16th International Fischer Symposium

a meeting on nanoscale electrochemistry

Program and Book of Abstracts

June 15-19, 2025
Kloster Seeon, Germany


Photo courtesy by Günter Standl

IFS 2025 Program

Sunday, June 15		Monday, June 16		Tuesday, June 17		Wednesday, June 18		Thursday, June 19	
09:00		09:00	**Todorova**	09:00	**Hellmuth Fischer Award**	09:00	**Robert**	09:00	**Drnec**
09:10		09:10		09:10	**Ceremony**	09:10		09:10	
09:20		09:20		09:20	**Award lecture**	09:20		09:20	
09:30		09:30		09:30	**Huang**	09:30		09:30	
09:40		09:40	Schramm Petersen	09:40		09:40	Durante	09:40	Wittstock
09:50		09:50		09:50		09:50		09:50	
10:00		10:00	Schuster	10:00	**Ding**	10:00	**Mertens**	10:00	Yeo
10:10		10:10		10:10		10:10		10:10	
10:20		10:20	Tong	10:20		10:20		10:20	Wang
10:30		10:30		10:30		10:30		10:30	
10:40		10:40	**Coffee break**	10:40	**Coffee break**	10:40	Gorostiza	10:40	**Coffee break**
10:50		10:50		10:50		10:50		10:50	
11:00		11:00		11:00		11:00	Facchin	11:00	
11:10		11:10	**Doblhoff-Dier**	11:10	**Chen**	11:10		11:10	**Arenz**
11:20		11:20		11:20		11:20	**Coffee break**	11:20	
11:30		11:30		11:30		11:30		11:30	
11:40		11:40		11:40		11:40		11:40	
11:50		11:50	Louisia	11:50	**Cordoba de Torresi**	11:50	**Savinova**	11:50	Brummel
12:00		12:00		12:00		12:00		12:00	
12:10		12:10	Vesztergom	12:10		12:10		12:10	Ozanam
12:20		12:20		12:20		12:20		12:20	
12:30		12:30	Spanos	12:30	Aarts	12:30	Sun	12:30	
12:40		12:40		12:40		12:40		12:40	
12:50		12:50		12:50		12:50	Nagra	12:50	
13:00	**Arrival**	13:00	**Lunch**	13:00	**Lunch**	13:00		13:00	**Departure**
13:10	**and registration**	13:10		13:10		13:10	Pittkowski	13:10	
13:20		13:20		13:20		13:20		13:20	
13:30		13:30		13:30		13:30	Oshchepkov	13:30	
13:40		13:40		13:40		13:40		13:40	
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14:00		14:00		14:00		14:00		14:00	
14:10		14:10		14:10		14:10	**Excursion**	14:10	
14:20		14:20		14:20		14:20		14:20	
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15:20		15:20		15:20		15:20		15:20	
15:30		15:30	**Round table discussion**	15:30	**Coffee break**	15:30		15:30	
15:40		15:40	**on publishing**	15:40		15:40		15:40	
15:50		15:50	**Poster session**	15:50	**Akbashev**	15:50		15:50	
16:00	**Coffee break**	16:00	**with coffee break**	16:00		16:00		16:00	
16:10		16:10		16:10		16:10		16:10	
16:20		16:20		16:20		16:20		16:20	
16:30	**Opening Fischer Seminar**	16:30		16:30	**Sakata**	16:30		16:30	
16:40	**Tutorial KristinaTschulik**	16:40		16:40		16:40		16:40	
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17:10		17:10		17:10	Amemiya	17:10		17:10	
17:20		17:20		17:20		17:20		17:20	
17:30		17:30		17:30	Jiang	17:30		17:30	
17:40		17:40		17:40		17:40		17:40	
17:50		17:50		17:50		17:50		17:50	
18:00	**Dinner**	18:00	**Dinner**	18:00	**Dinner**	18:00		18:00	
18:10		18:10		18:10		18:10		18:10	
18:20		18:20		18:20		18:20		18:20	
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19:00		19:00		19:00		19:00		19:00	
19:10		19:10		19:10		19:10		19:10	
19:20	**Opening remarks**	19:20		19:20		19:20		19:20	
19:30	**Opening lecture**	19:30	Yang	19:30	**Kley**	19:30		19:30	
19:40	**Koper**	19:40		19:40		19:40		19:40	
19:50		19:50	**Mol**	19:50		19:50		19:50	
20:00		20:00		20:00		20:00	**Conference dinner**	20:00	
20:10		20:10		20:10		20:10		20:10	
20:20		20:20		20:20		20:20		20:20	
20:30	Scherson	20:30	Switzer	20:30	**Concert**	20:30		20:30	
20:40		20:40		20:40		20:40		20:40	
20:50	Larsson	20:50	Brankovic	20:50		20:50		20:50	
21:00		21:00		21:00		21:00		21:00	
21:10	Valls Mascaro	21:10	Liu	21:10		21:10		21:10	
21:20		21:20		21:20		21:20		21:20	

Sesssions

▨	fundamental electrochemistry and interfaces	▨	operando studies
▨	single-entity and nanoscale effects	▨	electrocatalysis and energy sciene
▨	molecular systems	▨	electrodeposition and corrosion

16th International Fischer Symposium

a meeting on nanoscale electrochemistry

June 15-19, 2025
Kloster Seeon, Germany

Conference Chairs

Olaf Magnussen	*Kiel University, Germany*
Philippe Allongue	*CNRS, Ecole Polytechnique, France*
Kristina Tschulik	*Bochum University, Germany*

International Advisory Board

Peter Broekmann	*Bern University, Switzerland*
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Shi-Gang Sun	*Xiamen University, China*
Ulrich Stimming	*Technical University of Munich, Germany*

Local Organizing Committee

Olaf Magnussen (local organizer)

Jonas Bunge (conference secretary)

Institute of Experimental and Applied Physics
Kiel University
Olshausenstr. 40, 24098 Kiel, Germany

Phone: +49 431 880 4800
Fax: +49 431 880 4884
E-mail: fischer-symposium@email.uni-kiel.de
Website: www.fischer-symposium.org

Dear participants,

It is a pleasure to welcome you to the 16th International Fischer Symposium, a meeting on nanoscale electrochemistry. We hope this symposium will provide you with opportunities to present and discuss your results in a friendly and open atmosphere. For those who attend this meeting for the first time, the Fischer Symposium has traditionally been the place where the relations between electrochemistry and other fields of science are discussed and interdisciplinary approaches are developed. We hope that the 2025 edition will be in line with this tradition.

As usual, all contributions are presented in a plenary session spanning a variety of subtopics, including this year:

Fundamental electrochemistry and interfaces

Electrodeposition and corrosion

Single-entity and nanoscale effects

Molecular systems

Electrocatalysis and energy science

Operando studies

Invited talks willbe given by:

Andrew Akbashev	*Paul Scherrer Institute, Switzerland*
Matthias Arenz	*University of Bern, Switzerland*
Peng Chen	*Cornell University, United States*
Susana Cordoba de Torresi	*Universidade de São Paulo, Brazil*
Wei Ding	*Chongqing University, China*
Katharina Doblhoff-Dier	*Leiden University, Netherlands*
Christopher Kley	*Fritz-Haber Institute, Germany*
Marc Koper	*Leiden University, Netherlands*
Stijn Mertens	*Lancaster University, United Kingdom*
Arjan Mol	*Delft University of Technology, Netherlands*
Marc Robert	*Sorbonne Université, France*
Kaoruho Sakata	*High Energy Accelerator Research Organization, Japan*
Elena Savinova	*University of Strasbourg, France*
Mira Todorova	*Max Planck Institute for Sustainable Materials, Germany*

Program

Sunday, June 15th

13:00 – 16:00	Registration
16:00 – 16:30	Coffee break

International Fischer Seminar

16:30 – 16:40	Opening Fischer Seminar
16:40 – 17:50	Tutorial: Advanced electrochemical tools to characterise electrocatalysts **Kristina Tschulik**
18:00 – 19:20	Dinner

Fundamental Electrochemistry and Interfaces

Chair: Elena Savinova

19:20 – 19:30	Opening Remarks **Olaf Magnussen**
19:30 – 20:30	Opening Lecture: Electric double layer of platinum **Marc Koper**
20:30 – 20:50	The electrostatically stimulated oxidation of adsorbed carbon monoxide on polycrystalline Pt in aqueous acidic electrolytes **Daniel Scherson**
20:50 – 21:10	Platinum oxidation hinders the oxygen reduction reaction **Alfred Larsson**
21:10 – 21:30	Electrochemical oxidation and reduction of Au(111) in alkaline media **Francesc Valls Mascaro**

Photo courtesy by Günter Standl

Monday, June 16th

Fundamental Electrochemistry and Interfaces

Chair: Marc Koper

9:00 – 9:40	Electrochemical interfaces and reactions studied by using ab initio supercells **Mira Todorova**
9:40 – 10:00	Determining the potential of maximum entropy from ab initio molecular dynamics **Amanda Schramm Petersen**
10:00 – 10:20	Determination of the reaction volume ΔRV of electrode processes, an approach to address the role of water in electrochemical reactions **Rolf Schuster**
10:20 – 10:40	Experimentally quantifying local fields at electrochemical interfaces with the vibrational Stark effect **Yujin Tong**
10:40 – 11:10	Coffee Break

Chair: Daniel Scherson

11:10 – 11:50	(Atomistic) simulations of electrochemical interfaces: Bridging experiment and structural insight **Katharina Doblhoff-Dier**
11:50 – 12:10	Cation-anion interactions in the electric double layer resolved by in situ XPS **Sheena Louisia**
12:10 – 12:30	The effect of Interfacial pH shift on constant current hydrogen evolution from dilute acids **Soma Vesztergom**
12:30 – 12:50	Shining light on active site transformations for oxygen evolution reaction catalysts in PEM water electrolysis **Ioannis Spanos**
13:00 – 14:30	Lunch
15:30 – 15:50	Round table discussion on publishing *Chairs: Elena Savinova and Philippe Allongue*
15:50 – 17:50	**Poster session** with coffee break
18:00 – 19:30	Dinner

Electrodeposition and Corrosion

Chair: Mira Todorova

19:30 – 19:50	Video-STM studies of atomic-scale sulfide and halide dynamics at electrochemical interfaces **Chaolong Yang**
19:50 – 20:30	In-situ and nanoscopic corrosion studies using liquid-phase transmission electron microscopy **Arjan Mol**
20:30 – 20:50	Epitaxial single-domain metal-organic framework (MOF) thin films by electrodeposition **Jay Switzer**
20:50 – 21:10	Electrochemical synthesis of laminated structures for inductor application **Stanko Brankovic**
21:10 – 21:30	Electrochemical synthesis of high entropy nanoparticles and the exploration of the AgAuPd composition space for the oxygen reduction reaction **Menglong Liu**

Tuesday, June 17th

Hellmuth Fischer Medal Award

9:00 – 9:20	Hellmuth Fischer Medal award ceremony
9:20 – 10:00	Award Lecture: Four personal puzzles in interfacial electrochemistry **Jun Huang**

Photo courtesy by Günter Standl

Single-entity and Nanoscale Effects

Chair: Kristina Tschulik

10:00 – 10:40	Regulation of electrocatalysts based on confinement-induced properties **Wei Ding**
10:40 – 11:10	Coffee Break
11:10 – 11:50	Single-particle/single-molecule microscopy of (photo)(electro)chemistry **Peng Chen**
11:50 – 12:30	Plasmon-enhanced electrochemistry as strategy for sustainable development **Susana Cordoba de Torresi**
12:30 – 12:50	Local interrogation of the electrified solid-liquid interface with force microscopy **Mark Aarts**
13:00 – 14:30	Lunch break
15:30 – 15:50	Coffee Break

Operando Studies

Chair: Matthias Arenz

15:50 – 16:30	Ion intercalation, lattice instability and chemo-mechanical coupling in electrocatalysts **Andrew Akbashev**
16:30 – 17:10	Real-time observation of the solid-liquid interface of catalyst electrode for water electrolysis by soft X-ray absorption spectroscopy **Kaoruho Sakata**
17:10 – 17:30	Novel time-resolved soft X-ray absorption spectroscopy technique for operando observation of electrochemical reactions at solid-liquid Interface **Kenta Amemiya**
17:30 – 17:50	In-situ observation of the structure and performance evolution for atomic $Fe–N_4$ during thermal activation **Yanxia Jiang**
18:00 – 19:30	Dinner

Chair: Katharina Doblhoff-Dier

19:30 – 20:10	Nanoscale insights into electrocatalyst surfaces and electrochemical interfaces **Christopher Kley**
20:30	Concert

Wednesday, June 18th

Molecular Systems

Chair: Philippe Allongue

9:00 – 9:40	Ticking the CO_2 clock with molecular control. From fuels to complex molecules **Marc Robert**
9:40 – 10:00	EC-STM investigation of nitrate reduction reaction on iron-octaethylporphyrin adsorbed on Au(111) **Christian Durante**
10:00 – 10:40	Electric field switching of single molecules in a self-assembled monolayer **Stijn F. L. Mertens**
10:40 – 11:00	Long distance interprotein electron transport in redox proteins and photosynthetic complexes **Pau Gorostiza**
11:00 – 11:20	ORR electrocatalysis on Fe-Octaethylporphyrin under the fast electrochemical scanning tunnelling microscope. **Alessandro Facchin**
11:20 – 11:50	Coffee Break

Electrocatalysis and Energy Science

Chair: Ulrich Stimming

11:50 – 12:30	Electrooxidation of organic molecules on $Ni(OH)_2/NiOOH$ **Elena Savinova**
12:30 – 12:50	Studies of PEMFC non-precious metal catalysts **Shi-Gang Sun**
12:50 – 13:10	The potential-dependent structure of Pt_3Ni alloy electrocatalysts and its effect on electrocatalytic activity **Hassan Javed Nagra**
13:10 – 13:30	Multi-modal X-ray characterization to probe amorphization of oxygen-evolving electrocatalysts **Rebecca Pittkowski**
13:30 – 13:50	Insights from operando ATR-FTIR spectroscopy on Pt-CO Interaction in the presence of ionomer: From surface-adsorbed species to the interfacial electrolyte composition and structure **Alexandr Oshchepkov**
14:15 – 19:45	Excursion
20:00	Conference Dinner

Thursday, June 19st

Electrocatalysis and Energy Science

Chair: Shi-Gang Sun

9:00 – 9:40	Dynamic structural transformations in IrRu catalysts during oxygen evolution reaction **Jakub Drnec**
9:40 – 10:00	Tuning the electrooxidation of C_1 compounds by adjusting the surface concentration of foreign elements in nanoporous gold **Gunther Wittstock**
10:00 – 10:20	Electrochemical reduction of CO_2 into long-chain hydrocarbons **Boon Siang Yeo**
10:20 – 10:40	Probing the mechanism of cation-enhanced CO_2 reduction on copper in acidic media **Tao Wang**
10:40 – 11:10	Coffee Break

Chair: Susanna Cordoba de Toressi

11:10 – 11:50	How to address statistical relevance of data in electrocatalysis research? **Matthias Arenz**
11:50 – 12:10	Electroreduction of acetone on Pt/Ru model catalysts: The interplay of structure, activity, and selectivity **Olaf Brummel**
12:10 – 12:30	Understanding the impact of boron doping in methylated amorphous silicon electrodes for Li-ion batteries. **Francois Ozanam**
13:00	Departure

Photo courtesy by Günter Standl

Poster contributions

P 01 In situ HEGISAXS studies of the nanoscale restructuring mechanism of platinum single crystal electrodes
***Jan Ole Fehrs**, Timo Fuchs, Fabian Schröfel , Finn Schröter , Barbara Schröder , Jing Tian , Nick Merkel , Simon Kempf , Jakub Drnec , Valentín Briega-Martos , Serhiy Cherevko , and Olaf Magnussen*

P 02 Structural insights into the electrochemical double layer on Pt(111) by in situ surface X-ray diffraction
***Finn Schröter, J**an Ole Fehrs, Barbara Schröder, Andrea Sartori, Pol Salles Perramon, Jakub Drnec, and Olaf Magnussen*

P 03 Operando interfacial investigation on copper-based model catalysts for CO$_2$ electroreduction
***Jing Tian**, Carl Hendric Scharf, Jonas Bunge, Jan Ole Fehrs, Alex Chandraraj, Eric Liberra, Matias Herran, Arno Bergmann, Jochim Stettner, Beatriz Roldan Cuenya, and Olaf Magnussen*

P 04 Ionomer adsorption in catalyst inks as a function of ink solvent composition using contrast-variation small angle neutron scattering
***Martha Yael Stando**, Lionel Porcar, Arnaud Morin, Gerard Gebel, Jakub Drnec, and Stephanè Cotte*

P 05 Ethylene glycol partial oxidation on Co$_3$O$_4$ (001) surface: Pathway to two- and four-electron products and interplay between solute's surface coverage and aqueous solvation
***Falonne Bertholde Sharone Nkou,** and Stephane Kenmoe*

P 06 In-situ and operando characterization of electrochemical systems at the I07 beamline
***Francesco Carla**, Li Shao, and Jonathan Rawle*

P 07 EC-STM investigation on cyclic triimidazoles self-assembling on Au(111) as carbon nitride mimicking system for electrocatalytic studies
***Francesco Cazzadori**, Elena Lucenti, Elena Cariati, and Christian Durante*

P 08 Electrodeposition of CoPd ultra-thin films with low Co composition for magnetic memory applications
***Rippei Suzuki**, Mikiko Saito, and Takayuki Homma*

P 09 Influence of the shape of deposited area on Photoelectrochemical activity of TiO$_2$–multiwalled carbon nanotube film electrode prepared via sol–gel electrophoresis deposition
***Yuehai Yu**, and Mariko Matsunaga*

P 10 Implementation of a fast add-on module into an electrochemical scanning tunneling microscope
Alessandro Facchin, Marco Cautero, Leonardo Gregorat, Giuseppe Cautero, and ***Friedrich Esch***

P 11 Development of NiFe catalysts for the reverse water gas shift (RWGS) reaction und co-electrolysis conditions
Esperanza Ruiz, ***Maria Jose Escudero****, and Rocio Millan*

P 12 Hydrazine hydrate electrooxidation reaction mechanism on Ni electrode
Evgeniia Vorms*, Evgenii Strugovshchikov, Amandine Brige, Mykola Isaiev, Tristan Asset, Antoine Bonnefont, Marian Chatenet, Elena Savinova, and Alexandr Oshchepkov*

P 13 Supperlattice-like strcuture: Ordered mass transfer endows high quality output of fuel cell
Jian Wang*, Wie Ding, and Zidong Wei*

P 14 Electrolyte potentials during high voltage electrolysis and their implications for operando electrochemical measurements
Lukas Forschner*, Tim Bolter, Tima Jacob, and Albert K. Engstfeld*

P 15 Electrochemical questions answered using the echemdb database
Johannes M. Hermann*, Nicolas Hörmann, Maren-Kathrin Heubach, Nadine Wölfel, Nicolas Bergmann, Karsten Reuter, Timo Jacob, Julian Rüth, and Albert K. Engstfeld*

P 16 Influence of pH on the surface structure of Ni anodes under OER conditions
Justus Leist*, Annika Neufischer, Benjamin Schick, Sylvain Brimaud, Timo Jacob, and Albert K. Engstfeld*

P 17 Potential Dependent Surface Adlayer Structures on and Restructuring of Ru(0001) and Pt-Modified Ru(0001) Electrodes Under Reaction Conditions
Albert K. Engstfeld*, Joachim Bansmann, Zenonas Jusys, Jakub Drnec, and R. Jürgen Behm*

P 18 Suspension electrolyte for aqueous dual-ion batteries
Yitao He*, and Jiri Cervenka*

P 19 Electrocatalytic water oxidation with prussian blue analogues under magnetic field
Ferdi Karadas

P 20 Nature of the Au(111) interface in aqueous solution
Antonia Köhler*, Ralf Bechstein, Michael Reichling, and Angelika Kühnle*

P 21 In situ monitoring of oxygen permeation and Li_2O_2 formation in lithium-oxygen batteries
Nelly Nembot*, Marius Muhle, Marcel Reisch, Daniela Fenske, and Gunther Wittstock*

P 22 New insights on bipolar electrochemistry of microstructures
Franziska Kühling*, and Gunther Wittstock*

P 23 Time evolution of the potential of hard carbon/sodium metal cells upon stepwise temperature changes
Laurin Derr*, Steffen Braun, Krishnaveni Palanisamy, Christine Kranz, and Rolf Schuster*

P 24 Development of a microcalorimetric method for the determination of the reaction entropy of irreversible electrochemical processes and application to the oxidation of formic acid
Steffen Braun*, Katrin Bickel, and Rolf Schuster*

P 25 Microcalorimetric studies on magnesium deposition from $Mg[B(hfip)_4]_2$/DME electrolyte solutions
Daniel Metzger*, Franziska Karcher, Sibylle Riedel, Zhirong Zhao-Karger, and Rolf Schuster*

P 26 Zinc compound electrodeposition on HOPG using high-speed AFM
Tatsumi Naganuma*, Ryuto Ohashi, Cheng Yen Chieh, Mikito Ueda, and Hisayoshi Matsushima*

P 27 High-speed AFM observation of copper electrodeposition and dissolution behaviour on HOPG
Cheng Yen Chieh*, Ryuto Ohashi, Tatsumi Naganuma, Mikito Ueda, and Hisayoshi Matsushima*

P 28 Dynamic nucleation/dissolution of electrolytic nanobubbles during potential sweep by high-speed AFM
Ryuto Ohashi*, Tatsumi Naganuma, Cheng Yen Chieh, Mikito Ueda, and Hisayoshi Matsushima*

P 29 Influence of surface defects, oxygen groups, and alkali metals on H_2O_2 generation at carbon electrodes
Andre Olean-Oliveira*, Najeeb Hasnain, Ricardo Martinez-Hincapie, Ulrich Hagemann, Adarsh Jain, Doris Segets, Ioannis Spanos, and Viktor Colic*

P 30 Theory of electrochemical plasmonics
Lulu Zhang*, and Jun Huang*

P 31 How good is orbital-free density functional theory for metal-solution interfaces? Comparison with an orbital-based method for a 1D model
***Xiwei Wang**, Chenkun Li, and Jun Huang*

P 32 Operando X-ray diffraction studies of Co oxide model catalysts during alcohol oxidation and oxygen evolution reaction
***Carl Hendric Scharf**, Jing Tian, Jochim Stettner, Konrad Dyk, Anastasiia Kotova, Sebastian Reinke, Julia Linnemann, Fouad Maroun, and Olaf Magnus Magnussen*

P 33 Operando X-ray diffraction studies of structurally-defined Co oxide thin films during oxygen evolution: Skin layer formation and reactivity
***Jochim Stettner**, Tim Wiegmann, Canrong Qiu, Finn Reikowski, Carl Hendric Scharf, Mathilde Bouvier, Ivan Pacheco, Manon Bertram, Firas Faisal, Olaf Brummel, Jörg Libuda, Jakub Drnec, Philippe Allongue, Fouad Maroun, and Olaf Magnus Magnussen*

P 34 A newly-developed electrochemical video STM for adsorbate diffusion studies
***Fabian Schröfel**, Chaolong Yang, Knud Schröter, and Olaf Magnussen*

P 35 Implementation of a video STM for studies of electrochemical interfaces
***Knud Schröter**, Fabian Schröfel, Matthias Greve, Karsten Tarhouni, and Olaf Magnussen*

P 36 Au nanoparticle-catalyzed electron transfer to electrodes for enhanced biosensing sensitivity
*Seonhwa Park, and **Haesik Yang***

P 37 Connecting SEI structure and chemistry to electron-ion transport mechanisms and rates using redox probes
***Xiaokun Ge**, Lukas Köbbing, Andreas Kuhlmann, Maryam Nojabaee, Birger Horstmann, Jimun Yoo, and Hans-Georg Steinrück*

P 38 Differential electrochemical mass spectrometry to elucidate the mechanism of non-aqueous electrochemical reactions
***Aude Salame**, Christoph Bondü, and Marc T. M. Koper*

P 39 Understanding the constant phase element behaviour of the double layer capacitance of Pt(111)
***Katherine J. Levey**, Nicci L. Fröhlich, Lucas B. T. de Kam, Steffen Hardt, and Marc T. M. Koper*

P 40 Confining the electrical double-layer
***Marco Schöning**, Serge Lemay, and Marc T. M. Koper*

P 41 Exploring the metal nanoparticle/aqueous electrolyte interface by nanoimpact electrochemistry
Mahnaz Azimzadeh Sani*, and Kristina Tschulik*

P 42 Electrocatalysis at a liquid | liquid | solid triple phase boundary
Marius Spallek*, Christoph Bondü, and Kristina Tschulik*

P 43 Spectroelectrochemical analysis of water confinement and electrochemical CO_2 reduction at Au modified with covalent organic frameworks
Yannick Weidemann*, Pouya Hosseini, Andres Rodriguez Camargo, Bettina Lotsch, and Kristina Tschulik*

P 44 Dynamically dealloyed Au-Ag catalysts for acidic ethanol electrooxidation via nano-impacts electrochemistry
Hanxin Zhang*, Mahnaz Azimzadeh Sani, Dean-Robin Nettler, and Kristina Tschulik*

P 45 Electrochemical investigation of hydrogen transport in anodized aluminium oxide nanochannels
Luca Sicking*, Oliver Trost, Moksh Madan, Simon Ospina Velez, Tobias Binninger, Michael Eikerling, and Kristina Tschulik*

P 46 Statistical evaluation of IrO_x and RuO_x catalyst thin film OER measurements
Jonas Forner*, Gustav K. H. Wiberg, and Matthias Arenz*

P 47 Transforming nitrate into ammonia over kinetically stabilized Co metal-hydroxide composite foams: A complementary operando analytical approach
Nandu Ashtaman Pillai Syamaladevi*, Abhijit Dutta, Hridya Nedumkulam, Zsolt Szakaly, Soma Vesztergom, Jakub Drnec, Rebecca Katharina Pittkowski, and Peter Broekmann*

P 48 HMF electrooxidation on robust nickel-foam catalysts: pH effects on the electrolysis performance
Liliana Galvez Vazquez*, Abhijit Dutta, Soma Vesztergom, Romina Zaugg, Alexander Rudnev, and Peter Broekmann*

P 49 On the faradaically active surface area of metal foam electrodes
Zsolt Szakaly*, Xin Yu, Nandu Syamaladevi Ashtaman, Liliana Galvez Vazquez, Abhijit Dutta, Peter Broekmann, and Soma Vesztergom*

P 50 Electrocatalysis of the oxygen reduction at knitted polymers
Shumaila Razzaque*, Alla Dyachenko, Aimen Waqar, Katarzyna Dusilo, and Marcin Opallo*

List of Participants

Mark	Aarts	Leiden University	Netherlands
Ajay	Ajay	CAU Kiel	Germany
Andrew	Akbashev	Paul-Scherrer-Institute	Switzerland
Philippe	Allongue	Ecole Polytechnique Palaiseau	France
Kenta	Amemiya	KEK, Tsukuba	Japan
Matthias	Arenz	Bern University	Switzerland
Nandu	Ashtaman Pillai Syamaladevi	University of Bern	Switzerland
Mahnaz	Azimzadeh Sani	Ruhr University Bochum	Germany
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Stanko	Brankovic	University of Houston	USA
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Francesco	Cazzadori	Università degli Studi di Padova	Italy
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Ella	Dieball	CAU Kiel	Germany
Wei	Ding	Chongqing University	China
Katharina	Doblhoff-Dier	Leiden University	Netherlands
Jakub	Drnec	ESRF	France
Christian	Durante	Università degli Studi di Padova	Italy
Albert	Engstfeld	Ulm University	Germany
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Justus	Leist	Ulm University	Germany
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Stijn	Mertens	University Lancaster	UK
Daniel	Metzger	Karlsruhe Institute of Technology	Germany
Arjan	Mol	TU Delft	Netherlands
Tatsumi	Naganuma	Hokkaido University	Japan
Hassan Javed	Nagra	Leiden Institute of Chemistry	Netherlands
Falonne	Nkou	University Duisburg-Essen	Germany
Ryuto	Ohashi	Hokkaido University	Japan
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Marc	Robert	Sorbonne University	France
Kaoruho	Sakata	KEK, Tsukuba	Japan
Aude	Salamé	Leiden Institute of Chemistry	Netherlands
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Marco	Schönig	Leiden University	Netherlands
Amanda	Schramm Petersen	University of Copenhagen	Denmark
Fabian	Schröfel	CAU Kiel	Germany
Finn	Schröter	CAU Kiel	Germany
Knud	Schröter	CAU Kiel	Germany
Rolf	Schuster	Karlsruhe Institute of Technology	Germany

Luca	Sicking	Ruhr Universität Bochum	Germany
Marius	Spallek	Ruhr University Bochum	Germany
Ioannis	Spanos	MPI for Chemical Energy Conversion	Germany
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Jochim	Stettner	CAU Kiel	Germany
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Rippei	Suzuki	Waseda University	Japan
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Zsolt	Szakaly	Eötvös Lordánd University of Budapest	Hungary
Jing	Tian	CAU Kiel	Germany
Mira	Todorova	MPI for Sustainable Materials	Germay
Yujin	Tong	University of Duisburg-Esssen	Germany
Susana	Torresi	University of Sao Paulo	Brazil
Kristina	Tschulik	Ruhr-Universität Bochum	Germany
Francesc	Valls Mascaro	University of Innsbruck	Austria
Soma	Vesztergom	Eötvös Lordánd University of Budapest	Hungary
Evgeniia	Vorms	University of Strasbourg	France
Jian	Wang	Chongqing University	China
Tao	Wang	Xiamen University	China
Xiwei	Wang	Forschungszentrum Jülich	Germany
Yannick	Weidemann	Ruhr-Universität Bochum	Germany
Gunther	Wittstock	University of Oldenburg	Germany
Haesik	Yang	Pusan National University	South Korea
Chaolong	Yang	CAU Kiel	Germany
Boon Siang	Yeo	National University of Singapore	Singapore
Jimun	Yoo	Forschungszentrum Julich	Germany
Weilai	Yu	University of Toronto	Canada
Yuehai	Yu	Chuo University	Japan
Hanxin	Zhang	University of Chinese Academy of Sciences Beijing	China
Lulu	Zhang	Forschungszentrum Jülich	Germany
Zengming	Zhang	Forschungszentrum Jülich	Germany
Da	Zhu	Forschungszentrum Jülich	Germany

Abstracts

Oral presentations

Advanced electrochemical tools to characterise electrocatalysts

Kristina Tschulik
Analytical Chemistry II, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, 44801 Bochum, Germany
Kristina.tschulik@rub.de

The synthesis and physical characterization of (nano)catalyst materials is often done with atomic scale precision utilizing state-of-the-art techniques. Conversely, characterization of their electrocatalytic performance often relies on techniques that were developed more than a century ago and for much simpler systems, such as the classical Tafel analysis. This gap in the consideration level between material and electrochemical characterization limits our ability to design advanced nanomaterials for electrocatalysis and can be overcome by developing and utilizing advanced electrochemical methods. [1]

This is particularly relevant for precious metal free catalysts, such as transition metal oxide. These are highly promising catalysts for alkaline water splitting or selective oxidation of organic compounds, thanks to their relatively high abundancy and high catalytic activity. Due to their limited electrical conductivity they are often used as nanoparticles and their catalytic performance is assessed based on experiments at composite electrodes. Besides the nanocatalyst of interest, these electrodes contain catalytically inactive binders and conductive additives. This makes it highly challenging – if not impossible – to distinguish influences of catalyst properties from matrix effects. For example, observed effects of particle morphology on electrocatalytic activity may simply originate from different wetting/blocking of catalyst active sites by the used additives or by different iR drop across the composite film, instead of signifying different charge transfer kinetics.

Single nanoparticle electrochemistry allows to overcome this limitation by studying electrocatalysis at individual nanoparticles [2]. Employing this approach, particle property-activity relations and support effects can be determined experimentally. These experiments can be linked to advanced theory data, thanks to the comparably small size of the single particle electrochemical system. Complementary operando spectro-electrochemical investigations are equally essential for the design of non-precious-metal electrocatalysts, as these typically undergo substantial transformation [4], forming the catalytically active species only under operation conditions and converting back to less active species under ex situ conditions. [1] In this tutorial we will discuss single entity electrochemistry and spectro-electrochemical approaches applied to nanoscale materials.

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Electric double layer of platinum

Marc T.M. Koper
Leiden Institute of Chemistry, Leiden University, the Netherlands
m.koper@chem.leidenuniv.nl

Platinum is the most studied electrode material in electrocatalysis, but its double layer properties are still incompletely understood. Only Pt(111) has a true double layer window. However, the properties of the electric double layer of Pt(111) do not follow the classic Gouy-Chapman-Stern theory. Lower coordination sites and facets on platinum are always covered by either hydrogen or hydroxyl adsorbates, which have an important influence on its double layer properties, as I will demonstrate by recent results of double-layer measurements on stepped Pt single-crystal electrodes. In addition, we show that at low electrolyte concentrations, which are often necessary for double-layer measurements, Pt(111) displays strong constant-phase element behavior, which complicates the accurate measurement of its double layer capacitance. The possible origin of this nonideality will be discussed. Finally, the effect of adsorbates on the double-layer of platinum will be discussed on the basis on hydrogen-covered Pt(111).

The Electrostatically Stimulated Oxidation of Adsorbed Carbon Monoxide on Polycrystalline Pt in Aqueous Acidic Electrolytes

Arvind Singh Heer, Marc D. Rubin and Daniel Scherson*
Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106-7078
Corresponding Author email: dxs16@case.edu

Abstract

The oxidation of CO adsorbed, CO(ads), on a Pt(poly) disk electrode polarized at a fixed potential, was electrostatically stimulated by a Au electrode, SE, placed at the edge of the disk, while collecting time-, and spatially resolved images of the disk under normal incidence conditions. The optical assembly incorporated a light emitting diode, a telecentric lens equipped with a built-in prism that provides coaxial illumination, and a high-performance monochrome cooled camera. Shown in the red and black lines in the Left Panel, Fig. 1, respectively, are plots of the current flowing through the SE, i_{SE} and the Pt disk ,i_{Pt}, during stimulation. As indicated, i_{Pt} displays a prominent peak associated with the oxidation of CO(ads). A plot of the fraction of the original CO|Pt surface becoming oxidized as a function of the time elapsed, as determined from the integration of the transient in the Right Panel in this figure is provided in the Right Panel in this figure. A sequence of images from the Pt surface collected during the oxidation of CO(ads), is shown in Fig. 2**,** where the evolution of the dark and light areas affords clear evidence for the propagation of an oxidation front, until the entire surface is oxidized. This agrees with the interpretation of current transients collected from single crystal Pt facets, where the initiation of the oxidation was assumed to be triggered spontaneously from a defect along the edge of the facet [1]

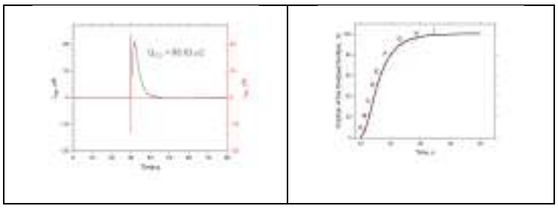

Fig. 1. Left Panel. Plot of the current flowing the SE (red) and Pt electrode (black) over the time region prior, during and following stimulation. Right Panel is a plot of the fraction of the original CO|Pt surface becoming oxidized as a function of the time elapsed, as determined from the integration of the transient in the Right Panel.

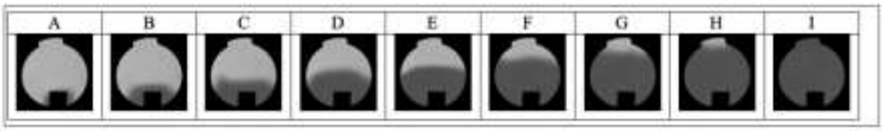

Fig. 2. Sequence of images from the Pt surface collected during the oxidation of adsorbed CO. The time at which the images were recorded is shown in red dots in the Right Panel in Fig. 1.

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Platinum Oxidation Hinders the Oxygen Reduction Reaction

Alfred Larsson[1,2]*, Andrea Grespi[1], Karen van den Akker[2], Auden Ti[1], Alexander Imre[3], Estephania Lira[1], Mahesh Ramakrishnan[4], Justus Just[4], Rik Mom[2], Marc Koper[2], Lindsay Merte[5], and Edvin Lundgren[1]

[1] Division of Synchrotron Radiation Research, Lund University, Lund, Sweden [2] Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands [3] Institute of Applied Physics, TU Wien, Vienna, Austria [4] MAX IV Laboratory, Lund University, Lund, Sweden [5] Materials Science and Applied Mathematics, Malmö University, Malmö, Sweden.

*Corresponding author: email: alfred.larsson@sljus.lu.se

Abstract

The oxygen reduction reaction (ORR) is essential for fuel cells, but limits their efficiency due to its large overpotential(*1*). The overbinding of oxygenated adsorbates such as OH on the surface of the Pt electrocatalysts is thought to play a critical role in this high overpotential. At open circuit potential, such oxygenated species can accumulate on the Pt surface, negatively affecting the performance during fuel cell start-up (*2*). Advances have been made in the understanding of the oxygen chemistry at Platinum surfaces (*3, 4*), but the topic is still debated, and the local oxide structure has remained elusive.

Here, we use electrochemical methods and *in situ* total reflection x-ray absorption spectroscopy (refleXAFS) to determine the local oxide structure and its effect on ORR activity. From the cyclic voltammograms in Fig. 1 (a), we show how the oxide reduction peak shifts with increasing upper vertex potential. This is also reflected in the ORR onset potential during the cathodic sweep as shown in Fig. 1 (b). refleXAFS allows us to determine the local oxide structure at anodic potentials already from 1 V vs. RHE for a polycrystalline platinum electrode, as shown in Fig. 1 (c) and (d). We further show that higher oxide coverages shift the apparent overpotential for ORR, and there is a coexistence of metallic and oxidized platinum at the surface until the mass transfer limited current is reached. We argue that the presence of the surface oxide hinders the onset of ORR due to the slow reduction of the oxide. The slow oxidation and reduction kinetics are caused by the rearrangement of Pt surface atoms to accommodate a Pt-Pt distance in the flat square planar PtO_2-like rows that are different from the bulk Pt-Pt distance.

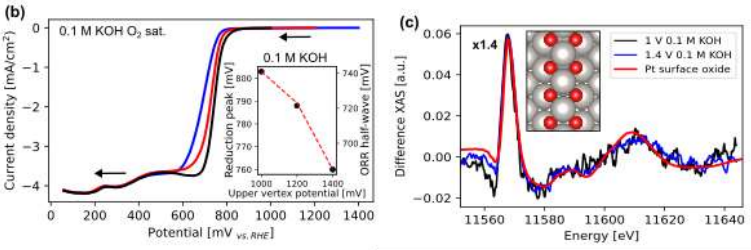

Figure 1. (a) Cyclic voltammogram for polycrystalline platinum at various upper vertex potentials. (b) ORR activity was measured from the cathodic sweep after holding at various upper vertex potentials. (c) Difference TR-XAS and a calculated spectrum of the oxide structure in (d) taken from Ref [1].

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Electrochemical Oxidation and Reduction of Au(111) in Alkaline Media

Toni Moser[1], Francesc Valls Mascaró[1*], Andrea Auer[1], and Julia Kunze-Liebhäuser[1]

[1] University of Innsbruck, Innsbruck, 6020 (Austria)

* Francesc.Valls-Mascaro@uibk.ac.at

Abstract

Gold is commonly used as a model electrode to investigate fundamental problems such as metal oxidation and degradation. In electrochemical environment, its oxidation starts through a place-exchange mechanism, in which gold surface atoms interchange their positions with the adsorbed oxygen atoms [1]. This process ultimately results in the nucleation and growth of adatom and vacancy islands, and hence in the roughening of the electrode [2-5]. In this work, we use Electrochemical Scanning Tunnelling Microscopy (EC-STM) to show that the place-exchange on Au(111) in alkaline media takes place in two steps. At mild oxidation potentials gold atoms are lifted from the terrace plane by less than a monolayer height. At higher oxidation potentials the lifted gold atoms are pushed out onto the terrace, thereby becoming adatoms that nucleate into adatom islands. Upon slow reduction of the surface oxide, the adatom islands vanish, while vacancy islands appear that remain metastable even at very low potentials.

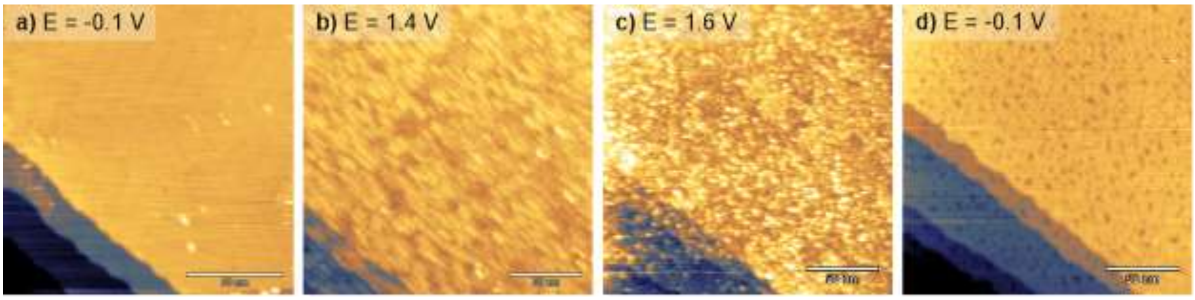

Figure 2. EC-STM images of Au(111) recorded in 0.1 M NaOH at different electrode potentials: **(a)** -0.1 V, **(b)** 1.4 V, **(c)** 1.6 V, and **(d)** -0.1 V after oxidation. All potentials are referenced to the Reversible Hydrogen Electrode (RHE).

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Electrochemical interfaces and reactions studied by using ab initio supercells

M. Todorova[1*], J. Yang[1], Z. Wang[1], S. Surendralal[1], F. Deißenbeck[1],

S. Wippermann[1,2], J. Neugebauer[1]

[1] Max Planck Institute for Sustainable Materials, Düsseldorf, 40237 (Germany)

[2] 2 Phillips-Universität Marburg, Marburg, 35032 (Germany)

* m.todorova@mpie.de

Abstract

Electrochemical interfaces are at the heart of many processes central to our quest of achieving a sustainable and greener future. The rational design and targeted optimization of processes such as hydrogen or oxygen evolution, material dissolution and others will hugely benefit from our understanding of the fundamental mechanisms driving electrochemical reactions and how these are affected by environmental changes.

Ab initio density functional theory calculations have been hugely successful in providing fundamental insights into various areas of application, but face challenges when modelling electrochemical interfaces. This is due, not least, to the necessity to describe a thermodynamically open system, which exchanges energy, electronic charge and ions with the environment, within the confines of a typical supercells size. In addition, large fluctuations of the electrostatic potential and field occur on the time and length scales relevant to chemical reactions, which need to be accounted for.

Focusing on some of these challenges, the presentation will discuss possible ways to overcome them, for example, by discussing differences in popular electrostatic boundary conditions [1] and how to achieve potential control without imposing artificial constrains on either the charge or the potential dynamics [2]. The used examples will be related to the Mg/H_2O [3,4] and Pt/H_2O [5] electrochemical interfaces.

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Determining the Potential of Maximum Entropy from *ab initio* Molecular Dynamics

Amanda S. Petersen[1*] **and Jan Rossmeisl**[1]
[1] Department of Chemistry, Center for High Entropy Alloy Catalysis,
University of Copenhagen, 2100 (Denmark)
* asp@chem.ku.dk

Understanding electrolyte structuring at the electrochemical interface is crucial for optimizing electrocatalysis, yet many aspects remain unresolved. Here, we present a computational framework based on *ab initio* molecular dynamics (AIMD) simulations to predict the potential of maximum entropy (PME) - a key descriptor of electric double layer (EDL) disorder, charge transfer efficiency, and electrocatalytic activity. By integrating AIMD with the generalized computational hydrogen electrode (GCHE), we reveal how electrolyte composition, alkali metal (AM) cation identity, and pH modulate PME values. Our approach successfully reproduces experimentally observed PME shifts [1-3] for Au_{pc} and Pt_{pc} electrodes - and uncovers the existence of multiple PME values within mixed-cation systems.

These findings challenge conventional electrolyte models, revealing a more complex interplay between cations, adsorbates, and interfacial disorder. This talk will highlight how our computational-experimental synergy enables quantitative PME predictions, offering a powerful strategy for tuning electrochemical interfaces. By bridging experiment and computation, we provide a pathway for rational design of electrochemical interface for next-generation energy applications.

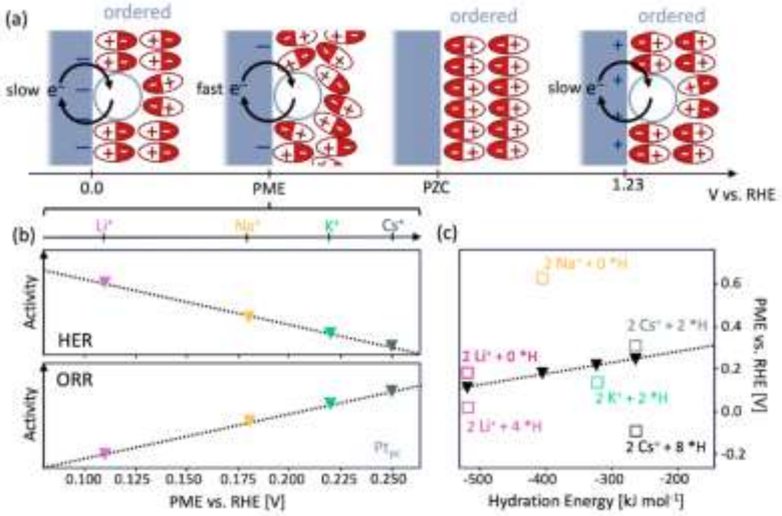

Figure 1. (a) At the PME, the interfacial water layer exhibits the highest disorder in the EDL. PME often aligns with the potential of zero charge (PZC). Grey circles indicate adsorbed species (e.g., intermediates) at the electrode surface. (b) Experimental PME trends [2] show that the hydrogen evolution reaction (HER) activity is enhanced by AM cations with higher hydration energies, while the opposite trend is observed for the oxygen reduction reaction (ORR). (c) Experimentally measured PME values (black) are co-plotted with computational predictions, highlighting the agreement between theory and experiment.

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Determination of the reaction volume $\Delta_R V$ of electrode processes, an approach to address the role of water in electrochemical reactions

Lisa V. Hirsch[1] **and Rolf Schuster**[1*]

[1] Karlsruhe Institute of Technology, Institute of Physical Chemistry, Karlsruhe, 76131 (Germany)

* rolf.schuster@kit.edu

Abstract

Water plays an important role for the energetics of electrochemical reactions. Apart from solvation of the ionic species in solution it impacts the structure of the interface and may strongly influence reaction pathways and transition states. [1,2]. Since water does not participate in the electrochemical current, electrochemical methods will yield rather indirect information on its role, e.g., from the behavior of the capacity and deviations from Gouy Chapman behavior [1]. Direct spectroscopic information is difficult to obtain, due to the large excess of bulk water.

Measuring the reaction volume may provide an alternative approach. The reaction volume gives the difference between the partial molar volumes of the products and reactants of a reaction. Beside the changes due to the intrinsic volumes of the reacting species the reaction volume is strongly influenced by the structure of water, which is sensitive to both, interaction with the strong fields near an ion in the bulk of the solution or in the double layer and structure making or breaking effects immanent to the chemical species.

We determine the reaction volume of electrode processes by measuring the response of the cell potential to a small pressure stimulus, similar to [3]. We couple a small pressure jump to the cell via a thin Teflon membrane and directly measure the potential variation. This method is tested by studying the Cu underpotential deposition (UPD) and sulfate adsorption on (111)-textured Au films in sulfuric acid. At highly positive potentials, where the electrode is covered by a densely packed sulfate adlayer, we found negligible reactions volumes for the electrode process, which is compatible with pure double layer charging. For potentials, where coadsorption of Cu and sulfate occurs, reaction volumes slightly above that of Cu bulk-deposition were found, signalling strong electrostriction of water in the Cu-sulfate UPD layer.

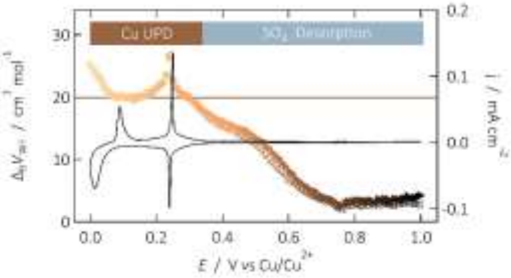

Figure 3 Reaction volume together with a Cyclic voltammogram (50 mV s^{-1}) for sulfate adsorption and underpotential deposition of copper on Au(111) from 10 mM Cu^{2+} in 0.1 M H_2SO_4. $\Delta_R V$ is given for the cathodic direction.

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Experimentally Quantifying Local Fields at Electrochemical Interfaces with the Vibrational Stark Effect

Yujin Tong[1*]

[1] University of Duisburg-Essen, Lotharstr. 1, D-47057 Duisburg, (Germany)

* Corresponding. yujin.tong@uni-due.de

Abstract

Understanding interfacial electric fields at electrochemical interfaces is crucial for elucidating charge transfer mechanisms, reaction kinetics, and electrocatalytic processes. The electrochemical vibrational Stark effect (EC-VSE) has emerged as a powerful tool to probe these fields at the molecular level. EC-VSE relies on the shift of vibrational frequencies of probe molecules in response to an external electric field, allowing for Ångstrom-scale mapping of local electrostatic environments. However, the conventional assumption of a linear relationship between vibrational frequency shift and field strength is increasingly challenged by experimental observations and theoretical studies [1,2].

This talk will explore the key factors influencing the accuracy of local field quantification via EC-VSE, including molecular symmetry changes under bias, strong-field effects, dipole-dipole coupling, and the structure of the electric double layer. Through a comparative analysis of various spectroscopic techniques — such as vibrational sum frequency generation (VSFG), infrared absorption, and surface-enhanced Raman spectroscopy (SERS) — we demonstrate how different interfacial environments influence vibrational Stark shifts and their interpretation. Particular emphasis will be placed on recent experimental findings that reveal nonlinear behaviors in EC-VSE and their implications for field estimation.

By critically examining the preconditions required for linear Stark tuning rate approximations, we aim to refine the methodologies for extracting reliable local field values from EC-VSE experiments. Ultimately, this work contributes to a deeper understanding of interfacial electrochemistry, with implications for energy conversion, molecular electronics, and catalysis.

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(Atomistic) simulations of electrochemical interfaces: Bridging experiment and structural insight

Katharina Doblhoff-Dier[1*]

[1] Leiden Institute of Chemistry, Leiden University, Leiden, Netherlands

* k.doblhoff-dier@lic.leidenuniv.nl

Abstract

Electrochemical processes are influenced on the atomic scale by the (structure of) the catalyst surface, (local) electric fields, and the (structure of) the electrolyte. Experiments often reveal the concerted effect of all these factors of influence, but it can be hard to reveal the (atomic scale) origin of an observation. Computational tools, on the other hand, have a difficult time to capture the entire (multi-scale) processes leading to a certain reaction outcome, but can help to reveal the (operando) structure of electrochemical interfaces, and – in particular – the electrolyte structure at the interface. This atomic scale insight can in turn be used to provide a physical interpretation for experimental observations and thus to foster rational design.

In this talk, I will discuss what we know (and do not know) about the potential profile at the interface that drives electrochemical reactions [1] (Figure 1) and discuss the behaviour of ions at charged interfaces and how this may influence electrochemical processes [2]. If time allows, I will also showcase how theoretical simulations at differing time and length scales can be used to reconcile seemingly contradictory experimental observations for the potential of zero charge and provide an atomic scale interpretation of the underlying effects [3].

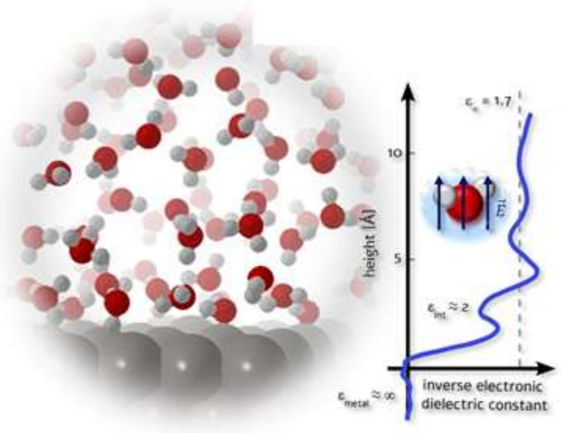

Figure 4. a) The electronic dielectric profile at the interface plays an important role in defining the potential profile at the interface. Using atomistic simulations and a combination of DFT simulations and machine learning approaches, the electronic dielectric profile at a Pt(111)/water interface can be computed [1]. **b)**

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Cation-anion interactions in the electric double layer resolved by in situ XPS

Sheena Louisia[1,2], **Rik Mom**[2] **and Marc Koper**[2*]

[1] CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, Paris, 75005 (France)

[2] Leiden Institute of Chemistry, Leiden, 2300 RA (Netherlands)

*m.koper@lic.leidenuniv.nl

Abstract

The application of X-ray photoelectron spectroscopy (XPS) for the study of electrochemical interfaces has seen some steady improvement over the last few years. So far, electrochemical XPS (EC-XPS), has enhanced our ability to monitor changes in the electrode's chemical composition during key reactions such as the hydrogen evolution reaction (HER) or the oxygen evolution reaction (OER). [1] Recent electrochemical studies have highlighted the crucial role water molecules and ionic species play during electrocatalytic processes [2], shifting the focus of interface investigation away from the surface toward the first molecular layers of electrolyte. Here, we combine the dip-and-pull geometry with EC-XPS to evaluate the composition and potential dependent response of electrolytic species at a metal-liquid interface. Using a polycrystalline Au foil in aqueous electrolytes, we compare the distribution of K^+ cations in the presence of non-specifically adsorbed (ClO_4^-) and chemically adsorbed anions (Cl^-). The application of EC-XPS to study these two systems reveals cation-anion interactions that stabilize a higher-than-expected concentration of K^+ cations within the double layer. Interestingly, this phenomenon observed with XPS is corroborated by electrochemical impedance spectroscopy (EIS) measurements. These results highlight how the application of EC-XPS to an electrochemical interface can offer new insights into the possible effects of cation-anion interactions on the double layer properties, possibly expanding our understanding of electrochemical interfaces beyond the classical Gouy-Chapman-Stern theory.

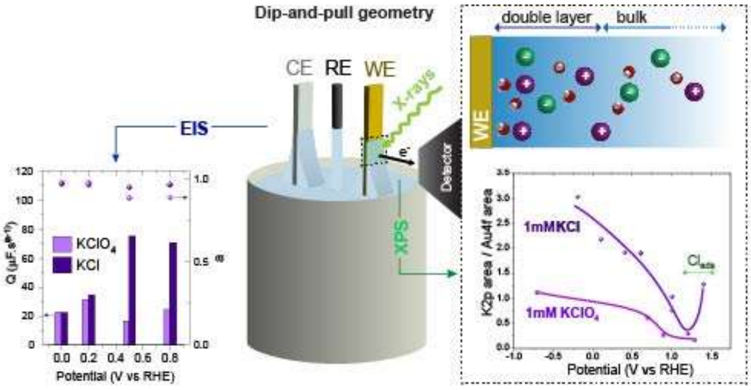

Figure 5. Comparison of a polycrystalline Au foil in 1 mM KCl and 1 mM $KClO_4$ indicates a stark capacitive difference using EIS (left) corroborated with a large K^+ cation concentration difference measured using EC-XPS (right) in the dip-and-pull geometry (center).

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The Effect of Interfacial pH Shift on Constant Current Hydrogen Evolution from Dilute Acids

Soma Vesztergom[1*], **Mária Ujvári**[1], **Zsolt Szakály**[1], **Peter Broekmann**[2], **Vitali Grozovski**[3]

[1] Eötvös Loránd University, H–1117 Budapest, Pázmány P. s. 1/A, Hungary

[2] University of Bern, CH–3012 Bern, Freiestrasse 3, Switzerland

[3] University of Tartu, EE–50411 Tartu, Ravila 14A, Estonia

* soma.vesztergom@ttk.elte.hu

Cathodic hydrogen generation from unstirred dilute acids (2<pH<7) often results in the vicinity of the electrode turning alkaline. Potential transients (Figure 1) recorded at constant current exhibit a sharp step at the moment of surface neutralisation, and the stepped chronopotentiograms convey important information with regard to the rate of both the electrode reaction and of reactant transport.

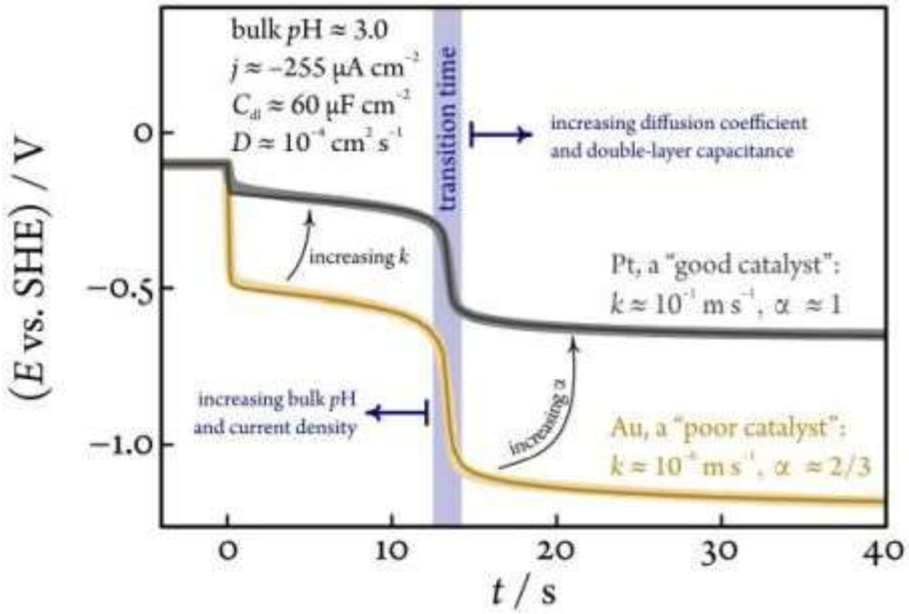

Figure 6. Chronopotentiograms of cathodic hydrogen evolution at two different (Au and Pt) electrodes, recorded in a mildly acidic solution. Measured data are plotted in light colours; the dark curves show fits based on the model presented in this contribution.

Here we present a robust model that, although it contains only three variable parameters, can fit experimentally obtained chronopotentiometric curves remarkably well. The reaction rate and charge transfer coefficients obtained from the fitting can be combined into a pH dependent exchange current density of the hydrogen evolution reaction. This parameter can be used for benchmarking the catalytic activity of different electrode materials, while the obtained diffusion coefficient can be applied in simple formulae to estimate the characteristic time of surface neutralisation and the rate of propagation of the neutrality front.

Shining Light on Active Site Transformations for Oxygen Evolution Reaction Catalysts in PEM Water Electrolysis

A. Lim,[1] M. Tesch[1], I. Spanos[1]*
[1]Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, 45470, Germany

* ioannis.spanos@cec.mpg.de

Abstract

Extending catalyst stability for the demanding oxygen evolution reaction (OER) in PEM water electrolysis, while at the same time keeping high catalytic activity and increasing catalyst utilization efficiency is challenging. Only the combination of operando spectro-electrochemistry can promote a deeper understanding on the interplay of different phenomena taking place during OER [1]. In this work we apply operando quick extended X-ray absorption fine structure spectroscopy (QEXAFS) and Surface Enhanced Raman Spectroscopy (SERS) [2] in order to identify the catalyst reactive species, follow their formation before OER which lead to final catalyst active phase and their dynamic transformation during a regeneration protocol which prolongs catalyst lifetime.

The underlying mechanisms studied via our operando analysis provide fundamental understanding of reaction mechanism but also guidance for the design of efficient OER catalysts optimized for their operation in technical devices.

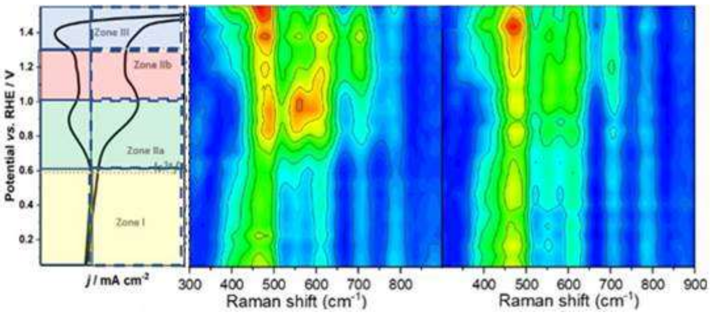

Figure 1. Operando SERS screening of potential-dependent transformation of μ_1 and μ_2 Iridium reactive species during cyclic voltammetry, leading to OER.

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Video-STM studies of atomic-scale sulfide and halide dynamics at electrochemical interfaces

Chaolong Yang[1], Reihaneh Amirbeigiarab[1], Sönke Buttenschön[2], Eckhard Pehlke[2*], and Olaf Magnussen[1*]
[1] Institute of Experimental and Applied Physics, Kiel University, 24098 Kiel (Germany)
[2] Institut für Theoretische Physik und Astrophysik
* pehlke@theo-physik.uni-kiel.de; magnussen@physik.uni-kiel.de

Atomic-scale processes at the electrode/electrolyte interface are keystones of many electrochemical reactions. In particular, strongly adsorbing species, such as halides, can substantially affect these processes. Here, we report new results on the molecular-scale dynamics of adsorbed sulfide and halides on Ag (100) and Au (100) electrode surfaces, obtained by electrochemical video-rate scanning tunneling microscopy (Video-STM) [1].

First, we report results on the surface diffusion of sulfur on Ag (100) in Br or I containing solution (Figure 1) [2]. At the positive end of the double layer range, where the halide coadsorbates form close-packed c(2x2) structures, the mobility of the atoms exponentially decreases with increasing potential, indicating a linear increase of the diffusion barrier with potential. However, in the negative potential range, where halides form a highly mobile lattice gas on the surface and the coverage increases with potential, a surprising increase in sulfide diffusion with potential is found. Furthermore, modelling of the Video-STM data suggests the presence of a second, minority diffusion pathway that always exhibits a positive potential dependence [3].

Second, the dynamics of adsorbed Br and S on Au(100) is discussed. Specifically, we observed the formation of Au_2Br_6 and Au_2S_2 complexes on the Au electrode. These complexes are stable, but can rotate and diffuse over the surface.

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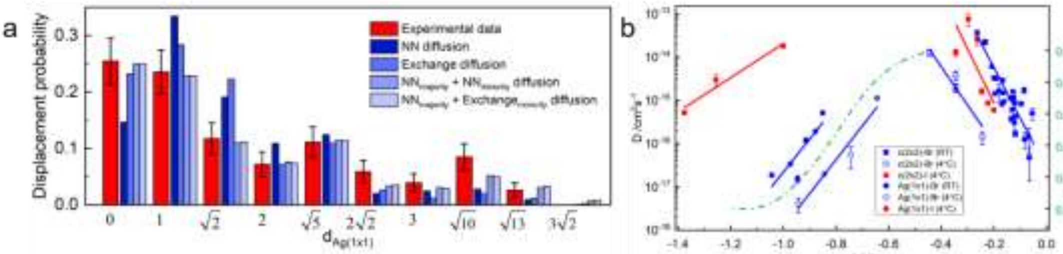

Figure 1. (a) Exemplary jump distribution function of the experimental data and best fits by 4 different models. (b) Potential dependent diffusion coefficients.

In-situ and nanoscopic corrosion studies using liquid-phase transmission electron microscopy

Arjan Mol[1*]

[1] Delft University of Technology, Department of Materials Science and Engineering, Delft, The Netherlands

* J.M.C.Mol@tudelft.nl

Abstract

High-strength aluminium alloys, widely applied in aerospace industries, may suffer from severe localized corrosion as a result of its relatively complex and heterogeneous microstructure. The corrosion initiation in such a critical alloy is governed by dynamic processes that take place at the nanoscale. A thorough understanding of the sequential stages of corrosion initiation is of pivotal importance to developing efficient inhibition strategies and demands high resolution techniques along with the ability of real-time recording of nanoscopic events.

However, until recently it has not been possible to unambiguously show the morphological and electrochemical characteristics during local corrosion of complex aluminium alloys. In particular, local corrosion initiation linked to nano- and microstructural heterogeneities, intermetallic particles (IMPs), take place relatively fast and at the nanoscopic scale, rendering the study of the early stages of corrosion experimentally extremely difficult. In our recent work, the dynamic evolution of site-specific local corrosion of aluminium alloys as from early-stage surface initiation at the nanoscale is studied, using a dedicated in-situ liquid phase-transmission electron microscopy (LP-TEM) experimental facility.

TEM, capable of revealing microstructural and compositional variations in alloys at atomic and nanoscopic scale, has been applied widely in corrosion studies but mostly ex-situ and quasi in-situ. These approaches are not straightforward as artefacts and contaminations might be introduced into the system during the ex-situ and quasi in-situ experiments, including dehydration of surfaces, and therefore may not fully represent the real conditions. With recent technological advances, thanks to the development of dedicated microelectronic mechanical systems (MEMS), it is now possible to fabricate components like nanoreactors (NRs) to study complicated corroding systems at the nanoscale in-situ. In fact, NRs employed in TEM studies enable to monitor morphological and compositional evolutions in materials in-situ as a result of interaction with aggressive environments like a gas or liquid [1].

We put efforts into providing direct evidence for the nanoscopic role of IMPs in aerospace aluminium alloy AA2024-T3 localized corrosion through quasi in-situ TEM and in-situ LP-TEM approaches. Quasi in-situ studies were implemented by intermittently exposing the Argon ion-milled thin samples to 0.01 M NaCl solution. For in-situ LP-TEM, the TEM specimens (lamellae) were first fabricated out of regions of interest with a FEI Helios focused ion beam. Then, the lamellae were transferred successfully to home-made NRs using the easy-lift technique. The NRs, equipped with an electrochemical configuration, were specially designed for corrosion studies. A Cs-corrected FEI Titan TEM was employed to perform real-time studies in scanning TEM (STEM) mode. Although a good resolution is still a major challenge for in-situ LP-TEM, the results revealed that intermetallic phases regardless of their types are active and prone sites to localized corrosion attack themselves and the observations finally show and elucidate initial stages of IMP-induced pitting corrosion and copper redistribution mechanisms in AA2024-T3 [2].

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Epitaxial Single-Domain Metal-Organic Framework (MOF) Thin Films by Electrodeposition

Jay A. Switzer,* **Xiaoting Zhang, John Z. Tubbesing**
Missouri University of Science and Technology, Rolla, MO 65409 (USA)
*jswitzer@mst.edu

Abstract

Metal-organic frameworks (MOFs) are highly porous materials that are built from metal ions coordinated by organic linker molecules.[1] Epitaxial MOFs with a single out-of-plane and in-plane orientation can produce films with a uniform pore size and open porosity. In previous work, we fabricated epitaxial single-domain Cu- BTC thin films by electrochemical conversion of Cu_2O, but the thickness of Cu-BTC was limited, and only the [111] orientation of Cu-BTC was achieved.[2]

In this presentation, we will discuss the production of epitaxial single-domain Cu-BTC MOF thin films by electrodeposition from solution precursors. The epitaxial Cu-BTC thin films were electrodeposited from a $Cu(NO_3)_2$-H_3BTC-H_2O_2 bath using H_2O_2 reduction to generate base to deprotonate the H_3BTC molecule. The Cu-BTC films can be grown to micrometer thicknesses, with Faradaic efficiencies up to 94%. Three different crystal orientations of epitaxial Cu-BTC thin films can be obtained with different substrates. Epitaxial single-domain Cu-BTC(100) grows on single-crystal Au(100) with a coincidence site lattice (CSL) mismatch of +1.11%. Epitaxial single-domain Cu-BTC(111) grows on epitaxial Cu_2O/Au(111) with a CSL mismatch of -0.91%. Twinned films of epitaxial Cu-BTC (110) are produced on Cu_2O/ Au(110) with a CSL mismatch of +0.12%. Epitaxial Cu-BTC(100) provides oriented square-shaped nano-channels with a 9 Å aperture, and epitaxial Cu-BTC(111) has oriented tetrahedral-shaped side pockets with triangular windows of internal diameter
3.5 Å.

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Electrochemical Synthesis of Laminated Structures for Inductor Application

Peter A. Quaye[1], Nafiseh Amiri[1] and Stanko R. Brankovic[1*]
[1] University of Houston, Houston, TX 77204, USA
* SRBrankovic@uh.edu

Abstract

Growing application of magnetic thin films and inductor chips for analog circuits in mobile phones, MEMS and defence sector technologies rise need for development of new alloys and structures with low energy losses during electromagnetic induction process. Miniaturization of the new device design require that these alloys and structures have the highest possible moment and resistivity in order to produce inductor chips with high specific inductance and minimum permeability loses related to Eddy currents[1,2].

We present work on development of electrodeposition process for 2.2-2.4 T CoFeX alloys and CoFeX/X laminated structures that show no permeability decrease over the wide frequency range up to 0.5 GHz. This is achieved by alloy bulk resistivity control adding a resistivity controlling element in the alloy X (X=O, P, C) and introducing a resistive barrier layer and lamination process to control the alloy layer thickness to be below the alloy skin depth. Therefore, achieving the structures with complete suppression of Eddy currents and lossless induction process. The schematics of deposition process is shown in Figure 1A. The one-laminate deposition includes a cycle consisting of two stages: (a)-CoFeX-alloy deposition (t_1, j_1) and (b)-electro-polymerization stage (PPY resistive barrier, t_2, E=-0.75 V). The process is repeated arbitrary number of times to create laminates with desired thickness. The representative data are shown in Figure 1B. The permeability and quality spectra from cavity induction measurements illustrate advantage of laminated structures over the bulk thin film alloy.

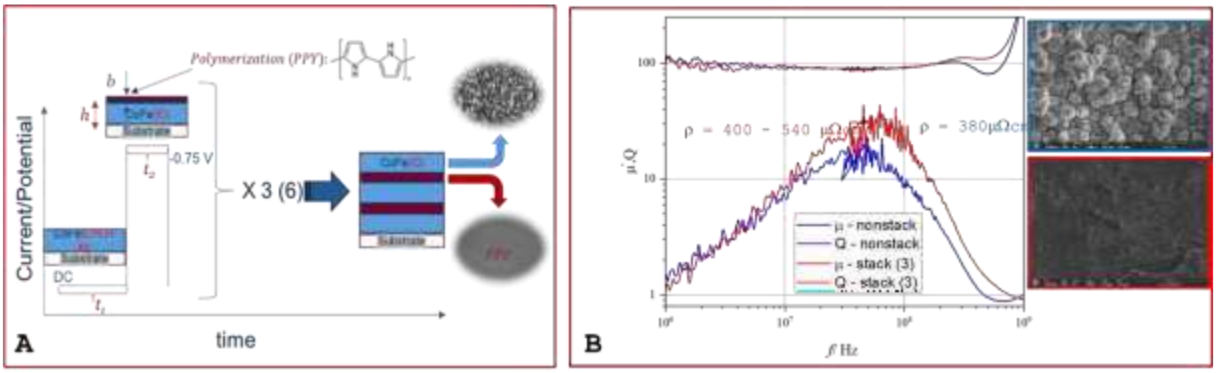

Figure 1. (A) Schematics of the laminate synthesis via electrodeposition and electro- polymerization steps. (B) Permeability and Q spectra from cavity measurements for thin film CoFeX alloy and CoFeX/X laminated structure. Insets show surface morphology of electrodeposits.

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Electrochemical Synthesis of High Entropy Nanoparticles and the Exploration of the AgAuPd composition space for the oxygen reduction reaction

Menglong Liu[1], Divyansh Gautam[1], Christian M. Clausen[2], Ahmad Tirmidzi[1], Gustav K.H. Wiberg[1], Jan Rossmeisl[2], and Matthias Arenz[1]*

[1] Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Bern, 3012 (Switzerland)

[2] Center for High Entropy Alloy Catalysis (CHEAC) Department of Chemistry, University of Copenhagen, KøbenhavnØ, 2100 (Denmark)

*matthias.arenz@dcb.unibe.ch

Abstract

Multi-metallic alloys such as high entropy alloys (HEAs) span an extensive compositional space, potentially offering materials with enhanced activity and stability for various catalytic reactions. However, experimentally identifying the optimal composition within this vast compositional space poses significant challenges. In this study, we present a medium-throughput approach to screen the composition – activity correlation of electrodeposited HEA nanoparticles. We apply the approach for exploring the **PdAgAu** composition subspace for the alkaline **Oxygen Reduction Reaction** (ORR). The PdAgAu alloy nanoparticles are synthesized electrochemically, characterized and evaluated for the ORR using a rotating disk electrode (RDE) setup. From 107 individual measurements, a **composition – activity correlation was constructed using Gaussian Process Regression**, pinpointing the optimal composition around Pd:Ag:Au = 86:7:7. The **experimental results are then compared to theoretical predictions** based on the well-established descriptor approach, results shown in Figure 1. This work provides valuable insights for the **efficient screening of multi-metallic catalysts for catalytic applications** and exemplifies advanced pathways on how to compare and analyse experimental data to simulations based on well-defined hypotheses.

Keywords: high entropy alloys, PdAgAu nanoparticles, oxygen reduction reaction, Gaussian Process Regression, composition-activity correlation.

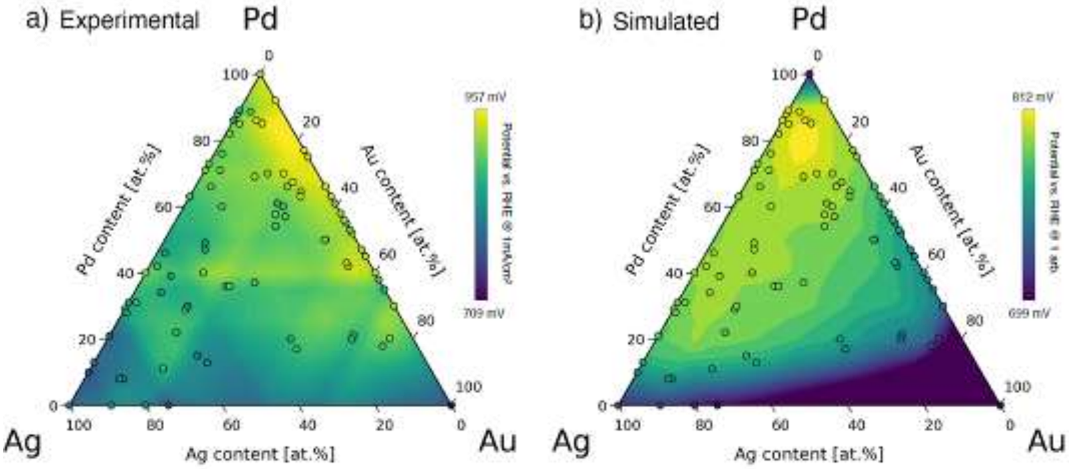

Figure 1. Composition-activity contour plots of experimental and simulated results

Four Personal Puzzles in Interfacial Electrochemistry

Jun Huang[1]*

[1] Institute of Energy Technologies, IET-3: Theory and Computation of Energy Materials, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

[2] Theory of Electrocatalytic Interfaces, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany

Email: ju.huang@fz-juelich.de

Abstract

It is a privilege for me to present my personal perspective on four persistent problems related to the structure and dynamics of electrochemical interfaces that have been puzzling me for the past decade, hoping that colleagues, especially younger researchers in the audience, will contribute to resolving them in the next decade.

The first puzzle is about the origin of constant phase element (CPE) I encountered in electrochemical impedance research.[1] There have been many explanations for the CPE in high frequency range, but none of them could explain the CPE in low-frequency range. In all these explanation schemes, CPE is associated with the frequency dispersion of the interfacial capacitance. I try to provide an explanation outside this category, which, trivially, attributes the low-frequency CPE to higher chance of side charge transfer processes in low-frequency range.

The second puzzle concerns the high capacitance values in the double-layer region of Pt(111) in weakly adsorbing electrolyte solutions. There are several explanations based on the premise that the capacitance is the double-layer capacitance corresponding to variation of the free charge density stored in the double layer upon potential change.[2,3] I will critically analyse measurements in the literature and will propose an alternative view where the capacitance is the total capacitance – the sum of double-layer capacitance and pseudo-capacitances of ionic adsorption processes.[4,5] A few observations on the cation and concentration dependence of the pseudo-capacitance will be given.

The third puzzle was met when we were developing density-potential functional theoretical (DPFT) approach with a statistical field theory of aqueous electrolyte solutions.[6] We found a criterion of the structural stability of liquid water, involving a few constants of water. The foundation of this mathematical criterion is unclear.

The last puzzle was found in benchmarking existing orbital-free kinetical energy functionals with exact results obtained from solving the Kohn-Sham equation, see a poster presented by Xiwei Wang in this symposium. We noticed persistent trends in the deviation between the popular Thomas-Fermi-von Weizsäcker theory and exact results. Understanding the origin will hopefully lead to the development of more accurate orbital-free methods for simulating electrochemical interfaces.

Acknowledgements

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Regulation of Electrocatalysts Based on Confinement-Induced Properties

Wei Ding *

[1] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331. (China)

* dingwei128@cqu.edu.cn

Abstract

The development of highly efficient and low-cost electrocatalysts is important for both hydrogen- and carbon-based energy technologies. The electronic structure and coordination features, particularly the coordination environment and the amount of low-coordination atoms, of the catalyst are key factors that determine their catalytic activity and stability in a particular reaction. The regulation and rational design of catalytic materials at the molecular and atomic levels are crucial to achieving precise chemical synthesis at the atomic scale. Recently, significant efforts have been made to engineer coordination features and electronic structures by reducing the particle size, tuning the composition of the edges, and exposing specific planes of crystals. Among these representative strategies, the methods based on the confinement effect are most effective for achieving precise chemical synthesis with atomic precision at the molecular and atomic levels. Under molecular or atomic scale confinement, the physicochemical properties are largely altered, and the chemical reactions as well as the catalytic process are completely changed. The unique spatial and dimensional properties of the confinement regulate the molecular structure, atomic arrangement, electron transfer, and other properties of matter in space. It not only adjusts the coordination environments to control the formation mechanism of active centers, but also influences the structural and electronic properties of electrocatalysts. Therefore, the adsorption of catalytic intermediates is altered, and consequently, the catalytic activity and selectivity are changed. The catalysts, produced by confinement significantly differ from those produced in an open system, showed unique advances in the field of fuel cells and material energy conversion.

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Single-particle/single-molecule microscopy of (photo)(electro)chemistry

Peng Chen*

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14854 (USA)

*pc252@cornell.edu

Abstract

This presentation will describe our recent work in developing and applying single-molecule/sub-particle-level imaging approaches to study photoelectrochemical and photoelectrocatalytic properties of semiconductor particles, important for many solar energy conversion technologies. In particular, it will present single-molecule super-resolution microscopy methods to image charge-carrier–selective redox reactions on single-particle photoelectrodes at nanometer resolution and measure sub-particle to whole-particle photoelectrochemistry, in correlation with ex situ scanning electron microscopy [1,2,3]. It will present the discovery of interfacet-junction effects on anisotropically shaped semiconductor particles that play key roles in their photoelectrochemical performance [3]. IT will also cover new super-resolution imaging methods to quantify molecular adsorption on surfaces of (photo)(electro)catalysts [2,4].

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Plasmon-enhanced electrochemistry as strategy for sustainable development

Susana I. Córdoba de Torresi[1*]
[1] Instituto de Química, Universidade de São Paulo, São Paulo, Brazil
* storresi@iq.usp.br

Abstract

Nanoelectrochemistry brings the advantage of using nanoparticles with unique properties when compared to their bulk counterparts. Among those properties, in the case of metals, there is the localized surface plasmon resonance (LSPR), which gives rise to valuable physical effects such as hot-carrier generation and local heating effect. However, not every metal presents the LSPR on the visible range of the spectrum and, thus, requires specific and costly apparatus to optimize LSPR outcomes. However, it makes a valuable challenge to tune the LSPR extinction band toward the visible spectrum through the rational design of nanoparticles. One strategy is to combine different metals with catalytic and plasmonic properties in hybrid nanostructures, allowing an improved energy harvesting and catalytic activity toward electrochemical reactions upon excitation at the visible spectrum. A systematic study of the synthesis of different bimetallic or hybrid semiconductor/metallic nanoestructures is presented. The materials exhibited the LSPR excitation in different regions of the visible range of the spectrum depending on their composition, size or geometry. Distinct electrochemical reactions were chosen to evaluate the LSPR excitation impact on the catalyst's activity and/or selectivity showing that each electrochemical reaction was affected differently by the LSPR excitation. This work provides a concise overview of the fundamental principles of LSPR; the mechanism of plasmon enhanced electrocatalysis; recent progress in plasmon-mediated electrocatalysis for the detection of analytes and the synthesis of chemicals such us green ammonia and urea. This idea is also to shed light on the areas where major advancements are required to further improve the field of plasmon-mediated electrocatalysis to achieve a major paradigm shift toward a sustainable future.

Acknowledgements

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Local Interrogation of the Electrified Solid-Liquid Interface with Force Microscopy

M. Aarts*[1], H. A. J. de Vries[1] and M.T.M Koper[1]
[1] Leiden Institute of Chemistry, Leiden, The Netherlands
*m.aarts@lic.leidenuniv.nl

Abstract

The electrified solid-liquid interface is inherently confined to the nanoscale, as potentials are rapidly screened by the reordering of charge in an electrical double layer (EDL) structure. Electrochemical rates are then determined by an interplay of the structure of both the solid electrode, as well as the liquid electrolyte. The nanometer length scale of the EDL poses challenges for its experimental characterization however. While the structure of the interface is highly localized and therefore spatially inhomogeneous on most practical electrodes, many conventional electrochemical techniques rely on macroscopic measurements.

We aim to tackle this issue using atomic force microscopy (AFM). While scanning probes excel at obtaining local topography, as the AFM probe interacts with the electrode surface inside the liquid medium, this **medium is also part of the region of interest** [1]. Indeed, AFM allows for continuous force measurements while the probe approaches/withdraws from the surface. These force-curves hold additional information on the local structure of the solid-liquid interface, such that both the solid electrode and the liquid electrolyte can be interrogated simultaneously.

We have recently demonstrated that force mapping is a powerful tool to observe potential-dependent electrode heterogeneities at the nanoscale [2]. In this contribution we use the AFM tip as a local electrostatic probe, interacting with the potential profile in the EDL. We employ metal probes to improve the force resolution at small tip radii (< 20 nm radius) as the surface charge on (insulating) silicon tips is strongly pH-dependent [3], which can be used in a bipotentiostat configuration for further control over the interaction force. We demonstrate the use of this method to visualize the evolution of the interface as a function of potential through the force curve (Figure 1). These potential-dependent force profiles are obtained on model gold electrodes in different electrolytes (varying pH, ionic strength, and ion identity) to extract **local** electrochemical quantities, such as the point of zero charge.

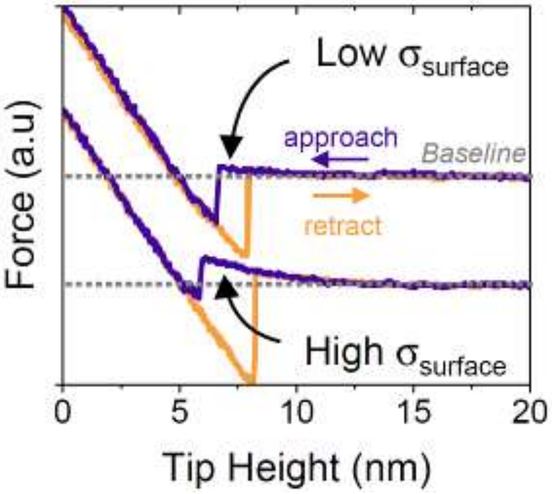

Figure 7. Force curves in 10 mM Na_2SO_4 for a polarized Pt AFM tip approaching a polarized gold electrode at different electrode potentials. The changing electrode surface charge ($\sigma_{surface}$) is evidenced by the repulsive (positive) interaction in the force profile.

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Ion Intercalation, Lattice Instability and Chemo-Mechanical Coupling in Electrocatalysts

Andrew Akbashev[1*]
[1] Paul Scherrer Institute, Villigen, 5232 (Switzerland)
* andrei.akbasheu@psi.ch

Abstract

When studying the stability of electrocatalysts, scientists mostly focus on the evolution of surfaces. However, electrocatalytic reactions can cause transformations in the bulk of the material, leading to a significant modification of their electronic and structural properties.

In my talk, I will focus on bulk transformations in electrocatalysts caused by intercalation reactions (mostly under oxygen evolution reaction). I will show how intercalation of ions can induce volumetric changes, chemo-mechanical coupling, anion redox and (ultimately) lattice instability in oxides and hydroxides. To study the nanoscale evolution of electrocatalysts, we had to employ a variety of characterization techniques - resonant inelastic X-ray spectroscopy (RIXS), *operando* X-ray/electron microscopy and atomic force microscopy, all performed on single-crystalline materials as model electrocatalysts. Our work highlights the need to account for the effects of ion insertion and de-insertion reactions on both stability and catalytic activity.

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Real-time Observation of the Solid-liquid Interface of Catalyst Electrode for Water Electrolysis by Soft X-ray Absorption Spectroscopy

Kaoruho Sakata[1*] **and Kenta Amemiya**[1]
[1] Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, 305-0801(Japan)
* kaoruho.sakata@kek.jp

Abstract

The oxygen evolution reaction (OER) of water electrolysis is bottleneck in electrochemical energy conversion compared with the hydrogen evolution reaction, therefore various studies have been attempted to improve the OER performance. However, it is still unclear about the detail of the reaction mechanism at the solid–liquid interface. In this study, the fluorescence-yield wavelength-dispersive X-ray absorption spectroscopy (XAS) in the soft X-ray region [1], which is recently developed in our group, was applied to observe the chemical states at the solid–liquid interface directly in real time during OER reaction. With this method, one spectrum with a photon energy range of ~ 10 eV can be obtained at once with a time resolution of ca. 3 ~ 10 s. For the electrochemical measurements during XAS observation, a dedicated electrochemical cell was attached to the XAS apparatus, and O K-edge and Co L-edge XAS data on the surface of a Co thin film working electrode, that is one of the effective OER catalysts was observed during sweeping the potential [2]. For the electrolyte, alkaline solution (NaOH, 0.1 M) was used. The three-electrode system comprised a Pt counter electrode and Ag/AgCl reference electrode (commercial one of BAS Inc.) which were inserted from the top of the cell (Fig. 1(a)). As results, when the electrode potential was shifted to a positive value, the peaks of the O K-edge at around 531 eV for molecule-like oxygen and around 529 eV for possibly precursor were detected, and the peak intensity changed in correlation with the electrode potential. The results can be expected to be one of the clues to clarify the electrochemical reaction mechanism at the solid–liquid interface of the OER catalysts. In addition, the reactions of Ru and Ru oxide OER catalysts in acidic media were also observed in the same manner (Fig. 1(b)) [3].

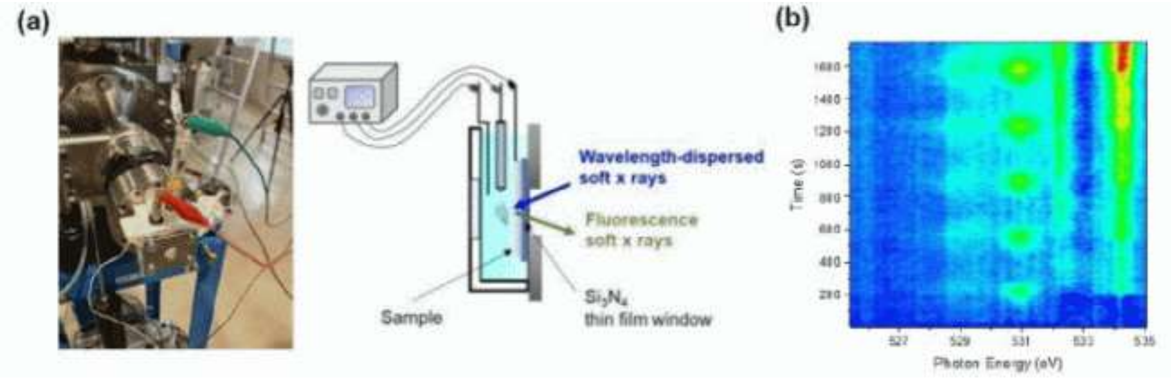

Figure 8. (a) Setup of the electrochemical cell for the XAS measurement, and **(b)** oxygen K-edge X-ray absorption spectra for Ru catalyst in acidic media during cyclic polarization in 0.1 M $HClO_4$ at 5 mV/s (the potential was swept from 0.5—1.3 V vs. Ag/AgCl). The map summarizes the development of the populations of oxygen containing species at the Ru surface during the first 5 cycles.

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Novel time-resolved soft X-ray absorption spectroscopy technique for *operando* observation of electrochemical reactions at solid-liquid Interface

Kenta Amemiya[1*] **and Kaoruho Sakata**[1]
[1] Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, 305-0801(Japan)
* kenta.amemiya@kek.jp

Abstract

The X-ray absorption spectroscopy is a powerful tool that enables quantitative identification of chemical species, and it has been used to observe electrochemical reactions at the solid-liquid interface. Although light elements such as oxygen play key roles in the electrochemical reactions, soft X rays are necessary to observe such elements, which makes the *operando* measurement for the solid-liquid interface difficult due to the short attenuation length of the soft X rays. Moreover, it usually takes a several minutes to record a soft X-ray absorption spectrum, so that there have been few reports on the time-resolved observation during the electrochemical reactions.

To overcome these drawbacks, a novel technique, fluorescence-yield wavelength-dispersive soft X-ray absorption spectroscopy, has been developed, by which an absorption spectrum is recorded in several seconds without scanning the monochromator [1]. The setup for the technique is schematically illustrated in Fig. 1. The wavelength-dispersed soft X rays, in which the wavelength (photon energy) continuously changes as a function of the position, illuminate the sample, and the emitted fluorescence X rays at each position are separately focused onto each position at a detector by two spherical mirrors. The absorption spectrum is obtained by plotting the intensity of fluorescence X rays as a function of the position on the detector. Moreover, a dedicated electrochemical reaction cell has been developed, in which the liquid electrolyte is separated from the beamline vacuum by a 200 nm-thick Si_3N_4 window, and a thin-film electrode and catalysts are supported on the Si_3N_4 window.

In this contribution, the principle of the developed technique will be presented in detail, as well as the examples for the real-time and *operando* observation of electrochemical reactions at the solid-liquid interface [2-4].

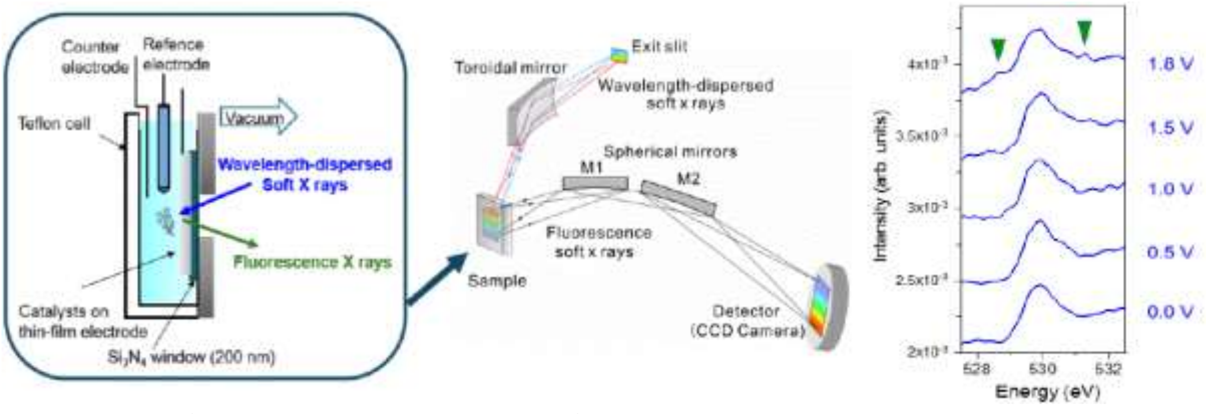

Figure 9. Setup for the wavelength-dispersive soft X-ray absorption spectroscopy with an electrochemical reaction cell (left), and oxygen K-edge X-ray absorption spectra for CoOx catalyst at different electrode potentials (right).

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In-situ Observation of the Structure and Performance Evolution for Atomic Fe–N_4 During Thermal Activation

Yanxia Jiang*, Shuhu Yin, and Shi-Gang Sun
Department of Chemistry, Xiamen University, Xiamen 361005, P. R. China
*yxjiang@xmu.edu.cn

Abstract

As sustainable and efficient oxygen reduction reaction (ORR) catalysts, Fe/N/C catalysts show great application potential[1]l. However, the preparation of Fe/N/C catalyst by pyrolysis is still a "black box". A thorough comprehension of the structural transformation of the Fe–N_4 active sites during thermal activation is essential to precisely regulate the catalytic performance of the Fe/N/C catalysts. In this work, in-situ heating XRD, TEM, XPS, XAS methods were designed to systematically study the structural evolution of atomic-scale from precusor $FeCl_2$ into Fe–N_4 sites during the thermal activation. It was determined that iron oxide was generated through thermal activation of the precursor, and the crystal phase of iron oxide underwent a complicated transformation process (Figure 1). The coordination arrangement of Fe atoms developed from Fe_2O_3 to Fe_3O_4 to FeO, and then into Fe–N_4 active site. Besides, the expansion, decomposition, diffusion, and "flow" of nanoparticles were directly observed. As the particle size of the formed FeOx nanoparticles increases beyond 10 nm, it can lead to severe particle aggregation; whileas the size of the nanoparticles below 7 nm, it can accomplish a 100% conversion of site density during the thermal activation process. Therefore, it is essential to regulate the size of the FeO_x nanoparticles so that it is below 7 nm. There are the following four suggestions for the rational design of Fe/N/C catalysts:(1) The FeO_x particle sizes must be reduced to less than 7 nm during pyrolysis process. With this, more Fe–N4 sites can be created; (2) Substances that decompose into acidic gases during the pyrolysis process, such as NH_4Cl, NH_4Br, and others, can be introduced. FeO_x can be produced and their development inhibited or even stopped by reacting with acidic gasses; (3) It is also possible to prevent iron oxide formation at its source, such as non-contact vapor deposition strategy[2]; (4) It is critical to investigate how the formed Fe active center may be employed effectively, such as the porous structure of catalyst are useful strategies for boosting site utilization. Overall, these strategies can be combined to improve the conversion and utilization of Fe active centers during pyrolysis process in high-performance Fe/N/C catalyst design.

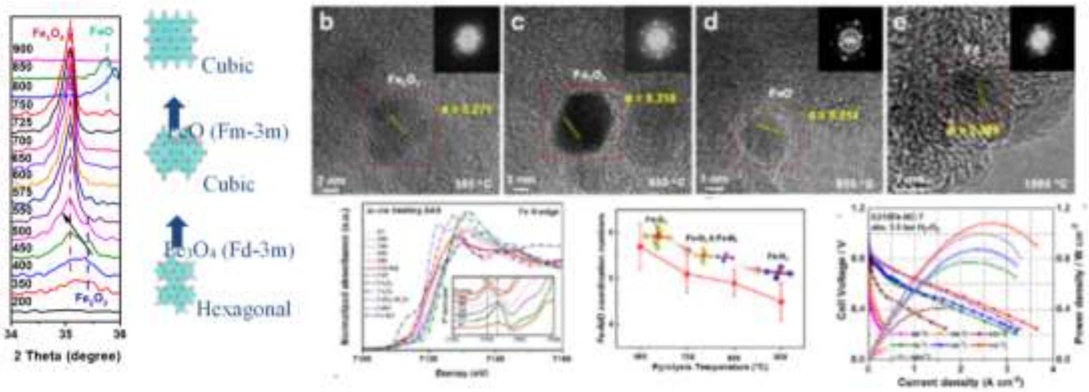

Figure 1. Left: In-situ heating XRD patterns of 0.015Fe-NC-T samples during in-situ heating experiments, and Right: Structure evolution of Fe precursor and performance of ORR. .

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Nanoscale insights into electrocatalyst surfaces and electrochemical interfaces

Christopher Kley[1*]

[1] Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, 14109 (Germany)

[2] Fritz Haber Institut der Max Planck Gesellschaft, Berlin, 14195 (Germany)

* christopher.kley@helmholtz-berlin.de

Abstract

In key electrocatalytic reactions such as $CO_{(2)}$ electroreduction ($CO_{(2)}R$) and oxygen evolution (OER), product selectivity and activity are strongly influenced by the nanoscale structure of electrode surfaces. Additionally, proton/electron transfer and reaction kinetics are highly sensitive to interfacial hydration structure, electrolyte/ionic composition, and surface-adsorbed species. Disentangling these structural and chemical factors, along with their dependence on applied potential, remains a fundamental challenge in electrocatalysis. In this talk, I will present our latest insights into (i) metal electrode reconstruction during $CO_{(2)}R$, (ii) reaction intermediates and interfacial hydration effects in CO_2R, (iii) the reversibility of surface *vs.* bulk transformations in OER catalysts, and (iv) interphasial viscosity variations in nanoconfined electrolytes. These findings are enabled by techniques including electrochemical atomic force microscopy (EC-AFM) and surface-enhanced infrared and Raman spectroscopy (SEIRAS, SHINERS). I will also discuss strategies for disentangling a catalyst's ensemble *vs.* local properties through nanoscale sensing of chemical and electrical properties.

Ticking the CO_2 clock with molecular control. From fuels to complex molecules

Marc Robert[1,2*]

[1] Sorbonne Université, Institut Parisien de Chimie Moléculaire, CNRS, F-75005, Paris (France)

[2] Institut Universitaire de France, F-75005, Paris (France)

* marc.robert@sorbonne-universite.fr

Abstract

Reduction of carbon dioxide has as main objective the production of useful chemicals and fuels - renewable fuels - in which solar energy would be stored. Molecular catalysts can be employed to reach this goal, either in photochemical or electrochemical (or combined) contexts. They may in particular provide excellent selectivity thanks to easy tuning of the electronic properties at the metal and of the ligand second and third coordination sphere. Based on thorough mechanistic studies, we have shown that such molecular catalysts may be tuned for generating all C1 products, including formaldehyde, methanol and methane, [1-5] but also C2+ products[6] and more complex molecules.[7] Our recent results will be discussed, using earth abundant metal (Fe, Co) porphyrins and phthalocyanines as well as related complexes as catalysts, being dispersed in solution or assembled at (semi)conductive materials.

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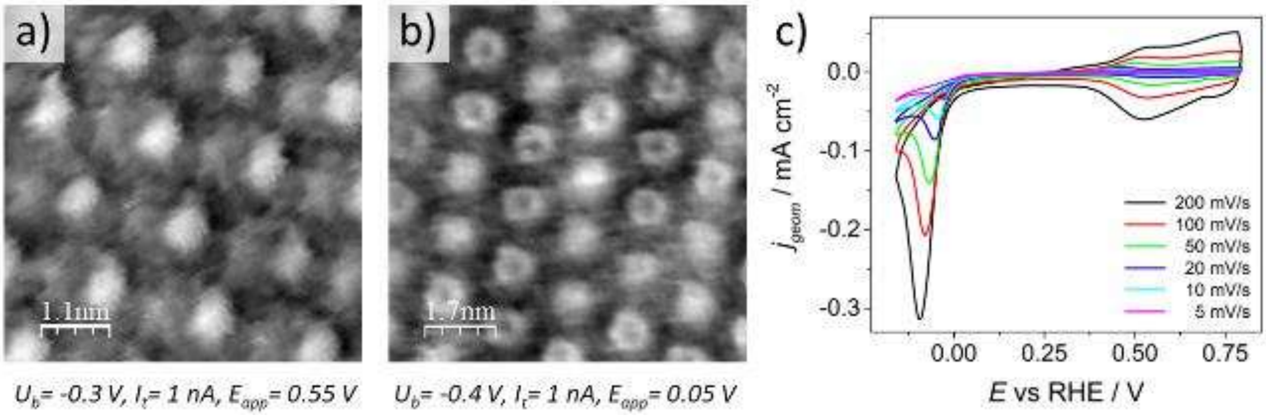
EC-STM investigation of Nitrate Reduction Reaction on iron-octaethylporphyrin adsorbed on Au(111)

Christian Durante*, **Silvio Reginato, Francesco Cazzadori**
University of Padova, Department of Chemical Sciences, via Marzolo, 1 - 35031 Padova, (Italy)
*christian.durante@unipd.it

Abstract

Nitrate reduction reaction (NO_3RR) is acquiring attention as an effective method to remove nitrate from drinking water and convert it to ammonia. The complete reduction to ammonia is recognized as a complex reaction, involving an $8e^-$ transfer and a variety of reaction pathways, each leading to different products. A promising candidate catalyst for this reaction is the M-N_4 single site, already known for its ability to catalyse oxygen reduction. Among 3*d* metals, iron exhibits good activity and selectivity towards ammonia [1] and has several benefits such as sustainability and low cost.

In this study, iron-octaethylporphyrins (FeOEP) adsorbed on an Au(111) single crystal are used to simulate the Fe-N_4 system. Their reactivity towards the reduction of various nitrogen oxides, specifically nitrate, nitrite, and nitric oxide, is investigated by EC-STM. A statistical method was then used to assess the differences in height and profile shape among the molecules. A bright, off-centre spot is observed on top of the molecules when nitrate is inserted into an acidic environment (fig. 1a), indicating a potential interaction with the active sites. However, in a neutral medium, no significant changes were revealed. In the case of nitrite, porphyrins were observed to adopt a "donut-like" structure when sufficient reductive potentials were applied (fig.1b); this behavior contrasts with the typical tunnelling shape of free-base octaethylporphyrins [3]. Furthermore, in the case of nitric oxide, a reduction peak was observed during cyclic voltammetry tests (fig. 1c), which differed from the electrochemical response of the previous species and allowed for direct observation of the active site activity.



U_b= -0.3 V, I_t= 1 nA, E_{app}= 0.55 V

U_b= -0.4 V, I_t= 1 nA, E_{app}= 0.05 V

Figure 1. High-resolution EC-STM images of FeOEP@Au(111) system in Ar-purged **a)** $HClO_4$ 0.1 M + HNO_3 1 µM and **b)** KNO_2 1 mM. **c)** Cyclic voltammetries of FeOEP@Au(111) system in NO-saturated $HClO_4$ 0.1 M.

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Electric Field Switching of Single Molecules in a Self-Assembled Monolayer

Stijn F. L. Mertens[1*]
[1] Department of Chemistry, Energy Lancaster and Materials Science Lancaster,
Lancaster University, Lancaster LA1 4YB (United Kingdom)
* s.mertens@lancaster.ac.uk

Abstract

In this talk, I shall discuss mechanisms for controlled switching of the structure and properties of 2D materials at solid–liquid interfaces, from the collective scale down to single-molecule manipulation, at ambient temperatures and pressures. The 2D materials are self-assembled structures of tailored organic molecules, and the switching events depend on tipping the balance between intermolecular and adsorbate–substrate interactions [1,2] through external stimuli: the interfacial potential at electrochemical solid–liquid interfaces [3-5], the chemical potential of ionic species in solution [6], or the electric field between an STM tip and the substrate [7], Figure 1.

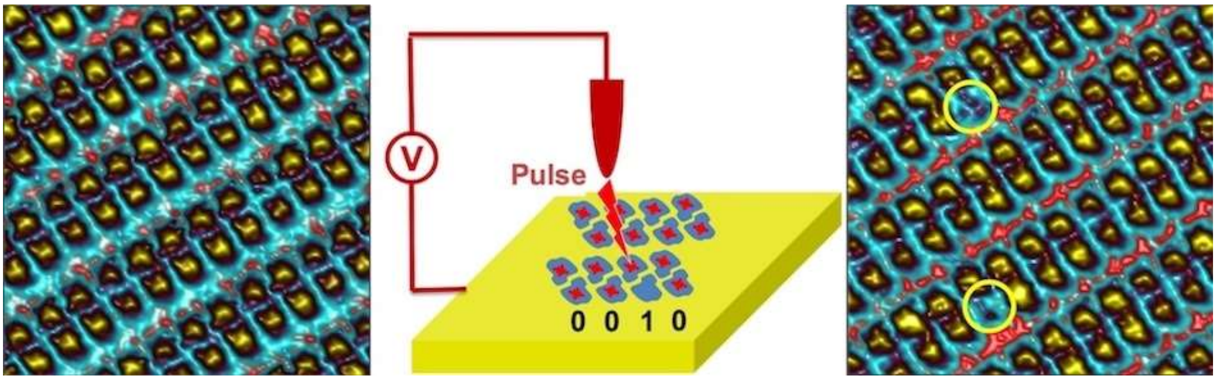

Figure 1. Scanning tunnelling micrograph of molecular monolayer before (left) and after (right) single-molecule switching.

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Long Distance Interprotein Electron Transport in Redox Proteins and Photosynthetic Complexes

Pau Gorostiza[1,2,3,*]

[1] Catalan Institution for Research and Advanced Studies (ICREA), Barcelona 08010

[2] Institute for Bioengineering of Catalonia (IBEC), Barcelona 08028

[3] Networking Biomedical Center in Bioengineering, Biomaterials, and Nanomedicine (CIBER-BBN), ISCIII, Madrid 28029

* pau@icrea.cat

Abstract

Interprotein electron transport is an essential process in cell respiration and photosynthesis. It takes place between redox proteins and complexes, and it displays an outstanding efficiency and environmental adaptability. Although the biochemistry of intraprotein electron transport processes is well characterized, nanoscale experimental methods are needed to understand the dynamics of inter-protein electron transport.

Electrochemical scanning tunneling microscopy (ECSTM) is a unique tool to study electronic materials and redox molecules including proteins. It offers single molecule resolution and allows working in aqueous solution, in nearly physiological conditions in the case of proteins, and under full electrochemical control [1]. ECSTM also allows performing conductance measurements by current-potential and current-distance tunneling spectroscopy [2], notably between cognate redox partner proteins.

Recent results of the laboratory in the respiratory [3, 4] and photosynthetic chains [5-8] (López-Martínez et al., 2019; Zamora et al., 2022; López-Ortiz et al., 2022 and 2023) will be discussed. They include the mechanism of long-distance electron transport between redox partner proteins through the aqueous solution, for example between cytochrome *c* - respiratory complex III [9], and between plastocyanin and photosystem I complexes [6, 7].

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ORR electrocatalysis on Fe-Octaethylporphyrin under the fast electrochemical scanning tunnelling microscope

Alessandro Facchin[1]*, **Friedrich Esch**[1]
[1]TUM School of Natural Sciences, Department of Chemistry, Chair of Physical Chemistry
Lichtenbergstr. 4, 85748 Garching (Germany)
* alessandro.facchin@tum.de

Abstract

To study electrocatalytic activity at the atomic scale, with elevated time resolution and under electrochemical potential control, we have implemented an add-on Fast-SPM (scanning probe microscopy) control module [1] into our electrochemical scanning tunneling microscope (EC-STM). We present recent results on the activity of single iron centers carried by octaethylporphyrin molecules (FeOEP) in the oxygen reduction reaction (ORR) on Au(111).

Instead of using a dedicated, fast instrument, [2,3] we accelerate a standard beetle-type EC-STM (Wandelt-type [4]). The FastSPM module allows (i) to take constant height movies (time resolution ~100 ms), (ii) to track single features under lateral and vertical feedback (time resolution ~500 µs), and (iii) to precisely position the tip on surface features for fast current detection (time resolution 5 µs).

In the EC-STM, movies taken in phosphate buffer electrolyte, either purged with Ar or saturated with O2, show reliable imaging over extended periods with high drift stability. We distinguish the Fe(III)/Fe(II) reduction upon appropriate working electrode potential variation and the adsorption of oxygen and its reduction reaction. Furthermore, the movies reveal the porphyrin mobility and the intermediate formation of confined, metastable phosphate adlayers upon potential cycling.

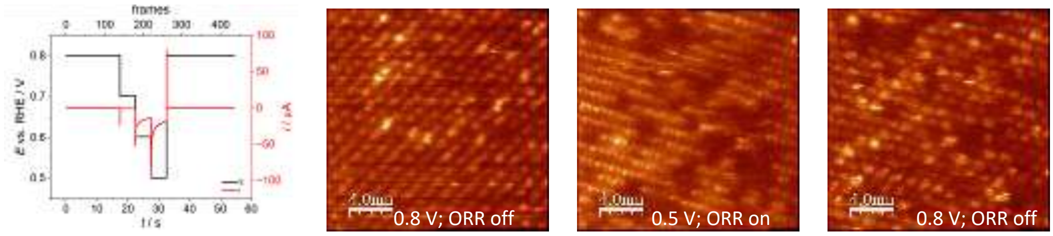

Figure 1. Chronoamperometric time series (left) and corresponding EC-STM frames (right) of FeOEP/Au(111) in O2-saturated phosphate buffer at pH 7. Image size: 20x20 nm2, tip bias +0.05 VRHE, tunneling current 3 nA, 8 frames per second (the black inset indicates the frame number).

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Electrooxidation of organic molecules on $Ni(OH)_2$/NiOOH

A. Medrano-Banda[1@], X. Shen[2], A. Bonnefont[3], A.G. Oshchepkov[1], T. Asset[1], E.R. Savinova[1*]

[1] ICPEES, UMR 7515 CNRS-University of Strasbourg, Strasbourg 6700 (France)
[@]Present address: Argonne National Laboratory, Lemont IL 60439 (USA)
[2] IC, UMR 7177 CNRS-University of Strasbourg, Strasbourg 67000 (France)
[3] LEPMI, UMR 5279 CNRS-Grenoble INP, Grenoble 38000 (France)
* Elena.Savinova@unistra.fr

Abstract

Ni and NiFe oxyhydroxides are among the most widely studied catalytic materials for the oxygen evolution reaction (OER) in alkaline media. It is however well known that along with water oxidation, NiOOH catalyses oxidation of various organic molecules. Fleischmann et al [1] have rationalized electrocatalysis on NiOOH electrodes through an EC' mechanism whereby $Ni(OH)_2$, in an electrochemical step, is converted in NiOOH, the latter reacting with a dissolved organic molecule in a chemical step recovering the $Ni(OH)_2$ species. This mechanism, however, is challenged in some recent publications.

Anodic oxidation of organic molecules occurring at potentials below the OER, has attracted much attention as the means to produce "green" hydrogen at lower voltages than required by the water electrolysis [2, 3].

In this presentation we will compare oxidation of various organic molecules (glucose and other sugars, mono alcohols, diols, urea, etc) on $Ni(OH)_2$/NiOOH [4-8]. We combine electrochemistry, operando spectroscopies and microkinetic modelling to unveil reaction mechanisms and understand why for some molecules the reaction 'onset' overlaps with the $Ni(OH)_2$/NiOOH phase transition, while for others the oxidation occurs at significantly lower potentials. We will show that Ni^{3+} species can be detected by operando X-ray absorption spectroscopy at potentials below the main peak of the $Ni(OH)_2$/NiOOH phase transition [6]. Armed with all the experimental and modelling results, we will then discuss tentative role of α-$Ni(OH)_2$/γ-NiOOH and the β-$Ni(OH)_2$/β-NiOOH phase transitions in the oxidation of various organic molecules.

Acknowledgements

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Studies of PEMFC Non-Precious Metal Catalysts

Yu-Cheng Wang, Zhi-You Zhou, Yan-Xia Jiang, Hong-Gang Liao, Shi-Gang Sun*
State Key Laboratory of surface and Interface Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China.
*sgsun@xmu.edu.cn

Abstract

The Proton Exchange Membrane Fuel Cells (PEMFCs) convert directly, and high-efficiently chemical energy stored in fuel molecules or hydrogen into electricity, and play a key role in the carbon neutralization target and hydrogen energy society. At present, platinum-based materials are the unique and un-replaceable catalysts employed in PEMFCs, while the rare resource and high price of platinum metals restricted the commercial wide applications of the PEMFCs. Due to the extremely sluggish kinetics of oxygen reduction reaction (ORR) at cathode of PEMFCs, 90% of total Pt amount used in a PEMFC is currently loaded in cathode, which presents the main obstacle in fast development of PEMFCs. Therefore, exploration of non-precious metal ORR catalysts (NPM-ORR catalysts) becomes urgent and challenging.

Extensive works have been done in past decades to develop NPM-ORR catalysts. Although key progresses and even breakthroughs reported[1,2], 3 key problems remain to be solved, i.e., the catalytic activity, the stability and the degradation mechanism. We have focused on these key problems and made significant progresses in recent years[3-18], including (1) Exploring the performance degradation mechanism of NPM-ORR catalyst by ·OH radical attacking, and enhancing the stability by introducing ·OH scavenger into the NPM-ORR catalysts; (2) Based on understanding the formation process of Fe-N4 active catalytic center through in-situ/Operando techniques, designing “surfaceization" strategy to increase significant the density of Fe-N4 sites, thus boosting the catalytic activity. Our achievements result unceasingly breaking records of high-power output of PEMFCs using the developed NPM-ORR catalysts.

Acknowledgements:

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The potential-dependent structure of Pt_3Ni alloy electrocatalysts and its effect on electrocatalytic activity

H.J Nagra, Leiden Institute of Chemistry, Leiden University

R.V. Mom, Leiden Institute of Chemistry, Leiden University

The distribution of elements within alloy nanoparticles is a critical parameter for their electrocatalytic performance. Here, we use the case of a Pt Ni alloy to show that this elemental distribution can dynamically respond to the applied potential, leading to strongly potential-dependent catalytic properties. Starting from the Pt-Ni core, Pt shell structure that Pt-Ni alloys form in acid electrolyte due to Ni leaching, our electrochemical X-ray photoelectron spectroscopy measurements show that the Ni atoms can be reversibly moved between the core of the particles and the near-surface region using the applied potential. Through potential jump measurements, we show that this Ni migration modulates the hydrogen evolution reaction activity of the particles by over 30% which is found to be stable over the long term. These observations highlight the potential of incorporating in situ restructuring of alloys as the final step in electrocatalyst design.

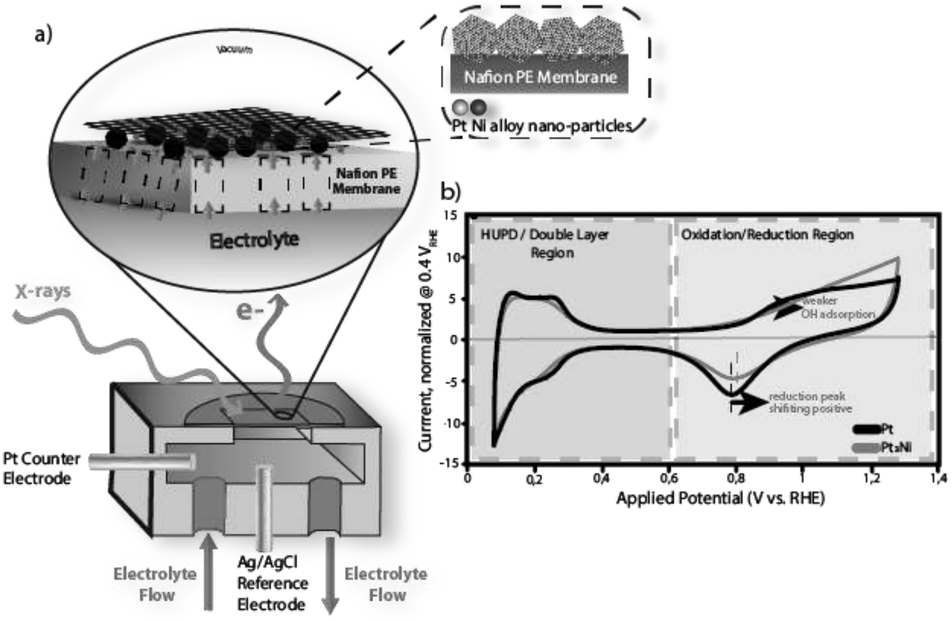

Figure j: Cell for electrochemical XPS measurements containing an MEA consisting of the Pt_3Ni catalyst sandwiched between a Nafion membrane and a bi-layer graphene. b) cyclic voltammograms of Pt and Pt_3Ni catalysts recorded in the XPS cell in 0.1 M H_2SO_4 at 50 mVs^{-1} ; highlighting Hydrogen Underpotential Deposition (HUPD), Double Layer (DL) and oxidation/reduction regions

Multi-modal X-ray characterization to probe amorphization of oxygen-evolving electrocatalysts

Rebecca K. Pittkowski*
Department of Chemistry, University of Copenhagen, Copenhagen, 2100 Denmark
* rebecca.pittkowski@chem.ku.dk

Abstract

Electrocatalytic water splitting is a key technology for using hydrogen as an energy vector. Catalyzing the oxygen evolution reaction (OER) effectively is especially important, as it is the kinetically more hindered reaction. For polymer electrolyte membrane (PEM) electrolysis, precious metals like Ir and Ru are, used which need to be used as efficiently as possible.[1] Nanoparticles (NPs) provide high surface-to-bulk-atom ratios required for minimizing the catalyst amounts. However, small NPs suffer frequently from instability in electrochemical environments, and the underlying degradation mechanisms and structural rearrangements are, so far, not fully understood

Synchrotron X-ray techniques using hard X-rays provide a set of valuable tools to probe the catalyst's structural changes during operation. The high penetration power of high-energy X-rays allows us through i*n-situ* and *operando* to monitor the evolution of atomic structures.[2] We can track changes in size and morphology with small-angle X-ray scattering (SAXS), while X-ray total scattering with PDF analysis provides insights into the atomic structure. Additional X-ray absorption spectroscopy measurements give insights into changes in the electronic structure of the catalyst material. When combining these characterization techniques in a multi-modal approach, it becomes possible to fully elucidate the structure of the NP catalyst under operating conditions.

With this approach, we could determine the structure of electrochemically oxidized Ir NPs. While the average NP size remains 1.5 nm, the catalytically active oxide only has a rutile structured local order in a cluster size or circa 8 Å. This difference can be attributed to the formation of an amorphous surface oxide. An Ir-O bond contraction is observed, which is confirmed as oxidation by XAS. Our analysis highlights the disordered nature of the OER active iridium oxide structure which could only be revealed by this multi-modal approach.[3] For a NiFeOOH catalyst in alkaline media, we found contrarily that no amorphization took place at OER conditions, but that the particles were decreasing in size due to dissolution.[4] This highlight the importance of precise structural characterization under operating conditions, to determine real structure-property relations.

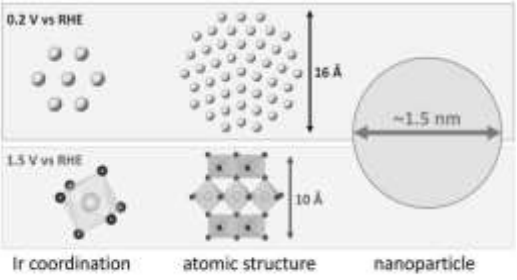

Figure 11. Information from *operando* characterization of Ir catalysts at different length scales

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Insights from Operando ATR-FTIR Spectroscopy on Pt-CO Interaction in the Presence of Ionomer: From Surface-Adsorbed Species to the Interfacial Electrolyte Composition and Structure

Alexandr G. Oshchepkov[1]*, **Tristan Asset**[1], **Elena R. Savinova**[1]
[1] ICPEES, UMR 7515 CNRS-University of Strasbourg, Strasbourg 67087 (France)
* aoshchepkov@unistra.fr

Abstract

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIRS) has emerged as one of the most powerful optical techniques for probing *operando* adsorbed species and recently gained particular attention when studying the electrode/electrolyte interface [1]. The electrooxidation of CO on Pt has been widely studied with *operando* ATR-FTIRS on single-crystal electrodes. However, little is known about the influence of the ionomer on the CO adsorption on Pt/C and especially on the composition and structure of the interfacial electrolyte, despite their likely impact on electrocatalytic performance [2].

In this talk, we will discuss how the use of *operando* ATR-FTIR spectroscopy can help to understand the effect of Nafion® ionomer on the acidic hydrogen oxidation reaction (HOR) on Pt/C in the presence of CO. While rotating disk electrode (RDE) data evidence the influence of the Nafion to Carbon ratio on the Pt surface depoisoning from pre-adsorbed CO (Figs. 1a,b), ATR-FTIRS results highlight differences in CO adsorption characteristics on Pt/C surfaces with and without ionomer (Fig. 1c). They also hint towards the influence of the ionomer on the interfacial water structure (Fig. 1d) and the potential of zero charge of Pt surface indirectly probed through monitoring perchlorate ion presence near the interface (Figs. 1b, d). These insights into complex interactions between the Pt surface, ionomer, electrolyte, hydrogen, and CO can aid in developing catalysts with enhanced CO tolerance.

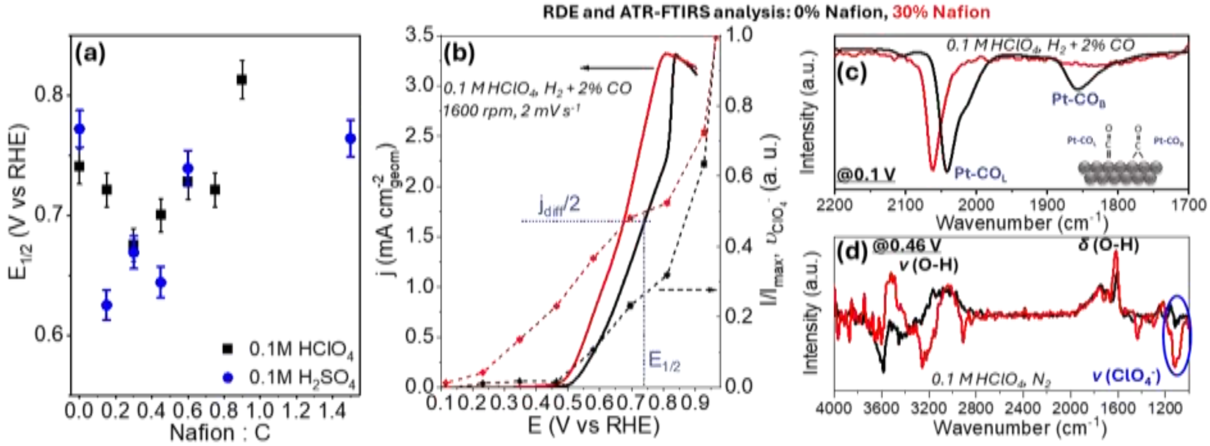

Figure 12. Effect of Nafion® concentration in the catalytic layer on (a) the half-wave potential ($E_{1/2}$) of the HOR diffusion currents derived from (b) RDE cyclic voltammograms for CO-poisoned Pt/C (solid curves); (c, d) difference spectra in the intervals of (c) 1700 – 2200 cm^{-1} (showing C-O vibrations at 0.1 V vs RHE), and (d) 1000 – 4000 cm^{-1} (showing vibrations of interfacial water and ClO_4^- anions at 0.46 V vs RHE). Dashed curves in panel (b) show the change in the normalized intensity of the ClO_4^- band with potential.

Acknowledgments

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Dynamic Structural Transformations in IrRu Catalysts during Oxygen Evolution Reaction.

H. Nedumkulam[1,2], T. Hrbek[2], M. Zlatar[3], S. Cherevko[3], I. Martens[1], M. Mirolo[1], P. Kůš[2], and J. Drnec[1*]

[1] ESRF, Grenoble, France, [2] Charles University, Prague, Czech Republic, [3] Forschungszentrum Jülich, Erlangen, Germany
* drnec@esrf.fr

Abstract

The electrocatalysis of the oxygen evolution reaction (OER) is crucial for the hydrogen economy. However, optimizing materials for this reaction is challenging due to the low stability of many highly active materials during activation and/or operation. Therefore, operando methods that can examine catalyst structure and morphology in operating electrochemical cells are essential for tracking transformations that cause deactivation and changes in activity.

An interesting class of catalysts for acidic water electrolysis is IrRu alloys. While pure Ir is a relatively stable catalyst, its activity is mediocre in acidic environments. On the other hand, Ru is an excellent catalyst for OER, but its stability in acidic environments is poor. Interestingly, the addition of a small amount of Ir to Ru makes the catalyst both more active and more stable than pure Ir [1,2].

We find that this counterintuitive result originates from the reorganization of the starting material at the atomic scale[3]. The complex structure of magnetron sputtered alloys undergoes rapid dissolution of both constituents when the electrode is polarized to OER conditions. This causes the formation of an IrO_x shell, which is more durable and active for structures with a rich Ru core. Operando WAXS measurements at high current densities and ICP-MS characterization reveal the intricate interplay between the dissolution rates and the morphology of the active material (Figure 1). The oxidation state of the surface Ir species indicates the formation of Ir^{4+} states at the expense of the less stable Ir^{3+} state. However, in this case, the Ir^{4+} also exhibits high activity, which we assign to the electronic interaction with the Ru core.

This discovery is not only fundamentally important for understanding the true active state of the material, but it can also guide the development of future Ir-based catalysts. The observed phenomenon likely extends beyond the bimetallic IrRu system and is likely common in other materials [4] that meet the requirements for efficient catalysis by reducing the price due to low Ir loading and extending the lifetime through controllable in-situ structural transformation.

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Tuning the Electrooxidation of C_1 Compounds by Adjusting the Surface Concentration Foreign Elements in Nanoporous Gold

Gunther Wittstock*[1] Alex. R. Silva Olaya[1] and Franziska Kühling[1*]
[1] Carl von Ossietzky University Oldenburg, School of Mathematics and Science, Institute of Chemistry, Oldenburg, 26129 (Germany)
* gunther.wittstock@uni-oldenburg.de

Nanoporous gold (NPG) is obtained by dealloying of an Au alloy with a less noble metal, e.g., Ag. It consists of struts, called ligaments, and pores with tunable sizes in the nanometer range. Despite an exhaustive removal of Ag during the dealloying process, Ag is never removed completely from NPG and may segregate to the surface during storage under air or during prolonged cycling in alkaline media.[1] The content of the less noble element or other elements deliberately deposited on the porous electrode surface have a pronounce effect on the catalytic activity for various reaction and were probed here for the oxidation of methanol and other C1 compounds.

Cyclic voltammetry of powdered material in cavity microelectrodes in alkaline media is a suitable technique to verify the presence of residual Ag without removing it or provoking coarsening.[2] The concentration of surface Ag can be manipulated by potential cycling the material in acidic solution to remove Ag from the surface of the ligaments and then deliberately dosing specific amounts of Ag to the surface by a potential-controlled under-potential deposition (UPD). Residual Ag has a prominent effect on the electrooxidation of methanol, formaldehyde and formate in alkaline media at NPG with different residual Ag content and in comparison to flat Au[3,4] and to nanoporous gold that is free of other metals due to a different preparation.[5]

The effect of surface Ag is significantly different in different potential ranges. Ag shifts the onset potential to a less positive value at the metallic surface. At oxide-covered surface, it enables the oxidation of methanol and formate at potential where no reaction occurs on pure gold.

The results were corroborated by XPS for surface composition, EDX for bulk concentration[6] and NMR for product identification.[4] Reaction sites were identified by selective blocking of surface sites by Pb UPD in alkaline solution.[3] Ag is suggested to act as a promoter during the abstraction of the ⍰-H atom in the rate-determining step.

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Electrochemical reduction of CO2 into long-chain hydrocarbons

Boon Siang Yeo[1,*]
[1] National University of Singapore, Singapore 117543
* chmyeos@nus.edu.sg

Abstract

We share our recent works related to the development of catalysts for the electroreduction of CO2 and CO feedstocks to C1-C6 alkanes and alkenes, which can be used as chemicals and fuels. We shall show how we probe the mechanistic pathways by which these products were formed by using probe molecules and density functional theory calculations. In particular, we reveal (a) the active sites of the catalysts at the nanometer scale, and (b) how the selectivities of the products, such as their linear / branching ratios, could be controlled. The electrocatalysts that were found to work well were unexpectedly based on nickel and cobalt, rather than copper, which is more generally known to electroreduce CO2 to C1-C3 products. Reasons for these differences in product selectivities would be discussed.

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Probing the mechanism of cation-enhanced CO_2 reduction on copper in acidic media

Zhi-Ming Zhang, Zhi-You Zhou, Tao Wang[1*], Shi-Gang Sun

[1] State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China

* twangxm@xmu.edu.cn

Abstract

Modulating the electric double layer through cations is a well-established strategy to enhance the efficiency of the CO_2 reduction reaction (CO_2RR). However, the underlying mechanism of cation-enhanced CO_2RR kinetics remains unclear. In this talk, we identify adsorbed CO_2 as a key intermediate using in situ attenuated total reflection surface-enhanced infrared absorption spectroscopy on Cu in an acidic electrolyte. Our findings show that adsorbed CO_2 only appears in the presence of cations. Time-resolved infrared spectra reveal that Li^+ enhances CO_2 adsorption more effectively than larger cations, but it also slows the hydrogenation kinetics of CO_2. Ab initio molecular dynamics simulations, along with spectroscopic data on water, indicate that the rigid water network around Li^+ restricts the approach of water protons to adsorbed CO_2. In contrast, larger cations like Na^+ create more flexible water networks that facilitate water reorientation, enhancing the proximity of hydrogen to CO_2 and thus improving CO_2RR.

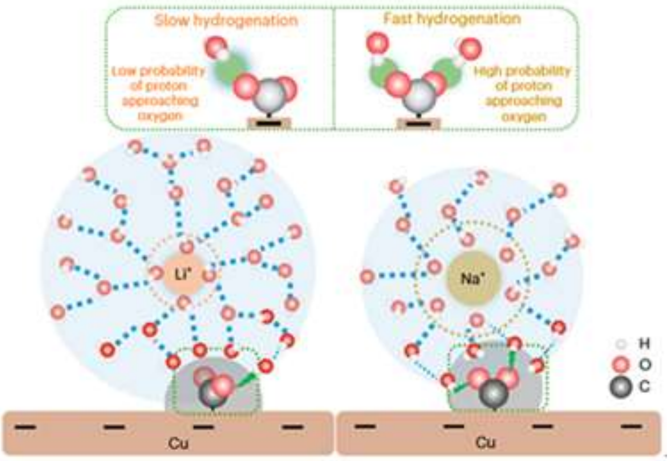

Figure 13. Figure example with appropriate caption format.

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How to address statistical relevance of data in electrocatalysis research?

Matthias Arenz*
[1] Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Bern, 3012 (Switzerland)
* matthias.arenz@unibe.ch

Abstract

The presentation of experimental data in electrocatalysis often lacks a clear discussion of statistical relevance, raising questions about reproducibility and data selection. Catalyst activity studies, for example, frequently report results without error bars and rely on representative data, leaving uncertainty about the true variability of measurements. When error bars are included, they are typically based on the standard deviation of only a few measurements, while more informative statistical tools, such as box plots, remain largely underutilized in electrocatalysis research. Additionally, it is often unclear whether all collected data are reported or if a selection process has taken place. While excluding experimental outliers, such as false negatives, can be justified to avoid misinterpretation, the criteria for such decisions are not always transparently communicated. In this talk, we critically examine these issues and explore strategies to improve the statistical robustness of electrocatalysis research. Drawing from our experience with NiFe metal foams for the alkaline oxygen evolution reaction (OER) [1] and high-entropy alloys for the oxygen reduction reaction (ORR), we discuss approaches to enhance data reporting practices, increase transparency in data selection, and ensure meaningful statistical interpretation in electrocatalytic studies.

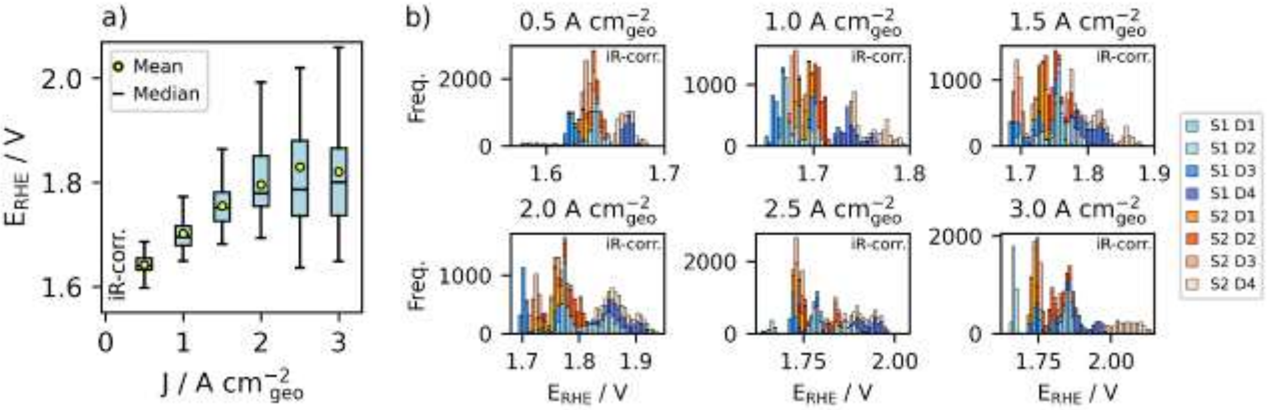

Figure 14. Summary of OER data of NiFe alloy foam, including data from eight individual measurements derived from two syntheses (S1 and S2). (a) Box plot of the potential required at different applied current densities in pulsed electrolysis measurements. It is seen that while mean and median values are aligned at lower current densities, the mean deviated to slightly higher potentials than the median at current densities above 2 A cm^{-2}. By consulting the respective histograms shown in (b), the data structure is clarified, and the contribution of each sample can be identified. The blue scheme depicts the four disks (D1-D4) of the initial synthesis, whereas the red scheme illustrates the disks from the repeated synthesis. Outliers are not shown, and bin size is not specifically normalized. Figure taken from ref. [1]. Copy right by the authors. Open access article under the CC BY license

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Electroreduction of Acetone on Pt/Ru Model Catalysts: The Interplay of Structure, Activity, and Selectivity

Robert Hübsch[1], Pankaj Kumar Samal[2], Frederike Jäschke[1], Tomáš Skála[2], Nataliya Tsud[2], Josef Mysliveček[2], Yaroslava Lykhach[1*], Olaf Brummel[1*], Jörg Libuda[1]

[1]Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

[2]Department of Surface and Plasma Science, Charles University, Prague, Czech Republic

* olaf.brummel@fau.de
* yaroslava.lykhach@fau.de

Abstract

The isopropanol/acetone system functions as an electrochemically active liquid organic hydrogen carrier (EC-LOHC).[1] [2] PtRu-based alloys are state-of-the-art catalysts for isopropanol electrooxidation.[1] [3] Utilizing the same alloys to catalyze the reverse reaction enables a complete conversion cycle between isopropanol and acetone within a single device.

In this study, we investigated the electrochemical reduction of acetone on well-defined Pt_xRu_{1-x} model surface alloys, prepared by surface science methods, with varying surface compositions. Our approach combined cyclic voltammetry (CV), ex-situ emersion synchrotron radiation photoelectron spectroscopy (SRPES), electrochemical infrared reflection absorption spectroscopy (EC-IRRAS), and differential electrochemical mass spectrometry (DEMS).

Through a systematic analysis, we established the structure-activity relationship for both well-ordered Pt_xRu_{1-x} alloys and surfaces subjected to a dealloying process. We found that the catalytically active state corresponds to ultra-small Pt aggregates supported on partially oxidized Ru(0001). This active state forms via dealloying and cannot be replicated by depositing ultra-small Pt aggregates on Ru(0001) in ultrahigh vacuum. Unlike Pt(110), which primarily produces the decomposition product propane,[4] the dealloyed catalysts selectively yield the target product isopropanol while suppressing propane formation.

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Understanding the impact of boron doping in methylated amorphous silicon electrodes for Li-ion batteries

Ngoc Tram Phung,[1] Yue Feng,[1] Catherine Henry de Villeneuve,[1] Michel Rosso[1] and François Ozanam[1*]

[1] PMC, CNRS, Ecole polytechnique, IP Paris, Palaiseau, 91120 (France)
* francois.ozanam@polytechnique.edu

Boron is a classical p-type dopant for silicon. In silicon electrodes for Li-ion batteries, it has been introduced for enhancing the material conductivity. However, this approach does not solve the major drawbacks of silicon electrodes, mechanical instability and imperfect surface passivation upon electrochemical cycling. Methylated amorphous silicon, a material deposited as thin films, has been shown to partially alleviate mechanical limitations as compared to pure (crystalline or amorphous) silicon. However, it is a resistive material: boron doping enhances its conductivity making the material better suited to battery applications. Surprisingly, as shown in the Figure below, doping also improves the stability of the material upon electrochemical cycling. The possible origins of this improvement are discussed.

The first most obvious origin of improved performance is the increase of the material conductivity, which decreases Ohmic losses. However, it does not appear to be the major factor of the improvement. Indeed, phosphorus doping is not as effective as boron doping [1], though it brings a comparable increase of the material conductivity.

Boron doping also affects the material mechanical properties. Methylated amorphous silicon is a material softer than amorphous silicon, ant it is thought to be the origin of its improved cycling performance. Boron doping makes methylated amorphous even softer [2]. The origin of the boron impact on the material hardness remains somewhat speculative, but a positive consequence of boron addition is to make the use of thicker electrodes possible.

A final benefice of boron addition could be sought for in terms of change in surface chemistry of the boron-doped material. We have investigated this possibility using operando infrared spectroscopy. Overall, the results show that boron doping efficiently limits the growth of the passivation layer and affects its composition, especially when combined to a high enough concentration of methyl groups in the material.

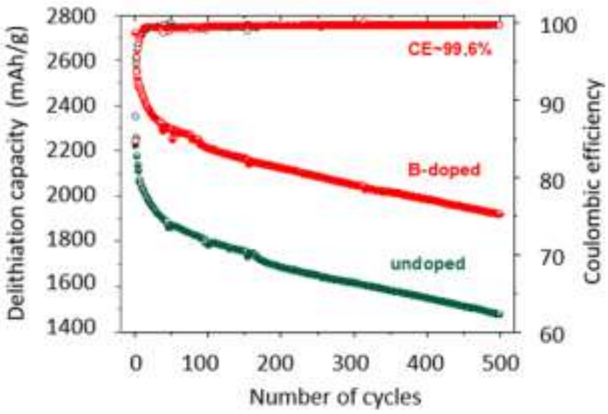

Figure. Delithiation capacity and Coulombic efficiency of 10% methylated amorphous Si thin-film electrodes as a function of the number of lithiation/delithiation cycles, for an undoped (green symbols) or a boron-doped (red symbols) electrode.

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Abstracts

Poster presentations

P 01

In situ HEGISAXS studies of the nanoscale restructuring mechanism of platinum single crystal electrodes

Jan Ole Fehrs[1*], **Timo Fuchs**[1], **Fabian Schröfel**[1], **Finn Schröter**[1], **Barbara Schröder**[1], **Jing Tian**[1], **Nick Merkel**[1], **Simon Kempf**[1], **Jakub Drnec**[2], **Valentín Briega-Martos**[3], **Serhiy Cherevko**[3], **Olaf Magnussen**[1*]

[1] Christian-Albrechts-Universität zu Kiel, Christian-Albrechts-Platz 4, 24118 Kiel (Germany);
[2] European Synchrotron Radiation Facility, 71 Av. des Martyrs, 38000 Grenoble (France);
[3] Forschungszentrum Jülich GmbH, Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IET-2), Cauerstr. 1, 91058 Erlangen (Germany)

**** fehrs@physik.uni-kiel.de, magnussen@physik.uni-kiel.de***

Platinum (Pt) electrocatalysts play a key role in polymer electrolyte membrane fuel cells (PEMFCs) due to their excellent activity and stability for the oxygen reduction reaction (ORR). Despite this, their long-term durability remains a significant challenge, mainly due to Pt dissolution and irreversible nanoscale restructuring during oxidation/reduction cycles (ORCs). While operando X-ray scattering studies have shed light on Pt oxidation and dissolution mechanisms [1–3], the link between Pt dissolution and nanoscale morphological changes is still under debate [3-5].

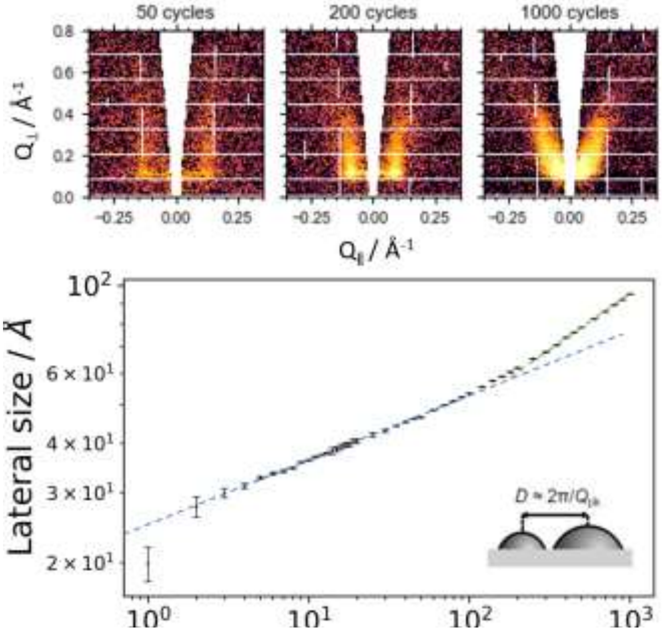

Figure 1: *Top:* HEGISAXS images of the Pt(100) sample after different numbers of ORCs up to 1.62 V vs. RHE in 0.1 M $HClO_4$. *Bottom:* Lateral size of the Pt nanoisland as a function of ORC count.

To address this uncertainty, our group has explored Pt oxidation using in situ surface crystallography [1,2] and grazing incidence small-angle X-ray scattering (GISAXS) [3], supported by Pt dissolution measurements and density functional theory. High-energy GISAXS (HEGISAXS) has revealed isotropic nanoscale mound formation on Pt(111) and Pt(100), and anisotropic features on Pt(110), following scaling behaviors that shift after approximately 100 ORCs in 0.1 M $HClO_4$. However, restructuring beyond 200 cycles has remained unexplored. Our most recent study focuses on this extended cycling regime using in situ HEGISAXS, specifically examining Pt(111) and Pt(100) surfaces in 0.1 M $HClO_4$ up to ~1000 ORCs and potentials as high as 1.62 V, where a crossover to mound facetting is observed. We show that this behavior can be explained by the atomic scale structure of the Pt surface oxide. By providing deeper insight into Pt surface evolution under prolonged ORC conditions, this work contributes to the broader understanding of Pt degradation in practical PEMFC environments.

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P 02

Structural insights into the electrochemical double layer on Pt(111) by in situ surface X-ray diffraction

Finn Schröter[1], Jan Ole Fehrs[1], Barbara Schröder[1], Andrea Sartori[2], Pol Salles Perramon[2], Jakub Drnec[2], Olaf Magnussen[1]*

1 Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24118 Kiel, Germany

2 European Synchrotron Radiation Facility, 38000 Grenoble, France

magnussen@physik.uni-kiel.de

Abstract

The structure of the electrochemical double layer at electrode surfaces is of key interest for understanding interfacial properties and electrochemical reactivity. Current progresses in ab initio molecular dynamics (AIMD) simulations allow a detailed description of the interface structure [1], but experimental verification of these predictions is still scarce. In the measurements presented here, we use high energy surface X-ray diffraction (HESXRD) to investigate the structure of the electrochemical double layer on single-crystal Platinum electrodes. The Pt(111) surface is arguably the most studied system for fundamental studies of electrode-electrolyte interfaces. Recent electrochemical measurements revisited this system and found evidence of a double layer structure that strongly deviated from the traditional Gouy-Chapman-Stern model. A structural influence of interfacial water has been proposed as a possible explanation for the deviations close to the potential of zero charge (PZC) [2,3]. Subsequent AIMD simulations indicate a voltage-dependent formation of layers of interfacial water molecules at distinct Pt(111)-water distances between 2-3 Å [4].

To investigate the arrangement of water molecules and ions near the Pt(111) surface we performed detailed measurements of the specular and non-specular crystal truncation rods (CTR) at beamline ID31 of the European Synchrotron Radiation Facility using photon energies of 75 keV. The fast, high-quality data acquisition allows significantly improved structural modelling compared to conventional SXRD. We will report first results on the structure of the interfacial water in the double layer at potentials around the PZC. In particular, we find significant potential-dependent shifts in the position of the first water layer, in good agreement with the predictions by AIMD.

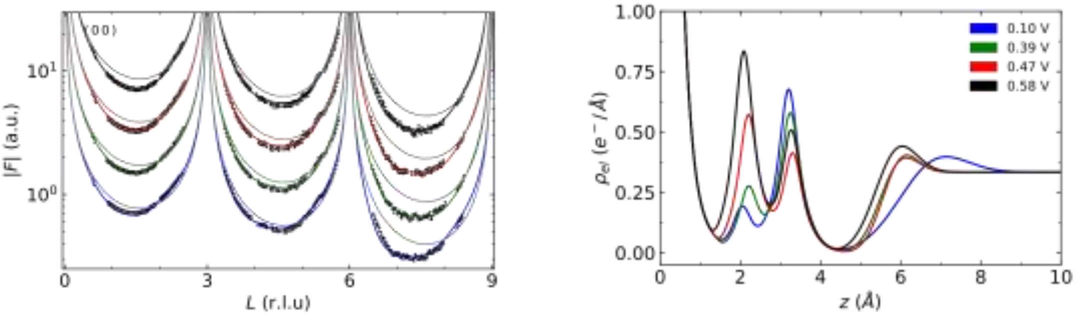

Figure 2. Specular CTRs and best fits of Pt(111) in 1 mM $HClO_4$ close to ϕ_{pzc} (left) and corresponding water density profiles along the surface normal direction (right), showing a potential-dependent rearrangement of the interfacial water.

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P 03

Operando interfacial investigation on copper-based model catalysts for CO_2 electroreduction

Jing Tian[1*], Carl Hendric Scharf[1], Jonas Bunge[1], Jan Ole Fehrs[1], Alex Chandraraj[1], Eric Liberra[2], Matias Herran[2], Arno Bergmann[2], Jochim Stettner[1], Beatriz Roldan Cuenya[2], Olaf Magnussen[1]
[1] Kiel University, Kiel, 24118 (Germany)
[2] Fritz-Haber-Institute of Max Plank Society, Berlin, 14195 (Germany)
***tian@physik.uni-kiel.de**

The electrochemical carbon dioxide reduction reaction (CO_2RR) driven directly by renewable electricity to produce high energy density C_2 products (e.g. ethylene, ethanol) offers a sustainable development strategy. This approach not only enables the storage of intermittent renewable energy, but also promotes the development of a carbon-neutral economy.[1,2] Despite its promising potential, the industrial implementation of this technology faces critical challenges, including low product selectivity, insufficient energy conversion efficiency, and poor catalyst stability. These challenges stem primarily from the lack of in-depth understanding of the nature of electrochemical solid-liquid interfaces, especially the characteristics under working conditions. As the critical active center for electrocatalytic reactions, the metal-electrolyte interface undergoes inevitable structural reconstruction during operation. The conventional research paradigm that relies on static interface fail to fully elucidate the structure-performance relationship of catalytic reactions. The development of in-situ/operando characterization technologies provide new opportunities for probing the dynamic evolution of these interfaces.[3,4] Here, the interface of Cu(100) based model catalyst systems under CO_2RR conditions were studied by operando surface X-ray diffraction (SXRD) and operando surface-enhanced Raman spectroscopy (SERS).

Specifically, we performed operando SXRD studies of Cu(100) electrodes that were decorated by submonolayer coverages of Ag in form of Ag(111) monolayer islands,[5] Crystal truncation rods (CTRs) of these electrodes were recorded in $KHCO_3$ solution at different potentials from the double layer (0 V) to the CO_2RR (-1.1 V) regime. The obtained results show a pronounced potential dependence of the interface structure. In particular, notable changes are observed below -0.4 V, i.e., in the potential regime where CO2RR starts.

Further in situ SXRD studies reveal the influence of cations on the interface structure of Cu(100) electrode and bicarbonate electrolyte. Specifically, we find notable differences in the intensity distribution along specular rod (00L) for Cs ions as compared to Li and K ions. In addition, SERS provides additional insights into cation effects on surface adsorbed species. As the potential decreases, the Raman signal of adsorbed CO appears, while in the presence of Cs ions, distinct Raman features attributable to hydroxyl or hydroxide species are observed.

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P 04

Ionomer adsorption in catalyst inks as a function of ink solvent composition using contrast-variation small angle neutron scattering

M. Y. Stando[1]*, **L. Porcar[1], A. Morin[2], G. Gebel[2,3], J. Drnec[4], S. Cotte[5]**

[1] Institut Laue-Langevin, [2] CEA-LITEN, [3] Université Grenoble Alpes, [4] The European Synchrotron Radiation Facility, [5] Toyota Motor Europe

*** Martha.y.stando@gmail.com**

Abstract

Proton exchange membrane fuel cell (PEMFC) based electric vehicles have been recognized as a promising zero-emission alternative to conventional vehicles, yet large scale commercialization requires progress in performance, cost, and durability, for which the catalyst layer (CL) is the most limiting component. Composed of Pt nanoparticle catalyst supported on carbon, embedded in a proton conductive ionomer, the CL is manufactured from a slurry where the above-mentioned components are dispersed in an alcohol/water mixture solvent. Although it is evident the structure of the CL has a direct impact on electrochemical performance, its structure, along with that of the ink it is manufactured from, remains largely unknown, leaving optimization reliant on a trial-and-error approach.

Developing a fundamental understanding of the catalyst ink structure is a promising starting point for optimization of the final CL structure and therefore electrochemical performance. Contrast variation small angle scattering (CV-SANS) is a suitable technique for structural analysis of multi-component, complex systems such as the catalyst ink and CL.[1,2] Due to the ease with which the contrast term can be adjusted through isotopic substitution of hydrogen by deuterium in the solvent system, scattering from undesired components can be minimized. Further scattering function deconvolution into partial scattering functions (PSFs) allows for structural analysis of each component that makes up the ink separately.

The effect of isopropanol (iPrOH) concentration in the ink solvent system on the degree of adsorption of ionomer to carbon particles was investigated using CV-SANS and extracted PSFs. Analysis of the ink structure suggested preferential adsorption of ionomer to Pt/C particles in a water-rich, 25:75 wt% iPrOH/water solvent (25PtHNP). Additionally, the increased degree of adsorption observed in the ink could be correlated to increased size domains related to the ionomer in resulting catalyst layers, as well as reduced proton transport resistance during electrochemical characterization.

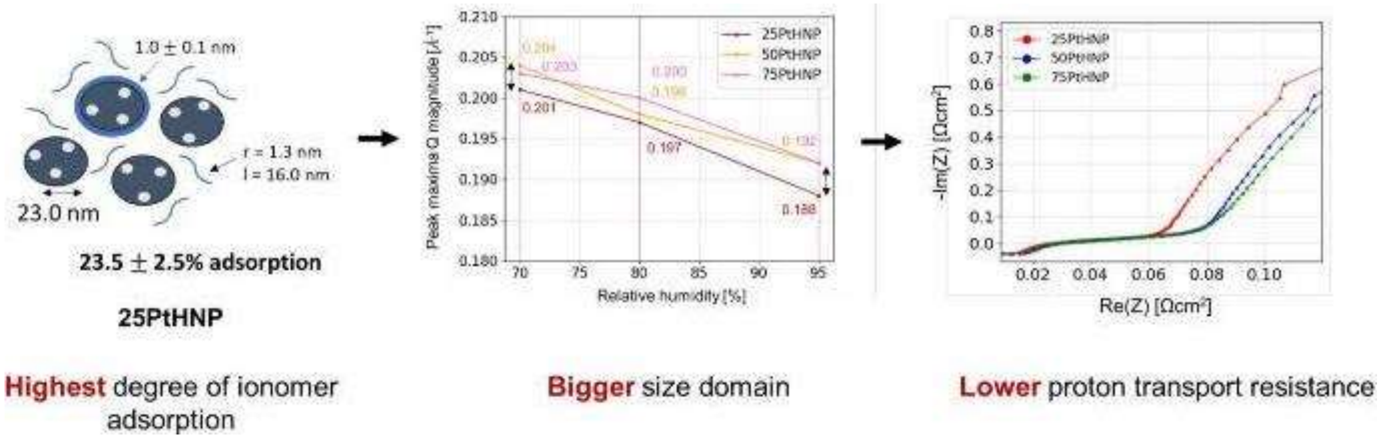

Figure 1. Correlation of catalyst ink/layer structures and impact on resulting electrochemical characterization.

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P 05

ETHYLENE GLYCOL PARTIAL OXIDATION ON Co_3O_4 (001) SURFACE: PATHWAY TO TWO- AND FOUR-ELECTRON PRODUCTS AND INTERPLAY BETWEEN SOLUTE'S SURFACE COVERAGE AND AQUEOUS SOLVATION

F. B. S. Nkou[1], and S. Kenmoe[1*]

[1] Department of Theoretical Chemistry, University of Duisburg-Essen, Universitätstr.2, D-45141, Essen (Germany)

*** stephane.kenmoe@uni-due.de**

Abstract

The oxidation of 2-propanol to acetone at the Co_3O_4 (001)/H_2O interface has been recently studied using ab-initio molecular dynamics to understand the roles of temperature, surface structure, and electrochemical environment [1]. In the same vein, we now study the case of a more complex molecule, namely ethylene glycol, on the same metal oxide surface to understand its oxidation processes. We study the system under both dry and humid conditions on the A- and B-terminated surfaces of Co_3O_4 at room temperature (300 K). Under dry conditions, a chemical reaction occurs, as the glycol coverage increases, with only a deprotonated ethylenedioxy compound formed as the oxidation product after a 20 ps simulation. We then considered cases with **varying ethylene glycol coverages**, both solvated and unsolvated in a **hydroxylated water film**. As expected, increased coverage results in more chemical reactions, including proton exchange and transfer, with products such as **glycolaldehyde**, **acetate**, **glycolic acid, glyoxal, hydrogen peroxide** and **dioxygen evolution**. We conclude that not only **water molecules play a key role in the oxidation process**, but the concentration of the diol and the presence of hydroxyl groups (both adsorbed and in the liquid film) act as proton donor and acceptors. Our work provides insight into the complex interplay between key factors governing the two-electron partial oxidation: **the role of solvation**, the relevant **solute's concentration range**, the **size of the active surface regions** as well as the **chemical state of interfacial water and its competition with ethylene glycol**.

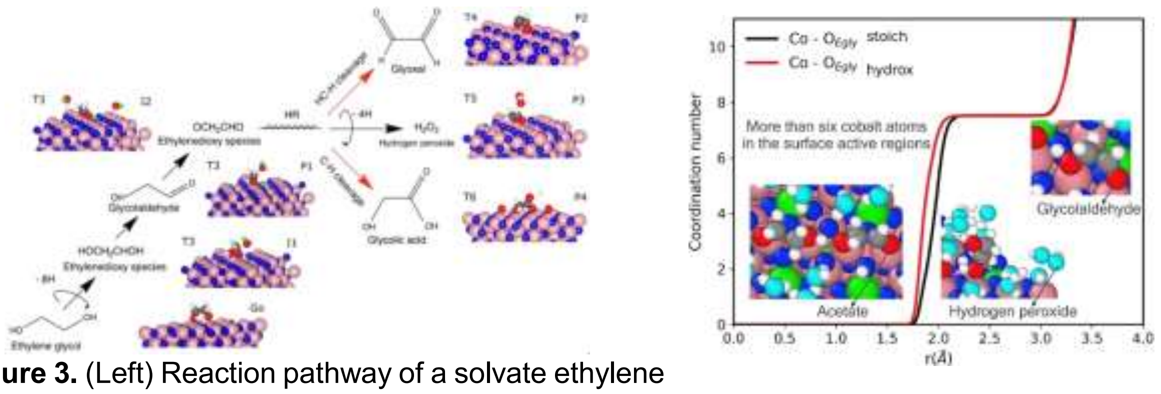

Figure 3. (Left) Reaction pathway of a solvate ethylene glycol molecule on the B-terminated (001) Co_3O_4 surface. (Right) Coordination number of ethylene glycol oxygen to cobalt sites at 0.25 ML coverage and observed products.

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P 06

In-situ and operando characterization of electrochemical systems at the I07 beamline

F. Carlà[1*], L. Shao[1], J. Rawle[1]

[1] Diamond Light Source Ltd, Didcot OX11 0DE (UK)

*** francesco.carla@diamond.ac.uk**

The I07 beamline at Diamond Light Source is a facility dedicated to the characterization of surfaces and buried interfaces using x-ray diffraction and scattering techniques in a variety of different sample environments. Thanks to the high flux and high energy (5-30keV) source provided by its undulator the beamline is particularly suitable for in-situ and operando experiments on surfaces and interfaces, which can be performed in conditions ranging from Ultra High Vacuum (UHV) to high pressure of gas and liquids. The beamline is also largely used for the characterization of thin films and buried interfaces.

The beamline is equipped with a versatile 2+3 circles diffractometer of operating in horizontal and vertical scattering geometry, capable of carrying payload up to 250kg. Different types of sample environments available at the beamline can be installed on the instrument (electrochemical cells, various environmental chambers, high temperature environment, high pressure catalysis reactor, compact UHV chamber) as well as bespoke setups. While the beamline can support a variety of different experiments, a significant part of the beamtime is dedicated to the characterization of electrochemical systems.

Different electrochemical setups are available for the I07 users, which allows to perform electrochemistry experiments in different conditions (electrodeposition, characterisation of absorbed layers, electrocatalysis, corrosion…). Custom setups developed by users can be also installed. A versatile system of detectors permits fast data acquisition and can be used to map the reciprocal space at different length scales. Surface dynamics can be also investigated in time-dependent experiment in the millisecond regime. A fluorescence detector is also available to perform XAS experiment in parallel with diffraction and scattering experiments, providing additional chemical information.

This contribution will showcase the beamline capabilities and will present different opportunities for in-situ/operando characterization of electrochemical systems.

P 07

EC-STM investigation on cyclic triimidazoles self-assembling on Au(111) as carbon nitride mimicking system for electrocatalytic studies

F. Cazzadori[1*], E. Lucenti[2], E. Cariati[3] and C. Durante[1]

[1] University of Padova, Department of Chemical Sciences, via Marzolo 1, 35131, Padova (Italy)

[2]Institute of Chemical Sciences and Technologies SCITEC- CNR, Milano 20133, Italy

[3] University of Milan, Department of Chemistry, via Golgi 19, 20133 Milano (Italy)

***francesco.cazzadori@phd.unipd.it**

Electrochemical Scanning Tunnelling Microscopy (EC-STM) is a powerful technique to study molecular electrocatalysts on well-defined surfaces, such Au single crystal, due to its single atom resolution and *in-Situ* operating conditions.[1] These strengths have been widely employed to study porphyrinoids in the electrocatalysis of important reactions, like the oxygen reduction reaction (ORR), leading to a deeper understanding of their reactivity with interesting application in the design of novel catalysts, sensors and microelectronics.[2,3] With similar scopes, the investigation is here extended to a new class of macrocyclic compounds, which consist of cyclic triimidazole (TT) derivatives. In fact, these molecules can represent a model system to study carbon nitride materials by forming 2d self-assemblies suitable for an on-surface polymerization process similarly to what already carried out with the parent compound 2,5,8Triazido-s-heptazine[4].

In this contribution TT@Au(111) in a 0.1 M $HClO_4$ electrolyte solution was investigated by EC-STM, which showed the formation of a highly ordered TT monolayer with hexagonal symmetry (Fig. 1a). The cyclic voltammetry measures revealed a potential-induced phase transition (Fig. 1b-d). Then, the electrolyte was saturated with O_2 to investigate a possible catalytic effect of the monolayer. In addition, Fe ions are added to the electrolyte solution, trying to exploit the coordination character of N atoms in the TTs, while performing EC-STM imaging to monitor the monolayer response.

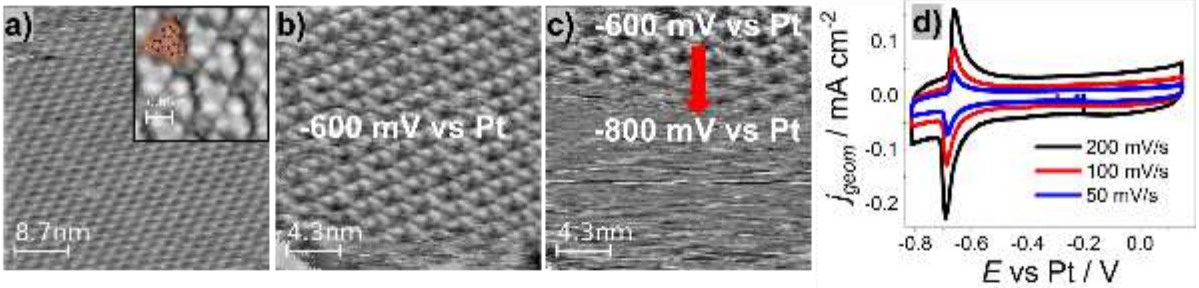

Figure 1. Au(111) in 0.1 mM TT and 0.1 M $HClO_4$ electrolytic solution saturated with Ar; a) EC-STM large scale image of TT monolayer with a zoomed inset, I_t = 1 nA, U_b = -200 mV, E_{WE} = -350 mV vs Pt; b-c) EC-STM image of TT monolayer I_t = 1.6 nA, U_b = -100 mV, the E_{WE} is outlined on the image; d) CV of the investigated system at different scan rate.

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P 08

Electrodeposition of CoPd Ultra-thin Films with Low Co Composition for Magnetic Memory Applications

Rippei Suzuki[1], **Mikiko Saito**[2] **and Takayuki Homma**[1,2*]

1 Department of Nanoscience and Nanoengineering, Waseda University, Tokyo, 169-8555 (Japan)

2 Research Organization for Nano and Life Innovation, Waseda University, Tokyo, 162-0041 (Japan)

*** t.homma@waseda.jp**

Abstract

With increasing demand for data processing, driven by advancements and widespread use of technologies such as artificial intelligence, there is a growing need for the development of new memory that offers large capacity, high speed, and low power consumption to bridge the data transfer speed gap between HDD or SSD and RAM. As a promising solution to this issue, 3D domain wall motion memory (3D-DWMM) composed of nanowires with alternating layers a few nanometres thick of high magnetic anisotropy material (recording layers) and low magnetic anisotropy material (domain wall layers) has been proposed [1]. In this memory, data is written by magnetization switching using Spin-Orbit Torque (SOT), and the written data is transferred to the upper layers by domain wall motion using Spin Transfer Torque (STT) and the use of materials with perpendicular magnetic anisotropy (PMA) and lower saturation magnetization (M_s) in the recording layers reduces the current required for device operation. Therefore, the fabrication of ultra-thin films with PMA and low M_s is essential for realizing 3D-DWMM. Lattice strain or small cobalt clusters in the Co alloy induce PMA in sputtered films, even with low Co content [2]. Ultra-thin Co films with PMA have also been electrodeposited [3], and the effects of lattice strain or small cobalt clusters on PMA have been studied in detail [3,4], supporting the possibility of fabricating Co alloy films with low M_s and PMA via electrodeposition. Moreover, electrodeposition is a simpler method than sputtering and previous studies have reported direct formation of structures required for 3D-DWMM like multilayered films [4] or nanowires [5]. Thus, electrodeposition is a promising method for fabricating 3D-DWMM. In this study, we aimed to fabricate CoPd thin films with PMA and low M_s using electrodeposition and investigate the effects of deposition conditions on their magnetic properties.

The composition of the electrodeposition bath is shown in Table 1. Electrodeposition was performed on 111-oriented Pt substrates (Si/SiO_2/Ti/Pt) at a constant potential of -750 mV vs. Ag/AgCl. Since the metal cation concentration in the bath was low and the conditions were diffusion-limited, the Co composition in the films changed in proportion to the Co^{2+} concentration in the bath. The composition of the films was evaluated by X-ray photoelectron spectroscopy. The out-of-plane magnetization curve of the fabricated CoPd thin film (2-3 nm thickness) was measured by the Magneto-Optical Kerr Effect (Figure 1), and it was confirmed that the films have PMA even in the Co composition range of 10-20 at.%. These results significantly contribute to the development of 3D-DWMM, and similar CoPd thin films are expected to be fabricated in nanowire templates in the future. In the presentation, the quantitative analysis results of magnetic properties such as PMA and M_s of the films and crystal structure analysis results by X-ray diffraction will also be discussed.

Table.1 Bath composition

$CoSO_4$	0.1 to 0.01 mM
$PdCl_2$ (+HCl)	0.3 mM
K_2SO_4	100 mM
KOH	Adjust to pH=4.0
Saccharine Na	0.1 mM

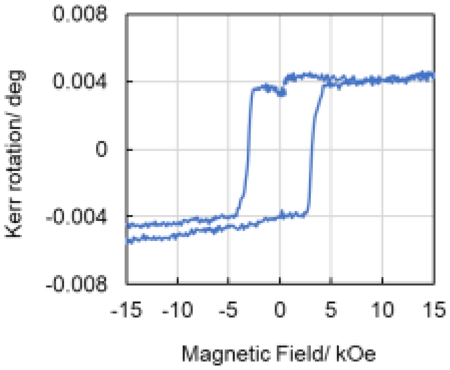

Figure 1. Out-of-plane magnetization curve of $Co_{10}Pd_{90}$

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P 09

Influence of the shape of deposited area on Photoelectrochemical activity of TiO_2–multiwalled carbon nanotube film electrode prepared via sol–gel electrophoresis deposition

Yuehai Yu[1] and Mariko Matsunaga[1*]
[1] Chuo University, Tokyo, 112-8551 (Japan)
*** matsunaga@elect.chuo-u.ac.jp**

Abstract

As environmental concerns have become increasingly pressing, photocatalytic water splitting for hydrogen production has attracted significant attention to reduce carbon dioxide emissions. However, the improvement in photocatalytic activity is still a critical focus. Among various strategies, composition of photocatalysis with a highly conductive material is a method for improving an efficiency in hydrogen generation.

In our previous study, TiO_2 was successfully composited with highly conductive multiwalled carbon nanotubes (MWCNT) by combining the sol–gel method and electrophoretic deposition (EPD), namely sol–gel EPD, to enhance the photoelectrochemical activity of TiO_2. Recently, we reported the effect of the TiO_2 sol/MWCNT ratio and additives in the bath [1] and the effect of the solvent in the bath [2] on the morphology and composition of the film, crystal structure of TiO_2, and other physicochemical properties influencing the photoelectrochemical activity.

In this study, the effect of the immersion geometry (i.e., triangle and rectangle with (a,b) identical surface area) of the ITO substrate during EPD on the photoelectrochemical activities of thin-film electrodes was investigated by focusing on the inner mechanical stress of the thin films. As a result, rectangular films with more mechanical stress within the film indicate an increased crystallite size of TiO_2 along with an increased anatase/(anatase+rutile) ratio, and large clacking in the film, resulting in superior photoelectrochemical activity than the film on the triangular area.

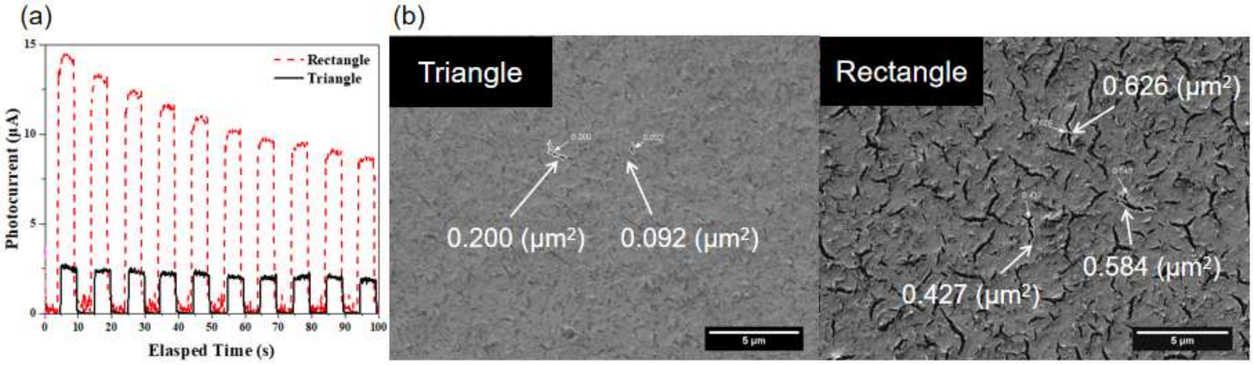

Figure 1. (a)The Photocurrent responses and (b) SEM images of the TiO_2-MWCNTfilm on triangle and rectangle areas.

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P 10

Implementation of a fast add-on module into an electrochemical scanning tunneling microscope

Alessandro Facchin[1*], Marco Cautero[2], Leonardo Gregorat[2],
Giuseppe Cautero[2], Friedrich Esch[1]

[1]TUM School of Natural Sciences, Department of Chemistry, Chair of Physical Chemistry

Lichtenbergstr. 4, 85748 Garching (Germany)

[2]Elettra-Sincrotrone Trieste S.C.p.A. Science Park, Strada Statale 14, km 163.5, 34149 Basovizza (Italy)

*** friedrich.esch@tum.de**

Abstract

Electrochemical scanning tunneling microscopes (EC-STMs) give the unique opportunity to study the dynamics of non-equilibrium processes upon electrochemical potential control, e.g. electrocatalytic activity, at the atomic scale and with elevated time resolution. To that purpose, we accelerate a standard beetle-type EC-STM (Wandelt-type [1]) by implementing a new add-on FastSPM control module [2], rather than using dedicated, fast instruments [3,4]. We present examples of systems that can be investigated, such as single iron centers carried by octaethylporphyrin molecules (FeOEP) and their activity in the oxygen reduction reaction (ORR) on Au(111).

The module allows the seamless transition between multiple measurement modes: (i) constant height image acquisition at frame rates of ~10 fps - e.g. for investigation of nanoparticle surface dynamics in reactive environments - and (ii) tracking of the apex of single nanoparticles down to 500 µs time resolution under full lateral and vertical feedback - e.g. for investigation of particle diffusion mechanisms and energetics. Moreover, the continuous drift correction in the background allows for (iii) drift-corrected positioning on specific surface features for fast current detection down to 5 µs time resolution.

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P 11

Development of NiFe catalysts for the Reverse Water Gas Shift (RWGS) reaction under co-electrolysis conditions

E. Ruiz[1*], M.J. Escudero[1] and E. Millán[1]

[1] CIEMAT, Madrid, 28040 (Spain)

*** esperanza.ruiz@ciemat.es**

Abstract

CO_2 and H_2O co-electrolysis in solid oxide electrolysis cells (SOEC) yields syngas with tuneable H_2/CO ratio to be further converted into synthetic fuels and chemicals. The RWGS reaction is considered the determining step of the co-electrolysis process. Conventional Ni/YSZ (nickel-yttria stabilized zirconia) cermet commonly used as cathode in SOEC exhibits high electrocatalytic activity and conductivity, but poor long term stability. CeO_2 has an excellent oxygen storage capacity and redox behaviour, and the addition of Gd in CeO_2 lattice (gadolinium doped ceria, GDC) could improve oxygen mobility and thermal stability, resulting in higher Ni dispersion, and, thus, in better catalytic performance for both RWGS and H_2O/CO_2 reduction reactions, while preventing coking and Ni sintering, which results in greater stability [1–2]. Partial replacement of Ni by Fe could also improve catalytic performance and stability by preventing Ni aggregation and coke deposition [2–4].

In this work, Ni-CeO_2, NiFe-CeO_2, Ni-GDC and NiFe-GDC catalysts, in the form of half-electrolyte (YSZ) supported cells, have been prepared and catalytically investigated for the RWGS reaction to assess their applicability as cathode for co-electrolysis in SOEC. Catalyst powders with a metal loading of 40 at% (3/1 for Ni/Fe systems) were prepared by sol-gel. Commercial YSZ powders were pressed and sintered to obtain dense electrolyte pellets (diameter ~ 8mm and thickness ~1 mm). Then, a porous YSZ layer was deposited onto one side of the pellet by tape casting. Finally, the electrode ink, prepared by mixing the catalyst powder with an ink vehicle, was deposited onto the porous YSZ layer by screen-printing. The prepared half-cells were loaded into a lab-scale reactor, pre-reduced in 10 % H_2/90 % N_2 at 800 °C for 2 h and tested under a typical co-electrolysis environment (35 % CO_2, 35 % H_2O, 10 % H_2 and N_2 balance) at different temperatures (600-800 °C) and atmospheric pressure. Regardless of the utilized catalyst, CO_2 was mainly converted to CO through the RWGS reaction, reaching CO selectivities close to 100%. In general, CO_2 conversion values were low (less than 23%) under the utilized operating conditions. Results showed that, the incorporation of Gd into the CeO_2 lattice of the Ni or NiFe based catalyst considerably enhances the catalytic activity for RWGS reaction, whereas the addition of Fe to the Ni-CeO_2 or Ni-GDC catalyst formulation slightly improves CO yields via the RWGS reaction, but neither of them seem to suppress carbon deposition, as was confirmed visually after the tests. Therefore, additional research is needed to optimize the cathode materials and operating conditions.

This study was financed by the Ministry of Science, Innovation and Universities of Spain with funds from the European Union NextGenerationEU (PRTR-C17.I1) and by the Autonomous Community of Madrid, within the framework of the GREENH2CM project, and by the Ministry of Science, Innovation and Universities of Spain (ECO-H2 project: PID2023-149998NB-I00).

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P 12

Hydrazine hydrate electrooxidation reaction mechanism on Ni electrode

E. Vorms[1*], E. Strugovshchikov[3], A. Brige[1], M. Isaiev[3], T. Asset[1], A. Bonnefont[2], M. Chatenet[2], E. Savinova[1], A. Oshchepkov[1]

[1] ICPEES, Strasbourg, 67087 (France)

[2]LEPMI, Grenoble, 38402 (France)

[3]LEMTA, Nancy, 54505, (France)

*evgeniia.vorms@etu.unistra.fr

Abstract

Considering the growing demand for electricity in mobility applications new approaches for its production are necessary, one of which is direct liquid fuel cells (DLFCs). The fuel oxidized at the anode is usually stored/stabilized in alkaline media, which allows to use non-noble metal catalysts. Hydrazine hydrate ($N_2H_4{\bullet}H_2O$) oxidation reaction (HHOR) seems to be an attractive for the investigation anode reaction, due to its low standard potential (-0.33 V *vs.* reversible hydrogen electrode (RHE)) and environmentally friendly products (N_2 and H_2O). Literature data on the HHOR are contradictory, with some studies reporting high activity (albeit less than that of Pt or Pd) of Ni at low potentials ($E < 0.4$ V *vs.* RHE) [1,2], while others reporting HHOR occurring above 0.8 V *vs.* RHE. To understand the reason for such discrepancy, a deeper insight into the HHOR mechanism on Ni is required, which is the focus of our study. The HHOR in alkaline media was studied by cyclic voltammetry (CV) on Ni electrodeposited on porous carbon (Ni/C) (**Figure 1**a). Products composition and Ni selectivity towards HHOR were studied with the help of *in situ* differential mass spectrometry (DEMS) and rotating disk electrode (RDE) experiments. Using *in situ* and *ex situ* X-ray photoelectron spectroscopy (XPS) N-containing adsorbates formation depending on the applied potential was investigated. Based on density functional theory (DFT) calculations the possibility of various N-containing adsorbates formation was evaluated. Isotope substitution experiments showed the importance of Ni-OH_{ad} formation for the HHOR on Ni. Furthermore, the likelihood of the dissociative and molecular adsorption of N_2H_4 on Ni was assessed by microkinetic modeling through comparison of simulated and experimental CVs (**Figure 1**). The results obtained provide new insights into the HHOR mechanism on Ni, which could guide the development of highly-active Ni-alloys for HHOR catalysis.

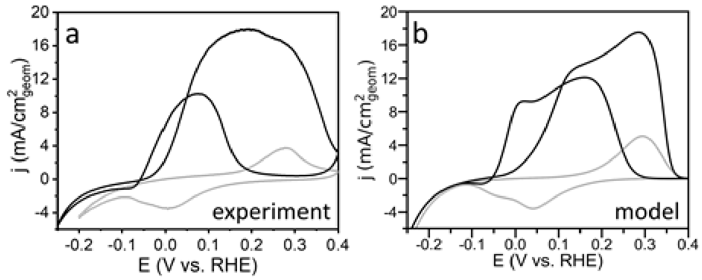

Figure 1. (a) Experimental and (b) corresponding simulated cyclic voltammograms recorded at 1600 rpm and 20 mV s^{-1} for Ni/C in 0.1 M NaOH (grey lines) and in 0.1 M NaOH + 5 mM N_2H_4 (black lines).

Acknowledgment: The authors acknowledge the financial support from the Jean Marie Lehn Foundation and are grateful to Dr. V. Papaefthimiou, Dr. A. Shavorskiy, Dr. R. Temperton, and Dr. I. Makarchuk for the help with XPS and TEM measurements.

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Supperlattice-like strcuture: Ordered mass transfer endows high quality output of fuel cell

Jian Wang, **Wei Ding,* and Zidong Wei * ***

[1] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331. (China)

*** dingwei128@cqu.edu.cn, zdwei@cqu.edu.cn**

Abstract

The current or voltage fluctuation in fuel cell operation is harmful to the fuel cell system and power application equipment. Here, we report a technique to eliminate such a fluctuation by the aid of new type of catalysts, superlattice-like mesoporous PtCo catalysts. The current fluctuation in fuel cells catalyzed by two invented catalysts are fixed at as low as 25 mA·cm-2 with a power of 0.75 W·cm-2 or 120 mA·cm-2 with a power of 1.01 W·cm-2, respectively, and no noticeable current decay were detected over 100 h. By contrast, a cell catalyzed by conventional Pt/C catalysts with the same Pt loading delivers a current fluctuation as large as 180 mA·cm-2 even at low power output of 0.30 W·cm-2, which also showed 32% current decay rate in 50 h. The superlattices-like mesoporous structure not only enhances the mass transfer and depresses the water flooding but also effectively increases the Pt utilization within its 3D carbon frameworks. Its power output is as high as 11.69 W·mgPt-1 (MEA), which is 46.1% higher than the 2025 target of DOE, USA, 8.0 W·mgPt -1(MEA).

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P 14

Electrolyte Potentials during High Voltage Electrolysis and their Implications for Operando Electrochemical Measurements

<u>Lukas Forschner</u>[1*], Tim Bolter[1], Timo Jacob[1] and Albert K. Engstfeld[1]

[1] Ulm University, Institute of Electrochemistry, Ulm, 89081 (Germany)

*** lukas.forschner@uni-ulm.de**

Abstract

Studying electrolysis at high voltages, from a few to several hundreds of volt, received increasing interest over the last decade for material modification and reactive species formation in an electrolyte. In addition to bubble formation, under these conditions Joule heating leads to the evaporation of the electrolyte, which eventually results in the ignition of a plasma within a thin vapour layer engulfing the electrode (plasma electrolysis – PE). In this work, we focus on the detection of H_2O_2 that forms in aqueous electrolytes in addition to O_2 and H_2 during anodic electrolysis in the presence of a plasma.

Earlier work from our group has illustrated an approach for the detection of H_2O_2 by electrochemical methods during PE,[1] similar to rotating ring disc setups used for studying H_2O_2 formation during the oxygen reduction reaction. By adopting a three-electrode setup into the PE cell and keeping the potential of a Pt wire working electrode >1.0 V_{RHE}, the H_2O_2 production can be related to the oxidation current. A key issue is, however, that the three electrodes of the probe setup are subject to potential shifts induced by significant voltage drops within the electrolyte caused by the low conductivity of the electrolyte (0.01 M KOH) and high currents (up to 1 A at 550 V). Thus, knowing the electrolyte potential distribution is key for reliable electrochemical probing. The implications of our measurements on the general understanding of *IR* drops in electrolytes in electrochemical systems will also be discussed.

By measuring the voltage between two reversible hydrogen reference electrodes placed at different locations in the electrolyte, we map the spatial distribution of the electrolyte potential during normal electrolysis at high voltages[2] and during PE. We compare these measurements to numerical COMSOL® simulations and discuss the effects of electrode placement during H_2O_2 detection. Figure 1 shows the evolution of the oxidation current (at >1.0 V_{RHE}) in a cyclic voltammogram of a Pt working electrode before, during, and after PE. Based on this analysis the H_2O_2 concentration can be monitored operando despite the interference of high electrolysis currents.

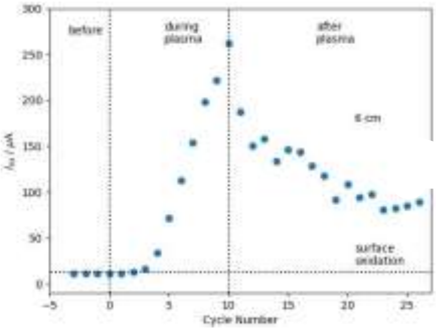

Figure 4. Oxidation currents inferred from cyclic voltammograms for a Pt wire probe electrode before, during, and after plasma electrolysis with a Au wire anode at 550 V in 0.01 M KOH.

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P 15

Electrochemical Questions Answered Using the echemdb Database

Johannes M. Hermann[1], **Nicolas Hörmann**[2], **Maren-Kathrin Heubach**[1], **Nadine Wölfel**[1], **Nicolas Bergmann**[2], **Karsten Reuter**[2], **Timo Jacob**[1], **Julian Rüth**[3], **Albert K. Engstfeld**[1]

[1] **Institute of Electrochemistry, Ulm University, Ulm, 89069 (Germany)**

[2] **Theory Department, Fritz-Haber-Institute der MPG, Berlin, 14195 (Germany)**

[3] **Julian Rüth GmbH, Güntersleben, 97261 (Germany)**

albert.engstfeld@uni-ulm.de, **johannes.hermann@uni-ulm.de**

The daily work of a scientist strongly depends on data available in databases or lookup tables, most simply the periodic table of elements. Information on electrochemical systems, physicochemical properties of electrodes or the electrolyte can be found in numerous databases, such as those provided by the National Institute of Standards and Technology (NIST, https://www.nist.gov), or in more specialized databases focussing on individual systems (see summary in Ref. [1]). In this work, we present an electrochemical database for interfacial electrochemistry, focussing on cyclic voltammetry (CV) data for single crystal model electrodes in contact with aqueous and non-aqueous electrolytes. Over the last century, these model systems have been detrimental to understanding more complex three-dimensional systems usually found in more applied research. Their well-defined properties allow seamless validation of experimental data across research institutions and facilitate the comparison with results from theory. In general, establishing/creating a database requires FAIR (findable, accessible, interoperable, and reusable) data. For published studies, (i) the data are usually stored as a trace in a figure, and (ii) the metadata, if available at all, are scattered across the text body, which limits machine readability and processing. To address these issues, the echemdb Github community[2] built a robust Python-based framework, allowing cross-disciplinary collaboration between data curators, developers, and researchers. The tools are extensible and applicable to other, more complex systems or research areas, including local research data management.[3] We created a new data extraction tool (svgdigitizer), which considers the peculiarities of CV data, such as multiple *y* (current) per *x* (potential) values, variable potential reference scales, and unavailable time axes. The data are stored in frictionless Data Packages,[4] including structured metadata, which are extracted manually from the publications. The openly available dataset is visualized on our website but can also be explored interactively using our Python-based unitpackage (builds on top of frictionless).[2]

We will showcase various database use cases. Most simply, we will illustrate how the availability of CVs in such a way will significantly improve finding such data compared to the classical text-based search. Furthermore, it allows for direct comparison between literature data and data recorded in the laboratory, highlighting differences between different sources.[5] Another example involves computational works aiming at simulating CVs, where the robustness of the employed approach can be validated against multiple datasets.[6] The extension of the framework and database for more complex systems will be demonstrated.

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Influence of pH on the surface structure of Ni anodes under OER conditions

<u>Justus Leist</u>[1*], Annika Neufischer[1], Benjamin Schick[1], Sylvain Brimaud[2], Timo Jacob[1], Albert K. Engstfeld[1]
[1] Ulm University, Institute of Electrochemistry, Ulm, Germany
[2] ZSW, Ulm, Germany
*** justus.leist@uni-ulm.de**

Abstract

In electrolyzers, the electrocatalytic splitting of aqueous electrolytes is typically impeded by the sluggish kinetics of the oxygen evolution reaction (OER) at the anode. Ni electrodes, which are oxidized under OER conditions, are employed in technology-mature alkaline electrolysis and have been studied intensively. In this study, we investigate the influence of potential ranges up to 3.5 V *vs.* RHE (reversible hydrogen electrode) and different pH values on the surface states of Ni electrodes and attempt a comprehensive depiction of possible surface changes, which have been previously obscured by bubble formation.

The OER characteristics are studied by means of cyclic voltammetry (CV) using Ni electrodes in alkaline solutions. CVs for different KOH concentrations are shown in Fig. 1a (region around the OER onset potential). Depending on the experimental conditions, electrolyte pH, electrolyte flow, and ionic strength, the features observed in current–voltage traces vary significantly in the OER region. Additional electrochemical quartz crystal microbalance measurements show potential-dependent changes in the electrode mass at high potentials and pH ≤ 12, which are concurrent with variations in the CVs. Furthermore, *in situ* Raman spectroscopy reveals a new band at 1040 cm^{-1} under comparable conditions (Fig. 1b). Additional density functional theory studies were performed on $Ni_xO_y(OH)_z$ structures to assign the bands in the Raman spectra. Based on this whole set of results, we elucidate concurrent changes in the surface structure during the OER at different pH values at high potentials and discuss possible undiscovered Ni-oxide surface structures. Furthermore, we rationalize the variations in the CVs to local pH changes at the electrode and address the impact of the pH and surface structure on OER kinetics and its mechanism.

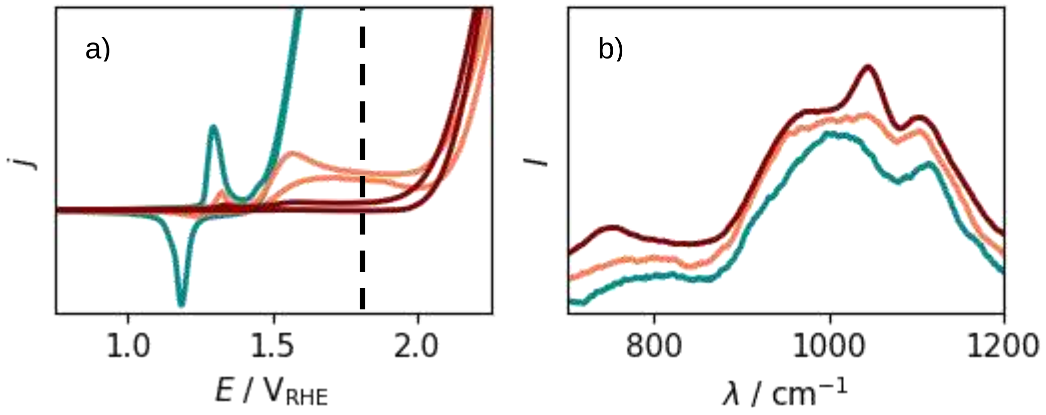

Figure 5. a) Cyclic voltammograms for the OER on Ni electrodes, recorded in 0.1 M (blue), 0.01 M (orange), and 0.001 M (red) KOH at 10 mV s^{-1}. $KClO_4$ was added to maintain a constant ionic strength of 0.1 M. b) Raman spectra of Ni deposited on Au electrodes recorded while applying a potential of 1.8 V *vs.* RHE in 0.1 to 0.001 M KOH (colors relate to the curves in a).

P 17

Potential Dependent Surface Adlayer Structures on and Restructuring of Ru(0001) and Pt-Modified Ru(0001) Electrodes Under Reaction Conditions

Albert K. Engstfeld*[1,2], **Joachim Bansmann**[1], **Zenonas Jusys**[1,3], **Jakub Drnec**[4] **and R. Jürgen Behm**[1,5]
[1] Ulm university, Institute of Surface Chemistry and Catalysis, Ulm, 89081 (DE)
[2] *pres. addr.*: Ulm University, Institute of Electrochemistry, Ulm, 89081 (DE)
[3] *pres. addr.*: Helmholtz Institute Ulm, Electrochemical Energy Storage, Ulm, 89081 (DE)
[4] ESRF, Experimental Division, grenoble, 38000 (FR)
[5] *pres. addr.*: Ulm University, Institute of Theoretical Chemistry, Ulm, 89081 (DE)
* albert.engstfeld@uni-ulm.de

Abstract

Over the last decades, fundamental research on the electrochemical/-catalytic properties of low-index single crystals has played an essential role in understanding and improving industrially relevant and more complex (electro-)catalyst materials. Some of the fundamental questions deal with the elucidation of the activity of specific sites on a catalyst material, which should ultimately reveal the most active site and the catalyst structure under reaction conditions, including potential dependent surface adlayer changes or possible restructuring phenomena, which can significantly alter the electrocatalytic activity.

In this work, we study the oxygen reduction reaction (ORR) on Ru(0001) and oxidation of carbonaceous species (CO and MeOH) in acid electrolytes on Pt-modified Ru(0001) electrodes, prepared under UHV conditions and studied in an electrochemical flow cell attached to the UHV chamber. For the ORR measurements, a flow cell with a collector electrode is used to monitor the reaction intermediate H_2O_2, and for the oxidation reactions, a differential electrochemical mass spectrometry (DEMS) cell is used. The electrodes are studied with scanning tunnelling microscopy (STM) before and after the electrochemical measurements under UHV conditions. Additional surface X-ray diffraction (SXRD) measurements provide insights into structural changes not observable from the STM images.

For the pure Ru(0001) electrodes, we show the impact of strongly adsorbing anions in H_2SO_4 electrolyte compared to $HClO_4$ on the features in cyclic voltammograms (CVs) in pure electrolytes[1] and the role of these species on the ORR mechanism on this electrode.[2] For Pt-submonolayer-modified Ru(0001) electrodes, we illustrate that modifying Ru steps by Pt adatoms shifts the onset potential for Ru step flow corrosion to more positive potentials, apparent from STM images.[3,4] The onset of the restructuring of the Pt islands is apparent from the CO oxidation traces recorded on these electrodes.[3,4,5] Finally, Pt-shell Ru-core model electrodes consisting of thin Pt films on Ru(0001) electrodes were studied in pure and CO/MeOH-containing electrolytes. For mono or bi-layer Pt films, we observed restructuring at similar potentials in pure and CO/MeOH-containing electrolytes compared to submonolayer-modified electrodes.[6] In turn, Ru(0001) electrodes with three to four layers are significantly more stable (up to 1.4 vs RHE), hence more stable than Pt(111) under these conditions. From additional SXRD measurements, we found that in the presence of carbonaceous species, the onset potential for reversible place exchange on the electrode shifts to higher potentials.[6] The role of the various adsorbates involved is discussed.

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P 18

Suspension Electrolyte for Aqueous Dual-Ion Batteries

Yitao He*, **Jiří Červenka**

Department of Thin Films and Nanostructures, FZU – Institute of Physics of the Czech Academy of Sciences, Cukrovarnická 10/112, 162 00 Prague 6, Czech Republic

*** yitao@fzu.cz**

Abstract

Dual-ion batteries (DIBs) have emerged as promising candidates for energy storage due to their cost-effectiveness, high operating voltage, and environmental friendliness. The electrolyte, which provides active ions during charge and discharge cycles, plays a crucial role in determining the capacity, energy density, and lifespan of DIBs. However, the reliance on high-concentration electrolytes using fully dissolved main salts often undermines their cost-efficiency. To address this, a novel salt particle suspension electrolyte (SPSE) system has been developed, leveraging a linear carbonate solvent with a trace amount of water. This innovative SPSE system was successfully applied in graphite||zinc and graphite||graphite DIBs. The SPSE offers a high surface anion concentration that minimizes concentration polarization, enhances anion utilization efficiency at the electrode surface, and ensures adequate anion supply even at low electrolyte concentrations. In particular, a 2 M solvated $Zn(OTf)_2$-based SPSE was developed by capitalizing on the low solubility of the main salt in dimethyl carbonate (DMC) and modulating the solvation structure with trace water. Unlike traditional fully dissolved electrolytes, the undissolved solvated salt particles in SPSE not only maintain ion mobility but also mimic the functionality of high-concentration electrolytes at lower concentrations. The zinc metal-anode-free expanded graphite||graphite DIB cells employing this SPSE achieved outstanding performance, including a discharge capacity of 178.66 mAh g^{-1} at 10 mA g^{-1}, with a high discharge platform of approximately 2.0 V. These results underscore the potential of SPSE in advancing DIB technology by combining superior electrochemical performance with cost-effective electrolyte formulations, paving the way for the transition from liquid to semi-solid systems in energy storage applications.

P 19

Electrocatalytic Water Oxidation with Prussian Blue Analogues under Magnetic Field

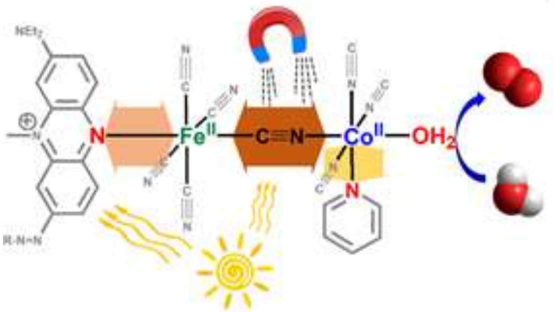
Ferdi Karadaş[1*]

[1] ***Department of Chemistry, Bilkent University, Bilkent, Çankaya, Ankara, 06800, Turkey***

**** karadas@fen.bilkent.edu.tr***

Abstract

CoFe Prussian blue analogues (CoFe PBAs) have been established as robust and efficient water oxidation catalysts (WOCs).[1] CoFe PBAs could easily be prepared by reacting Co^{2+} ions with a cyanoferrate precursor in a protic solvent at room temperature. Several strategies have recently been employed to enhance the catalytic activity of PBAs. For example, proper functional groups could be integrated into a CoFe PB structure to tune electronic properties of the catalytic cobalt site.[2] Furthermore, the intermetallic charge transfer between Co and Fe sites could be utilized to develop magnetic field- and light-responsive electrocatalysts.[3] Improvements of ≈11 % and ≈57 % were achieved under magnetic field (0.2 T) and light irradiation (100 mW cm^{-2}), respectively, when working at fixed overpotential, $\eta=0.6$ V at pH 7. The observed enhancements strongly tie in with the intermetallic charge transfer (IMCT) intensity between Fe and Co sites. Herein, these strategies will be presented and the effect of charge transfer in the catalytic process will be highlighted.



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P 20

Nature of the Au(111) interface in aqueous solution

A. Köhler[1], R. Bechstein[1], M. Reichling[2] and A. Kühnle[1*]

[1] Physical Chemistry I, Faculty of Chemistry, Bielefeld University, Bielefeld, 33615 (Germany)

[2] Institut für Physik, Universität Osnabrück, Osnabrück, 49076 (Germany)

***kuehnle@uni-bielefeld.de**

Abstract

Solid-liquid interfaces are omnipresent in the fields of electrochemistry, geochemistry and biochemistry [1-3]. A prototypical system to study electrode interfaces is the Au(111) surface in contact with aqueous solution. For understanding the reactivity of this system, it is crucial to elucidate the interfacial structure at the molecular level. However, reliable molecular-level experimental data addressing the solvation structure of the Au(111) interface are largely lacking.

Here, we present two- and three-dimensional (2D- and 3D) atomic force microscopy data. In pure water, 2D-measurements reveal stripe-like structures at the Au(111)-water interface, which can be assigned to hydrocarbons [4,5]. These stripes are not visible in concentrated sodium chloride solution. In a vertical slice extracted from a 3D map, we find a layered structure with interlayer distances of 0.4 nm in case of pure water, while layers with distances of 0.3 nm are revealed in concentrated sodium chloride solution. Our 3D results indicate that the layers measured in pure water do not originate from water layers as these should have a distance of 0.3 nm. Thus, despite an extremely thorough preparation procedure, contaminations are present at the Au(111)-water interface. In the presence of sodium chloride, however, typical hydration layer distances of 0.3 nm are obtained.

Our results demonstrate the difficulty to obtain a clean Au(111)-water interface under ambient conditions, highlighting the general significance of contamination at interfaces.

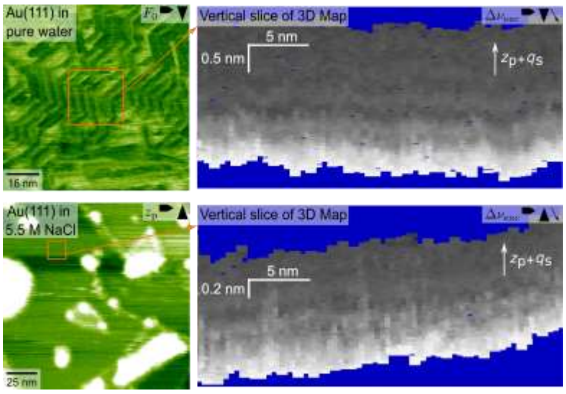

Figure 6. Top: 2D-AFM image of an Au(111) crystal immersed in pure water. A vertical slice (orange dotted line) was extracted from the 3D scan area (orange square). Bottom: 2D-AFM image of an Au(111) crystal immersed in 5.5 M NaCl. A vertical slice was extracted similar to the situation discussed before for pure water.

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P 21

In situ monitoring of oxygen permeation and Li_2O_2 formation in lithium-oxygen batteries

Nelly Nembot[1], Marius Muhle[1], Marcel Reisch[2], Daniela Fenske[2],
Gunther Wittstock[1]*
[1] Carl von Ossietzky University, Faculty of Mathematics and Natural Science,
Institute of Chemistry, D-2611 Oldenburg (Germany)
[2] Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM,
Wiener Straße 12, D-28359 Bremen (Germany)
*** gunther.wittstock@uni-oldenburg.de**

Titanium carbide (TiC)-based cathodes seems to be an alternative to carbon cathodes in lithium-oxygen batteries (LOBs) because TiC reduces greatly side reactions (arising from electrolyte and electrode degradation) compared to carbon and offers better reversible formation/decomposition of Li_2O_2, the lack of which is the main cause of failure of LiOBs [1]. This study investigates oxygen permeation and Li_2O_2 formation in LiOB cathodes (uncoated and TiC-coated carbon paper) during cycling using scanning electrochemical microscopy (SECM) in the generation-collection (GC) mode. A microelectrode (ME) placed at a closed distance to the gas-diffusion electrode detects the oxygen influx at different states of charge [2]. ME passivation is mitigated by a pulse amperometric detection with removal of Li_2O_2. Li_2O_2 formation is analyzed with X-ray photoelectron spectroscopy (XPS), using a second microelectrode to collect Li_2O_2 from the organic electrolyte solution.

Figure 1 shows XPS high resolution spectrums,of those samples , indicating the **presence of TiC** at C 1s binding energy of 283 eV and Ti 2p at 455 eV, on the coated sample .SECM GC mode results quantify oxygen permeation and Li_2O_2 formation.

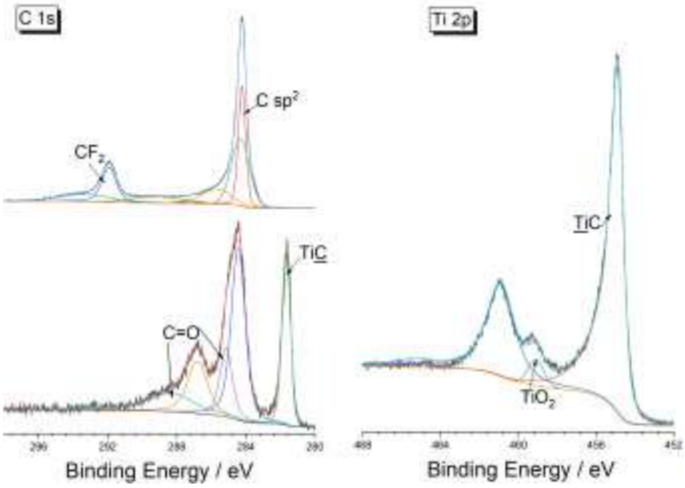

Figure 1: XPS high resolution spectrums of C 1s, and Ti 2p of uncoated (upper panel) and coated (lower panel) samples.

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New Insights on Bipolar Electrochemistry of Microstructures

F. Kühling[1] and G. Wittstock[1*]

[1] Carl von Ossietzky University of Oldenburg, School of Mathematics and Science, Institute of Chemistry, Oldenburg, 26129, (Germany)

* gunther.wittstock@uni-oldenburg.de

Abstract

In bipolar electrochemistry, oxidation and reduction occur on the same electrode body, the so-called bipolar electrode, which is not physically connected to a power supply. The reactions at the bipolar electrode are induced by a voltage drop in the solution, which is caused by applying a voltage between two feeder electrodes.[1] In an open set-up, an ionic current, the so-called bypass current, flows through the electrolyte solution in parallel to the electronic current within the bipolar electrode. In a closed setup, the entire current passes through the bipolar electrode.[1] While bipolar electrodes are common in fuel cells[2], other stacked electrochemical reactors[3] or in fluidized bed reactors,[4] they have occasionally been used in material science and in electroanalysis, where the wireless nature is attractive for the integration of micrometer and nanometer sized electrodes.[1] So far, the complexity of the setup and the resulting potential distributions make it challenging to precisely control the potential of the bipolar electrode. This contribution explores cell conditions that allow wireless electrochemistry with potential control on one side of the bipolar electrode, which is usually necessary for electroanalytical applications.

In this work, a closed bipolar setup was used with two interconnected microelectrodes as bipolar electrode. This particular setup has been extensively used by Zhang and coworkers to investigate the fundamentals of bipolar electrochemistry.[5–7] We investigated the influence of the size of the feeder electrodes and reactions at them on voltammetric experiments. Moreover, the potential of one side of the bipolar electrode was set by a redox couple in one half-cell of the closed setup. The influence of a varying bipolar efficiency on the capacitive current and on the required voltage between the feeder electrodes was also investigated. The bipolar efficiency is the ratio between the current through the bipolar electrode and the current between the feeder electrodes. Compared to previous reports,[8] in which the bipolar efficiency was changed by varying the diameter of the bipolar electrode, the bipolar efficiency was changed in this work by systematically varying the bypass current. This has the advantage that the influence of a changing interface between the bipolar electrode and the solution is avoided. We are currently investigating the time constant of bipolar setups in comparison to conventional three-electrode setups by chronoamperometry and electrochemical impedance spectroscopy. The accelerated responsiveness of bipolar electrochemical setups in their closed configuration could be promising for investigations of current transient of short time scales.

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P 23

Time evolution of the potential of hard carbon/sodium metal cells upon stepwise temperature changes

Laurin Derr[1*], Steffen Braun[1], Krishnaveni Palanisamy[2], Christine Kranz[2] and Rolf Schuster[1]

[1] Institute of Physical Chemistry, Karlsruhe Institute of Technology, Karlsruhe, 76131 Germany

[2] Institute of Analytical and Bioanalytical Chemistry, Ulm University, 89081 Ulm, Germany

*** laurin.derr@kit.edu**

Abstract

The temperature-dependence of the equilibrium potential of an electrochemical cell is directly correlated to its reaction entropy. This correlation was, e.g., used by Mercer et al. to determine the entropy of the sodiation of hard carbon (HC), a common anode material for sodium-ion batteries (SIBs), at different states of charge (SoCs).[1,2] They explained the variation of the entropy with the SoC by the interplay between interlayer and pore filling with increasing Na content in the HC.

Here, we followed the evolution of the open circuit potential (OCP) of HC/Na metal coin cells upon fast temperature changes at different SoCs of the HC (see Fig.1). For long times (t > 2500 s), a new equilibrium cell potential is reached. With the deviation from the initial potential, the entropy of the full cell can be determined. It varies with the SoC between -10 and 6 J mol^{-1} K^{-1}, in line with the results from Mercer et al.[1]

Right after the temperature change (t > 2000 s), two essential features in the OCP evolution were identified. The initial minimum of the OCP, less than 10 s after the temperature change, can be explained with an uneven cooling of both electrodes due to the coin cell geometry. The following positive overshoot, which is most pronounced at 0 % SoC (Fig.1, red curve), might be attributed to different kinetics of the equilibration of the HC composite electrode and the Na metal electrode.

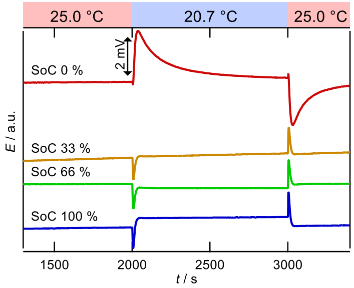

Figure 7. Open circuit potential of a HC/Na metal cell at different SoCs of the HC. From t = 2000 to 3000 s the cell temperature was reduced from 25.0 °C to 20.7 °C.

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P 24

Development of a microcalorimetric method for the determination of the reaction entropy of irreversible electrochemical processes and application to the oxidation of formic acid

S. Braun*, **K. Bickel and R.Schuster**

KIT, Karlsruhe, 76131 (Germany)

*** steffen.braun@kit.edu**

Abstract

Electrochemical microcalorimetry can be an important tool to determine the reaction entropy via the heat generated in an electrochemical reaction. The measurements usually start from chemical equilibrium and by driving the reaction with short (10 ms) current pulses it is possible to measure small changes in temperature [1]. The described method is limited to reversible reactions at small overpotentials, such as the deposition/dissolution of metals or the adsorption/ desorption of molecules.

This method was extended to measure similar effects for irreversible reactions. It makes use of the stationary current caused by the ongoing reaction at a certain potential. By briefly interrupting the reaction, the system, which was in thermal equilibrium, shows a temperature change due to the missing heat contribution from the reaction. Based on the change in temperature, the reversible heat and the entropy of the reaction can be determined. Figure 1 shows an example of the temperature and potential response following such a short pulse for the fast electron transfer reaction between $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ in aqueous solution. This reaction was used to validate the method.

A first application was the determination of the reaction entropy for the irreversible oxidation of formic acid on Au(111), which takes place at high overpotentials (η > 1 V) [2].

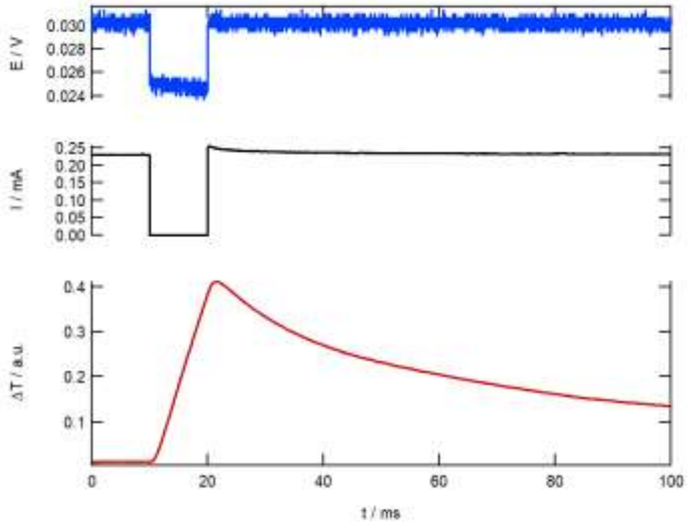

Figure 8. Potential (blue) and temperature (red) response to a 10 ms interruption of the current (black) in 0.1 M $K_4[Fe(CN)_6]$ + 0.1 M $K_3[Fe(CN)_6]$ with Au-WE, Pt-CE and Pt-RE.

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P 25

Microcalorimetric studies on magnesium deposition from $Mg[B(hfip)_4]_2$/DME electrolyte solutions

Daniel Metzger[1*], Franziska Karcher[1],

Sibylle Riedel[2], Zhirong Zhao-Karger[2,3] and Rolf Schuster[1]

[1] Institute of Physical Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe (Germany)

[2] Helmholtz Institute Ulm, Electrochemical Energy Storage, 89081 Ulm (Germany)

[3] Institute of Nanotechnology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen (Germany)

***daniel.metzger@kit.edu**

Abstract

Magnesium metal is a promising anode material for future battery systems, due to its high volumetric capacity and its ability to deposit in a homogenous morphology.[1] Therefore, a fundamental understanding of the deposition process itself, aging phenomena of surfaces and the influence of additives is desirable.

Using electrochemical microcalorimetry, we are able to obtain both, thermodynamic and kinetic information about the deposition and dissolution of magnesium. The measurement of the reversibly exchanged heat at a single electrode enables the determination of the reaction entropy, while time-resolved measurements of this quantity allow conclusions on the kinetics of the reaction.

Here we investigate the deposition and dissolution of magnesium in 0.3 M $Mg[B(hfip)_4]_2$ in DME and the influence of borohydride additives ($TBABH_4$ and $Mg(BH_4)_2$) on these processes. In all investigated electrolyte solutions, the reaction entropy for magnesium deposition was determined to be 520 ± 70 $J K^{-1} mol^{-1}$, which is indicating a strong solvation of the Mg^{2+}-ion in DME. Time-resolved measurements of the reversibly exchanged heat show that the heat evolution significantly slows down after one hour of aging under open-circuit conditions. After activation by potential cycling of the aged surface the same heat evolution as on a fresh surface is found. These observations are attributed to the growth of an adsorption layer on the electrode surface, which is (partly) removed by the activation step.

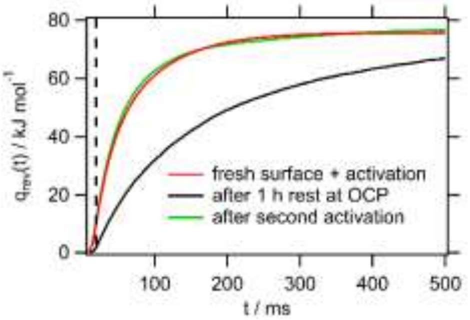

Figure 1. Reversibly exchanged heat $q_{rev}(t)$ at a single electrode upon the deposition of Mg^{2+} from 0.3 M $Mg[B(hfip)_4]_2$ in DME electrolyte solution.

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Zinc Compound Electrodeposition on HOPG using High-Speed AFM

Tatsumi Naganuma[1]*, Ryuto Ohashi[1], Cheng Yen Chieh[1],

Mikito Ueda[1] and Hisayoshi Matsushima[1]

[1] Faculty of Engineering, Hokkaido University, Sapporo, 060-8628 (Japan)

*** naganuma.tatsumi.h0@elms.hokudai.ac.jp**

Introduction

The fabrication of zinc thin films via electrodeposition has attracted attention as a low-cost and highly controllable technique compared to conventional methods such as sputtering and chemical vapor deposition (CVD) [1]. The morphology and crystal structure of deposited zinc is significantly influenced by the pH and Cl^- concentration of the solution. Especially, the Cl^- plays crucial role in determining the growth morphology of ZnO and may induce complex oxide formation [2]. Additionally, Zn^{2+} reacts with Cl^- to form zinc chloride complexes, which reduces the concentration of free Zn^{2+} in the solution and consequently alters the ZnO deposition rate [3]. However, there have been few reports on in-situ nanoscale observations of surface changes during electrodeposition and dissolution. In this study, the high-speed atomic force microscopy (HS-AFM) is applied for observing the zinc nucleation and dissolution depending on the various electrochemical conditions.

Experimental Methods

Experiments were conducted using an electrochemical AFM cell. Highly oriented pyrolytic graphite (HOPG) was used as the working electrode, a zinc wire as the counter electrode, and a hydrogen-absorbed Pd wire as the reference electrode. The electrolyte was a 1.0 mM zinc chloride solution. A potentiostat was used to control the deposition and dissolution processes from -1.0 V to 2.0 V. HS-AFM imaging was performed in dynamic mode with a scanning area of 300 nm^2 and a scanning speed of 1 fps.

Results and discussion

The nucleation and growth process of the deposits was observed at constant potential for 270 seconds (Fig. 1). At 47 s after starting electrodeposition, the nuclei (~11 nm in height) and needle-like structures (~5 nm in height) appeared on the HOPG surface. (Fig. 1(a)). Subsequently, the needle continuously grew and formed a ring shape (Fig. 1(b)). Interestingly at 64 s, the ring form was broken due to the high mobility of the needle tip (Fig. 1(c)). At 68 s, the two needles met each other and the new nucleation occurred inside of the ring (Fig. 1(d)).

In our presentation, we will discuss the dynamic processes of nucleationa, growth and dissolution during potential scanning.

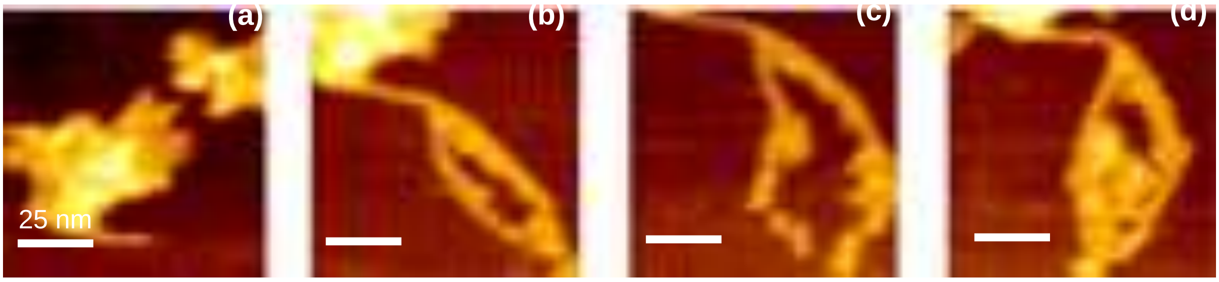

Fig.1 Sequence of HS-AFM images of Zn electrodeposition on HOPG at (a) 47 s, (b) 63 s, (c) 64 s, (d) 68 s (Potential : -265m V).

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High-Speed AFM Observation of Copper Electrodeposition and Dissolution Behavior on HOPG

Cheng Yen Chieh*, Ryuto Ohashi, Tatsumi Naganuma, Mikito Ueda and Hisayoshi Matsushima

[1] Hokkaido University, Faculty of Engineering, Hokkaido, Japan

*** yenchieh.cheng.c6@elms.hokudai.ac.jp**

Abstract

Copper (Cu) has a significant impact in many areas. Cu nanowires has been applied for transparent conductive electrodes due to its excellent conductivity. Moreover, they can be one of candidates for the new generation of IC chip internal interconnects, which helps to reduce interconnect resistance and delay [1]. Electrochemical nucleation and growth occur very fast on the nanoscale; therefore, we have employed high-speed atomic force microscopy (HS-AFM) for the in-situ observation [2, 3]. HS-AFM can observe nano-interfacial phenomena at a maximum speed of 50 frame s^{-1}. In this study, we aimed to observe the nucleation, growth, and dissolution process of Cu during electrolysis using HS-AFM.

The experimental cell was a three-electrode system. Highly oriented pyrolytic graphite (HOPG) was used for the working electrode as an HS-AFM substrate. The counter electrode and the reference both were Cu wire. The electrolyte was from 1~3 mM $CuSO_4 \cdot 5H_2O$ + 50 mM H_2SO_4. Electrolysis was conducted at a constant potential in the range of -900 to 900 mV. HS-AFM was operated in dynamic mode, and the scanning size was 2000 × 2000 nm^2

Figure 1 shows the dependency of Cu nucleation on the potential. The Cu nucleation can be observed from -300 mV to -900 mV. It is very interesting to note that the particle size becomes smaller as the negative potential increases. The particles grow on top of each other in an island-like manner. In this presentation, we will discuss the dynamic behavior of Cu nucleation, growth, and dissolution by HS-AFM videos.

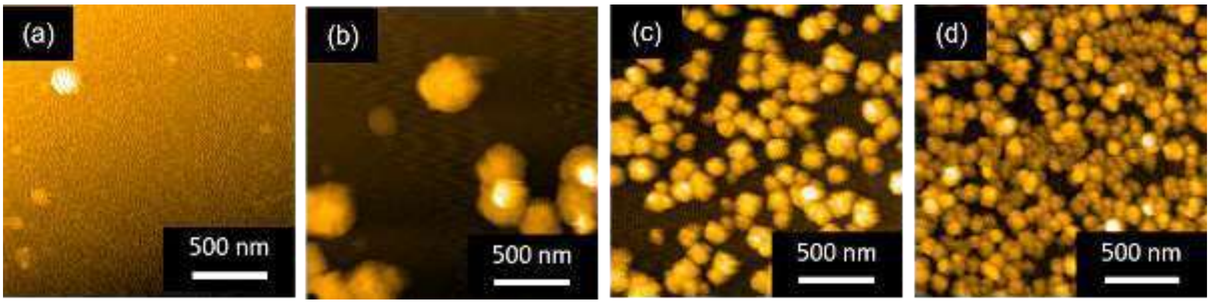

Figure 1. Typical picture of Cu electrodeposition at various potentials of (a) OPC, (b) -400 mV, (c) -600 mV and (d) -800 mV.

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Dynamic Nucleation/Dissolution of Electrolytic Nanobubbles during Potential Sweep by High-Speed AFM

Ryuto Ohashi*, **Tatsumi Naganuma, Cheng Yen Chieh,**

Mikito Ueda and Hisayoshi Matsushima

Faculty of Engineering, Hokkaido University, Sapporo, 060-8628 (Japan)

***ryuto.ohashi@elms.hokudai.ac.jp**

Introduction

An understanding of nano-sized bubbles (NBs: nanobubbles) on electrode surfaces is essential for efficient gas evolution reactions. NBs have been observed by atomic force microscopy (AFM). AFM showed three shapes of NBs: (1) hemispherical cap-shaped NB (Cap NB), (2) nano/micropancake with a flattened top surface, and (3) their composite form, nanobubble-on-pancake. Particularly, Cap NBs are characterized by a very large water-side contact angle (CA). To investigate the reason why NBs form in these unique shapes, dynamic observation of nucleation and growth is indispensable. Recently, high-speed atomic force microscopy (HS-AFM) has been applied to the in-situ observation of electrochemical interfacial phenomena. We studied electrolytic hydrogen Cap NBs using HS-AFM [1]. In this study, the formation and dissolution processes of NBs during potential sweep will be presented.

Experimental

The experimental AFM cell was a three-electrode system. The working electrode was highly oriented pyrolytic graphite (HOPG). The counter and quasi-reference electrodes were Pt wires. The electrolyte was H_2SO_4 solution (5 mmol L^{-1}). After the measurement, the quasi-reference electrode was corrected by hydrogen-absorbing Pd (Pd-H). The potential was swept from −1000 to 1600 mV versus Pd-H at 20 mV s^{-1}. HS-AFM capture rate was 0.5 frames s^{-1} and scan area were less than1000 × 750 nm^2 in tapping mode.

Results and Discussion

When the potential was swept in the anodic direction, nanopancakes were initially formed. When the potential reached the gas evolution potential, Cap NBs (A-Cap NBs: Anodic Cap NBs) were nucleated on the nanopancake. The typical A-Cap NB was 7.5 nm in height and 40 nm in width. When the potential was scanned in the cathodic direction, Cap NBs (C-Cap NBs: Cathodic Cap NBs) were nucleated on the HOPG surface at hydrogen evolution potential. Typical C-Cap NB was 6.0 nm in height and 28 nm in width.

The CAs of A-Cap NBs on nanopancake and C-Cap NBs on HOPG were compared (Figure 1). The mean CAs were 161 ± 5° and 147 ± 9°, respectively. This suggests that nanopancake is more hydrophobic than HOPG. We will show the formation/dissolution process of electrolytic NBs during potential sweep by HS-AFM.

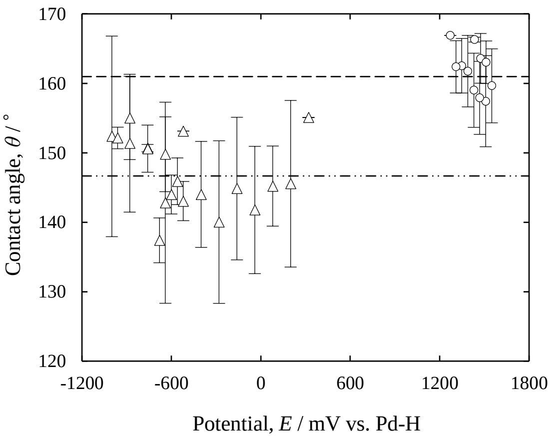

Figure 1 Scatter plots for CAs of A-Cap NBs (circle) and C-Cap NBs (triangle) versus potential. Error bars indicate standard deviations and the dotted lines represent the mean value for each NBs.

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P 29

Influence of Surface Defects, Oxygen Groups, and Alkali Metals on H_2O_2 Generation at Carbon Electrodes

André Olean-Oliveira[ab]*, Najeeb Hasnain[a], Ricardo Martínez-Hincapié[a], Ulrich Hagemann[bd], Adarsh Jain[c], Doris Segets[bc], Ioannis Spanos[a] and Viktor Čolić[ab]*

[a]Max-Planck Institute for Chemical Energy Conversion; [b]CENIDE – Center for Nanointegration Duisburg-Essen; [c]Institute for Energy and Materials Processes – Particle Science and Technology (EMPI-PST), University of Duisburg-Essen; [d]Interdisciplinary Center for Analytics on the Nanoscale (ICAN), University of Duisburg-Essen

*****Andre Olean-Oliveira, andre.oliveira@cec.mpg.de and Viktor Čolić, viktor.colic@cec.mpg.de

Hydrogen peroxide (H_2O_2) is an environmentally friendly oxidant, considered crucial for future “green chemistry”. One promising approach of its synthesis is based on the electrocatalytic reduction of dissolved oxygen (oxygen reduction reaction - ORR) to H_2O_2 using carbon-based materials as catalysts[1]. Despite several reports of carbon-based materials presenting high faradaic efficiency (FE) for H_2O_2 generation, higher current densities for H_2O_2 production in acidic conditions are desirable[2]. Therefore, understanding this reaction's mechanism is crucial for developing and applying carbon-based materials in industrially relevant conditions. The present study aims to investigate the electrochemical ORR over carbon-based model electrodes, such as the basal and edge planes of pyrolytic graphite (PG-Basal and PG-Edge) as well as glassy carbon electrode (GC) and the influence of defects, oxygen functional groups (OFGs) and the presence of alkali metals in the electrolyte on the activity and selectivity toward H_2O_2 generation. We use fresh polished PG-Edge and PG-Basal (Ø = 3.81 mm) and GC (Ø = 5.00 mm) electrodes to investigate the ORR selectivity toward H_2O_2 production. By atomic force microscopy (AFM) the electrode surfaces were characterized and showed roughness square of 6.7, 12, and 17 nm for GC, PG-Edge, and PG-Basal, respectively. The x ray photoelectron spectroscopy (XPS) showed that PG electrodes hold around 9% of OFGs against 2% of GC. RRDE measurement revealed faradaic efficiency (FE %) for H_2O_2 generation of 51% and 80%, and 76% to PG-Edge, PG-Basal, and GC, respectively, in absence of alkali cations. The hypothesis for the trend is based on the mechanism of reaction, using *in situ* Raman, the D peak associated to defects in the graphite sheets, showed to be affected during ORR measurement for PG electrodes, and no variation using GC. Therefore, the mechanism seems to be driven by outer sphere mechanism against inner sphere presented by the GC and PG electrodes, respectively[3]. The impact of alkaline cations on the interaction between active sites and reaction intermediates was assessed, revealing a significant influence. Both PG-basal and PG-edge exhibited an increase in their Faradaic efficiency (FE) in the presence of alkali cations, except for Li^+. For example, PG-basal recorded FE values of approximately 80% in the absence of Cs^+ and around 90% when Cs^+ was present. Although both PG-basal and GC electrodes achieve high FE for H_2O_2 production, alkali cations affect their selectivity differently: PG-basal promotes H_2O_2 formation, whereas GC favors H_2O generation[4]. This behavior is linked to the potential of maximum entropy (PME), here determined by electrochemical step potential impedance spectroscopy measurements (SP-EIS). Therefore, the findings of this study provide valuable insights into the effect of cations on carbon-based materials in ORR and serve as a foundation for future research in this field.

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P 30

Theory of electrochemical plasmonics

<u>Lulu Zhang</u>^{1,2} and Jun Huang^{1,2*}

^{1} Institute of Energy Technologies, IET-3: Theory and Computation of Energy Materials, Forschungszentrum Jülich, Jülich, 52425, Germany

^{2} Theory of Electrocatalytic Interfaces, Faculty of Georesources and Materials Engineering, RWTH Aachen University, Aachen, 52062, Germany
*** ju.huang@fz-juelich.de**

Abstract

Recent experiments have shown that the electron-photon interactions at nanoparticles, reflected in the localized surface plasmon resonance (LSPR) spectrum, are sensitive to the electronic and ionic structure of the electric double layer (EDL) formed at the nanoparticles.[1,2] However, it is very challenging to resolve the molecular structure of the EDL from LSPR measurements, because existing theoretical methods of simulating metal-solution interfaces are difficult to treat electro-ionic interactions in the EDL on the mesoscale (1-100 nm) under constant potential conditions. The density-potential functional theoretic (DPFT) scheme for modeling EDLs[3-6] offers a viable approach for calculating and interpreting the LSPR of EDL at nanoparticles.

In this work, we extend the DPFT framework from equilibrium to nonequilibrium conditions where the EDL is perturbed by an incident optical field. Following the well-established procedure in the field of quantum plasmonics,[7] we convert the time-dependent equations to the frequency space via Fourier transform, calculate the first-order variation in the electron density and the polarizability $\alpha(\omega)$, and then obtain photo-absorption cross section $\sigma(\omega)$ from $\alpha(\omega)$. We use the model to study the influence of the EDL parameters on the calculated LSPR, laying the base for the inversion problem, namely, extracting the EDL parameters from measured LSPR.

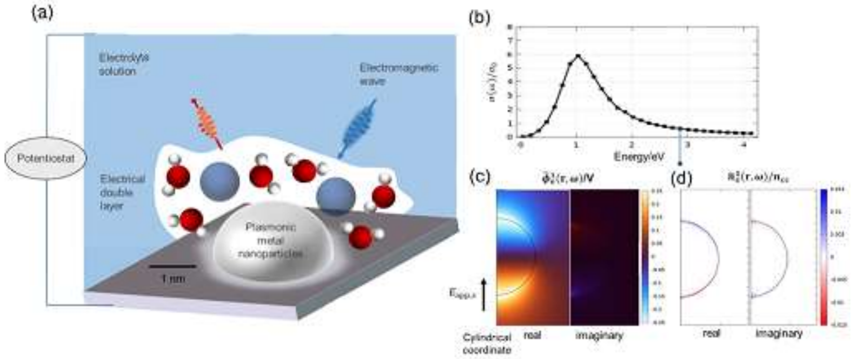

Figure 9. (a) Schematic of the EDL at plasmonic metal nanoparticle and solution interface. The blue wave represents a beam of light, while the red wave means the LSPR. (b) Photo-absorption cross section obtained by DPFT model for Au nanoparticle with the radius as 5 nm in vacuum. (c) The first-order variation in the electric potential and (d) the electron density at 2.9 eV (429 nm, 700 THz) in terms of the real part and imaginary part.

Acknowledgement

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How good is orbital-free density functional theory for metal-solution interfaces? Comparison with an orbital-based method for a 1D model

Xiwei Wang[1,2], Chenkun Li[1,2], Jun Huang[1,2*]
[1] IET-3, Forschungszentrum Jülich GmbH, Jülich, 52425 (German)
[2] Theory of Electrocatalytic Interfaces, Faculty of Georesources and Materials Engineering, RWTH Aachen University, Aachen, 52062 (German)
**** ju.huang@fz-juelich.de***

Abstract

Orbital-free density functional theory is a linearly scaling method approximating the kinetic energy density with an explicit functional of electron density, such as Thomas-Fermi-von-Weizsäcker (TFvW) functional[1],[2]. However, the approximation of kinetic energy density functional (KEDF) for electrical double layers is limited by unverified accuracy[3] .To benchmark the accuracy of KEDF, an orbital-based method should be established. Kohn-Sham-Poisson-Boltzmann (KSPB) Theory[4], which gives an unified orbital-based description to the metal-solution interfaces, combining Kohn-Sham equation and Poisson-Boltzmann equation with coupling relationship between the quantum behavior of electron density and electrostatic potential.

Here, we develop a KSPB model using in-house Matlab code as the orbital-based benchmark and compare the results for electrical double layers with an orbital-free model with TFvW functional. Both models are implemented for the simplest one-dimensional structure, eliminating structural complexity and focusing more on orbital-free kinetic energy functional itself. In addition, the symmetric structure (solution-metal-solution) is designed for easier boundary condition controlling. The double layer capacitance curves from KSPB model and orbital-free model show that TFvW with θ_T =0.7 predicts the potential of zero charge, but overestimates the electron spillout, resulting in higher double layer capacitance at more negative electrode potentials.

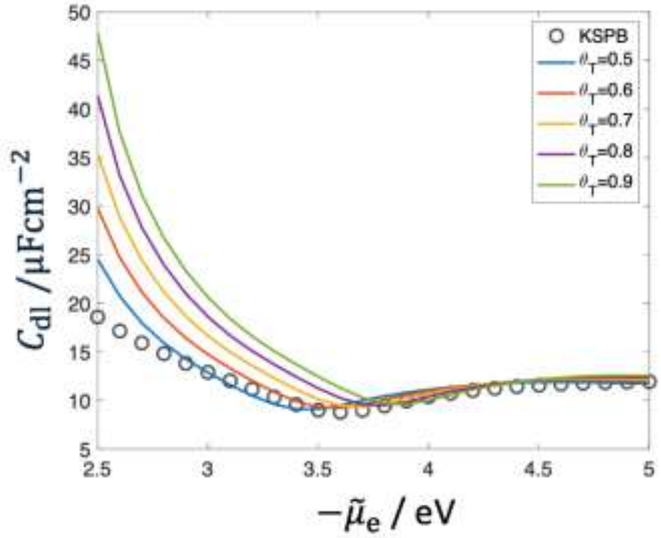

Figure 1. Double layer capacitance comparison between KSPB model and an orbital-free model with Thomas-Fermi-von-Weizsäcker functional

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Operando X-ray diffraction studies of Co oxide model catalysts during alcohol oxidation and oxygen evolution reaction

C.H. Scharf[1], J. Tian[1], J. Stettner[1], K. Dyk[1,2], A. Kotova[3], S. Reinke[3], J. Linnemann[3], F. Maroun[4], O.M. Magnussen[1*]

[1] Institute of Experimental and Applied Physics, Kiel, 24098 (Germany)

[2] Saule Research Institute, Wrocław, 54-427 (Poland)

[3] Chair of Analytical Chemistry II, Ruhr University Bochum, Bochum, 44801 (Germany)

[4] Physique de la Matière Condensée - Ecole Polytechnique - CNRS, Palaiseau, 91128 (France)

*magnussen@physik.uni-kiel.de

Abstract

Understanding the relationship between the surface structure of electrocatalysts under reaction conditions and their catalytic properties is of fundamental importance for the improvement of sustainable energy systems and industrial processes. Transition-metal oxides, such as Co_3O_4, are among the best precious-metal-free electrode materials for the anodic oxygen evolution reaction (OER) in alkaline electrolysis which is a key reaction in the chemical conversion of renewable energy [1-5]. Moreover, they are an important class of catalysts for the selective oxidation of organic compounds in the liquid phase [6].

Here, we present *operando* SXRD studies of OER model catalysts, consisting of thin epitaxial Co_3O_4(111) films electrodeposited on Au(111) substrates [7]. Our recent studies have shown that calcinating the samples by thermal annealing leads to the complete absence of potential-dependent changes on calcinated Co_3O_4, indicating that no reversible skin layer is formed. These calcination-induced structural changes of the Co_3O_4 catalysts affect the OER activity at low current densities. In addition, we performed combined electrochemical impedance spectroscopy (EIS) and *operando* SXRD measurements on as-prepared and annealed Co_3O_4 thin films. The EIS data exhibit clear characteristic changes upon annealing and allow to distinguish between different elementary processes at the catalyst interface, enabling us to identify correlations between these processes and the skin layer formation. These results provide detailed insights into the potential-dependent structure of Co_3O_4 catalysts and the OER mechanism.

Furthermore, similar *operando* SXRD studies for ethylene glycol (EG) oxidation on Co_3O_4 films revealed similar structural changes, even though they appear to be less pronounced under alcohol oxidation conditions, especially at higher EG concentrations. These studies will contribute to a deeper understanding of structure and reactivity of Co_3O_4 catalysts during liquid phase oxidation catalysis.

We acknowledge financial support by the Deutsche Forschungsgemeinschaft via special research area TRR 247, project B10 (project no. 388390466).

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Operando X-ray Diffraction Studies of structurally-defined Co oxide thin Films during Oxygen Evolution: Skin Layer Formation and Reactivity

**J. Stettner[1], T. Wiegmann[1], C. Qiu[1], F. Reikowski[1], C. Scharf [1], M. Bouvier[2],
I. Pacheco[2], M. Bertram[3], F. Faisal[3], O. Brummel[3], J. Libuda[3], J. Drnec[4],
P. Allongue[2], F. Maroun[2], O.M. Magnussen[1*]**
[1] Institute of Experimental and Applied Physics, Kiel, 24098 (Germany)
[2] Physique de la Matière Condensée - Ecole Polytechnique - CNRS, Palaiseau, 91128 (France)
[3] Interface Research and Catalysis, Universität Erlangen-Nürnberg, Erlangen, 91054 (Germany)
*** magnussen@physik.uni-kiel.de**

Abstract

The need for environmental friendly and sustainable energy conversion has triggered renewed interest into the electrochemical and photoelectrochemical splitting of water. A key challenge in this field is the development of economically viable electrocatalyst materials for the oxygen evolution reaction (OER) [1]. Transition metal oxides, such as Co_3O_4, present good catalytic properties and stability in alkaline solution under ambient conditions.

Previous studies of different groups, including us, have shown for Co_3O_4 in alkaline electrolytes a fast, reversible transition of the near-surface region under pre-OER conditions, where a sub-nm thick $CoO_x(OH)_y$ skin layer without long range order forms. Using synchrotron-based operando X-ray diffraction and electrochemical measurements on structurally well-defined, ≈ 20 nm thick Co_3O_4 films, we found that the formation of this skin-layer is accompanied by a reversible compression of the underlying Co_3O_4 lattice [2]. These structural changes start well below the onset of the OER, which indicates that the they have to be attributed to the oxide electrochemistry but not by the OER reaction itself. In a more recent work of our group, we investigated Co_3O_4 films with substantially differing morphologies, revealing a clear correlation between the skin layer volume and the OER reactivity and suggesting that the skin layer is an OER active interphase [3].

Here, we present systematic comparative studies of the potential- and pH-dependent structure and structural stability of Co_3O_4 and CoOOH films, using operando X-ray diffraction, atomic force microscopy, and electrochemical measurements. We found that Co_3O_4 films exhibit for all pH values reversible, potential-dependent skin layer formation, whereas CoOOH films were structurally perfectly stable under all experimental conditions [4]. However, for lower pH values, the Co_3O_4 surface roughens, partial dissolution occurs and the skin layer volume slightly increases. OER reactivity decreases, which may be explained by blocking effects of buffer phosphate ions incorporated or adsorbed in the Co_3O_4 skin layer surface. Apart from the pH value, we also studied the dependence on the main cation in the electrolyte and on processing temperatures up to 52°C. Whereas we found no evidence for main cation choice influence, elevated temperatures result in a larger skin layer volume. However, also at elevated temperatures all potential-induced Co_3O_4 structural modifications are highly reversible.

In total, we have shown that the reversible formation of a skin layer and Co_3O_4 lattice compression, strongly coupled to the OER reactivity, is occurring over a wide range of electrolytes and technologically relevant temperatures. These results will help providing a knowledge base for a deeper understanding of OER reaction mechanism on the atomic-scale level.

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A Newly-Developed Electrochemical Video STM for Adsorbate Diffusion Studies

Fabian Schröfel[1], **Chaolong Yang**[1], **Knud Schröter**[1], **Olaf Magnussen**[1]*
[1] **Institute for Experimental and Applied Physics, Kiel University, Kiel, 24118 (Germany)**
*** magnussen@physik.uni-kiel.de**

Abstract

The observation of many dynamic processes at the solid-liquid interface requires special instrumentation because their high rates make them inaccessible to a wide range of common experimental techniques. For example, diffusion rates of adsorbed atoms and molecules are often in the range from 0.1 to 100 s^{-1}. High-speed scanning tunneling microscopy (video STM) achieves imaging rates of >10 s^{-1} while also providing a spatial resolution sufficient for the identification of individual atoms. It has therefore proved to be a valuable tool for the quantitative analysis of such processes.

Our group has long been operating a unique custom-designed electrochemical video STM, which has allowed to reveal many intriguing details on various surface dynamic phenomena [1]. However, advances in electronics components and computing power in recent years have opened room for improvement with regards to usability and avoiding limitations of the old design. For that reason, we developed a new electrochemical video STM that is based on a commercial STM controller and home-built add-on instrumentation for electrochemical control and high-speed image acquisition [2]. Among other things, the new instrument allows a much more flexible selection of the scan speed that ranges from conventional imaging rates, where the scan is operated by the commercial controller in constant-current mode, up to beyond video rate, where our video controller performs a constant-height scan. Additionally, the control of the new instrument is now fully software-based and therefore more accessible, more user friendly, and more easily extensible than its predecessor, which relied heavily on analog controls.

In this presentation, we will demonstrate that the new video STM is capable of *in situ* video-rate imaging electrode surfaces with atomic resolution (Fig. 1) and investigate the effect of different scan parameters, such as imaging rate and tip path. We will present investigations of sulfur diffusion on Cu(100) and Ag(100) surfaces, a system that is particularly well suited for video STM measurements due to its experimental accessibility. It has been the focus of recent studies of our group, in which we revealed a strong potential dependence of the diffusion coefficient in the presence of a halide adlayer [3]. In our more recent work, we specifically focus on sulfur adsorbates in halide-free electrolytes and show that this system exhibits a similar potential dependence.

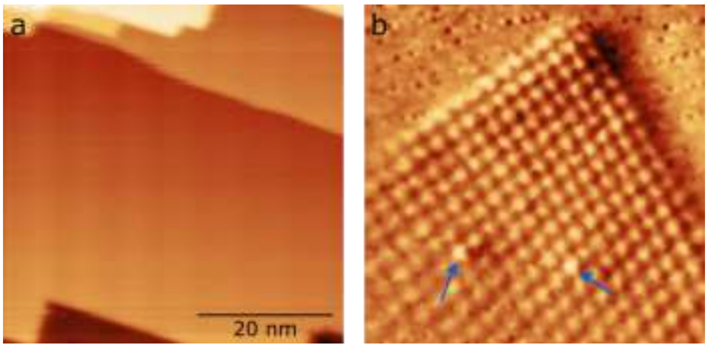

Figure 1. Cu(100) covered with an ordered c(2x2) adlayer of Cl imaged with the new video STM. (a) Large-scale image recorded in conventional constant-current mode. (b) Snapshot from a video recorded at 9 images/s after changing to the fast-scanning constant-height mode. The Cl lattice is clearly visible. The arrows indicate diffusing S atoms.

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Implementation of a video STM for studies of electrochemical interfaces

Knud Schröter, Fabian Schröfel, Matthias Greve, Karsten Tarhouni, Olaf Magnussen*
Institute for Experimental and Applied Physics, Kiel University
Leibnizstraße 19, 24118 Kiel, Germany
*** magnussen@physik.uni-kiel.de**

Abstract

The atomic-scale understanding of processes at the interface between solid electrodes and liquid electrolytes is of high importance for electrochemical energy storage and conversion. Electrochemical scanning tunnelling microscopy (ECSTM) is a key technique for the investigation of these interfaces and as such, it has seen widespread use. However, the image acquisition in a conventional ECSTM is a rather slow process, requiring tens of seconds or minutes per image.

To help understand the precise reaction mechanisms of atomic and molecular species at solid-liquid interfaces, their movement and interactions need to be resolved, which requires higher imaging rates. High-speed STMs (video STMs) are capable of operating at rates >10 images per second, which is sufficiently fast to observe and quantitatively study a wide range of surface dynamic processes, e.g., surface diffusion and growth [1]. However, this technique has not been widely employed, mainly because of the instrumental requirements.

A video STM recording at a rate >10 images per second implies a line frequency in the order of several kHz. Moving the tip at such high speeds is prone to excite mechanical resonances, which can easily lead to unpredictable tip movements and thus distorted images. To avoid this problem, a video STM requires a particularly rigid scanner and good knowledge of its mechanical response. Furthermore, the data acquisition rate quickly reaches a few MHz when increasing the scan speed. Conventional measurement and control electronics are not capable of such rates, neither does any commercial control software provide the fast scan generation and data processing capabilities required. For this reason, all existing video-rate STM studies have been performed with home-built setups that employ highly specialized hardware impeding reproducibility of the experiments.

In this contribution, we present a new high-speed ECSTM developed and built in our group. The basis for our setup is a Nanonis SPM controller by SPECS, which we have combined with a custom scanner and coarse approach control. A self-built bipotentiostat facilitates operation in electro-chemical environment. Recently, we made further modifications to this setup to enable video-rate imaging. These include a custom high-bandwidth preamplifier integrated into the scan head close to the tip and an FPGA-based control software, which features highly optimised data processing capabilities. Additionally, we devised a novel dual-stack scanner design with two independent piezo stacks, whose characteristics are specifically tailored to the requirements of slow and high-speed scans, respectively.

The whole setup is designed to be versatile: It can operate in air as well as in electrolyte and in both slow and high-speed mode. The system allows easy and fast switching between these modes and thus facilitates finding suitable areas on the sample for video measurements.

We will present technical details of the setup with a particular focus on the high-speed components and show in situ as well as ex situ images and videos that we recorded with our setup to demonstrate its performance in slow and fast operation mode.

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Au nanoparticle-catalyzed electron transfer to electrodes for enhanced biosensing sensitivity

Seonhwa Park[1] and Haesik Yang[1*]

[1] Pusan National University, Busan, 46241 (Korea)

*** hyang@pusan.ac.kr**

Abstract

Metal nanoparticle (NP)-catalyzed electron transfer (ET) from a reducing agent to a metal complex enhances signal detection in biosensors. For optimal ET, the metal complex must facilitate rapid outer-sphere reactions, exhibit high water solubility, and penetrate bio/organic layers on the metal NPs effectively. Our research highlights that $Ru(NH_3)_6^{3+}$ and ferrocenmethanol are particularly effective for these purposes. Among reducing agents, ammonia-borane (AB) promotes swift ET catalyzed by metal NPs, with Au, Pt, and Pd nanoparticles showing comparable catalytic efficiency. The pseudo-second-order rate constant for ET catalyzed by 20-nm Au NPs from AB to $Ru(NH_3)_6^{3+}$ is notably high at $1.4 \times 10^8\ M^{-1}\ s^{-1}$, nearing the diffusion-controlled limit. Even with proteins like immunoglobulin G and bovine serum albumin adsorbed onto the Au NPs, their catalytic activity remains mostly intact. Utilizing this Au NP-catalyzed ET approach, we achieved a low detection limit of 10 pg/mL for prostate-specific antigen in human serum.

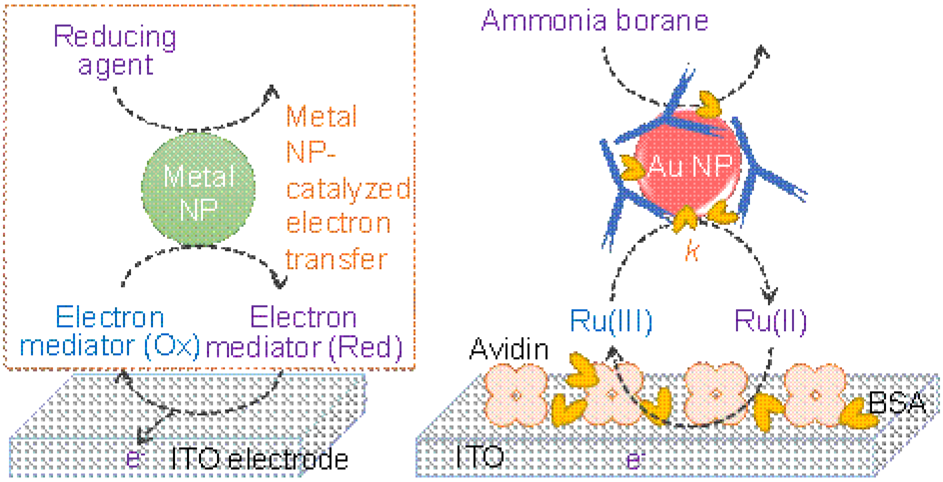

Figure 10. Schematic diagram of metal nanoparticle (NP)-catalyzed electron transfer.

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P 37

Connecting SEI Structure and Chemistry to Electron-Ion Transport Mechanisms and Rates Using Redox Probes

X. Ge[1,2,*], L. Köbbing[3,4], A. Kuhlmann[1,2], M. Nojabaee[3], B. Horstmann[3,4,5], J. Yoo[1], H-G. Steinrück[1, 2]

[1] Forschungszentrum Jülich GmbH, Institute for a Sustainable Hydrogen Economy (INW), Jülich, 52428 (Germany)
[2] RWTH Aachen University, Institute of Physical Chemistry, Aachen, 52074 (Germany)
[3] German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Stuttgart, 70569 (Germany)
[4] Helmholtz Institute Ulm (HIU), Ulm, 89081 (Germany)
[5] Ulm University, Faculty of Natural Sciences, Ulm, 89081 (Germany)
***: x.ge@fz-juelich.de**

Abstract

The Solid Electrolyte Interphase (SEI) originates in the thermodynamic instability of electrolyte moieties on the negatively polarized anode surface. As a result, there is a (electro)chemical reduction of electrolyte moieties, which may react with Li ions and form solid, insoluble products on the anode surface. This SEI limits both electron and solvent transport while permitting Li ion transport, kinetically stabilizing the interface. [1] Despite its importance, several questions regarding central processes related to the SEI remain unresolved, such as the precise SEI formation mechanisms as well as electron and ion transport through the SEI. [2,3]

The objective of our study is (1) to unravel the mechanisms and rates of electron and ion transport across the SEI and (2) to establish a correlation between these processes and the structural and chemical parameters of the SEI. For this purpose, we use ferrocene redox molecules to quantify the rate and mechanism of electron transfer from electrodes to redox molecules. Here, we focused on an SEI composed “exclusively” of LiF (denoted as “LiF-SEI”) on a Pt electrode. We designed our LiF-SEI to be simplified enough to avoid chemical interaction between multiple components within SEI.

LiF selectively generated on Pt electrode through the electrocatalytic reduction of HF (30 - 60 ppm) present in LP40 (1 M $LiPF_6$ in EC/DEC=50/50 (v/v)) electrolyte. [4] The generated LiF-SEI was investigated by *in situ* redox probe experiment with multiple cyclic voltammetry (CV) for its electrochemical interface characterization. In the initial stage of the ferrocene experiments, LiF-SEI is effective in passivating the electrode. Upon multiple scans and/or time passed, the passivation of LiF gradually diminishes. This implies a change in the electronic and/or physical structure of LiF-SEI. To investigate more detailed transport mechanisms of both electron and Li ion through the LiF-SEI, as well as its physicochemical properties, electrochemical impedance spectroscopy (EIS) and electrochemical quartz crystal microbalance (EQCM) experiments were carried out. The mechanistic understanding gained at the atomic and continuum level will permit a direct rationalization of the observed nucleation, growth and evolution of SEI, and test whether electron tunneling plays a role in capacity fading. [5]

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P 38

Differential Electrochemical Mass Spectrometry to Elucidate the Mechanism of Non-Aqueous Electrochemical Reactions

A. Salamé[1], C. J. Bondue[2] and M. T. M. Koper[1*]

[1] Leiden Institute of Chemistry, Leiden University, Leiden, 2300 RA (The Netherlands)

[2] Laboratory of Electrochemistry & Nanoscale Materials, Ruhr-University Bochum, 44780 Bochum, (Germany)

*** m.koper@lic.leidenuniv.nl**

Abstract

Differential Electrochemical Mass Spectrometry (DEMS) is an experimental technique which allows the online and quantitative detection of volatile products formed during electrochemical reactions through mass spectrometry.

DEMS has already been successfully used in our group to study the reduction of nitrates on platinum [1], investigate the competition between hydrogen evolution and carbon dioxide (CO_2) reduction on gold [2], and even elucidate the electrochemical reduction of CO_2 catalyzed by a supported molecular catalyst [3]. Most of these studies were realized in aqueous media. Indeed, the use of DEMS in non-aqueous – organic – solvents remains scarce.

Our setup consists in a two-compartment flow cell (**Fig. 1**) [4], allowing simultaneous measurement of Faradaic current, mass variations and product formation rate, as a function of the electrode potential.

In this poster, we provide a didactic overview of our DEMS setup, present the key questions we have answered thanks to it, and define our upcoming challenge: develop the use of DEMS for the study of non-aqueous electrochemical reactions.

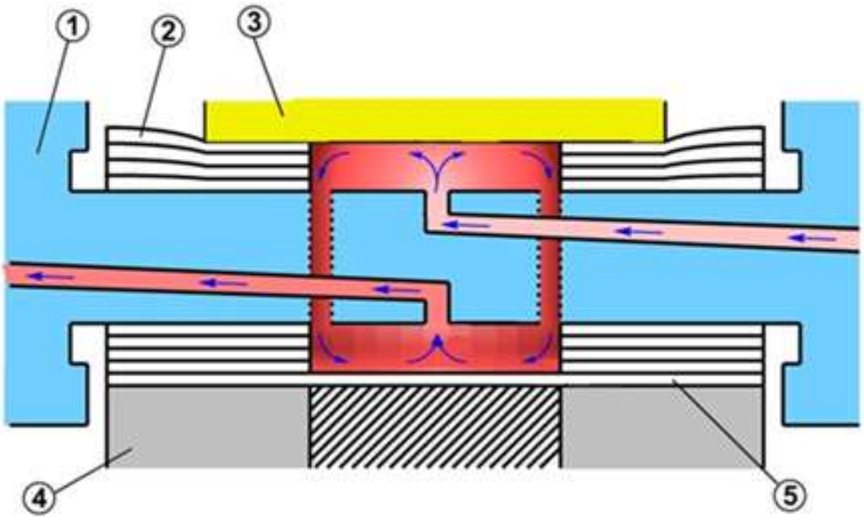

Figure 11. Scheme of the two-compartment flow cell. 1: Cell body; 2: PTFE spacer (upper compartment); 3: Working electrode; 4: Steel holder; 5: PTFE membrane

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P 39

Understanding the Constant Phase Element Behaviour of the Double Layer Capacitance of Pt(111)

<u>Katherine J. Levey</u>,[1,*] Nicci L. Fröhlich,[1] Lucas B.T. de Kam,[1] Steffen Hardt,[1]
Marc T.M. Koper[1]
[1] Leiden Institute of Chemistry, Leiden University, Leiden (the Netherlands)
*** k.j.levey@lic.leidenuniv.nl**

Abstract

The formation of the electrochemical double layer (EDL) upon the application of a potential difference is fundamentally present in all electrochemical processes, however its significance is frequently underestimated. Understanding how this highly non-linear nanoscale region impacts larger macroscale properties is crucial, particularly when considering its implications for electrocatalytic reactions occurring at the interface. A model system for studying EDL effects is the Pt(111)/$HClO_4$ interface which uniquely displays a well-defined double-layer window. In this potential region, the adsorbate-free surface is ideally polarisable as interfacial H_2O does not dissociate. In contrast, lower-coordinated Pt facets such as Pt(110) and Pt(100) dissociate water more readily. However, recent work by Fröhlich *et. al.* demonstrated that, when using electrochemical impedance spectroscopy (EIS) to measure the capacitance minimum in low (0.1 mM) electrolyte concentrations, the EDL behaves as a non-ideal capacitor.[1] In this case, the interface is better modelled by a constant phase element (CPE). The exponent of the CPE element (which quantifies CPE behaviour) exhibited a minimum at the potential of zero charge, where the net charge on the electrode surface is zero. The deviation from idea behaviour increased with an increase in the electrode size and decrease in the electrolyte concentration. While previous work has attributed similar capacitive dispersion effects to surface roughness and specific ion adsorption,[2,3] for the Pt(111) interface in the double-layer window (*i.e.*, adsorbate-free), we ascribe this dispersion to an inhomogeneous capacitance distribution across the electrode surface.[4]

To investigate the role of the electrode geometry plays in the observed CPE behaviour, we have developed a 2D numerical model using the coupled Poisson-Nernst-Planck equations. This single model spans fully from the nm to mm length scales and captures the effects of ohmic potential drop, ion migration and the potential dependence of the EDL structure by employing a simple Gouy-Chapman-Stern model in 2D.[5] In addition, the model extends upon previous work to account for the real-world geometry of the hanging meniscus electrode set-up used in corresponding experimental measurements. Our model highlights the interconnected nature of the nano and macro length scales, where the differences in the diffusivity of the H^+ and ClO_4^- significantly influences the potential dependence of the CPE exponent. While this model accounts for certain aspects of the observed experimental behaviour, it also highlights the absence of a universal approach to modelling this complex and elusive interface.

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P 40
Confining the electrical double-layer

Marco Schönig[1*], **Serge Lemay**[2] **and Marc Koper**[1]

[1] Leiden University, Leiden, 2311EZ (The Netherlands)

[2] University of Twente, Enschede, 7522NH (The Netherlands)

*** m.schonig@lic.leidenuniv.nl**

Abstract

Nanoporous electrodes play a crucial role in modern energy storage and conversion technologies. However, despite their ubiquitous usage, the impact of nanoscale geometrical confinement on their electrochemical properties remains poorly understood. This is particularly relevant when the pore dimensions become so small that the double layers of opposing sides overlap. A key challenge in studying this phenomenon is the need for precise experimental control to enable systematic investigations [1].

In this contribution, we present a fabrication approach for gold slit electrodes with tuneable slit sizes, adjustable with nanometre precision. The fabrication process involves a series of deposition and lithography steps utilizing a sacrificial chromium layer [2].

By varying the electrolyte concentration—and thereby modulating the double-layer extension—we compare the capacitive response of a 5 nm slit electrode in H_2SO_4 under confined and unconfined conditions (Fig. 1). Additionally, we analyse the charging behaviour using pulsed chronopotentiometry and impedance spectroscopy. Finally, we explore the potential of ATR-IR spectroscopy to understand the effect of double-layer confinement on the interfacial water structure[3].

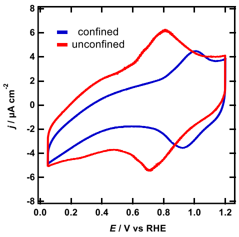

Figure 12. Cyclic voltammogram of a 5nm Au slit electrode in 0.001 M H_2SO_4 (blue) and 0.1 M H_2SO_4 (red); scan rate 50 mV s^{-1}.

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Exploring the Metal nanoparticle/Aqueous Electrolyte Interface by Nanoimpact Electrochemistry

M. Azimzadeh Sani[1] **and K. Tschulik**[1*]

[1] **Ruhr University Bochum, Bochum, 44801 (Germany)**

*** Kristina.Tschulik@rub.de**

Abstract

The advancement and enhancement of sustainability-focused systems, such as renewable energy conversion and storage devices, requires a molecular level comprehension of solid/liquid interfaces. At the interface of a charged electrode with an electrolyte, electrons, solvent molecules, and ions form a structure called electric double layer (EDL). Nanoimpact electrochemistry is a high-throughput technique that enables the study of the EDL properties at individual nanoparticles [1]. In this method, nanoparticles dispersed in the electrolyte solution of interest make electrical connection with a current collector electrode upon collision [2]. Consequently, the nanoparticle's potential equilibrates with that of the electrode, and a transient current signal becomes measurable. This signal reveals the amount of charge required for the rearrangement of the EDL, corresponding to the applied potential. As a result, the EDL capacitance of the nanoparticles can be extracted without any ambiguities caused by overlaying effects relevant for the ensemble measurements commonly used for studying nanoparticles. In this work, we investigate how different ions affect the EDL capacitance of platinum nanoparticles, shedding new light on the underlying structure and interactions at the EDL.

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Electrocatalysis at a Liquid | Liquid | Solid Triple Phase Boundary

M. Spallek[1], **C.J. Bondü**[1] **and K. Tschulik**[1*]

[1] Ruhr University Bochum, Bochum, 44801 (Germany)

*** Kristina.Tschulik@rub.de**

Abstract

Functionalization of biomass-derived platform chemicals is becoming increasingly relevant due to a paradigm shift in the chemical industry induced by the expansion of electrified transportation. That is, conventional crude-oil based platform chemicals, which are obtained as by-products of fuel production, will have decreased economic relevance in the future. Alternatively, biomass from regenerative sources can be converted to valuable building blocks for the chemical industry. In this scope, electrocatalysis is a promising tool in the valorization of biomass-derived organic molecules towards a vast amount of fine chemicals and fuels.[1] However, to achieve economically relevant reaction rates, that is current densities, high concentrations of organic reactants need to be employed. Additionally, electrolytes need high concentrations of either OH^- or H^+ as they are necessary reactants in the electrochemical oxidation reaction or electrochemical hydrogenation, respectively.[2] This poses a problem because a vast number of organic molecules can enter unwanted side-reactions, which include the degradation to polymers, resulting in a decreased product yield and blocking of the electrode surface.[3,4] Aldehydes are especially prone to aldol reactions and Cannizzaro disproportionation, while furoic compounds can undergo ring-opening followed by further degradation.

In our work, we prevent undesired degradation pathways of biomass-derived molecules by separating them from waterborne reactants. That is, organic reactants are employed in an organic phase, which is in contact with the aqueous electrolyte containing OH^- or H^+. The electrocatalyst (i.e., Au) is placed on a nanoporous membrane directly at the interface of both liquids, so a triple phase boundary is formed (Figure 1). Using butanal oxidation as a model reaction, we show that the organic reactant first has to partition into the aqueous electrolyte before it can react with the waterborne hydroxide at the catalyst surface. When the extraction process is rate limiting, this prevents the organic reactants from accumulating and therefore degrading in the aqueous electrolyte. Using this motif, we can achieve high current densities (250 mA/cm^2) with excellent yields demonstrated for the oxidation of biomass-derived furfural to furoic acid.

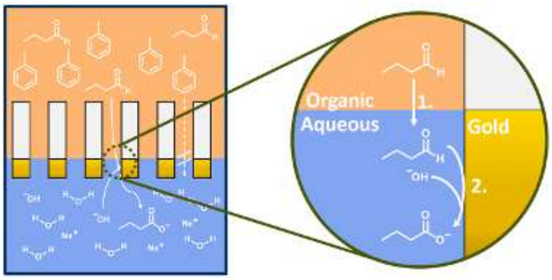

Figure 13. Schematic representation of the liquid | liquid | solid triple phase boundary at nanopores. 1. Extraction into the aqueous electrolyte. 2. Electrocatalytic reaction.

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P 43

Spectroelectrochemical Analysis of Water Confinement and Electrochemical CO_2 Reduction at Au modified with Covalent Organic Frameworks

Yannick Weidemann[1*], Pouya Hosseini[1], Andrés Rodríguez Camargo[2], Bettina Lotsch[2], Kristina Tschulik[1]
[1]Ruhr University Bochum, 44801 Bochum, Germany
[2]Max Planck Institute for Solid State Research, Stuttgart 70569, Germany
*** Yannick.Weidemann@ruhr-uni-bochum.de**

Abstract

The distinct electrochemical behaviour one can achieve by the introduction of nanoscale confinement, has led to a growing interest in the study of the effects introduced by such an environment. Their effects can span changes to the electrochemical double layer but also manifest as a changed electrocatalytic response.[1]–[3] The systematic study of these effects requires a tuneable and reproducible way to introduce confinement and operando techniques, which provide direct insight on the changes to the electrochemical behaviour. In this work, we present a method to introduce such confinement by modification of a bulk electrode surface with 2D covalent organic framework (COF) films. Furthermore, we employed electrochemical surface enhanced infrared absorption spectroscopy (EC-SEIRAS) to directly probe the effect of the COF films on the potential-dependent behaviour of hydrogen-bonded water in 0.1 M $KClO_4$ solutions as well as their effect on the Au-catalysed electrochemical CO_2 reduction reaction (CO_2RR). Three different COF films, with pore sizes of 2.5 nm, 2.7 nm and 2.9 nm respectively, were used. Two of them belong to an isoreticular series, meaning their topology is identical, but an additional benzene ring increases the pore size for one of them. The third one offers an additional Azo functionality in its linker, thereby allowing to disentangle plain pore size related effects and effects caused by different chemical functionality. First, we focussed our studies on hydrogen-bonded water at the interface to confirm the presence of confinement. We found that, the first two COFs led to an enhanced response of the water network to the applied potential resulting in more severe change of the vibrations related to hydrogen-bonded water (3500-3200 cm^{-1}) as well as a shift of their band centre to lower wavenumbers with increasing pore size. Thereby suggesting that depending on the pore-size, the change in the water network will be dominated by water with different degree of hydrogen-bonding. The Azo-functionalized COF resulted in a suppression of change in the hydrogen-bonded water network within the same potential range. This suggests either an already strong network or inhibition to form a network. Similar trends in changed behaviour compared to the unconfined system were also observed during electrocatalytic CO_2RR. The two isoreticular COFs showed an accumulation of CO_3^{2-}, while the COF with a larger pore size showed a simultaneous increase in HCO_3^-. This again indicates a pore size dependent effect causing distinct mass transport inside the pores. Furthermore, it also showed a very strong signal for gaseous CO inside the pores suggesting a longer retention time. A similar trend for CO could be seen with Azo-functionalized COF, but without the accumulation of HCO_3^- and CO_3^{2-}. Overall, these COFs prove a reliable system to induce confinement and allow for better understanding of the resulting effects on electrocatalysis, which in turn may enable better utilisation of confinement effects in electrocatalysis or sensing.

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Dynamically Dealloyed Au-Ag Catalysts for Acidic Ethanol Electrooxidation via Nano-impacts Electrochemistry

HX. Zhang,[1,2] **M.A. Sani,**[1] **DR. Nettler,**[1] **and Prof. Dr. K. Tschulik** [1*]
[1]Ruhr-University Bochum, Universitätsstr. 150, Bochum, 44801 (Germany)
[2]University of Chinese Academy of Sciences, Beijing, 100190 (PR China)

*** kristina.tschulik@rub.de, zhanghanxin21@mails.ucas.ac.cn**

Abstract

Ethanol Electrochemical Oxidation (EOR) serves as a crucial reaction in Direct Ethanol Fuel Cells (DEFCs), playing a pivotal role in advancing clean energy technologies. Ethanol demonstrates distinct advantages over hydrogen and methanol as a fuel source, including high energy density, renewable production through biomass fermentation, and safer storage and transportation characteristics. These properties render ethanol a promising green energy carrier for applications such as portable electronic devices and electric vehicles. [1]

Dealloyed materials such as dealloyed Au-Ag nanoparticles have emerged as promising electrocatalysts for alcohol oxidation,[2,3] due to their porous structure formed by selective corrosion, which increases their surface area and active sites. This enhances their catalytic performance while reducing material usage and overall costs.[4] Understanding the electrochemically induced morphological and compositional changes of these nanoparticles is essential for optimizing porosity, composition, and catalytic performance. However, the heterogeneous nature of nanoparticles makes it difficult to achieve a comprehensive understanding through conventional electrochemical techniques, which average signals from large particle ensembles and are influenced by factors like mass transport and conductivity effects. The development of Nano-impacts Electrochemistry in recent decades has provided a powerful tool for single-particle level investigation and characterization of particle concentration, size, composition, and catalytic activity, overcoming the limitations of traditional methods.[5]

This study investigates the dealloying of individual Au-Ag nanoparticles and the subsequent ethanol oxidation on the dealloyed particles under varying potentials via Nano-impact Electrochemistry. By tracking transient current signals generated by individual particles colliding with an electrode, we try to reveal the dynamic structural evolution of dealloyed Au-Ag nanoparticles, including Ag dissolution and pore formation, while simultaneously measuring their catalytic activity for EOR. This approach allows us to establish direct correlations between structural changes and variation in EOR activity, clarifying the underlying "structure-performance" relationship. These findings offer theoretical insights for the design of next-generation bimetallic EOR catalysts and introduce a methodology for single-particle-level monitoring of catalyst modification and performance, to advance DEFC and electrocatalytic energy conversion.

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P 45

Electrochemical Investigation of Hydrogen Transport in Anodized Aluminium Oxide Nanochannels

<u>Luca Sicking</u>[1*], Oliver Trost[1], Moksh Madan[1], Simon Ospina Velez[2], Tobias Binninger[2], Michael Eikerling[2], Kristina Tschulik[1*]

[1]Chair of Analytical Chemistry II, Electrochemistry and Nanoscale Materials, Ruhr University Bochum, 44801 Bochum, Germany

[2]Theory and Computation of Energy Materials (IET-3), Institute of Energy Technologies, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

***luca.sicking@rub.de, kristina.tschulik@rub.de**

Abstract

Understanding the complex mass transport and reaction mechanisms in nanostructured materials is essential for designing state-of-the-art devices in energy technology, for example fuel cells and electrolyzers. [1] Here, especially the transport of produced hydrogen (H_2) through nanoscale pores and channels plays a key role for the effectiveness of modern setups. [2]

A suitable model system portraying a highly ordered structure is anodized aluminium oxide (AAO). The reproducible synthesis allows to produce macro-scale AAO membranes, while retaining the periodic hexagonal arrangement of cylindrical pores with varying diameter, interpore distance, and channel length. [3] By placing an electrode at the pore bottom and another one on top of the membrane while keeping the pores open, a double sided AAO electrode can be fabricated. This special electrode design allows for studying mass transport and reaction processes inside the (nano)-confined space between the two electrodes.

Utilizing this AAO electrode in pump-probe experiments, generating H_2 at the bottom of the channel and collecting it at the top, reveals a characteristic current response. Comparing the transferred charge at both electrodes allows for insight into the collection efficiency of the system. Additionally, the short delay of the oxidative wave at the top electrode can be directly linked to the transport of H_2 along the channel. Therefore, the key mass transport parameters, e.g. the diffusion coefficient of hydrogen, can be extracted from the current transients and can be linked to experimental parameters like pump potential, pump duration, or the AAO pore diameter.

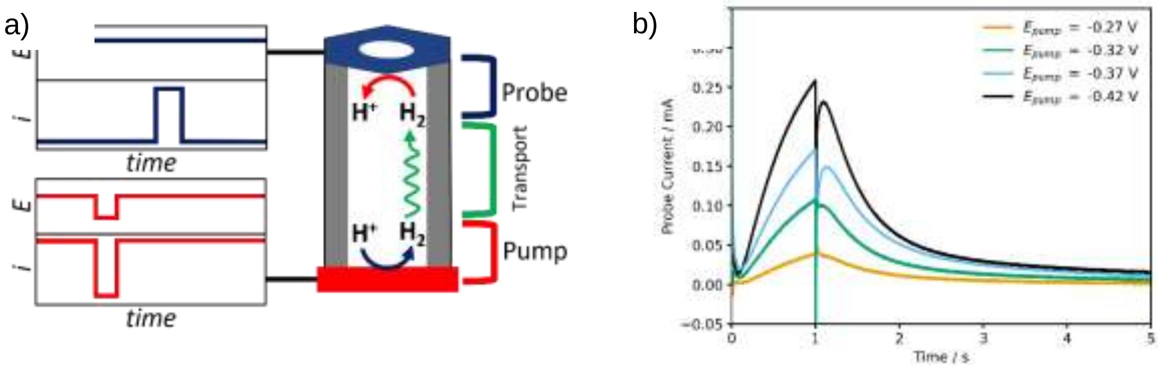

Figure 1. a) Schematic of the two-sided AAO electrode for pump-probe experiments with a pump electrode at the bottom and a probe electrode at the top of the AAO channel. b) Characteristic current response at the probe electrode when applying varying potentials at the pump electrode.

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Statistical Evaluation of IrO_x and RuO_x Catalyst Thin Film OER Measurements

Jonas Forner [1*], Gustav K. H. Wiberg [1], and Matthias Arenz [1]

[1] Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Switzerland

*** E-Mail: jonas.forner@unibe.ch**

Abstract

Iridium (Ir) and ruthenium (Ru) nanoparticles are among the most efficient catalysts for the oxygen evolution reaction (OER) in acidic media. However, when tested as thin films their performance can vary due to factors such as film morphology, substrate interactions, and measurement conditions. To ensure statistical reliability, a sufficient number of independent experiments must be conducted to account for these variations and obtain meaningful data.

This study highlights the importance of statistical validation in OER measurements for IrO_x and RuO_x nanoparticle thin films. We demonstrate that single or few measurements can lead to misleading conclusions, particularly when assessing intrinsic activity, as variations in catalyst distribution, film thickness, and electrochemical conditions can significantly affect the observed performance. By applying statistical analysis to a dataset of repeated experiments, we identify the minimum number of replicates required for reproducible and statistically significant results. Furthermore, we discuss the implications of inadequate sampling on data interpretation, emphasizing how insufficient statistical validation can lead to overestimation or underestimation of catalytic activity. Our findings underline the necessity of rigorous experimental design in electrocatalysis research, ensuring accurate benchmarking and comparability across studies while reducing the risk of data misinterpretation.

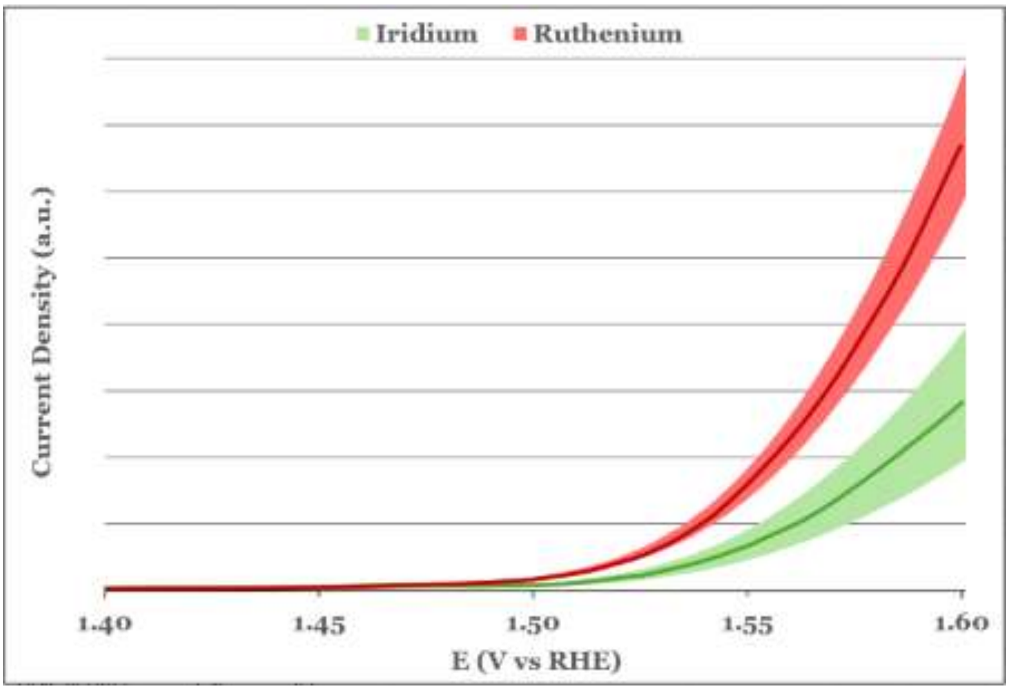

Figure 14. Proposed visualization of mass-specific current density (J) as a function of potential (E vs. RHE) for Ir and Ru nanoparticle thin films, with shaded areas representing hypothetical data spread to illustrate statistical variation.

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Transforming Nitrate into Ammonia over Kinetically Stabilized Co Metal-Hydroxide Composite Foams:

A Complementary *Operando* Analytical Approach

N. Ashtaman Pillai Syamaladevi[1], A. Dutta[1], H. Nedumkulam[2], Z. Szakaly,[3] S. Vesztergom[1,3], J. Drnec[2], R.K. Pittkowski[4], and P. Broekmann[1]

[1]National Centre of Competence in Research (NCCR) Catalysis; Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Switzerland

[2]European Synchrotron Radiation Facility (ESRF), Grenoble, France

[3]Eötvös Loránd University, Budapest, Hungary

[4]University of Copenhagen, Denmark

Abstract

A porous Co-based metal-oxide foam catalyst has been fabricated using the dynamic hydrogen bubble template (DHBT) electrodeposition technique in combination with thermal annealing (6 h at 300 °C). Electrolysis data demonstrate excellent performance characteristics of this novel Co composite catalyst for the electrochemical nitrate reduction reaction ($\mathrm{NO_3^-RR}$), attaining near-unity Faradaic efficiency for ammonia at comparably low (over)potentials of $E = -0.2$ V vs. RHE. Complementary digital simulations confirm that the electrochemically active surface area –relevant to the $\mathrm{NO_3^-RR}$ – is not constant, but highly dynamic, due to rapid nitrate depletion in the interior of the three-dimensional foam catalyst, occurring in the absence of extra electrolyte convection on a millisecond time scale. An active inner surface of the 3D foam catalyst can, however, be recovered, e.g. under conditions where the $\mathrm{NO_3^-RR}$ is superimposed on the gas-evolving hydrogen evolution reaction (HER), which allows for effective electrolyte replenishment inside 3D catalyst materials. The establishment of such a 'self-convective' system is considered the physical origin for the observed high partial current densities for ammonia, which exceed several hundred milliamperes per square centimeter (geometric surface area).

A combination of complementary *operando* analytical techniques (X-ray absorption, X-ray diffraction, and Raman spectroscopy) and electrochemical analysis reveals the in situ evolution of a high-performance 'tandem' catalyst during electrolysis consisting of β-$Co(OH)_2$ and metallic Co serving as the active phase for the $\mathrm{NO_3^-RR}$ and HER, respectively. The co-existence of β-$Co(OH)_2$ and metallic Co, evidenced by *operando* XAS and XRD measurements during simultaneous $\mathrm{NO_3^-RR}$ /HER, suggest a substantial kinetic stabilization of β-$Co(OH)_2$ as active phase for the nitrate-to-ammonia conversion.

P 48

HMF electrooxidation on robust nickel-foam catalysts: pH effects on the electrolysis performance

L. Galvez Vazquez[1*], **A. Dutta**[1], **S. Vesztergom**[2], **R. Zaug Z**[1]. **A. Rudnev**[3], **and P. Broekmann**[1]

[1] **University of Bern, Bern, 3012 Bern (Switzerland)**

[2] **Eötvös Lorand University, 1117 Budapest (Hungary)**

[3] **Russian Academy of Sciences, 119071 Moscow (Russia)**

*** liliana.galvez@unibe.ch**

Abstract

Produced from biomass, 5-hydroxymethylfurfural is a key platform chemical for manufacturing value-added compounds. Remarkably, the electrochemical oxidation of HMF to 2,5-furandicarboxylic acid (FDCA), a key precursor for bio-based polyethylene furanoate plastics, has gained popularity as a green and efficient replacement for conventional anode reactions in power-to-value electrolysers. This study mainly addresses the **essential role of alkalinity and OH^-/HMF concentration ratios** on the response of NiOOH-based electrocatalysts in the electrochemical HMF oxidation reaction (HMFOR).

Voltammetric and potentiostatic studies show that the solution pH significantly affects the reaction rate and the selectivity of the products in the HMFOR. Higher alkalinity promotes selective oxidation towards FDCA. However, a high solution pH accelerates the degradation of HMF to unwanted byproducts and adds complexity to the isolation of FDCA. An ideal OH-/HMF concentration ratio of 2 to 4 was found to provide a balance between maximizing the FDCA production rate and reducing alkali consumption. Additionally, the study highlights the importance of **upholding sufficient OH^- ion availability** during prolonged electrolysis to guarantee efficient catalyst performance and system stability.

These results provide a crucial understanding for the optimization of HMFOR systems, opening the way for sustainable and economically viable production of FDCA and other bio-derived chemicals.

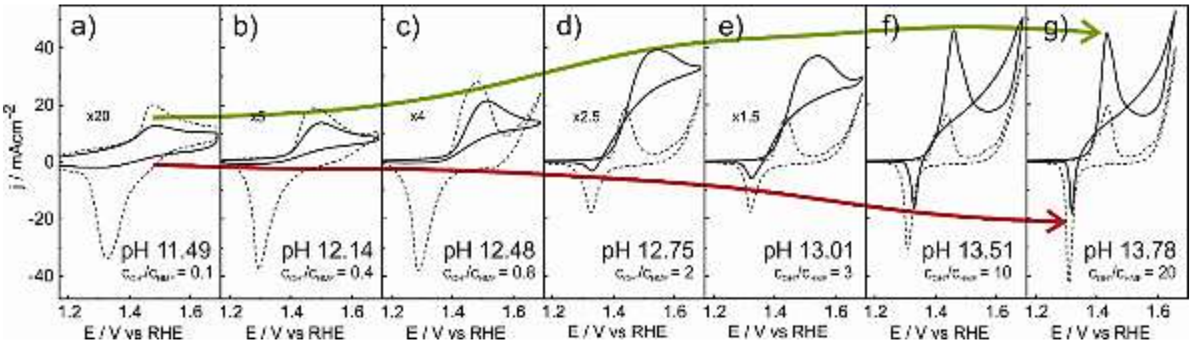

Figure 1. CVs of Ni-foam electrodes in solutions of different pH with (solid curves) and without (dashed curves) 0.05 M HMF.

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On the Faradaically Active Surface Area of Metal Foam Electrodes

Zsolt Szakály[1*], Xin Yu[2], Nandu Syamaladevi Ashtaman[2],
Liliana Gálvez Vázquez, Abhijit Dutta[2], Peter Broekmann[2], Soma Vesztergom[1]
[1] Eötvös Loránd University, H–1117 Budapest, Pázmány P. s. 1/A, Hungary
[2] University of Bern, CH–3012 Bern, Freiestrasse 3, Switzerland
* zsolt.szakaly@ttk.elte.hu

The application of dynamic hydrogen bubble templating (DHBT) allows the pereparation of hierarchically structured metal foam electrodes that can effectively be used for the catalysis of many technologically relevant electrolytic processes, including nitrate and CO_2 reduction, as well as anodic processes alternative to oxygen evolution.

By changing the process parameters of foam deposition (the applied current density, the composition of the galvanic bath and the deposition duration), basic metrics of the deposited foam structure can be customized and foams of different characteristic pore size, opening angle, and thickness can easily be created. The overall surface area of the deposited foams is usually orders of magnitudes higher than the geometric area of the substrate — however, not all of it can actually contribute to Faradaic reactions that are already mass-transport limited.

The aim of this presentation is to create a simple model that can predict the (Faradaically) effective surface area of metal foams of different geometries, under various hydrodynamic conditions of electrolysis where convection defines a known diffusion layer thickness. The model is based on an approximation that the Faradaically effective surface can be estimated as the area of a diffusion front placed at a known Euclidean distance from the foam structure, and that the foam itself can be described as a statistical ensemble of truncated conical holes placed inside a quasi-planar surface. Approximations of the model can be proven valid by 3D simulations of material transport. As statistical data on the pore sizes and foam thickness can be obtained by the analysis of scanning electron microscopy images (Figure 1.a and b), using the conical pore model (Figure 1.c) and the assumption of a finite diffusion layer thickness δ, we can predict the Faradaically active surface area of foam electrodes (Figure 1.d). Our predictions are in good agreement with the results of model experiments (using a viologen redox system), and can pave the way towards a knowledge-driven optimization of foam electrode properties applied in industrial processes.

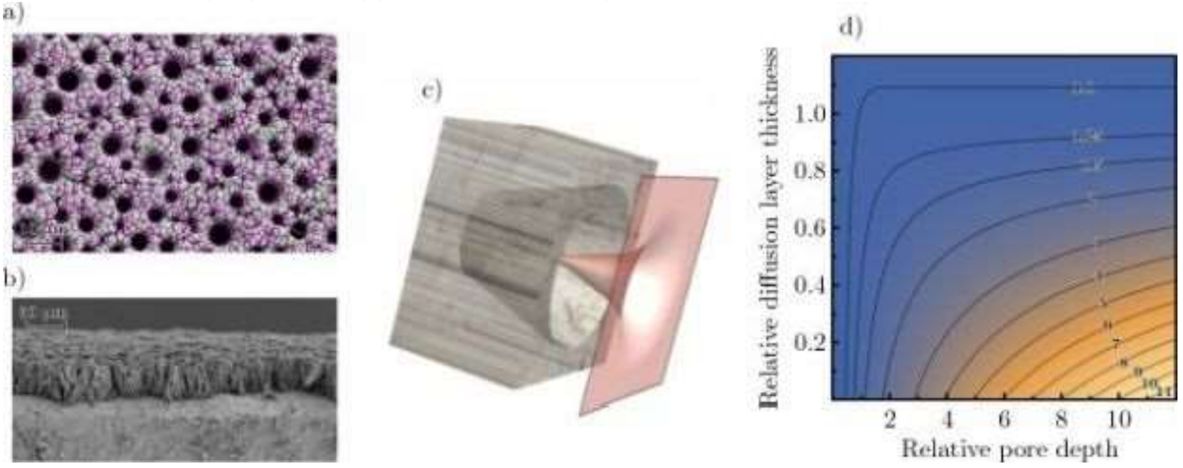

Figure 15. (a, b) Top and side-view of SEM images of a nickel foam. (c) Three-dimensional representation of a truncated conical pore with a semi-penetrating diffusion layer. (d) Current increase vs. the diffusion layer thickness and pore depth (both relative to the pore opening radius), shown as a contour plot.

P 50

Electrocatalysis of the oxygen reduction at knitted polymers

<u>Shumaila Razzaque,</u> Alla Dyachenko, Aimen Waqar, Katarzyna Dusilo and Marcin Opallo[1*]
[1] Institute of Physical Chemistry, PAN, Warsaw, (Poland)
*** srazzaque@ichf.edu.pl**

Abstract

Designing and exploring a non-metalated electrocatalysts for efficient oxygen reduction reactions (ORR) is an imperative for commercializing fuel cell and metal-air batteries. Unlike conventional metal-based catalysts, knitted polymers provide a sustainable and cost-effective alternative, while mitigating issues related to metal scarcity and environmental pollution.[1] They can be designed with specific functional groups, heteroatom doping (e.g., nitrogen, sulfur, or phosphorus), and controlled porosity, enhancing their catalytic activity, electron transfer efficiency and stability. [2]

The knitting is unique and facile in constructing the interconnected polymer chains forming hierarchical pores, responsible for the efficient charge transport and mass diffusion during the electrocatalytic process. Moreover, this approach enables the seamless integration of diverse aromatic monomers with tailored electronic and structural properties. Polymeric network is formed through covalent cross-linking, typically facilitated by external linking agents such as formaldehyde dimethyl acetal or other electrophilic cross-linkers. They help connect aromatic units via methylene or other robust linkages, creating a highly porous, interconnected matrix. Aromatic monomers, such as benzene, pyridine, thiophene, and their derivatives, possess distinct electron distribution that significantly impact the catalytic performance of the polymers. Additionally, the knittng is scalable, and it does not require complex synthetic procedures or expensive precursors, making it an attractive route to design next-generation electrocatalysts for fuel cells and metal-air batteries. [2,3]

In this study, we demonstrate, hypercrosslinked polymers (HCPs) provide an effective platform for ORR by offering a high surface area, abundant active sites and tailored electronic properties without the need for high-temperature treatment. [4]

For ORR electrocatalysis, we designed an electrocatalyst based on a copolymer of non-planar triphenylbenzene and nitrogen-rich triphenylamine. The introduction of nitrogen functionalities improves electron density, facilitating oxygen adsorption, activation, and subsequent reduction. Additionally, the hypercrosslinked structure enables rapid charge transfer and mass transport, ensuring efficient ORR kinetics. Tafel slope value (0.067 V dec^{-1}) indicates the efficient electrocatalytic activity and fast reaction kinetics. The lack of H_2O_2 product detected by scanning electrochemical microscopy suggests 4-electron path. [4] A key advantage of this system is its ability to maintain high activity in both alkaline and acidic media, overcoming frequent limitation of non-metal catalysts.

Beyond copolymer-based systems, we also explored ORR activity in HCPs synthesized from single aromatic monomers. These materials exhibited measurable catalytic performance, confirming that hypercrosslinking itself plays a crucial role in generating ORR-active sites. Our findings highlight HCPs networks as a new class of sustainable, metal-free electrocatalysts capable of driving efficient ORR. Further optimization of HCP-modified electrodes may lead to significant improvements in ORR performance, advancing the development of energy conversion technologies.

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