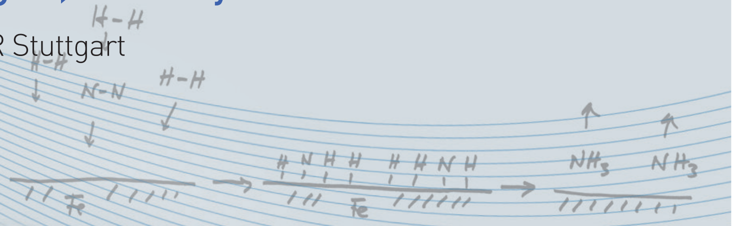
International

2nd Ertl Symposium on
Surface and Interface Chemistry

24-27 June 2012 in Stuttgart, Germany

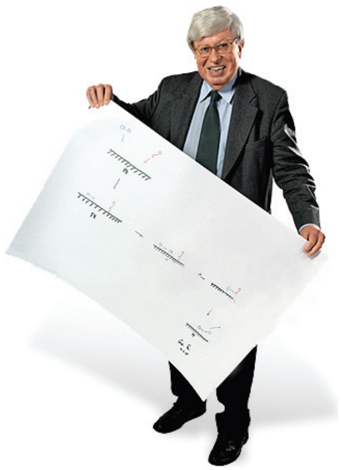
hosted by the Ertl Center & DLR Stuttgart



Prof. Dr. Gerhard Ertl
Nobel Laureate 2007
Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, Germany
“for his studies of chemical processes on solid surfaces”


24-27 June, 2012 in Styttgart, Germany
2nd Ertl Symposium on Surface and Interface Chemistry
GIST
Gwangju Institute of Science and Technology

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.

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 - 1st Ertl symposium	- 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 and food. All these global problems are seeking scientific solutions, especially from chemistry, and in this connection electrochemistry and catalysis are of tremendous importance, in particular for energy conversion and pollution control. It is expected that the Ertl symposium on Surface and Interface Chemistry will play a significant role in these attempts, and we wish great success to all the people involved in this enterprise

Honorary Chairman

Gerhard Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Ertl Center for Electrochemistry and Catalysis, GIST

Symposium Chairmen

K. Andreas Friedrich
German Aerospace Center (DLR) Stuttgart
Jaeyoung Lee
Ertl Center for Electrochemistry and Catalysis/RISE
School of Environmental Science and Engineering, GIST

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Young Dok Kim (Sungkyunkwan Univ.)
Bongjin Simon Mun (Hanyang Univ.)
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Sabine Winterfeld (DLR)
Gregory Jerkiewicz (Queen's Univ.)
Hye Jin Lee (Kyungpook National Univ.)
Seung-Hyeon Moon (GIST)
Elena R. Savinova (Univ. Strasbourg)
Sunghyun Uhm (IAE)
Nobert Wagner (DLR)
Martin Wolf (FHI der MPG)

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Key Topics

Nanoscale Surface and Interface
Heterogeneous Catalysis and Electrocatalysis
Complex Chemical Kinetics

Speakers

Gerhard Ertl [FHI der MPG & Ertl Center]
Alexander A. Auer [MPI for Chemical Energy Conversion]
Artur Braun [EMPA]
Angel Cuesta [CSIC]
Markus Eiswirth [FHI der MPG]
Gerd Ganteför [Univ. Konstanz]
Renate Hiesgen [HS-Esslingen]
Gregory Jerkiewicz [Queen's Univ.]
Young Dok Kim [Sungkyunkwan Univ.]
Hye Jin Lee [Kyungpook National Univ.]
Olaf Magnussen [Univ. Kiel]
Karl J.J Mayrhofer [MPI für Eisenforschung]
Bongjin S. Mun [Hanyang Univ.]
Punit Parmananda [IIT Bombay]
Micheál D. Scanlon [EPFL]
Igor Schreiber [ICT Prague]
Rolf Schuster [KIT]
Germano Tremiliosi-Filho [Univ. São Paulo]
Norbert Wagner [DLR]
Malte Behrens [FHI der MPG]
Christa L. Brosseau [Saint Mary's Univ.]
Zhifeng Ding [UW Ontario]
Marvin Esterfelder [Süd-Chemie AG]
Christoph Hartnig [Rockwood Lithium]
Henrik Jensen [Univ. Copenhagen]
Ludwig A. Kibler [Univ. Ulm]
Marc T.M. Koper [Leiden Univ.]
Dong Chan Lim [KIMS]
Daniel Mandler [Hebrew Univ. of Jerusalem]
Guido Mul [Univ. Twente]
Masatoshi Osawa [Hokkaido Univ.]
Elena R. Savinova [Univ. Strasbourg]
Günther G. Scherer [PSI]
Robert Schlögl [FHI der MPG]
Peter Strasser [TU Berlin]
Hamilton Varela [Univ. São Paulo]
Martin Wolf [FHI der MPG]

Tutorial Courses

Key Technologies for Electrochemistry - Gregory Jerkiewicz (Queen's Univ.)
for Surface Science - Bongjin Simon Mun (Hanyang Univ.)

Abstract submission by 30 April 2012

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

Conference fees & Registration

- Regular participants: €350 Students: €200
  The symposium registration fee includes a copy of the book of abstracts, lunch, coffee break and conference dinner.
- Registration https://dlr-tt.meetingmasters.de

Program

	June 24	June 25	June 26	June 27	June 28	Time
08:00-09:00	Arrival & Registration	Registration				60
09:00-10:50		Jaeyoung Lee & K. Andreas Friedrich	Renate Hiesgen & Guido Mul	Norbert Wagner & Artur Braun		110
		OS J. Lee & K.A. Friedrich **PL Gerhard Ertl** AL1 Hamilton Varela AL2 Hye Jin Lee	**KL03 Martin Wolf** OP1 Youngkook Kwon OP2 Peter Bogdanoff **KL04 Gerd Ganteför**	**KL08 Peter Strasser** IL18 Bongjin S. Mun IL19 Marvin Estenfelder IL20 Renate Hiesgen		
10:50-11:20		Coffee Break				30
11:20-13:10		Bongjin S. Mun & Daniel Mandler	Zhifeng Ding & Rolf Schuster	Ludwig A. Kibler & Hye Jin Lee		110
		KL01 Robert Schlögl IL01 Guido Mul IL02 Alexander A. Auer IL03 Elena R. Savinova	**KL05 Daniel Mandler** IL11 Christa L. Brosseau IL12 Malte Behrens IL13 Gregory Jerkiewicz	**KL09 Masatoshi Osawa** IL21 Igor Schreiber IL22 Olaf Magnussen OP5 Chinmoy Ranjan		
13:10-14:30		Lunch				80
14:30-16:10	Bongjin S. Mun **Tutorial 1** Key Tech. for Surface Sci. (15:00-16:30)	Gerd Ganteför & Karl J.J. Mayrhofer	Marc T.M. Koper & G. Tremiliosi-Filho	Peter Strasser & Olaf Magnussen		100
		IL04 Artur Braun IL05 Christoph Hartnig IL06 Punit Parmananda IL07 Dong Chan Lim	IL14 Zhifeng Ding IL15 Henrik Jensen IL16 Micheál D. Scanlon IL17 Rolf Schuster	**KL10 Marc T.M. Koper** IL23 Young Dok Kim IL24 Markus Eiswirth CR Hye Jin Lee		
16:10-16:40	Coffee Break & Photograph time (Monday)			Excursion & Culture Night		30
16:40-18:30	Gregory Jerkiewicz **Tutorial 2** Key Tech. for Electrochem. (17:00-18:30)	Elena R. Savinova & Malte Behrens	Masatoshi Osawa & Alexander A. Auer			110
		KL02 Günther G. Scherer IL08 Norbert Wagner IL09 Karl J.J. Mayrhofer IL10 Angel Cuesta	**KL06 G. Tremiliosi-Filho** OP3 I. Herrmann-Geppert OP4 U. Kamachi Mudali **KL07 Ludwig A. Kibler**			
18:30-20:30	**Welcome reception** (Commundo Tagungshotel)	Hamilton Varela Young Dok Kim Christa L. Brosseau	Gregory Jerkiewicz & Punit Parmananda			120
		POSTER Session	**Symposium Dinner & Award Ceremony** (Ertl Prize & Best Poster Award)			

- Plenary Lecture, PL (45min): 1
- Award Lecture, AL (30min): 2
- Oral Presentation, OP (20min): 5
- Opening speech and Closing remarks (5min): 2
- Keynote Lecture, KL (35min): 10
- Invited Lecture, IL (25min): 24
- Tutorial Course, TC (90min): 2

June 24th (Sunday) at Commundo Tagungshotel

TC (Tutorial Course, 90min), PL (Plenary Lecture, 45min), KL (Keynote Lecture, 35min), AL (Award Lecture, 30min), IL (Invited Lecture, 25min), OP (Oral Presentation, 20min)		Time
Program		
15:00–16:30	**TC-01 Bongjin Simon Mun** (Hanyang University, South Korea) ▶ Noble techniques in surface science	90
16:30 –17:00	Coffee Break	30
17:00 –18:30	**TC-02 Gregory Jerkiewicz** (Queen's University, Canada) ▶ Electrochemical quartz-crystal nanobalance: Design, calibration and applications to interfacial electrochemistry and electrocatalysis	90
18:30 –20:30	Welcome reception	120

Starry Night by Vincent van Gogh in 1889

June 25th (Monday) at STEP

Program		Time
09:00–10:50	Session 1: Jaeyoung Lee & K. Andreas Friedrich **Opening of the Symposium** J. Lee & K. Andreas Friedrich **PL Gerhard Ertl** (Fritz-Haber-Institute of MPG, Germany) ▶ Reactions at surfaces: From atoms to complexity **AL-01 Hamilton Varela** (University of São Paulo, Brazil) ▶ Decoupling parallel pathways for CO_2 production during the oscillatory electrooxidation of methanol on platinum **AL-02 Hye Jin Lee** (Kyungpook National University, South Korea) ▶ Creating highly selective and sensitive electrochemical sensors with micro-water/organic gel interfaces and biofunctionalized nanoparticles	110
10:50–11:20	**Coffee Break**	30
11:20–13:10	Session 2: Bongjin Simon Mun & Daniel Mandler **KL-01 Robert Schlögl** (Fritz-Haber-Institute of MPG, Germany) ▶ Material dynamics of OER electrodes **IL-01 Guido Mul** (University of Twente, The Netherlands) ▶ Photocatalysis for solar fuels: Challenges and opportunities **IL-02 Alexander A. Auer** (MPI für Chemical Energy Conversion, Germany) ▶ Quantum chemical investigations of Pt-nanoparticles as catalysts in the oxygen reduction reaction **IL-03 Elena R. Savinova** (University of Strasbourg, France) ▶ An ambient pressure XPS investigation of potential driven processes in a membrane-electrode assembly of a high temperature PEM	110
13:10–14:30	**Lunch**	80
14:30–16:10	Session 3: Gerd Ganteför & Karl J.J. Mayrhofer **IL-04 Artur Braun** (EMPA, Switzerland) ▶ The role of defects in hematite for solar water splitting, and its experimental assessment with x-ray and photoelectron spectroscopy methods **IL-05 Christoph Hartnig** (Rockwood Lithium, Germany) ▶ Development activities for energy storage applications **IL-06 Punit Parmananda** (Indian Institute of Technology Bombay, India) ▶ Noise induced regularity in electrochemical systems **IL-07 Dong Chan Lim** (Korea Institute of Materials Science, South Korea) ▶ Spontaneous formation of ZnO nanoripples and surface modification for ling-term stable organic photovoltaics	100
16:10–16:40	**Coffee Break & Photograph Time**	30

June 25th (Monday) at STEP

Program		Time
16:40–18:30	Session 4: Elena R. Savinova & Malte Behrens **KL-02 Günther G. Scherer** (Paul Scherrer Institut, Switzerland) ▶Polymer electrolyte fuel cells: Some technological aspects of electrocatalysis **IL-08 Norbert Wagner** (German Aerospace Center, Germany) ▶Electrochemical characterization of silver gas diffusion electrodes during oxygen reduction in alkaline solution **IL-09 Karl J.J. Mayrhofer** (MPI for Eisenforschung, Germany) ▶Stability of electrode materials for electrochemical energy conversion **IL-10 Angel Cuesta** (Institute of Physical Chemistry Rocasolano, Spain) ▶Adsorbed formate: An electrocatalytic crossroads	110
18:30–20:30	Poster Session: Hamilton Varela & Young Dok Kim & Christa L. Brosseau	120

June 26th (Tuesday) at STEP

Program		Time
09:00–10:50	Session 5: Renate Hiesgen & Guido Mul	110
	KL-03 Martin Wolf (Fritz-Haber-Institute of MPG, Germany) ▶ Dynamics of electron transfer and solvation processes at water/metal interfaces	
	OP-01 Youngkook Kwon (Leiden University, The Netherlands) ▶ Highly selective electro-oxidation of glycerol to dihydroxyacetone on platinum in the presence of bismuth	
	OP-02 Peter Bogdanoff (Helmholtz Zentrum Berlin für Materialien und Energie, Germany) ▶ Electrochemical activity of ruthenium disulphide in the oxygen evolution reaction	
	KL-04 Gerd Ganteför (University of Konstanz, Germany) ▶ The quest for new clustrer materials	
10:50–11:20	**Coffee Break**	30
11:20–13:10	Session 6: Zhifeng Ding & Rolf Schuster	110
	KL-05 Daniel Mandler (The Hebrew University of Jerusalem, Israel) ▶ Local deposition of shape controlled nano-objects by scanning electrochemical microscopy (SECM)	
	IL-11 Christa L. Brosseau (Saint Mary's University, Canada) ▶ Electrochemical PM-IRRAS studies of cholera toxin binding at a model biomembrane surface	
	IL-12 Malte Behrens (Fritz-Haber-Institute of MPG, Germany) ▶ Nanostructured catalysts for energy conversion	
	IL-13 Gregory Jerkiewicz (Queen's University, Canada) ▶ Surface and materials science, and electrochemical analysis of nickel foams	
13:10–14:30	**Lunch**	80
14:30–16:10	Session 7: Marc T.M. Koper & Germano Tremiliosi-Filho	100
	IL-14 Zhifeng Ding (The University of Western Ontario, Canada) ▶ Strategy for efficient and cost-effective absorber layers of thin film solar cells	
	IL-15 Henrk Jensen (University of Copenhagen, Denmark) ▶ Protein adsorption at biomimetic interfaces: The role of electrostatic interactions, dielectric layers and charge regulation	
	IL-16 Micheál D. Scanlon (EPFL, Switzerland) ▶ Electrocatalysis at soft interfaces	
	IL-17 Rolf Schuster (Karlsruhe Institute of technology, Germany) ▶ Electrochemical microcalorimetry	
16:10–16:40	**Coffee Break**	30

June 26th (Tuesday) at STEP

Program		Time
16:40–18:30	Session 8: Masatoshi Osawa & Alexander A. Auer **KL-06 Germano Tremiliosi-Filho** (University of São Paulo, Brazil) ▶ Glycerol electro-oxidation on gold: The influence of the gold nanoparticle coverage degrees **OP-03 Iris Herrmann-Geppert** (Helmholtz-Zentrum Berlin für Materialien und Energie, Germany) ▶ Photoelectrooxidation of water on hematite thin films **OP-04 U. Kamachi Mudali** (Indira Gandhi Centre for Atomic Research, India) ▶ Superhydrophobic surfaces through micro-nano surface modification and their corrosion evaluation by electrochemical impedance spectroscopy **KL-07 Ludwig A. Kibler** (University of Ulm, Germany) ▶ Electrooxidation of methanoic acid on Au(111): The autocatalytic role of adsorbed formate	110
18:30–20:30	Gregory Jerkiewicz & Punit Parmananda **Symposium Dinner & Award Ceremony (Ertl Prize & Best Poster Award)**	120

June 27th (Wednesday) at STEP

Program		Time
09:00–10:50	Session 9: Norbert Wagner & Artur Braun	110
	KL-08 Peter Strasser (Technical University Berlin, Germany) ▶ Core-shell nanoparticle electrocatalysts for PEMFC cathodes: New insights in their intraparticle fine structure and size-dependent morphology **IL-18 Bongjin Simon Mun** (Hanyang University, South Korea) ▶ *In-situ* oxidation study of Pt(110) and its interaction with CO **IL-19 Marvin Estenfelder** (Süd-Chemie AG, Germany) ▶ Heat management in chemical reactions - Challenge and opportunity for catalyst development **IL-20 Renate Hiesgen** (University of Applied Sciences Esslingen, Germany) ▶ Microscopic analysis of current and mechanical properties at solid electrolyte membranes by AFM	
10:50–11:20	**Coffee Break**	30
11:20–13:10	Session 10: Ludwig A. Kibler & Hye Jin Lee	110
	KL-09 Masatoshi Osawa (Hokkaido University, Japan) ▶ Electrocatalytic oxidation of formate on Pt in neutral and alkaline media studied by surface-enhanced infrared absorption spectroscopy (SEIRAS) **IL-21 Igor Schreiber** (Institute of Chemical Technology, Prague, Czech Republic) ▶ Patterns of signal spreading in planar anisotropic networks of excitable cells: Application to cardiomyocytes **IL-22 Olaf Magnussen** (University of Kiel, Germany) ▶ *In situ* surface x-ray scattering as a tool for studies of nanoscale structural changes during electrochemical processes **OP-05 Chinmoy Ranjan** (Fritz-Haber-Institue of MPG, Germany) ▶ Electrochemical oxidation of Pt single crystalline surfaces	
13:10–14:30	**Lunch**	80
14:30–16:10	Session 11: Peter Strasser & Olaf Magnussen	100
	KL-10 Marc T.M. Koper (Leiden University, The Netherlands) ▶ Electrocatalysis for solar fuels **IL-23 Young Dok Kim** (Sungkyunkwan University, South Korea) ▶ Oxidation of toluene on bare and TiO$_2$-covered NiO-Ni(OH)$_2$ nanoparticles **IL-24 Markus Eiswirth** (Fritz-Haber-Institue of MPG, Germany) ▶ Chemical kinetics and algebraic geometry **Closing Remarks (Hye Jin Lee)**	
16:10–16:40	**Excursion & Culture Night**	

List of Oral Presentations

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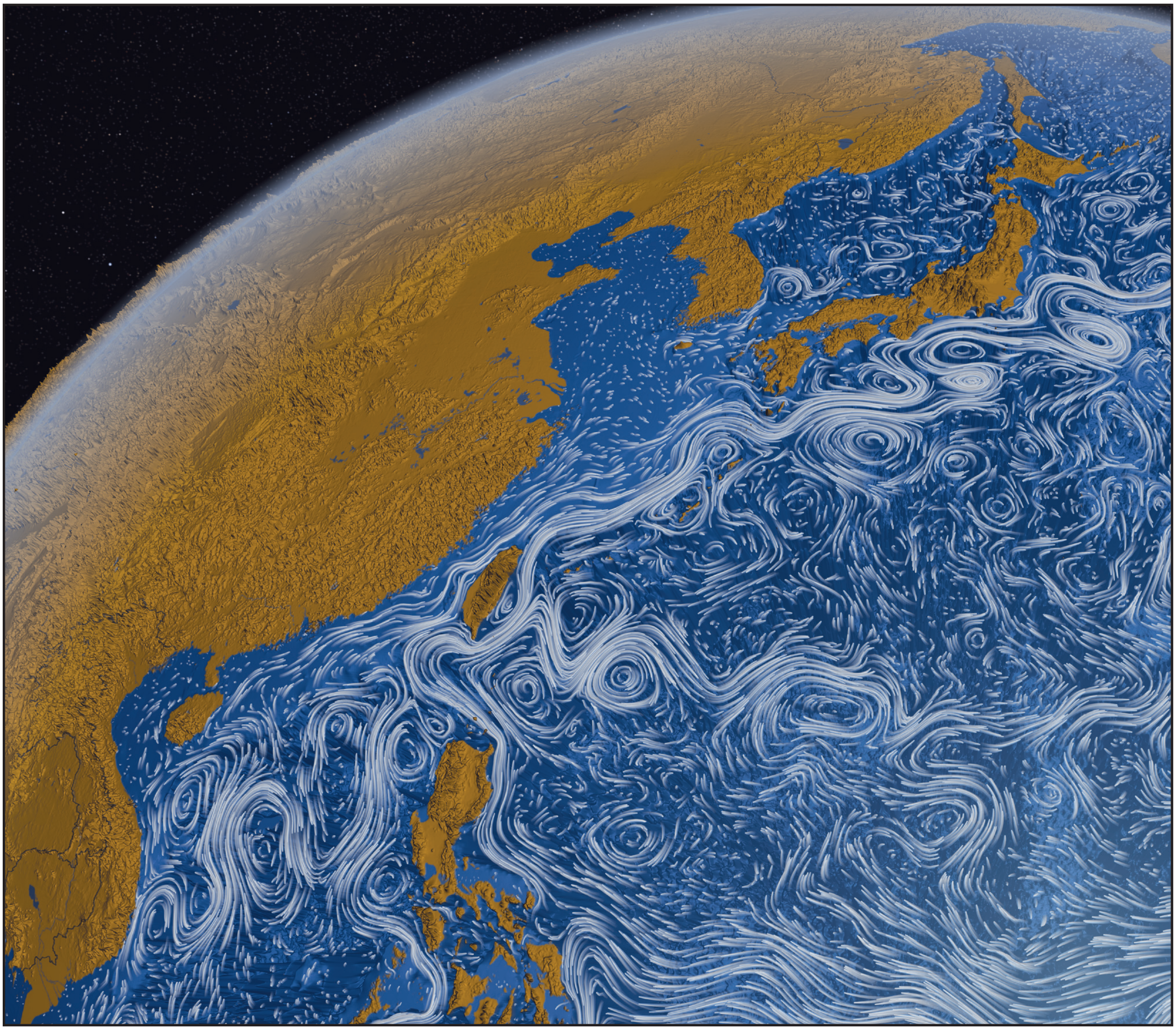
Oral Session



NASA. http://svs.gsfc.nasa.gov/vis/a000000/a003800/a003827/index.html

Noble techniques in surface science

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The advances in surface science often come with the emergence of new instrumentation. Scanning tunneling microscope is a good example. Nowadays, the instrumentations become highly complicated as the problems in surface science become more complex and demanding. One of the recent major progresses in the surface science instrumentation is the refinement of *in-situ* spectroscopy using synchrotron radiation sources.

In this tutorial, the various synchrotron-based *in-situ* surface science spectroscopic tools will be introduced, include ambient pressure x-ray photoelectron spectroscopy, x-ray emission spectroscopy, and x-ray absorption spectroscopy.

Electrochemical quartz-crystal nanobalance: Design, calibration and applications to interfacial electrochemistry and electrocatalysis

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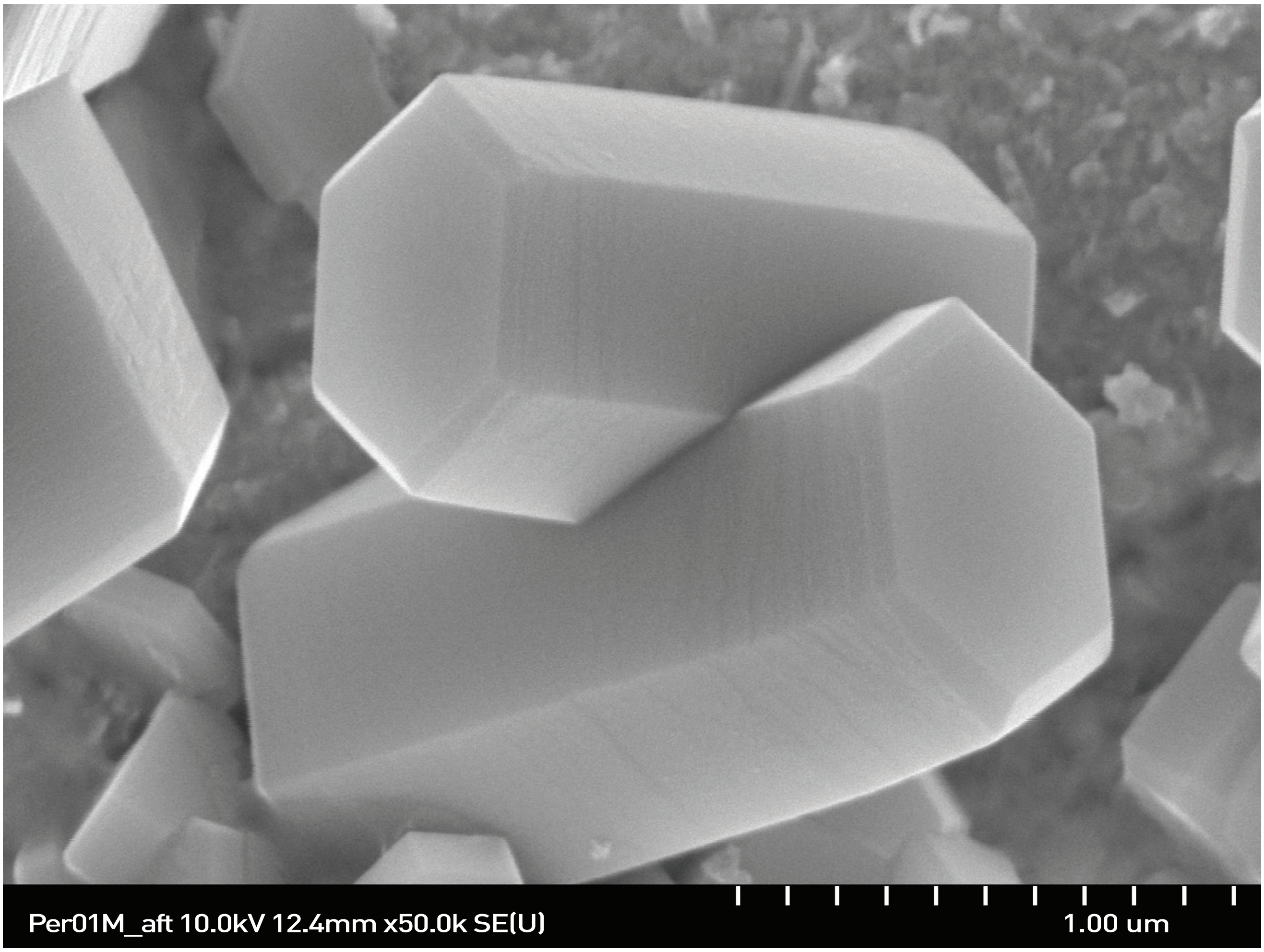
Research in interfacial electrochemistry and electrocatalysis is cross-disciplinary in nature and requires the application of complementary techniques in order to acquire detailed understanding of electrochemical phenomena. Electrochemical methods measure parameters such as potential, current, charge, double-layer capacitance, and charge transfer resistance. Thermochemical research allows determination of thermodynamic state functions of electrochemical processes. Materials science methods image the three-dimensional structure and analyze the bulk chemical composition of electrode materials, while surface science techniques shed light on their surface chemical composition and arrangement of atoms. Vibrational spectroscopy techniques play an important role in identifying reaction intermediates and products formed at electrodes. While electrochemical techniques shed light on the charge balance of electrochemical process and thermochemical approaches on its energy balance, few techniques examine its mass balance.

Electrochemical quartz-crystal nanobalance (EQCN) is a unique technique that measures interfacial mass changes accompanying electrochemical phenomena. Initially, the technique had a detection limit in the μg cm^{-2} range and was known as a microbalance; it was successfully used in research on electrodeposition and electro-polymerization. However, recent advances in the experimental setup design (*e.g. improved mechanical and electromagnetic isolation, adhesive-free quartz-crystal attachment, impurity-free quartz-crystal holder that allows quick electrode exchange, glass-Teflon electrochemical cells*) resulted in a major enhancement of the mass detection limit that at present is below 1 ng cm^{-2}, hence the name "nanobalance".

The tutorial course on EQCN targets an audience with both electrochemistry and non-electrochemistry background. It is at a level suitable for established researchers, post-doctoral fellows and graduate students. It is designed to stimulate interest in EQCN and to demonstrate that it can be applied in research on a variety of electrochemical phenomena. The course covers the following subjects: (i) the theoretical principals governing EQCN; (ii) the experimental setup design; (iii) the quartz-crystal holder and electrochemical cell design; and (iv) the calibration procedures used to determine the constant (C_f, calibration constant or sensitivity contact) that is employed to convert a frequency change (Δf) to a mass variation (Δm). The conversion of Δf to Δm is done using a simplified Sauerbrey equation ($\Delta m = -C_f\Delta f$). It is a common practice to calculate the value of C_f using the Sauerbrey equation $C_f = [\sqrt{(\rho_q\mu_q)}]/(2nf_o^2)$ but this value of C_f applies to an ideal system. The difference between the calculated and experimental values of C_f is as much as 25-30% and has a profound impact on quantitative (*vs.* qualitative) interpretation of EQCN data. Thus, experimental evaluation of C_f is of great importance to EQCN research.

Finally, the tutorial course presents and discusses several examples of application of EQCN to interfacial electrochemical phenomena and electrocatalytic reactions. It ends by reviewing challenges encountered in EQCN research and presents future research opportunities.



Ertl Center for Electrochemistry and Catalysis

Reactions at surfaces: From atoms to complexity

Gerhard Ertl

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Energy barriers in the course of surface reactions may be overcome by thermal activation or (if charged particles are involved) by electric fields. These principles are underlying heterogeneous catalysis and electrocatalysis, respectively. This overview will illustrate, mainly with carbon monoxide oxidation as an example, the kind of information which may be obtained on the atomic scale. Under certain conditions the interplay between reaction and transport processes may give rise to the formation of spatio-temporal concentration patterns on mesoscopic scale as described in the framework of nonlinear dynamics.

Decoupling parallel pathways for CO_2 production during the oscillatory electrooxidation of methanol on platinum

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As in the case of most small organic molecules, the electro-oxidation of methanol to CO_2 is believed to proceed through a so-called dual pathway mechanism. The direct pathway proceeds *via* reactive intermediates such as formaldehyde or formic acid, whereas the indirect pathway occurs in parallel, and proceeds *via* the formation of strongly adsorbed carbon monoxide. Despite the extensive literature on the electrooxidation of methanol, no study to date distinguished the production of CO_2 from direct and indirect pathways, and only indirect proofs are available. Working under oscillatory conditions, we were able to decouple, for the first time, the direct and indirect pathways that lead to CO_2 during the oscillatory electro-oxidation of methanol on platinum [1]. The CO_2 production was followed by differential electrochemical mass spectrometry and the individual contributions of parallel pathways were identified by a combination of experiments and numerical simulations. Moreover, we have also investigated the role of anion adsorption on both direct and indirect pathways.

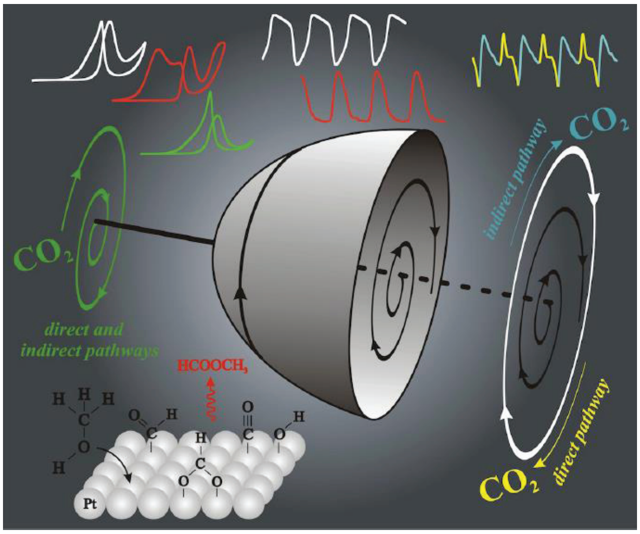

Fig. 1. Pictorial view of the separation of the two pathways leading to CO_2 production during the oscillatory electrooxidation of methanol on platinum.

References

[1] R. Nagao, D.A. Cantane, F.H.B. Lima, H. Varela, Phys. Chem. Chem. Phys., 2012, **14**, 8294.

Creating highly selective and sensitive electrochemical sensors with micro-water/organic gel interfaces and biofunctionalized nanoparticles

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In this paper, we demonstrate our latest advances made on developing highly selective and sensitive amperometric sensors for environmental and biological applications. The first part of my talk will include novel amperometric anion selective sensors based on the transfer reaction of anions across a polarized microhole array interface between the aqueous and the organic gel (3% polyvinylchloride-nitrophenyloctylether) phase. Prior to the anion-selective sensing, we evaluated thermodynamic parameters including the half-wave transfer potentials, the formal transfer potentials and the formal Gibbs transfer energies of hydrophilic anions such as ClO_4^-, Br^-, NO_3^-, I^- and SCN^-. As a demonstration, an $HCrO_4^-$ selective detection platform was created based on measuring current changes due to the assisted transfer of $HCrO_4^-$ across the polarized water/organic gel by an $HCrO_4^-$ selective ionophore, Aliquat 336. The second part of my presentation is a novel nanoparticle enhanced amperometric biosensor for the femtomolar detection of Immunoglobulin E (IgE) which utilizes both DNA aptamer-functionalized nanoparticles and a surface enzymatic reaction. A surface sandwich assay was designed *via* the specific adsorption of IgE onto a gold electrode surface that was pre-modified with a monolayer of aptamer-nanoparticle conjugates followed by the specific interaction of alkaline phosphatase (ALP) conjugated anti-IgE. Anodic current measurements of the ALP catalyzed oxidation of the enzyme substrate 4-aminophenylphosphate (APP) were then used for establishing a detection limit in the 5 fM range of IgE.

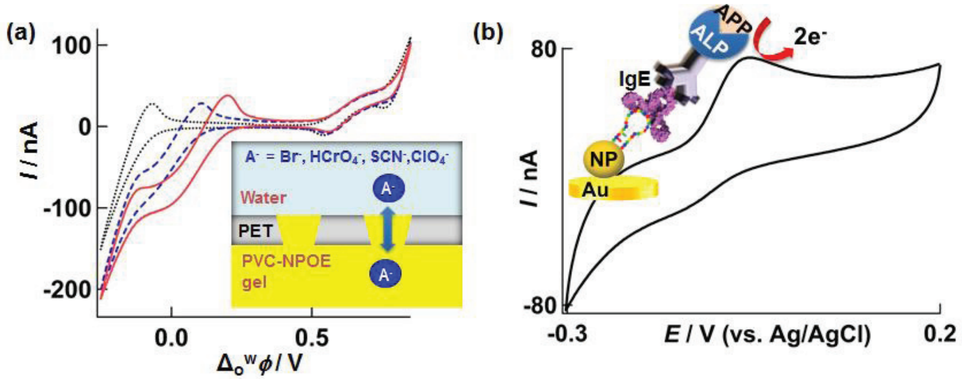

Fig. 1. (a) Representative cyclic voltammograms showing the transfer reaction of anions across a 66-microhole array interface between the water and organic gel phases. (b) A typical cyclic voltammogram for the detection of IgE *via* the formation of a surface sandwich complex of anti-IgE-ALP/IgE/IgE-aptamer coated NPs on gold electrodes followed by the anodic current measurement of ALP catalytic reaction with the substrate APP.

Material dynamics of OER electrodes

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Electrochemical water splitting is a key process in the implementation of large-scale regenerative electricity as replacement for nuclear or fossil power stations. The technology of electrolysis is despite massive scientific and technological efforts hampered by several factors such as static and cycling stability, use of noble metal electrodes, over-potentials that mostly aggregate to the limited function of the oxygen evolution reaction.

We studied this process under realistic load conditions over various forms of Pt with electrochemical techniques and with *in-situ* XPS all elucidating the formation of Pt compounds during operation. High-resolution electron microscopy of cross-sectioned electrodes relates the chemical instability to dimensional instability and elucidates pathways of electrode degradation.

A comparative study of Pt, Ir, and Ru reveals that all elements are subject to drastic and substantial chemical transformations irrespective of their metallic or oxidic states. This is a typical sign of structural dynamics as pre-requisite for high electro-catalytic performance. Possible strategies for kinetic stabilization or for alternative material developments are derived.

Photocatalysis for solar fuels: Challenges and opportunities

Guido Mul

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Photocatalysis is based on the use of light activated catalysts in chemical conversion. Catalysts usually consist of (combinations of) crystalline semiconductors (TiO_2 is by far the most applied and investigated), or light absorbing isolated sites supported on silica-based materials, like Ti-SBA-15. Photocatalysis holds promise in production of solar fuels from H_2O and CO_2 (means to store energy). Practical application is as of yet not feasible because of problems in light management. First, most (stable) photocatalysts require UV radiation to be activated, rather than visible light. Photo excitation by visible light is desired to increase the potential of solar light for catalyst activation (40% of solar light encompasses wavelengths in the visible). Second, often more than 99% of the photo excited states in semiconductor catalysts recombine, before chemical conversion is initiated. After discussing the implications of these phenomena for practical application, recent developments and strategies in tackling these challenges will be presented (see Fig. 1).

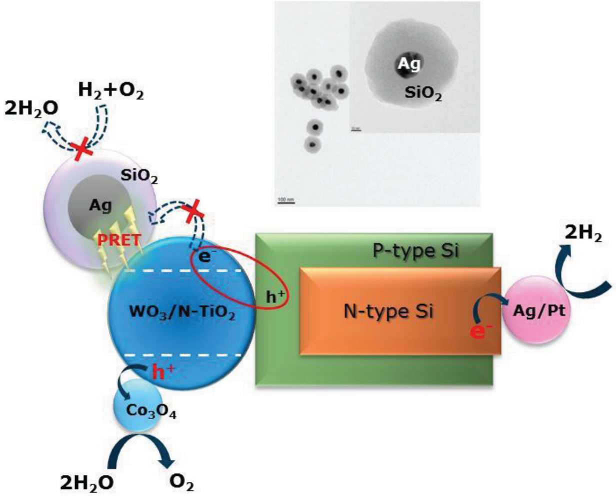

Fig. 1. Schematic representation of a Si based construct for solar water splitting. The construct consist of a Si p/n junction, which upon photoexcitation provides electrons for (Ag or Pt catalyzed) hydrogen generation. The holes are recombined with photoexcited electrons produced in semiconductors absorbing different wavelengths as compared to Si, such as WO_3 or N-doped TiO_2. The holes in the semiconductor are available for Co_3O_4 catalyzed water oxidation. Silica protected Ag particles (see TEM insert) potentially provide enhancement in efficiency by plasmon resonance energy transfer.

Quantum chemical investigations of Pt-nanoparticles as catalysts in the oxygen reduction reaction

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Proton exchange membranes fuel cells (PEMFCs) are an important component of the hydrogen cycle in which hydrogen and oxygen are used as energy carrier for example for automotive technologies or for large-scale energy storage systems.

The key component in PEMFCs is the catalysts for the oxygen reduction reaction (ORR) which in current application are platinum nanoparticles on a carbon support. While PEMFCs are already used for example for public transportation [1], these devices are not without shortcomings.

The performance of low temperature PEMFC is mainly limited by the slow kinetics of the platinum catalyzed ORR on the cathode side [2-5]. Here, a detailed understanding of the relevant mechanisms on nanoparticles can help to optimize the catalyst. A promising system towards more effective and cheaper catalysts is core-shell particles of Pt-alloys [6-10]. However, the stability against dissolution of the lesser noble component and the segregation properties of these systems are critical for the overall catalyst efficiency. Furthermore, the deadhesion of Pt nanoparticles from the supporting carbon materials are a problem for the lifetime of PEMFCs [11,12].

In our work we focus on quantum chemical studies of nanoparticles as catalysts for the ORR. This study includes detailed investigations of the mechanism of the ORR on Pt-nanoparticles and non-Pt catalysts, the stability and segregation properties of Pt-alloy nanoparticles as well as simulations of cluster + support model systems that will hopefully aid experimentalists to design catalysts systems with increased activity and stability.

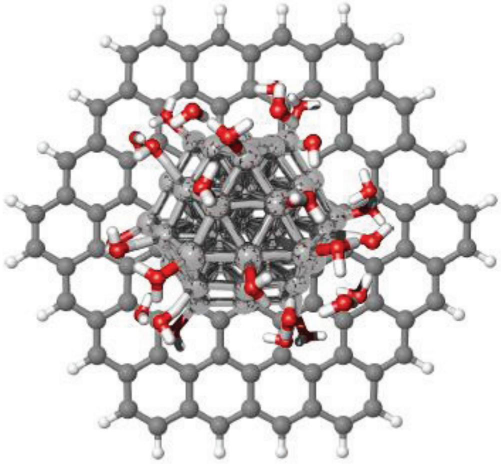

Fig. 1. Computational laboratory: Pt_{37} cluster on support model including explicit solvent.

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An ambient pressure XPS investigation of potential driven processes in a membrane-electrode assembly of a high temperature PEM

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Polymer electrolyte membrane fuel cells (PEMFCs) are considered as one of the most promising environmentally-friendly technologies for transportation and decentralized energy production. Major constraints impeding large-scale commercialization of PEMFCs are their high cost and yet insufficient durability. High temperature polymer electrolyte fuel cells (HT PEMFC) is a subkind of PEMFC that use phosphoric acid imbibed polymer membranes instead of sulfonated polymers like Nafion® or its analogs [1]. The advantage of a HT PEMFC is the possibility to increase the operating temperature up to 150 ~ 200°C which renders them much higher tolerance to contaminations and simpler water and heat management. Unfortunately, along the said advantages they suffer from slower ORR kinetics usually attributed to the adsorption of phosphoric acid at the metal/electrolyte interface as well as to the low O_2 solubility in phosphoric acid [2]. Hence, an understanding of the state of the interface between catalytic Pt nanoparticles and the phosphoric acid-imbibed polymer membrane *in situ* under potential control is of paramount importance for the dissemination of this attractive technology.

Photoelectron spectroscopy (PES) is one of the most powerful techniques for surface studies since it is very sensitive to the composition and the oxidation state of components located on the surface and in the near-surface region of materials. However, application of PES requires ultra-high vacuum thus severely restricting the range of electrochemical systems which can be investigated. Recent advances in vacuum and analyzer technologies have resulted in the development of specialized instruments at synchrotron facilities which allow performing the so-called Ambient Pressure Photoelectron Spectroscopy (APPES) measurements in the pressure range of millibars [3]. Development of the APPES has boosted *in situ* studies of various catalytic [4] and recently also electrocatalytic [5] systems. Recently, Zhang *et al*. [5] applied APPES to study a single-chamber solid oxide fuel cell at 750°C in 1 mbar reactant gases. However, *in situ* monitoring of the metal/polymer electrolyte interfaces relevant to PEMFCs so far has not been possible.

Here we will present the results of an *in situ* study of the interface between Pt nanoparticles and phosphoric acid imbibed polymer membrane under potential control. The measurements were performed at the BESSY synchrotron facility in Berlin (beamline ISISS, operated by Fritz-Haber Institute) which allows measurements at pressures in the millibar range. MEAs were prepared by chemical deposition of ultrathin Pt layers directly onto the high temperature polymer membrane. The preparation technique provides highly extended three phase boundary between the membrane, the catalyst and the gas phase which is of key importance in this study. We will show that the approach employed allows *in situ* probing the potential distribution, as well as the observation of various potential-driven processes including Pt surface oxide formation, as well as adsorption and migration of phosphoric acid in the catalytic layer.

Acknowledgements
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The role of defects in hematite for solar water splitting, and its experimental assessment with X-ray and photoelectron spectroscopy methods

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Solar water splitting by photo-electrochemical cells (PECs) is a prospective green concept for hydrogen generation, but a number of materials related issues need to be overcome before this concept can turn into a technology which can compete against non-sustainable hydrogen generation methods. “Cost” is one such issue and practically requires that only affordable components be considered for PEC. Hematite, α-Fe_2O_3 satisfies this condition, but its electronic structure suffers from several deficiencies, the origin of which is not completely understood, despite of decades of ever recurring research efforts on this interesting metal oxide.

In the context of energy storage and conversion, structural and electronic defects play a critical and even functional role. Recent advancement of synchrotron spectroscopy methods in Berkeley and Berlin allow us to monitor the evolution of remnant and transitional defects at the surface, in the Schottky depletion layer and in the bulk of hematite depending on synthesis routes, process parameters, and operation conditions such as bias potential and illumination with solar light. A bias of 600 mV generates remnant defect states in the upper Hubbard band of un-doped hematite, whereas Si-doped hematite possesses such state already prior to bias. Resonant photoemission spectroscopy shows that continued exposure to such a bias yields electron hole doping to an extent that the valence band spectrum shifts towards the Fermi level. Interestingly, the shift scales systematically with the bias. *Operando* soft X-ray absorption spectroscopy under applied electrochemical bias and illumination produces two transitional defect states in the valence band, one of which is an O2p-type hole and scales with the depletion layer depth and constitutes a transition into the charge transfer band, whereas the other is an Fe3d-type hole transition into the upper Hubbard band. In contrast to established literature, both states contribute equally to the solar water splitting.

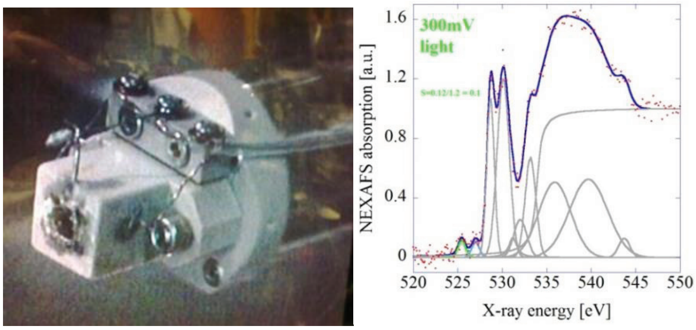

Fig. 1. Photoelectrochemical NEXAFS liquid cell for PEC *operando* studies and NEXAFS spectrum of hematite under light and bias with two transitional defect states.

Development activities for energy storage applications

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Fuel cells and batteries play an important role for a sustainable energy supply in the forthcoming years. For stationary and mobile applications both solutions are required to ensure a reliable and environmentally friendly energy storage technology.

The research challenges for these two technologies are completely different: both low and high temperature PEM fuel cells represent a mature technology that already found the entrance to the market. Main requirements are durability and long term stability, where degradation phenomena of all employed components have to be taken into account. In the best case, the individual contributions and potential failure modes can be monitored separately and accelerated procedures can be defined to shorten experimental observation times without missing essential aspects. Two approaches to study degradation phenomena in high temperature PEM fuel cells are presented and discussed.

The development of next generation batteries, especially lithium metal based technologies such as the lithium/sulfur battery, has at the current stage some fundamental problems to solve before real long term tests can be initiated. In the second part of this presentation some trends of new materials for the lithium/sulfur technology will be discussed and the key requirements for tailor-made solutions are highlighted.

Noise induced regularity in electrochemical systems

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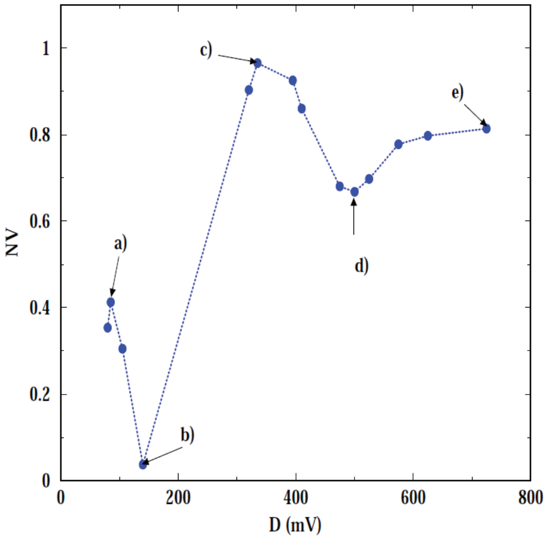
We study the interaction of noise and nonlinear dynamics in simulations and experiments. Both external and internal noise sources are considered. For appropriate noise and system parameters, a variety of interesting and counterintuitive phenomena are observed. It includes the inception of numerous well known resonance effects such as Coherence Resonance, Periodic Stochastic Resonance and Aperiodic Stochastic Resonance. Furthermore, the possibility of noise assisted pattern formation is explored. These results indicate that noise, used judiciously, can induce regularity in nonlinear systems.



Spontaneous formation of ZnO nanoripples and surface modification for Long-term stable organic photovoltaics

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3-D nanostructured ZnO thin films were wet-chemically fabricated on indium tin oxide (ITO) substrate as electron-collecting layers of inverted organic solar cells (IOSC). In addition, ZnO and TiO_2 ultra-thin films were deposited on 3-D ZnO surfaces using atomic layer deposition method. Ultrathin ZnO and/or TiO_2 layers with a mean thickness of less than 5 nm could enhance photovoltaic performance of the inverted organic solar cell; in particular, short-circuit current (J_{sc}) and power conversion efficiency (PCE) was increased by deposition of ultra-thin layer. A higher thickness of additional oxide thin film resulted in reduced photovoltaic performance. Evidence is provided that recombination of electrons and holes on the surface of 3-D ZnO can be quenched by ultra-thin layer. And also, this additional process turned out to increase stability of the IOSC significantly.

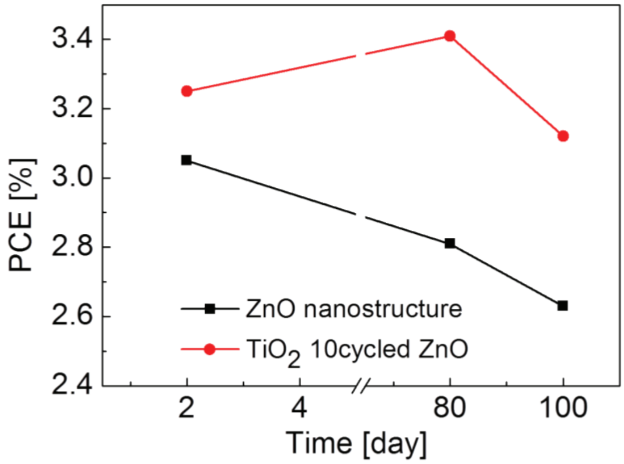

Fig. 1. Highly stable OPV over than 100 days without encapsulation.

Polymer electrolyte fuel cells – Some technological aspects of electrocatalysis

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Polymer electrolyte fuel cells (PEFCs) utilize an acidic polymer ion exchange membrane as solid electrolyte. As a consequence, precious metal catalysts, *e.g*. platinum and its alloys, have to be employed. In addition, the fuel cell operation mode requires specific interfacial electrode/electrolyte properties.

Our work is related to the development of H_2/O_2 polymer electrolyte fuel cells for automotive power trains. In this context, we investigate electrodes with low precious metal loading, prepared by sputtering, and their performance in the fuel cell [1,2]. A further topic concerns the aging behavior of carbon supported platinum electrodes under load following duty cycles specific for automotive applications [3,4]. In this context, the study of platinum/carbon model electrodes in aqueous acidic electrolytes serves to gain a better insight into the stability of these electrodes [5].

Some examples of our current research topics will be presented.

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Electrochemical characterization of silver gas diffusion electrodes during oxygen reduction in alkaline solution

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In order to analyze in detail the kinetics of the oxygen reduction reaction (ORR) and the influence of the porous electrode structure on the electrode performance in alkaline solution (10 M NaOH) at 80°C electrochemical impedance measurements (EIS) and cyclic voltammograms (CVs) have been performed. The investigated electrodes were technical silver gas diffusion electrodes (GDE) and porous silver membranes with different pore radii ranging from 0.2 μm to 5 μm. Silver gas diffusion electrodes were used as cathodes for the oxygen reduction reaction in alkaline solution, as oxygen depolarized cathodes (ODC) in NaCl electrolysis and as cathodes in Li-air batteries.

Electrochemical impedance spectra (EIS) were recorded at different current densities in the frequency range from 50 mHz to 100 kHz. The measured impedance spectra (Fig. 1) can be simulated using an equivalent circuit [1,2] taking into account the kinetic of the oxygen reduction reaction and the porous structure of the electrode.

The used equivalent circuit (model) is the cylindrical-pore model proposed by Göhr, where the impedance elements of the pore's wall surface are the double layer capacity (C_{dl}), charge transfer resistance (R_{ct}) and impedance elements of oxygen adsorption or heterogeneous surface reaction ($R_{ad/het}$ and $C_{ad/het}$).

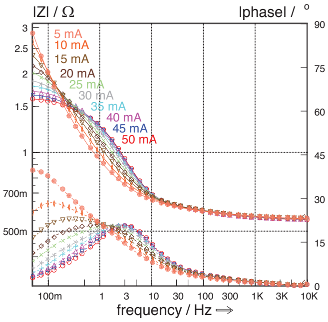

Fig. 1. Bode representation of impedance spectra measured at different current densities during oxygen reduction reaction on Ag-GDE in 10 N NaOH, 80°C.

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Stability of electrode materials for electrochemical energy conversion

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Continuous electrochemical flow reactors for efficient conversion of electrical energy into chemicals and vice versa, *i.e.* fuel cells, become increasingly important for our energy sustainability and environmental concerns. The search for improved electrocatalyst materials, which constitute the core of electrochemical energy conversion devices, has been typically dominated by the optimization of kinetic activity of catalysts and efficiency of whole cells. However, also the stability of the materials is highly important for a potential commercialization, if not even more important, and should at least always be considered in parallel. In this presentation I will demonstrate how such investigations are done on a fundamental level, and what can be learned from these studies for large scale applications. The focus will be on the methodological developments from our group, as well as typical noble metal catalysts as used in low-temperature fuel cell electrochemical reactors.

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Adsorbed formate: An electrocatalytic crossroads

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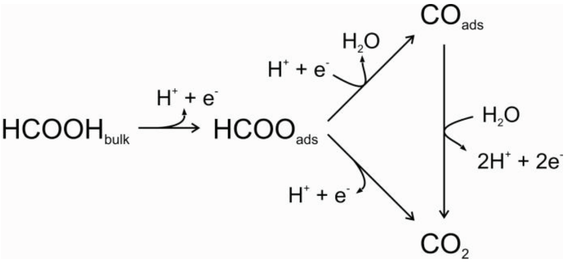
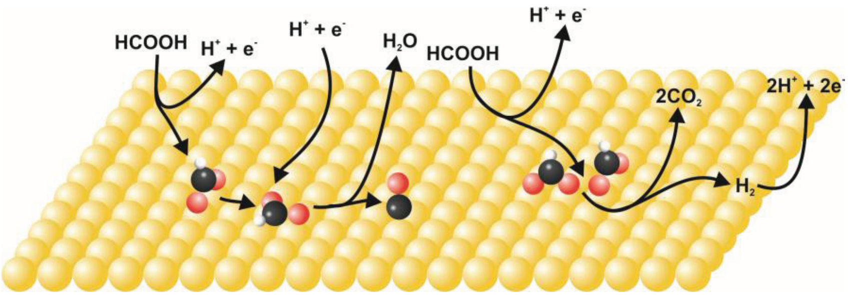
The reaction mechanisms of the direct and indirect pathways of formic acid electrooxidation have been studied on Au and Pt electrodes, respectively, using time-resolved ATR-SEIRAS [1-3].

Regarding the direct path, ATR-SEIRAS reveals that the current due to formic acid oxidation increases quadratically with the formate coverage, and that the slope of i *vs.* θ_{formate} is potential-independent. This indicates that the rate-determining step in the oxidation of adsorbed formate to CO_2 is a bimolecular reaction between adjacent formate species [2,3].

The first stage in the indirect path, that corresponds to the dehydration of formic acid to adsorbed CO can be studied on Pt electrodes at potentials negative enough to avoid the oxidation of adsorbed CO. Time resolved ATR-SEIRA spectra recorded during the dehydration of formic acid on Pt allow to detect the reaction intermediate in the dehydration of formic acid, and to unveil the corresponding reaction mechanism. Adsorbed formate is also the intermediate in the indirect path and is, hence, the key reaction intermediate, common to both the direct and indirect paths, the latter following an unusual electrochemical mechanism, in which an oxidation is immediately followed by a reduction [1,3].



These results have been combined with previous knowledge regarding the atomic-ensemble requirements of the direct and indirect paths [4,5] in order to obtain a detailed description of the reaction mechanism.



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Dynamics of electron transfer and solvation processes at water/metal interfaces

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Electron transfer across interfaces and solvation processes are of vital importance in different areas of physics, chemistry and biology. When an electron is injected in a polar medium, such as water or ammonia, the excess charge will be rapidly screened by the reorientation of the surrounding molecular dipoles. Generation of such excess electrons in liquids involves either photoionization of solvent molecules or doping with *e.g.* alkali atoms, involving possibly perturbing interactions of the system with the parent cation. In our work we use a science approach to electron solvation and interfacial charge transfer. In the case of polar adsorbate layers on metal surfaces, the substrate acts as an electron source from where photoexcited carriers are injected into the polar adlayer. This approach allows also the investigation of heterogeneous electron transfer, as the excited solvated electron population continuously decays back to the metal substrate. In this manner, electron transfer and solvation processes are intimately connected at any polar adsorbate-metal interface.

In this talk I will discuss experiments on the ultrafast dynamics of photoinduced electron transfer and solvation processes at D_2O-ice-metal interfaces. With the aid of femtosecond time-resolved two-photon photoelectron spectroscopy we can unveil all elementary processes like the charge injection across the interface, the subsequent electron localization and solvation, and the dynamics of electron transfer back to the substrate. For *amorphous* NH_3- and D_2O-layers these processes occurs typically on a femto- to picosecond timescale. However, this is fundamentally different for *crystalline* ice layers where we monitor the stabilization of trapped electrons at the ice vacuum interface continuously from femto-seconds up to minutes. Recently we have extended these studies to ice layer doped with alkali ions leading to the formation of electron alkai-water complexes.

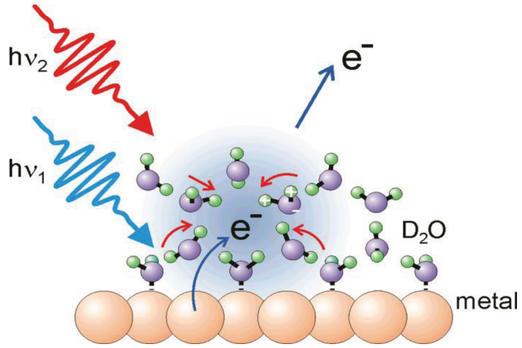

Fig. 1. Schematic illustration of photoinduced electron transfer and solvation processes at water-ice/metal interfaces probed by femtosecond time-resolved two-photon photoelectron spectroscopy.

Highly selective electro-oxidation of glycerol to dihydroxyacetone on platinum in the presence of bismuth

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In recent years, there has been a growing interest in converting glycerol to valuable chemicals. Glycerol, a surplus byproduct of biodiesel, can be selectively transformed to functionalized feedstocks such as dihydroxyacetone and glyceric acid. In heterogeneous catalysis, several monometallic (Pt, Pd, Au) and bimetallic catalysts (Pt-Bi, Au-Pt) have been investigated and revealed that the Pt-Bi bimetallic system shows a promising conversion and selectivity toward DHA at low pH and mild operating conditions.

In this work, we show that the selective conversion of glycerol to DHA is achieved by electro-catalytic oxidation on a carbon-supported platinum (Pt/C) electrode in a bismuth-saturated acidic solution [1]. This high selectivity is related to a selective blocking of the Pt electrode by Bi adatoms confirmed by online HPLC [2,3] and FT-IR analysis. The schematic diagram of the selective oxidation of glycerol is described in Fig. 1.

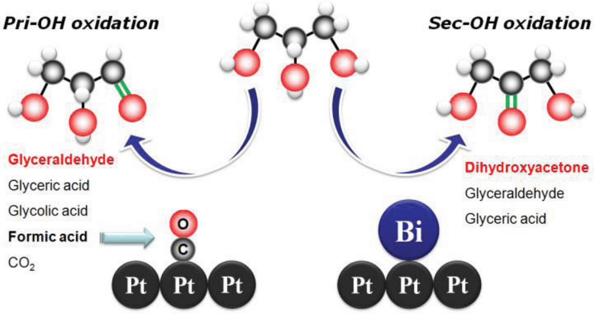

Fig. 1. Schematic diagram of the selective oxidation of glycerol.

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Electrochemical activity of ruthenium disulphide in the oxygen evolution reaction

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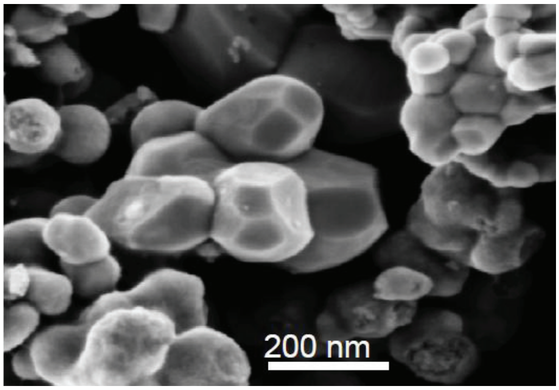
We present single crystals of the compound semiconductor RuS_2 (laurite) which show light-assisted electro-oxidation of water in acidic electrolytes. The material is distinguished by an indirect band gap of 1.36 eV and a direct transition at 2.2 eV. Since the formation of RuS_2 single crystals *via* high temperature growth techniques is not suitable for the production of technical devices the preparation and characterisation of RuS_2 nano particles as well as RuS_2 thin layers were investigated, too. Thin layers have been prepared using reactive magnetron sputtering from a ruthenium metal target and H_2S as sputter gas. The substrate temperature, the gas pressure and gas composition (ratio S:Ar) during the sputter process reveal a strong influence on the electrochemical activity and stability towards water oxidation in acidic media. RuS_2 nanoparticles are prepared by a chemical precipitation route combined with a post annealing step. Depending on the preparation conditions well facetted nanocrystals with sizes ranging from 200 to 20 nm have been achieved.

Layers and particles were characterized by X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM, EDX) and microwave conductivity measurements. The electrochemical activity has been determined by Differential Electrochemical Mass Spectroscopy (DEMS) with and without light. Although absorption measurements confirmed the established optical band transitions and microwave conductivity analysis reveals the generation of photo-induced charge carriers, only small photoeffects were observed so far. This fact can be explained by deep traps and recombination sites in the bulk and at the surfaces. Attempts how to overcome this limiting property will be discussed.



The quest for new cluster materials

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Until today there are only very few materials consisting of size-selected clusters. The most famous example is Fullerite, the third phase of pure carbon besides diamond and graphite. It is a crystal of C_{60} "soccer ball" clusters. The scarcity of cluster materials is somewhat surprising since in the gas phase a wealth of many clusters with many exciting properties has been identified. One major obstacle synthesizing cluster materials from gas phase clusters is the relative large amount of clusters needed. Nanoclusters consisting of a well-defined number of atoms represent the "high end" of nanoscience and can be synthesised in extremely small amounts only. In addition, a ligand shell is not favourable. Ligands tend to mask the advantageous chemical and electronic properties of the nanoparticles. Ideally, new cluster materials need to be build bottom-up from well-defined monosized clusters at ultraclean conditions. A short review on new developments in this field is given and first results [1] are presented.

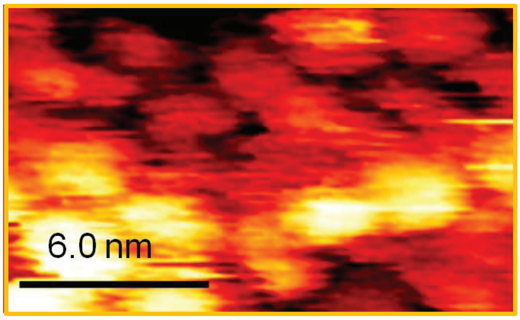

Fig. 1. STM picture of a material synthesized by the deposition of size-selected Mo_{30} cluster anions. At room temperature individual clusters are still discernible.

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Local deposition of shape controlled nano-objects by scanning electrochemical microscopy (SECM)

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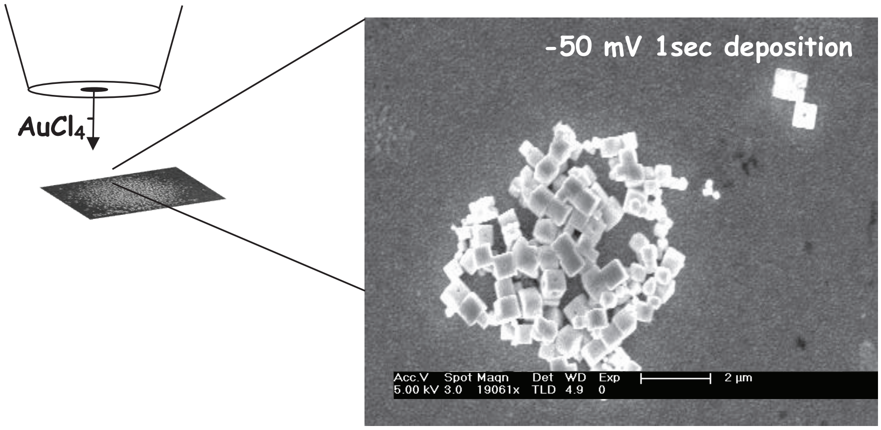
The formation of anisotropic nano-objects such as nanorods and nanoprisms have gained substantial interest due to their interesting size and shape-dependent properties, which can be used in a variety of applications such as photovoltaic cells, surface enhance Raman spectroscopy and many other fields. This has motivated the development of various synthetic approaches by which the aspect ratio and shape can be controlled. Metallic anisotropic nano-object, and in particular those made of gold, have attracted much of these efforts. Numerous approaches have been described, among them are seed mediated growth method with different modifications, photochemical, template, electrochemical and sonochemical methods. These synthetic methods with combination of modern extraction techniques have enabled achieving high efficiency in the formation of nano-objects with controlled size and aspect ratio.

Once these nano-objects are made the challenge is to place them onto surfaces in either repetitive structures or locally in order to form nanostructures that could be used later as catalysts, sensors, etc.

We have been using scanning electrochemical microscopy (SECM) as a means of patterning surfaces with nanoparticles. We have developed different approaches for the local deposition of nano-objects such as metallic nanoparticles. More recently we have addressed the challenge of locally depositing anisotropic nano-objects such as nanorods. The latter are grown locally by controlling the flux of metal ions and their chemical or electrochemical reduction. We will discuss different approaches such as using self-assembled monolayers to control the local growth of nano-objects.



Electrochemical PM-IRRAS studies of cholera toxin binding at a model biomembrane surface

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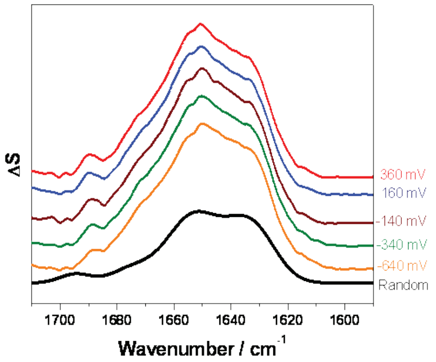
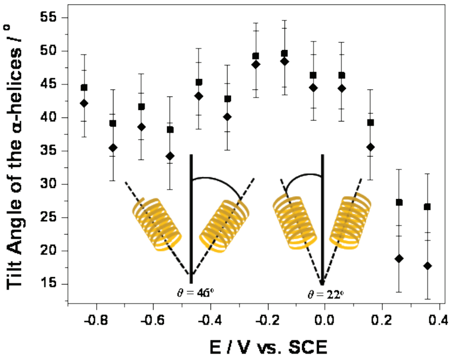
Differential capacitance, chronocoulometry and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) measurements were used to characterize structural and orientational changes induced in a model biological membrane upon binding of the cholera toxin binding unit. The data presented in this work show that binding of the toxin to the membrane results in a decrease in the number of *gauche* conformers, a result of constriction of the lipids by the interaction of the toxin with the glycolipids. The bound toxin induces some defects in the membrane, as was seen from differential capacitance measurements; however, these defects are not significant enough to cause measurable changes in the average orientation of the membrane lipids. The main difference that was observed was that binding of the toxin to the membrane caused a marked decrease in the hydration of the membrane, most likely due to seclusion of the membrane from the aqueous electrolyte because of the massive protein layer. In addition, a voltage-dependent opening of the helical pore of the B subunit of cholera toxin was observed.





Nanostructured catalysts for energy conversion

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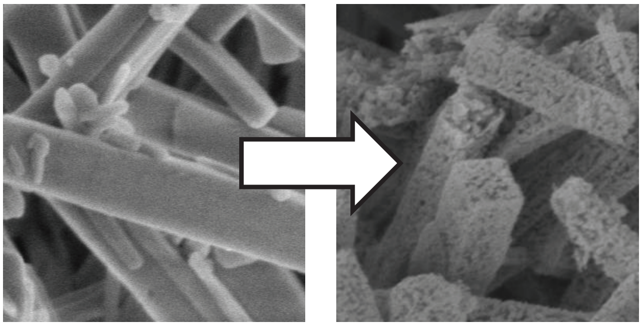
Catalytic processes have great potential for the conversion of CO_2 into useful chemicals like methanol, which can be used, *e.g.*, as an alternative and sustainable synthetic combustion fuel. Alternatively, it can be turned into synthesis gas as a feedstock for chemical industry. Both reactions require hydrogen as reactant, which can be obtained by electrolytic water splitting using renewable energy. Water electrolysis as well as CO_2 conversion reactions require new stable and active catalysts. A precursor approach for feasible preparation of such materials will be presented for abundant transition metal catalysts like systems containing Cu, Mn or Ni. Well-defined precursor compounds with mixed cationic lattices can be transformed by controlled thermal decomposition into nanostructured composite catalysts. The figure shows a mixed Cu, Zn formate precursor before and after calcination. As can be seen in the SEM images, porosity is developed by decomposition of the formate anions. After reduction of the Cu component, the resulting Cu/ZnO catalyst shows high activity for the synthesis of methanol from CO_2/H_2.



Surface and materials science, and electrochemical analysis of nickel foams

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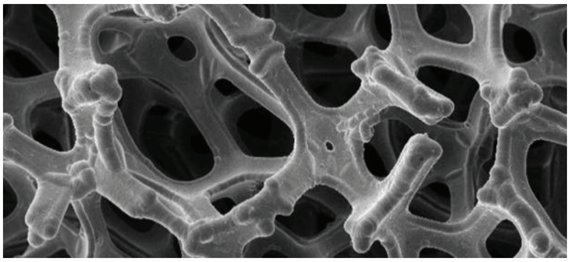
Metallic foams are a form of porous materials possessing a large specific surface area (A_s) and an open-pore structure. Nickel foams (*Fig.*) are fairly new materials and are of importance to electrochemical energy-storing and energy-generating devices, such as batteries, electrochemical supercapacitors and alkaline fuel cells. This contribution reports on the materials science, surface science and electrochemical characterization of commercial Ni foams.



An analysis of their structure by scanning electron microscopy (SEM) demonstrates that they possess interconnected struts that generate small and large pentagonal pores of ca. 50 and 500 μm in size. Surface-chemical analysis by X-ray photoelectron spectroscopy (XPS) reveals that the Ni foams have oxidized and metallic sections within their surfaces, although their fabrication involves sintering in an oxidizing atmosphere at a high temperature and storage in done under ambient conditions (moist air). XPS is used to examine the ratio of the areas of oxidized and metallic sections. The native oxide/hydroxide layer on the Ni foam surface can be removed either by chemical etching or by thermal reduction in a H_2 (g) atmosphere. Chemical etching of the Ni foams results in removal of the native oxide/hydroxide without altering the three-dimensional structure but increases the roughness (R) of the Ni struts and, consequently, the electrochemically active surface area (A_{ecsa}). Reduction of the Ni foams in a H_2 (g) atmosphere at T = 500°C reduces the native surface oxide/hydroxide but does not increase R or A_{ecsa}. Cyclic-voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are used to analyze the electrochemical behaviour of the Ni foams in 0.5 M aqueous KOH solution. As-received, chemically etched, thermally reduced and electro-oxidized Ni foams produce distinct CV profiles, whose features are assigned to oxidized and metallic sections within the Ni foam surfaces. The conclusions drawn on the basis of XPS measurement are confirmed by the results of CV examination. The application of CV-XPS or EIS allows *in-situ* determination of A_{ecsa} and A_s of the chemically etched and thermally reduced Ni foams. The values of A_s determined through the CV-XPS measurements agree with those produced by the EIS analyses. Thus, any of the two approaches can be successfully applied to determine A_{ecsa} and A_s of Ni materials having an extended three-dimensional structure and a large surface area.

Strategy for efficient and cost-effective absorber layers of thin film solar cells

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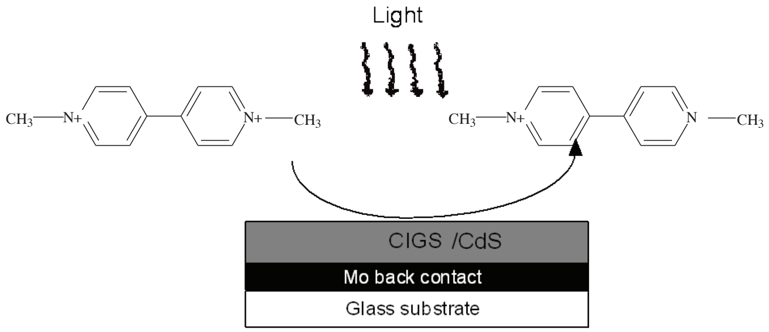
One of the most important challenges for modern sciences and technologies is to develop clean renewable energy resources such as $CuInGaSe_2$ (CIGS) type thin film solar cells. The efficiency, capital investment and production cost of absorber layers in the solar cells have attracted much attention to researchers.

Herein, $CuInS_2$ nanocrystals were easily prepared by one-pot reaction. The composition, structures and photoreactivity of the prepared nanocrystals were investigated by electron dispersive X-ray (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman microspectroscopy as well as scanning photoelectrochemical microscopy.



Photoelectrochemistry was employed to investigate photoreactivity of the nanocrystal films, in a solution of methyl viologen to evaluate their photoconversion. Photoelectrochemical measurements are powerful to characterize the properties of the thin films without making full solid devices.

Protein adsorption at biomimetic interfaces: The role of electrostatic interactions, dielectric layers and charge regulation

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The understanding of protein adsorption is important for a wide range of scientific disciplines including surface engineering and catalysis. Compared to chemical entities having a permanent charge, the adsorption of small ampholytes and proteins is more complicated as the proton concentration near a charged surface can be significantly different from in bulk solution [1].

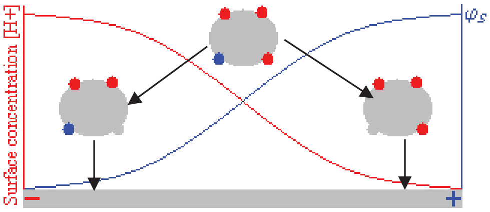

Fig. 1. The proton concentration near a chargedsurface is dependent on the surface potential. The interfacial proton gradient may lead to interfacial charge regulation of an adsorbing protein [1].

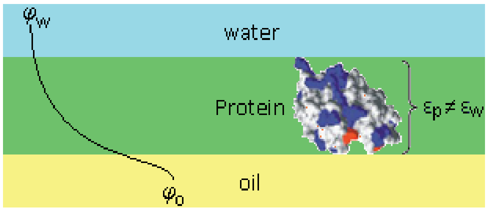

Fig. 2. At an Interface between immiscible Electrolyte Solutions (ITIES) an adsorbing protein may lead to radical changes in the dielectric properties of the interfacial region which in turn lead to charge regulation [2].

Electrochemistry at ITIES is well suited for studying protein adsorption as it offers the possibility of controlling the potential difference between the bulk water and oil phases and enable measurement of protein adsorption by impedance based techniques. In this work we have developed a theoretical model for protein adsorption which takes into account protein charge regulation and formation of dielectric layers. The model successfully explains experimental results and for the first time rationalizes some counter intuitive results which could not be predicted form simple electrostatic considerations. In addition to understanding protein adsorption, the present work will also have relevance in understanding the catalytic performance of ampholytes at interfaces and for quantifying protein stability in heterogenous systems.

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Electrocatalysis at soft interfaces

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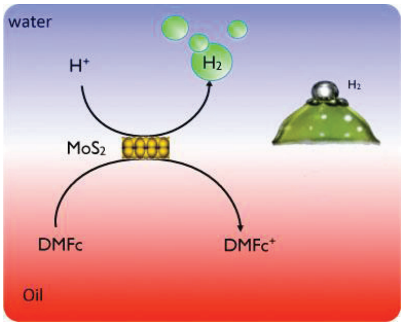
This lecture will review our recent work aimed at investigating electrocatalytic reactions at soft interfaces [1].

First, we shall present recent results in the field of molecular electrocatalysis for the 4-electron oxygen reduction at liquid-liquid interfaces using amphiphilic molecular rafts based on porphyrins subunits able to reduce oxygen to water with a good selectivity [2,3].

Then, we shall present recent studies in the field of aqueous protons reduction by lipophilic electron donors in the presence of nano-Schottky assemblies adsorbed at the interface as illustrated below, and discuss hydrogen production and photo-reduction at polarised liquid interfaces [4-6].



Finally, we shall present some recent results in the field of electrochemistry in supercritical CO_2 containing ionic liquids. We shall present dark CO_2 reduction by metallocenes, and some electrocatalytic cycles at the water-supercritical CO_2 interface [7].

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Electrochemical microcalorimetry

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The measurement of heat effects upon electrochemical reactions provides valuable information on the entropy of reaction, *i.e.*, entropic contributions of all reactants, including those of the reacting ions as well as of solvent molecules and double layer charging. Here we present an experimental approach where sensitive pyroelectric heat detection is combined with pulsed electrochemistry. This allows to measure heat effects of surface electrochemical reactions with small conversions down to a few percent of a monolayer with respect to the sample surface [1,2].

As an example, Fig. 1 shows the temperature decrease of the electrode upon the potential-induced phase transition in a sodiumdodecylsulfate adlayer (SDS) on Au from a hemi-micellar phase to a compact bilayer. The temperature change can be rationalized in terms of the entropy of solvation of the SDS molecules.

In addition, we will discuss the role of entropy for the stabilization of under-potentially deposited Cu and compare our measurements of the entropy of H-adsorption on polycrystalline Pt with results obtained by temperature dependent cyclic voltammetry.

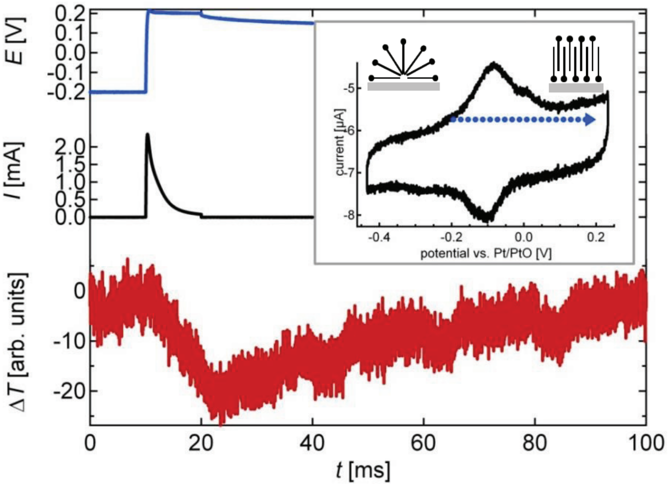

Fig. 1. Temperature and cell current transients during a potential induced phase transition in a sodiumdodecylsulfate adlayer on Au. The inset shows the corresponding cyclic voltammogram. The arrow indicates the potential step.

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Glycerol electro-oxidation on gold:
The influence of the gold nanoparticle coverage degrees

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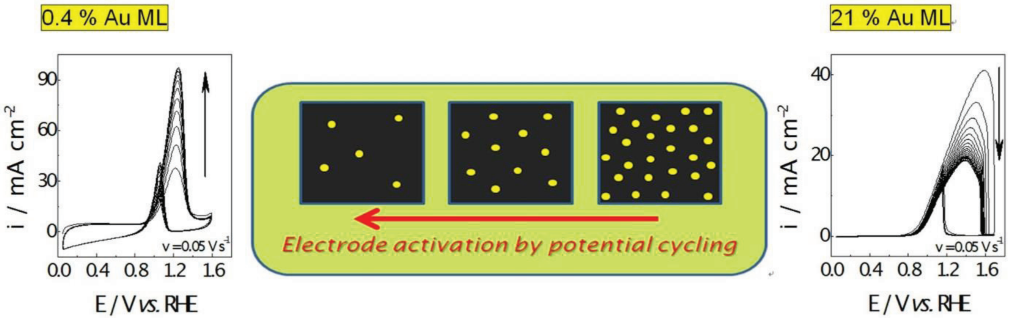
Glycerol is obtained as a co-product during the biodiesel synthesis. Because of the increasing interest in the biodiesel as a fuel, in a short timescale, the glycerol production will surpass its current demand for cosmetic and pharmaceutical uses. For that reason, an alternative application in a Direct Glycerol Fuel Cells (DGFC) for the exceeding glycerol can be proposed for cogeneration of electricity and chemicals.

Gold exhibit very good catalytic activity for glycerol oxidation in alkaline environment [1]. Thus, this work intends to show comparative studies between bulk and nanostructured gold towards the glycerol oxidation. Au nanoparticles were deposited on glassy-carbon electrode with different coverage degrees by exposing the glassy carbon support to gold salt containing electrolyte for distinct times between 0.1 - 45 s at 0.25 V *vs*. Ag/AgCl. The resulting particles are in the range between 50 - 250 nm. The electrode coverage with Au particles increased as a function of the increasing deposition time. It was verified that the electrode activity for glycerol oxidation tends to decrease with increasing electrodeposition time, and the Au particles obtained for 45 s displayed very similar activity compared to the bulk Au electrode.



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Photoelectrooxidation of water on hematite thin films

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Hematite is a promising photoanode material for the oxygen evolution reaction (OER) due to its appropriate valence band position with respect to the electrochemical redox-potential of H_2O/O_2 and its high stability in a broad pH range. However, this semiconductor also possesses disadvantages like low mobility and short diffusion length of photogenerated charge carriers. For this reason these charge carriers are recombining rapidly after excitation with light being trapped in the volume or on the surface of the oxide before reaction of holes at the electrode/electrolyte interface with water molecules can occur.

The here presented contribution depicts hematite thin layers synthesized by a sol-gel process. Only low photoelectrochemical activity was obtained on this pristine material. To overcome this problem, the layers were treated by annealing and by oxygen plasma as well as by anodic polarization, respectively. Surface modification as well as structural perfection in the bulk was yielded lowering recombination probability of excited charge carriers. XPS analysis of the plasma treated material indicates the formation of an oxygen species at the surface which might be responsible for the OER-activity. Combination of bulk and surface treatments lead to a highly active photoelectrocatalyst whose photocurrent curves are kinetically controlled. Differential electrochemical mass spectroscopy (DEMS) measurements in 1 M KOH show an onset potential of the photocurrent and the oxygen evolution about 300 mV more negative than the thermodynamic potential of the OER.

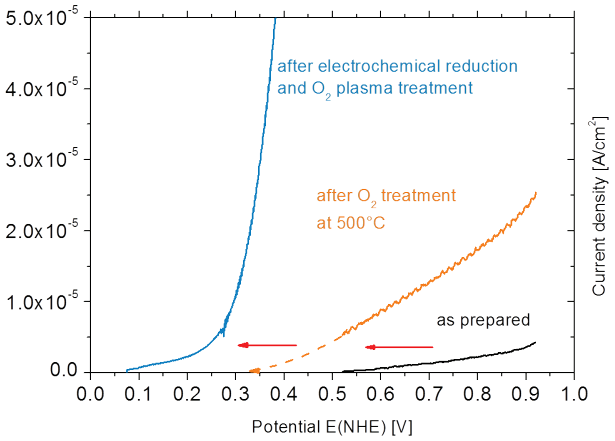

Fig. 1. CV measurements under illumination (400 mW tungsten halogen lamp) in 1 M KOH.

Superhydrophobic surfaces through micro-nano surface modification and their corrosion evaluation by electrochemical impedance spectroscopy

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Corrosion can be defined as the degradation of a material due to its reaction with its environment, where degradation implies deterioration of physical, mechanical and chemical properties of the material. There are a number of ways by which corrosion can be controlled, but the choice of a corrosion control method depends upon economics, simplicity, reliability, performance, and a number of other technical considerations. In the present investigation, a novel and facile method is adapted to improve the corrosion resistance of titanium and chrome-moly steel, the two important materials used in nuclear power plants and reprocessing applications. Learning from nature has lead scientists to unbelievable inventions. One such finding is the superhydrophobicity or the 'lotus effect' which is exhibited by lotus leaves, cabbage leaves, wings of butterflies, legs of water striders to name a few. Superhydrophobic materials have widespread applications ranging from self-cleaning windshields to fabrics to electronic chips. For the current research, we have successfully employed superhydrophobic surface modification to improve the corrosion resistance of titanium and 9Cr-1Mo steel in sea water and nitric acid media. To begin with, a detailed microscopic examination of the lotus leaves was carried out which revealed a micro-nano rough feature combined with a superficial wax-like coating. To achieve these two requirements in titanium, first it was mechanically polished followed by pickling and then anodized. The anodized samples were dip coated with a low surface energy material either a higher fatty acid like myristic acid or silane. The AFM and SEM images (Fig. 1) of surface modified titanium indicated a micro-nano texture and the contact angle was around 150°. A systematic study has also been carried out to evaluate the influence of various electrolytes on the wetting behavior and the corrosion resistance of titanium. Titanium was anodized in different media, namely (i) H_2SO_4+HF, (ii) H_3PO_4+HF, (iii) H_2SO_4, (iv) H_3PO_4, and (v) HF. The electrolytes played a significant role on the texturing of titanium which in turn resulted in surfaces ranging from hydrophilic to superhydrophobic. Electrolytes containing phosphoric acid lead to hydrophilic titanium while sulphuric acid electrolytes lead to superhydrophobic titanium. Open circuit potential and electrochemical impedance spectra (Fig. 2) for surface modified titanium in 0.1, 0.5 and 1 N nitric acid and sea water were recorded which showed improved corrosion resistance as compared to control samples. The antimicrobial activity of these superhydrophobic Ti surfaces was studied by exposing them to predominant biofilm former, *Pseudomonas* species culture in sea water. Anodized and coated titanium showed two order lesser bacterial attachment compared to the control titanium sample. The present study revealed the influence of different electrolytes on the superhydrophobic surface modification and their corrosion and biofouling resistance. The successful modification of titanium directed us to employ a similar approach for 9Cr-1Mo ferritic steel. The superhydrophobic surface was prepared by mechanical polishing and chemical etching to make the surface rough and coated with Silane, a low surface energy material. This resulted in superhydrophobic 9Cr-1Mo ferritic steel with water contact angle around 148° which showed good corrosion resistance in sea water medium. Further work is in progress to improve the water contact angle, stability and corrosion resistance by coating with siloxanes.

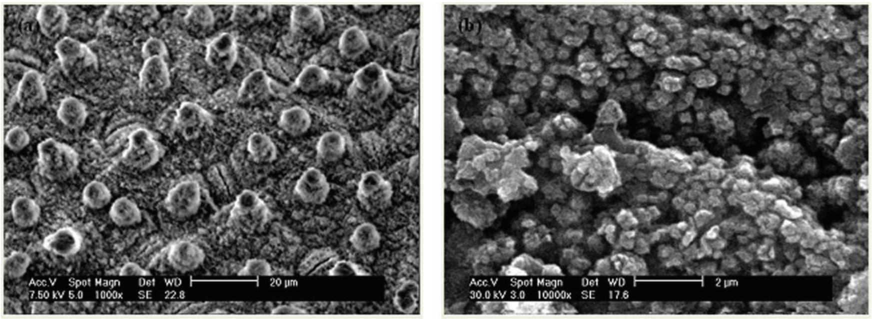

Fig. 1. SEM morphology of (a) lotus leaf showing micro-nano features and (b) anodized Ti surface showing similar morphology.

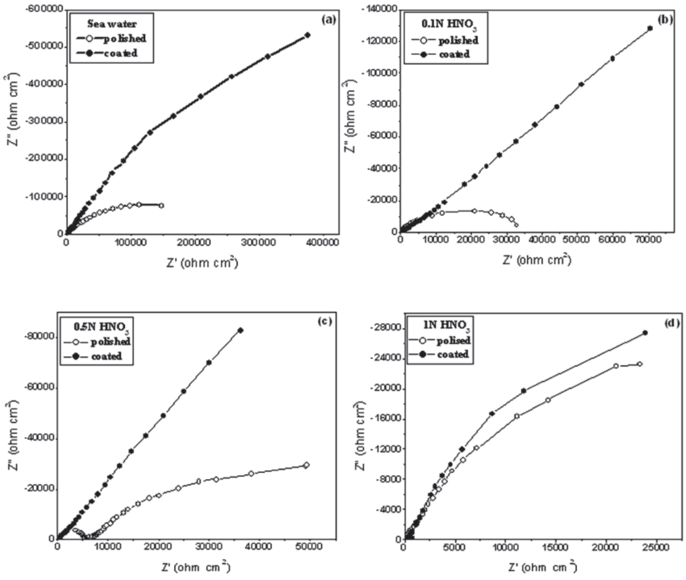

Fig. 2. ElS spectra of control and superhydrophobic surfaces of Ti in sea water and nitric acid media.

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Electrooxidation of methanoic acid on Au(111): The autocatalytic role of adsorbed formate

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New information obtained by FTIR spectroscopy is available for formic acid on polycrystalline Au [1]. In order to establish the structure sensitivity of this fundamental electrocatalytic oxidation reaction, the behaviour of aqueous formic acid was studied on Au single crystal electrode surfaces in the potential region negative to the oxidation of the electrode surface.

Electrochemical measurements including fast-scan voltammetry have been performed to study the specific adsorption of formate on Au(111) as a function of electrode potential for different formic acid concentrations. A previously unknown phase transition within the formate adlayer on Au(111) occurs at a coverage of about 0.25 monolayers. Simultaneously, a pronounced current jump for the formic acid oxidation reaction occurs (Fig. 1), which underpins the electrocatalytic role of adsorbed formate. The steady-state oxidation of formic acid shows a characteristic current maximum at constant formate coverage. A simple rate-law is presented, which explains these experimental findings.

It will be discussed, how the presence of adsorbed formate impacts the reaction mechanism of formic acid oxidation, and if the (auto)catalytic role of formate can be mimicked by other adsorbates, *e.g.*, acetate.

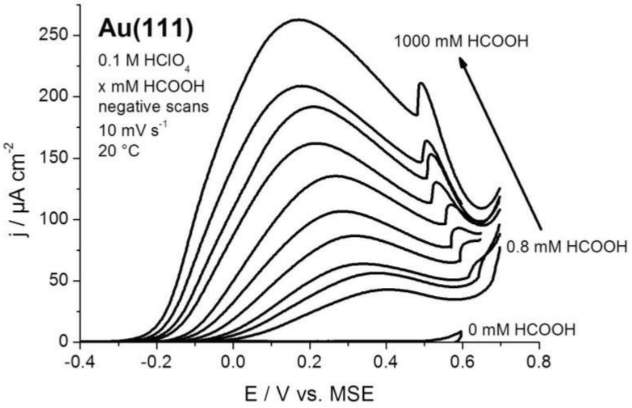

Fig. 1. Current-potential curves for Au(111) in 0.1 M $HClO_4$ + x mM HCOOH. The current jump between 0.5 and 0.6 V arises from a structural phase transition within the adsorbed formate adlayer.

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Core-shell nanoparticle electrocatalysts for PEMFC cathodes: New insights in their intraparticle fine structure and size-dependent morphology

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Core-shell Pt nanoparticles, prepared by chemical dealloying of non-noble metal rich Pt-Cu, Pt-Co, or Pt-Ni precursor alloys show favorable catalytic activities for the electroreduction of molecular oxygen and have recently emerged as promising candidates for PEMFC cathode electrocatalysts. We have started to unravel the origin of their surface catalytic reactivity and found evidence for strong links to the structural and compositional characteristics of the catalyst particles.

Based on detailed scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) studies, we have recently investigated the intraparticle fine structure of the core-shell nanoparticle catalysts at the subnanometer level. We find that a two-phase single core shell structure – often proposed as the structurally and catalytically dominant feature – appears to be an oversimplified model for dealloyed core shell particles. Instead a more complex multi-shell structure exhibiting a non-monotonoous compositional profile of the less noble component appears to a dominant structural feature. We further report how sensitively the active catalyst particle morphology depends on its initial size.

In-situ oxidation study of Pt(110) and its interaction with CO

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Using ambient pressure x-ray photoelectron spectroscopy, high-pressure scanning tunneling microscopy, and density functional theory calculations, the oxidation states of Pt(110) surface under oxygen gas environment are monitored. Only chemisorbed oxygen is observed at low oxygen pressure while nanometer-sized islands of multilayered α-PtO_2-like surface oxide form along with chemisorbed oxygen at higher pressure (0.5 Torr of O_2). Interestingly, both of these oxygen species show a very similar reactivity to CO gas. The spectroscopic features of the surface oxide are similar to the oxide observed on Pt nanoparticles of a similar size, which could help to understand the previous *in-situ* single crystal model catalysis works.

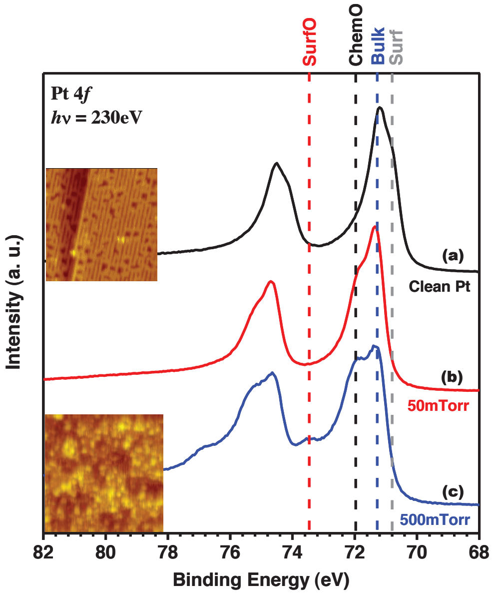

Fig. 1. Pt 4f spectra and STM images taken at different pressure conditions.

Heat management in chemical reactions – Challenge and opportunity for catalyst development

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Mass- and heat transfer are key processes in heterogeneously catalyzed chemical reactions. In order to get meaningful results both need to be addressed in an adequate manner already in an early stage of catalyst development. A well-controlled heat management during a chemical reaction requires an alignment of process conditions, reactor design and the properties of the catalyst. In the presentation the implication of heat transfer processes on the design of a catalyst test rig is shown. In industrial case studies it will be demonstrated how the challenge of heat management has been addressed in the respective cases.

Microscopic analysis of current and mechanical properties at solid electrolyte membranes by AFM

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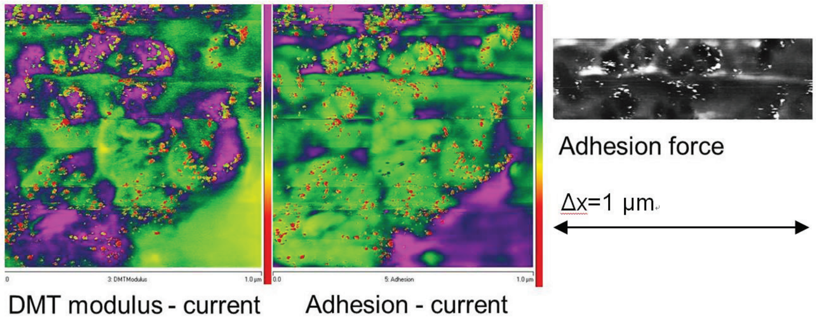
One of the challenges in the further development of membranes for polymer-electrolyte fuel cells is to ascertain a high and homogeneous ionic conductivity. In proton-conducting membranes water transport and conductivity are closely connected by the electro osmotic drag.

Characterization of the conductivity of different fuel cell membranes at the nanometer scale has been performed by advanced tapping mode atomic force microscopy techniques, the so-called PeakForce QNM© and PeakForce TUNA© (Bruker Corp.). The conductivity of different types of solid electrolyte membranes as well as their mechanical properties has been analysed.

AFM yields high resolution images of the conductive structure at membrane surfaces and some insight into the bulk conducting network. The correlation of conductivity with other mechanical properties like *i.e.* adhesion force, deformation, and stiffness, simultaneously measured with the current, gives an indication of subsurface phase separations and phase distribution at the surface of the membrane. In more detail, subsurface regions containing water can be discerned from dry subsurface volume. The distribution of conductive pores at the surface can clearly be identified by water droplet formation.



DMT modulus - current Adhesion - current

Fig. 1. PeakForce QNM©-tapping mode AFM images measured with conductive tip on Nafion© 112 membranes with 1 micrometer side length. **Left side:** DMT modulus (stiffness) with current signal subtracted (red), middle: adhesion force with current signal subtracted (red). **Right side:** adhesion force.

Electrocatalytic oxidation of formate on Pt in neutral and alkaline media studied by surface-enhanced infrared absorption spectroscopy (SEIRAS)

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Formic acid is believed to be oxidized to CO_2 on Pt electrodes *via* the dual pathways mechanism; a major reaction pathway *via* a reactive intermediate and a minor pathway *via* adsorbed CO (poison). Based on systematic time-resolved SEIRAS measurements, Samjeské *et al*. [1-4] proposed that the adsorbed formate is the reaction intermediate in the non-CO pathway (formate pathway). On the contrary, Chen *et al*. [5,6] claimed that adsorbed formate is a site-blocking spectator and the direct decomposition of weakly adsorbed *molecular formic acid* carries most of the oxidation current (direct pathway). If formic acid were directly oxidized to CO_2 *via* a weakly adsorbed formic acid molecule as Chen *et al*. claimed, the oxidation current should decrease as the pH value of the solution is increased. However, a larger oxidation current flows in neutral and weak alkaline solutions ($3 < pH < 10$) than in strong acid. The result indicates that the direct pathway does not work or is negligible if any. SEIRAS coupled to cyclic voltammetry shows that formate in neutral and weak alkaline solutions is oxidized *via* adsorbed formate, as in acid. In strong alkaline solutions ($pH > 10$), on the other hand, formate cannot be adsorbed on the electrode due to the oxidation of the surface, and hence oxidation current decreases significantly. We will discuss that formate oxidation in strong alkaline solutions occurs *via* the CO pathway.

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Patterns of signal spreading in planar anisotropic networks of excitable cells: Application to cardiomyocytes

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Networks of excitable cells, such as neurons, astrocytes, cardiac and certain smooth muscle cells, are connected to each other *via* gap junctions allowing to transfer a signal from one cell to another. The cells, especially in the heart muscle, are densely packed, creating a network possessing a complex connectivity pattern with connections to some neighbors having more gap junctions than to the others. Thus an anisotropic network arises, with varying number of connected neighbors and varying coupling strength. As a result, the wave of excitation spreading through such a network displays certain degree of irregularity.

For example, in the cardiomyocytes the cells are coupled in intercalated discs at the cell's endpoints with the preference to linear chain formation in a horizontal direction, but cells may be also coupled by their sides and/or by their edges, thus leading to vertical and diagonal direction of coupling. We choose spatially 2-D arrangement involving several thousands of cells and explore the relation between the topological arrangement of the network and the wave patterns created. Based on known proportions of coupling directions (horizontal, vertical, diagonal) in different parts of the heart tissue we observe varying tendency of the normally circular waves emitted from a location of an external stimulus toward developing spirals and complex spiralling patterns. Apart from the network topology, this feature also strongly depends on the coupling strength.

In-situ surface x-ray scattering as a tool for studies of nanoscale structural changes during electrochemical processes

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Electrochemical phase formation processes, such as deposition, dissolution, or oxidation reactions, are of major technological importance, *e.g.* in microfabrication or energy storage. However, direct determination of the associated structural changes on the atomic or nanometer scale still is a major experimental problem, especially under technologically relevant conditions, *e.g.* at high reaction rates, complex electrolyte compositions (*e.g.* in the presence of polymers), or during substantial gas evolution.

In this talk I will demonstrate that surface x-ray scattering methods using the high-brilliance beam of modern third-generation synchrotron sources are a powerful tool for *in situ* studies of electrode reactions, able to overcome many of the above obstacles. *In situ* grazing incidence x-ray diffraction (GIXD) nowadays allows direct investigations of metal growth and dissolution [1-3], giving detailed insight on the influence of the atomic-scale interface structure on the growth behavior at a time resolution down to 5 ms, enabling studies at growth rates of 11 ML per second [3] (Fig. 1). As a novel development, *in situ* grazing incidence small angle x-ray scattering (GISAXS) provides data on the time-dependent surface morphology, including island shapes, characteristic lateral dimensions, and surface roughness during the growth process. X-ray reflectivity measurements even allow studies of phase formation processes at liquid-liquid interfaces [4], which are otherwise inaccessible to structure-sensitive techniques. The application of these methods will be illustrated, using various electrochemical deposition and dissolution processes as examples.

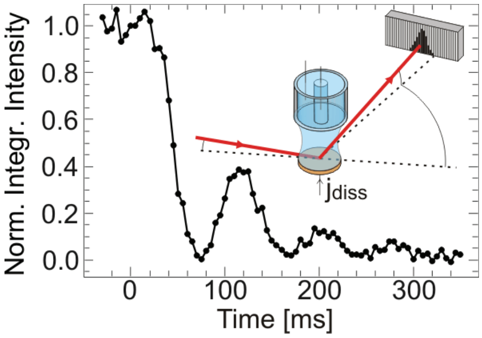

Fig. 1. Fast GIXD experiment (scattering eometry indicated in inset), showing intensity oscillations at (the (1,1,0.1) reflection due to layer-by-layer dissolution of Au(001) in Cl-containing electrolyte at 1.07 $V_{Ag/AgCl}$ with a dissolution rate of 11 ML per second [3].

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Electrochemical oxidation of Pt single crystalline surfaces

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Platinum oxygen interaction in electrochemical media was explored by oxidizing single crystalline Pt surfaces. Pristine single crystalline surfaces Pt(111), Pt(100) and Pt(110) were taken into the extreme anodic potentials during electrochemical cycling of the electrodes. Oxidation/reduction based disordering of Pt electrodes is one prominent aspect of such potential cycling. The CVs for all the disordered surfaces are different from their pristine surface counter parts but remain unique. Disordering process happens on all Pt surfaces. Anion adsorption protects Pt(111) from disordering upto 1.45 V.

Disordered single crystalline surfaces show different activities for oxygen evolution in the order Pt(111) > Pt(100) > Pt(110). Electrochemical impedance measurements obtained under oxygen evolution condition indicate a growing charge transfer resistance with time interpreted as formation of an oxide film on the surface that inhibits charge transfer.

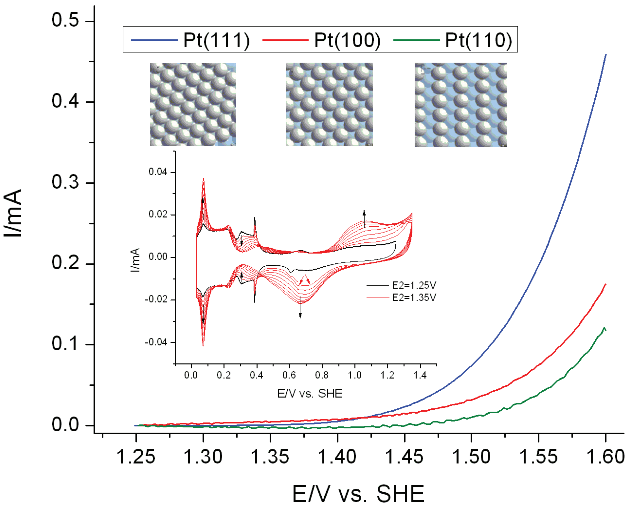

Fig. 1. Oxidation of Pt single crystalline surfaces.

Electrocatalysis for solar fuels

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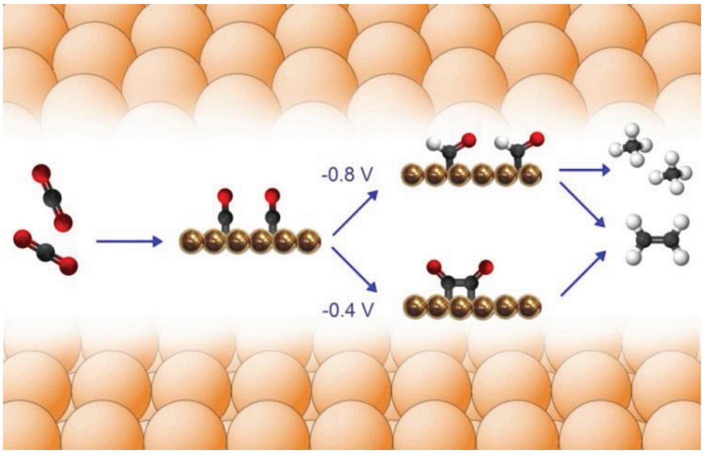
The efficient generation of fuels generated by solar energy, either directly or *via* the intermediate generation of electricity, requires catalysts for multi-electron transfer reactions. In this talk, I will describe our recent results on the mechanisms of the electrocatalytic reduction of carbon dioxide and carbon monoxide on copper electrodes, and on the mechanism of oxygen evolution on gold and other electrodes. Electrochemical measurements are complemented by *in situ* spectroscopy, online mass spectrometry and first-principles density functional theory calculations, to identify key intermediates and critical steps in the relevant reaction pathways.



Oxidation of toluene on bare and TiO_2-covered NiO-$Ni(OH)_2$ nanoparticles

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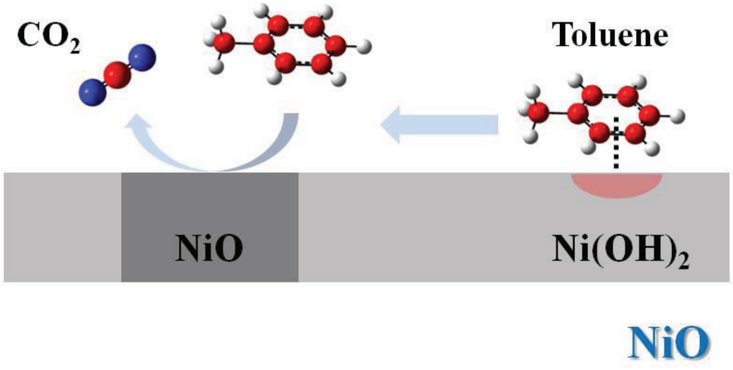
Oxidation of toluene was catalyzed by bare and TiO_2-covered NiO-$Ni(OH)_2$ nanoparticles under humid air. For deposition of TiO_2, atomic layer deposition was used. Bare NiO-$Ni(OH)_2$ showed a significantly high activity for toluene oxidation. When TiO_2 islands were deposited on NiO, formation of CO_2 as a result of total oxidation of toluene was completely suppressed at 180°C, even though the substrate surface was only partially covered by TiO_2. We suggest that TiO_2 islands preferentially blocked the active sites for total oxidation of toluene under our experimental conditions. Based on the XPS data, catalyst surfaces consisted of NiO, $Ni(OH)_2$, and NiO was active for toluene total oxidation, whereas $Ni(OH)_2$ was not. Studies of change in the activity of a heterogeneous catalyst upon preferential decoration of specific surface sites can shed light on the structures and properties of catalytically active sites.



Chemical kinetics and algebraic geometry

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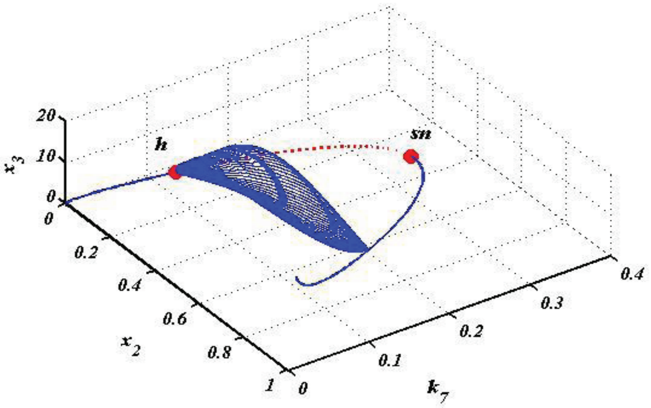
Using a combination of methods from linear algebra (stoichiometric network analysis SNA) and algebraic geometry (polynomial rings) nonlinear chemical reaction equations can be solved for all physically possible steady states and hence the complete stability analysis of the steady states can be achieved. While SNA allows to obtain the complete set of steady states in reaction coordinates (convex parameters) and existence proofs of local bifurcations, the solution in the original kinetic parameters can be achieved by defining a polynomial ring on the kinetic equations and transformation to a Groebner basis which gives restrictive binomials in the form of a toric variety which can be readily transformed into kinetic parameters resulting in a family of curves depending on the rate constants. The procedure is demonstrated using the oscillatory electro-oxidation of methanol.

The methods presented are useful in model development in particular for multistable and oscillatory systems for which several rate constants are unknown since the complete set of stationary states can be determined analytically and checked for instabilities.



Bifurcation analysis of a model of galvanostatic methanol oxidation exhibiting a Hopf (h), saddle-loop and saddle-node (sn) bifurcation for increasing current (k_7). Limit cycle oscillations are shown in blue in phase space; they originate in the Hopf bifurcation and die by collision with the saddle point.

2^{nd} **Ertl Symposium on**
Surface and Interface Chemistry

Poster Session

Redox flow batteries with combined hydrogen generation

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The development of intermittent renewable energy sources necessitates the development of appropriate means of energy storage. Among the various possibilities, redox flow batteries are of particular interest for stationary applications due to their flexibility, scalability and their expected long lifetime [1-3]. In order to improve their flexibility, and indirectly their energy density, the production of hydrogen by redox flow batteries would be profitable as a second level of storage, for when an of electricity is being produced or for smaller installations. Furthermore, hydrogen is considered as a potential energy carrier for energy transportation. The system we are proposing converts the energy contained in a charged redox flow battery into hydrogen and oxygen through two catalyzed chemical reactions. A cerium-vanadium redox flow battery is utilized as illustrated in Fig. 1. Molybdenum-based catalysts deposited on silica particles are used for the regeneration of V(III), through a reaction between protons and V(II) that produces hydrogen. Similarly, IrO_2 nanoparticles deposited on silica particles catalyze the oxygen formation reaction, through Ce(III) regeneration. Both electrolytes are then separated from the catalysts by filtration, and the discharged redox mediators react again at the electrodes of the redox flow battery.

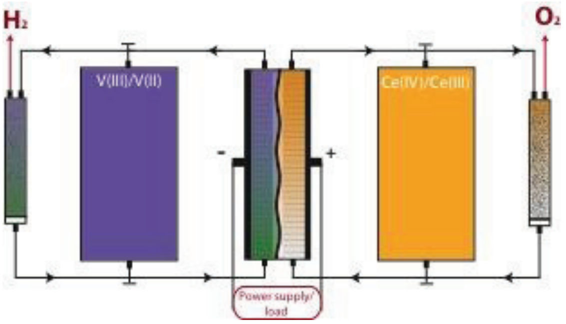

Fig. 1. Scheme of a vanadium/cerium redox flow battery used for hydrogen generation.

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Development of self-supporting MPLs for investigations of water transport in PEM fuel cells

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The performance of a polymer electrolyte membrane (PEM) fuel cell has a strong dependence of its water management. The membrane needs humidity to have sufficient ion conductivity. But at high humidity, especially at high current densities, flooding of the electrodes can occur and consequently the available active area begins to decrease. The primary purpose of a micro porous layer (MPL) on a gas diffusion layer (GDL) is the effective wicking of liquid water from the catalyst layer into the diffusion media as well as reducing electrical contact resistance with the adjacent layers.

In synchrotron radiography studies the importance of liquid water pathways through the porous structure for the water management is proven [1]. These pathways can be formed by natural cracks in the MPL and the texture of the carbon fibre substrate or by artificial pore paths through the GDL. With artificial paths in a carbon fibre GDL produced by laser perforation an overall performance gain has been obtained [2].

To get additional information about the function of the MPL as an interconnection between the reaction layer and the macro porous carbon fibre substrate a self-supporting MPL was developed. This allows the manufacturing and the following treatments of the MPL independent from the GDL substrate. This MPL consists of a thin nonwoven of synthetics coated on one side with a mixture of carbon and PTFE produced by the dry spraying technology [3]. It is possible to perforate this layer alone and press it with the non coated side on a commercial GDL without MPL (Sigracet® GDL 25BA from SGL). Thus it was feasible to perform experiments for investigation of the influence of artificial pores in the MPL on the water management. As a consequence, the liquid water transport of nonperforated GDL/MPLs is compared to the perforation of both layers as well as to the exclusive perforation of MPL and the GDL, by means of *in-situ* synchrotron imaging.

Further measurements, in particular $U_{cell}(i)$-curves up to limiting current densities and electrochemical impedance spectra were done in a 5 cm^2 fuel cell setup, to obtain a correlation of the global intrinsic properties of the MPL, like through-plane permeability, electrical conductivity or hydrophobicity, with fuel cell performance.

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Lateral and vertical chemical imaging of proton exchange fuel cell (PEFC) components with FTIR microspectroscopy

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For the characterisation of large area samples, such as fuel cell components it is desirable to analyse the samples in the macroscopic and in the microscopic scale. In particular the chemical changes after longer operation times are of high importance for a detailed understanding of the degradation of polymer fuel cells. Thus, a method for chemical imaging of such materials is crucial for comprehensive studies.

The application of a focal plane array detector (FPA) with a reflective measurement mode allows for chemical imaging in the micrometer range without damaging the sample. The vertical resolution leads to reduced spectral intensities from areas out of the focal plane. This property gives the possibility to characterise the chemical structure of macroporous media in vertical direction.

Such a structure in gas diffusion layers (GDL) with thicknesses of a few hundred of micrometers and fibers in various heights enables chemical view into deeper layers of the material. In consequence, spectroscopic imaging requires imaging not only in lateral directions, but through various vertical positions as well.

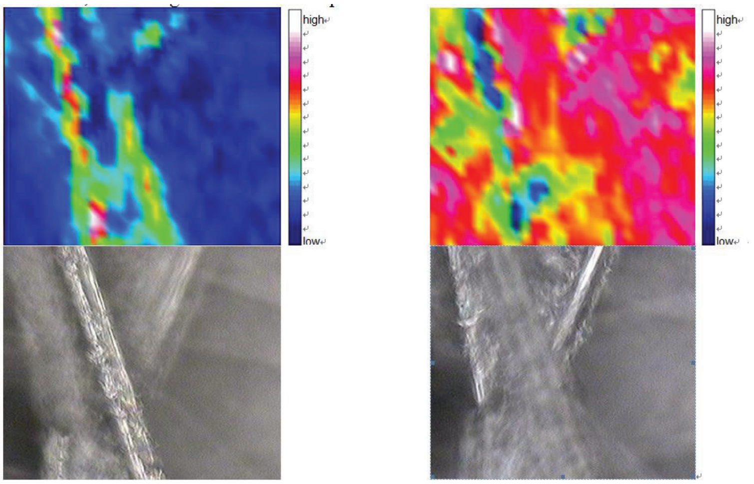

Fig. 1. Left: Chemical mapping of the C-F vibration and corresponding optical image of a GDL, focused on a surface fibre. PTFE rich areas on the fibre edge appear highlighted. **Right**: Chemical mapping of the C-F vibration and corresponding optical image of the same lateral position, focused on a deeper region. PTFE rich areas are in red colors while areas above the focal plane yield less intensity (field of view 120 x 110 μm).

Potential oscillations observed during electro-oxidation of methanol on Pt studied by ATR-SEIRAS

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The highly surface sensitive technique of surface enhanced infrared absorption spectroscopy (SEIRAS) in an attenuated total reflection (ATR) configuration, using a platinum film on a Si prism as working electrode, has been employed to study the spontaneous potential oscillations observed during electro-oxidation of methanol when a constant applied current is asked. Carbon monoxide adsorbed linearly, CO_L, was the main adsorbed specie observed in the induction period and within the oscillatory regime.

In long time experiments the potential oscillations were followed by nearly two thousand seconds and a continuous decay in CO_L band intensity with time was detected along with an increase in the amplitude of potential oscillations and in the mean potential (regarded as the area under a potential cycle divided by the period of this cycle), which is an indicative that adsorbed oxygenated species accumulate on the surface and could be the parameter responsible by the drift in oscillations. Looking in a short time scale, Fig. 1, was possible to found that the band position of CO_L oscillates in-phase with potential curve and that the coverage of CO_L oscillates in a low range of monolayer.

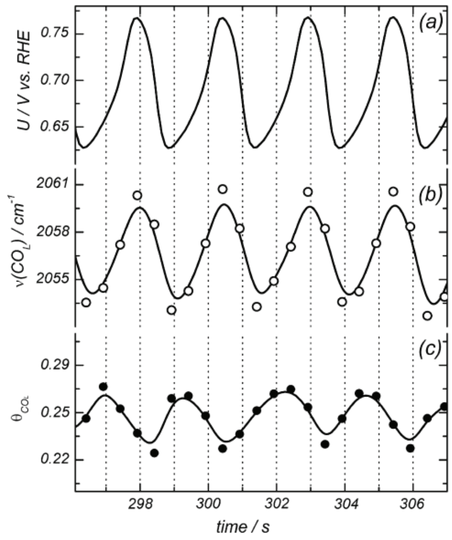

Fig. 1. (a) Potential oscillations during the galvanostatic electro-oxidation of methanol under a constant applied current of 0.18 mA cm^{-2}, (b) band position and (c) CO_L coverage, recorded simultaneously with the electrochemical experiment. Spectral and time resolutions were 8 cm^{-1} and 500 ms, respectively. Electrolyte: $[H_2SO_4]$ = 0.5 M + $[CH_3OH]$ = 0.1 M.

Studies of femtosecond time-resolved photoelectron spectroscopy of Au_3^- $(H_2O)_m$ clusters : Alteration of cluster relaxation dynamics of metal clusters by water molecules

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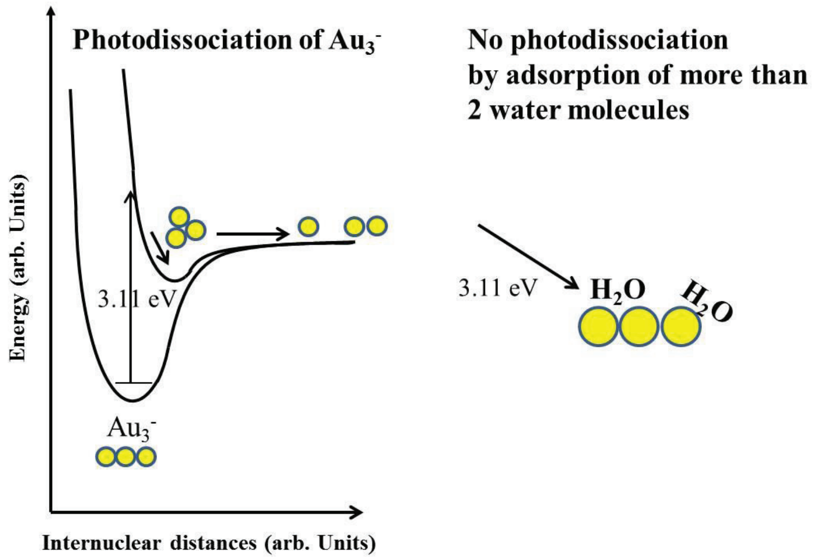
Relaxation dynamics of optically excited states of Au_3^- and $Au_3^-(H_2O)_m$ were studied *via* femtosecond time-resolved photoelectron spectroscopy (fsTRPES). Au_3^- exhibits photo-dissociation into either (Au_2^- + Au_1) or (Au_2 + Au_1^-) with a time constant of 1.6 ns. One water molecule adsorbed on Au_3^- opened new photo-induced dissociation channels with a much shorter time constant. More than one water molecules on Au_3^- inhibited photo-dissociation, most likely as a result of facile dissipation of excess energy of optically excited states by nuclear motions of clusters. Photochemical path can be controlled by adjusting the number of water molecules interacting with the ionic species.



Stabilizing electrochemical times series during formaldehyde oxidation by negative galvanodynamic sweep

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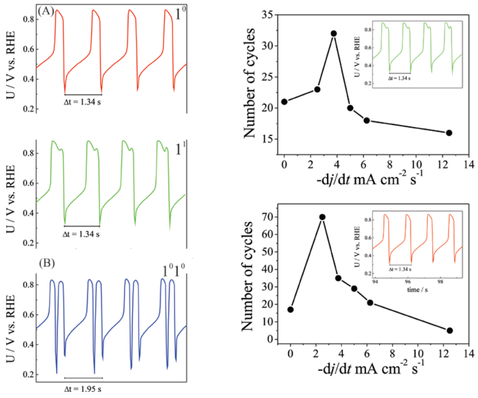
In this work we studied the stabilization of the oscillatory patterns during the formaldehyde oxidation on polycrystalline platinum electrodes in acid media by means of negative galvanodynamic sweep. The time-dependent bifurcation parameter is related to a slow sub-process coupled with the feedback loops as consequence of the subsequent accumulation of the mean oxygenated species coverage on the surface. Spontaneous temporal pattern transitions were observed under the evolution of the drift, following a concatenation of the oscillatory period. In order to compensate this drift, a negative galvanodynamic sweep was employed aiming diminish the changes suffered by the polycrystalline electrode surface during the formaldehyde oxidation. Similar procedure was adopted to methanol oxidation [1]. Now using another molecule, such as formaldehyde, good period stabilizations were obtained, proving that this method can be thought as generic stabilization procedure. The oscillatory patterns (A) observed during the formaldehyde oxidation on polycrystalline Pt electrode in a positive galvanodynamic sweep show an interesting behavior. Applying a negative galvanodynamic sweep to compensate the spontaneous drift under a galvanostatic measurement, it was possible to increase the number of cycles 2.5 and 3.5 times for the oscillatory patterns 1^1 and 1^0, respectively. Now, we are looking for stabilizing other oscillatory pattern ($1^0 1^0$) that appears during the formaldehyde oxidation as depicted in (B) by galvanodynamic sweep. As a consequence, it allows obtaining additional insights on the mechanistic details underlying the electro-oxidation of formaldehyde. Finally, we expect that the application of this method to other oscillatory patterns might bring a deeper understanding about the reaction mechanism far from the thermodynamic equilibrium.



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In-situ XRD and electrochemical characterization of cathodes for Li-S batteries

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Li-S batteries undergo significant structural and morphological changes during cycling. As a result, the specific capacity of the battery decreases considerably, especially in the first cycles. In order to optimize the performance of the cell, it is highly important to understand the degradation processes of sulfur cathode under operating conditions.

In the present work, x-ray diffraction (XRD) and electrical impedance spectroscopy (EIS) were measured during cycling. The formation of crystalline products was monitored *in-situ* and semi-quantitatively determined by analysis.

Impedance measurements were performed during the first cycle at a frequency range of 1 MHz to 60 mHz. Impedance spectra were investigated at several states of charge distinguishing the impedance contributions of the different physical/chemical phenomena occurring in the battery. Furthermore, the aging during cycling was studied until fifteen cycles.

Our results provide new insights into the discharging and charging processes of Li-S batteries by means of XRD and EIS characterization.

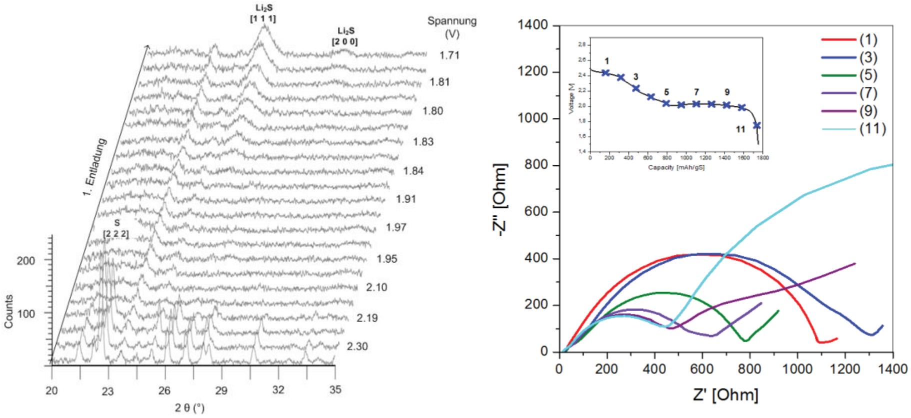

Fig. 1. X-ray diffraction patterns (left) and EIS Spectra (right) collected in the first discharge process of a Li-S battery.

In situ video-STM studies of Pt in electrochemical environment

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Polymer electrolyte fuel cells (PEFCs) are regarded as efficient power generator for stationary and mobile applications in the next generation, due to their high power density, near-zero pollutant emission and low operating temperature. In polymer electrolyte fuel cells (PEFCs), the carbon-supported platinum electrode is commonly used to catalyze both the anodic oxidation of hydrogen and the cathodic reduction of oxygen. It has been established experimentally that the dissolution, coalescence and agglomeration of Pt nanoparticle at the cathode, changes the morphology of the catalyst layer from the initial state during the lifetime of fuel cell. These results in a loss of cell performance, which is one of the problems to be overcome for practical operation [1]. It is know that Pt oxidation/reduction at positive potential leads to substantial restructuring of the electrode surface, as revealed by *in-situ* STM studies of single crystal electrodes [2,3]. However, the detailed atomic-scale mechanisms of these dynamic processes are still unclear.

In this study, an *in-situ* STM with highly time resolution (video-STM) was employed to studies of Pt(111) surfaces in electrochemical environment, to evaluate the dynamic behavior of the Pt(111) surface in 0.1 M $HClO_4$ and 0.1 M H_2SO_4 solution during potential cycles. As illustrated in Fig. 1, atomic resolution images could be obtained in both electrolyte solutions. First results on the Pt oxidation and dissolution behavior will be discussed.

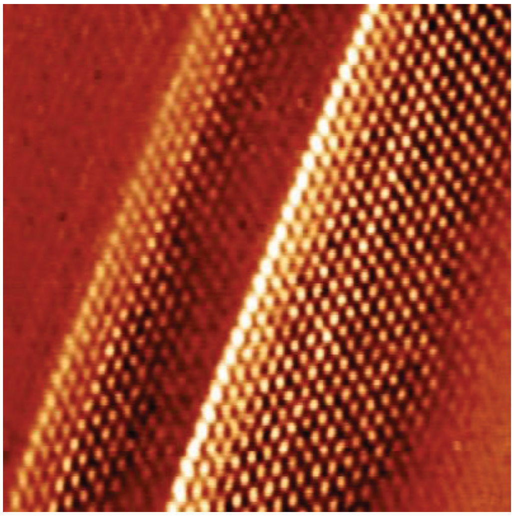

Fig. 1. Atomic resolution video-STM image of Pt(111) in 0.1 M $HClO_4$ solution at 0.3 V *vs*. RHE (6.5 × 6.5 nm^2), showing two terraces with steps along the close-packed lattice directions.

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Methanol reactions on bimetallic Ru(0001)-based surfaces under UHV-conditions

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The adsorption and reactions of methanol are of technological relevance for the DMFC. Thereby, it is desirable to influence the chemical selectivity of catalysts to convert methanol to CO_2 instead of CO which acts as a catalyst poison. In this context we present a detailed study on thermally induced methanol reactions on a number of functionalized bimetallic layers and surface alloys performed by means of FTIRAS, TPD, and XPS in the temperature range 20 – 600 K.

In particular, the experiments focus on the identification of fundamental reaction steps and stable species as well as on the variation of surface parameters, such as the thickness of a deposited metal (Cu or Pt) or the density and order of co-adsorbates (*e.g.* O).

It is found that on the clean surfaces either the dehydrogenation pathway is observed or no reactions occur. The CO_2 producing path, on the other hand, can be opened by the co-adsorption of oxygen; in parallel, the CO formation rate is decreased. Generally, only disordered and/or dilute surface oxygen layers promote methanol reactions; in the case of dense and ordered O-overlayers they passivate the surfaces effectively. A significant drawback of adding oxygen is the reaction of the oxygen atoms with methanolic hydrogen to gaseous water.

As on oxygen covered Pt_xRu_{1-x}/Ru(0001) surface alloys with a Pt contents x = 50 – 80% the drain of H atoms is limited and they nonetheless exhibit CO_2 as a final product, they represent a compromise regarding a suitable catalyst material for a DMFC as compared with the other systems investigated by us (see Fig. 1).

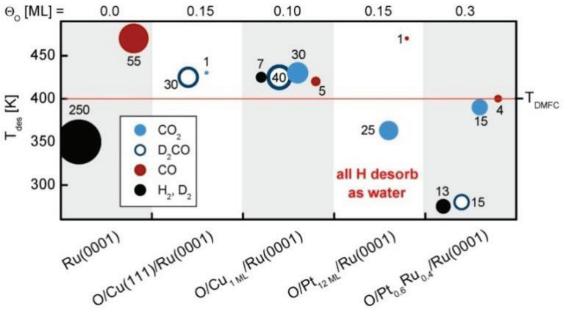

Fig. 1. Desorption temperatures (vertical scale) and quantities (symbol size) of final products (given in percentage of initially chemisorbed methanol) from methanol reactions on the layers indicated in the figure. Note that desorbing water is not included. The initial oxygen coverages are given at the top of the figure. The horizontal line labels the typical operation temperature of a DMFC.

Biphasic water splitting by osmocene

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Solar water splitting is undoubtedly a key challenge and in the quest for solar fuels hydrogen is definitely a major target with many industrial applications ranging from transportation to carbon dioxide mitigation. In this context, we have studied hydrogen evolution reaction through the reduction of aqueous protons by decamethylferrocene in water/1,2-dichloroethane interfaces since 2009 [1] and later on the catalytic HER by MoS_2 [2] and carbon based MoS_2 catalysts [3].

The analogy of ferrocene, osmocene works as a photocatalyst for water splitting in acidic aqueous solutions [4]. However, the low solubility of osmocene in water phase greatly limited its applications. For the first time, the photo-reactivity of osmocene with protons was studied in a biphasic system under anaerobic conditions. The mechanisms were investigated and elucidated experimentally and computationally. We carried out biphasic reactions by mixing an organic phase containing osmocene with an aqueous phase containing protons. Hydrogen and $[Cp_2Os^{III}–Os^{III}Cp_2]^{2+}$ were evidenced as photo-reaction products as confirmed by gas chromatography and proton nuclear magnetic resonance (NMR). Furthermore, $[Cp_2Os^{III}–Os^{III}Cp_2]^{2+}$ was found by NMR to split water to form $[Cp_2Os^{IV}(H^-)]^+$ and $[Cp_2Os^{IV}(OH^-)]^+$, which releases O_2 under light. The dimerization property of osmocene was also observed by electrochemistry. Reaction mechanisms suggested by experiments corroborate DFT computations. This study gives important insights on the mechanism of biphasic water splitting property of osmocene. Inspired by the bimetallic dimers of osmocene, mixed metal dimers could be potential candidates for water splitting catalysts.

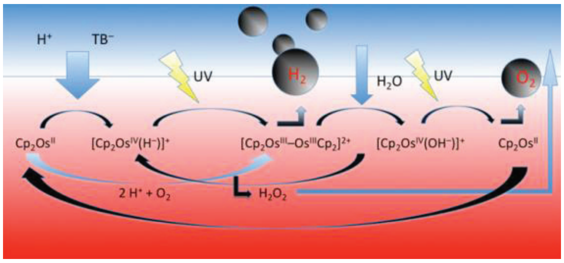

Fig. 1. Schematic of the global reactions of water splitting by osmocene at water/1,2-dichloroethane interfaces

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Effect of bulk concentration on dynamical stability of a model electrocatalytic process on a spherical electrode surface

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The effect of bulk concentration on the appearance of Hopf instability and saddle-node one in a model electrocatalytic process on a spherical electrode surface with apreceding homogeneous chemical reaction in the Nernst diffusion layer under potentiostatic conditions is investigated using electrochemical impedance spectroscopy method. It is shown that at low values of bulk concentration the system can demonstrate spontaneous periodic current oscillations and bistability. The last one disappears at high values of bulk concentration. The effective rate of a preceding chemical reaction regulates the regions of the instabilities in question in an opposite way (Fig. 1). This is also true for a change in electrode radius.

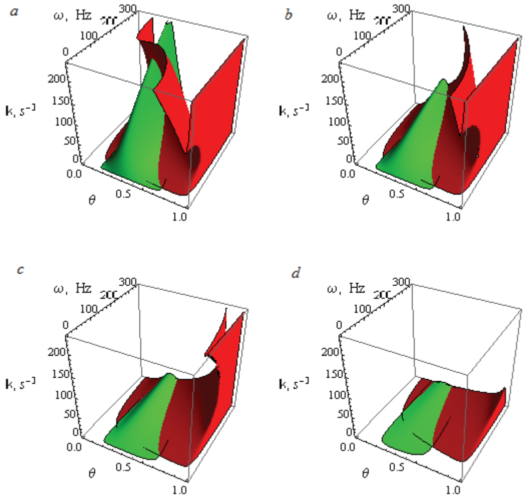

Fig. 1. Zero surfaces of the imaginary and real components of the system impedance as function of frequency ω, electrode surface coverage by adsorbate θ and the effective rate of a preceding chemical reaction k for various c_0 values (10^{-6} mol cm^{-3}): (a) 9, (b) 11, (c) 15, and (d) 25. The intersection of these surfaces yields the Hopf bifurcation points, namely, bifurcation values of frequency ω_H, electrode surface coverage by adsorbate θ_H and the effective rate of a preceding chemical reaction k_H.

Microscopic investigation of PEMFC cross sections by AFM and SEM

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Proton Exchange Membrane Fuel Cells (PEMFCs) are on the way towards commercialisation but degradation of its components is still an issue. Degradation of the electrolyte membrane can cause failure of the cell and therefore limits its lifetime.

The aim of this work is to examine cross sections of aged membrane electrode assemblies (MEAs) at microscopic scale in order to analyse alterations caused by fuel cell operation. Measurements have been performed on various MEAs aged for 1600 hours at open circuit voltage. The analysed MEAs differ in the Nafion® membrane type used, *i.e.* especially in thickness.

Cross sections of those MEAs were investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDX). The advanced AFM tapping mode Peak Force QNM© (Bruker Corp.) allows not only to get height data but also information about mechanical properties of the sample surface.

Using those analytical tools, platinum particles were detected inside the membrane. Particles are distributed in the whole cross section area with larger particles concentrating in a band parallel to the electrodes. The high resolution AFM data yields particle size distribution. Furthermore SEM images revealed thinning of the membrane.

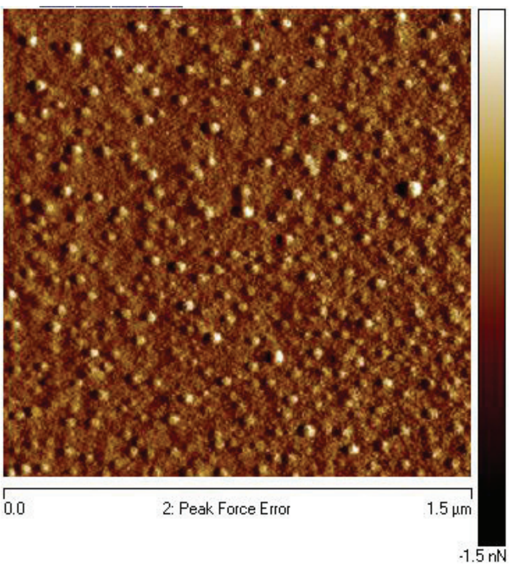

Fig. 1. PeakForce QNM©-tapping mode AFM image measured on aged Nafion© 117 membrane with 1.5 μm side length: Peak Force image shows platinum particles.

FTIR spectroscopic imaging of aged fuel cell components

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Regarding fuel cells as an environmentally friendly energy converter one of the major unsolved problems is an insufficient lifetime. In polymer electrolyte fuel cells humidity management is a key point for their performance. Thus the degradation of the gas diffusion layers (GDL) and microporous layers (MPL) therein are the key point for the understanding of reduced fuel cell lifetimes.

The characterization with FTIR spectroscopic imaging utilizes the presence of a polyester fleece as carrier the MPL. The measurements were performed in attenuated total reflection (ATR), resulting in an information depth in the range of ~100 nm. Characteristic C-F modes at 1200 cm^{-1} and 1150 cm^{-1} and C=O vibration modes at 1700 cm^{-1} were used for mapping the amount of polyester detectable beneath the layers composed of polytetrafluoro ethylene (PTFE) and carbon powder. Areas of high C=O intensities were identified in diffusion layers of aged fuel cells, which were not present in the pristine samples, showing a reduction of the PTFE thicknesses.

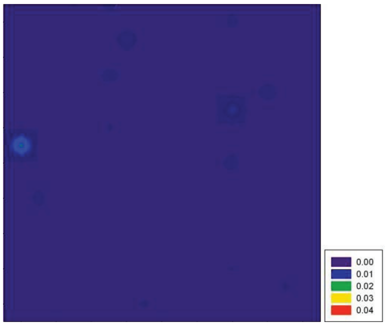

Fig. 1. Chemical image of C=O vibrational intensities related to the polyester concentration of a pristine MPL.

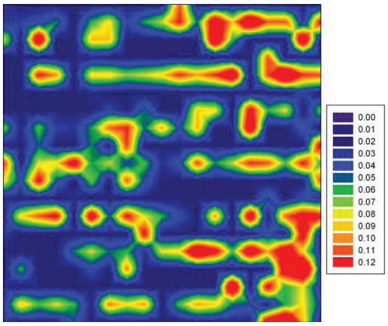

Fig. 2. Chemical image of C=O vibrational intensities related to the polyester concentration of a degraded MPL (reduced contrast).

Enzymatic fuel cell based on carbon nanostructured electrodes

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One-compartment biofuel cells are considered as an attractive power sources and they are in high demand for small biomimetic-based medical devices [1].

This kind of cells needs very active and tolerant catalysts which are highly-important for mixed-reactant system applications. Therefore, Buckypapers (BPs) were fabricated from commercially available carbon nanotubes (CNTs) and decorated with redox enzymes [1-4]. BP is mesoporous, highly conductive, flexible and mechanically stable material [2]. A high enzyme molecules loading on BP can be achieved due to its large mesoporous surface area which enhances also the utilization and electroactive surface area (*i.e.* coverage effect).

The enzymatic cathodes based on bilirubin oxidase or laccase [4] decorated-BP electrodes showed significant enhancements of bioelectrocatalytic performance with direct electron transfer for molecular dioxygen reduction reaction [3,4].

Using such three-dimensional electrodes based on BP or redox hydrogel matrix can solve the problems associated with the use of traditional two-dimensional electrodes. The performance of the cells was studied depending on the operation conditions. The highest power output of 26 μW cm^{-2} at + 0.20 V was achieved in O_2-saturated solution (pH 7.2 at 37°C) with a physiological glucose concentration of 5 mM. Moreover, in contrast to the literature, our bioelectrochemical system seems to be more effective and reproducible in O_2-saturated phosphate buffer solution than air [5].

Furthermore in this contribution, our progress on synthesizing novel carbon nanostructures by inductively coupled radio frequency (RF) plasma enhanced chemical vapour deposition (PECVD) will be presented as well. The resulting vertically-aligned carbon nanostructures (CNs) of 2D carbon nanowalls (Fig. 1a) and 1D nanofibers (Fig. 1b) can be controlled and grown on different surfaces. These nanostructures can accelerate the bioelectrocatalytic reactions by facilitating the mass transport and thus the rapid diffusional fluxes of reactants and products to internal surfaces.

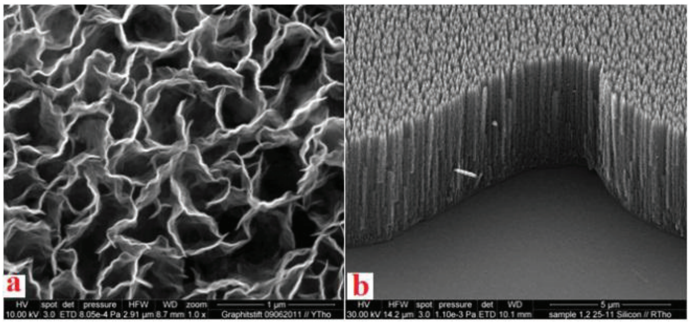

Fig. 1. SEM images of different vertically-aligned carbon nanostructures: (a) carbon nanowalls, (b) carbon nanofibers (scale bar 1 μm).

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Amperometric detection of proteins using biologically modified quasi-spherical gold nanoparticles

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In this poster, we demonstrate a novel nanobio hybrid sandwich assay platform based on the combined use of aptamer coated quasi-spherical gold nanoparticles (d = ~50 nm) and a surface-site selective enzyme reaction for the ultrasensitive detection of proteins. Immunoglobulin E (IgE) was used as a model target protein which possesses two different epitopes for separate ligands (*i.e.,* IgE specific aptamer and anti-IgE) providing an easy configuration of surface sandwich assay platform. IgE was detected *via* the first specific binding of IgE onto IgE-aptamer-nanoparticle conjugate modified gold electrodes followed by the specific adsorption of alkaline phosphatase (ALP) conjugated anti-IgE. The surface complex of NPs-IgE-aptamer/IgE/anti-IgE-ALP on gold electrodes were then reacted with the substrate 4-aminophenylphosphate (APP) resulting in the oxidative current changes as a function of the IgE concentration. The effect of the quasi-spherical gold nanoparticle on the protein sensing signals was also demonstrated by comparing the anodic current signal changes associated with the surface ALP oxidation of APP with a gold electrode upon which for the IgE aptamer was directly immobilized.

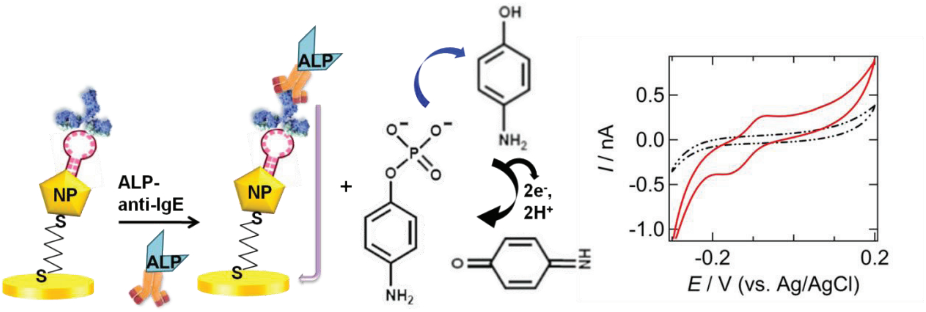

Fig. 1. (Left) Schematics showing nanobio hybrid electrochemical immunoassays for IgE detection. (Right) A representative cyclic voltammogram for 20 fM IgE detection using an IgE specific aptamer-nanoparticle conjugate modified gold electrode with anti-IgE-ALP and APP.

Flow induced dispersion analysis: A new approach for instant ELISA

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Rapid quantification of complex protein based biomarkers from small amounts of sample is a serious limitation in decentralized (point-of-care) molecular theranostics. In this project we develop a new approach based on Flow Induced Dispersion Analysis (FIDA). This methodology is based on the fact that large molecules diffuse slowly and small molecules diffuse comparatively faster. When a molecule interacts with a ligand its apparent diffusivity becomes that of the complex. The apparent diffusivity is thus dependent on the fraction of complexed and non-complexed analyte which in turn is given by the non-covalent analyte-ligand affinity constant as demonstrated recently for small molecules [1]. We have extended the system to include fluorescently marked BSA (BSAfc) and an antibody against BSA (IgG) as well as fluorescein interacting with Human Serum Albumin (HSA). In Fig. 1 is shown a peak corresponding to fluorescein from which the peak variance is obtained by fitting the raw data to a Gaussian peak shape. A non-covalent affinity constant may be obtained by fitting a binding curve (purple curve in Fig. 2) to the appropriate binding model. It may also be used to construct a standard curve for quantifying HSA in human plasma samples; in this application fluorescein is serving as an indicator molecule.

A simple membrane filtration has proved to be sufficient sample pretreatment for applying FIDA on human plasma samples. The results indicate that the FIDA methodology is a viable option for decentralized instant ELISA tests.

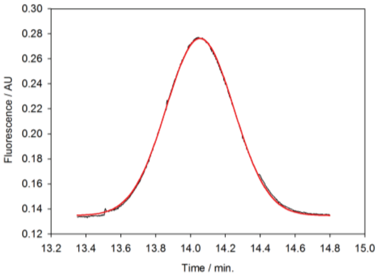

Fig. 1. Fluorescent signal of 10 nl 50 nM fluorescein in 30% Human Plasma / 67 mM phosphate buffer pH 7.4. Capillary length 65.3 cm, pressure 50 mbar. Red curve is fit to Gaussian peak shape.

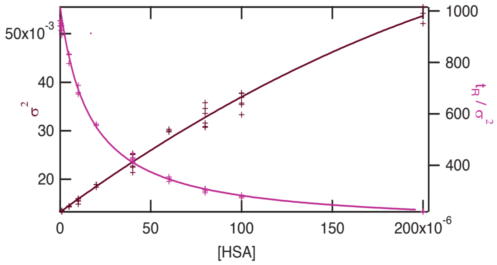

Fig. 2. Peak variance σ^2 of fluorescein obtained from Gaussian fit versus HSA concentration (black curve) for quantifying HSA in unknown human plasma samples. Peak appearance time t_R of fluorescein divided by σ^2 for assessing non-covalent affinity constant between fluorescein and HSA (purple curve).

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In-situ characterization of deactivation behaviour of Pd in an electro-oxidation of formic acid

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Pd is the most attractive anode catalyst in an electrocatalytic oxidation of formic acid (HCOOH). In spite of its superior activity to Pt-based catalysts Pd still has not been regarded as an anode catalyst in direct formic acid fuel cells (DFAFCs) in terms of its fast deactivation. Although much effort has been given to solve this problem, deactivation mechanism is still unclear. In this study, lost activity of Pd anode was restored by applying cathodic bias potentials. The effects of consecutive cathodic bias on Pd and other cell components also evaluated and this approach seems to be a fast and corrosion-free reactivating way for long-term operation of DFAFCs with high performances. In addition surface and structural changes of Pd anode in active and passive states were examined by *in-situ* characterization of XANES and EXAFS which can provide experimental observations to elucidate the origin of deactivation mechanism of Pd in an electro-oxidation of HCOOH.

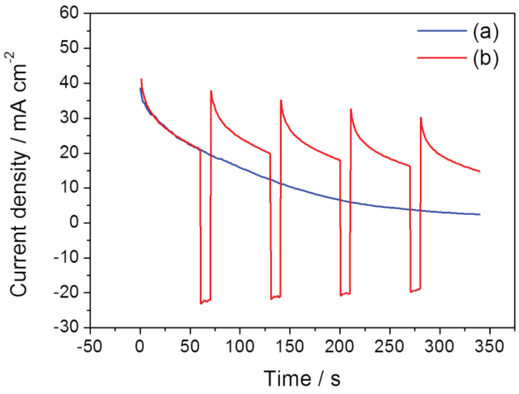

Fig. 1. Current density profile of Pd anode applying (a) constant oxidation potential of +0.3 V and (b) pulsed potential method (+0.3 V for 60 s, -0.4 V for 10 s) in 2 M HCOOH and 0.5 M $HClO_4$.

Pyrolytic carbon infiltrated nanoporous alumina layer reducing contact resistance at the interface between aluminum current collector and active carbon material

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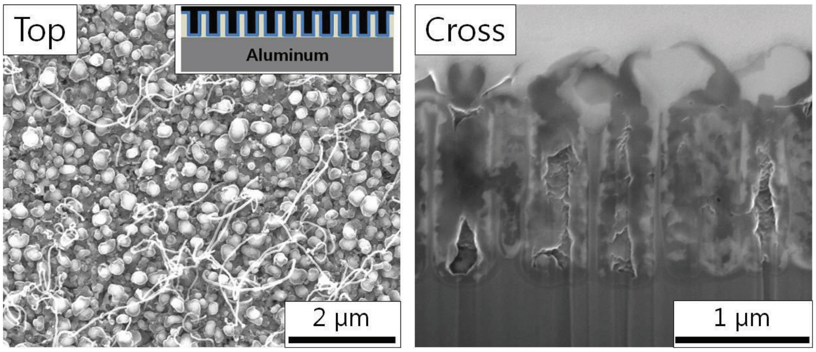
We fabricated a highly conductive pyrolytic carbon layer that penetrates into nanoporous alumina channels and that strongly adheres to an aluminum (Al) current collector in order to reduce the contact resistance at the interface between a carbon active material and an Al current collector. The fabrication method includes the following processes: (i) Al anodization, (ii) alumina etching, (iii) nickel seed layer deposition on the alumina surface, and (iv) chemical vapor deposition of pyrolytic carbon grown by the catalytic nickel layer. From SEM and EDX analyses, we confirmed that the pyrolytic carbon could be uniformly placed into an alumina nanoporous template on the Al substrate. Based on measurements of the transverse resistance and electrochemical capacitor tests, the fabricated composite layer of pyrolytic carbon and nanoporous alumina significantly reduced contact resistance of Al/carbon interface due to the highly conductive pyrolytic carbon formed through the nano-porous alumina on the Al surface. Therefore the developed composite layer of pyrolytic carbon and porous alumina demonstrated a potential as an intermediate layer that is able to improve the power performance of electrochemical capacitors.



Charge-transfer loss factors of dye-sensitized solar cells

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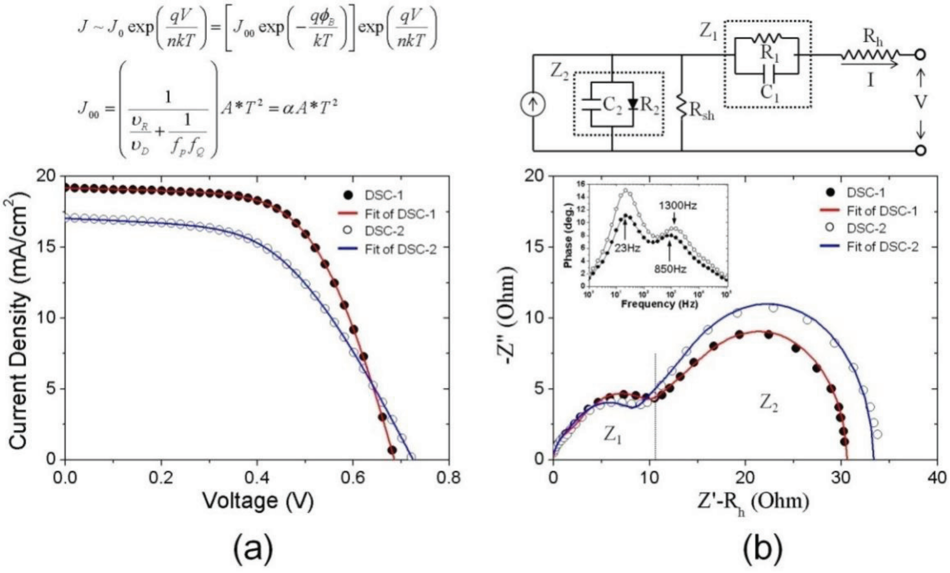
Charge-transfer loss factors of dye-sensitized solar cells (DSCs) were studied by a modified junction diode model and electrochemical impedance spectroscopy (EIS). In the modified junction diode model, the ideal barrier height (0.9 eV) condition of DSCs gives the reverse saturation current density on the order of ~10^{-6} mA/cm^2 at least. When the characteristics of DSCs are deviated from the ideal conditions, the subsidiary charge-transfer loss factor can be quantified by thermionic-emission diffusion, which represents the recombination of oxidized redox with charge-carriers tunneling through the TiO_2 barrier quantum mechanically by means of thermionic-emission diffusion. This charge-transport process is in good agreement with the result obtained from EIS. The real barrier height, converted to the open-circuit voltage is deterministic in overall device performance by the total charge-transfer loss factors.



$$J \sim J_0 \exp\left(\frac{qV}{nkT}\right) = \left[J_{00}\exp\left(-\frac{q\phi_B}{kT}\right)\right]\exp\left(\frac{qV}{nkT}\right)$$

$$J_{00} = \left(\frac{1}{\frac{\upsilon_R}{\upsilon_D}+\frac{1}{f_p f_Q}}\right) A^*T^2 = \alpha A^*T^2$$

Fig. 1. Current-voltage curves and their fitting (a), and Nyquist plots and their fitting (b) of DSCs. The inset in Fig. 1(b) shows the bode plots related to the charge-transfer loss factors.

Capacitance behavior of supercapacitor electrodes of heat-treated single-wall carbon nanohorns

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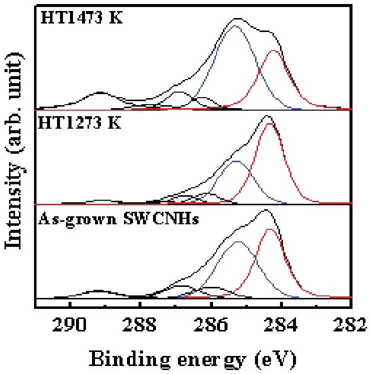
Single-wall carbon nanohorn (SWCNH) is composed of graphene sheet that forms tubular shape with a conical cap, and several thousand of the SWCNHs form stable spherical bundle structure whose diameter is 80 ~ 100 nm. The SWCNHs have a unique chemical structure with sp^2 and sp^3 bonding, coincidently. The space between adjacent walls of SWCNHs provides interstitial pores, functioning as attractive potential fields for various guest molecules.

The SWCNHs were heat-treated at 1273 K and 1473 K under high vacuum condition, respectively. The SWCNH samples before and after heat-treatment were characterized by FESEM, HRTEM, XPS, Raman spectroscopy, and N_2 adsorption at 77 K. Then, capacitance behaviors of the SWCNH supercapacitor electrodes were investigated.

The heat-treatment promoted the transformation between sp^2 and sp^3 bonding, leading to meaningful changes in the specific surface area of SWCNHs. Specific capacitances of SWCNH electrodes dramatically increased after heat-treatments.



Acknowledgements

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Nanoparticle-enhanced biosensing platforms for environmentally toxic agents

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In this poster, a simple and highly sensitive nanoparticle-enhanced biosensing platform for the detection of environmentally toxic reagents including Ni(II) ions and phenol is described. A surface sandwich platform requiring two different bioreceptors for a single target molecule was designed to provide a direct detection of target molecules. For the detection of Ni(II) ions two receptors known to strongly bind to Ni(II), polyhistidine and nitrilotriacetic acid were utilized; A NTA coated Au chip was exposed to selectively interact with Ni(II) ions in water samples followed by the adsorption of polyhistidine coated quasi-spherical gold nanoparticles The sequential adsorption process of forming the surface sandwich complex of NTA/Ni^{2+}/polyhistidine-gold nanoparticles was monitored a surface sensitive technique, surface plasmon resonance (SPR). Various interfering divalent cations such as Ca(II), Zn(II) were also investigated for the selectivity of the proposed sandwich method for Ni(II). Another example is to detect directly phenol by the use of anti-phenol from two different organs; An anti-phenol from mouse immobilized on a chemically modified Au chip surface was exposed to phenol followed by the adsorption of anti-phenol from rabbit coated Au nanoparticles. A significant change in SPR signal was observed when the surface complex of anti-phenol/phenol/anti-phenol-NPs. Both nanoparticle-enhanced biosensing methods for Ni(II) and phenol established a superb detection limit of 0.05 ppb concentration.

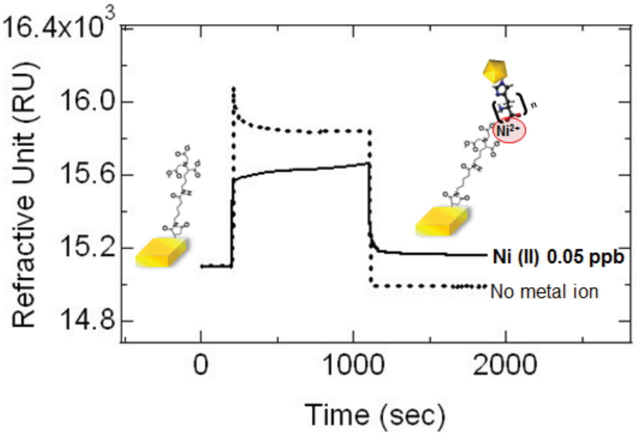

Fig. 1. A representative real time SPR signal changes upon the adsorption of polyhistidine coated NPs onto the surface complex of Ni(II)/NTA.

Enhancement of performance by graphene-supported sulfur cathode for Li-S battery

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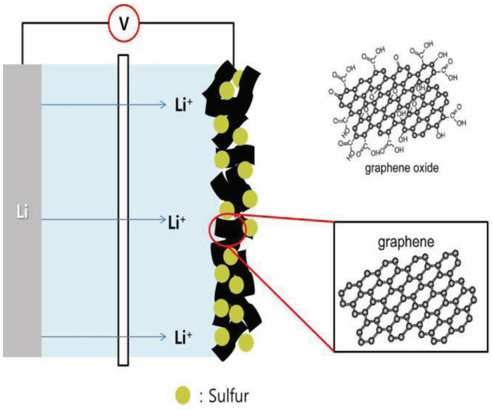
Because of fossil fuel depletion and environmental problems, demand of high-capacity energy storage system (ESS) becomes dramatically increased, especially for the electric vehicles (EVs). Up to now, ESS is based on the lithium ion batteries system and lithium ion battery technology has been developed, but they have a limitation of capacity from using the graphite carbon materials. Thus, new concept of batteries, which can store the energy more than the lithium ion batteries, should be needed.

To achieve developing a new high-capacity ESS, there are proper alternative, metal-air and lithium-sulfur batteries. In particular, sulfur element shows the high capacity (1,672 mAh g^{-1}) and theoretically 2~3 times higher than lithium-ion battery, as well as non-toxic and low cost materials. However, electrical conductive materials should be included in the cathode of lithium-sulfur batteries because sulfur and their compounds are electrical insulators.

In addition, many of researchers are using graphene materials because graphene has a 2-D sheet, high electrical conductivity and their high surface area. Recently, to make the graphene, there are two approaches, using chemical vapor deposition (CVD) method, and chemical reduction from graphene oxides. rGO shows a relatively lower electrical conductivity than the graphene synthesized by CVD because of defect sites, but their defect sites can be an active sites to enhancing charge and discharge reaction from the recent report [1].

In this work, rGO with high specific area was used as a sulfur support to enhance cycle performance for lithium-sulfur battery.



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Lab-scale continuous electrowinning system for refining highly concentrated sodium hydroxide solution

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The concentrated sodium hydroxide solution (50 wt.%) is required to produce silicon solar cell. However, the alkaline solution contains more than a ppm of iron and nickel impurities dissolved from enrichment facility. Therefore, additional process has to be considered in order to remove the impurities and improve the performance of solar cell. Though existing methods (*e.g.* ion exchange resin) can be applied to reduce the metal concentration, they need regeneration or cleaning process.

Electrowinning is an electrochemical technique to reduce metal ion in solution. This system doesn't need any regeneration process. Also, it can be easily designed and operated due to its simple structure. Furthermore, nickel and platinum electrodes have much longer lifetime than ion exchange resin.

The aim of this work is purification of highly concentrated alkaline solution. In this research, various conditions of electrowinning operation such as electrode material, temperature of electrolyte and current density are optimized. These factors change the result of metal reduction significantly. The optimized condition is applied to continuous electrowinning system, and economic value of the system is evaluated.

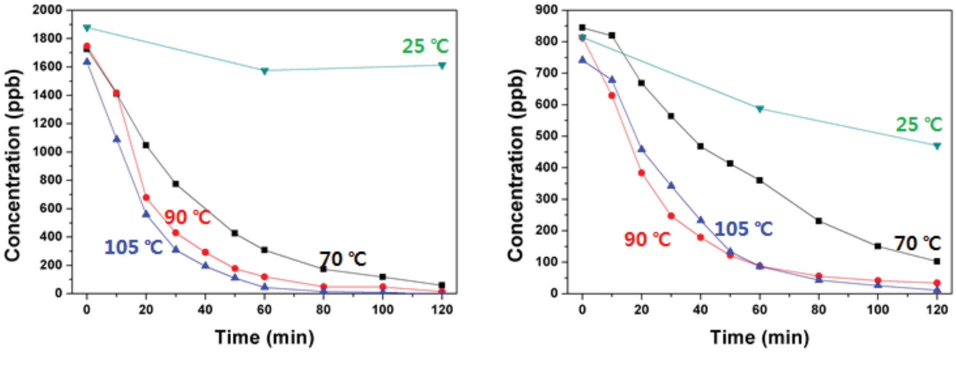

Fig. 1. Concentration change of iron (left) and nickel (right) by electrowinning with different temperature.

Enhanced electrochemical performance of WO_3 nanostructures prepared by photoelectrochemical anodization

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Semiconductive tungsten oxide has attracted great attention in electrode of photocatalytic water splitting device due to excellent electron transfer and corrosion resistance in acidic solution. Especially, compared to TiO_2, WO_3 has low bandgap energy (2.5 ~ 2.8 eV), showing high photoelectrochemical response in not only visible but UV light region.

In this study self-organized tungsten oxide (WO_3) nanostructure films are prepared by photoelectrochemical anodization in 10 wt.% K_2HPO_4/glycerol electrolyte. Thickness of WO_3 film prepared by photoelectrochemical anodization is around twice the thickness of that prepared by simple anodization without illumination. The increase in thickness is ascribed to the acceleration of dissolution at the edge by holes and the formation of a protective crystallized oxide film during illumination. The photocurrent value of film prepared by photoelectrochemical anodization is practically two times higher than for film prepared with general anodization. The photocurrent is 0.28 mA cm^{-2} at 1.5 V (*vs.* Ag/AgCl 3 M KCl) in 0.33 M H_3PO_4 under AM 1.5 illumination.

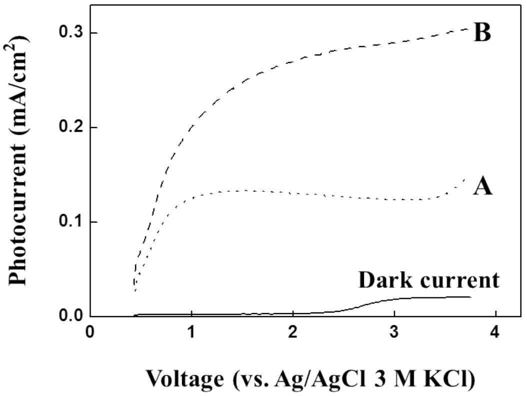

Fig. 1. Photocurrent response of WO_3 films prepared for 20 h by (A) general anodization and (B) photoelectrochemical anodization.

N-doped TiO_2 thin films from N-coordinated Ti precursors by MOCVD for photoelectrochemical applications

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N-doped titanium dioxide (TiO_2) thin films from N-coordinated Ti precursors were grown on Si(100) and indium tin oxide coated borosilicate glass (ITO/glass) substrates by metal organic chemical vapour deposition (MOCVD). Titanium amide-gaunidinate complex, $[Ti(NMe_2)_3(guan)]$ (guan = *N,N'*-diisopropyl-2-dimethylamidoguanidinato), has been developed to compensate the thermal instability of the parent alkylamide $[Ti(NMe_2)_4]$. Both these compounds were tested as single source precursors for N-doped TiO_2 by varying the deposition temperature. Structure and morphology of TiO_2 thin films on Si(100) substrate were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). For the determination of N content in the films, Rutherford back scattering (RBS), nuclear reaction analysis (NRA), and secondary ion mass spectrometry (SIMS) were performed. Optical and photoelectrochemical properties of TiO_2 thin films on ITO/glass substrate were also examined. N-doped TiO_2 film grown from $[Ti(NMe_2)_3(guan)]$ at 600°C exhibited the lowest optical absorption edge (2.95 eV) and the highest visible light photocurrent response. As compared to undoped TiO_2, it showed enhanced photocurrents under visible light irradiation, while in the UV-light the photoconversion efficiency decreased significantly.

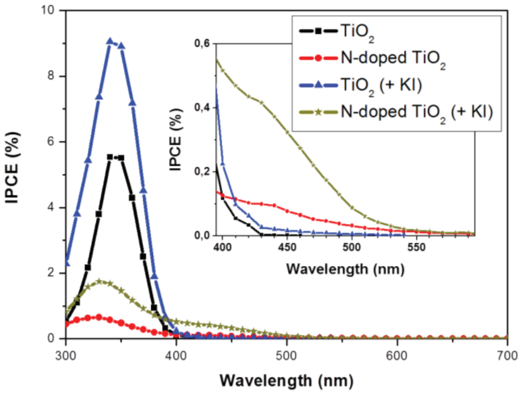

Fig. 1. Incident photon-to-current efficiency (IPCE) spectra recorded in Na_2SO_4 (0.1 M) electrolyte or Na_2SO_4 (0.1 M) + KI (0.1 M) at 0.5 V *vs.* Ag/AgCl for TiO_2 and N-doped TiO_2 thin films (inset : zoomed plots in the visible light region).

Electronic structure of chemisorbed oxygen on Pt(111) surface

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Pt is the most widely investigated catalyst for oxidation of NO_x (storage/reduction system) and CO (exhaust system), and for oxygen reduction and oxidation of H_2 and hydrocarbon (fuel cell). Consequently, oxidation-bonding process in Pt-based catalyst system is the most important physics of electrochemical reactions. However, detailed interaction and principal mechanism of chemisorbed oxygen bonding on the Pt surface remains poorly understood.

By using state-of-art angle resolved photoemission spectroscopy (ARPES), the electronic structures of chemisorbed oxygen on Pt(111) surface is investigated, unveiling the bonding interaction between chemisorbed atomic oxygen and Pt(111) surface. Density functional calculation (DFT) with the local density approximation (LDA) is utilized to explain the result of ARPES, pointing out the roles of sub-d band structures. It is found that d_{xz} and d_{yz} orbitals involve with small charge transfer while dz^2 orbital makes strong hybridization with oxygen atom.

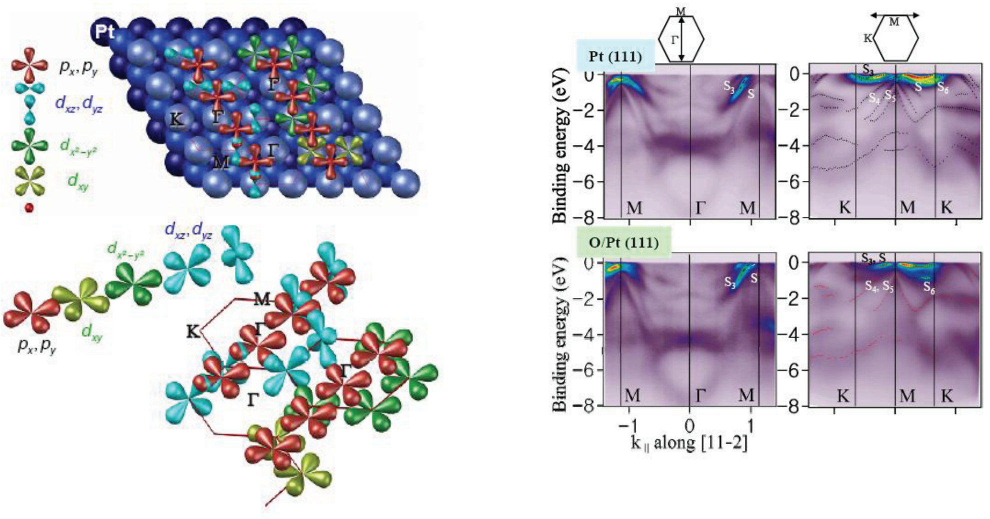

Fig. 1. Orbital configuration and surface electronic band structure.

Chromate anion transfer reaction across microhole-array liquid/gel interface for sensing applications

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In this poster, we demonstrate an amperometric Cr(VI) sensitive and selective sensor utilizing the transfer reaction of various anionic hexavalent chromium species at the polarized 66 microhole array interface between water and polyvinylchloride-2-nitrophenyloctylether (PVC-NPOE) gel phase. A hydrophobic organic supporting electrolyte, tetraoctylammoniumtetrakis(pentafluorophenyl)borate (TOATB), which extends a potential window range towards the more negative potential was synthesized and incorporated into the gel phase to voltammetrically characterize each hexachromic anion transfer behavior. The transfer behaviours of the three hexachromic anion species including $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ across the water/gel interface were investigated using cyclic voltammetric and differential pulse stripping voltammetry at different Cr(VI) concentrations and electrolyte pH ranges. In addition, a $HCrO_4^-$ selective sensor was developed based on the measurement of the current response associated with the assisted transfer reaction of $HCrO_4^-$ anion by the $HCrO_4^-$ selective ionophore, Aliquat 336 across the microhole array-water/organic gel interface. The current response was found to be linear as a function of Cr(VI) concentration range from 0.5 M to 100 M.

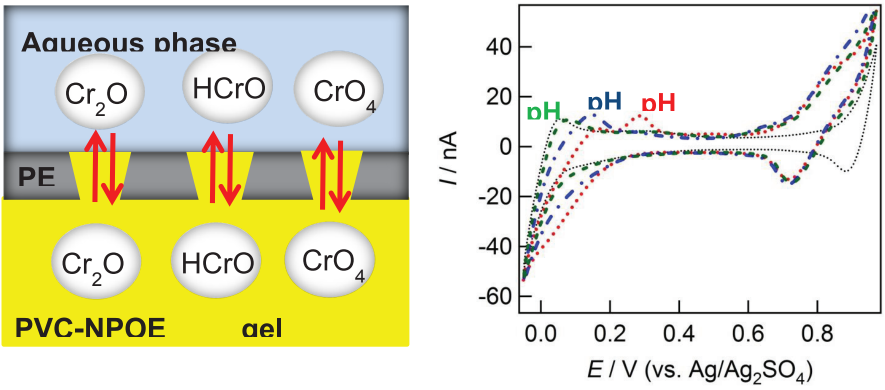

Fig. 1. (Right) A schematic showing the transfer reaction of different hexachromic anionic species including $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} ions. (Left) A series of cyclic voltammograms for the transfer of various hexachromic anionic species across the 66 microhole array aqueous/ PVC-NPOE gel interface at different pH conditions in the presence of 100 μM TMA^+ ions as an internal reference. Voltammograms were obtained at pH 10, pH 7 and pH 4 in the presence of 200 μM Cr(VI) with 10 mM Na_2SO_4 . Scan rate = 20 mV s^{-1}.

High efficient organic photovoltaics with interface modified 3-D ZnO nanoripples

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A simple method for spontaneous formation of nanoripples on ZnO thin films was developed, and these nanostructured ZnO films were used as hole-blocking layer in inverted organic solar cells. Moreover, the size (height) of nanoripples on ZnO surface could be controlled in the range of several tens of nanometers. Among various ZnO films, surface structures with ~70 nm-high nanoripples resulted in the best photovoltaic performance of the organic solar cell. In addition, ZnO and TiO_2 ultra-thin films were deposited on 3-D ZnO surfaces using atomic layer deposition. Ultrathin ZnO and/or TiO_2 layers with a mean thickness of less than 5 nm could enhance photovoltaic performance of the inverted organic solar cell; in particular, short-circuit current (J_{sc}) and power conversion efficiency (PCE) was increased by deposition of TiO_2 layers. A higher thickness of additional oxide thin film resulted in reduced photovoltaic performance. Evidence is provided that recombination of electrons and holes on the surface of ZnO can be quenched by ultra-thin layer. And also, this additional process turned out to increase stability of the IOPV significantly without additional encapsulation process.

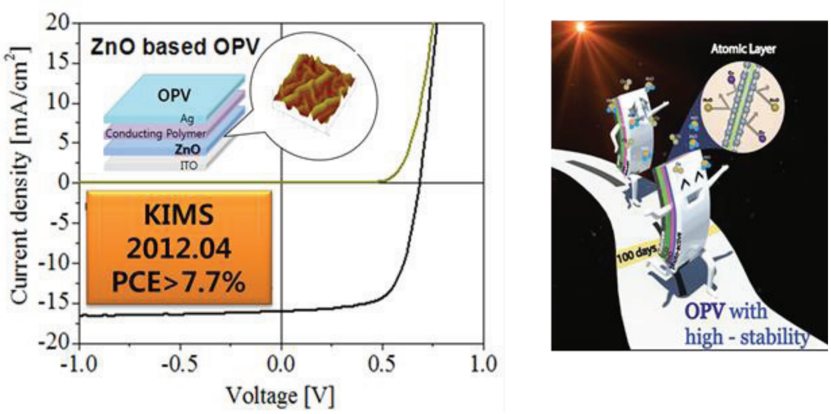

Fig. 1. OPV with high-efficiency & high-stability.

Non-linear phenomena during the electro-oxidation of borohydride on platinum

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Borohydride is being largely studied as an alternative fuel to be used in low temperature fuel cells [1]. Most of these studies are focused on mechanistic and applied aspects. The present work illustrates our recent findings on the nonlinear kinetics present during the electro-oxidation of borohydride on platinum and in alkaline media. The first aspect to be discussed concerns the autocatalysis observed during the open circuit interaction between borohydride and an oxidized platinum surface [2]. Overall, the autocatalytic surface reduction took place in very short times, around 0.5 s, which is about two-three orders of magnitudes faster than that for methanol [3] and hydrogen [4]. Furthermore, the chemical reduction was found to proceed *via* a two-step transient, which in turn, seems to be connected to the two humps observed in the backward sweep in the cyclic voltammogram under comparable conditions. Finally, spontaneous current oscillations have been also found in this system. Fig. 1 illustrates the occurrence of such oscillations under potentiostatic control in the presence of an external resistance, and during the backward sweep. Altogether, our results illustrate the complex nature of the electro-oxidation of borohydride on platinum and call for further experimental and numerical investigation on this important reaction.

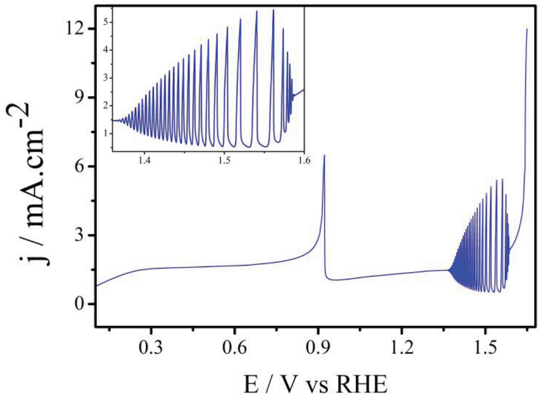

Fig. 1. Current oscillations during the electro-oxidation of borohydride 5 mM on platinum. Electrolyte: NaOH M; External Resistance: 500 Ω ; Sweep Rate: 10 mVs^{-1}; T = 25±1°C.

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Turing patterns in a cyclic array of four coupled continuous stirred tank reactors and their usage as parallel logic gates

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We focus on finding proper parameters for occurrence of spatially non-uniform (Turing) patterns in the model of four diffusively coupled continuous stirred reactors in a cyclic array with equal transport rate coefficients of the activator and inhibitor. As an example, we chose a simple biochemical reaction - the core model of glycolysis proposed by Moran and Goldbeter [1]. There are two species in the model: ATP (activator) and ADP (inhibitor). The autocatalysis is due to the enzyme phosphofructokinase mediating the conversion of ATP into ADP. Negative feedback on the enzyme comes from the lower parts of the glycolysis reaction chain.

The system was analysed with the use of one-parametric and two-parametric numerical continuation. Parameters were set upon construction of a bifurcation diagram so that coexistence of multiple Turing patterns occurred, which enabled to use transitions between them as a means of creating parallel logic gates.

In order to propose logic gate technique with parallel computing, specific perturbation values were found. The resulting logic functions are complex combinations of a set of basic functions NOT, OR, NOR, AND, NAND, XOR, XNOR.

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Negatively and positively carved silicon *via* laser interference lithography for use in lithium-ion batteries

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We demonstrated Si pillar- and well-arrays (SPA and SWA) as tailored electrode materials, in which the well-ordered and periodic morphologies are formed on the Si electrodes thin-film *via* laser interference lithography (LIL) with a successive dry etch process. For asystematic study, the fabricated Si nanopattern arrays have been controlled in terms of the pattern size, etch depth, and periodicity. Two different patterns of negatively or positively carved Si electrodes exhibited highly improved cycle performance as a consequence of the enlarged surface area and the nanoscale pattern effects. The improved electrochemical features of carved Si electrodes could be attributed to the low internal resistance, facilitated charge transport, and facile stress relaxation by engraving Si into periodic nanopatterns. The SWA showed the highest energy density, rate capability, and cycling retention among the prepared Si electrodes. Consequently, the carved Si electrode prepared through a LIL exhibit a superior Li storage capacity, high rate capability, and long cycling properties, indicating their potential application as anode materials in high-energy density Li-ion battery.

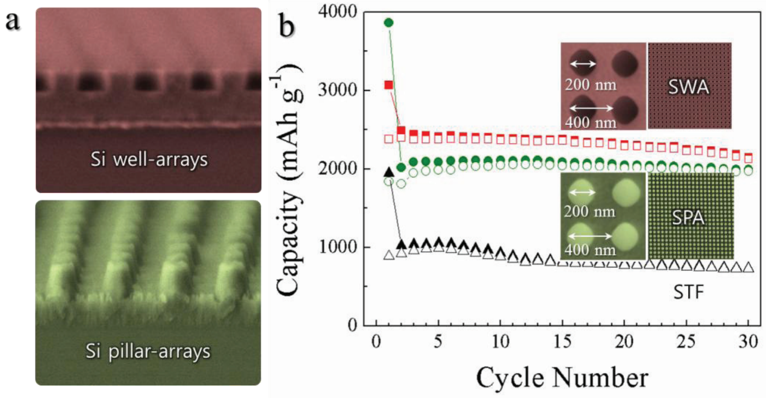

Fig. 1. (a) Images of the positively and negatively carve Si arrays for Li-ion storage. (b) Capacity *vs.* cycle number of the prepared Si electrodes. The inset figures present magnified images of the plane-view of the prepared Si electrodes.

Shape versus electrochemical activity of gold nanoparticles

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Physical and chemical properties of nanoscale gold materials depend mainly on their size, structure and shape due to the quantum confinement effect. Thereby, these last years, various applications in catalysis, electronics, sensors, optical devices and biotechnology have emerged. Furthermore, gold nanomaterials are suggested as electrodes for oxidizing glucose [1] through the development of an alternative detection system. Studying chemical reactions on a well-defined structure provides fundamental data and guidelines on the surface reactivity necessary to understand and design novel catalytic materials. Shape and size controlled gold nanoparticles present interesting surface structure which are worthy of investigate.

From Slot *et al.* [2] and seed-mediated growth approaches [3,4], three different shapes of gold nanoparticles were synthesized. The TEM images obtained show spherical nanoparticles as well as nanorods and nanocubes with a high yield. Electrochemical characterizations of these nanoparticles are evaluated through underpotential deposition (UPD) of lead [5]. The voltammetric profiles have shown that spherical nanoparticles are single crystals with (111) and (110) as dominant faces, whereas gold nanorods resulted in the seed-mediated synthesis method present rounded lateral facets with (110) and (111) reflection planes on the long side, and (100) and (111) at the end faces. As electrochemical results, gold nanorods and spherical particles in alkaline solution have shown high catalytic activity towards glucose oxidation. The reaction process begins at 0.2 V *vs*. RHE for the nanorods and at 0.3 V *vs*. RHE for spherical nanoparticles.

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Kinetic instabilities and the Stern-Brocot tree in electrochemical systems

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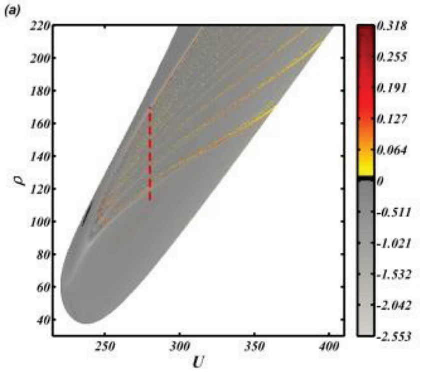
The understanding of complex phenomena manifested by nature has provided an excellent exercise to the human intellect. Phenomena such as spatiotemporal patterns on the fur of animals, biological rhythms and social behavior can be modeled by ordinary differential equations. Examples of complex behavior are rather abundant in chemical and electrochemical systems [1,2]. In this work we discuss the dynamic behavior of a dimensionless electrochemical model formed by a set of three nonlinear differential equations proposed by Krischer [3] as shown below:

$$\varepsilon\frac{d\phi}{dt}=-k(\phi)c(1-\theta)+\frac{U-\phi}{\rho},\quad \mu\frac{dc}{dt}=-k(\phi)c(1-\theta)+1-c \quad\text{and}\quad \frac{d\theta}{dt}=\theta_0(\phi)-\theta .$$

For this set of equations ϕ describe the double layer potential, c the concentration of electroactive species and θ the surface coverage of an inhibiting species. The control parameters are ε the time-scale for the evolution of the electrode potential, μ the time-scale of the temporal evolution of the concentration, U the applied voltage, and ρ the total resistance. The kinetic constants $k(\phi)$ and $\theta_0(\phi)$ represent rate and coverage respectively. The result for the system under study is shown in Fig. 1(a) and 1(b) that displays the Lyapunov and period diagrams.

Observe the formation of ridges separated by intervals of chaotic lines. Each region between the chaotic lines there is a well defined periodic domain, which can be described by Stern-Brocot numerical sequence. This behavior becomes clearer in Fig. 1(c), where the existence of two numerical sequences corresponding to the two arms in the Stern-Brocot tree emerges.



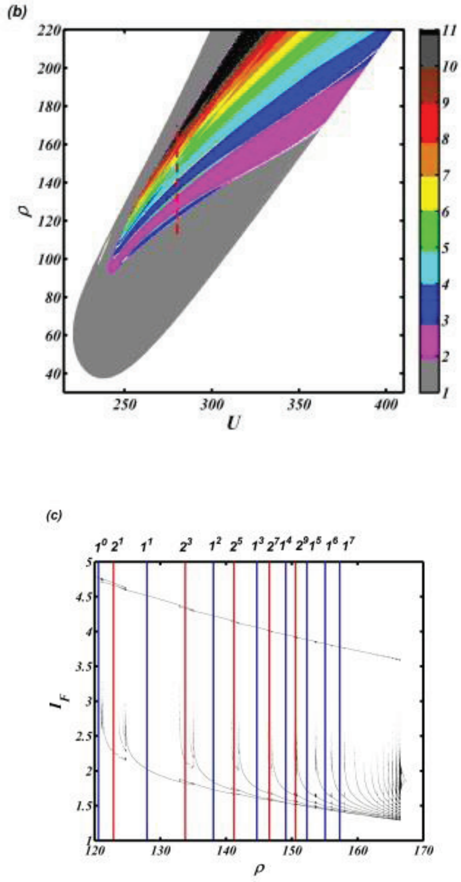


Fig. 1. (a) Lyapunov's diagram, where the colormap indicate the regions with positive (red color scale), negative (gray color scale), and zero (black color) exponents. (b) Period diagram with the colormap indicating the morphologic period of oscillations in bifurcation. The region of chaos is not represented in the Fig. (b) and the region with periods above of 10 is represented by black color. (c) Orbital diagram concerning the dashed line in red, Fig. (a) and (b). The blue and red lines represent two different types of distinct sequences calling of A and B.

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High capacity porous germanium (PGe) as lithium-ion battery anode by electrochemical etching

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Lithium-ion and lithium-air batteries are promising technologies that can offer high energy capacity and longer cycle life for various applications. In order to improve the performance of lithium batteries, the development of higher capacity anode material using practical and scalable methods is necessary to replace the widely used low capacity carbon-based materials. Although germanium has a lower theoretical capacity than silicon, it has far greater lithium ion diffusivity and lower volume change than silicon during cycling. Here, we present the single-step synthesis of porous germanium (PGe) fabricated using anodic electrochemical etching and its electrochemical activity as Li-ion battery anode. Different porous structures of Ge were formed *via* HF electrolyte concentration, current density and etching time variations. The structure and morphology were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), X-ray diffraction (XRD) and electrochemical measurements were taken. Cyclic voltammetry measurements and galvanostatic discharge-charge half-cell tests show that porous germanium provides excellent capacity and cycling stability. The use of PGe drastically improves the cyclability compared to the bare Ge wafer due to the better accommodation of volume changes during cycling.

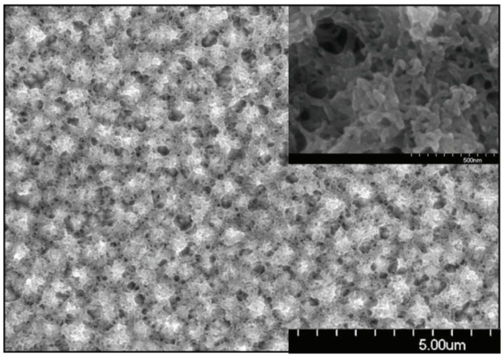

Fig. 1. Scanning electron micrographs of the electrochemically etched PGe (inset image shows the network of mesoporous structures for the same sample at higher magnification).

A comparison of spatiotemporal instabilities of formic acid and methanol on poly Pt at low conductivities

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The nonlinear dynamics of the electrooxidation of methanol and formic acid on a polycrystalline platinum ring under low electrolytes conductivity are investigated in acidic media at room temperature (295 K). For various electrolyte conductivities, the spatiotemporal distribution of the double layer potential was observed using potential microprobes and setting the reference and working electrodes at a close distance from each other. In the case of formic acid, which presents bistability and show a higher catalytic behavior under presence of bismuth ad-atoms [1], the low electrolyte's conductivity influences the apparition of local patterns and the breaking of the continuity of travelling patterns without suppressing the oscillations at a wide range of the anodic potential, justified by the low coupling through the surface of the electrode. In the case of the methanol electrooxidation, although the presence of oscillations under the effect of external resistance has been previously reported [2], a low electrolyte's conductivity not necessarily implies an oscillatory behavior under potentiostatic conditions over the anodic range.

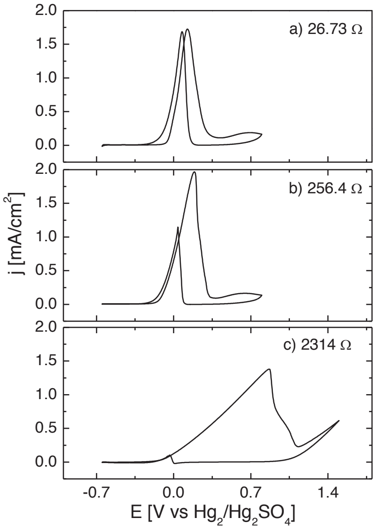

Fig. 1. Cyclic voltammogram for the electrooxidation of 0.03 M CH_3OH in a) 0.1 M, b) 0.01 M, and c) 0.001 M $HClO_4$ on platinum. Scan rate kept at 10 mV s^{-1}.

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Properties of aliphatic acetate as 3rd cosolvents in electrolytes for Li-ion cells with improved low-temperature performance

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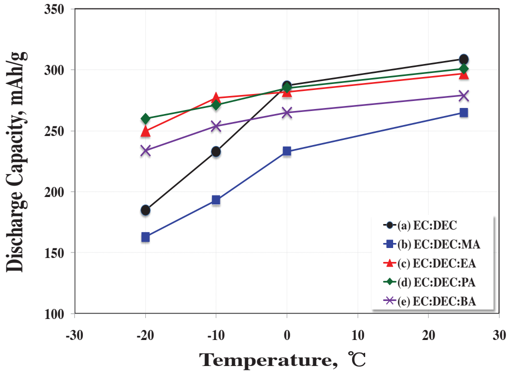
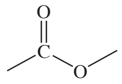
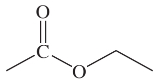
In an attempt to improve the electrolyte for Li-ion cell useful in a wide operation temperature, we have investigated some ternary electrolyte containing aliphatic acetate (methyl acetate (MA), ethyl acetate (EA), propyl acetate (PA), or butyl acetate (BA)) as 3rd cosolvents to improve the discharge capacity and cycle life at low-temperature. We have studied performance of Li-ion cells containing these electrolytes at various temperatures by using chronopotentiometry, cyclic voltammetry, and impedance spectroscopy. Two electrolyte systems, EC:DEC:EA and EC:DEC:PA, showed the very interesting overall performance including initial performance at -20°C , discharge capacity and cycle life at room temperature.

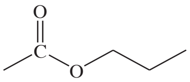




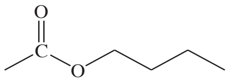
Methyl Acetate (MA)
m.p.: -98 ℃
b.p.: 58 ℃
η: 0.385 cP



Ethyl Acetate (EA)
m.p.: -84 ℃
b.p.: 77 ℃
η: 0.426 cP



Propyl Acetate (PA)
m.p.: -95 ℃
b.p.: 102 ℃
η: 0.551 cP



Butyl Acetate (BA)
m.p.: -74 ℃
b.p.: 126 ℃
η: 0.73 cP

Fabrication of length-controlled ZnO nanostructures by anodization of sputtered Zn for dye-sensitized solar cells

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Dye-sensitized solar cells (DSSCs) are a photoelectrochemical system consisted of two electrodes, organic or metallorganic-complex dyes and liquid electrolytes that generally contain I^-/I_3^- redox couples. The photosensitized anode is constructed with the N-type oxide semiconductor, mainly TiO_2, and dye molecules. Recently, ZnO has been attracted attentions as alternative to TiO_2 due to an energy band structure and physical properties similar to those of TiO_2. In addition, ZnO has high electronic mobility and easy crystallization. Moreover, ZnO with various nanostructures can be produced through diverse methods such as hydrothermal method, sol-gel synthesis, chemical bath deposition and electrochemical deposition.

In this study, we focused on fabrication of photosensitized electrode using nanostructured ZnO. ZnO nanowires were grown on a Zn foil by anodization in $KHCO_3$ aqueous solution. Subsequently, they were used for electrodes of DSSC. We found that the cell did not operate properly because of rapid reduction reaction between Zn metal underneath the ZnO nanowries and iodine redox couples. Therefore, anodization of a thickness-controlled Zn film, which was deposited directly onto FTO glass by sputtering, was carried out to prevent remaining Zn from the reduction reaction. The structures were immersed in N719 dye and assembled with iodine based electrolyte. DSSC performance was measured by using a solar simulator under AM 1.5 simulated sunlight at 100 mW/cm^2.

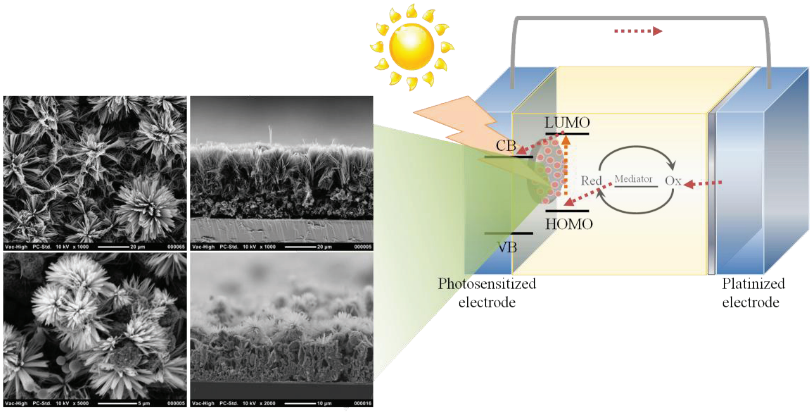

Fig. 1. Schematic diagram of DSSCs and SEM images of ZnO nanowires on FTO glass substrate.

Oscillatory electro-oxidation of formic acid on intermetallic Pt_3Sn surfaces

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The electro-oxidation of formic acid on platinum is one of the most well-studied electrochemical systems under oscillatory regime [1,2]. It is known that the presence of surface modifiers strongly impacts the kinetics of the electro-oxidation itself but also the oscillatory dynamics [3]. Herein we present results on the oscillatory electro-oxidation of formic acid on intermetallic Pt_3Sn [4]. Fig. 1 exemplifies the oscillatory dynamics observed in this system at two different normalized applied currents [5], and oscillations on Pt are also given for reference. Remarkable differences are observed in the oscillation's morphology, period and amplitude. Moreover, the stability of the oscillatory state is strongly influenced by the presence of tin, and much longer (in the range of about 6 hours) oscillations were found for the Pt_3Sn surface. This is a previously unseen effect and might be due to the low potential at which oxygenated species are formed on tin, which prevents the early collision of the limit cycle with the oxygen evolution branch, as commonly observed on platinum.

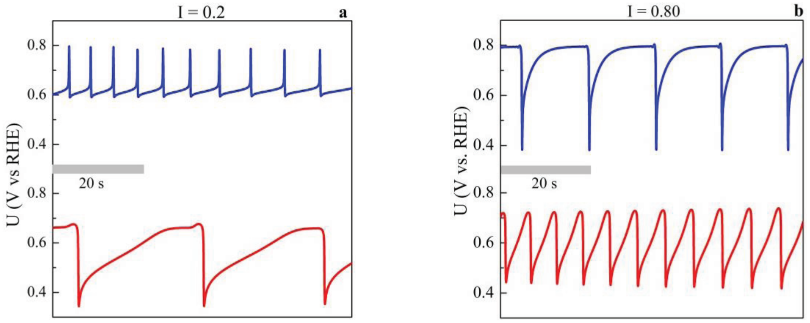

Fig. 1. Time-series registered during the electro-oxidation of by formic acid on Pt (blue) and on Pt_3Sn (red) with normalized applied current [5] (a) $I_N = 0.20$, and (b) $I_N = 0.80$ (b). Electrolyte: aqueous solution with $[H_2SO_4] = 0.1$ mol L^{-1} and $[HCOOH] = 0.5$ mol L^{-1}.

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Co complexes catalyst onto gently reduced graphene surface for oxygen evolution reaction

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Oxygen evolution and reduction reaction (OER/ORR) is a key reaction for unitized regenerative fuel cell (URFC) and energy storage technologies and its most important issue is an efficiency of the catalysts [1]. Regarding to the reason, tremendous studies have focused on the development of catalyst on its catalytic reactions, especially, to achieve OER/ORR bi-functional catalytic activity is considered as benefit and challenge. Regarding to OER/ORR catalyst, Co is the most common among non-noble metals, which has been studied over a decade aside Ni, Fe, Mn and Pb. Up to now, there are number of researches employed solely Co to state its electrocatalytic activity, but, the seldom was done on any existing supportive materials.

Graphene is holding a variety of attractive and unique properties, due to its dense honeycomb crystal structure. Therefore, graphene is expected to provide promising nanoscale building blocks for innovational composition such as support material for various nanoparticles [2].

This study presents an approach to deposit two different forms of cobalt nanoparticles, cobalt oxalate (CoC_2O_4) and organo-cobalt [$C_2Co_2(CO)_6$] [3] which are dissolute in water-based solution. Herein, graphene was obtained from gently reduced graphene oxide by ammonia solution with intermediate heat treatment. Both cobalt complexes, which have alkali preference, will be combined in graphene water-based solution to obtain CoC_2O_4 and [$C_2Co_2(CO)_6$] graphene-based composite. The alteration on graphene surface morphology will be characterized and determined, so as their electrocatalytic performance in OER and ORR. This approach is anticipated to provide an optional application of graphene-based materials to further practice as catalyst, in particular.

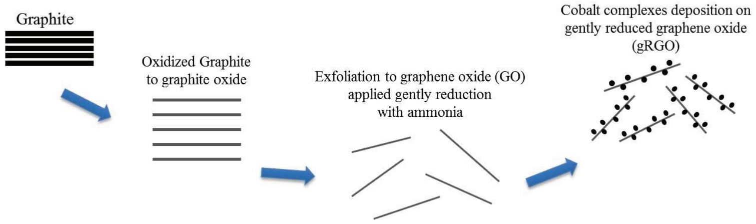

Fig. 1. Scheme showing the route of cobalt complexes deposition on graphene sheet.

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Manganese-iron non-precious metal catalysts for oxygen reduction reaction (ORR) in alkaline and acid

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Fuel cells have been recognized as clean energy-converting devices due to their high efficiency and low emissions. However, two major technical gaps limit their commercialization: cost and reliability. Currently, platinum (Pt)-based catalysts and their corresponding cathode catalyst layers are among the major causes of limited performance and high cost for proton exchange membrane (PEM) fuel cells, although these are the most promising and practical fuel cell catalysts [1]. Some approaches to cost reduction and performance improvement have been put forward and researched for many years. However, there has been no real breakthrough yet [2].

Two approaches to reducing catalyst cost are currently being actively pursued: one is to reduce Pt loading, and the other is to explore non-noble catalysts. In the short-term, catalysts containing low amounts of Pt are the priority and are also practical, but in the long term, non-noble metal catalysts would be the better solution.

Manganese-iron catalysts derived from polyaniline (PANI), Mn^{II} and Fe^{III} chloride supported on commercial carbon Ketjenblack EC 300J and 600J synthesis by high temperature treatment were characterized for reduction of oxygen using RDE, both in acid and alkaline electrolytes.

Rotating disk electrode (RDE) measurements was used to evaluate the catalyst performance. Additionally temperature programme desorption (TPD) and thermogravimetry analysis (TGA) were also applied for active site characterization.

Investigations were conducted with the aim of achieving better activity and stability of the synthesized catalysts. The results of this study show that for Mn-based catalyst an increase in Mn-content causes a tremendous increase in catalyst performance, suggesting that metal has a dominant part in the active sites formation. Although manganese-based catalysts showed an acceptable activity but Mn-Fe catalysts showed more positive onset potential.

The catalysts were employed to coat an electrode surface in order to optimize their catalyzed ORR activity. The formed catalyst layers containing different catalyst loads of 300, 500, 600, 800, and 1000 $\mu g\ cm^{-2}$ tested using RDE technique. It was found that by increasing the catalyst loading we can achieve a higher activity, then reached a saturation point with 1000 $\mu g\ cm^{-2}$, additionally it should be mentioned that film with 1000 $\mu g\ cm^{-2}$ is not stable, resulting in removal of catalyst from the electrode surface. Cyclic voltammetry (CV) showed a better activity in alkaline in comparison to benchmark Pt 20% and acceptable activity in acid.

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Nanoporous TiO_2/SiO_2 prepared by atomic layer deposition as adsorbents of methylene blue in aqueous solutions

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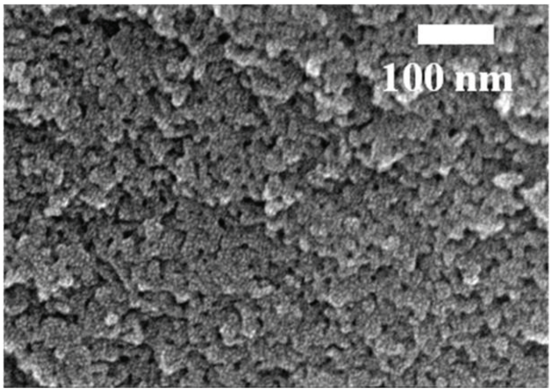
TiO_2 films supported by porous SiO_2 with high surface area were synthesized by atomic layer deposition (ALD). Porous structure of SiO_2 could be maintained even after deposition of TiO_2 using 500 ALD cycles (figure). All the TiO_2-covered SiO_2 samples showed comparable methylene blue (MB) adsorption abilities to that of bare ones. Moreover, MB adsorption capability of TiO_2/SiO_2 was almost fully recovered by simple re-annealing process, whereas MB adsorption capacity of bare SiO_2 was not fully recovered by the same treatment. FT-IR study demonstrated that thermal decomposition of adsorbed MB molecules was much facilitated in the presence of TiO_2 films, hence preventing deposition of surface-bound species created on the adsorbents surface during the thermal treatment process. Photocatalytic activity of TiO_2/SiO_2 samples was also investigated as a function of TiO_2 film thickness, and the result will be discussed.



Ultrathin TiO_2 films on ZnO electron-collecting layers of inverted organic solar cell

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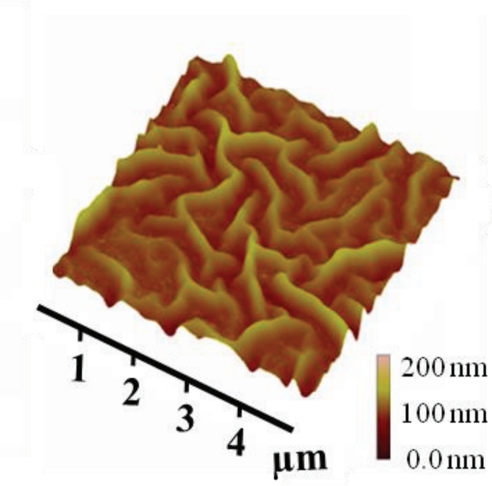
Nanostructured ZnO thin films (figure) were fabricated on Indium Tin Oxide (ITO) as hole-blocking and electron-collecting layers of inverted organic solar cells. In addition, TiO_2 thin films were deposited on ZnO surfaces using atomic layer deposition. Ultrathin TiO_2 layers with a mean thickness of less than 3 nm could enhance photovoltaic performance of the inverted organic solar cell; in particular, short-circuit current (J_{sc}) and power conversion efficiency (PCE) were increased by deposition of TiO_2 layers. A higher thickness of TiO_2 resulted in reduced photovoltaic performance. Studies on electronic structure using photoelectron spectroscopy showed that the TiO_2 layers should act as barrier for the electron-collection on ZnO. However, recombination of electrons and holes on the surface of ZnO can be quenched by TiO_2, resulting in an improved efficiency of the IOSCs. It is demonstrated that atomic layer deposition with a precise control of film thickness can be of potential application for fabrication of energy devices.



Analysis of sodium concentration in $CuInGaSe_2$ (CIGS) thin films using laser-induced breakdown spectroscopy (LIBS)

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$CuIn_{1-x}Ga_xSe_2$ (CIGS) solar cells are a great candidate of next-generation solar cells to replace the silicon solar cells due to many attractive characteristics such as high optical absorption coefficient, high conversion efficiency and low material cost. Recently CIGS solar cell with an active area of 0.5 cm^2 made by ZSW exhibits the highest efficiency over 20% using soda-lime glass (SLG) substrate. The effect of a SLG substrate in CIGS devices has been interpreted as being due to Na diffusion into the absorber layer during high temperature processing. Many recent CIGS researches highlight ways to improve the optoelectronic properties of CIGS absorber films and their dependence on the stoichiometry of absorber *via* various analysis techniques such as ICP-AES, XRF, and SIMS, etc. However, it is not still easy to find an accurate analysis technique possible to measure even small amount of Na included in CIGS film, which significantly influences on the grain growth and electrical properties of CIGS crystals.

Herein, we monitored carefully the Na content along with other elements in the SLG substrate and CIGS film fabricated on SLG using laser-induced breakdown spectroscopy (LIBS) in air to investigate the effect of Na on the formation of CIGS crystalline films. In addition, its structural properties and photovoltaic properties were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), incident photon-to-electron conversion efficiency (IPCE) and I-V measurement under the simulated illumination of 100 mW cm^{-2}.

Acknowledgements

This work was supported by the Core Technology Development Program for Next-generation Solar Cells of Research Institute for Solar and Sustainable Energies (RISE), GIST and partially by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-0028271).

Voltammetry in super critical CO_2 fluids

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Over the past 25 years a number of publications have emerged, exploring electrochemistry in supercritical CO_2 [1-4], with and without polar co-solvents. However, the publications are few, and extensive studies of the system with regards to the interplay of co-solvent, the enhancement of mass transport and the influence on diffusion coefficients and reaction kinetics have not been reported. In particular, investigations on the macro scale are highly scarce, owing to the low relative permittivity of $scCO_2$ and poor solvation of ionic species as electrolytes, thus resulting in high resistivity and ohmic drop in voltammetry.

Recently the synthesis of a highly lipophilic ionic liquid, that is soluble in $scCO_2$ and organic co-solvent, has permitted macroscale voltammetric studies to be performed in the supercritical fluid with little ohmic distortion. Herein we present voltammetric investigations of well-known redox couples and electrochemical systems in the supercritical medium, focusing on the interplay of co-solvent and the apparent steady-state voltammetry observed at moderate scan rates.

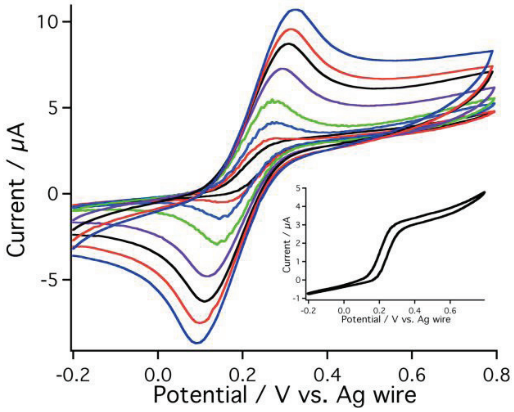

Fig. 1. Cyclic voltammograms at increasing scan rates of the decamethylferrocene (DMFc) redox couple on a gold macro electrode. Supercritical CO_2 fluid at 100 bar and 313 K, acetonitrile co-solvent at a 0.5 molar ratio, ionic liquid electrolyte 10 mM and DMFc 0.5 mM.

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In situ study of structural transformation of alloy nanoparticles to high active fuel cell catalysts

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Renewable energy conversion and storage using chemistry has become a pivotal issue in solving the global energy challenge. In particular fuel cells, owing to their high efficiency and fuel flexibility, will play a critically important part to use electrochemical energy for storage in molecular bonds. However, high catalyst cost and limited catalyst durability at the fuel cell electrodes have long hampered a broader technology deployment of fuel cells, in particular of low temperature Polymer Electrolyte Fuel Cells.

Typically, nanoscale materials such as nanoparticles are employed as catalytically active electrode components. This is because nanoparticles offer a large electrochemical surface area, which is indispensable for useful electrochemical power densities. However, the large surface area of the nanoparticles also tends to be unstable due to their high surface energy. Previous studies have evidenced that catalytic Pt nanoparticles grow and coarsen, resulting in reduced surface areas, which in turn, manifests itself as degradation of cell performance.

We modified the composition of the NP catalyst by adding a less noble metal in the particle structure. Electrochemical characterization of the prepared alloy nanoparticles indicated significantly enhanced catalyst activity towards the oxygen reduction reaction with increasing number of potential cycles. We performed *in situ* anomalous small angle x-ray scattering experiments in terms of understanding the mechanism of intra particle dynamics. Corresponding pair distribution function analysis provided by high energy x-ray diffraction measurements supported our hypothesis on reformation of the alloy nanoparticles (Fig. 1).

Our findings afford outstanding knowledge on particle structure trajectories, which is indispensible for the design of a strongly improved fuel cell catalyst.

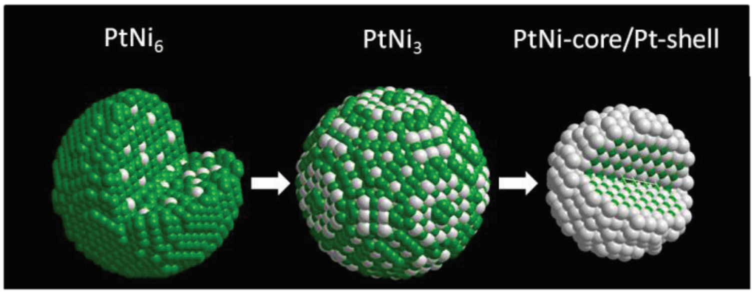

Fig. 1. Mechanism of PtNi alloy particle reformation during electrocatalysis.

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Controlling water retention in polymer electrolyte fuel cells

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The power performance of the polymer electrolyte fuel cell (PEFC) is strongly influenced by interdependent properties such as water and heat management, porosity and internal structure of the gas diffusion layer (GDL). Insufficient humidification of the membrane leads to elevated cell resistance, while excess water can block oxygen diffusion, resulting in mass transfer limitation. Therefore, GDLs should possess the combined and balanced properties of water repellency and attraction. This thereby enables an effective integration of the fuel cell system by lowering the auxiliary power consumption without the need for humidification subsystems.

In this study, we report on our approach; one is preparing a superhydrophobic GDL for autonomous humidification in PEFC, even under fully humidified conditions with a much lower air flow rate. The other is to prepare ultrathin hydrophilic TiO_2 coating on top of microporous layer of GDL for a stable operation under low humidification without external humidifying subsystems.

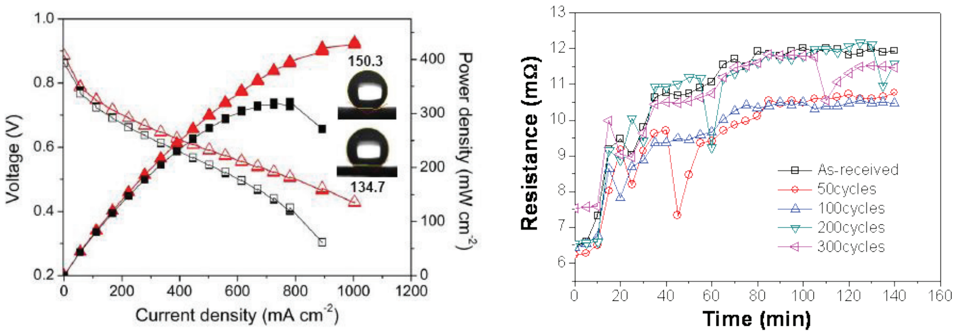

Fig. 1. Current voltage polarization curves on the effect of superhydrophobic GDL by PDMS coating (left) and high frequency resistance variation as a function of time on hydrophilic TiO_2 coated GDL by atomic layer deposition (right).

Photoelectrochemical water splitting using polymeric carbon nitride films on chalcopyrite as new thin-film photocathodes

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Hydrogen production through photoelectrochemical water splitting is one of the attractive ways to convert solar energy to sustainable chemical energy [1]. Very recently, graphitic carbon nitride (g-C_3N_4), a metal-free and abundant material, exhibits promising photocatalytic activity for hydrogen production from water under visible light illumination in the presence of a sacrificial donor [2]. Here, we will present new results concerning the application of g-C_3N_4 films deposited onto p-type polycrystalline $CuGaSe_2$ and $CuInS_2$ thin-film semiconducting absorbers as photocathodes for the production of hydrogen from acidic aqueous solutions. Graphitic carbon nitride thin-films have been successfully achieved by thermal condensation from dicyandiamide precursor heated until 550°C under inert gas conditions. Morphological and structural studies of g-C_3N_4 thin-films suggest a high porosity of the films consisting of a network of nanocrystallites. Additionally, X-ray photoemission spectroscopy has been performed to study the surface/near-surface chemical composition of the g-C_3N_4 film. Fourier transform infrared spectroscopy and Raman spectroscopy have been also measured on these g-C_3N_4 thin-films and reveal the same chemical composition and vibrational properties as reported for g-C_3N_4 powders. It is thereby shown that the process of dicyandiamide polycondensation is a suitable method for fabrication of g-C_3N_4 thin films on semiconductor supports. Photoelectrochemical investigations clearly prove hydrogen evolution under visible light illumination. Moreover, the electrodeposition of small amount of metal co-catalytic nanoparticles like Pt or Rh on such photocathodes strongly improves the production of hydrogen. Finally, it is shown for the first time that conversion of solar energy to hydrogen by water splitting can be successfully achieved by the fabrication of g-C_3N_4/chalcopyrite based heterostructures [3].

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An electrochemical insight to highly sulfonated polymer electrolyte membranes reinforced by electrospun nanofibers for efficient water behaviors in fuel cells

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In this study, we report structural feasibility of an electrospun nonofiber porous substrate (NFPS) as a mechanical support to reinforce highly sulfonated polyelectrolyte membranes for fuel cells. Highly sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) was mechanically reinforced by electrospun and cross-linked bromomethylated poly(2,6-dimetyl-1,4-phenylene oxide) (cBPPO) NFPS. The membranes were successfully fabricated without additional surface conducting layers. Especially, the affinity between hydrophilic conducting SPPO and hydrophobic reinforcing cBPPO NFPS was considerably improved partially due to the same backbone structure. The SPPO base membranes with high water swelling of 90% was significantly suppressed to 20% by the mechanical strength of cBPPO NFPS. The proton conductivities of the prepared membranes showed from 0.03 to 0.08 S/cm, and greatly enhanced energy conversion efficiencies were confirmed in a low temperature H_2/O_2 fuel cell. Furthermore, the prepared thin membranes possessed sufficient water uptake and IEC under reduced swelling ratio. Based on the physicochemical properties of the membranes, such structural advantages for efficient water diffusion through the thin membranes were quantified from their polarization behaviors based on Fick's diffusion law.

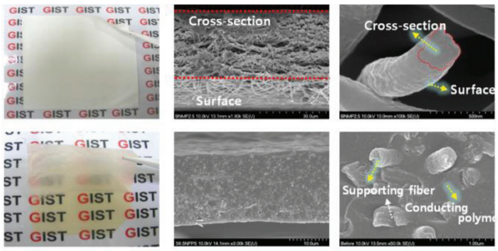

Fig. 1. Photographs and SEM images of the electropun nanofiber porous substrate (NFPS) and the synthesized composite polymer electrolyte membranes.

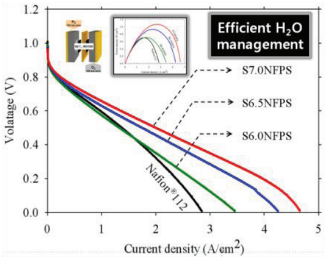

Fig. 2. Polarization behaviors of NFPS based composite polymer electrolyte membranes.

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Role of water in electrocatalytic Cl_2 evolution reaction at RuO_2 based electrodes - Understanding of electrocatalysis as a resonance phenomena

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The reaction path of the Cl_2 evolution reaction (CER) was investigated by combining electrochemical and spectroscopic methods.

During CER electron transfer proceeds at a reconstructed, oxidized surface, which have properties that are different from those observed at open circuit conditions. The conventional interpretation of electrocatalysis namely the effect of the electrode material on the reaction rate does not specify the impact of the solvent on faradaic process at the electrode/electrolyte interface, whereas the theory of electron transfer postulates the importance of the solvent. However, it is not really clear how the solvent contributes to the rate of an electrochemical reaction, especially if the reaction proceeds through adsorbed intermediates.

In the seminal paper of Trasatti [1] it was demonstrated that the work functions of metals in solution are practically the same than those of metals in vacuum. At the same time it was assumed that the solvent behaves like a dielectric continuum that shifts the absolute scale of reactivity to the same extent for all metals, due to the water dipoles that alter the surface potential at the solid/liquid interface.

The state of the RuO_2 surface during CER was analysed *in situ* with Raman spectroscopy, by monitoring vibrations of the crystal lattice of RuO_2 and changes in the surface concentration of adsorbed species as a function of the electrode potential. It was observed that water is crucial in the oxidation of Cl^- ions at RuO_2 based electrodes through the formation of an oxygen-containing layer (more precisely an OH adlayer), which is a key prerequisite for electrocatalytic Cl_2 formation. Water is understood not just as a medium that allows adsorption of intermediates, but also as an integral part of intermediate formed during the electrochemical reaction.

Within this work new insights were obtained concerning a better general understanding of electrocatalysis. Of particular importance is the observation that the electrocatalytic reaction is strongly dependent on the characteristic vibrations of chemical bonds in the crystals used as a catalyst. Instead of using of thermodynamic catalytic descriptors in the form of the adsorption energy of intermediates, the vibration frequencies of the crystal lattice were utilized as a dynamic catalytic descriptor. Interpretation of the newly constructed “volcano”-curve revealed that electrocatalysis is a resonance phenomena, established between the electrode surface and chemical species in the electrochemical double layer.

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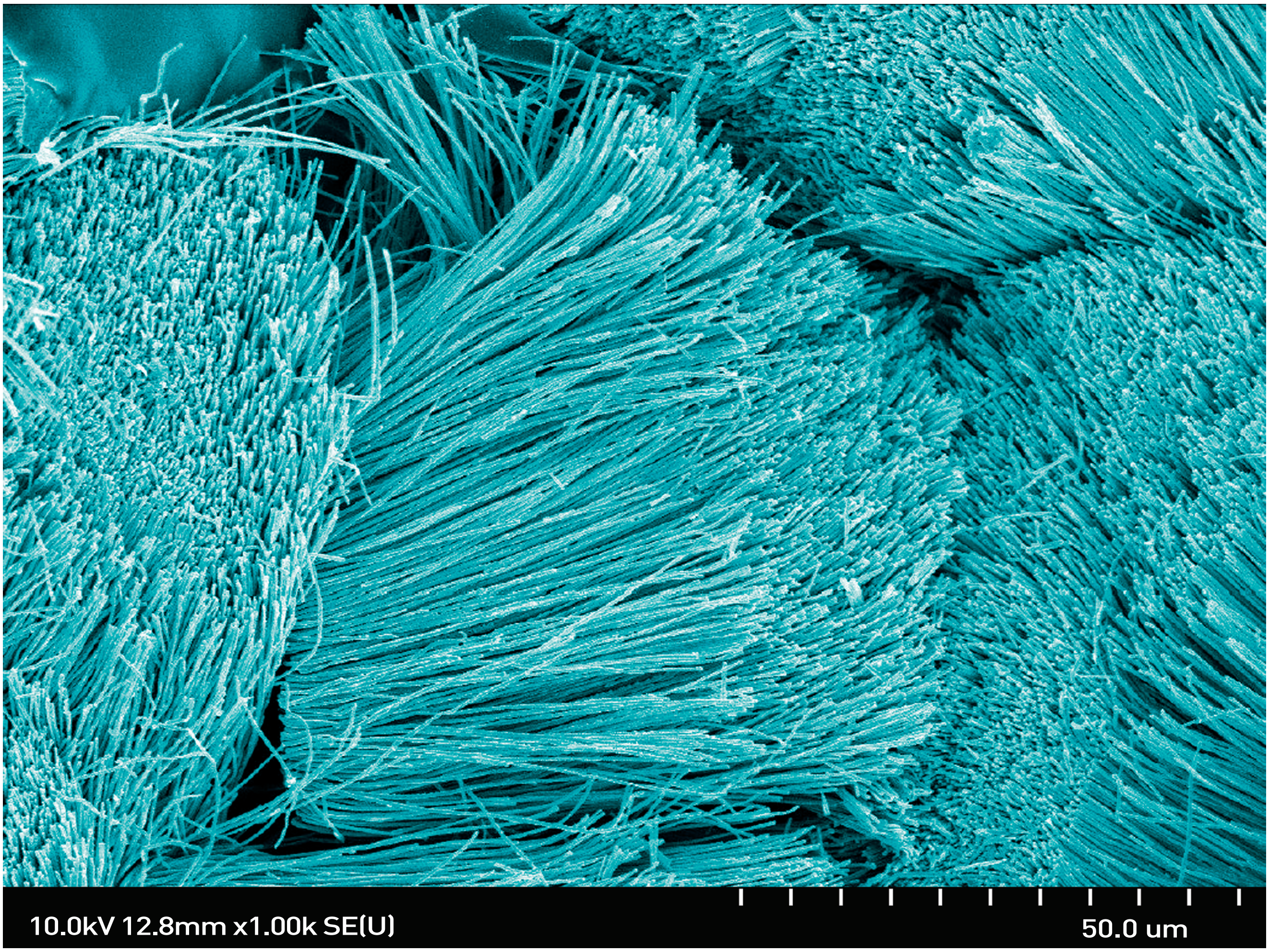

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With best regards,

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