water splitting process. For these reasons, the necessity to seek new alternative electro-catalyst has been emphasized, and transition metal based catalysts recently have been got attraction due to the possibility to utilize in alkaline media. In this study, we suggest that improved mesoporous structures that are naturally and artificially created during heat treatment step affect to OER performance. In particular, the mesoporous structures around 3-9 nm might be responsible for the OER activity rather than the total amount of metal in Me-CNFs. Overall, this could lead better understanding to transition metal based water oxidation catalysts, which could be extended to the preparation of non-metal OER electro-catalyst with excellent activity and stability for energy efficient chemical energy storage and conversion cells in alkaline media.

# Activity and Stability of Hierarchical Microporous-Mesoporous Carbon Supported Pt-Catalysts in PEMFC Application

Silver Sepp, Jaak Nerut, Kersti Vaarmets, Indrek Tallo, Heisi Kurig, Enn Lust
*Institute of Chemistry, University of Tartu*
*14a Ravila Str. 50411, Tartu, Estonia*
*e-mail: silver.sepp@ut.ee*

Proton exchange membrane fuel cell (PEMFC) is one of the most promising candidates as a clean power source in various applications. The instability of carbon supports in fuel cell working conditions is the major obstacle hindering the commercialization of PEMFCs. Therefore novel carbon supports are being sought for fuel cell application [1, 2]. Hierarchical microporous-mesoporous carbon supports were synthesized applying various conditions. Prepared materials exhibited high specific surface area, but they differed from one another in their structural properties, such as pore size distribution and the ratio of micro- and mesopores volumes [2, 3].

The platinum nanoparticles were deposited onto the carbon support using the sodium borohydride method. Thermogravimetric analysis, X-ray diffraction, low temperature nitrogen sorption and high resolution transmission electron microscopy methods were used to characterise the structure of synthesised materials. Prepared catalysts were used as cathodes in the single cell measurements. For comparison the experiments were also conducted using the most common commercial carbon Vulcan XC72 as the catalyst support. The polarization and power density curves were used to evaluate the activity of the materials synthesized. The electrochemically active surface area was used to estimate the contact surface of platinum nanoparticles and Nafion electrolyte. The resistance of electrolyte, polarization resistance and activation energy values have been calculated from electrochemical impedance spectroscopy data. It was found that synthesized carbon supports are suitable for PEMFC application due to their high catalytic activity and oxidation/reduction stability.

## References

[1] E. Härk, J. Nerut, K. Vaarmets, I. Tallo, H. Kurig, J. Eskusson, K. Kontturi, E. Lust, J. Electroanal. Chem. 2013, 689, 176-184.

[2] S. Sepp, E. Härk, P. Valk, K. Vaarmets, J. Nerut, R. Jäger, E. Lust, J. Solid State Electrochem. 2014, 18(5), 1223 – 1229.

[3] K. Vaarmets, J. Nerut, E. Härk, E. Lust, Electrochim. Acta 2013, 104, 216 - 227.

## Acknowledgements

This work was supported by Estonian Centre of Excellence in Research Project TK117T "High-technology Materials for Sustainable Development", Material Technology Program project No. 3.2.1101.12-0014, Material Technology Program project No. 3.2.1101.12-0019, Estonian Energy Technology Programme project No. SLOKT 10209T, Project of European Structure Funds 3.2.0601.11-0001, Estonian target research project IUT20–13 and ESF Grant ETF8865.

# Mesoporous Graphene as a Synergistic Electrocatalyst Matrix for High-Performance Hydrogen Evolution and Oxygen Reduction Reaction

Jingjing Xiao,[a] Yujie Liu,[a] Huiying Xu,[a] Lei Liao,[a] Hubert H. Girault,[b] and Baohong Liu [a,*]

[a] *Department of Chemistry, Fudan University, Shanghai 200433, China*
[b] *Laboratoire d'Electrochemie Physique et Analytique École Polytechnique Fédérale de Lausanne CH-1015 Lausanne, Switzerland*
*E-mail address：bhliu@fudan.edu.cn*

It has become more urgent and inspiring to find clean and cheap energy to meet the rapid increase in global demand in recent years. Functional carbon materials such as mesoporous graphene and reduced-graphene-oxide have been developed as electrochemical catalyst supports for energy applications owing to their good chemical stability and electrical conductivity, and high electrocatalytic activity.

As a clean and sustainable energy, hydrogen serves as one of the most promising candidates for replacing fossil-based fuels in the future. Lowering the overpotential of hydrogen evolution reaction (HER) is therefore of great importance. The catalysts morphology and electrical conductivity are the two key factors that influence electrocatalytic efficiency. Inspired by previous advances, we also present a highly active and stable electrocatalyst for hydrogen evolution based on *in situ* formation of $MoS_2$ nanoparticles on mesoporous graphene foams ($MoS_2$/MGF). The electrode reactions are characterized by electrochemical impedance spectroscopy and the reaction mechanism has been investigated.

Oxygen reduction reaction (ORR) at the cathode in fuel cells has also attracted considerable attention. To balance the anchoring sites and conductivity of the catalyst supports is a dilemma in ORR. Nitrogen-doped mesoporous graphene (N-MG) with large surface area, high porosity, and superior intrinsic conductivity has been developed to address this issue. Using N-MG as the backbone, a hybrid catalyst of $Co_3O_4$ nanocrystals embedded on N-MG ($Co_3O_4$/N-MG) was prepared for the electrocatalytic ORR in alkaline media. The $Co_3O_4$/N-MG showed high catalytic activity for the four-electron ORR, giving a more positive onset potential and a higher current density. With improved electrocatalytic activity and durability, the $Co_3O_4$/N-MG can be an efficient nonprecious metal catalyst and potentially used to substitute the platinum-based cathode catalysts in fuel cells and metal-air batteries.

Reference:
1. L. Liao, J. Zhu, X.Bian, L. Zhu, M. D. Scanlon, H. H. Girault and B.Liu, *Adv.Funct.Mater.*, 2013, **23**, 5326.
2. J. Xiao, X. Bian, L. Liao, S. Zhang, C. Ji, and B. Liu, *ACS Appl. Mater. Interfaces,* 2014, **6**, 17654.

# Time Stability Tests for Pt-Nanoclusters Modified Carbide Derived Carbons Catalysts in 0.5 M $H_2SO_4$ Solution

Kersti Vaarmets, Silver Sepp, Jaak Nerut, Enn Lust
*Institute of Chemistry, University of Tartu*
*Ravila 14A, Tartu, Estonia*
*e-mail: Kersti.Vaarmets@ut.ee*

Carbon supported platinum catalysts are widely used in PEMFC applications. The instability of these catalysts in harsh fuel cell working conditions is the main problem hindering the large-scale usage of the fuel cell technology in commercial applications [1].

Hierarchical microporous-mesoporous carbon supports C($Mo_2C$) were prepared from molybdenum carbide using high temperature chlorination method at different synthesis temperatures from 600 °C to 1000 °C. The Pt-nanoparticles were deposited onto the carbon support using the $NaHB_4$ method [2,3]. The X-ray diffraction, low temperature nitrogen sorption and thermogravimetric analysis (TGA) were used to characterize the catalysts prepared.

Corrosion and electrochemical-active surface area (ECA) changes of the platinum based catalysts supported onto carbon were evaluated using an accelerated durability test (ADT). The value of ECA and oxygen electroreduction reaction kinetics of the catalysts were determined after 10, 100, 1000, 3000, 10 000, 20 000 and 30 000 cycles (in oxygen (99.999%, AGA) saturated 0.5 M $H_2SO_4$ aqueous solution, from 0.6 V to 1.0 V vs RHE, at 50 mV $s^{-1}$) [4]. ECA was estimated in the solution saturated with nitrogen (99.999%, AGA) using cyclic voltammetry at different potential sweep rates from 30 to 1000 mV $s^{-1}$. The rotating disc electrode method was used to evaluate oxygen electroreduction kinetics in solution saturated with oxygen at rotation rate 1600 rev $min^{-1}$ and at potential scan rate 20 mV $s^{-1}$ within the region of potentials from 0.05 V to 1.05 V vs RHE.

The platinum content in the catalyst was determined before and after the ADT using electrochemical dissolution of platinum from the electrode in 6 M HCl solution. The content of Pt in the catalysts before the ADT was in a good agreement with the TGA data.

The main decrease in ECA took place during first 1000 cycles and the ECA value stabilizes thereafter. The half wave potential depends weakly on the number of cycles measured.

Electrochemical impedance spectra were obtained at 0.6 V vs RHE within ac frequencies from 0.01 to 10 000 Hz to determine the changes of the electrolyte resistance and capacitance values.

## References

[1] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345–352.
[2] K. Vaarmets, J. Nerut, E. Härk, E. Lust, Electrochimica Acta 104 (2013) 216–227.
[3] E. Lust, K. Vaarmets, J. Nerut, I. Tallo, P. Valk, S. Sepp, E. Härk, Electrochimica Acta 140 (2014) 294–303.
[4] U.S Department of Energy, Office of Energy Efficiency and Renewable Energy, Rotating Disk-Electrode Aqueous Electrolyte Accelerated Stress Tests for PGM Electrocatalyst/Support Durability Evaluation (2011).

## Acknowledgements

This work was supported by Estonian Centre of Excellence in Research Project TK117T "High-technology Materials for Sustainable Development", Material Technology Program project No. 3.2.1101.12-0014, Material Technology Program project No. 3.2.1101.12-0019, Estonian Energy Technology Programme project No. SLOKT 10209T, Estonian target research project IUT20–13 and ESF Grant ETF8865.

# Effect of Crystal Structure of $TiO_2$ Nanotube Array on Capacitive and Oxidant-generating Properties Formed by Electrochemical Self-doping

Seonggeun Lee[a], Choonsoo Kim[a], and Jeyong Yoon[a,*]

[a]*School of Chemical and Biological Engineering, College of Engineering, Institute of Chemical Process, Seoul National University (SNU), Gwanak-gu, Daehak-dong, Seoul 151-742, Republic of Korea*
*ibbal2523@naver.comr*

$TiO_2$ nanotube array (NTA) has emerged as one of the useful one-dimensional $TiO_2$ nanostructure in the various fields of energy conversion, storage and water treatment.[1] Nevertheless, the use of $TiO_2$ NTA as an electrode material has limited due to its semi-conductive nature. Although many efforts including metal/nonmetal doping and thermal hydrogen method have led to the enhanced metallic characteristic, their complicated processes has been considered as one of the obstacles for application of $TiO_2$ NTA as electrode materials. Recently, attention for $TiO_2$ NTA as electrode materials has been greatly increased with the electrochemical self-doping as the novel doping methods to enhance their electronic properties with coloration phenomenon. This coloration has been well known as the electrochromic effect which is attributed to the electron transfer reaction with small cations interaction in metal oxide. Many researches have successfully demonstrated the enhanced capacitive and oxidant-generating properties of electrochromic $TiO_2$ NTAs fabricated with the electrochemical self-doping. However, these previous studies have focused on the enhanced electrochemical properties of the electrochromic $TiO_2$ NTAs, and thus, the understanding of electrochromic $TiO_2$ NTAs has remained unclear.[2,3]

Therefore, the aim of this study was to examine the effect of crystal structure of $TiO_2$ nanotube on capacitive and oxidant-generating properties formed by electrochemical self-doping. According to the crystal structure of $TiO_2$ NTA, the electrochromic $TiO_2$ NTAs exhibited significantly different the capacitive and oxidant-generating properties. These results suggest the crystal structure can play a critical role to enhance the electrochemical properties of electrochromic $TiO_2$ NTAs.

We believe these results can offer deep understanding of these electrochromic $TiO_2$ NTA leading to the new opportunities for great success as a promising electrode material in application of supercapacitor and oxidant-generating anode.

## References

[1] P. Roy, S. Berger, P. Schmuki, $TiO_2$ nanotube: synthesis and applications, *Angew. Chem. Int. Ed.*, 50, 2904-2939 (2011)

[2] C. Kim, S. Kim, J. Choi, J. Lee, J. Kang, Y. Sung, J. Lee, W. Choi, J. Yoon, Blue $TiO_2$ nanotube array as an oxidant generating novel anode material fabricated by simple cathodic polarization, *Electrochim. Acta*, 141, 113-119 (2014)

[3] C. Kim, S. Kim, J. Lee, J. Kim, J. Yoon, Capacitive and oxidant generating properties of black-colored $TiO_2$ nanotube array fabricated by electrochemical self-doping, *ACS Appl. Mater. Interfaces*, 7, 7486-7491 (2015)

# Soft-template approach to One-pot synthesis of Mesoporous Fe/N/C for Non-precious metal catalyst of Oxygen reduction

Yeongdong Mun,[a] Min Jeong Kim,[b] Young-Eun Sung,[b] Jinwoo Lee[a]

[a] *Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH),*
*77 Cheongam-ro, Nam-gu, Pohang, Republic of Korea*
[b] *School of Chemical & Biological Engineering, Seoul National University,*
*1 Gwanak-ro, Gwanak-gu, Seoul, Republic of Korea*
*digitaly@postech.ac.kr*

Low-temperature operating fuel cell with polymer electrolyte is a candidate for power generator for vehicles or house heating in next generation, due to its high energy conversion efficiency and eco-friendly product. However, oxygen reduction reaction (ORR) which occurs at the cathode of fuel cells is a huge obstacle for operation of fuel cell, because of its sluggish kinetics. Even if platinum can accelerate ORR fairly, price and scarcity of platinum are another big problems in commercialization of fuel cells.

For the substitution of platinum catalyst in cathode, non-precious metal catalysts (NPMCs) have been developed by many researchers. Fe/N/Cs, which are iron-containing nitrogen doped-carbons, have shown the high ORR activities among various kinds of NPMCs. Fe/N/Cs are generally synthesized by heat-treatment of iron, nitrogen, and carbon containing precursor at high temperature (> 800 °C) in inert atmosphere.

There are two important factors to make Fe/N/C with high ORR activity. One is active site. Fe-$N_x$/C site that iron ion is coordinated to nitrogen functionalities in carbon basal plane is the most probable active site for ORR. It is important for developing high performance Fe/N/C for ORR by controlled synthetic method. Another crucial factor for Fe/N/Cs is accessibility to the active sites. Generally, fuel cell cathodes made of NPMC have high mass transport resistance, because of thick catalyst layer. The high mass transport resistance interrupts the kinetics of reaction and makes the utilization of catalyst surface inefficient. Thus, control of nanoporosity is important to make high performance Fe/N/C catalyst in fuel cell operation.

We report, a simple soft-template synthesis to ordered mesoporous Fe/N/C catalyst (m-FePhen-C) with Fe-$N_x$/C sites by direct incorporation of Fe-$N_x$/C analogous catalyst precursor to block co-polymer assembly. MEA fabricated with m-FePhen-C showed 140% higher power density than that with commercial Pt/C in alkaline fuel cell MEA test. To our best knowledge, this high performance of MEA with NPMC as compared to commercial material has not been reported. We attribute it to the Fe-$N_x$/C sites from Fe-$N_x$/C analogous catalyst precursor and the facile mass transport through well-developed mesopores in m-FePhen-C.

# Characterization of amorphous Ir-oxohydroxides for the Oxygen Evolution Reaction

C. Massué, V. Pfeifer, S. Cap and R. Schlögl
*Fritz-Haber-Institute of the Max-Planck Society*
Faradayweg 4-6, 14195 Berlin
*cmassue@fhi-berlin.mpg.de*

Hydrogen production through water splitting in proton exchange membrane (PEM)-based electrolysers has come under focus as a suitable chemical energy storage solution. Indeed, PEM-electrolysers allow for the production of high-purity $H_2$ at high pressures. However they require an acidic electrolyte, which threatens the electrocatalysts used to minimize overpotentials, especially in the anodic Oxygen Evolution Reaction (OER): Under these conditions, most transition metal oxides exhibit high corrosion rates.[1] So far, only Ir-based electrocatalysts retained noteworthy activities for longer periods in acidic OER. Producing the right chemical state of iridium is critical: Authors often emphasized the key role of amorphous Ir-oxohydroxides in high-current, stable OER-electrocatalysis in contrast to crystalline $IrO_2$.[2-4] The importance of amorphous, hydrated Ir-species was more recently confirmed by the investigation of Ir-catalysts produced by the groups around P. Strasser and K. Mayrhofer.[5,6] In order to understand the link between the chemical nature of the precursor phase and the observed OER-performance, we developed an innovative synthesis procedure for the synthesis of such amorphous Ir-oxohydroxides.

The OER-performance of our Ir-oxohydroxides outperformed the benchmarks recently reported by McCrory et al.[7] However, the study of their chemical nature proved to be a challenge. Indeed the Ir-oxohydroxide phase is XRD-amorphous and transforms rapidly into metallic $Ir^0$ under reducing conditions, even under mild electron beams, hindering structural studies in electron microscopy. In order to study the chemical bonds present in such Ir-oxohydroxides, Raman-spectroscopy had to be applied at very low laser intensities with high collection times in order to avoid crystallization of $IrO_2$. We could however detect the presence of Raman-modes already observed under OER-conditions for Ir-based electrocatalysts, suggesting a close relation between our as prepared compounds and the active Ir-electrocatalyst.[8] The Ir-oxohydroxides were also investigated using XPS- and NEXAFS-measurements at the BESSY II/HZB synchrotron radiation source. Furthermore, diffuse reflectance infrared spectroscopy (DRIFTS) was used to study the sample surface during CO-adsorption experiments. Our findings suggest that our synthesis procedure gives access to a class of Ir-oxohydroxides exhibiting a high amount of air-stable reactive oxygen species. If these surface sites are already close in nature to the active electrocatalyst under OER-conditions, this might explain their outstanding OER-performance.

(1) Kötz, R.; Stucki, S.; Scherson, D.; Kolb, D. M. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, *172*, 211.
(2) Frazer, E. J.; Woods, R. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1979**, *102*, 127.
(3) Beni, G.; Schiavone, L. M.; Shay, J. L.; Dautremont-Smith, W. C.; Schneider, B. S. *Nature* **1979**, *282*, 281.
(4) Vuković, M. *J Appl Electrochem* **1987**, *17*, 737.
(5) Cherevko, S.; Reier, T.; Zeradjanin, A. R.; Pawolek, Z.; Strasser, P.; Mayrhofer, K. J. J. *Electrochemistry Communications* **2014**, *48*, 81.
(6) Reier, T.; Teschner, D.; Lunkenbein, T.; Bergmann, A.; Selve, S.; Kraehnert, R.; Schlögl, R.; Strasser, P. *J. Electrochem. Soc.* **2014**, *161*, F876.
(7) McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. *J. Am. Chem. Soc.* **2015**, *137*, 4347.
(8) Hintermair, U.; Sheehan, S. W.; Parent, A. R.; Ess, D. H.; Richens, D. T.; Vaccaro, P. H.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 10837.

# N-graphene-$NbO_x$ Hybrid Nanosheets with Sandwich-Like Structure as Electrocatalyst for Oxygen Reduction Reaction

Jingjing Xiao, Lei Liao, Qingbin Wu, Baohong Liu* and Yi Tang*

*Department of Chemistry, Fudan University, Shanghai 200433, China*
*E-mail address：bhliu@fudan.edu.cn; yitang@fudan.edu.cn*

Energy issues attract increasing concerns in recent years for the fast exhaustion of fossil fuel. Oxygen reduction reaction (ORR) is crucial to a number of renewable energy applications such as metal-air batteries, water splitting and fuel cells. Despite a lot of effort, the catalysts for ORR today are still far from the expected level, and new strategies towards ORR catalysts with high efficiency and low cost remain a great challenge.

Recently, nitrogen-doped graphene (N-graphene)-based materials were found efficient in ORR. It is commonly believed that nitrogen doping on graphene could provide the enhanced coupling between graphene layer and metal sites by offering nucleation and anchor sites, and the generated N-metal species could be the ORR active sites, ensuring the N-graphene-based materials as promising substitutes for platinum-based ORR materials. We also noted that a new type multilayered hybrid material with graphene and $TiO_2$ nanosheets were fabricated via layer-by-layer deposition, which was reported with efficient cross-surface charge percolation ability and has been applied in some electrocatalytic and photocatalytic systems.

Considering the remarkable features of multilayered hybrid for charge transfer and N-graphene for promotion in ORR, a hybrid of nitrogen-doped graphene (N-graphene) and $NbO_x$(x=2~2.5) semiconductor nanosheets with sandwich-like structure has been designed and synthesized via a strategy of intercalation-in situ carbonization. The obtained multilayer hybrid material exhibits quite positive onset potential of ORR, good stability and excellent selectivity for ORR with high methanol tolerance. The enhanced performance could be attributed to the active oxygen vacancy from the partial reduction of Nb (V) during the carbonization process and the synergetic coupling effect resulting from the molecular level contact of N-graphene and $NbO_x$(x=2~2.5) nanosheets, which makes it a promising substitute of platinum-based materials for renewable energy applications.

Reference:
1. Q. Wu, L. Liao, Q. Zhang, Y. Nie, J. Xiao, S. Wang, S. Dai, Q. Gao, Y. Zhang,X. Sun, B. Liu*, Y. Tang*, *Electrochimica Acta*, 2015, **158**, 42.

# Amorphous Cobalt Silicate Hydroxide Electrocatalyst for Water Oxidation

Ju Seong Kim[†], Eun-Suk Jeong[†], Hyunah Kim[†], Inchul Park[†]and Kisuk Kang[*,†,‡]

[†]Department of Materials Science and Engineering, [‡]Research Institute of Advanced Materials (RIAM), Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-742, Republic of Korea

The development of highly active and cost-effective electrocatalyst to evolve oxygen gas is a major challenge in water splitting systems. We report an amorphous cobalt silicate (a-CoSi) and it exhibit a high catalytic activity toward oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The catalyst was fabricated by rapid precipitation method at room temperature in aqueous solution, which enables facile mass production. In the electrochemical water splitting, the catalyst exhibits a current density of 10 mA $cm^{-2}$ at an overpotential of 360 mV for OER and an overpotential of 170 mV for HER. At 1st CV of a-CoSi in KOH electrolyte, irreversible transformation was observed with oxidation of $Co^{2+}$ to $Co^{3+}$. Extended X-ray absorption fine structures (EXAFS) analysis reveals that the local structure of a-CoSi is composed of edge-sharing $CoO_6$ octahedra which is similar with local structure of CoOOH. This study demonstrates the promising catalytic activity of amorphous transition metal silicate for oxygen evolution reaction and provides general strategies to synthesis of amorphous electrocatalyst material.

# Electrochemical degradation of glassy carbon under the condition for oxygen evolution in acidic vs. alkaline media

Youngmi Yi, Gisela Weinberg, Mark Greiner, Sylvia Becker*, Robert Schlögl
*Max-Planck institute for chemical energy conversion*
*Stiftstreet 34-36, 45470 Mülheim an der Ruhr, Germany*
*youngmi.yi@cec.mpg.de*

As cost-effective and metal-free electrocatalyst currently receives great attention for energy storage and conversion, carbon materials have been extensively utilized for either a catalyst support or catalyst itself. Carbon is a very attractive material for electrochemical systems because of high electrical conductivity, a structural diversity and relatively low cost. Many research reported that novel developed carbon materials, such as carbon nanotube, graphene, and mesoporous carbon, have reasonable electrocatalytic activity for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Furthermore, they show a comparable activity with metal or metal oxides, e.g. Pt, Ir, Ni or Co. However, carbon is thermodynamically oxidized to carbon dioxide at above 0.2 V *vs.* SHE, we should consider the stability of carbon materials. Although carbon has large overpotential for the oxidation, carbon oxidation at high anodic potential for OER is inevitable. In other words, oxygen evolution on carbon electrode is accompanied by carbon oxidation. Therefore, owing to carbon corrosion, carbon degrades at the condition for OER.

In this study, we focus on carbon materials at the oxidizing condition of OER. Glassy carbon was chosen for the first starting material to understand the electrochemical degradation of carbon. Glassy carbon is commonly used as an electrode in electrochemistry and the electrode substrate for the deposition of OER catalysts. The glassy carbon was oxidized at high anodic potential for OER, and then the morphological and structural change of carbon before and after the oxidation was investigated by microscopic analysis, Raman, infrared and X-ray photoelectron spectroscopy. The corrosion behavior of the carbon towards electrochemical oxidation is different in acidic and alkaline media. Figure 1 shows the SEM images of glassy carbon before and after the electrochemical oxidation. The smooth surface of glassy carbon turns into rough surface structures by oxidation. Carbon oxidized in acidic media seems to form a thin layer on the surface, whereas the one in alkaline media exhibits significant holes by dissolution of carbon. In EDX, we can see clearly the increase in oxygen content after the oxidation in acidic media. It is inferred that the surface oxides are formed by the oxidation of carbon in acidic media. On the other hand, the carbon in alkaline media dissolves itself during the oxidation, resulting in the colored electrolyte. The presented stability studies are of crucial importance for the electrochemical community.

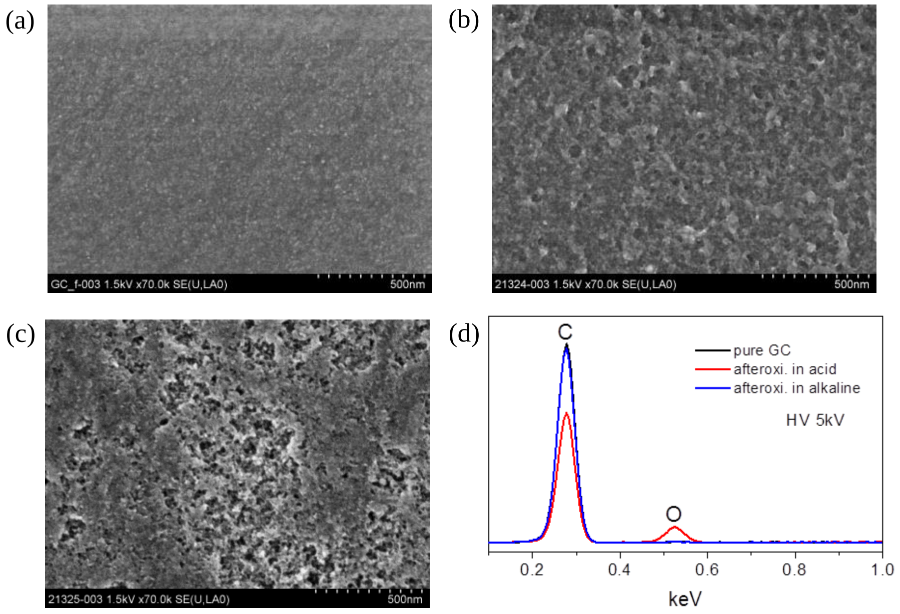


Figure 1. SEM images of (a) pure glassy carbon, glassy carbon after electrochemically oxidized at 1.8 V vs. RHE for 24 h in (b) 0.5 M $H_2SO_4$, (c) 0.1 M KOH and (d) EDX analysis.

# Controlling of Specific Adsorption in Oxygen Reduction Reaction by Modification of Platinum-Based Nanocatalysts

Mi-Ju Kim[1,2], Yun Sik Kang[3], Yung-Eun Sung[1,2,*]
*[1]School of Chemical & Biological Engineering, Seoul National University (SNU),*
*Seoul 151-744, Republic of Korea*
*[2]Center for Nanoparticle Research, Institute for Basic Science (IBS),*
*Seoul 151-744, Republic of Korea*
*[3]Fuel Cell Research Center, Korea Institute of Science and Technology (KIST),*
*Seoul 136-791, Republic of Korea*
*ysung@snu.ac.kr*

Specific adsorption on electrode surface degrades the activity of surface reaction on the electrode of electrochemical devices. This phenomenon, however, is inevitable for certain devices including polymer electrolyte membrane fuel cells and phosphoric acid fuel cells as the devices are composed of the electrolyte which contains the specifically adsorbed anions. To attenuate its detrimental effect on the electrode, the requirements are understanding and governing specific adsorption. Researches concerning specific adsorption have been focused on single crystal metal electrodes in many decades while the research on the electrode composed of nanoparticles is still insufficient.

Platinum is well known for its high catalytic activities toward many electrochemical reactions. It has been reported that heterogeneous catalysts containing platinum exhibit considerable improvement in catalytic activity than pure platinum. It leads to encouraging various studies for platinum-based catalysts such as platinum-transition metal alloys and modified platinum nanostructure, particularly in oxygen reduction reaction. According to these studies, it is widely believed that the catalytic activity improvement of platinum-based catalysts results from the change in the electronic and geometric structure of platinum. These structural changes could affect also adsorption phenomena of adsorbate as well as oxygen species such as OH and OOH, and eventually influence specific adsorption on the electrode surface.

In this regard, we have studied the effect of specific adsorption on the platinum alloy nanocatalysts by using the electrolyte containing phosphoric acid. Based on our results, we demonstrate the control of the adsorption of phosphoric acid on the surface of the catalyst via the post treatments on platinum-cobalt nanocatalyst. Two different post treatments, etching and annealing, were used to induce the change of the surface properties including the interaction with phosphate anions. Owing to these changes, each catalyst exhibited different ORR activities in the electrolyte containing phosphoric acid, which result from controlled specific adsorption behaviors.

# Rotating-ring disk electrodes: Effect of the choice of the redox mediator on the Ring collection efficiency; Case of adsorption of $CN^-$ anions on platinum

Daniela Wintrich, Wolfgang Schuhmann, Justus Masa

Analytical Chemistry and Center for Electrochemical Sciences-CES
Ruhr-Universität Bochum, NC04/788, D-44780 Bochum (Germany)
Fax: (+)49 234 3214683
Justus.masa@rub.de

Rotating ring-disk electrodes (RRDE) are widely used for studying the mechanism and selectivity of electrode reactions. A critical parameter of the RRDE is its collection efficiency, which has to be independently calibrated for individual electrode surfaces. For the oxygen reduction reaction (ORR), the ferrocyanide/ferricyanide redox couple is commonly used for calibration of the ring collection efficiency. In the case of RRDE electrodes with a glassy carbon disk and a platinum ring, we observed drastic discrepancy between the computed and experimentally determined values of the collection efficiency attributable to the strong adsorption of cyanide anions on the platinum ring. This effectively reduces the electrochemical surface area of the ring and thus it collection efficiency thereby affecting the accuracy of the selectivity and mechanistic studies. In this presentation, we demonstrate that reversible redox couples without strong adsorption or poisoning tendencies on platinum give more consistent results between theoretical and experimental collection efficiencies and should thus be preferable for calibration of the collection efficiency of RRDE electrodes with a platinum ring.

# Fuel Heterogeneity in Solid Oxide Carbon Fuel Cells: Carbon Disproportionation and its Reverse Reaction

Hansaem Jang,[a] Youngeun Park,[a] Jaeyoung Lee[a,b]
[a] *Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea.*
[b] *Ertl Center for Electrochemistry and Catalysis, Research Institute for Solar and Sustainable Energies, GIST, Gwangju, 500-712, South Korea.*
*Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea.*
*jaeyoung@gist.ac.kr, luxuriest@gist.ac.kr*

Solid oxide carbon fuel cell is a potential technique, turning intrinsic chemical energy of solid carbonaceous materials into electricity [1]. In carbon fuel cells based on solid oxide, oxygen ($O_2$) is provided to a cathode at which oxygen gas becomes oxide ion ($O^{2-}$) and the resultant ion reaches an anode surface through the defects within a solid oxide electrode. The electrochemical reaction between carbon and oxide ion results in the production of carbon monoxide (CO; *via* partial oxidation of carbon) and/or carbon dioxide ($CO_2$; *via* complete oxidation of carbon) with electrons. Subsequently, the resultant CO is also able to be further electrochemically oxidized into $CO_2$ with the emission of electrons. Moreover, CO is more readily available as fuel than solid-state fuels, since it is a gas-state oxidizable material and is more reachable to triple phase boundary (TPB) at which fuel, electrolyte and current collector are met together and hence electrochemical reactions happen. In fact, at the elevated temperature, CO can be provided not only by partial oxidation of carbon but by reverse Boudouard reaction (RBR; $C(s) + CO_2(g) \rightarrow 2CO(g)$) as well [2]. Two distinctly different viewpoint on RBR-derived CO has been suggested. One is as a fuel loss since gaseous fuel can be more naturally ventilated without being electrochemically oxidized, therefore not all CO can take part in electrochemical reactions and the rest would be found at the exhaust [3]. The other is as a crucial fuel, being further electrochemically oxidized into $CO_2$ [4]. However, the role of CO in this technique is still in ambiguity. In this sense, the authors have attempted to demonstrate the effect of CO in solid oxide carbon fuel cells.

## References

[1] D. Cao, Y. Sun, G. Wang, J. Power Sources, **167** (2007) 250.
[2] H. F. Abbas, W.M.A. W. Daud, Int. J. Hydrogen Energy, **35** (2010) 141.
[3] S. Giddey, S.P.S. Badwal, A. Kulkarni, C. Munnings, Prog. Energy Combust. Sci., **38** (2012) 360.
[4] T. M. Gür, Chem. Rev., **113** (2013) 6179.

# Surface stability of Pt skin-layer in $Pt_3Ni(111)$ under oxidation environment

H.C. Lee[1], G. H. Kim[1], B.M. Kim[2], C.K. Jeong[2], T. Ryo[3], H. Kondoh[3], S. Toru[4], B. Mao[5], Z. Liu[5],
H.G. Lee[6], W.X. Li[7], P. N Ross[5], B. S. Mun[1]

*[1] Department of Physics and Photon Science, School of Physics and Science,*
*Ertl Center for Electrochemistry and Catalysis, Gwangju Institute of Science and Technology, Korea*
*[2] Department of Applied Physics, Hanyang University, ERICA, Korea*
*[3] Department of Chemistry, Keio University, Tokyo, Japan*
*[4] Department of Science, Faculty of Education, Hirosaki University, Aomori, Japan*
*[5] Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*
*[6] Department of Chemistry, Sookmyung Women's University, Seoul, Korea*
*[7] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,*
*Dalian 116023, China*
*bsmun@gist.ac.kr*

Using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS), the stability of surface skin layer is investigated under various temperature and oxygen pressure conditions, e.g. the surface chemical compositions, depth profile, and oxidation states. A clear segregation of Ni element to the surface is observed as the oxygen pressure and temperature are varied. As the temperature and pressure are elevated, the formations of $Ni_2O_3$, $NiO_x$, and NiO are observed on surface while Pt atom starts to reduce its adsorbed oxygen. Under reducing condition, i.e. UHV, both of NiOx and NiO oxide get reduced. The DFT calculation is employed to explain the formation of oxide under oxidation condition in the alloy.

# Processing and Electrochemical Performance of Metal Foam Supported Solid Oxide Fuel Cells with Nanostructured Anode and Thin-film Electrolyte

Feng Han[1], Robert Semerad[2], Patric Szabo[1] and Rémi Costa[1]

*[1]German Aerospace Center*
*Institute of Engineering Thermodynamics*
*Pfaffenwaldring 38-4, D-70569 Stuttgart / Germany*
*feng.han@dlr.de*
*[2]Ceraco Ceramic Coating GmbH*
*Rote-Kreuz-Str.8 , D-85737 Ismaning / Germany*

The processing and electrochemical performance of a novel designed metal foam supported solid oxide fuel cell (SOFC) with nanostructured anode and yttria-stabilized zirconia (YSZ) - gadolinium doped ceria (GDC) bi-layer electrolyte is reported in this work. The prepared cells are supported by NiCrAl metal foam, which has been impregnated with a La-substituted $SrTiO_3$ (LST) nickel cermet as electrical conductive material. An LST-GDC anode functional layer with average pore size in the micrometer range was deposited onto the metal foam support. Porosity-graded YSZ layers were dip-coated with a fine suspension containing nanoparticles in order to obtain intermediate supporting layers for the electrolyte. The macroporous and mesoporous YSZ layer with pore size of less than 100 nm was loaded with Ni nanoparticles to serve as a nanostructured anode, while the microporous YSZ layer with pores size of less than 2 nm serves as a quasi-hermitic and pure ionic conductive electrolyte. Successively, a gas-tight GDC electrolyte was deposited by EB-PVD method. The thickness of the gas-tight thin-film YSZ-GDC bi-layer electrolyte was less than 3 µm. Half cells with size up to 90 cm² were successfully produced showing an air leakage rate down to 0.5 $Pa \cdot m \cdot s^{-1}$ satisfying the gas-tightness quality control threshold of the state of the art metal supported SOFCs at DLR. Button cells with 4x4 cm² active $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathodes showed an OCV of 1.02 V at 750°C and power density up to 320 mW/cm² was obtained at 0.7 V.

# Preparation of WC/MMT nanocomposite and its electrocatalytic activity for methanol oxidation

Wei Yang[1], Guohua Li[1,2,*], Jing Gao[1]
[1]*School of Chemical Engineering, Zhejiang University of Technology*
[2]*State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology*
*Hangzhou* 310014, *Zhejiang, P R China*
**E-mail: nanozjut@zjut.edu.cn*

Tungsten carbide (WC) can be used as an alternative electrocatalyst to replace platinum in electrocatalysis, due to its catalytic behavior is similar to that of platinum[1], and its higher tolerance to CO、$H_2S$ poisoning[2]. But the catalytic activity of WC is much lower than that of platinum. Composite is one of the efficacious approaches to improve the catalytic activity of WC[3].

Tungsten carbide and montmorillonite (WC/MMT) nanocomposite was prepared through combining an impregnation approach with a reduction-carbonization method, using exfoliated MMT as a support. The sample was characterized by X-ray diffraction, scanning electron microscope and transmission electron microscope. The results show that the crystal phase of the sample is composed of monotungsten carbide (WC), bitungsten carbide ($W_2C$) and MMT, and tungsten carbide is distributed on the outer surface of MMT. The electrocatalytic activity for methanol oxidation of the nanocomposite was tested by a cyclic voltammetry (CV) in acidic solution. It was found that WC/MMT nanocomposite is electrocatalytic active to methanol oxidation and its activity is better than that of 5% Pt/C's (E-ETK). These imply that the exfoliated MMT is one of the excellent composite carriers to improve the electrocatalytic activity of WC, and can be used as a support for other catalysts.

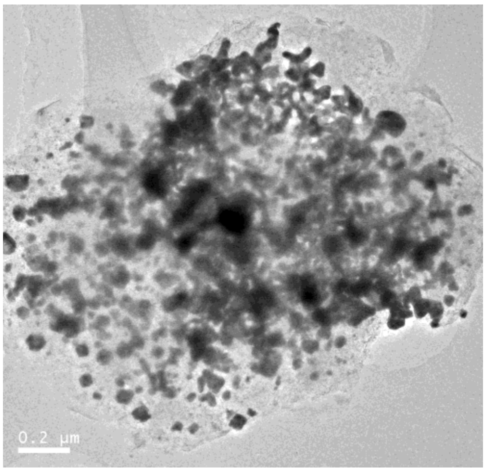


Fig.1 TEM image of WC/MMT sample

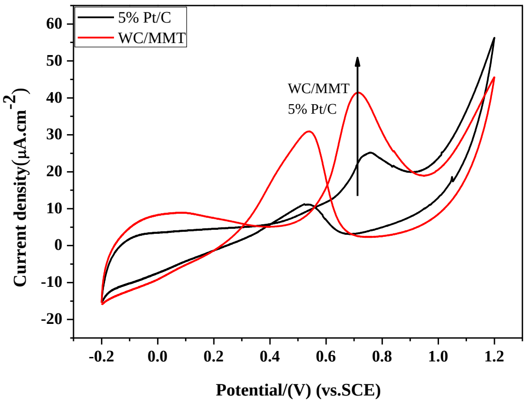


Fig.2 Cyclic voltammograms of WC/MMT and 5% Pt/C Samples at scan rate 100 mV·s$^{-1}$

References

[1] Levy, R. B.; Stauffer, M. C. *Science*, **1973,** *181*, 547.

[2] Palanker, V. S.; Gajyev, R. A.; Sokolsky, D. V. *Electrochim. Acta*, **1977,** *22*, 133.

[3] Rahsepar, M.; Pakshir, M.; Nikolaev, P.; Safavi, A.; Palanisamy, K.; Kim, H. *Appl. Catal. B-Environ.* **2012,** *127*, 265.

# Preparation of Tungsten Carbide with Different Morphologies and Their Electrochemical Properties

Haibiao Sun[1], Guohua Li[1,2,*], Jing Gao[1]
*1 School of chemical engineering, Zhejiang University of Technology*
*2 State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology*
*Zhejiang University of Technology, Hangzhou 310032 P.R. China*
**E-mail: nanozjut@zjut.edu.cn*

Tungsten carbide (WC) possesses a catalytic property similar to platinum catalyst's[1], and higher tolerance to CO poisoning [2], but its catalytic activity is much lower than that of platinum [3]. How to improve its electrocatalytic activity is a hot research topic.

Tungsten carbide nanoslice and nanorod were prepared by combining a hydrothermal method with an in-situ reduction and carbonization approach, while tungsten carbide microsphere was fabricated by a spray drying and an in-situ reduction and carbonization approach stepwise. The samples were characterized by X-ray diffraction, scanning electron microscope, transmission electron microscope. The results show that the crystal phase of nanoslice, nanorod and microsphere is $WC/W_2C$, WC/W and $WC/Fe_3W_3C$, respectively; the nanoslice is composed of nanoparticle and mesopore, its width is around 700 nm, and its thickness is about 90 nm; the diameter of the nanorod is around 100 nm with a length between 0.5 and 1.0 μm; while the diameter of the microsphere is about 1.2 μm with some surface wrinkles. The electrocatalytic activity of the samples for methanol oxidation was investigated using cyclic voltammetry. The results show that the electrocatalytic activity for methanol oxidation of the nanoslice is the best among the three catalysts, that of the nanorod is the mediate, and that of the microsphere is the weakest. These imply that the electrocatalytic activity of tungsten carbide can be adjusted by controlling its morphology, furthermore, the preparation of tungsten carbide nanomaterials with different morphologies is one of the efficacious ways to improve the electrocatalytic property of tungsten carbide.

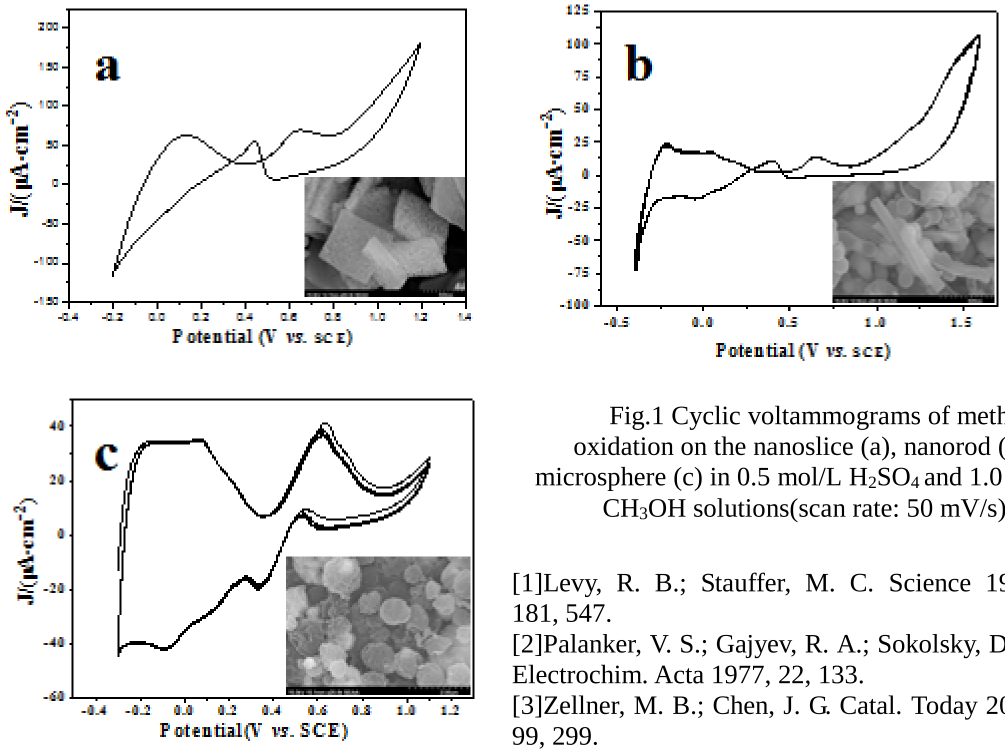


Fig.1 Cyclic voltammograms of methanol oxidation on the nanoslice (a), nanorod (b), microsphere (c) in 0.5 mol/L $H_2SO_4$ and 1.0 mol/L $CH_3OH$ solutions(scan rate: 50 mV/s)

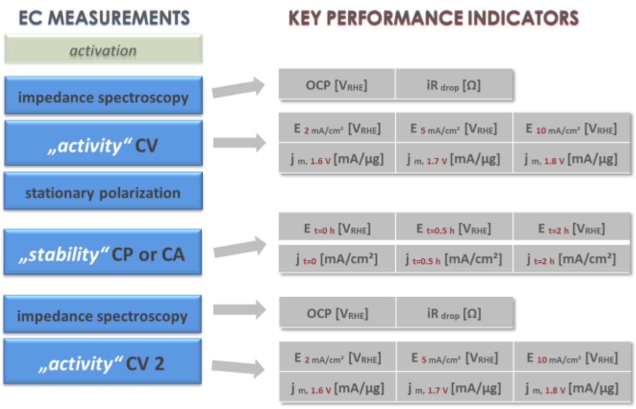
[1]Levy, R. B.; Stauffer, M. C. Science 1973, 181, 547.
[2]Palanker, V. S.; Gajyev, R. A.; Sokolsky, D. V. Electrochim. Acta 1977, 22, 133.
[3]Zellner, M. B.; Chen, J. G. Catal. Today 2005, 99, 299.

# Standardized Measurements for Oxygen Evolution Reaction-Rotating Disk Electrode Measurements and Beyond

Sebastian Neugebauer, Ioannis Spanos, Youngmi Yi, Sebastien Cap, Robert Schlögl
*Max Planck Institute for Chemical Energy Conversion*
*Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany*
*sebastian.neugebauer@cec.mpg.de*

The oxygen evolution reaction (OER) is without doubt one of the most studied reactions in electrocatalysis. Due to its significance in a sustainable energy scenario [1, 2], the quest for cost-efficient, highly stable electrocatalysts for OER is ongoing. A considerable amount of research is directed at replacing pricey catalysts based on precious metals. So far, it seems that a breakthrough is still not reached and a clear understanding of structure-function relationships is not yet established. A factor that might contribute to such a gap in knowledge is the fact that a lot of data in the literature is not easily comparable. One of the standard techniques to evaluate new electrocatalysts for OER is the rotating disk electrode technique (RDE [3]). There is, however, no standardized protocol to conduct these measurements and, in consequence, drawing conclusions from a set of different studies is not straightforward. A drawback of many electrocatalytic studies is to focus the evaluation of a catalyst on the so-called activity mostly represented by a value for the overpotential needed to start driving oxygen evolution. Long-term stability is, however, of utmost importance in the application of electrocatalysts. It seems that thorough studies on the stability of electrocatalysts are only slowly receiving the deserved attention.

Starting from existing attempts at standardization [4], we evaluated the many factors influencing the electrochemical response of electrocatalyst-modified electrodes in RDE experiments. Among those factors are electrode-specifics such as electrode material, use of different binders and loadings, electrolyte and measurement parameters such as scanrate. In conclusion, we adapted a series of electrochemical measurements to evaluate the activity and, most importantly, stability of powder-like electrocatalysts via a RDE methodology. The methodology involves the definition of key performance indicators (KPI) as shown below and includes the change in KPI upon stability testing.



Within the scope of a multi-partner project we evaluated the between-lab reproducibility of the proposed sequence of measurements. The results from thirteen identical experimental set-ups including same-model potentiostats and glass-free electrochemical cells using a standard electrode based on commercially available nickel cobalt oxide nanopowder are presented. It is demonstrated that the values for e.g. overpotential vary over a range of about 15 mV and stability measurements are not easily reproduced. It is concluded that proper statistics are mandatory in RDE experiments and the studied systems are undergoing dynamic changes. In addition, an argument is made that RDE measurements can only be the starting point for electrocatalyst evaluation and should never be regarded as complete characterization. The need for pre/post ex-situ analysis and in-situ analysis is stressed and some examples of such analysis using the standard electrode mentioned above are presented.

[1] R. Schlögl, ChemSusChem **3**, 209 (2010)
[2] I. Katsounaros, S. Cherevko, A. R. Zeradjanin, K. J. J. Mayrhofer, Angew. Chem. Int. Ed. **53**, 102 (2014)
[3] K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. Stamenkovic, M. Arenz, N. M. Markovic, Electrochim. Acta **53**, 3181 (2008)
[4] C. L. C. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, J. Am. Chem. Soc. **135**, 16977 (2013)

# Enhancement of the Photovoltaic Performance of Dye Sensitized Solar Cell using $TiO_2/SnO_2$ Nanofibers as a Photoanode

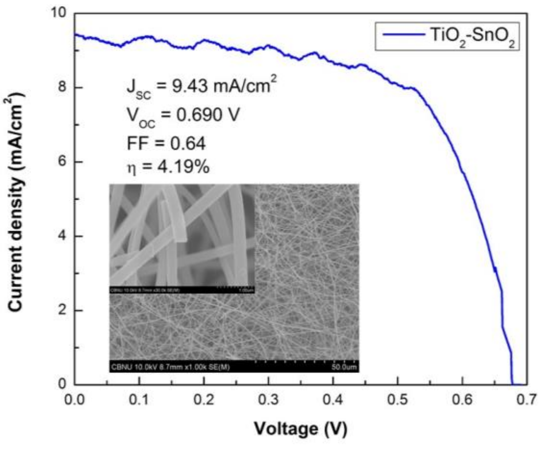
Ibrahim M A Mohamed[a]*, M. Shaheer Akhtar[b] and Nasser A M Barakat [a,c]

[a] *Bionanosystem Engineering Department, Chonbuk National University, Jeonju 561-756, Republic of Korea*
[b]*New & Renewable Energy Material Development Center (NewREC), Chonbuk National University, Jeonbuk 561-756, Republic of Korea*
[c]*Chemical Engineering Department, Faculty of Engineering, Minia University, El-Minia, Egypt.*

** Corresponding author: Bionanosystem Engineering Department, Chonbuk National University, Jeonju 561-756, Republic of Korea.*
*E-mail: imaashour20080@gmail.com*

## Abstract

Dye sensitized solar cells have attracted much attention, because it directly converts solar light into electrical power without any environmental effect. Experimentally, this work fabricates a novel photoanode to enhance the light harvesting and photovoltaic performance of dye sensitized solar cell. The novel electrode composed of one-dimensional $TiO_2/SnO_2$ nanofibers which is synthesized by a facile and one-step technique of electrospinning. The studied material was characterized by field emission scanning electron microscope, Transmission electron microscopy, X-ray diffractometer, UV-Visible spectrophotometer and thermal gravimetric analysis. X-ray diffraction revealed that the investigated $TiO_2$ nanoparticles exhibit anataste phase. $TiO_2$/ $SnO_2$ nanofibers are studied as a photo anode substrate to increase the performance of DSSCs. The results indicate that the presence of tin oxide enhance the amount of dye absorption which leads to high migration of electrons from the photosensitizer to the conduction band of the collection electrode. Accordingly, remarkably improved power conversion efficiency of 4.19 % was reported in case of utilizing $SnO_2$ incorporated $TiO_2$ nanofibers as working electrode based DSSCs which is higher than that of the conversion efficiency in case of pristine TiO2 nanofibers (i.e. 1.54%).



# Feature performance of activated carbon charcoal as anode material on power generation in single air cathode MFC using food waste water

**Hend Omar Mohamed[1], M. Obaid[1] and Nasser A. M. Barakat[1,2,*]**

[1]Bio-Nanosystem Engineering Department, Chonbuk National University, Jeonju 561-756, Republic of South Korea

[2]Chemical Engineering Department, Faculty of Engineering, Minia University, Minia, Egypt

**Corresponding author:** N.A.M. Barakat, E-mail: *nasser@jbnu.ac.kr*

Microbial Fuel Cells (MFCs) is the charming technology which can add waste source to renewable energy list during bio catalytic reaction using very small creatures called microorganism as a catalyst. This study investigates the performance of different types of anode materials to generate power from industrial food wastewater without any pretreatment or addition of biological or chemical mediator using single air cathode MFC. The results indicated that the greatness of this study lies in two reason, firstly that the microorganisms existing in wastewater can behave as exogenous microorganism as they have the ability to produce and transfer electrons to the anode surface without external electron shuttles. Secondly, the results proved that MFC based on activated carbon anode achieved the highest power generation although the utilized anode is a price-less material which strongly recommend exploiting the proposed MFC in simultaneous treatment and power generation from the investigated waste. Power and current generated from activated carbon, graphite , carbon cloth and carbon paper anode materials were 338, 175 ,78 and 57 mWm-$^{2}$, and 1.16, 0.3, 0.2 and 0.143 mA, respectively. Overall, this study opens new prospects for the energy production and waste water treatment in the same time with the lowest cost.

***Keywords**:* Microbial fuel cell; food waste; Activated carbon anode

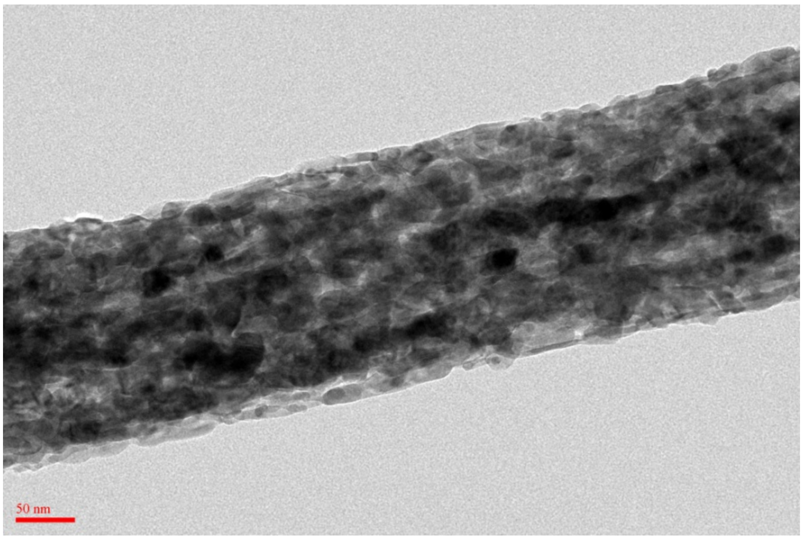
# Photo-assisted& electro-oxidation of organic pollutants using Zirconium Doped Titanium Dioxide Nanofibers

Ahmed S. Yasin[a] ,Nasser A.M. Barakat[a,b,*]
[a]Bionanosystem Engineering Department, Chonbuk National University, Jeonju 561-756, Republic of Korea
[b]Chemical Engineering Department, Faculty of Engineering, Minia University, Minia, Egypt

In this study, the features and characterization of a photo-assisted electro-oxidation process of the organic pollutants is examined using novel $TiO_2/ZrO_2$ nanofibers. All experiments were carried out in a three electrodes cell, and it was presented the impacts of electrolyte mixing, different supporting electrolytes on the observed current density. The observed results in this work have revealed that the thermally prepared anode of titanium Dioxide, doped with zirconia, displays photo-activity also it can be utilized for the treatment of the effluents. The degradation of prepared methelyne blue is obtainable, and the results exhibit that the influence of titania is reduced compared with that of the nanocomposite, attributed to the presence of the zirconia. Therefore, this study introduces effective treatment for the organic pollutants accompanied with simultaneous production of electric energy.

Keywords

Electrochemical oxidation; Photoelectrocatalysis; Titanium dioxide.



HR-TEM and TEM image of the $TiO_2/ZrO_2$ nanofibers

# Room-Temperature Synthesis of Nanostructured Transition Metal Nitride Electrocatalysts for Oxygen Evolution Reaction

Jin Soo Kang, Heejong Shin, Yoonjun Son, Dong Young Chung, Yung-Eun Sung*

*Center for Nanoparticle Research, Institute for Basic Science (IBS) and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea.*

**E-mail: ysung@snu.ac.kr*

Oxygen electrocatalysis is one of the most important reactions for the development of renewable energy conversion technologies. Recent advances in catalysts for oxygen reduction reaction, which is the rate determining step in fuel cell operation, are reinforcing positive outlooks on hydrogen-energy utilization in the near future. For this reason, importance of reliable and economic hydrogen fuel supply is on a rapid growth, and catalysts for water electrolysis are under intensive investigations. In general, the rate of electrochemical water dissociation is limited by oxygen evolution reaction (OER) due to its sluggish kinetic. Therefore high-performance OER catalysts are required for the efficient water electrolysis, and wide range of transition metal compounds have been reported as active materials. Among them, nitrides exhibit excellent properties such as high conductivity and activity, but high-temperature heat treatment in toxic ammonia atmosphere is often inevitable for the synthesis of nitride catalysts. Herein, our works in the synthesis of nanostructured nitride materials at room-temperature in inert condition will be presented. Complete nitridation of low-cost early transition metals were verified by various physicochemical analyses including X-ray diffraction, photoelectron and absorption spectroscopy, and the activity and stability of nitride catalysts were evaluated by electrochemical measurements.

# Behaviour of Birnessite Coated Electrodes Operated as Water Oxidation Anodes

M.Sc. Jonas Ohms[a], Dr. Philipp Hillebrand[b] Prof. Dr. Philipp Kurz[a]
*[a]Institut für Anorganische und Analytische Chemie and*
*Freiburger Materialforschungszentrum (FMF)*
*Albert Ludwigs Universität Freiburg, Albertstaße 21, 79104 Freiburg (Germany)*
*[b]Helmholtz Zentrum Berlin, Institut für Solare Brennstoffe*
*Hahn-Meitner-Platz 1, 14109 Berlin (Germany)*
*jonas.ohms@ac.uni-freiburg.de*

The efficient catalysis of the four-electron process of water to molecular oxygen is a central challenge for the development of devices for the production of solar fuels. This is equally true for artificial leaf-type structures and electrolyser systems. Inspired by the composition of the oxygen evolving complex of Photosystem II, the biological catalyst for this reaction, synthetic routes for calcium manganese oxides have been developed by our working group. We were able to successfully use these materials as heterogeneous catalysts for water oxidation. In screenings where $Ce^{4+}$ was used as chemical oxidant, calcium-containing, layered manganese oxides from the birnessite mineral family clearly emerged as most active oxide phase.[1],[2]

As a first step towards the application of these manganese oxide catalysts in the context of electrocatalysis, screen-printing methods were investigated to coat conductive surfaces like flourine doped tin oxide (FTO) with presynthesized manganese oxides.[3] We are able to prepare highly porous electrodes which facilitate water-oxidation in aqueous electrolytes at pH 7 with overpotentials of 400-500 mV, thereby producing current densities of > 1mA*$cm^{-2}$ for up to 20 hours.

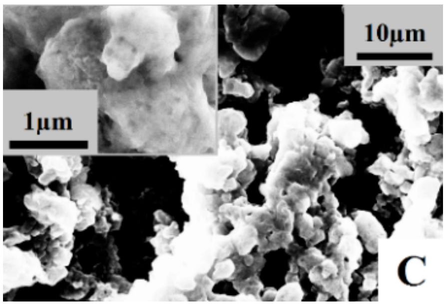


**Figure 1:** SEM-micrograph of a porous calcium-birnessite electrode.

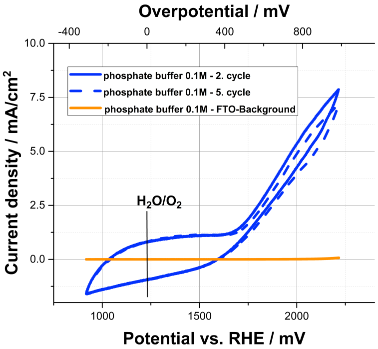


**Figure 2:** Cyclic voltammogram of a calcium-birnessite electrode (1/15M phosphate buffer, 20 mV/s).

As a subsequent optimization step, the dependence of the electrocatalytic activity on nature, concentration and pH of the electrolyte was investigated thoroughly. These experiments were supported by X-ray photoelectron spectroscopy which was used to study the interaction of the bulk manganese oxide and the electrolyte. From the results of these studies, we conclude that the electrolyte plays a crucial role in electrocatalytic water oxidation by manganese oxides, exceeding simple pH effects.

In subsequent comparative studies, the established screen printing method was used to prepare FTO-electrodes coated with various manganese oxide phases (e.g. hausmannite, manganosite and hollandite) in order to compare OER-activities. We encountered strong variations of the electrocatalytic activities depending on the oxide phases and also on the average oxidation state of the manganese centres.

In the near future, we will build on the referred comparative study by preparing coatings of various manganese oxides on glassy carbon or other carbon-based supports using Nafion or similar polymers as coating agents. First results of this study will be shown in this poster presentation.

[1] C. E. Frey, Ph. Kurz, *Dalton Trans.* **43**, 4370 (2014).
[2] C. E. Frey, Ph. Kurz, *Chem. Eur. J.* **21**, 14958 (2015).
[3] S. Y. Lee et al., *ChemSusChem*, **7**, 3442 (2014).

# Impact of air contaminants on automotive fuel cells under realistic operating conditions – dynamic drive cycle

Anja Talke (1), Ulrich Misz (2), Gerhard Konrad (1), Angelika Heinzel (2)
*(1) Daimler AG, Neue Str. 95, D-73230 Kirchheim/Teck-Nabern*
*(2) ZBT GmbH, Carl-Benz-Str. 201, D-47057 Duisburg*
anja.talke@daimler.com

Fuel cells are a promising option for the automobile industry to meet the requirements for future mobility. They combine a very low environmental impact with the advantages of high ranges and low refueling times. To achieve a successful market introduction of fuel cell vehicles a reduction of costs and an increase of lifetime of the fuel cell system is desirable. It is known from several studies that common air contaminants like nitrogen oxides or ammonia have a negative impact on the cathode of a fuel cell. With respect to fuel cell vehicles it is indispensable to execute further research under realistic operating conditions. This is necessary to get a better understanding of actual impacts of air contaminants on vehicles and to facilitate the development of effective remedies.

For this reasons experiments with air contaminants were carried out using a dynamic drive cycle. The fuel cell hardware was an automotive ten-cell stack with an active area of 300 $cm^2$ of each cell and a loading of 0.4 mg $cm^{-2}$ Pt/C at the cathode. The used drive cycle is one of the rare cycles existing as a 93 km long route in the area of Stuttgart, Germany. The route was introduced by the German automobile magazine "auto motor und sport" to test realistic fuel consumptions of cars and is shown in Figure 1. The drive cycle consists of a mix of sections like city traffic, country roads and highways. Furthermore it offers a diversified height profile and therefore many load changes. The drive cycle was translated in a load profile for a fuel cell and adapted to match the requirements of the test bench. This approach allows a maximum realistic experimental design for the first time.

Besides the realistic drive cycle the experiments included the usage of a varying contaminant concentration. In ambient air there is a quite low background concentration of air contaminants plus the occurrence of short contaminant peaks with significantly increased concentrations. For this reason the influence of contaminant peaks were tested by introducing a high concentration of contaminants in the air feed only for a few seconds. In addition the influence of contaminants at the different sections was tested by introducing contaminants only at the high load phases for example. This should simulate the influence of air contaminants divided for the different sections like highways and provide a better understanding.

The present results clearly confirm the severity of the influence of air contaminants on automotive fuel cells. They show a harming impact of air contaminants even at a realistic load cycle with permanently changing conditions like air feed, humidity and pressure. The data is also compared to steady state and semi-dynamic experiments to quantify the differences and facilitate the influence of the variation of the particular operating conditions.

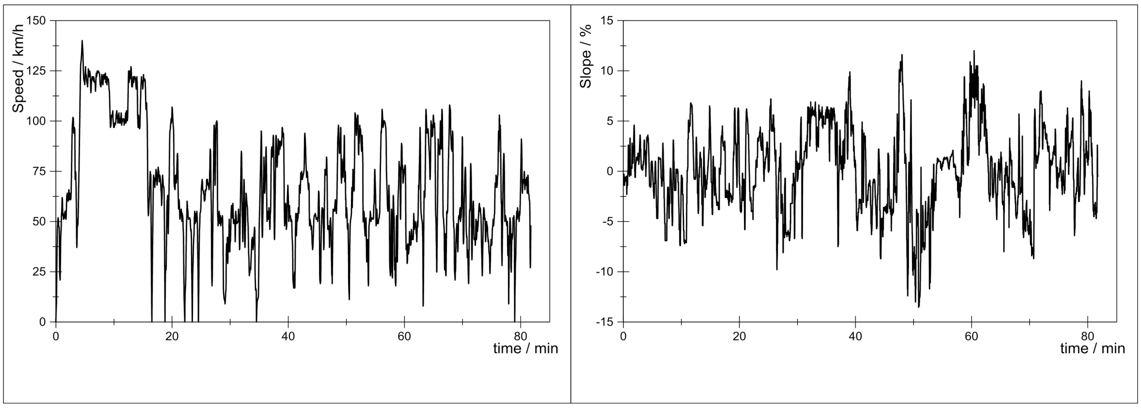


Figure 1: Speed and Slope of the "auto motor und sport" test route near Stuttgart, Germany

# Heteroatom doped graphitic Carbon Nitride Nanostructures as Efficient Catalyst for Oxygen Evolution Reaction

Vinayak S. Kale†‡§, Uk Sim‖§, Ki Tae Nam‖, Taeghwan Hyeon†‡

*† Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 151-742, Korea*
*‡ School of Chemical and Biological Engineering and Institute of Chemical Processes, Seoul National University, Seoul 151-742, Korea*
*‖Department of Materials Science & Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 151-744, Korea.*
*§ These authors contributed equally to this work.*
*e-mail address: vinayakskale@snu.ac.kr*

Analogues to graphene, graphitic carbon nitride (g-$C_3N_4$) which contains C, N, and H in trace amount have fascinated scientists to consider as a catalyst for many applications. It is a medium bandgap semiconductor, which can be efficiently used as a catalyst for photochemical splitting of water. The world's biggest energy problem will be solved if we can succeed in the splitting of water into $H_2$ and $O_2$ gas using solar energy and by using suitable semiconductor photocatalysts. Domen *et al* showed g-$C_3N_4$ is a good visible light absorber with proper band gap and have capability to dissociate water molecule. It is stable in water as well as non-toxic, cheap and easily available.[1] Another report from Zheng *et al* showed the synthesis of g-$C_3N_4$ with nitrogen-doped graphene (N-Gr), showed excellent electrocatalytic Hydrogen Evolution Reaction (HER) application since this composite possesses unique molecular structure and electronic properties.[2] Still this composite has not beaten the best Pt catalyst, it showed to be similar electrocatalytic HER activity with the well-known metallic catalysts like nanostructured $MoS_2$ materials. These significant reports along with many other reports underline the importance of the non-metal/metal-free based systems in the area of catalysis. Particularly g-$C_3N_4$ is being explored recently although its basic structure has been know from very long time. Along with this, g-$C_3N_4$ can act as a catalyst for broad variety of reactions like electrocatalyst for Oxygen Reduction Reaction (ORR), Oxygen Evolution Reaction (OER) in fuel cells, oxidation reactions (alkanes, olefins, alcohols, heteroatoms, photodegradation of pollutants), many hydrogenation reactions and as a basic catalyst for NO decomposition, activation of bonds, F-C reactions as well as. We have synthesized g-$C_3N_4$ nanostructures by a novel method which has been used for various electrocatalytic reactions such as HER, OER and ORR. The nano-structuring of g-$C_3N_4$ has improved the electrocatalytic activities compared to bulk g-$C_3N_4$. To further improve the conductivity and catalytic properties, these nanostructures of g-$C_3N_4$ have been doped with heteroatoms. It has been already well known that doping of particular heteroatom like Phosphorus (P), Iodine (I), Fluorine (F), Sulfur (S) can alter many properties.[3] Heteroatom doped g-$C_3N_4$ nanostructures has showed excellent electrocatalytic performances. Heteroatom doping in g-$C_3N_4$ nanostructures has been proven by many techniques/characterizations.

References:

1 Xinchen Wang, Kazuhiko Maeda, Arne Thomas, Kazuhiro Takanabe, Gang Xin, Johan M. Carlsson, Kazunari Domen and Markus Antonietti, *Nat. Mater.* **2009***, 8,* 76- 80.
2 Yao Zheng, Yan Jiao, Yihan Zhu, Lu Hua Li, Yu Han, Ying Chen, Aijun Du, Mietek Jaroniec and Shi Zhang Qiao *Nat. Commun.* **2014**, *5*, 3783-3791
3 Yuanjian Zhang, Toshiyuki Mori, Jinhua Ye, and Markus Antonietti *J. Am. Chem. Soc.* **2010**, *132*, 6294-6295

# Anion-conducting ionomer binders for solid alkaline fuel cells

Mun-Sik Shin[1], Moon-Sung Kang[1], Hyoung-Juhn Kim[2] and Jin-Soo Park[1*]
[1]*Department of Environmental Engineering, College of Engineering, Sangmyung University, 31 Sangmyungdae-gil, Dongnam-gu, Cheonan, Chungnam Province 330-720, Republic of Korea*
[2]*Fuel cell Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Republic of Korea*
**energy@smu.ac.kr*

Solid alkaline fuel cells (SAFCs) are recently being highlighted to 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. This solid electrolytes were prepared by quaternized polymers having a function to exchange anions. According to the recent works, alkaline 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. For fuel cell applications, membrane-electrode assemblies should be prepared for solid alkaline fuel cells. 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.

## ACKNOWLEDGMENTS

This research is supported in part by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2014R1A1A1006067) and by the KIST Institutional Program (Project No. 2E24841).

## REFERENCES

[1] J.S. Yang, L.N. Cleemann, T. Steenberg, C. Terkelsen, Q.F. Li, J.O. Jensen, H.A. Hjuler, N.J. Bjerrum, R.H. He, High Molecular Weight Polybenzimidazole Membranes for High Temperature PEMFC, Fuel Cells, 14 (2014) 7-15.
[2] L.C. Jheng, S.L.C. Hsu, B.Y. Lin, Y.L. Hsu, Quaternized polybenzimidazoles with imidazolium cation moieties for anion exchange membrane fuel cells, Journal of Membrane Science, 460 (2014) 160-170.
[3] H.Y. Hou, S.L. Wang, Q.A. Jiang, W. Jin, L.H. Jiang, G.Q. Sun, Durability study of KOH doped polybenzimidazole membrane for air-breathing alkaline direct ethanol fuel cell, Journal of Power Sources, 196 (2011) 3244-3248.
[4] K.J.W.Y. Soo, An Investigation into Polybenzimidazoles as Anion Exchange Membranes, Science: Department of Chemistry, 2013.
[5] Z. Xia, S. Yuan, G. Jiang, X. Guo, J. Fang, L. Liu, J. Qiao, J. Yin, Polybenzimidazoles with pendant quaternary ammonium groups as potential anion exchange membranes for fuel cells, Journal of Membrane Science, 390-391 (2012) 152-159.

# Cationic Pore-filled Polyelectrolyte Membranes for Electrochemical Energy Conversion Processes

Do-Hyeong Kim, Jin-Soo Park, Moon-Sung Kang
*Department of Environmental Engineering, Sangmyung University, 31, Sangmyungdae-gil, Dongnam-gu, Cheonan-si, Chungnam 330-720, Republic of Korea*

Polyelectrolyte membranes (or ion-exchange membranes) which consist of a polymer backbone with fixed charge groups have been widely used in various water treatment processes for the desalination of brackish water, the production of table salt, the recovery of valuable metals from effluents of metal-plating industry and so on. Recently, the polyelectrolyte membranes have also gained increased industrial importance in the electrochemical energy conversion and storage processes such as reverse electrodialysis, fuel cells, and redox flow batteries. Especially, in recent years, direct liquid fuel cells using anion-exchange membranes (AEMs) have attracted significant attention as promising alternative energy sources owing to their merits such as the use of non-noble and low cost electro-catalyst, low membrane cost, and low fuel crossover rate etc. However, the ion conductivity of AEMs in not as high as those of proton-exchange membranes (PEMs) such as Nafion and the long-term stability of AEMs in a strong alkaline condition should be improved more for practical applications. In this work, therefore, we have developed pore-filled polyelectrolyte membranes (PFPEMs) with structurally stable anion-exchange groups for the applications to efficient alkaline direct liquid fuel cells. The PFPEMs composed of a highly inert and tough porous substrate and a polymer with stable anion-exchange groups that fills the pores can provide both high ion conductivity and excellent mechanical properties. Additionally the PFPEMs could be produced in a cheaper way by a roll-to-roll continuous process. The PFPEMs with a film thickness below 50 μm have been successfully prepared and characterized via various electrochemical analyses. As a result, they were shown to possess excellent electrochemical and mechanical properties. Their electrochemical characteristics have also been optimized for the successful applications to various energy conversion processes including alkaline direct liquid fuel cells.

This work was supported in part by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Korea government (MSIP) (2015R1A1A1A05001486) and the Technology Innovation Program funded by the Korea government (MOTIE) (No. 10047796).

.