

O 64: Focussed Session: Solid-liquid Interfaces I

Organizers: M. Arenz (University of Copenhagen), P. Broekmann (Universität Bern), A. Flügel (BASF)

This focused session will offer an interdisciplinary discussion forum for experimental and theoretical work - including aspects in experimental and theoretical method development - in the field of electrochemical energy conversion, energy storage and nano-galvanic processes. The focus of the session is on the question what electrochemical surface science and an atomic level understanding have contributed so far and will contribute in the future to the development of new catalytic materials with advanced properties on a technological level.

Time: Thursday 10:30–13:00

Location: H31

Topical Talk O 64.1 Thu 10:30 H31 Cooperative Phenomena at the Solid/Liquid Interface — •KATHARINA KRISCHER — TU München, Germany

Complex forms of organization are often the result of nonlinear interactions between their basic building blocks. As a consequence, the system's properties cannot be explained by extrapolating knowledge about the molecular structure of the components which build up the system. Rather, in addition, information about their mutual interactions is required.

In the talk I will summarize the current state of understanding of self-organization processes occurring at the electrode|electrolyte interface with emphasis on spatial pattern formation, cooperative phenomena in ensembles of microelectrodes and non-Markovian processes at nanoelectrodes.

O 64.2 Thu 11:00 H31 Capacity of Electrochemical Interfaces — •MANUEL LANDSTORFER and WOLFGANG DREYER — Weierstrass Institute for Applied Analysis and Stochastics (WIAS)

The differential capacity $C = dq_M/dU$, where q_M is the metal (surface) charge and U the applied potential difference between the bulk metal and the bulk electrolyte, of an electrode/electrolyte interface is unique *tool* to characterize and investigate combinations of various electrode and electrolyte materials. Classical thermodynamic and continuum mechanical descriptions of the electrode/electrolyte interface only treat the electrolyte environment (in terms of Poisson-Boltzmann equations and its generalizations) in the derivation of an explicit function $C = C(U)$ [3,4]. In contrast, we will model the interface as electrode domain Ω_M and an electrolyte domain Ω_E which share a common singular surface Σ . Based on free energy formulations for the electrolytic solution and the singular surface, as well as contact conditions for the chemical potentials, we derive explicit functions $C = C(U)$ for various types of interfaces:

- metal - dilute electrolyte - no adsorption
- metal - strong electrolyte/ionic liquid - no adsorption
- metal - electrolyte - various adsorption models

Our results are compared to experimental data which allows for a determination of model parameters in our free energy formulation.

Topical Talk O 64.3 Thu 11:15 H31 Electrochemical energy conversion - interesting challenges for Surface Scientists — •HARRY E. HOSTER — Technische Universität München, TUM CREATE, 10-02 CREATE Tower, Singapore 138602

I will highlight important contributions by Surface Science towards a better understanding of options and limits of improving electrodes for low-temperature fuel cells and metal-air batteries. Structure-property relationships for bimetallic electrocatalysts in fuel cells can be elegantly observed and quantified in electrochemical studies involving particularly well-defined bimetallic surfaces. Preparation and imaging methods in vacuum provide optimum control of structure and composition of such model electrodes. For typical fuel cell reactions like O_2 reduction, H_2 oxidation, or CO oxidation I will show that by this approach we can not only screen metal combinations and surface compositions for optimum performance, but also identify the roles of distinct metal surface atoms and ensembles in adsorption and reaction.

Similar to fuel cells, cathodes of metal-air batteries must be active for electrochemical oxygen reduction. The energy drawn from a metal-air cell, however, results from the formation of a solid state metal-oxide film hosted by the cathode. Using the example of a $Li-O_2$ model cell I will illustrate how nucleation and growth of that film can give rise to serious history dependent limitations of the available energy content.

New types of batteries also mean new challenges for Surface Scientists. We have to tackle these challenges by new efforts in developing and improving experimental and theoretical methods.

O 64.4 Thu 11:45 H31 CO Electrooxidation on Pt monolayer island modified Ru(0001) electrodes — •STEPHAN BECKORD, ALBERT K. ENGSTFELD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

Bimetallic catalysts often show catalytic properties which strongly differ from those of the respective pure components. One example are PtRu catalysts, which are used, e.g., in direct methanol oxidation fuel cells (DMFC) because of their improved tolerance towards CO compared to Pt catalysts. We here report results of a study on the CO oxidation characteristics on structurally well defined PtRu bimetallic surfaces, consisting of a Ru(0001) substrate partly covered by Pt monolayer islands. To elucidate possible correlations between structure and catalytic properties, the Pt coverage was systematically varied. The surfaces were prepared by Pt evaporation under ultra high vacuum (UHV) conditions at elevated temperatures to form hexagonal islands, and characterized structurally by scanning tunneling microscopy (STM). The electrocatalytic CO oxidation was investigated in an electrochemical flow cell attached to the UHV system. In interpreting the resulting data, we take advantage of the result of earlier studies in our group on the gas phase adsorption of CO or hydrogen on similar surfaces [1], and on the electro-adsorption of hydrogen or OH on these surfaces in acid electrolyte [2]. [1] H. Hartmann et al, PCCP 14 (2012) 10919 [2] H. Hoster et al, JPC B 108 (2004) 14780

15 min. break

Topical Talk O 64.5 Thu 12:15 H31 Interaction of Pt-nanoparticles with graphitic carbon structures - a computational study — •ALEXANDER A. AUER, WOLFGANG B. SCHNEIDER, and UDO BENEDIKT — Max-Planck Institut für Chemische Energie Konversion

In heterogeneous electrocatalysis, often the lifetime and stability of a catalyst are the bottleneck for the performance of a catalyst. For the oxygen reduction reaction, for example, usually Pt Nanoparticles on amorphous carbon are and one degradation mechanism that is frequently observed is the detachment of nanoparticles from the support.

While the attachment of nanoparticles to carbon surfaces in electrocatalysis is interesting in itself, the question arises what the basic interaction of metallic structures and conjugated carbon structures is in general.

In this contribution we present work on the interaction of platinum nanoparticles in the size of a few atoms up to 1 nm with graphitic carbon structures, modelled by patches of graphene, using quantum chemical methods. We focus on the type and strength of interaction as well as the possibility to increase adhesive forces. Furthermore, some insights will be discussed on how electrochemical reactions can be modelled using quantum chemical methods including the electrochemical potential and explicit or implicit representations of the solvent.

O 64.6 Thu 12:45 H31 Interfacial water properties at room temperature: a comparison between PBE and RPBE-D3 — •TANGLAW ROMAN and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

In studying the properties of solid-liquid interfaces at ambient temperature, using ab initio molecular dynamics (AIMD) is advantageous because of its reliable description of metal-water interaction. In this

talk we will be discussing results of investigations motivated by the suggestion that the dispersion-corrected RPBE functional (RPBE-D3) gives a more reasonable description of both the intermolecular water-water and water-metal interaction, compared with the more popular PBE functional [1]. More specifically, we point out differences between PBE and RPBE-D3 results for room-temperature interfacial water structure on three surfaces: (1) ideal Pt(111), (2) pseudomorphic Ru monolayer on Pt, on which water more strongly adsorbs, and (3)

hydrogen-covered Pt, on which water more weakly adsorbs [2]. Three trajectories are used for each case, made distinct by how the interfacial bilayer is initially configured: H-up, H-down, and completely random in terms of both water molecule positions on the Pt surface and molecular orientation.

- [1] K. Tonigold, A. Groß, J. Computational Chem. 33 (2012) 695.
- [2] T. Roman, A. Groß, Catalysis Today, in press.