O 71: Focus Session: Nanoscale Insights into Interfacial Electrochemistry II

Time: Wednesday 15:00–17:15 Location: HE 101

O 71.1 Wed 15:00 HE 101

From nanoparticle shapes to mechanisms: modeling the oxygen evolution reaction at IrO_2 nanoparticles from first-principles — •Daniel Opalka, Jakob Timmermann, Christoph Scheurer, and Karsten Reuter — Technische Universität München

The efficiency and commercial viability of proton-exchange membrane (PEM) electrolysers depends critically on the anode catalyst. Chemical stability requirements currently limit the available catalyst materials to iridium oxide based materials. Experiments identified the surface morphology and associated iridium hydroxo groups as important factors in the oxygen evolution reaction mechanism, but the relevant structural features in operating PEM cells remain elusive. In this contribution we develop an ab initio thermodynamics based scheme to predict the surface stoichiometry and composition of individual IrO_2 facets as a function of the applied potential. Combined within a Wulff construction this yields the shape of IrO_2 nanoparticle catalysts at operating conditions. The determined potential-dependent transformations of surface hydroxo groups furthermore allow to conclude on Faradaic charge transfer processes as observed in cyclovoltammetric experiments. From this atomistic picture we finally derive a mechanistic model which explains important reaction steps in the water oxidation reaction.

O 71.2 Wed 15:15 HE 101

Selective solvent-induced stabilization of polar oxide surfaces in an electrochemical environment — •Su-Hyun Yoo, Mira Todorova, and Jörg Neugebauer — Department of Computational Materials Design, Max-Planck-Insitut fuer Eisenforschung GmbH, Duesseldorf, Germany

Solid/liquid interfaces are at the heart of many problems of practical importance, such as water electrolysis and batteries, photo catalytic water splitting, electro catalysis or corrosion. Understanding what surface structures form when the solid is immersed in an aqueous electrolyte is therefore of particularly high interest. Focusing on the ZnO(0001) surface as a typical example of a polar oxide surface, we study the thermodynamic stability of its surface reconstructions subject to the environmental conditions. We find that solvation effects are highly selective: They have little effect on surfaces showing a metallic character, but largely stabilize semiconducting structures, particularly those that have a high electrostatic penalty in vacuum. We will show that this selectivity has direct consequences for the surface phase diagram and discuss the mechanisms by which it is triggered.

[1] S.-H. Yoo, M. Todorova and J. Neugebauer (submitted)

Invited Talk O 71.3 Wed 15:30 HE 101

XPS of ionic liquids: from half-cell to in situ electrochemical measurements — •Annette Foelske-Schmitz[1], Markus Sauer[1], Daniel Weingarth[2], and Rüdiger Kötz[3] — [1]TU Wien, Vienna, Austria — [2]Heraeus Holding GmbH, Hanau, Germany — [3]Paul Scherrer Institut, Villigen, Switzerland

XPS is widely accepted to be a powerful tool to study electrochemically induced changes of the electrode/electrolyte interface. As electrochemical experiments are commonly performed under atmospheric pressure, XPS is usually not applied directly in the analyser chamber. Therefore, three experimental approaches may be distinguished: (i) ex situ, (ii) quasi in situ, and, (iii) in situ EC XPS [1]. The in situ approach may be realised using UHV compatible electrolytes such as ionic liquids (IL). IL are also known to provide large electrochemical stability windows making them attractive for certain electrochemical applications, such as double layer capacitors or lithium ion batteries. In this contribution quasi in situ [2] and in situ [3] EC XPS setups as well as half-cell measurements of IL [4] will be presented and discussed with respect to investigations of interfacial behaviour, stability windows, and interpretation of XPS data.

[1] A. Foelske-Schmitz, Ref. Mod. Chem., Mol. Sci. Chem. Eng., Elsevier, in press [2] A. Foelske-Schmitz, D. Weingarth, R. Kötz, Electrochim. Acta 56 1032 (2011)[3] D. Weingarth, A. Foelske-Schmitz, A. Wokaun, R. Kötz, Electrochem. Commun. 13 619 (2011)[4] A. Foelske-Schmitz, M. Sauer, JESRP, in press

15 min. break

Invited Talk O 71.4 Wed 16:15 HE 101

Single-Molecule Switching in 2D Materials at Solid-Liquid Interfaces — •Stijn F. L. Mertens — TU Wien, Institut für Angewandte Physik, 1040 Vienna, Austria

Living organisms are full of sophisticated molecular machines, and unravelling their structure and function continually inspires man-made nanotechnology, with expected applications from tribology to data storage.

In my talk, I will 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 include self-assembled structures of tailored organic molecules but also hexagonal boron nitride, an atomically thin insulator. The switching events invariably depend on tipping the balance between intermolecular and adsorbate-substrate interactions, and may be controlled by a number of external stimuli: the interfacial potential at electrochemical solid-liquid interfaces, the chemical potential of ionic species in solution, intercalation of atomic species, or the electric field between an STM tip and the substrate.

References: Angew. Chem., Int. Ed. 53, 12951 (2014); Chem. Commun. 50, 10376 (2014); Small 1702379 (2017); Nature 534, 676 (2016)

O 71.5 Wed 16:45 HE 101

Electrochemical STM Imaging of J-Aggregates Immobilized on Au(111) — •Iris Dorner[1], Matthias Müllner[1], Ulrike Diebold[1], Jürgen Hauer[2], Graig N. Lincoln[3], and Stijn F.L. Mertens[1] — [1]TU Vienna, Institute of Applied Physics, Wiedner Hauptstr. 8-10/134, 1040 Vienna, Austria — [2]TU Munich, Associate Professorship of Dynamic Spectroscopy, Department of Chemistry, Lichtenbergstr. 4, 85748 Garching, Germany — [3]TU Vienna, Photonics Institute, Gusshausstr. 27, 1040 Vienna, Austria

J-aggregates are supramolecular assemblies of organic dye molecules with characteristic optical and exciton transport properties and have captured interest in photochemistry, photonics and materials science. Although widely characterized in spectroscopic experiments, models for their structure have been waiting for experimental evidence.

We present electrochemical scanning tunnelling microscopy studies with submolecular resolution of the J-aggregate-forming molecule 5,5',6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidacarbocyanine (TTBC). On bare Au(111), the molecules do not form an ordered structure, which we ascribe to kinetic trapping. If the gold substrate is modified by an iodide adlayer, favourable electrostatic interactions and enhanced lateral diffusion of TTBC yield long-range ordered structures that reflect the hexagonal symmetry of the substrate. Ongoing work aims to reveal to what extent the TTBC adlayer structure is representative of J-aggregates in solution.

O 71.6 Wed 17:00 HE 101

Nanoscale monitoring of temperature dependent lithium particle growth for solid state electrolytes — •Valon Lushta[1], Sebastian Badur[1], Dirk Dietzel[1], Bernhard Roling[2], and André Schirmeisen[1] — [1]Institute of Applied Physics, Justus-Liebig-University Gießen, D-35392 Gießen, Germany — [2]Department of Chemistry,Philipps-University of Marburg, D-35032 Marburg, Germany

Solid-state batteries are a promising approach to safer and more reliable electrochemical energy storage. However, compared to current liquid electrolytes these materials only show a low ion conductivity. In this context, understanding ion transport processes on the nanoscale is considered crucial for the development of improved solid electrolyte systems. Here we have employed a novel approach, where nanoscopic metallic lithium particles are deposited on a solid electrolyte surface by a biased AFM tip [1,2]. To verify, that quantitative values for the local ion mobility can indeed derived by this method, we have monitored the particle volume as a function of the sample temperature for the example of a Ohara lithium ion glass ceramic. From this data the Arrhenius activation energy for ion diffusion could then be calculated and was found to be in good accordance to macroscopic reference data. Additionally, we managed to perform high resolution mapping of the ion mobility by decreasing the particle volumes to only a few 10 nm^3.

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[1] S. Jesse et al., *Nano Lett. 11*, 4161-4167 (2011)

[2] J. Kruempelmann et al., *Electrochem. Comm. 18*, 74-77 (2012)