

4th Ertl Symposium on Chemical Processes on Solid Surfaces

11-13 October 2016 in Berlin, Germany I hosted by the FHI der MPG & GIST Ertl Center

Water at Interfaces



Prof. Dr. Gerhard Ertl Nobel Laureate 2007

Fritz-Haber-Institut der Max-Planck-Gesellschaft Berlin, Germany "for his studies of chemical processes on solid surfaces"

Gerhard Ertl

Born in 1936 in Bad Cannstadt, Germany. PhD in Physical Chemistry in 1965 from Technische Universität München, Germany. Prof. Emeritus, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany. Ertl has laid the foundation of a scientific discipline through his enormously systematic and thorough studies. He has often returned to the same problem in surface chemistry decade after decade in order to use new experimental methods to obtain answers to questions posed earlier. His ability to describe in detail how an experiment is to be designed and interpreted has helped him to provide the methodological platform for an entirely new area of research.



The Ertl Center			
	Agenda of the Ertl Center		
The first period (2008-2010)	The second period (2011-2014)	The third period (2015-beyond)	
- Foundation of the center	- Center of excellence (COE) in electrochemistry and catalysis research	- Continuous research	

Role of the Ertl Center

- Bridge between basic research and industrial applications
- Encouragement of continuous research in Electrochemistry and Catalysis (Surface Science)
- Focused on international collaboration
- Promotion of "practical Learning" movement (DASAN)
- Organization of Ertl symposium

Introduction

At the beginning of the 21st century our world is facing serious problems with regards to environment, climate, energy conversion, raw materials, water and food. All these global problems are seeking scientific solutions, especially from physical chemistry and electrochemistry, and in this connection analysis and dynamics are of tremendous importance, in particular Chemical Processes on Solid Surfaces: "Water at Interfaces". It is expected that the 4th Ertl symposium will provide a good opportunity in these attempts, and we wish great success to all the people involved in this enterprise.



Organizing and Scientific Committee

Markus Eiswirth Hye Jin Lee Jaeyoung Lee Robert Schlögl Martin Wolf FHI der MPG & GIST Ertl Center Kyungpook National University GIST Ertl Center & SESE (Co-Chair) FHI der MPG & MPI-CEC (Co-Chair) FHI der MPG

Symposium Secretariat

Dorothea DammFHI der MPGJae Kwang LeeGIST Ertl CenterEmailertl@gist.ac.kr / damm@fhi-berlin.mpg.deFax+82 62 715 2434 (Korea)+49 30 8413 4401 (Germany)



Key Topics

Water Splitting and vice versa Electrified Interface Surface Analysis and Dynamics Computational Physical Chemistry

Award Lectures (2016 Ertl Prize Winner)

Bongjin Simon MunGIST Ertl Center & DPHPeter StrasserTU Berlin

Keynote, Invited and Contributed Speakers

Mischa Bonn	MPI Mainz
Saskia Buller	MPI-CEC
Kramer Campen	FHI der MPG
Jinsub Choi	Inha University
Zhifeng Ding	The University of Western Ontario
Hajo Freund	FHI der MPG
Renate Hiesgen	University of Applied Sciences, Esslingen
Saman Hosseinpour	MPI Mainz
Timo Jacob	University of Ulm
Henrik Jensen	University of Copenhagen
Young Dok Kim	SKKU
Axel Knop-Gericke	FHI der MPG
Marc T. M. Koper	Leiden University
Hye Jin Lee	Kyungpook National University
Sergey Levchenko	FHI der MPG
Angelos Michaelides	University College London
Bridget Murphy	Kiel University
Sebastian Neugebauer	MPI-CEC
Enrico Pizzutilo	MPIE
Beatriz Roldan Cuenya	Ruhr-University Bochum
Rolf Schuster	KIT
Hyun Ook Seo	SKKU & University of Konstanz
Shamil Shaikhutdinov	FHI der MPG

Dongyoon Shin	GIST Ertl Center
Marc Willinger	FHI der MPG
Bo-Qing Xu	Tsinghua University
Youngmi Yi	MPI-CEC

Abstract Submission by 31 August 2016

150-300 words with illustration and pictures in WORD file E-mail submission: ertl@gist.ac.kr

Conference Fee & Registration

 ▶ Regular participants: € 350
 Students: € 200
 The symposium registration fee includes a copy of the book of abstracts, lunch, coffee break and conference dinner.
 Payment: in CASH at the registration desk upon arrival.

Conference Venue

The 4th Ertl Symposium on Water at Interfaces will be held in the Harnack-House, the conference venue of the Max Planck Society, around 200 meters from U3 Thielplatz. The symposium venue can easily be reached by the well-established public traffic system in Berlin. For details of the location, see: http://www.harnackhaus-berlin.mpg.de http://www.fhi-berlin.mpg.de/reach.epl



U3 Thielplatz

Special Issue

The symposium proceedings will be published in a special issue of **Catalysis Today** on <u>Water</u> <u>at Interfaces</u>. Articles will be subject to the standard peer review for an Elsevier journal. The Catalysis Today website is active for this special issue (WAIT) and contributions can be uploaded starting **15 October 2016.** The deadline for submission of manuscripts is **31 December 2016.** Guest Editors: Jaeyoung Lee (Ertl Center & SESE, GIST), Bongjin Simon Mun (DPH & Ertl Center, GIST) and Young Dok Kim (SKKU)

Program

Time	Time Tuesday (10/11) Wednesday (10/12) Thursday (Goethe-Saal Goethe-Saal Laue-S		Thursday (10/13) Laue-Saal	
08:30 - 09:00	30		Regist	ration
09:00 - 10:40	100		Young Dok Kim Award Lecture 2 / 40 Peter Strasser Invited 5 / 30 Jinsub Choi Invited 6 / 30 Henrik Jensen	Marc Willinger Invited 10 / 30 Shamil Shaikhutdinov Contributed Oral 8 / 20 Enrico Pizzutilo Contributed Oral 9 / 20 Saman Hosseinpour Invited 11 / 30 Sergey Levchenko
10:40 - 11:00	20	Arrival & Registration	Coffee	Break
11:00 - 12:30	90		Beatriz Roldan Cuenya Keynote 2 / 40 Hajo Freund Contributed Oral 2 / 20 Saskia Buller Invited 7 / 30 Kramer Campen	Peter Strasser Keynote 5 / 40 Axel Knop-Gericke Invited 12 / 30 Marc Willinger Contributed Oral 10 / 20 Sebastian Neugebauer Closing Remarks / 5 Markus Eiswirth
12:30 - 14:00	90		Lur	nch
14:00 - 16:00	120	Hye Jin Lee Opening Address / 5 Robert Schlögl Welcome Address / 5 Gerhard Ertl Award Ceremony /10 Award Lecture 1 / 40 Bongjin Simon Mun Invited 1 / 30 Marc T. M. Koper Invited 2 / 30 Renate Hiesgen	Zhifeng Ding Keynote 3 / 40 Mischa Bonn Contributed Oral 3 / 20 Hye Jin Lee Contributed Oral 4 / 20 Rolf Schuster Contributed Oral 5 / 20 Youngmi Yi Contributed Oral 6 / 20 Yound Dok Kim	City Tour
16:00 - 16:30	30	Coffee (Photograph Tir	: break me on Tuesday)	(or MANGAN Project Conference - Sebastian Neugebauer)
16:30 – 18:30	120	Sebastian Neugebauer Keynote 1 / 40 Bo-Qing Xu Contributed Oral 1 / 20 Dongyoon Shin Invited 3 / 30 Beatriz Roldan Cuenya Invited 4 / 30 Timo Jacob	Henrik Jensen Keynote 4 / 40 Angelos Michaelides Contributed Oral 7 / 20 Hyun Ook Seo Invited 8 / 30 Zhifeng Ding Invited 9 / 30 Bridget Murphy	
18:30 – 20:30	120	Timo Jacob Jaeyoung Lee Poster Session	Bongjin Simon Mun Symposium Dinner & Poster Award Ceremony	Culture Night

11 October (Tuesday)

	AL (Award Lecture, 40min), KL (Keynote Lecture, 40min), IL (Invited Lecture, 30min), OP (Oral Presentation, 20min)	
	Program	Time
12:00 - 14:00	Registration	120
	Opening Address : Robert Schlögl	14:00
14:00 - 14:20	Welcome Address : Gerhard Ertl	14:05
	Award Ceremony	14:10
	Session 1: Hye Jin Lee	
	 AL-01 Bongjin Simon Mun (Gwangju Institute of Science and Technology, Korea) Oxygen Adsorption on Pt & Pt Alloys 	14:20
14:20 - 16:00	IL-01 Marc T. M. Koper (Leiden University, The Netherlands) ▶ Water at Stepped Platinum Surfaces	15:00
	 IL-02 Renate Hiesgen (University of Applied Sciences Esslingen, Germany) Ionomer in Fuel Cell Membranes and Electrodes Investigated at High Humidity by Atomic Force Microscopy 	15:30
16:00 - 16:30	Coffee Break	30
	Session 2: Sebastian Neugebauer	
	 KL-01 Bo-Qing Xu (Tsinghua University, China) ▶ Active Site Structures in Aniline-Derived Fe-N-C Electrocatalysts for Oxygen Reduction Reaction 	16:30
16:30 - 18:30	 OP-01 Dongyoon Shin (Gwangju Institute of Science and Technology, Korea) On the Origin of Electrocatalytic Water Oxidation on Cobalt Derived Edge Plane Rich Mesoporous Carbon Nanofiber 	17:10
	IL-03 Beatriz Roldan Cuenya (Ruhr-University Bochum, Germany) ▶ Selectivity Control in the Electroreduction of CO ₂ over Nanostructured Catalysts	17:30
	IL-04 Timo Jacob (Ulm University, Germany) ▶ Measuring an Electrocatalyst's Vital Signs: the Need for in <i>Operando</i> Studies	18:00
18:30 - 20:30	Poster Session: Timo Jacob, Jaeyoung Lee	120



12 October (Wednesday)

	Program	Time
08:30 - 09:00	Registration	30
	Session 3: Young Dok Kim	
	 AL-02 Peter Strasser (Technical University Berlin, Germany) Free Electrons to Molecular Bonds and Back: Materials and Electrocatalysis of Energy Conversion 	9:00
07:00 - 10:40	IL-05 Jinsub Choi (Inha University, Korea) ► High Aspect Ratio Anodic TiO ₂ Nanotubes with Dopants for Water Oxidation	9:40
	 IL-06 Henrik Jensen (University of Copenhagen, Denmark) Tunable Partitioning and Extraction of Drug Compounds and Their Metabolites at Interfaces between Immiscible Electrolyte Solutions (ITIES) 	10:10
10:40 - 11:00	Coffee Break	20
	Session 4: Beatriz Roldan Cuenya	
	 KL-02 Hajo Freund (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) The Structure of Oxide Surfaces and Its Interaction with Water 	11:00
11:00 - 12:30	 OP-02 Saskia Buller (Max-Planck-Institute for Chemical Energy Conversion, Germany) ▶ Carbon Based Electrode Materials 	11:40
	IL-07 R. Kramer Campen (Fritz-Haber-Institute of the Max-Planck-Society, Germany) ▶ Probing the Mechanism of the Hydrogen Evolution Reaction on Au	12:00
12:30 - 14:00	Lunch	90
	Session 5: Zhifeng Ding	
	 KL-03 Mischa Bonn (Max-Planck-Institute for Polymer Research, Germany) The Water Surface: Complex, Dynamic and Wet 	14:00
	OP-03 Hye Jin Lee (Kyungpook National University, Korea) ▶ Reduction Process of Carbon Dioxide at an ITIES	14:40
14:00 - 16:00	 OP-04 Rolf Schuster (Karlsruhe Institute of Technology, Germany) Microcalorimetric Investigation of Charge-Neutral Anion Coadsorption and Substitution Processes during the Cu and Ag Underpotential Deposition on Au(111) 	15:00
	OP-05 Youngmi Yi (Max-Planck-Institute for Chemical Energy Conversion, Germany) ▶ Carbon Materials for Oxygen Electrocatalysis	15:20
	 OP-06 Young Dok Kim (Sungkyunkwan University, Korea) Superhydrophobic Surfaces Prepared by Dimethylsiloxane-Coated Nanoparticles: Fundamental Studies and Applications 	15:40
16:00 - 16:30	Coffee Break	30

12 October (Wednesday)

	Program	Time
	Session 6: Henrik Jensen	
	 KL-04 Angelos Michaelides (University College London, United Kingdom) ► Unravelling the Mysteries of the Water-Solid Interface with Statistical Mechanics and <i>ab initio</i> Simulations 	16:30
	UP-07 Hyun Ook Seo (Sungkyunkwan University, Korea) ▶ Light-induced Oxidation of Poly(3-Hexy(thiophene-2,5-diyl) Thin Films on ZnO Buffer Layers:	17:10
16:30 - 18:30	Impacts of Humidity, Underlying Metal-Oxides, and the Wavelength of Visible Lights	
	IL-08 Zhifeng Ding (The University of Western Ontario, Canada)	
	 Hydrophilicity/Lipophilicity of Phosphonium Ionic Liquids as Determined at Electrified Interfaces 	17:30
	IL-09 Bridget Murphy (Kiel University, Germany) ▶ Investigating the Atomic Scale Structure of Liquid Metal - Electrolyte Interface with X-rays	18:00
18:30 - 20:30	Symposium Dinner & Poster Award Ceremony	120

13 October (Thursday)

	Program	Time
08:30 - 09:00	Registration	30
	Session 7: Marc Willinger	
	IL-10 Shamil Shaikhutdinov (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) ▶ Interaction of Water with Metal Supported Silicate Films	9:00
09:00 - 10:40	 OP-08 Enrico Pizzutilo (Max-Planck-Institut für Eisenforschung, Germany) Activity and Stability of Pore Confined Pt-Co Alloyed Catalyst for the Oxygen Reduction Reaction (ORR) 	9:30
	OP-09 Saman Hosseinpour [Max-Planck-Institute for Polymer Research, Germany] ▶ Water Structure at the TiO ₂ /Water Interface	9:50
	IL-11 Sergey V. Levchenko (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) ▶ <i>Ab initio</i> Study of Adsorbed Water Phases at Alkaline Earth Metal Oxide Surfaces	10:10
10:40 - 11:00	Coffee Break	20
	Session 8: Peter Strasser	
	 KL-05 Axel Knop-Greicke (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) The Electronic Structure of Iridium Oxides Active in Water Splitting 	11:00
11:00 - 12:30	IL-12 Marc Georg Willinger (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) ▶ Oscillatory Red-Ox Behavior of Active Metal Catalysts Observed by <i>in situ</i> Electron Microscopy	11:40
	OP-10 Sebastian Neugebauer (Max-Planck-Institute for Chemical Energy Conversion, Germany) ▶ MANGAN - Standardized Electrochemical Measurements for the Oxygen Evolution Reaction	12:10
	Close of Symposium (Markus Eiswirth)	12:30
12:35 - 14:00	Lunch	85
14:00 - 18:30	City Tour (or MANGAN Project Conference – Sebastian Neugebauer)	
18:30	Culture Night	

List of Oral Presentations

AL-01	Bongjin Simon Mun	Oxygen adsorption on Pt & Pt alloys	1
IL-01	Marc T. M. Koper	Water at Stepped Platinum Surfaces	2
IL-02	Renate Hiesgen	Ionomer in Fuel Cell Membranes and Electrodes Investigated at High Humidity by Atomic Force Microscopy	3
KL-01	Bo-Qing Xu	Active Site Structures in Aniline-Derived Fe-N-C Electrocatalysts for Oxygen Reduction Reaction	5
0P-01	Dongyoon Shin	On the Origin of Electrocatalytic Water Oxidation on Cobalt Derived Edge Plane Rich Mesoporous Carbon Nanofiber	6
IL-03	Beatriz Roldan Cuenya	Selectivity Control in the Electroreduction of \mbox{CO}_2 over Nanostructured Catalysts	7
IL-04	Timo Jacob	Measuring an Electrocatalyst's Vital Signs: the Need for in Operando Studies	8
AL-02	Peter Strasser	Free Electrons to Molecular Bonds and Back: Materials and Electrocatalysis of Energy Conversion	9
IL-05	Jinsub Choi	High Aspect Ratio Anodic TiO_2 Nanotubes with Dopants for Water Oxidation	10
IL-06	Henrik Jensen	Tunable Partitioning and Extraction of Drug Compounds and Their Metabolites at Interfaces between Immiscible Electrolyte Solutions (ITIES)	11
KL-02	Hajo Freund	The Structure of Oxide Surfaces and Its Interaction with Water	12
0P-02	Saskia Buller	Carbon Based Electrode Materials	13
IL-07	R. Kramer Campen	Probing the Mechanism of the Hydrogen Evolution Reaction on Au	14
KL-03	Mischa Bonn	The Water Surface: Complex, Dynamic and Wet	15
0P-03	Hye Jin Lee	Reduction Process of Carbon Dioxide at an ITIES	16
0P-04	Rolf Schuster	Microcalorimetric Investigation of Charge-Neutral Anion Coadsorption and Substi- tution Processes during the Cu and Ag Underpotential Deposition on Au(111)	17
0P-05	Youngmi Yi	Carbon Materials for Oxygen Electrocatalysis	18
0P-06	Young Dok Kim	Superhydrophobic Surfaces Prepared by Dimethylsiloxane-Coated Nanoparticles: Fundamental Studies and Applications	19
KL-04	Angelos Michaelides	Unravelling the Mysteries of the Water-Solid Interface with Statistical Mechanics and <i>ab initio</i> Simulations	20

List of Oral Presentations

OP-07	Hyun Ook Seo	Light-induced Oxidation of Poly[3-HexyIthiophene-2,5-diyl] Thin Films on ZnO Buf- fer Layers: Impacts of Humidity, Underlying Metal-Oxides, and the Wavelength of Visible Lights	21
IL-08	Zhifeng Ding	Hydrophilicity/Lipophilicity of Phosphonium Ionic Liquids as Determined at Electri- fied Interfaces	22
IL-09	Bridget Murphy	Investigating the Atomic Scale Structure of Liquid Metal - Electrolyte Interface with X-rays	23
IL-10	Shamil Shaikhut- dinov	Interaction of Water with Metal Supported Silicate Films	24
0P-08	Enrico Pizzutilo	Activity and Stability of Pore Confined Pt-Co Alloyed Catalyst for the Oxygen Reduc- tion Reaction (ORR)	25
OP-09	Saman Hosseinpour	Water Structure at the TiO_2 /Water Interface	26
IL-11	Sergey V. Levchenko	Ab initio Study of Adsorbed Water Phases at Alkaline Earth Metal Oxide Surfaces	27
KL-05	A. Knop-Gericke	The Electronic Structure of Iridium Oxides Active in Water Splitting	28
IL-12	Marc Georg Willinger	Oscillatory Red-Ox Behavior of Active Metal Catalysts Observed by <i>in situ</i> Electron microscopy	29
OP-10	Sebastian Neuge- bauer	MANGAN - Standardized Electrochemical Measurements for the Oxygen Evolution Reaction	30

List of Poster Presentations

PP-01	Qiao-Ling Dai	Model Reaction Studies of Water Effects on the Surface Acidity of Several Solid Acid Catalysts	33
PP-02	F. Dionigi	NiFe Layered Double Hydroxide Electrocatalyst for Water and Seawater Oxidation	34
PP-03	M. Fitzner	On the Role of Pre-Critical Fluctuations in Heterogeneous Ice Nucleation	35
PP-04	Lukas Gierster	Ultrafast Electron Transfer-Induced $\rm CO_2$ Activation at a ZnO Surface	36
PP-05	Wen Ju	Transition Metal Functionalized Nitrogenated Carbon Based Catalyst for Direct Electrochemical CO $_2$ Reduction to CO and Hydrocarbons	37
PP-06	Il Hee Kim	Temperature Regulated-Chemical Vapor Deposition for Incorporating Metal Nanoparticles into Mesoporous Media: Simple Strategy for Preparation of Cata- lyst with Activity and Stability	38
PP-07	Sarah B. King	Energetics, Dynamics and Reactivity of Excess Electrons in Polar Solvents	39
PP-08	Yoobin Koh	Chemical States of Palladium Nanoparticles Supported on Nanodiamond and Onion-like-Carbon during CO Oxidation	40
PP-09	Gibaek Lee	Anodic ${\rm TiO_2}$ Hollow Microcones as Advanced Anodes for Lithium-Ion Batteries	41
PP-10	Hojoon Lim	Characterizing Surface Oxidation States of Vanadium Thin Films with <i>in situ</i> Ambient Pressure X-ray Photoelectron Spectroscopy	42
PP-11	Anna K. Mechler	Hybrid Materials of Non-Precious Metal Catalysts with Ultra-Low Platinum Load- ings for the Oxygen Reduction Reaction	43
PP-12	Hong Nhan Nong	Operando X-ray Absorption Spectroscopy Study of IrNiOx Core-Shell Nanopar- ticles as Highly Active Water Oxidation Electrocatalysts	44
PP-13	Zarina Pawolek	A Gastight RDE Setup to Investigate the Selectivity of Electrochemical Oxygen and Chlorine Evolution	45
PP-14	Dongyoon Shin	Effect of Transition Metal Induced Pore Structure on Oxygen Reduction Reaction of Electrospun Fibrous Carbon	46
PP-15	Sunghyun Uhm	Efficient Structured Catalysts for CO Oxidation	47
PP-16	J. J. Velasco-Vélez	Soft X-ray Photoelectron Spectroscopy at Solid-Liquid Electrified Interfaces: Revealing Electrochemistry in Action	48
PP-17	Youngmi Yi	Biomass-Based Hydrothermal Carbon Disc for Electrocatalytic Water Splitting	49
PP-18	Hyeonseok Yoo	The High Performance Anodic $\rm TiO_2$ Electrode Consisting of $\rm IrO_2-RuO_2$ Catalysts for Water Oxidation Application	50
PP-19	Youngseok Yu	The Role of Surface Oxide during CO Oxidation on Pt(110)	51
PP-20	Zi-Fei Yuan	Effect of the Support Acid-Base Property on the Selectivity Control of Au- Catalysis for Glycerol Oxidation in Base-Free Water	52
PP-21	M. Zanatta	Local Measurement of pH Gradient on Microstructured Electrodes Using SICM	53





Oxygen Adsorption on Pt & Pt Alloys

Bongjin Simon Mun^{1,2,*}

¹ Department of Physics and Photon Science, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea ² Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju, Republic of Korea

E-mail: bsmun@gist.ac.kr (B. S. Mun)

In surface science, the oxygen adsorption on Pt surface has been one of the most important research subjects mainly due to its critical roles in heterogeneous catalyst research. Over the years, with the advance of surface science experimental tools and DFT calculation, the fundamental understandings of chemisorbed oxygen on Pt surface have made the significant progress.

In this presentation, I will present the various oxygen adsorption properties on Pt and Pt alloys that have been studied in our group with the application of x-ray photoelectron spectroscopy. The focus of the presentation will be given on how surface electronic structure is correlated to the oxygen adsorption behavior.



Fig. 1. Fermi surface mapping of Pt(111) and Pt₃Ni (111) measured with angle resolved XPS.

Water at Stepped Platinum Surfaces

Manuel J. Kolb, Cansin Badan, Angela den Dunnen, Federico Calle-Vallejo, Ludo B. F. Juurlink, <u>Marc T. M. Koper</u>

Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands

E-mail: m.koper@chem.leidenuniv.nl (M. T. M. Koper)

The structure of water at platinum surfaces is highly sensitive to the structural, electronic and chemical properties of the underlying platinum substrate. In this talk I will summarize our recent experimental and computational results on the influence of step geometry, step density, water coverage, and the presence of adsorbed atomic hydrogen and oxygen, on the interfacial structure of water in contact with a platinum surface. The implications on (electro-)catalytic surface reactivity will also be discussed briefly.



Ionomer in Fuel Cell Membranes and Electrodes Investigated at High Humidity by Atomic Force Microscopy

Renate Hiesgen^{1,*}, Tobias Morawietz¹, Michael Handl¹, K. Andreas Friedrich²

¹ University of Applied Sciences, Kanalstr. 33, Esslingen 73728, Germany ² Institute of Engineering Thermodynamics, German Aerospace Center, Pfaffenwaldring 38-40, Stuttgart, 70569, Germany

E-mail: renate.hiesgen@hs-esslingen.de (R. Hiesgen)

Ionomers are widely used ionically conducting polymers, i.e. in sensors, fuel cells and water as well as brine electrolyzes. In PEM fuel cells and –electrolyzes, the proton conductions membranes as well as the ionically conducting phase in the electrodes consist of ionomer such as Nafion or Aquivion. In such ionomers, the proton conduction is based on a nano-segregation into a hydrophobic and a hydrophilic phase. To obtain a proton flow, a continuous ionically conducting network which has large enough water channels to allow structure diffusion of bulk water is needed.

Using material-sensitive atomic force microscopy (AFM), the properties of different ionomer membrane cross-sections were investigated at high humidity. Differences in the structure of the waterrich phase and the formation of a continuous proton conductive network were as investigated [1].

The analysis of the thickness and distribution of the ionomer component in the electrode has proven to be difficult [2]. Using vacuum-based techniques such as high-resolution electron microcopy leads to drying out and shrinking of the ionomer, also the contrast between carbon and ionomer phase is small without staining [3]. With material-sensitive AFM applied to cross-sections of electrodes, the ionomer phase gives a high contrast to platinum-coated carbon particles. At cross-sections of differently prepared electrodes, the thickness and distribution of the ionomer phase was evaluated before and after fuel cell operation.

More insight into the properties of such thin ionomer films was derived using material-sensitive AFM measurements at ultra-thin Nafion layers deposited on platinum.



Fig. 1. (a) AFM capacitive current mapping of bulk Nafion[®] with bright water-rich phase. (b) Capacitive current mapping of 10 nm-thick Nafion[®] layer. (c) AFM adhesion force mapping of a bulk fuel cell electrode cross-section, measured at 75% relative humidity. (d) Distribution of thickness of ionomer layers in anode of commercial fuel cell after 235 h of operation, measured at 60% RH.

Acknowledgements

The research leading to these results has received funding from the European Union's Seventh Framework Programm (FP7/ 2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n°303452, "IMPACT— Improved Lifetime of Automotive Application Fuel Cells with ultra low Pt-loading", and grant agreement n° 621237, "INSIDE- In -situ Diagnostics in Water Electrolyzers"

References

- R. Hiesgen, T. Morawietz, M. Handl, M. Corasaniti, K. A. Friedrich, Electrochim. Acta, 162 (2015) 86.
- [2] S. Holdcroft, Chem. Mater., 26 (2014) 381.
- [3] M. Lopez-Haro, L. Guétaz, T. Printemps, A. Morin, S. Escribano, P. -H. Jouneau, P. Bayle-Guillemaud, F. Chandezon, G. Gebel, Nat. Commun., 5 (2014) 5229.

Active Site Structures in Aniline-Derived Fe-N-C Electrocatalysts for Oxygen Reduction Reaction

Nan-Hong Xie, Bo-Qing Xu*

Innovative Catalysis Program, Department of Chemistry, Tsinghua University, Beijing 100084, China

E-mail: bqxu@mail.tsinghua.edu.cn (B. -Q. Xu)

Iron and nitrogen co-doped carbon (Fe-N-C) catalysts are considered as the promising alternatives to Pt-based electrocatalysts for oxygen reduction reaction (ORR) in fuel cells and metal-air batteries. However, the earlier Fe-N-C catalysts always contained co-existing active and inactive Fe-involving entities that disturb clear identification of the active site structures. We present herein a new preparative approach that allows systematic variation of the density of the doped Fe and N atoms (and thus the surface active site density as well) but can avoid involvement of Fe_xS, FeO_y, Fe_zC and metallic Fe in aniline-derived Fe-N-C catalysts. Careful characterizations of these Fe-N-C samples with multiple techniques, including XRD, Raman, TEM, HAADF-STEM, XPS, ⁵⁷Fe Mössbauer spectroscopy and XANES/EXAFS, are conducted in conjunction with electrochemical measurements of the intrinsic ORR activity to identify the possible most active sites and to establish correlation between the number of such active sites and the kinetic ORR rate. The data clearly point to that those isolated or atomically dispersed Fe^{II} species in coordination structures of Fe^{II}-N₄ are serving as the most active sites for the ORR.



Fig. 1. (a) LSV curves for the Fe-N-C-*x* catalysts in O_2 -saturated 0.1 M KOH, (b) catalytic ORR activity and stability by half-wave potentials of the Fe-N-C-6 and Pt/C (E-TEK) catalysts, (c) correlation between the kinetic ORR activity and concentration of the electrochemically active Fe^{II} species (EAFC) in the Fe-N-C-*x* catalysts.

On the Origin of Electrocatalytic Water Oxidation on Cobalt Derived Edge Plane Rich Mesoporous Carbon Nanofiber

Dongyoon Shin¹, Xianghua An¹, Myounghoon Choun¹, Jaeyoung Lee^{1,2,*}

¹ Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea

² Ertl Center for Electrochemistry and Catalysis, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, South Korea

E-mail: shingoon@gist.ac.kr (D. Shin)

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

Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi, K. Hashimoto, Nat. Commun., 4 (2013) 2390.
 T. Y. Ma, S. Dai, M. Jaroniec, S. Z. Qiao, Angew. Chem.-Int. Edit., 53 (2014) 7281.
 J. Zhang, Z. Zhao, Z. Xia, L. Dai, Nat. Nanotechnol., 10 (2015) 444.

Selectivity Control in the Electroreduction of CO₂ over Nanostructured Catalysts

Beatriz Roldan Cuenya

Department of Physics, Ruhr-University Bochum, 44708 Bochum, Germany

E-mail: Beatriz.Roldan@rub.de (B. R. Cuenya)

The electrocatalytic reduction of CO_2 to industrial chemicals and fuels is a promising pathway to sustainable electrical energy storage and to an artificial carbon cycle, but is currently hindered by the low energy efficiency and low activity displayed by traditional electrode materials.

Using colloidal synthesis, nanoparticles (NPs) with well-defined size and interparticle distance were prepared and tested as catalysts for CO_2 electroreduction. Cu NP catalysts displayed a drastic increase in activity and selectivity for H_2 and CO with decreasing NP. Hydrocarbon (methane and ethylene) selectivity was increasingly suppressed with decreasing NP size. For Au NPs, a drastic increase in current density was observed with decreasing NP size, along with a decrease in faradaic selectivity towards CO. The H_2/CO product ratio could be tailored by tuning the NP size. In addition, interparticle distance is also a critical parameter for controlling reactivity. For largely spaced NPs, selectivity to CO is enhanced. On the contrary, for closely spaced NPs we find that hydrocarbon selectivity is enhanced, since the re-adsorption of reaction intermediates on neighboring NPs can facilitate the multi-step pathway required for hydrocarbon production.

Another critical parameter for selectivity control in nanostructured electrocatalysts is the chemical state. We will discuss new oxide-derived (plasma-treated) metal catalysts (Cu and Ag-based) that can reduce CO_2 with lowered overpotential and improved ethylene selectivity. Insights into the catalyst reaction mechanism which were unraveled using structural and chemical information obtained under o*perando* conditions via X-ray absorption fine-structure spectroscopy will be presented. Finally, the role of the NP shape, in particular, the presence of (100) facets in Cu nanocubes and the evolution of the NP structure and dispersion under reaction conditions will be discussed based on *operando* electrochemical AFM data.



⁴th Ertl Symposium on Chemical Processes on Solid Surfaces

Measuring an Electrocatalyst's Vital Signs: the Need for in *Operando* Studies

Timo Jacob

 ¹ Institute of Electrochemistry, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany
 ² Helmholtz-Institute-Ulm (HIU), Helmholtzstrasse 11, D-89081 Ulm, Germany

E-mail: timo.jacob@uni-ulm.de (T. Jacob)

Batteries, fuelcells, photocells and many other applications are powered by fundamental electrochemical processes. Compared to surface science under UHV conditions, electrochemical systems combine a wide variety of additional effects. These range from the presence of an electrolyte and a multi-component environment to reaction conditions such as finite temperature, pressure, and electrode potential. Due to this complexity our knowledge of the ongoing processes is mostly limited to the macroscopic regime. However, nowadays interface-sensitive experiments together with theoretical modeling are able to provide deeper insights into structures and processes at the atomic level. This fundamental knowledge makes the development and/or design of improved (electro-)catalysts possible.

Following general overview of а electrochemistry, Ι will compare the concepts of surface science and electrochemistry in detail, addressing both their similarities and differences. Using apparently simple electrocatalytic reactions as model systems, the effects of the reactive surrounding as well as environmental parameters will be successively explored. It turns out that pure and perfect catalyst models, which are often used in literature, are in many cases insufficient.

Finally, these concepts will be extended from single crystals to the nanoregime, where nanostructured surfaces and particles are often used for electro-catalytic reactions. Taking transition metal alloys as an example, we will show that nanoparticles are not rigid objects but often change their morphologies and compositions under reaction conditions. Thus, understanding the dynamic nature of



Fig. 1. Schematic model of the dynamic behavior of AuPd(111) in the hydrogen evolution regime.

these catalysts is crucial in our efforts to further extend our ability to rationally design multicomponent (electro-)catalysts.

4th Ertl Symposium on Chemical Processes on Solid Surfaces

Free Electrons to Molecular Bonds and Back: Materials and Electrocatalysis of Energy Conversion

Peter Strasser

Department of Chemistry, Chemical Engineering Division, Technical University Berlin, Germany

E-mail: pstrasser@tu-berlin.de (P. Strasser)

Electrochemistry and Electrocatalysis play pivotal roles in the science and technology of chemical energy storage and conversion. Devices such as electrolyzers, photoelectrochemical cells, or fuel cells constitute electrochemical reactors where all relevant molecular processes occur. There, storage and conversion is put into effect via molecular bond making and breaking, catalyzed at electrified interfaces of an ion conductor and an electrocatalyst material. For these reactions to occur with the smallest possible energy losses and the utmost atom efficiency, nanostructured multi-component electrode materials have proven indispensable, because they offer substantial advantages in atomic dispersion, often resulting in energy efficiency and performance benefits.

All this taken together is why energy-related electrocatalysis and the science of nanomaterials have formed an irrevocable symbiosis. The successful development of novel nanostructured electrocatalyst materials, however, requires insight into the relation between their atomic-scale structure and their catalytic performance. Unraveling such relations is thus a scientific priority.

In this talk, I will highlight some advances of our recent work on the design and understanding of structure-activity relations of nanostructured electrocatalytic materials and their liquid-solid interfaces.



Fig. 1. The electrocatalytic production and conversion of fuels/chemicals from and into electricity depends critically on the efficient electrocatalytic oxygen reduction and evolution reaction.

High Aspect Ratio Anodic TiO₂ Nanotubes with Dopants for Water Oxidation

Hyeonseok Yoo, Jinsub Choi*

Department of Chemistry and Chemical Engineering, Center for Design and Applications of Molecular Catalysts, Inha University, Incheon 402-751, Korea

E-mail: jinsub@inha.ac.kr (J. Choi)

In the study, TiO_2 nanotubes with a doping of various catalysts, such as MnO_2 , Pt, RuO_2 and/or IrO_2 , were prepared by novel doping processes for water oxidation applications. We demonstrated that most catalysts can be homogeneously doped into TiO_2 nanotubes with high aspect ratio by the single step anodization, in which negatively-charged precursors are simultaneously incorporated into TiO_2 films during anodic oxidation of Ti. Since for some cases, the precursors were decomposed into the positively charged metal ions, which were deposited on the counter electrode instead of the simultaneous doping during the single step anodization, the potential shock method, in which the high positive bias is shortly imposed on the prepared TiO_2 nanotubes in the precursor solution immediately after the first anodization, was introduced. Advanced techniques such as underpotential shock method, which was developed to suppress the aggressive chloride ions involved in some precursors, will be discussed in detail.



Fig. 1. SEM images of anodic TiO_2 nanotubes without (a, b) and with IrO_2/RuO_2 dopants (c, d). Fig.1 (a, c) and (b, d) show the top and bottom side view, respectively.

Tunable Partitioning and Extraction of Drug Compounds and Their Metabolites at Interfaces between Immiscible Electrolyte Solutions (ITIES)

Andrea M. Nadal, David Fuchs, Nickolaj J. Petersen, Steen H. Hansen, Stig Pedersen-Bjergaard, <u>Henrik Jensen</u>

Department of Pharmacy, Faculty of Health and Medical Sciences, University of Copenhagen, Denmark

E-mail: henrik.jensen@sund.ku.dk (H. Jensen)

Electrochemistry in aqueous solution usually involves solid conductive electrode materials at which redox reactions can be controlled and/or studied, however, there exist other formats for studying charge transfer processes. Electrochemistry at ITIES may be used for studying ion transfer processes or biphasic electron transfer reactions taking place at the boundary between water and oil. Using basic electrochemical concepts, it is possible to characterize these processes in great detail as well as to obtain thermodynamic and kinetic information.



Fig. 1. Drawing of traditional electrochemical ITIES system (a), sandwiched ITIES setup for extraction of charged drug compounds (b) and voltage dependent extraction curves (c).

As illustrated in figure 1 we have adapted electrochemistry at ITIES (Fig. 1a and 1b) to practical applications involving extraction of drug compounds and their metabolites from plasma and liver microsomes [1-3]. It is possible to utilize the applied potential to introduce selectivity in the extraction process (Fig. 1c), and the entire protocol can be fully automated using a microfluidic based system [3]. A mathematical model is used to predict the extraction efficiency [4]. Finally, the influence of ion paring in the extraction process will be discussed along with future applications.

References

- [1] M. A. Deryabina, S. H. Hansen, H. Jensen, Anal. Chem., 83 (2011) 7388.
- [2] N. J. Petersen, J. S. Pedersen, N. N. Poulsen, H. Jensen, C. Skonberg, S. H. Hansen, S. Pedersen-Bjergaard, Analyst, 137 (2012) 3321.
- [3a] D. Fuchs, H. Jensen, S. Pedersen-Bjergaard, C. Gabel-Jensen, S. H. Hansen, N. J. Petersen, Anal. Chem., 87 (2015) 5774.
- [3b] D. Fuchs, S. Pedersen-Bjergaard, H. Jensen, K. D. Rand, S. H. Hansen, N. J. Petersen, Anal. Chem., 88 (2016) 6797.
- [4] C. Huang, H. Jensen, K. F. Seip, A. Gjelstad, S. Pedersen-Bjergaard, J. Sep. Sci., 39 (2016) 188.

The Structure of Oxide Surfaces and Its Interaction with Water

Hajo Freund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Chemical Physics, Faradayweg 4-6, 14195 Berlin, Germany

E-mail: freund@fhi-berlin.mpg.de (H. Freund)

Knowledge on oxide surface structures is of fundamental importance towards understanding its reactivity towards water. We report on several surface structures recorded via LEED and scanning tunneling microscopy. We make a particular point of using LEED, a technique that has come out of fashion for oxides for all the wrong reasons.

Results on transition metal and simple oxides are presented. Adsorption of water has been studied in addition using infrared spectroscopy as well as single crystal micro calorimetry. The standard models for dissociative and molecular adsorption are discussed. Parallel to the experimental work, theoretical studies are carried out and their results are mentioned as well.

H ₂ O/V ₂ O ₃ (0001)/Au(111) and W(110)	Abu Haija, M.; Guimond, S.; Uhl, A.; Kuhlenbeck, H.; Freund, H. J.: Adsorption of water on thin V ₂ O ₃ (0001) films. <i>Surf. Sci.</i> 2006 , <i>600</i> , 1040-1047.
H ₂ O/Fe ₃ O ₄ (111)/Pt(111)	Dementyev, P.; Dostert, KH.; Ivars-Barceló, F.; O'Brien, C. P.; Mirabella, F.; Schauermann, S.; Li, X.; Paier, J.; Sauer, J.; Freund, HJ.: Water Interaction with Iron Oxides. <i>Angew. Chem. Int. Ed.</i> 2015 , <i>54</i> , 13942-13946.
H ₂ O/FeO(111)/Pt(111)	Ringleb, F.; Fujimori, Y.; Wang, H. F.; Ariga, H.; Carrasco, E.; Sterrer, M.; Freund, H. J.; Giordano, L.; Pacchioni, G.; Goniakowski, J.: Interaction of water with FeO(111)/Pt(111): Environmental effects and influence of oxygen. <i>J. Phys. Chem. C</i> 2011 , <i>115</i> , 19328-19335.
H ₂ O/CaO(100)/Mo(100)	Fujimori, Y.; Zhao, X.; Shao, X.; Levchenko, S. V.; Nilius, N.; Sterrer, M.; Freund, HJ.: Interaction of Water with the CaO(001) Surface. <i>J. Phys. Chem.</i> C 2016 , <i>120</i> , 5565-5576.
	Zhao, X.; Shao, X.; Fujimori, Y.; Bhattacharya, S.; Ghiringhelli, L. M.; Freund, HJ.; Sterrer, M.; Nilius, N.; Levchenko, S. V.: Formation of Water Chains on CaO(001): What Drives the 1D Growth? <i>J. Phys. Chem.</i> <i>Lett.</i> 2015 , <i>6</i> , 1204-1208.
H ₂ O/MgO(100)/Ag(100)	Włodarczyk, R.; Sierka, M.; Kwapień, K.; Sauer, J.; Carrasco, E.; Aumer, A.; Gomes, J. F.; Sterrer, M.; Freund, HJ.: Structures of the Ordered Water Monolayer on MgO(001). <i>J. Phys. Chem. C</i> 2011 , <i>115</i> , 6764-6774.

^{4&}lt;sup>th</sup> Ertl Symposium on Chemical Processes on Solid Surfaces

Carbon Based Electrode Materials

Saskia Buller^{1,*}, Pascal Düngen¹, Jan Straten¹, Sylvia Becker (née Reiche)¹, Robert Schlögl^{1,2}

¹ Max-Planck-Institute for Chemical Energy Conversion, Mülheim, Germany ² Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany

E-mail: saskia.buller@cec.mpg.de (S. Buller)

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 [1]. The knowledge-based development of electrode materials of our research is focused on compound materials of carbons as conductive base material and transition metals as catalytic active sites.

Carbon materials fulfill the requirements of a conductive support that provides high surfaces areas as well as specific functional groups that are able to anchor catalytic active metal oxides. Systematic changes of the synthesis parameter, like pH or the addition of urotropine for the incorporation of nitrogen in the graphitic layers, are performed. Variations of the initial pH mainly influence the degree of condensed graphitic layers that are performed during the autoclave process [2]. Whereas the nitrogen n-type doping enhances the electron transfer processes of the mechanically stable disc electrodes that can be obtained after the annealing of the hydrothermal carbon (HTC). The characterization of carbon support materials by Raman spectroscopy and thermal analysis was refined from original practice to gain better qualitative and quantitative knowledge about the surface functional groups. This novel opportunity allows the detailed investigation of the anchoring sites that are required for the deposition and stabilization.

Gaseous as well as wet deposition techniques are applied, leading to small cluster, adsorbed colloidal particles or single atom sites depending on the method (Fig. 1). The atomic layer deposition (ALD) process is a gas phase technique that is self limiting and very specific in regard to the reactivity of the metal-organic precursor with distinct functional groups. The reactivity of explicit functional groups could be approved in accordance to results from computational chemistry. With this deep insight about the support and the formed bond between carbon and deposited metal oxide we can develop homogeneously distributed well-defined carbon metal compounds.



Fig. 1. TEM images reveal the influence of different deposition techniques. a) small cluster by wet impregnation on MWCNT, b) adsorbed colloidal particles generated by laser ablation on HTC, c) single atoms covalently bonded on MWCNT by atomic layer deposition.

References

[1] Buller, Strunk, J. Energy Chem., 25 (2016) 17.

[2] Reiche, Kowalew, Schlögl, ChemSusChem, 16 (2015) 579.

Probing the Mechanism of the Hydrogen Evolution Reaction on Au

Yujin Tong, François Lapointe, R. Kramer Campen

Fritz-Haber-Institute of the Max-Planck-Society, 4-6 Faradayweg, Berlin, Germany

E-mail: r.k.campen@fhi-berlin.mpg.de (R. K. Campen)

While the hydrogen evolution reaction (HER) was first demonstrated on Au more than 225 years ago, its mechanism remains controversial. Theoretical studies suggest that HER proceeds via an interfacial solvated e⁻ stabilized by water molecules with one OH pointed towards the Au [1]. From an experimental point of view detecting either of these species is challenging: the former because its lifetime is short and the latter because it requires probing small populations of interfacial water molecules in the presence of a much larger number of bulk-like waters nearby [2]. Here we describe experimental approaches that allow us to address both halves of this problem. We probe the interfacial solvated e by initiating hydrogen evolution at a Au/water interface using an intense, femtosecond, UV pulse to promote an electron from gold's fermi level into water's conduction band and track the fate of this electron with fs time resolution both optically, using interface specific sum frequency generation spectroscopy, and electrochemically, via a double-pump, laser induced perturbation of the open circuit potential. In parallel we demonstrate the existence of a population of interfacial water molecules with an OH group pointing towards Au and describe its potential dependence using a sum frequency scheme resonant with water's OH stretch. Taken together this work suggests that (i) a population of water molecules with one OH group pointing towards Au exist over a wide range of potentials (ii) at circumneutral pH, at the gold/water interface the delocalized, conduction band, solvated electron has a potential dependent lifetime of 150-250 fs (iii) conduction band electrons relax to form localized solvated electrons the great majority of which have a potential dependent lifetime of 1-18 ps while a small fraction live for much longer, > 40 ps, and drive chemistry. These results furnish a potential-dependent, mechanistic picture of the transfer of electrons from gold into liquid water, the first step in hydrogen evolution.



References

- [1] Pang et al., Electrochim. Acta, 101 (2013) 272.
- [2] Velasco-Velez et al., Science, 346 (2014) 831.

^{4&}lt;sup>th</sup> Ertl Symposium on Chemical Processes on Solid Surfaces

The Water Surface: Complex, Dynamic and Wet

Mischa Bonn

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

E-mail: bonn@mpip-mainz.mpg.de (M. Bonn)

Water surfaces and interfaces are ubiquitous, not just in nature (e.g. at the boundaries of cells, in rain drops, oceans, rivers and lakes) but also in many technological applications (such as electrochemistry and photocatalytic water splitting). Water is a rather unique liquid, owing to its strong intermolecular interactions: strong hydrogen bonds hold water molecules together. At the surface of water, the water hydrogen-bonded network is abruptly interrupted, conferring properties on interfacial water different from bulk water [1].

We elucidate the structure and structural dynamics of interfacial water using surfacespecific vibrational spectroscopy of interfacial water molecules, with femtosecond time resolution. Specifically, we find that the interface is structurally more heterogeneous and shows faster dynamics than bulk water [2,3]. We show that the control over the water interfacial structure and dynamics allow ice nucleating proteins to accelerate the nucleation of ice, through a subtle interplay of interfacial water arrangement and accelerated heat transport away from the surface [4].

Finally, we show that the evaporation of water - i.e. the release of individual water molecules from the bulk into the gas phase - is not a purely stochastic event. Rather, the evaporation follows one specific pathway, involving a delicately timed, concerted motion of several water molecules to 'launch' a single molecule from the surface (see picture) [5].



References

- [1] M. Bonn, Y. Nagata, E. H. G. Backus, Angew. Chem.-Int. Edit., 54 (2015) 5560.
- [2] C. S. Hsieh, M. Okuno, E. H. G. Backus, J. Hunger, Y. Nagata, M. Bonn, Angew. Chem.-Int. Edit., 31 (2014) 8146. (VIP paper)
- [3] S. T. van der Post, C. S. Hsieh, M. Okuno, Y. Nagata, H. J. Bakker, M. Bonn, J. Hunger, Nat. Commun., 6 (2015) 8384.
- [4] R. Pandey et al., Sci. Adv., 2 (2016) e1501630.
- [5] Y. Nagata, K. Usui, M. Bonn, Phys. Rev. Lett., 115 (2015) 236102.

Reduction Process of Carbon Dioxide at an ITIES

Hye Jin Lee^{*}, Shinta Jeshycka

Department of Chemistry, Kyungpook National University, Daegu 41566, South Korea

E-mail: hyejinlee@knu.ac.kr (H. J. Lee)

Over the past decades, the electrochemistry at an interface between two immiscible electrolyte solutions (ITIES) has attracted great attentions in research fields of biomimic studies, pharmaceutical, electroanalytical and also energy related applications. In this talk, we will highlight our recent efforts on utilizing voltammetric investigation for CO₂ reduction processes to produce CO or HCOO⁻ across the ITIES. Cyclic and linear sweep voltammetries in addition to chronoamperometry were employed to monitor the reduction process of CO₂ in the organic phase in contact with the aqueous phase enriched with proton. As an example, the aqueous electrolyte composed of perchloric acid which serves as a proton source to the organic electrolyte solution [i.e. propylene carbonate (PC) with 0.1 M tetrabutylammoniumperchlorate (TBAClO₄)]. Different types and materials of working electrodes including gold mesh, platinum wire, gold nanoparticles, copper were investigated for formate (or formic acid) and CO production. Quantitative analyses for the generation of HCOOH, HCOO⁻ and CO gas were performed using high performance liquid chromatography, ion chromatography and gas chromatography-mass spectroscopy, respectively. In addition, an interfacial molecular catalyst pair was introduced at the ITIES to facilitate both the CO_2 reduction process in the organic phase to produce formate and H_2 generation in the aqueous phase and some of preliminary results will also be discussed.



Fig. 1. (a) Schematics showing CO_2 reduction at ITIES and (b) preliminary linear sweep voltammetry data for CO_2 reduction in the organic phase compared to the cases where no CO_2 was introduced.

Microcalorimetric Investigation of Charge-Neutral Anion Coadsorption and Substitution Processes during the Cu and Ag Underpotential Deposition on Au(111)

Stefan Frittmann, Rolf Schuster

Institute of Physical Chemistry, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany

E-mail: rolf.shuster@kit.edu (R. Schuster)

Measuring the reversible heat exchange at an electrode during an electrochemical reaction provides direct access to the reaction entropy of the electrochemical process, including all side processes like coadsorption or substitution of ions or ordering of the solvent water. As demonstrated in the figure, we can measure the Peltier heat, i.e., the reversibly exchanged molar heat during surface electrochemical processes like Ag or Cu underpotential deposition (UPD) with minute conversions of a few percent of a monolayer. This allows recording the Peltier heat, dependent on the actual potential, that is for the corresponding state of the surface system, hence obtaining independent thermodynamic information in addition to the charge balance.

Here we apply this method to the UPD of Ag and Cu on Au(111) in sulfate and perchlorate containing solutions, in order to determine the participation of anions during the UPD formation [1,2]. It is well accepted that for Ag UPD the anion coverage only negligibly changes during the UPD proceeds while Cu UPD proceeds via strong coadsorption of anions and Cu²⁺. From the course of the reaction entropy and the charge balance we can determine the anion coverages during the UPD. In addition, highly positive reaction entropy upon the completion of the first metal monolayer indicates charge neutral substitution of anions by oxygenated species from decomposition of water.



References

[1] S. Frittmann, V. Halka, R. Schuster, Angew. Chem.-Int. Edit., 55 (2016) 4688.

[2] S. Frittmann, R. Schuster, J. Phys. Chem. C, (2016) accepted.

Carbon Materials for Oxygen Electrocatalysis

Youngmi Yi, Sakeb Hasan Choudhury, Marina Prenzel, Saskia Buller, Sylvia Becker, Robert Schlögl

Max-Planck-institute for chemical energy conversion, Stiftstreet 34-36, 45470 Mülheim an der Ruhr, Germany

E-mail: youngmi.yi@cec.mpg.de (Y. Yi)

A growing interest in cost-effective and metal-free electrocatalysts has stimulated to extensive research on carbon materials for catalysts itself in renewable energy conversion and storage such as fuel cells, direct solar driven water splitting, hydrogen production from water electrolysis, and rechargeable metal-air batteries. The overall efficiency of energy-related technologies has been limited by sluggish kinetics of oxygen electrocatalysis, that is oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Many research reported ORR and OER activity of novel developed carbon materials, such as carbon nanotube, graphene and mesoporous carbon. 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 the OER/ORR environment, as carbon is oxidized at high potential. In particular, oxygen evolution on a carbon electrode is accompanied by carbon oxidation.

We present the structural and chemical effect of carbon materials for OER/ORR performance. 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 graphite flake and carbon nanotube (CNT). To control chemical properties of carbon materials, nitrogen and oxygen-containing functional groups were introduced by a low pressure plasma discharge and chemical modification. Fig. 1 shows representative data of this work. Depending on the structured carbon, ORR and OER activity is different. CNT shows higher activity than graphite flake and glassy carbon. Furthermore, nitrogen incorporated on CNT (N-CNT) has more positive potential for ORR and the comparable oxidation activity to metal and metal oxide catalyst. In the electrochemical stability test, pure CNT degrades rapidly due to carbon corrosion, while N-CNT has a stable performance at high anodic potential for OER environment. It can therefore be inferred that nitrogen on carbon structures activates and stabilizes electrocatalytic oxygen-involving reaction. This work provides design guideline for further materials and the potential of carbon electrocatalyst to replace metal and metal oxide for energy applications.





Superhydrophobic Surfaces Prepared by Dimethylsiloxane-Coated Nanoparticles: Fundamental Studies and Applications

Young Dok Kim, Hyun Ook Seo, Eun Ji Park

Department of Chemistry, Sungkyunkwan University, Suwon, Republic of Korea

E-mail: ydkim91@skku.edu (Y. D. Kim)

Ultrathin film of dimethylsiloxane (DMS) can be deposited on a variety of surfaces of nanostructures using vapor deposition method. This method is shown to be applicable to various solid surfaces independent of the chemical composition of the surface, due to the van der Waals nature of the interaction between DMS and substrate. Typically, a thickness of 2-3 nm of the film of DMS can be achieved using this method with a high conformality of the film structure. Deposition of DMS-coated nanoparticles on solid surface can result in superhydrophobic phenomenon, i.e., water droplets are fully repelled from such surfaces. We show that our simple technique for the fabrication of superhydrophobic surfaces can be applied to diverse fields as follows.

- i) DMS-coated mesoporous materials and nanoparticles can selectively capture organic pollutants under humid atmosphere and aqueous solution, and this can be exploited in pre-concentration of analytes for analytical instrument.
- ii) Use of superhydrophobic fabric can be useful for selective removal of spill-oil from water-oil mixtures.
- iii) Superhydrophobic and optically transparent surfaces can also be prepared (figure). Self-cleaning behavior of such surface cane useful in many applications.



Unravelling the Mysteries of the Water-Solid Interface with Statistical Mechanics and *ab initio* Simulations

Angelos Michaelides

Thomas Young Centre, University College London, United Kingdom

E-mail: angelos.michaelides@ucl.ac.uk (A. Michaelides)

There are few molecules, if any, more important than water. Yet remarkably little is known about how it interacts with solid surfaces, particularly at the all important atomic-level. This is true despite widespread general interest and compelling environmental and economic incentives. For example, water-solid interactions play a crucial role in the activity of fuel cells, the chemistry of the atmosphere, global warming, corrosion, catalysis, the operation of membranes, and so on. In this talk I will discuss some of our recent work in which we have been using classical and quantum molecular dynamics approaches as well as advanced electronic structure methods to better understand the structural and dynamical properties of water-solid interfaces. This will include work focused on understanding the formation of ice [1-3], confined water in nanocapiliaries [4], and water diffusion and friction [5-7].

References

[1] M. Fitzner, G. C. Sosso, S. J. Cox, A. Michaelides, J. Am. Chem. Soc., 137 (2015) 13658.

[2] S. J. Cox, S. M. Kathmann, B. Slater, A. Michaelides, J. Chem. Phys., 142 (2015) 184704.

[3] S. J. Cox, S. M. Kathmann, B. Slater, A. Michaelides, J. Chem. Phys., 142 (2015) 184705.

[4] J. Chen, G. Schusteritsch, C. J. Pickard, C. G. Salzmann, A. Michaelides, Phys. Rev. Lett., 116 (2016) 25501.

[5] G. Tocci, L. Joly, A. Michaelides, Nano Lett., 14 (2014) 6872.

[6] M. Ma, G. Tocci, A. Michaelides, G. Aeppli, Nat. Mater., 15 (2016) 66.

[7] L. Joly, G. Tocci, S. Merabia, A. Michaelides, J. Phys. Chem. Lett., 7 (2016) 1381.

Light-Induced Oxidation of Poly(3-Hexylthiophene-2,5-diyl) Thin Films on ZnO Buffer Layers: Impacts of Humidity, Underlying Metal-Oxides, and the Wavelength of Visible Lights

Hyun Ook Seo, Dae Han Kim, Myung-Geun Jeong, Sang Wook Han, Eun Ji Park, Il Hee Kim, Kwang-Dae Kim, Young Dok Kim

Department of Chemistry, Sungkyunkwan University, 440-746 Suwon, Republic of Korea

E-mail: seoho83@gmail.com (H. O. Seo)

We have studied the oxidation behavior of P3HT (Poly(3-Hexylthiophene-2,5-diyl)) layers (average thickness ~ 40 nm) deposited on ZnO substrates, which would be relevant for many organic/inorganic electronic devices. We have studied the impacts of humidity, underlying metal-oxides, and the wavelength of incident visible light on the photo-induced oxidation of P3HT layers using an X-ray photoelectron spectroscopy and UV-visible absorption spectroscopy. Our experimental results revealed that the photo-induced oxidation behaviors of P3HT films were influenced by the humidity, interface structure, and wavelength of the incident visible light. Furthermore, we have found that the oxidation of P3HT films resulted in the significant reduction of its light absorption in the visible light range, indicating that the study of oxidation behaviors of P3HT films is essential to understand the performances of organic solar cells.



Hydrophilicity/Lipophilicity of Phosphonium Ionic Liquids as Determined at Electrified Interfaces

T. Jane Stockmann, Ryan Guterman, Paul J. Ragogna, Zhifeng Ding*

Department of Chemistry, The University of Western Ontario, 1151 Richmond Street, London Ontario, N6A 5B7, Canada

E-mail: zfding@uwo.ca (Z. Ding)

Ionic liquids (ILs) have become valuable new materials for a broad spectrum of applications including as additives or components for new hydrophobic/hydrophilic polymer coatings. However, fundamental information surrounding IL molecular properties is still lacking. With this in mind, the electrified micro-interface between two immiscible electrolytic solutions (micro-ITIES), for example between water 1,2-dichloroethane, has been used to evaluate the hydrophobicity/lipophilicity of 10 alkylphosphonium ILs. By varying the architecture around the phosphonium core, chemical differences were induced, changing the lipophilicity/hydrophilicity of the cations. Ion transfer (IT) within the polarizable potential window (PPW) was measured to establish a structure-property relationship. The Gibbs free energy of IT and the solubility of their ILs were also calculated. Phosphonium cations bearing either three butyl, or three hydroxypropyl groups with a tunable fourth arm displayed a wide variety of easily characterizable IT potentials. The tributylphosphonium ILs however, were too hydrophobic to undergo IT within the PPW. Utilizing a micro-ITIES (25 µm diameter) housed at the tip of a capillary in a uniquely designed pipette holder, we were able to probe beyond the traditional potential window and observe ion transfer of these hydrophobic phosphonium ILs for the first time. A similar trend in lipophilicity was determined between the two subsets of ILs by means of derived solubility product constants. The above results serve as evidence towards the validation of this technique for the evaluation of hydrophobic cations that appear beyond the conventional PPW and of the lipophilicity of their ILs.



References

- [1] T. J. Stockmann, Z. Ding, J. Phys. Chem. B, 116 (2012) 12826.
- [2] T. J. Stockmann, J. Zhang, A. M. Montgomery, Z. Ding, Anal. Chim. Acta, 821 (2014) 41.
Investigating the Atomic Scale Structure of Liquid Metal - Electrolyte Interface with X-rays

Bridget Murphy

Ruprecht Haensel Laboratory, Kiel University, Leibnizstr. 19, D-24098 Kiel, Germany

E-mail: murphy@physik.uni-kiel.de (B. Murphy)

Electrochemical interfaces between immiscible liquids lately receive renewed interest, both for fundamental insight as well as for applications in nanomaterial synthesis. In this feature article we demonstrate that the atomic scale structure of these previously inaccessible interfaces nowadays can be explored by *in situ* synchrotron based X-ray scattering techniques. Exemplary studies of a prototypical electrochemical system - the liquid mercury electrode in pure NaCl solution - reveal that the liquid metal is terminated by a well-defined atomic layer. This layering decays on lengths scales on 0.5 nm into the Hg bulk and displays a potential and temperature dependent behaviour that can be explained by electrocapillary effects and contributions of the electronic charge distribution on the electrode [1]. In similar studies of nanomaterial growth, performed for the electrochemical deposition of PbFBr, a complex nucleation and growth behaviour is found, involving a crystalline precursor layer prior to 3D crystal growth [2]. *Operando* X-ray scattering measurements provide detailed data on the processes of nanoscale film formation [3].



Fig. 1. Atomic-scale structure and corresponding density profile of a liquid-liquid interface.

References

- [1] A. Elsen, B. M. Murphy, B. M. Ocko, L. Tamam, M. Deutsch, I. Kuzmenko, O. M. Magnussen, Phys. Rev. Lett., 104 (2010) 105501.
- [2] A. Elsen, S. Festersen, B. Runge, C. T. Koops, B. M. Ocko, M. Deutsch, O. H. Seeck, B. M. Murphy, O. M. Magnussen, Proc. Natl. Acad. Sci. USA, 110 (2013) 6663.
- [3] B. M. Murphy, S. Festersen, O. M. Magnussen, Nanoscale, 8 (2016) 13859.

Interaction of Water with Metal Supported Silicate Films

Shamil Shaikhutdinov

Department of Chemical Physics, Fritz-Haber-Institute of the Max-Planck-Society, Faradayweg 4-6, Berlin 14195, Germany

E-mail: shaikhutdinov@fhi-berlin.mpg.de (S. Shaikhutdinov)

Ultrathin oxide films grown on metal substrates become important materials for modern technological applications. In addition, such films are considered as suitable models to elucidate the atomic structure and mechanism of chemical reactions at oxide surfaces. The talk addresses interaction of water with well-defined silicate films [1]. In particular, direct visualization of hydroxo-species and rational approach to control surface hydroxylation will be discussed [2,3].



Fig. 1. STM image and IRA-spectrum (inset) of a hydroxylated single-layer silicate film on Ru(0001).

References

- [1] S. Shaikhutdinov, H. J. Freund, J. Phys. Condens. Matter, 27 (2015) 443001.
- [2] B. Yang et al., J. Phys. Chem. Lett., 5 (2014) 1701.
- [3] X. Yu et al., Phys. Chem. Chem. Phys., 18 (2016) 3755.

Activity and Stability of Pore Confined Pt-Co Alloyed Catalyst for the Oxygen Reduction Reaction (ORR)

Enrico Pizzutilo

Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

E-mail: pizzutilo@mpie.de (E. Pizzutilo)

The long-term performances of polymer electrolyte fuel cells (PEMFCs) are strongly correlated to the electrocatalyst durability, rather than its initial activity. Due to the interplay of different degradation mechanism (carbon corrosion, dissolution, detachment, Oswald ripening and agglomeration), a straightforward interpretation of the impact of a single mechanism is quite difficult.

Our group recently exploited the possibility of encapsulating the catalyst nanoparticles (4 nm) inside the pores of a partially graphitic carbon support material, the so-called "hollow graphitic spheres (HGS). The pore confinement was shown to successfully hinder common degradation mechanisms as agglomeration and particle detachment, thus improving the overall catalyst durability compared to commercially available Pt/C catalyst. Therefore, the HGS can be regarded as an ideal support to study the impact of de-alloying without the superposition of agglomeration which may change the particle size distribution and thus the activity.

In this context, PtCo alloys with distinct atomic ratios were synthesized (Pt, Pt₅Co, Pt₃Co and PtCo, see Figure 1) and encapsulated in the HGS, that were synthesized via a multistep hard templating route. This work focuses on the investigation of their activity and stability. In addition, the influence on the degradation of key parameters, such as upper and lower potential limit (UPL-LPL), scan rate was investigated in detail on the PtCo@HGS sample which showed the highest initial activity. Besides standard electrochemical techniques, advanced analytical tools such as inductively-coupled plasma mass spectrometer (ICP-MS) and online electrochemical mass spectrometer (OLEMS) have been used to evaluate the impact of dissolution/de-alloying and carbon corrosion respectively. Finally, TEM images provided a complete picture of the degradation on the nanoscale.





Water Structure at the TiO₂/Water Interface

Saman Hosseinpour, Fujie Tang, Mischa Bonn, Yuki Nagata, Ellen H. G. Backus

Max-Planck-Institute for Polymer Research, Mainz, Germany

E-mail: hosseinpour@mpip-mainz.mpg.de (S. Hosseinpour)

Photocatalytic splitting of water using sun light for production of hydrogen as an environmentally-friendly, storable, transportable, cost efficient and abundant energy source has received much attention in the last decades. Despite the large number of studies focusing on determining and increasing the efficiency of the water splitting process on semiconducting materials especially on TiO₂, fundamental questions regarding the exact mechanisms of this process at the molecular level are still not answered. For example, it is unclear what the correlation is between different interfacial structures and the efficiency of the splitting process. The main reason is the absence of an appropriate analytical tool that can specifically probe the electrode/water interface. In this study we utilized conventional sum frequency generation spectroscopy (SFG) to determine the structure and conformation of interfacial water molecules at the anatase TiO₂/bulk water interface. We compared the results with the simulated SFG spectra through ab initio Molecular Dynamics (MD) simulation and those obtained through phase sensitive SFG measurements. Our results indicate that interfacial water spectrum at the hydroxylated TiO₂ features water molecules which are directly bonded to the bridging oxygen of TiO₂ as well as water molecules H-bonded to their neighboring water molecules. Furthermore we studied the dynamics of the water splitting reaction over the range of few femto seconds to hundreds of picoseconds upon UV irradiation with UV pump-SFG probe. The preliminary timeresolved results show a strong water pH dependency of the relaxation/re-orientation of the water molecules.



Fig. 1. (left) SFG spectra of the TiO₂/water interface in the -OH stretching frequency region for different ratios between H₂O and D₂O. The spectrum with open circle symbols is calculated from 100% H₂O curve assuming no coupling between the water molecules. (top right) Experimentally measured SFG intensity spectra (red) vs. the intensity spectra constructed from the phase resolved measurements (blue). (bottom right) $Im(\chi(2))$ (red) and $Re(\chi(2))$ (blue) for 100% H₂O and 50% H₂O.

Ab initio Study of Adsorbed Water Phases at Alkaline Earth Metal Oxide Surfaces

Xunhua Zhao, Sergey V. Levchenko, Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin 14195, Germany

E-mail: levchenko@fhi-berlin.mpg.de (S. V. Levchenko)

Interaction of water with metal-oxide surfaces is ubiquitous in both natural and industrial environments. However, atomic-scale information on water/oxide interfaces is still limited. In this work, we use electronic-structure calculations and *ab initio* atomistic thermodynamics to identify atomic structure of stable adsorbed water phases at MgO, CaO, and SrO (100) surfaces as a function of coverage, temperature, and pressure.

Density-functional theory combined with the self-consistent many-body dispersion approach [1] is employed to calculate total energies. We find a range of H_2O chemical potentials where ordered onedimensional adsorbed water structures are thermodynamically stable at CaO(001). This is in agreement with scanning tunneling microscopy studies of CaO films exposed to water [2]. At MgO(001) and SrO(001), thermodynamically stable one-dimensional adsorbed water structures are not found. The formation of the one-dimensional structures on CaO(001) is explained by the balance between adsorbate-adsorbate and adsorbate-surface interactions. Our first-principles analysis of vibrational frequencies and core-level shifts also helps to explain the infrared and X-ray photoemission spectra observed for water adsorbed at CaO(001), and their dependence on coverage [3].



Fig. 1. Stable adsorbed water structures at CaO(100) surface, calculated vibrational spectra, and calculated and experimental X-ray photoemission spectra as a function of water coverage.

References

- [1] A. Tkatchenko et al., Phys. Rev. Lett., 108 (2012) 236402.
- [2] X. Zhao et al., J. Phys. Chem. Lett., 6 (2015) 1204.
- [3] Y. Fujimori et al., J. Phys. Chem. C, 120 (2016) 5565.

The Electronic Structure of Iridium Oxides Active in Water Splitting

V. Pfeifer^{1,2}, T. E. Jones1, J. J. Velasco Vélez^{1,3}, R. Arrigo^{1,3}, M. Hävecker^{1,3}, <u>A. Knop-Gericke¹</u>, R. Schlögl^{1,3}

¹ Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany ² Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany ³ Max-Planck-Institut für Chemische Energiekonversion, Mülheim a.d. Ruhr, Germany

E-mail: knop@fhi-berlin.mpg.de (A. Knop-Gericke)

Iridium oxide based electrodes are promising candidates for electrocatalyzing the oxygen evolution reaction (OER) in acidic media. To gain a deeper understanding of their electronic structure, we combined X-ray photoemission spectroscopy (XPS) and the near-edge X-ray absorption fine structure (NEXAFS) of benchmark catalysts with theoretical calculations. Our investigations reveal a pre-edge feature in the O K-edge of the 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 O 2p hole states (formally O^L) and the latter as formally Ir^{III} species [1].

Using CO oxidation, we found that the additional oxygen species identified in amorphous IrO_x are extremely electrophilic, oxidizing CO to CO_2 at room temperature. The exceptional reactivity of these formally O^{I} species is suspected to play a critical role in the OER by reacting with OH/H_2O to form the OOH intermediate, which likely explains the exceptional OER activity of amorphous IrO_x . Like in biological water splitting, the electrophilic oxygen in IrO_x seems to be an optimal precursor site for the nucleophilic attack of (preadsorbed) water during the O–O bond formation process. Likewise flexibility in the oxidation state for iridium is needed for electrophilic oxygen formation in iridium, which is apparently found in IrO_x [2].

To follow the formation of such highly defective amorphous iridium oxide surfaces on metallic iridium during the OER and as a function of the applied potential, we have developed an electrochemical cell based on the proton exchange membrane Nafion[®] [3] compatible with the Near-Ambient-Pressure XPS setup of the ISISS beamline at the synchrotron BESSYII/HZB.

Fig. 1. Three-electrode in situ cell with sputtered Ir working, Pt wire counter, and Ag/AgCl reference electrode. Water supplied from the rear diffuses through the desiccation cracks of the sputtered electrodes and the PEM and delivers the reactant molecules to the reaction chamber. While XPS and NEXAFS are measured, the gas composition in monitored by on line QMS.



References

- [1] V. Pfeifer, T. E. Jones, J. J. Velasco Vélez, C. Massué, M. T, Greiner, R. Arrigo, D. Teschner, F. Girgsdies, M. Scherzer, J. Allan, M. Hashagen, G. Weinberg, S. Piccinin, M. Hävecker, A. Knop-Gericke, R. Schlögl, Phys. Chem. Chem. Phys., 18 (2016) 2292.
- [2] V. Pfeifer, T. E. Jones, S. Wrabetz, C. Massué, J. J. Velasco Vélez, R. Arrigo, M. Scherzer, S. Piccinin, M. Hävecker, A. Knop-Gericke, R. Schlögl, (2016) submitted.
- [3] R. Arrigo, M. Hävecker, M. E. Schuster, C. Ranjan, E. Stotz, A. Knop-Gericke, R. Schlögl, Angew. Chem.-Int. Edit., 52 (2013) 11660.

Oscillatory Red-Ox Behavior of Active Metal Catalysts Observed by *in situ* Electron Microscopy

Marc Georg Willinger^{*}, Jing Cao, Ramzi Farra, Zhu-Jun Wang, Robert Schlögl

Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany

E-mail: willinger@fhi-berlin.mpg.de (M. G. Willinger)

State-of-the-art transmission electron microscopes are equipped with aberration correctors and provide images of atomic arrangements at sub-Ångstrom resolution. Due to various interactions between the electron beam and the observed material, it is possible to locally identify atomic species and even their chemical state using different detectors and spectroscopic tools. Although catalyst materials are generally characterized by a high structural complexity and a related tendency to sensitively act on intense electron beam irradiation, electron microscopy has contributed tremendously to our understanding of catalyst synthesis, particle- support interactions and reaction-induced modifications. However, since the observations are generally performed in vacuum, the recorded images and acquired spectroscopic data describe catalytic relevant material in a thermodynamic equilibrium state that is far away from the relevant active state. In order to move from imaging in vacuum to the observation of active catalysts, we have implemented commercially available sample holders for *in situ* studies of catalysts in their reactive state inside a transmission electron microscope and adapted an environmental scanning electron microscope for the investigation of surface dynamics on active catalysts. Using these two tools we are now able to cover a pressure range from 10^{-4} mbar to 10^{3} mbar and a spatial resolution ranging from the mm to the sub-nm scale.

Presently we are investigating the behavior of metal catalysts during hydrocarbon partial oxidation and decomposition reactions as well as structural dynamics during oscillatory redox reactions. The observations are performed in real-time and under conditions in which the active state of the catalyst can be monitored. The ability to directly image the active catalyst and associated morphological changes at high spatial resolution enables us to refine the interpretation of spatially averaged spectroscopic data that was obtained under otherwise similar reaction conditions, for example during near-ambient-pressure *in situ* XPS measurements.



Fig. 1. (a) and (b) show the aspect of a copper surface in a H_2/O_2 (20:1) atmosphere at 0.2 mbar and 650 °C. Image (b) was recorded 8 minutes after (a) at the identical location using in-situ SEM. Scanning TEM images (c) and (d) were recorded in-situ and reveal dynamic shape changes of Cu nanoparticles caused by concurrent oxidation and reduction processes in an H_2/O_2 atmosphere. Image (d) was recorded 3 s after image (c).

MANGAN - Standardized Electrochemical Measurements for the Oxygen Evolution Reaction

Sebastian Neugebauer¹, Ioannis Spanos¹, Youngmi Yi¹, Sebastien Cap², Robert Schlögl^{1,2}

 ¹ Max-Planck-Institute for Chemical Energy Conversion, Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany
 ² Fritz-Haber Institute of the Max-Planck-Society, Faradayweg 4, 14195 Berlin, Germany

E-mail: sebastian.neugebauer@cec.mpg.de (S. Neugebauer)

In basically all sustainable energy scenarios, the generation of hydrogen by water splitting plays a most important role [1]. Consequently, the anodic reaction of electrochemical water splitting, the oxygen evolution reaction (OER), is one of the most studied reactions in electrocatalysis [2]. As it typically exhibits sluggish kinetics, the quest for cost-efficient, highly stable catalysts for OER is ongoing. So far, it seems that no breakthrough has been reached and a clear understanding of structure-function relationships of OER catalysts 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 are not easily comparable.

Easily the most common method to start evaluating an electrocatalyst are measurements using a rotating disk electrode (RDE, [3]). However, there is not one standardized way of conducting these measurements and the influence of various parameters such as electrolyte, rotation speed, scan rates etc. on the observed numerical performance indicators such as overpotentials, current densities etc. is enormous. Starting from existing attempts at standardization [4], we adapted a series of electrochemical measurements to evaluate the performance of powder-like electrocatalysts via a RDE methodology. The methodology involves the definition of key performance indicators (KPI) as shown in the figure below.



As many studies focus only on the activity of a given catalyst, a sequence was incorporated to also retrieve information on the stability of the catalyst. Within the scope of a multi-partner project that deals with manganese-based catalysts for water splitting, MANGAN, we evaluated the between-lab reproducibility of the proposed sequence of measurements. The results from thirteen identical experimental set-ups are presented. 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 insitu analysis is stressed and an example of such analysis are presented.

Acknowledgements

Funding by the German Ministry for research an education (BMBF) within the framework of MANGAN (FK 03EK3545) is gratefully acknowledged.

References

[1] R. Schlögl, ChemSusChem, 3 (2010) 209.

- [2] I. Katsounaros, S. Cherevko, A. R. Zeradjanin, K. J. J. Mayrhofer, Angew. Chem.-Int. Edit., 53 (2014) 102.
- [3] K. J. J. Mayrhofer, D. Strmenik, B. B. Blizanac, V. Stamenkovic, M. Arenz, N. M. Markovic, Electrochim. Acta, 53 (2008) 3181.
- [4] C. L. C. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, J. Am. Chem. Soc., 135 (2013) 16977.

4th Ertl Symposium on Chemical Processes on Solid Surfaces

Poster Session



Model Reaction Studies of Water Effects on the Surface Acidity of Several Solid Acid Catalysts

Qiao-Ling Dai, Bo Yan, Bo-Qing Xu*

Department of Chemistry, Tsinghua University, Beijing 100084, China

E-mail: bqxu@mail.tsinghua.edu.cn (B. -Q. Xu)

Solid acids are widely used as heterogeneous catalysts in oil procession, chemical and pharmaceutical industries. Characterizations of the catalyst surface acidic property are usually conducted with well "dried" samples or under conditions without the presence of water, which cannot meet the present need for knowledge about the catalyst surface acidic property relevant to the reactions involving water or in water-containing system; e.g., many of the acid catalyzed reactions for the valorization of bio-derivative platform molecules are conducted in the presence of a large amount of water. Catalytic model reactions are in-situ chemistry probes to the catalyst surface property close to or under the reaction conditions. Two test reactions, 1) the dehydration of 2-propanol (2-PO) and 2) the skeletal isomerization of 3,3-dimethylbut-1-ene (33DMB), are used here to probe the water effects on the surface acidity of several solid acids. The first reaction is well-known for measuring the overall acidity (Lewis and Brønsted) and the second the Brønsted acidity. Table 1 shows the catalyst activity data for the two reactions at H₂O/2-PO \approx 1.0 and H₂O/33DMB \approx 0.7. The rate of 2-PO dehydration is lowered more or less in the presence of water when compared to that measured in the absence of water, revealing a poisoning effect of water to the reaction. For the 33DMB isomerization reaction, water presence leads to higher reaction rate over WO₃/ZrO₂, and thus higher Brønsted acidity at the WO₃/ZrO₂ surface. But, the 33DMB isomerization rate is significantly lowered due to water presence over the other catalysts measured (WO₃/Al₂O₃, SiO₂-Al₂O₃, HZSM-5 and Ta₂O₅·nH₂O) except γ -Al₂O₃, which is a typical solid Lewis acid and shows little activity for 33DMB isomerization. These results demonstrate that the impacts of water on the surface acidity are dependent of the nature of the solid acids.

	D	2	-PO dehydrati	on	33D	MB isomerizat	ion
Solid acid	Kxn. Temp.	H ₂ O/2-PO	Conv. ^a	Rxn rate ^{b,c}	H ₂ O/33DMB	Conv. ^a	Rxn rate ^{b,d}
	(C)	(mol/mol)	(%)	$(\mu mol h^{-1} m^{-2})$	(mol/mol)	(%)	(µmol h ⁻¹ m ⁻²)
WO ₃ /ZrO ₂	150	1.0	9.6 (13.8)	334 (539)	0.7	24.6 (21.2)	2091 (1771)
WO ₃ /Al ₂ O ₃	150	1.0	3.0 (8.2)	14 (50)	0.6	7.8 (14.1)	560 (1281)
SiO ₂ -Al ₂ O ₃	150	1.0	1.3 (6.1)	4(19)	0.7	23.3 (25.1)	123 (1458)
H-ZSM-5	150	1.0	10.9 (14.4)	21 (27)	0.6	14.0 (20.1)	471 (650)
Ta ₂ O ₅ ·nH ₂ O	200	0.9	5.4 (9.4)	35 (60)	0.6	22.7 (29.3)	309 (417)
γ -Al ₂ O ₃	200	0.9	7.1 (14.9)	33 (85)	0.7	0.5 (3.6)	3 (22)

Table 1. Activity of some solid acids for 2-PO dehydration and 33DMB isomerization in the presence and absence of water.

The catalytic reactions were conducted in a continuous flow fixed-bed reactor at atmospheric pressure over $30 \sim 100 \text{ mg}$ catalyst with varying partial H₂O pressures, $5 \sim 8 \text{ kPa } 2\text{-PO}$ or $9 \sim 10 \text{ kPa } 33\text{DMB}$ in N₂ at GHSVs = $0.02 \sim 0.2 \text{ m}^3 \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$.

^a the number outside the parenthesis shows the conversion in the presence of water while the one inside the parenthesis in the absence of water. ^b the number outside the parenthesis shows the catalytic rate in the presence of water while the one inside the parenthesis in the absence of water; $^{c}TOS = 0 \sim 1$ h. ^d TOS = 5 min.

NiFe Layered Double Hydroxide Electrocatalyst for Water and Seawater Oxidation

F. Dionigi, T. Reier, Z. Pawolek, M. Gliech, P. Strasser

Technical University Berlin, Berlin, Germany

E-mail: fabio.dionigi@mailbox.tu-berlin.de (F. Dionigi)

Generation of hydrogen and oxygen from seawater electrolysis is an attractive process to store energy from renewable resources since seawater is more abundant than fresh water and many arid zones have access to seawater. A grand challenge in seawater electrolysis is the selectivity, because in this condition chlorine evolution reaction (CIER) competes with oxygen evolution reaction (OER).

NiFe layered double hydroxide (LDH) has been reported as a good OER catalyst in alkaline electrolytes [1,2]. For this reason it was selected in our study as promising catalyst for seawater oxidation [3]. NiFe LDH was synthesized by homogeneous precipitation and in operando wide angle x-ray scattering (WAXS) was performed at synchrotron facilities to investigate the OER active structure.

The activity and stability for seawater oxidation have been investigated in chloride containing electrolytes mimicking seawater conditions with basic and near neutral pH [3]. The electrochemical experiments are combined with products analysis in order to estimate O_2 -selectivity (Fig. 1).

Despite the effect of the other ions present in seawater has not been tested yet, NiFe LDH shows promising results for its application as anode in a seawater electrolyzer operating under alkaline pH.



Fig. 1. Quadrupole mass spectrometer currents for O_2 and Cl_2 for NiFe LDH on Vulcan.

References

- F. Dionigi, P. Strasser, "NiFe-Based (Oxy)hydroxide Catalysts for Oxygen Evolution Reaction in Non-Acidic Electrolytes", Adv. Energy Mater., (2016) doi:10.1002/aenm.201600621.
- [2] M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, J. Am. Chem. Soc., 135 (2013) 8452.
- [3] F. Dionigi, T. Reier, Z. Pawolek, M. Gliech, P. Strasser, ChemSusChem, 9 (2016) 962.

On the Role of Pre-Critical Fluctuations in Heterogeneous Ice Nucleation

M. Fitzner^{*}, G. C. Sosso, A. Michaelides

London Centre for Nanotechnology, Department of Physics and Thomas Young Centre, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

E-mail: martin.fitzner.14@ucl.ac.uk (M. Fitzner)

Being the first step in the fascinating mechanism of phase transitions, nucleation governs a large variety of processes found in nature and industry, e.g. the crystallization of pharmaceuticals, cloud formation or intracellular freezing. It is well understood that most of these events occur heterogeneously, that is at the interface with a foreign phase. Despite the growing effort to elucidate this phenomenon the theoretical understanding today remains incomplete and is one of the main obstacles to a comprehensive control of nucleation.

In here, we studied the heterogeneous nucleation of ice by means of unbiased molecular dynamics simulations of coarse-grained water in contact with two different fcc model substrates. Surprisingly, despite the equality of the nucleation rate in both systems, the precritical fluctuations differ drastically. The substrate that nucleates the basal face of ice shows an increase in the size and presence of ice-like clusters near the surface. On the other hand the system that nucleates the prism face does not alter the fluctuations compared to the homogeneous case. The latter is inconsistent with the heterogeneous classical nucleation theory that predicts an increase of pre-critical fluctuations in any case.

Our findings indicate a previously unreported failure of one of the most applied nucleation theories. Subsequently it is insufficient to judge the nucleating capabilities of an impurity by its pre-critical cluster fluctuations. Furthermore, the differences in the nucleation of basal and prism face might be general and represent two different nucleation channels in nature's most common phase transition.



Ultrafast Electron Transfer-Induced CO₂ Activation at a ZnO Surface

Lukas Gierster, Sesha Vempati, Julia Stähler

Department of Physical Chemistry, Fritz-Haber-Institute of the Max-Planck-Society, Faradayweg 4-6, 14195 Berlin, Germany

E-mail: gierster@fhi-berlin.mpg.de (L. Gierster)

Since many years, ZnO has been used as a catalyst which facilitates the conversion of carbon dioxide into valuable chemicals such as methanol [1]. CO₂, which is the lowest energy carbon oxide species, needs to be activated in order to start the hydrogenation. Recent experimental and theoretical work showed that CO₂ adsorbs in a bent configuration with tridentate chemical binding on the ZnO (10-10) surface [1,2]. However, the energies of the frontier molecular orbitals of the adsorbed CO₂ molecules in the chemical reaction are still not known. We investigate this question using two-photon photoelectron spectroscopy (2PPE), which gives access to occupied and unoccupied electronic states and the dynamics therein. Static photoelectron spectroscopy shows that the work function of the surface increases considerably upon CO_2 adsorption possibly due to a (partial) reduction of the molecules and their dipole moment. A time-resolved pump-probe experiment suggests that electrons are injected from the ZnO substrate into the CO_2 molecules after above band gap photoexcitation of the substrate. The injected electrons populate the CO_2 LUMO, which subsequently shifts down in energy (see Fig. 1). This leads to a built up of an electronic state just below the Fermi energy within few picoseconds, which is likely to be related to the activated CO_2 molecules.



Fig. 1. Sketch of the 2PPE pump-probe measurement. The pump pulse excites electrons across the bandgap of ZnO leading to electron transfer to the CO_2 LUMO. The LUMO shifts below the Fermi energy E_F , which is detected by photoemission from a delayed probe pulse.

References

K. Kotsis et al., Z. Phys. Chem., 222 (2008) 891.
 Q. -L. Tang, Q. -H. Luo, J. Phys. Chem. C, 117 (2013) 22954.

Transition Metal Functionalized Nitrogenated Carbon Based Catalyst for Direct Electrochemical CO₂ Reduction to CO and Hydrocarbons

<u>Wen Ju</u>¹, Alexander Bagger², Ilya Sinev³, Ana Sofia Varela¹, Guangping Hao⁴, Beatriz Roldan Cuenya³, Jan Rossmeisl², Stefan Kasel⁴, Peter Strasser¹

 ¹ Department of Chemistry, Chemical Engineering Division, Technical University Berlin, Berlin, Germany.
 ² Department of Chemistry, University of Copenhagen, Universitertsparken 5, 2100 Kobenhavn, Denmark
 ³ Department of Physics, Ruhr-University Bochum, 44708 Bochum, Germany
 ⁴ Department of Inorganic Chemistry, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany

E-mail: w.ju@mailbox.tu-berlin.de (W. Ju)

The direct CO_2 electro-reduction reaction (CO2RR) has attracted renewed attention since it allows recycling the waste CO_2 into carbon based fuels. Among them, the mixture of the 2 electrons reduction products, CO and H₂, which is also known as syn-gas, can be coupled to a subsequent gas phase-catalytic Fischer-Tropsch process. The noble metal Au is known as an efficient catalyst to produce the 2 electrons reduction products, however, earth abundant materials as the catalyst for this process is still desired.

Recently, we have reported a class of Metal-containing N-doped carbon based catalyst (M-N-C) as an exceptionally promising molecular catalyst for the CO2RR into H_2 , CO and trace amount of hydrocarbons. Based on that, we explore various transition metals derived M-N-C catalysts for CO2RR in both experimental and theoretical study and find that the catalytic performance shows a strong dependence on the nature of the metal site in nitrogen cage. For instance, doping of Co make the M-N-C catalyst HER favoring whereas the Fe, Mn, Fe shows a positive effect to generate CO. It is dramatic that Ni derived catalyst outperforms the Gold benchmark at high over-potential. Interestingly, minute amount of CH₄ is observed on Fe and Mn doped catalysts, which is consistent with our DFT prediction.



4th Ertl Symposium on Chemical Processes on Solid Surfaces

Temperature Regulated-Chemical Vapor Deposition for Incorporating Metal Nanoparticles into Mesoporous Media: Simple Strategy for Preparation of Catalyst with Activity and Stability

<u>Il Hee Kim</u>, Sang Wook Han, Eun Ji Park, Myung-Geun Jeong, Hyun Ook Seo^{*}, Young Dok Kim^{*}

Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Republic of Korea

E-mail: shyloveuni@gmail.com (I. H. Kim), seoho83@gmail.com (H. O. Seo), ydkim91@skku.edu (Y. D. Kim)

We have developed a novel strategy to incorporate metal oxide nanoparticles into mesoporous substrate. Using this chemical vapor deposition method with regulating reactor temperatures sequentially from lower temperature for evaporation of inorganic metal precursors to higher temperature for oxidation of the precursors under ambient pressure conditions, we were able to decorate the internal structure of a mesoporous Al₂O₃ bead (size of ~ 1 mm) with metal oxide nanoparticles without clogging the pores. Metal oxide-deposited Al₂O₃ catalyst fabricated by the aforementioned method showed catalytic activity for CO oxidation. Additionally, iron oxide-deposited Al₂O₃ catalyst did not show significant deactivation at 100 °C, and maintained high activity even after annealing at 900 °C, and the catalyst. We showed that our new strategy could be widely applied for the incorporation of various nanoparticles into mesoporous supports, and the catalysts prepared by the strategy have potential for application as oxidation catalysts in industrial processes due to the simplicity of their fabrication process as well as the high and stable catalytic performance.



Energetics, Dynamics and Reactivity of Excess Electrons in Polar Solvents

Sarah B. King, Daniel Wegkamp, Katharina Broch, Julia Stähler

Department of Physical Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

E-mail: king@fhi-berlin.mpg.de (S. B. King)

The majority of water in the universe is in the amorphous solid water (ASW) phase, making solid phase reactions on ASW of considerable interest [1]. Dimethylsulfoxide (DMSO) is a ubiquitous polar solvent in chemistry and it has been identified as a possible electrolyte in lithium-oxygen batteries, a potential battery technology with extremely high theoretical energy density [2]; however excess electrons in DMSO have not been investigated in detail. In our current work, we investigate the formation, relaxation and reactivity of electronic states in thin films of both frozen solvents on the Cu(111) surface using time- and angleresolved two-photon photoemission. UV-induced electron injection into > 15 bilayers of ASW from a Cu(111) surface produces a long-lived electronic state at the ASW/vacuum interface with decay times on the order of seconds, fourteen orders of magnitude longer than the solvated electron in few-bilayer ASW films on metal surfaces [3]. The long lifetime of the trapped electron allows for a reaction of the excess electrons with the ASW surface, producing hydroxide anions at the ASW/vacuum interface. In a few monolayers of DMSO we observe a long-lived localized electronic state with a decay time of a few seconds that is consistent with formation of the solvated electron in DMSO. Preliminarily, this solvated electron appears to be populated via initial formation of a delocalized electronic state followed by ultrafast localization and formation of the solvated electron in DMSO. Addition of co-adsorbed oxygen molecules results in apparent reactivity of the solvated electron with oxygen.



References

- [1] P. Jenniskens, D. F. Blake, Astrophys. J., 473 (1996) 1104.
- [2] D. G. Kwabi et al., MRS Bull., **39** (2014) 443.
- [3] J. Stähler et al., J. Am. Chem. Soc., 137 (2015) 3520.

Chemical States of Palladium Nanoparticles Supported on Nanodiamond and Onion-like-Carbon during CO Oxidation

<u>Yoobin Koh</u>¹, Hojoon Lim¹, Youngseok Yu¹, Geonhwa Kim¹, BeomgyunJeong², Ethan Crumlin³, Liyun Zhang⁴, Dangsheng Su⁴, Bongjin Simon Mun^{1,5,*}

¹ Department of Physics and Photon Science, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea

² Division of Material Science Research, Korea Basic Science Institute, Daejeon, Republic of Korea ³ Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, USA

⁴ Shenyang National Laboratory for Materials Science Institute of Metal Research,

Chinese Academy of Sciences, Shenyang, China

⁵ Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju, Republic of Korea

E-mail: kyb702@gist.ac.kr (Y. Koh), bsmun@gist.ac.kr (B. S. Mun)

Recently, it is reported that palladium nanoparticles supported on Nanodiamond (Pd NPs /ND) exhibit superior catalytic activity in CO oxidation compared to palladium nanoparticles supported on Onionlike carbon (Pd NPs /OLC) [1]. It is suggested that the superior catalytic activity is due to the change in electronic structure of Pd NPs on carbon material that weaken the interaction between Pd NPs and CO. Considering the desorption rate of CO from catalytic surface is critical, the above argument is plausible, but lacks of supporting evidences. The purpose of this study is to suggest a mechanism that can explain difference in reactivity of Pd NPs /ND and Pd NPs OLC by looking into how the chemical states of Pd NPs on carbon varies under reaction condition. Using ambient pressure X-ray photoemission spectroscopy (AP-XPS), in situ CO oxidation of Pd NPs /ND and Pd NPs /OLC samples were investigated. Powdered samples (Pd NPs /ND and Pd NPs /OLC) were deposited onto the gold covered silicon wafer by drop-casting method. Samples were hydrogen annealed to remove graphitic layers and then exposed to 20 mTorr of CO and 100 mTorr of O2 gas mixture. With gradual increase in the temperature, CO oxidation reaction on Pd NPs /ND occurred at 408 K while that on Pd NPs /OLC occurred at 454 K, indicating the lower activation energy of Pd NPs /ND during CO oxidation process. Meanwhile, the analysis of high resolution Pd 3d spectra reveal that there are three peaks, i.e. surface Pd oxide, bulk Pd oxide, and Pd-Carbon (Pd-C). In the case of Pd NPs /ND, the intensity of surface Pd oxide peak increases during CO oxidation reaction, indicating the participation of Pd oxide in CO oxidation process.



Fig. 1. Schematic of CO oxidation of Pd NPs /ND and Pd NPs /OLC samples.

References

[1] L. Zhang et al., Angew. Chem.-Int. Edit., 54 (2015) 15823.

Anodic TiO₂ Hollow Microcones as Advanced Anodes for Lithium-Ion Batteries

Oonhee Rhee, Jinsub Choi, Gibaek Lee*

Nano & Energy materials Lab., Department of Chemical Engineering, Inha University, Incheon, South Korea

E-mail: gibaek@inha.ac.kr (G. Lee)

Recently, electrochemical energy storage systems are becoming increasingly important with respect to their use in portable electronic devices, medical implantable devices, hybrid electric (HEV) and electric vehicles (EVs), and storage of solar and wind energies. Rechargeable lithium-ion battery is one of the most promising systems for them due to its high energy density and long cycle life. Especially, nanostructured materials have led to significant improvements of physical and mechanical properties in lithium-ion batteries (LIB). Among them, nanostructured TiO₂ is one of potential candidates that can substitute conventional graphite anode owing to nontoxicity, chemically stability and low processing cost. It has been already reported that TiO₂ electrode with various morphologies, such as nanotubes, nanobelts, nanorods, nanowire and so on, has been successfully used as anode material for LIBs showing safety and inherent overcharge protection.

Herein, highly ordered TiO_2 microcones were prepared by anodization of a Ti foil under specific conditions. The as-prepared TiO₂ microcones had a hollow core and anatase phase, which were confirmed by SEM, XRD and TEM with EDS mapping. The electrochemical measurements of the TiO₂ microcone electrodes were evaluated as anode for LIB, exhibiting excellent cycle performance. The areal capacity of TiO₂ microcones was much higher than that of TiO₂ nanotubes and the remarkable cycle stability was observed over 500 charge/discharge cycles. Consequently, the cycled TiO₂ microcone electrodes preserved the original morphology of TiO₂ microcones due to probably a hollow structure and low volume expansion.

Keywords: titanium dioxide, anodization, microcones, anode, lithium-ion batteries



Characterizing Surface Oxidation States of Vanadium Thin Films with *in situ* Ambient Pressure X-ray Photoelectron Spectroscopy

<u>Hojoon Lim</u>¹, Yoobin Koh¹, Youngseok Yu¹, Beomgyun Jeong², Geonhwa Kim¹, Howon Kim³, Ethan Crumlin⁴, Honglyoul Ju³, Bongjin Simon Mun^{1,5,*}

¹ Department of Physics and Photon Science, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea
² Division of Material Science Research, Korea Basic Science Institute, Daejeon, Republic of Korea

³ Department of Physics, Yonsei University, Seoul, Republic of Korea ⁴ Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, USA ⁵ Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju, Republic of Korea

E-mail: ghwns4006@gist.ac.kr (H. Lim), bsmun@gist.ac.kr (B. S. Mun)

Vanadium thin film exhibits distinct physical and chemical properties that depend on its oxidation states. Consequently, it becomes important to have a good control of oxidation states of vanadium film for the study of intrinsic physical properties of vanadium oxides and its practical applications to industry [1]. In this study, the thermal oxidation process of vanadium thin films is characterized in operando condition with ambient pressure X-ray photoemission spectroscopy (AP-XPS). Spectra analysis for 5 nm vanadium thin film show that VO₂ has maximum growth at 200 mTorr oxygen pressure. Interestingly, as the surface temperature increase to 200 °C under elevated oxygen pressure of 200 mTorr, V_6O_{13} is developed significantly while V_2O_5 starts to reduce. Also, as the oxygen pressure increases, the spectra of 20 nm vanadium thin film show the reduction of VO₂ component and the formation of V_2O_5 at 250 °C. In addition, Raman spectroscopy measurement, a more bulk sensitive analytic tool than XPS, shows the oxidation states of both films, including VO₂, V_6O_{13} , and V_2O_5 , supporting the results of depth profiling measurement with in situ AP-XPS. The ex situ temperature-dependent resistivity measurements on the grown thin films show very weak metal-insulator transition only for 20 nm film.



References [1] J. Yoon et al., Appl. Surf. Sci., **353** (2015) 1082.

Hybrid Materials of Non-Precious Metal Catalysts with Ultra-Low Platinum Loadings for the Oxygen Reduction Reaction

Anna K. Mechler^{1,†}, Andrea Zitolo², Deborah Jones¹, Frederic Jaouen^{1,*}

 ¹ Université Montpellier, ICGM - Equipe AIME, Place Eugène Bataillon, 34095 Montpellier, France
 ² Synchrotron SOLEIL, L'orme des Merisiers, BP 48 Saint Aubin, 91192 Gif-sur-Yvette, France
 [†] current affiliation: Max-Planck-Institute for Chemical Energy Conversion, Department of Heterogeneous Reactions, Stiftstrasse 34 – 36, 45470 Mülheim, Germany

E-mail: Anna.Mechler@cec.mpg.de (A. K. Mechler), Frederic.Jaouen@univ-montp2.fr (F. Jaouen)

Non-precious metal catalysts (NPMC) are promising materials to replace Pt-based materials at the cathode of polymer electrolyte membrane fuel cells. However, their activity and especially their stability still do not match the current targets, as for example defined by the U.S. Department of Energy [1,2]. On the other hand, different routes are investigated to significantly lower the Pt loading, which however arises new problems in terms of oxygen transport, stability, and material handling. Especially, for very low amounts the current densities are too low for a reasonable application in fuel cells [3,4].

In an approach to combine both methods, ultra-low Pt amounts (< 5 wt.%) are deposited onto a Febased NPMC, resulting in highly dispersed and small Pt nanoparticles. The Fe-NPMC is derived from iron acetate, phenanthroline, and a Zn-based metal organic framework [5]. The deposited Pt nanoparticles are expected to build a hybrid structure with the Fe-NPMC support, in which the different active sites positively interact with each other.

The activity for the oxygen reduction reaction of different hybrid catalysts is tested in rotating disc electrode studies as well as in single fuel cell tests. The stability is monitored over 50 h at constant potential in the fuel cell. The performance is then put into context with the microstructure properties of the materials. Those are characterized, for instance, by X-Ray absorption spectroscopy to elucidate the interaction of Pt, Fe, and N active sites.



References

- U.S. Department of Energy, Multi-Year Research, Development and Demonstration Plan: Technical Plan -Fuel Cells, (2014).
- [2] F. Jaouen, E. Proietti, M. Lefèvre, R. Chenitz, J. -P. Dodelet, G. Wu, H. T. Chung, C. M. Johnston, P. Zelenay, Energy Environ. Sci., 4 (2011) 114.
- [3] T. A. Greszler, D. Caulk, P. Sinha, J. Electrochem. Soc., 159 (2012) F831.
- [4] A. Brouzgou, S. Q. Song, P. Tsiakaras, Appl. Catal. B-Environ., 127 (2012) 371.
- [5] E. Proietti, F. Jaouen, M. Lefèvre, N. Larouche, J. Tian, J. Herranz, J. -P. Dodelet, Nat. Commun., 2 (2011) 416.

Operando X-ray Absorption Spectroscopy Study of IrNiO_x Core-Shell Nanoparticles as Highly Active Water Oxidation Electrocatalysts

Hong Nhan Nong¹, Tobias Reier¹, Hyung-Suk Oh¹, Peter Strasser^{1,2}

¹ Department of Chemistry, Technical University Berlin, Strasse des 17. Juni 124, TC 03, 10623 Berlin, Germany

² Ertl Center for Electrochemistry and Catalysis, Gwangju Institute of Science and Technology, Gwangju 500-712, South Korea

E-mail: hongnhan.nong@gmail.com (H. N. Nong)

Electrocatalytic oxidation of water is expected to play an important role in the development of energy conversion and storage technologies, since it provides electrons to reduce protons to hydrogen fuel or to reduce carbon dioxide to carbon-containing fuels [1,2]. However, the slow rate of the water oxidation remains a main challenge and requires design of highly active and stable electrocatalysts [3,4]. Among the materials that catalyze OER, iridium oxide is one of the most appropriate OER catalysts, combining excellent activity and stability, especially in acidic media [4,5]. As a consequence, understanding how the water oxidation occurs on this electrocatalyst in detail is important for the design of highly active OER catalysts. Here we show the study of the $IrNi@IrO_x$ metal-oxide core-shell nanoparticles with significantly enhanced intrinsic activity compared to the pure $Ir@IrO_x$ nanoparticles - one of the most active and stable electrocatalysts for water oxidation [4-7]. We probed the electronic and local geometric structure of Ir sites in Ir@IrO_x and IrNi@IrO_x in operando condition using X-ray absorption spectroscopy. Ir-O bond distance in IrNi@IrOx was significantly shortened compared to in Ir@IrOx. We demonstrate that the electronic and geometric structure of the metal center, which may determine the electrophilicity of oxygen ions, play an essential role in activity of the electrocatalyst. This finding paves a way to the molecular machinery of highly active electrocatalysts for water oxidation.



Fig. 1. Ir sites under OER in the IrO_x shell of Ir@IrO_x and in the Ni-depleted IrO_x shell of IrNi@IrO_x core-shell NPs. $(0 < \delta_1 < \delta_2)$. O_T is terminal oxygen (can be - OH, = O, or - OH₂). The curved lines denote O_T or bridging atoms (Ir for bridging O and vice versa). For the IrNi@IrO_x core-shell NPs, Ni atoms were leached out during electrochemical oxidation step resulting in Ni-depleted hole-doped IrO_x shell.

References

- [1] H. Dau et al., ChemCatChem, 2(7) (2010) 724.
- [2] G. A. Olah, A. Goeppert, G. K. S. Prakash, J. Org. Chem., 74(2) (2009) 487.
- [3] H. -S. Oh et al., Chem. Sci., 6(6) (2015) 3321.
- [4] T. Reier, M. Oezaslan, P. Strasser, ACS Catal., 2(8) (2012) 1765.
- [5] S. Cherevko et al., Catal. Today, 262 (2016) 170.
- [6] H. N. Nong et al., Chem. Sci., 5(8) (2014) 2955.
- [7] T. Reier et al., J. Am. Chem. Soc., 137(40) (2015) 13031.

A Gastight RDE Setup to Investigate the Selectivity of Electrochemical Oxygen and Chlorine Evolution

Zarina Pawolek, Tobias Reier, Peter Strasser

Department of Chemistry, Technical University Berlin, Strasse des 17. Juni 124, TC 03, 10623 Berlin, Germany

E-mail: zarina@mailbox.tu-berlin.de (Z. Pawolek)

Fuelcells, running with hydrogen and air, constitute an environmentally friendly way of mobile energy supply. However, the required hydrogen fuel must be produced on an environmentally friendly basis as well. In this context, electrochemical water splitting is the most promising technology. Since only a small part of the water resources available on earth is fresh water, it is interesting to use saline seawater instead. In saline water the anode reaction of water electrolysis, the oxygen evolution reaction (OER), has to compete with the chlorine evolution reactions, a setup is required in which the gas composition can be continuously probed while the electrocatalytic reaction is running. Since mass transport effects are of great potential impact for the selectivity between OER and CIER, it is necessary to provide a controlled mass transport regime. An established way of controlling the mass transport velocity in electrochemical devices is the use of a rotating disc electrode (RDE). Furthermore, the setup must resistant the very corrosive wet chlorine gas.

Facing these requirements, we have built a gas tight RDE setup, which makes it possible to quantitatively probe the evolved amount of oxygen and chlorine during the reaction with a suitable time resolution. Accordingly, in our contribution we will present this setup and show some examples of measurements that have been done using an iridium oxide model catalyst.



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

Dongyoon Shin¹, Xianghua An¹, Myounghoon Choun¹, Jaeyoung Lee^{1,2,*}

¹ Electrochemical Reaction and Technology Laboratory, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, South Korea

² Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju 500-712, South Korea

E-mail: shingoon@gist.ac.kr (D. Shin), jaeyoung@gist.ac.kr (J. Lee)

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, Catal. Today, 260 (2016) 82.

- [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, Chin. J. Catal., 35 (2014) 891.

Efficient Structured Catalysts for CO Oxidation

Sunghyun Uhm, Minhye Seo, Sooyoung Lee

Advanced Materials & Process Center, Institute for Advanced Engineering, Yongin 17180, South Korea

E-mail: electrik@iae.re.kr (S. Uhm)

Catalyst shaping is an important issue, with a need to balance performance, strength, and pressure drop across the catalyst system. Honeycomb-type ceramic catalyst supports have been designed for use in high-temperature gas streams to allow the minimum pressure drop across the support while maintaining thermal, mechanical, and chemical stability. However, the fabrication techniques used to produce catalysts on honeycomb ceramics are becoming progressively more complex and should be better controlled to improve the catalyst utilization at the same time.

We present our recent experimental results on the Ni catalyst coating by temperatureregulated chemical vapor deposition into alumina pores on aluminum honeycomb which is fabricated by well-controlled anodization. The catalytic activity for CO oxidation is also discussed briefly.



Soft X-ray Photoelectron Spectroscopy at Solid-Liquid Electrified Interfaces: Revealing Electrochemistry in Action

J. J. Velasco-Vélez^{1,*}, V. Pfeifer², M. Hävecker¹, R. Schlögl^{1,2}, A. Knop-Gericke²

¹ Max-Planck-Institute for Chemical Energy Conversion, Germany ² Fritz-Haber-Institute of the Max-Planck-Society, Germany

E-mail: velasco@fhi-berlin.mpg.de (J. J. Velasco-Vélez)

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 and element specific techniques able to monitor the electronic structure in aqueous environment hinders the total understanding of such processes. We have overcoming this issue recently by developing a new electrochemical setup based in a bi-layer of graphene (BLG) membrane, see Fig. 1a. This membrane is transparent to the photoelectrons generated close to the solid liquid interface but still leak tight to the liquids enabling X-ray spectroscopy in situ, i.e. during electrochemical reactions [1]. To prove the operation concept, we further decorated the graphene layer with catalyst material such as Ir (see Fig. 1b) achieving reliable electrochemical performance (see Fig. 1c). This setup allows to record spectra under different bias polarization revealing changes in the electronic structure, which are related to variations in the oxidation state and are believed to be the active sites in the reaction (see Fig. 1d). In the symposium, we will present some of our actual results in electroplating, electrical-double layer formation and electrocatalytic processes which are within the most relevant topics in electrochemistry. Furthermore, our method opens the way for studies of virtually any solid-liquid interface, which was not possible with techniques such as X-ray absorption in fluorescence mode used until now. This includes electrode batteries, photocatalytic processes, atmospheric phenomena and biological processes as photosynthesis and nitrogen fixation that occur under aqueous conditions and are essential for life.



Fig. 1. (a) Sketch of the liquid flow cell and schematic drawing of the Si_3N_4 grid coated by a BLG. (b) TEM image of a BLG decorated with Ir nano-particles ranging from 2 nm to 5 nm. (c) CV performed with the electrochemical cell filled with 50 mM H₂SO₄, counter and reference electrode were Pt and Ag/AgCl respectively (d) Ir 4f and K 2p spectra collected under open circuit potential (OCP) and oxygen evolution reaction.

References

[1] J. J. Velasco-Velez et al., Angew. Chem.-Int. Edit., DOI:10.1002/ange.201506044R2.

Biomass-Based Hydrothermal Carbon Disc for Electrocatalytic Water Splitting

Youngmi Yi, Natalia Kowalew, Marina Bukhtiyarova, Saskia Buller, Sylvia Becker, Robert Schlögl

Max-Planck-institute for chemical energy conversion, Stiftstreet 34-36, 45470 Mülheim an der Ruhr, Germany

E-mail: youngmi.yi@cec.mpg.de (Y. Yi)

Increasing interest in sustainable energy requires energy conversion and storage systems which are highly efficient, low cost, and environmental-friendly. The production of hydrogen by splitting water using intermittent renewable energy sources is a critical technology in energy-related systems. The main reactions of water electrolysis are hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Noble metals (Pt, Ru, Ir), transition metals or metal oxides (Ni, Co) have been used as electrocatalysts in these reactions. However, metal-based catalysts suffer from not only scarcity and high cost, but also the release of metal ions in water during the electrolysis. Carbon materials as metal-free catalysts have an attention to produce hydrogen efficiently and reduce environmental issue.

In this study, the carbon disc synthesized by hydrothermal carbonization from biomass feedstocks was applied for water electrolysis. We obtained different properties of hydrothermal carbon (HTC) by adjusting initial synthesis pH. The material synthesis at pH 0 yields particles of broad size distributions and highly condensed carbon scaffolds. In contrary, HTC materials synthesized at pH 6 consist of smaller particles of approximately 500 nm in diameter in homogeneous size distribution. Due to the advantageous binding properties of HTC, the materials can be pressed into pellets prior thermal treatment and thus yield binderfree carbon disc. The HTC disc as an electrode shows an interesting activity and stability which is comparable with metal and metal oxide for HER and OER. Specially, we have studied the OER stability of HTC disc caused by the carbon oxidation at high anodic potential. Since carbon is thermodynamically unstable, the higher oxidation current of the HTC discs comes from not only oxygen evolution by oxidizing water, but also carbon oxidation. Through this study, we could find the possibility of biomass-derived carbon disc used for an electrode material in water electrolysis.



Fig. 1. (a) SEM of hydrothermal carbon synthesized by adjusting initial synthesis pH, and (b) HER and OER activity of HTC pH 6 measured in acidic media.

The High Performance Anodic TiO₂ Electrode Consisting of IrO₂-RuO₂ Catalysts for Water Oxidation Application

Hyeonseok Yoo, Kiseok Oh, Gibaek Lee, Jinsub Choi*

Department of Chemistry and Chemical Engineering, Center for Molecular Catalysts and Applications (BK21 plus program), Inha University, Yonghyun Dong 253, 22212, Incheon, South Korea

E-mail: dbwlsqkr2814@korea.com (H. Yoo), jinsub@inha.ac.kr (J. Choi)

 TiO_2 has been considered as a favorable electrochemical electrode for a long time because of excellent chemical and physical stability. Among the numerous methods for the preparation of TiO_2 with a large surface area, anodization has known as very practical method owing to relatively simple and inexpensive processes. Especially, in case of highly ordered anodic TiO_2 nanotubes (NTs), additional binder is not usually necessary to prepare the electrodes. However, since TiO_2 shows typical insulating properties, electrochemical catalysts are essentially required for electrode applications. Among the numerous electrochemical catalysts, IrO_2 and RuO_2 are the well-known catalysts for water oxidation applications. Nonetheless, a uniform doping of electrochemical catalysts into the TiO_2 NTs is difficult due to its high-aspect-ratio structure. In this study, we discuss the simultaneous doping process for binary catalysts, IrO_2 and RuO_2 , into anodic TiO_2 NTs by single-step anodization. Especially, IrO_x nanoparticles (NPs) are synthesized as an intermediate media from $IrCl_3$. We found that the IrO_x can be converted to IrO_4 - through selective dissolution in the electrolyte, which can be simultaneously doped into TiO_2 nanotubes during anodization.



Fig. 1. SEM (a) and TEM EDS mapping images (b-e) of anodic TiO_2 nanotubes with IrO_2/RuO_2 dopants. (c), (d) and (e) are corresponded to Ti, Ir and Ru, respectively.

The Role of Surface Oxide during CO Oxidation on Pt(110)

<u>Youngseok Yu</u>¹, Hojoon Lim¹, Yoobin Koh¹, Geonhwa Kim¹, Beomgyun Jeong², Daehyun Kim³, Isegawa Kazushia³, Ueda Kohei³, Kazuhiko Mase³, Ethan Crumlin⁴, Hiroshi Kondoh³, Bongjin Simo Mun^{1,5,*}

¹ Department of Physics and Photon Science, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea

² Division of Material Science Research, Korea Basic Science Institute, Daejeon, Republic of Korea ³ Department of Chemistry, Keio University, 3-14-1 Hyuoshi, Kohoku-ku, Yokohama, Kangawa 223-8522, Japan

⁴ Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, USA

⁵ Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju, Republic of Korea

E-mail: YuYoo@gist.ac.kr (Y. Yu), bsmun@gist.ac.kr (B. S. Mun)

In surface science, the pressure gap between UHV model system ($\sim 10^{-9}$ Torr) and high-pressure practical system (≥ 760 Torr) has been recognized for many years due to possible surface modification and different reaction [1]. In 2002, with environmental STM study, Frenken et al. proposed two separate mechanisms to explain the CO oxidation on Pt(110) surface, i.e. the Langmuir-Hinshelwood (LH) mechanism for low reactivity surface under UHV condition and the Mars-Van Krevelen (MK) mechanism for highly reactive surface under elevated pressure condition. On the other hand, Goodman et al. interpreted the chemically active state with hyperactive state and supported the LH mechanism. In this presentation, we investigate the CO oxidation on Pt(110) surface with ambient pressure x-ray photoelectron spectroscopy near hyperactive states. First, under O gas pressure at 200 mTorr and CO gas pressure at 40 mTorr, i.e. $O_2/CO = 5$, the chemical states of O *Is* and Pt *4f* are monitored as surface temperature is increased. Then, once the enhancement of CO oxidation occurs, ~ 550 K, the O_2/CO ratio is varied from 5 to 3.33, 2, and 1.43. Interestingly, even after O_2/CO ratio is reduced, the reaction rate increases while surface oxides formed at $O_2/CO = 5$ also increase, indicating that catalytically active site is the surface oxide.



Fig. 1. (a) Mass spectra intensity of CO_2 and CO as surface temperature under 200 mTorr of O_2 and 40 mTorr of CO. (b) At T<550 K, surface is covered by CO (532.5 eV), i.e. poisoning, and it takes a low reaction rate. (c) XP spectrum taken under T>553 K reveals the chemisorbed oxygen (529.8 eV) and the surface oxide (531.3 eV).



Effect of the Support Acid-Base Property on the Selectivity Control of Au-Catalysis for Glycerol Oxidation in Base-Free Water

Zi-Fei Yuan, Zhan-Kun Gao, Bo-Qing Xu*

Department of Chemistry, Tsinghua University, Beijing 100084, China

E-mail: bqxu@mail.tsinghua.edu.cn (B. -Q. Xu)

Glycerol (GL) is an important platform molecule in bio-refinery, whose valorization by catalytic aerobic oxidation in water usually produces various products. Under the co-presence of a base (NaOH), oxide-supported Au nanoparticles (NPs) were identified as efficient catalysts for producing glyceric acid with fairly high selectivity (GLA) (40~70%). However, our recent study disclosed that when the GL oxidation was conducted in base-free water, the Au catalysts would show a specific selectivity for producing dihydroxyacetone (DHA), instead of GLA. Thus, the presence of a base (NaOH) can modify the direction (selectivity) of Au-catalyzed GL oxidation in water, which motivates us to further investigate how the support surface acid-base property of Au NPs would affect the product selectivity. A series of Au/MgO-Al₂O₃ catalysts are prepared in this work by varying the molar Mg/Al ratio (x) in the supporting materials to tune the acid-base property at the support surface. Increasing x of the sample results in continued decrease in the acidity but increase in the basicity of the support surface, as determined from NH₃- and CO₂-TPD, respectively, as listed in Table 1. For the catalytic GL oxidation in NaOH-free water, Au NPs supported on the most acidic and least basic MgO-Al₂O₃ shows the highest activity for GL oxidation and the highest selectivity for DHA production. Increasing the basicity or lowering the acidity at the support surface leads to continuously improved selectivity for GLA but lowered selectivity for DHA (Table 1). These correlations disclose for the first time that the support acid-base property inversely affects the formation of DHA and GLA, demonstrating that the support acidity/basicity of Au catalysts is a key to the selectivity control for GL oxidation in base-free water.

Acidity ^b		Basicity ^c	Rxn	GL	Product sel. $(C\%)^d$								
x	$(\mu mol/m^2)$	$(\mu mol/m^2)$	(h)	(%)	DHA	GLA	LA	TTA	GCA	AC	OA	CO_2	FA
0	0.94	0.05	3	11.9	81.7	4.4	0.3	0.3	2.6	4.6	1.2	4.9	0.0
0.10	0.48	0.13	0.5	16.4	74.1	9.1	0.3	0.2	5.6	2.2	1.9	4.6	1.6
0.15	0.41	0.25	0.5	13.8	67.3	13.4	0.2	0.3	8.6	1.7	2.4	4.8	1.3
0.45	0.33	0.38	2	11.7	63.1	19.0	1.0	0.5	9.5	1.8	1.9	2.7	0.5
1.40	0.30	0.45	4	15.6	52.8	24.5	0.7	1.2	10.2	5.0	2.7	1.3	1.6
2.50	0.36	0.67	4	11.7	42.2	33.4	1.7	2.4	8.5	6.4	1.5	2.6	1.7
3.70	0.29	0.77	8	12.4	22.2	44.3	2.5	3.8	13.4	8.9	2.1	2.2	0.6
4.81	0.01	0.80	12	13.9	10.9	49.0	3.2	5.1	14.1	10.6	2.3	4.4	0.4

Table 1. Aerobic oxidation of GL over Au/MgO-Al₂O₃(x) samples^{*a*}

^{*a*} Rxn conditions: 0.1 M GL 20 mL, GL/Au (mol/mol) = 250, 80 °C, 10 bar, 900 rpm. ^{*b*} Catalyst surface acidity obtained by NH₃-TPD measurement. ^{*c*} Catalyst surface basicity obtained by CO₂-TPD measurement. ^{*d*} DHA = dihydroxyacetone, GLA = glyceric acid, LA = lactic acid, TTA = tartronic acid, GCA = glycolic acid, AC = acetic acid, OA = oxalic acid, FA = formic acid.

References

M. S. Ide, R. J. Davis, Accounts Chem. Res., 47 (2013) 825 and references therein.
 S. S. Liu, K. Q. Sun, B. Q. Xu, ACS Catal., 4 (2014) 2226.

Local Measurement of pH Gradient on Microstructured Electrodes Using SICM

<u>M. Zanatta</u>¹, N. El Habra², F. Visentin², G. Pozza³, A. Zambon^{1,4}, N. Elvassore^{1,4}, M. Giomo¹, G. Brusatin^{1,4}

¹ Industrial Engineering Department, University of Padova, Via Marzolo 9, 35131 Padova, Italy
² Institute of Condensed Matter Chemistry and Technologies for Energy, National Research Council of Italy, Corso Stati Uniti 4, 35127 Padova, Italy

³ Physics and Astronomy Department, University of Padova, Via Marzolo 8, 35131 Padova, Italy ⁴ Venetian Institute of Molecular Medicine (VIMM), Via Orus 2, 35129 Padova, Italy

E-mail: michele.zanatta.1@studenti.unipd.it (M. Zanatta)

In fuel cells, formation of pH gradients at electrodes is a major issue since it may lead to ohmic losses, but it was never measured locally: in this work we present local pH measurement via open circuit potential (OCP) measurements on a microstructured Pt/Au electrode using the device described below, setting the foundations for further studies on photocatalysts' activity towards water splitting reactions. Scanning ion conductance microscopy (SICM) is an imaging technique useful for pH mapping (thus revealing the preferential sites of the watersplitting reactions): the integration of this technique with a three-electrode electrochemical system provides simultaneous information on the topographical imaging of a nanostructured sample and on the electrochemical and catalytic activity of the sample itself (Fig. 1a). This integration is provided by coating the borosilicate micropipette with a 150 nmthick Pt layer (deposited via MOCVD) that acts as a WE. In order to achieve maximum resolution for the simultaneous topography and electrochemical measurements just a small area of the coated surface is in contact with the electrolyte: a fully insulating coating was studied, created and tested via cyclic voltammetry (CV), using an industrial spray paint (signal intensity lying just above the noise region). The thickness of the coating is estimated to be 500 μ m. The tip was opened putting it in contact with a small quantity of xylene. Pipettes were then characterized with CVs in Ru(NH₃)₆Cl₃, both in standard three-electrode cell and in a SICM-integrated three-electrode system: results of both set-ups were coherent thanks to a good overlap of CVs and calibration curves. Before use, each pipette is calibrated performing OCP measurements in solutions with different pH, ranging from 1 to 12. Finally, a microstructured Pt/Au electrodes array was prepared via lithographic technique and it is currently being studied with the integrated device described above (Fig. 1b).



Fig. 1. Schematic representation of (a) the experimental set-up and (b) microstructured electrodes array (each sample supports four replicas).

⁴th Ertl Symposium on Chemical Processes on Solid Surfaces

4th Ertl Symposium on Chemical Processes on Solid Surfaces

Presenter Index



Presenter Index

В	Mischa Bonn	Max-Planck-Institute for Polymer Research	15
	Saskia Buller	Max-Planck-Institute for Chemical Energy Conversion	13
С	R. Kramer Campen	Fritz-Haber-Institute of the Max-Planck-Society	14
	Jinsub Choi	Inha University	10
	Beatriz Roldan Cuenya	Ruhr-University Bochum	7
D	Qiao-Ling Dai	Tsinghua University	33
	Zhifeng Ding	The University of Western Ontario	22
	F. Dionigi	Technical University Berlin	34
F	M. Fitzner	University College London	35
	Hajo Freund	Fritz-Haber-Institut der Max-Planck-Gesellschaft	12
G	Lukas Gierster	Fritz-Haber-Institute of the Max-Planck-Society	36
Н	Renate Hiesgen	University of Applied Sciences Esslingen	3
	Saman Hosseinpour	Max-Planck-Institute for Polymer Research	26
J	Timo Jacob	Ulm University	8
	Henrik Jensen	University of Copenhagen	11
	Wen Ju	Technical University Berlin	37
Κ	Young Dok Kim	Sungkyunkwan University	19
	Il Hee Kim	Sungkyunkwan University	38
	Sarah B. King	Fritz-Haber-Institut der Max-Planck-Gesellschaft	39
	A. Knop-Gericke	Fritz-Haber-Institut der Max-Planck-Gesellschaft	28
	Yoobin Koh	Gwangju Institute of Science and Technology	40
	Marc T. M. Koper	Leiden University	2
L	Hye Jin Lee	Kyungpook National University	16
	Gibaek Lee	Inha University	41
	Sergey V. Levchenko	Fritz-Haber-Institut der Max-Planck-Gesellschaft	27
	Hojoon Lim	Gwangju Institute of Science and Technology	42
М	Anna K. Mechler	Max-Planck Institute for Chemical Energy Conversion	43
	Angelos Michaelides	University College London	20
	Bongjin Simon Mun	Gwangju Institute of Science and Technology	1
	Bridget Murphy	Kiel University	23

Presenter Index

- N
 Sebastian Neugebauer
 Max

 Hong Nhan Nong
 Tech

 P
 Zarina Pawolek
 Tech
- Enrico Pizzutilo S Rolf Schuster Hyun Ook Seo Shamil Shaikhutdinov Dongyoon Shin

Peter Strasser

- U Sunghyun Uhm
- V J. J. Velasco-Vélez
- W Marc Georg Willinger
- X Bo-Qing Xu
 Y Youngmi Yi
 Hyeonseok Yoo
 - Youngseok Yu Zi-Fei Yuan
- Z M. Zanatta

30	Max-Planck-Institute for Chemical Energy Conversion
44	Technical University Berlin
45	Technical University Berlin
25	Max-Planck-Institut für Eisenforschung
17	Karlsruhe Institute of Technology
21	Sungkyunkwan University
24	Fritz-Haber-Institut der Max-Planck-Gesellschaft
6, 46	Gwangju Institute of Science and Technology
9	Technical University Berlin
47	Institute for Advanced Engineering
48	Max-Planck-Institute for Chemical Energy Conversion
29	Fritz-Haber-Institut der Max-Planck-Gesellschaft
5	Tsinghua University
18, 49	Max-Planck-Institute for Chemical Energy Conversion
50	Inha University
51	Gwangju Institute of Science and Technology
52	Tsinghua University
53	University of Padova



GWANGJU

A relatively small city in Asia with wonders quite unrevealed reaching out to the world with your convention partner, Gwangju Convention & Visitors Bureau

KDJ Center 1F, Sangmunuriro 30, Seo-gu, Gwangju, Korea / Tel, +82-62-611-3623 Fax, +82-62-611-3612 / www.gwangjucvb.or.kr

