O 96: Solid-Liquid Interfaces III: Reactions and Electrochemistry II

Time: Friday 10:30–13:00 Location: TRE Phy

O 96.1 Fri 10:30 TRE Phy

First step of the oxygen reduction reaction on Au(111): A computational study of the electrified metal/water interface — •Elias Diesen, Alexandra M. Dudzinski, Hendrik H. Heenen, Vanessa J. Bukas, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin, Germany

While significant insight has been gained in recent years by first-principles simulations of electrochemical processes, crucial methodological challenges remain, especially for accurate determination of reaction energies under operando conditions. One open question is how to represent the constant electrode potential in simulations of an electrified water/metal interface, where the periodic simulation setup requires a constant charge in the simulation cell throughout the reaction. Here we compare different levels of treatment of the electrochemical interface: explicit *ab initio* molecular dynamics, an implicit solvent model, and a sawtooth-potential electric field in vacuum, for the case of O_2 adsorption on Au(111). We find that all methods agree qualitatively in predicting significantly enhanced O_2 binding at more reducing conditions. Important quantitative differences, however, are also presented and discussed. Umbrella sampling simulations shed light on the underlying free-energy landscape at varying potentials, while assessing the level of detail required in first-principles models of the electric double layer.

O 96.2 Fri 10:45 TRE Phy

Multiscale simulation of nanostructured electrocatalytic systems by coupling neural network surrogates and continuum models — •Younes Hassani Abdollahi[1,2], Jürgen Fuhrmann[3], and Sebastian Matera[1,2] — [1]Institut f. Mathematik, Freie Universität Berlin, Berlin, Germany — [2]Fritz Haber Institute of the Max Planck Society, Berlin, Germany — [3]Weierstraß-Institut f. Angewandte Analysis u. Stochastik, Berlin, Germany

The kinetic Monte Carlo method (kMC) is the physically most sound approach for addressing the kinetic interplay of elementary processes at electrocatalytic surfaces but also comes at high computational costs. Therefore, computationally efficient surrogate models are highly desirable which allow the utilization of kMC simulation results in coarser scale simulations.

Using the oxygen reduction reaction on Pt(111) as a prototypical example, we investigate regression neural networks as surrogates to reproduce the stationary TOF as a function of all reaction conditions, i.e. electrostatic potential, concentrations, and temperature. We found that a relatively shallow network serves as an appropriate choice. This surrogate is then coupled to a conservative and thermodynamically consistent Finite Volume discretization of a nanofluidic model. The resulting hybrid mesoscale model will be employed to discuss the interplay of the nanostructure, transport, and kinetics.

O 96.3 Fri 11:00 TRE Phy

Modeling Transport Effects on Selectivity in Electrochemical CO_2 Reduction — •Hendrik H. Heenen[1,2], Georg Kastlunger[2], Vanessa J. Bukas[1], Karsten Reuter[1], and Karen Chan[2] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]Technical University of Denmark, Lyngby, Denmark

Product selectivity in the electrochemical CO_2 reduction reaction (eCO_2RR) is known to change considerably with non-obvious parameters such as catalyst morphology or reactor design. In this work we explore the proposition that these parameters are related to selectivity through transport mediated desorption and adsorption of key intermediates. The mesoscopic morphology of a catalyst can be characterized by a measurable loading or roughness which determines the so-called active surface area. This area may in turn determine the selectivity by controlling the fate of desorbing (closed shell) intermediates along the reaction path: either to re-adsorb and further react on the surface, or to entirely leave the catalyst surface and form an early not fully-reduced product. We specifically show this competition in the reaction toward acetate which we propose to be governed by a solution reaction. Combining *ab initio* energetics, microkinetic and transport modeling in a multi-scale approach, we predict complex selectivity toward acetate with almost quantitative agreement to experiment. Finally, we demonstrate that the same principle applies to other important intermediates in the eCO_2RR. Mesoscopic transport thus provides an alternative or, at least, complementary explanation to changes in selectivity that are otherwise attributed to active sites changes, to doping, or to alloying.

O 96.4 Fri 11:15 TRE Phy

Kinetics of the initial step in Pt electrochemical oxidation — Jan Ole Fehrs[1], Timo Fuchs[1], •Olaf Magnussen[1], Chentian Yuan[2], David Harrington[2], Valentin Briega Martos[3], Serhiy Cherevko[3], and Jakub Drnec[4] — [1]Christian-Albrechts Universität zu Kiel — [2]University of Victoria — [3]Helmholtz Institute Erlangen-Nürnberg for Renewable Energy — [4]European Synchrotron Radiation Facility

A key event in electrochemical metal oxidation is extraction of a metal atom from its lattice site to a location in a growing oxide. The direct observation of this fundamental step is difficult for base metals that actively corrode, because of the difficulty of producing clean surfaces and the speed of the oxidation. However, use of noble metals allows preparation of clean surfaces that are well-defined on the atomic scale, and for which in situ methods can directly observe this extraction. Here we show by fast simultaneous electrochemical and high-energy surface X-ray diffraction measurements, performed at the ID31 beamline of the European Synchrotron Radiation Facility with a photon energy of 70 keV, that the initial extraction of Pt atoms from Pt(111) is a fast, potential-driven process whereas charge transfer for the related formation of adsorbed oxygen occurs on a slower time scale. Electrochemical oxidation is therefore inherently different from gas-phase thermal oxidation, where the extraction must be driven by the chemisorption of oxygen species on the surface.

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O 96.5 Fri 11:30 TRE Phy

CO oxidation on Pt layers on Ru(0001): A UHV-STM, DEMS, and SXRD study — •Albert K. Engstfeld[1], Lukas Forschner[1], Mario Löw[2], Zenonas Jusys[2], Joachim Bansmann[2], R. Jürgen Behm[2], and Jakub Drnec[3] — [1]Ulm University, Institute of Electrochemistry, D-89069 Ulm — [2]Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm — [3]ESRF, F-38000 Grenoble

According to the Sabatier principle, the performance of an (electro)catalyst material is determined by the fine balance between the binding strength of the reactants, reaction intermediates, and products to the catalyst surface. By changing the structural properties of the substrate, the electronic structure and in turn, also the binding of the species can be modified to tune the performance of the catalyst material. However, also the electrode‘s stability plays a crucial role in assessing the catalyst‘s performance.

Here we present results on the CO (and MeOH) electrooxidation on Pt layers with different thicknesses deposited on Ru(0001) under UHV conditions. The structural properties are studied by means of STM under UHV conditions before and after the electrochemical measurements. The electrocatalytic properties are studied in a flow cell (in a DEMS configuration) attached to the UHV chamber. This approach allows for disentangling surface redox processes from catalytic processes. Additional SXRD measurements provide additional insights into the stability of the electrodes. In combination, we discuss the fine balance between surface reactivity and electrode stability.

O 96.6 Fri 11:45 TRE Phy

Electrochemical Roughening of Stepped Platinum Surfaces — •Francesc Valls Mascaró[1], Marc Koper[1], and Marcel Rost[2] — [1]Leiden Institute of Chemistry, Leiden University — [2]Huygens-Kamerlingh Onnes Laboratory, Leiden Institute of Physics, Leiden University

Platinum is the model catalyst to be used in electrochemical energy conversion devices due to its high activity. Nevertheless, its industrial applicability is limited, as it degradates during fuel cell operation. This has been extensively studied by Cyclic Voltammetry and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [1, 2]. It is well known that this degradation is linked to the nucleation and growth of platinum nanoislands on initially atomically flat terraces [3, 4, 5, 6]. However, there is no insight yet on the role of steps on this roughening process. In this work, we combine Cyclic Voltammetry and Electrochemical Scanning Tunneling Microscopy to study the stability of different stepped platinum surfaces upon oxidation-reduction cycling. Surprisingly, the electrochemical results indicate that neither 2D nor 3D (for Pt(533)) and no 3D (for Pt(553)) roughness develops, although we clearly observe island formation in the STM, and thus an increase in the step lengths and roughness.

[1] Topalov, A. et al., Chem. Sci., 5, 631 (2014) [2] Sandbeck D. J. S. et al., ACS Appl. Mater. Interfaces, 12, 25718 (2020) [3] Jacobse, L. et al., Nat. Mater. 17, 277 (2018) [4] Jacobse, L. et al., ACS Cent. Sci. 5 (12), 1920 (2019) [5] Rost, M. J. et al., Nat. Commun. 10, 5233 (2019) [6] Ruge, M. et al., J. Am. Chem. Soc., 139, 4532 (2017)

O 96.7 Fri 12:00 TRE Phy

Shaping the electrochemical interfaces of high-performance photoelectrodes by dedicated corrosion — •Matthias M. May[1,2], Erica A. Schmitt[1,2], Margot Guidat[1,2], Mario Löw[2], Anna-Lena Renz[1], Marco Flieg[1], Max Nusshör[1], Vibhav Yadav[1], Jongmin Kim[1], and Moritz Kölbach[1] — [1]Universität Tübingen, Institute of Physical and Theoretical Chemistry, Tübingen, Germany — [2]Universität Ulm, Institute of Theoretical Chemistry, Ulm, Germany

Photoelectrodes for highly efficient solar water splitting often involve III-V semiconductors, which exhibit only a limited stability under operating conditions due to (electro)chemical corrosion. Yet photoelectrochemical *in situ* functionalisation, which also involves dedicated corrosion, can effectively create an interphase that passivates the solid-liquid interface in a similar manner as solid-electrolyte interphases in batteries [1].

We show how this approach can be used to also electronically passivate III-V/Si dual junction photoelectrodes. A full understanding of the underlying photoelectrochemistry is, however, not yet achieved. To improve this understanding, we study the structural evolution of the interface in the electrolyte, using *operando* reflection anisotropy [2], improving the control of functionalisation and catalyst photoelectrodeposition.

[1] May and Jaegermann, Curr. Opin. Electrochem. **34** (2022) DOI:10.1016/j.coelec.2022.100968. [2] Löw et al., RSC Adv. **12** (2022) DOI:10.1039/D2RA05159A.

O 96.8 Fri 12:15 TRE Phy

Understanding the Interfacial Capacitance of 2D Materials in an Implicit Water Environment — •Hedda Oschinski[1,2], Karsten Reuter[1], and Nicolas G. Hörmann[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]Technical University of Munich, Munich, Germany

The interfacial capacitance (C) is a central quantity in electrochemistry. For metal electrodes, C is dominated by the double layer capacitance that derives from the potential drop in the solvent. However, the finite density of states (DOS) in semiconducting 2D electrodes alters the picture and leads to a vanishing C around the point of zero charge. This entails a challenge in describing the energy-potential relation and the connected field effects when considering adsorbates. To explore this challenge, we study the interfacial capacitance for 2D metal halides MX_2, using density-functional theory in a continuum solvent environment. We break down C into a DOS-filling-related quantum capacitance and the double layer capacitance. Our analysis demonstrates that such a separation into individual components is not straightforward. Nevertheless, the qualitative behavior of C can be rationalized, making this study a first step towards better understanding of 2D, in particular semiconducting, electrodes.

O 96.9 Fri 12:30 TRE Phy

Initial Stages of Cathodic Corrosion of Au(111) in an Ionic Liquid — •Maren-Kathrin Heubach[1], Fabian M. Schuett[1], Areeg Abdelrahman[1], Ludwig A. Kibler[1], and Timo Jacob[1,2,3] — [1]Institute of Electrochemistry, Ulm University, Ulm, Germany. — [2]Helmholtz-Institute-Ulm (HIU), Ulm, Germany. — [3]Karlsruhe Institute of Technology, Karlsruhe, Germany.

At potentials negative of 0 V *vs.* SHE, noble metal surfaces can be etched by a phenomenon called 'cathodic corrosion'.[1] For this process, absence of protons and presence of stabilising cations and adsorbed hydrogen at the electrode-electrolyte interface are required.[2] Even if the presence of water plays an important role,[3] in non-aqueous electrolytes such as ionic liquids, cathodic corrosion can take place as well.[4]

In this study, the cathodic corrosion of Au(111) in the hydrophobic ionic liquid *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide ([MPPip][TFSI]) was studied by *in situ* scanning tunnelling microscopy. Hereby, the formation of equidistant holes at the so-called 'elbows' of the Au(111) herringbone reconstruction was observed. Additionally, it was found that the water content plays a crucial role in the corrosion potential and extent. The higher the water content, the less negative is the onset potential of the cathodic corrosion and the more pits are formed at this potential.

[1] T. J. P. Hersbach, *et al.* Curr. Opin. Electrochem. **2021**, *26*, 100653. [2] A. I. Yanson, *et al.* Angew. Chemie Int. Ed. **2011**, *50*, 6346-6350. [3] M. M. Elnagar, *et al.* Electrochem. Sci. Adv. **2021**, e2100175. [4] F. Lu, *et al.* RSC Adv. **2013**, *3*, 18791.

O 96.10 Fri 12:45 TRE Phy

Parameters Determining Electrode Modification by High Voltage Electrolysis — •Lukas Forschner, Evelyn Artmann, Timo Jacob, and Albert K. Engstfeld — Institute of Electrochemistry, Ulm University, Ulm, Germany

Applying a sufficiently high voltage between two gas-evolving electrodes of different sizes in an aqueous electrolyte can lead to transition from normal electrolysis (NE) to Contact Glow Discharge Electrolysis (CGDE). Due to Joule heating, the electrolyte temperature increases significantly until enough solvent evaporates to form a stable gas sheath around the smaller electrode in which a plasma is ignited. Both in the NE and the CGDE region, the electrode surface can be altered significantly, e.g., by the formation of a Au oxide film[1] or nanoparticles.[2]

During high voltage electrolysis, there are several factors which could influence the restructuring of an electrode surface. First, to disentangle these processes, we measured the distribution of the electric potential in the electrolyte during NE using reversible hydrogen reference electrodes.[3] We found, supported by a COMSOL® model, that the potential distribution mainly depends on the electrolyte conductivity and the cell geometry. Furthermore, we show that the amount of Au oxide formed on a Au electrode during NE is more closely correlated to the current (density) than the voltage (usually provided in the literature).

[1] Artmann et al., *ChemPhysChem* **22** (2021) 2429. [2] Allagui et al., *Electrochim. Acta* **93** (2013) 137. [3] Forschner et al., (2022, submitted).