AIT AUSTRIAN INSTITUTE OF TECHNOLOGY
TOMORROW TODAY

CEST competence center

INVITATION

WORKSHOP **SIMULATIONS OF/AT ELECTRODE INTERFACES**

The AIT Austrian Institute of Technology and CEST
invite you to the workshop:

»SIMULATIONS OF/AT ELECTRODE INTERFACES«

Date	**Tuesday, 25th September 2012**
Location	CEST Centre of Electrochemical Surface Technology Viktor-Kaplan-Straße 2, 2700 Wiener Neustadt

Programme

15.00 **Arrival (coffee served)**

Chairman: **Wolfgang Knoll**, AIT

15.30 **Chistoph Kleber**
Welcome at CEST

16.00 **Egbert Zojer**
Institute of Solid State Physics, Graz University of Technology, Graz, Austria
“Using Quantum-Mechanical Modeling to Understand the Electronic Properties of Metal-Organic Interfaces”

16.45 **Jürgen Fleig**
Institute for Chemical Technologies and Analytics, Vienna University of Technology
“Electrode Reactions in Solid State Ionics: Concepts, Models, Simulations”

17.30 **Bernhard Gollas**
Institute for Chem. and Tech. of Mat.,
Graz University of Technology, Graz, Austria
"Modelling of Electrochemical Processes at Cone-Shaped Microelectrodes"

18.15 Departure for Dinner at Domheurigen
Domplatz 2, 2700 Wiener Neustadt (http://hartigs-heurigen.gusti.at/)

Date **Wednesday, 26th September 2012**

Location **CEST Centre of Electrochemical Surface Technology**
Viktor-Kaplan-Straße 2, 2700 Wiener Neustadt

Programme

Chairman: **Christoph Kleber**, CEST

09.00 **Stefan Freunberger**
Institute for Chemistry and Technology of Materials,
Graz University of Technology, Graz, Austria
"Fuel Cell Simulation on Various Relevant Length Scales"

09.45 **Siva Palani**
EADS Innovation Works, Munich, Germany
"Simulation of Galvanic Corrosion"

10.30 **Renate L. C. Naumann**
AIT Austrian Institute of Technology GmbH AIT, Vienna, Austria
"Modelling Studies of Electronic Wiring and Proton Transfer
in a Multi-Redox Center Protein: Cytochrome c Oxidase"

11.15 Coffee Break

12.00 **Rainer Gotsbacher**
Technopol Wiener Neustadt, ecoplus. Niederösterreichs
Wirtschaftsagentur GmbH
"Chances for Network Activities Based on the Smart Frame Network"

12.15 **Jacek Lipkowski**
Department of Chemistry, University of Guelph,
Guelph, Ontario, Canada
"Ordered Molecular Films; from Fundamentals to Corrosion Protection, Production of Metals, Biosensors and Molecular Electronics"

13.00 End of Workshop

»SIMULATIONS OF/AT ELECTRODE INTERFACES«

September 25/26, 2012

CEST Centre of Electrochemical Surface Technology
Viktor-Kaplan-Straße 2, 2700 Wiener Neustadt

Egbert Zojer
Institute of Solid State Physics, Graz University of Technology, Graz, Austria

“Using Quantum-Mechanical Modeling to Understand the Electronic Properties of Metal-Organic Interfaces”

The absolutely crucial role that interfaces play for applications like organic (opto)electronic devices is increasingly acknowledged. In the present contribution, quantum-mechanical simulations are used to gain an in-depth understanding of the electronic properties of such interfaces, in particular those formed between metal electrodes and molecular monolayers. The focus is on understanding the fundamental differences between covalently (typically thiolate-) bonded self-assembled monolayers and layers consisting of strong donors or acceptors that undergo a charge-transfer reaction with the substrate. The electronic properties of the former are often dominated by collective/cooperative effects that electronically decouple the various parts of the SAM and result in SAM-properties qualitative differing from those of the individual molecules. Such effects can also be exploited to realize unexpected transport characteristics of suitably designed layers. The properties of charge-transfer monolayers, on the other hand, are typically determined by Fermi-level pinning. The first part of the talk will focus on reviewing these fundamental aspects for a number of examples; subsequently, deviations from the “conventional” behavior will be discussed. These include Fermi-level pinning in SAMs, the underlying mechanism, workarounds, and how it can lead to an anti-correlation between molecular dipole moments and SAM-induced work-function changes. Additionally, a coverage induced transition from a charge-transfer monolayer type situation to an upright-standing SAM with markedly different electronic properties will be mentioned and the talk will be concluded by discussing, how the internal electric fields in a “distributed-dipole” SAM can impact its electronic structure in a way reminiscent of the quantum-confined Stark effect commonly observed in semiconductor heterostructures.

Jürgen Fleig
Institute for Chemical Technologies and Analytics
Vienna University of Technology

"Electrode Reactions in Solid State Ionics: Concepts, Models, Simulations"

Crystalline solid electrolytes are highly relevant in a number of electrochemical applications, ranging from sensors to batteries to fuel cells and electrolysis cells. Similar to electrochemical cells based on liquid electrolytes, redox reactions have to take place at the electrodes in order to allow for current flow and establishment of equilibrium EMFs. For cells based on metal cation conducting solid electrolytes these electrode reactions exhibit many similarities to their liquid counter parts. As soon as (oxide) anion or proton conducting materials come into play, distinct differences are found: The corresponding reactions involve gas phases and gas molecules are completely unsolvable in crystalline electrolytes. Accordingly, electrode surfaces rather than electrode/electrolyte interfaces may play a key role in solid state electrochemistry.

In this talk it will be shown how this affects the theoretical concepts and models used to quantify and simulate electrode reactions in solid state ionics. Emphasis is put on the oxygen reduction and oxidation reaction which is the main cause of overpotentials in solid oxide fuel cells and solid oxide electrolysis cells.

Bernhard Gollas
Institute for Chem. and Tech. of Mat.,
Graz University of Technology, Graz, Austria

"Modelling of Electrochemical Processes at Cone-Shaped Microelectrodes"

The scanning electrochemical microscope (SECM) can be considered the most important instrumental development in analytical electrochemistry over the past two decades [1]. Its application in the investigation of local electrochemical processes on real world samples has increased over the last years due to the availability of reliable electrode tips and methodological improvements [2]. One of the crucial developments is the electrochemical imaging at constant tip-substrate distance. This is necessary particularly for rough or tilted samples, because the tip current (imaging signal) depends not only on the local reactivity of the sample surface, but also on the tip-substrate distance. Apart from the invention of the shear-force controlled constant distance mode [3], there have been attempts to combine SECM with atomic force microscopy to make use of the precise force feedback control in the AFM for constant distance imaging in SECM. The successful combination of these two methods has been demonstrated some 10 years ago [4,5], but its routine use was hampered by the availability of reliable bifunctional AFM tips with integrated electrodes. We have tried to overcome this limitation in a collaborative effort by developing a microfabrication process for cone-shaped AFM-SECM tips based on robust semiconductor processing steps [6]. The electrochemical behaviour of the tips was modelled in order to estimate how the tip geometry influences their performance. The presentation will thus highlight the dependence of diffusion controlled currents at conical electrodes on tip geometry [7], expressions describing feedback approach curves with such tips [8], as well as their imaging capabilities [9].

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[2] G. Wittstock, M. Burchardt, S. E. Pust, Y. Shen, C. Zhao, Angew. Chem., Int. Ed. 2007, 46, 1584-1617.
[3] K. B. Ballesteros, A. Schulte, W. Schuhmann, Chemistry 2003, 9, 2025-2033.
[4] J. V. Macpherson, P. R. Unwin, Anal. Chem. 2000, 72, 276-285.
[5] C. Kranz, G. Friedbacher, B. Mizaikoff, A. Lugstein, J. Smoliner, E. Bertagnolli, Anal. Chem. 2001, 73, 2491-2500.
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[7] K. Leonhardt, A. Avdic, A. Lugstein, I. Pobelov, T. Wandlowski, M. Wu, B. Gollas, G. Denuault, Anal. Chem. 2011, 83, 2971-2977.
[8] K. Leonhardt, A. Avdic, A. Lugstein, I. Pobelov, T. Wandlowski, B. Gollas, G. Denuault, submitted.
[9] K. Leonhardt, A. Avdic, A. Lugstein, I. Pobelov, T. Wandlowski, B. Gollas, G. Denuault, manuscript in preparation.

Stefan Freunberger
Institute for Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria

“Fuel Cell Simulation on Various Relevant Length Scales”

In polymer electrolyte fuel cells (PEFC) charge and mass transport and the intimately connected heat and current density distribution on all scales is of high interest for improving power density, which is associated to performance and costs. Despite considerable improvements, the major voltage losses in PEFCs arise from poor oxygen reduction kinetics, mass transport limitations and a high resistance of dehydrated ionomer. Catalyst activity and membrane conductivity are material specific properties. However, associated mass transport limitations and the hydration level of the ionomer are highly influenced by structural properties of the gas distributors. This is the morphology of the catalyst layer, mass transport properties of the micro porous layer (MPL) and the gas diffusion layer (GDL), and the flow field geometry. In terms of flow field geometry both the geometry of channels and ribs, the layout of the channels over the cell area, and the relative flow direction of the reactants come into play.

In this talk I will cover modeling efforts and associated experimental diagnostic of phenomena embracing all these length scales.1-7 Both steady state and dynamic models are discussed.

1 Freunberger, S. A., Reum, M., Evertz, J., Wokaun, A. & Buchi, F. N. Measuring the Current Distribution in PEFCs with Sub-Millimeter Resolution. J. Electrochem. Soc. 153, A2158-A2165, doi:10.1149/1.2345591 (2006).

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3 Freunberger, S. A., Wokaun, A. & Buchi, F. N. In-Plane Effects in Large-Scale PEFCs. J. Electrochem. Soc. 153, A909-A913, doi:10.1149/1.2185282 (2006).

4 Schneider, I. A., Freunberger, S. A., Kramer, D., Wokaun, A. & Scherer, G. G. Oscillations in Gas Channels: Part I. The Forgotten Player in Impedance Spectroscopy in PEFCs. J. Electrochem. Soc. 154, B383-B388, doi:10.1149/1.2435706 (2007).

5 Tehlar, D., Flueckiger, R., Wokaun, A. & Buechi, F. N. Investigation of Channel-to-Channel Cross Convection in Serpentine Flow Fields. Fuel Cells 10, 1040-1049, doi:10.1002/fuce.201000034 (2010).

6 Zaglio, M., Schuler, G., Wokaun, A., Mantzaras, J. & Buechi, F. N. Parameter extraction from experimental PEFC data using an evolutionary optimization algorithm. European Physical Journal-Applied Physics 54, doi:23409 10.1051/epjap/2011100190 (2011).

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Siva Palani,
EADS Innovation Works
Munich, Germany

"Simulation of Galvanic Corrosion"

Renate L. C. Naumann
AIT Austrian Institute of Technology GmbH,
Vienna, Austria

“Modelling Studies of Electronic Wiring and Proton Transfer in a Multi-Redox Center Protein: Cytochrome c Oxidase”

Electronic wiring of multi-redox center membrane proteins such as the cytochrome c oxidase (CcO) from R. sphaeroides has been achieved by oriented immobilization on a conducting surface via his-tag technology. Immobilization is followed by reconstitution a protein-tethered bilayer lipid membrane.

We use chemical reaction kinetics to explore the stepwise electron (ET) and proton transfer (HT) reactions of CcO. Proton transport is investigated in terms of a sequence of second order redox reactions, each of them affected by protonations of electron donors and acceptors. We assume fixed rather than shifting pK values, used in previous studies. Proton pumping can thus be simulated particularly when separate proton uptake and release sites are assumed rather than the same proton pump site for every ET step. In order to test these assumptions, we make use of a model system developed earlier, which allows to study direct ET of redox enzymes by electrochemistry. A four-ET model of CcO had been developed making it highly likely that electrons are transferred from the electrode to CuA. Thereafter electrons are transferred along the sequence heme a, heme a3 and CuB. Regarding HT, we consider protonation equilibria of the oxidized and reduced species for each of the four centers. Moreover, we add oxygen/H2O as the terminal (fifth) redox couple including protonation of reduced oxygen to water. Finally we arrive at a kinetic model comprising five redox couples describing a string of second order reactions with protonations. Modeling studies are directly compared with experimental data obtained in the absence and presence of oxygen. As a result, we can show that proton pumping can be modeled in terms of protonation-dependent redox kinetics.

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C. Nowak, M. G. Santonicola, D. Schach, J. Zhu, R. B. Gennis, S. Ferguson-Miller, D. Baurecht, D. Walz, W. Knoll, R. L. C. Naumann, Conformational Transitions and Molecular Hysteresis of Cytochrome c , Oxidase: Varying the Redox State by Electronic Wiring, SoftMatter 2010, 6, 5523–5532

Rainer Gotsbacher
Technopol Wiener Neustadt
ecoplus. Niederösterreichs Wirtschaftsagentur GmbH

"Chances for Network Activities Based on the Smart Frame Network"

Jacek Lipkowski
Department of Chemistry, University of Guelph, Guelph, Ontario, Canada

“Ordered Molecular Films; from Fundamentals to Corrosion Protection, Production of Metals, Biosensors and Molecular Electronics”

I will describe formation, structure and reactivity of thin films of amphiphilic molecules deposited onto a metal surface at the metal-solution interface. Specifically, I will discuss how these molecules aggregate to form monolayer or bilayer films and what is their stability in the presence of electric fields that are on the order of 107 V/m. I will show how these fields affect ordering of molecules within the film and how they cause a phase transitions in the film. I will then discuss various applications of molecular films in corrosion protection, metal electrodeposition, biosensors and molecular electronics.

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