

O 61: Focus Session: Nanoscale Insights into Interfacial Electrochemistry I

Time: Wednesday 10:30–13:00

Location: HE 101

Invited Talk

O 61.1 Wed 10:30 HE 101

Bias-dependent local structure of water molecules at a metallic interface — ●MARIA VICTORIA FERNANDEZ-SERRA — Physics and Astronomy department, Stony Brook University, Stony Brook NY 11794, USA

Understanding the local structure of water at the interfaces of metallic electrodes is a key issue in aqueous-based electrochemistry. Nevertheless a realistic simulation of such a setup is challenging, particularly when the electrodes are maintained at different potentials. To correctly compute the effect of an external bias potential applied to truly semi-infinite surfaces, we have combined Density Functional Theory (DFT) and Non-Equilibrium Green's Function (NEGF) methods. This framework allows for the out-of-equilibrium calculation of forces and dynamics, and directly correlates to the chemical potential of the electrodes, which is introduced experimentally. I will review how the structure and work function of solvated Pd and Au electrodes depends on the nature of the water/metal interactions and relate this to the nature of the electrode and its surface charge.

Invited Talk

O 61.2 Wed 11:00 HE 101

Optical imaging of surface chemistry and dynamics in confinement — ●SYLVIE ROKE — Laboratory for fundamental BioPhotonics (LBP), Institute of Bioengineering (IBI), and Institute of Materials Science (IMX), School of Engineering (STI), and Lausanne Centre for Ultrafast Science (LACUS), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland

Electrochemical processes, chemical surface reactions and transformations at interfaces depend strongly on the local electrostatic environment as well as on nanoscale structures. In addition, structural heterogeneities, confinement, and flow critically influence surface chemical processes. Here, we image the interfacial structure and dynamics of water in a microscopically confined geometry in three dimensions and on millisecond time scales with a 3D structurally illuminated wide-field second harmonic microscope. Image contrast reports on the orientational order of interfacial water, induced by charge-dipole interactions between water molecules and surface charges. The images are converted into surface potential maps. Spatially resolved surface acid dissociation constant $pK_{a,s}$ values are determined for the silica deprotonation reaction by following pH induced chemical changes on the curved and confined surfaces of a glass micro-capillary immersed in aqueous solutions. These values ranged from 2.3 to 10.7 along the wall of a single capillary, because of surface heterogeneities. Water molecules that rotate along an oscillating external electric field were also imaged.

O 61.3 Wed 11:30 HE 101

Molecular dynamics study of the Mg(0001)/H₂O interface in an ab initio electrochemical cell — ●SUDARSAN SURENDRALAL¹, MIRA TODOROVA¹, MICHAEL W. FINNIS², and JÖRG NEUGEBAUER¹ — ¹Department of Computational Materials Design, Max-Planck-Institut für Eisenforschung GmbH., Düsseldorf, Germany — ²Department of Materials, Imperial College London, United Kingdom

Ab-initio modelling using density functional theory (DFT) provides important insight into the understanding of reactions at electrochemical interfaces. However, there is no commonly used method to tune the electrode potential in these simulations due to constraints imposed by the periodic boundary conditions common to many DFT codes. This is a major challenge for computational electrochemistry since it hampers observation of reactions under conditions of an applied potential. Utilizing semiconductor concepts, we have designed an approach to realize a potentiostat in standard periodic boundary DFT codes. Our approach allows the control of the electrode potential of the system by controlling the magnitude of charge transfer between two electrodes. Using this method, we study the Mg(0001)/H₂O interface under anodic polarisation conditions. The high corrosion rate under these conditions is a severe technological challenge and has thus been extensively studied. The atomistic mechanisms, however, could so far not be identified. Using the new approach, we are able to observe dissociation events, proton transfer as well as H₂ evolution and to identify a novel and hitherto not considered reaction mechanism.

O 61.4 Wed 11:45 HE 101

Influence of near surface defects of GaAs on the electrolyte structure in KOH solutions — ●ALRIK STEGMAIER and HANS HOFSSÄSS — 2. Physikalisches Institut, Georg-August Universität Göttingen

The electrolyte-semiconductor interface is a very active area of research. While the electrolyte structure at ideal, defect-free semiconductor surfaces is relatively well understood, the influence of surface near defects, applied potential differences and strong electrolytes, as found in many applications, is much more difficult to understand.

Here we present our latest results of our investigation of the structure of the electrolyte for defects near the <100>-GaAs - KOH/water interface at large pH values. For this classical and ab initio molecular dynamics simulations are combined with continuum models and impedance measurements for proton irradiated GaAs.

Invited Talk

O 61.5 Wed 12:00 HE 101

Charge Transfer at the Single Molecule Level with Metal and Semiconductor Electrodes — ●RICHARD NICHOLS¹, ANDREA VEZZOLI¹, RICHARD BROOKE², NICOLÒ FERRI¹, SIMON HIGGINS¹, and WALTHER SCHWARZACHER² — ¹Department of Chemistry, University of Liverpool, L69 7ZD, UK — ²University of Bristol, Bristol BS8 1TL, UK

We have exploited STM based methods for making single molecule measurements on a wide variety of molecular targets from short molecular bridges to redox active organometallic molecular wires. Such measurements have been made as 2-terminal determinations and also under electrochemical control with electrolytes including ionic liquids. Recently we have extended such measurements to semiconductor electrodes. We have shown that it is possible to make measurements of single molecules connected at one end to gallium arsenide and at the other end to a gold STM tip. Using this methodology we can record current-voltage response of semiconductor-molecule-metal devices and measure the electrical conductance of single molecules in such junctions. As well as showing that it is possible to form single molecule devices contacted to the semiconductor gallium arsenide we have also recently demonstrated that such single molecule devices show a strong photocurrent response. The photo-current response in these junctions can be controlled through the choice of the semiconductor doping density, the molecular bridge and also the light intensity and wavelength. To conclude potential future applications in single-molecule semiconductor (photo-) electrochemistry will be discussed.

O 61.6 Wed 12:30 HE 101

In-operando Vibrational Spectroscopies in Electrochemical Environment from First-principles — ●FRANCESCO NATTINO¹, OLIVIERO ANDREUSSI^{1,2}, and NICOLA MARZARI¹ — ¹Theory and Simulations of Materials (THEOS) and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, Station 12, CH-1015 Lausanne, Switzerland. — ²Institute of Computational Science, Università della Svizzera Italiana, Via Giuseppe Buffi 13, CH-6904 Lugano, Switzerland.

Electrocatalysis is expected to play a key role in the development of a clean energy cycle, from energy harvesting to transformation and storage. Spectroscopic techniques able to work under potential control can extremely contribute to design novel catalyst materials by providing insight on the mechanism of target electrochemical reactions. In this context, theory has the task to decipher the precious information that *in-operando* experimental techniques are able to provide.

We present here first-principles calculations on key reaction intermediates of two electrochemical processes: the oxidation of a gold single crystal surface and the carbon dioxide reduction on copper metal electrodes. Vibrational adsorbate frequencies are computed in a realistic electrochemical environment, exploiting an accurate implicit solvation model to mimic the electrolyte solutions. Our results complement very recent surface enhanced Raman spectroscopy (SERS) experiments and surface enhanced IR absorption (SEIRA) measurements, contributing to shed light on the reaction mechanism of the two electrocatalytical processes considered.

O 61.7 Wed 12:45 HE 101

Quasi-atomistic insight into Au oxide reduction under real-

istic working conditions — •JONAS H. K. PFISTERER, ULMAS E. ZHUMAEV, and KATRIN F. DOMKE — Max Planck Institute for Polymer Research, Mainz, Germany

The rational design of improved electrochemical devices, e.g. fuel cells, depends on the atomistic understanding of the underlying reaction processes under realistic working conditions. The ability of tuning the Fermi level and employing highly sensitive molecular detection methods can provide valuable insights into molecular adsorption/desorption on the surface. Here, we investigate the reduction of AuOx surfaces in contact with an electrolyte by in-situ surface-enhanced Raman scattering (EC-SERS). We have performed potential-jump experiments in which we stepwise vary the applied potential to induce either AuOx

formation or Au surface recovery. As a function of potential, we observe a splitting of the AuOx/(AuOH) peak at 585 cm^{-1} into two peaks that are assigned to AuOx and AuOH based on H/D exchange experiments. Further, the AuOH peak exhibits Raman intensity oscillations with time that can possibly be ascribed to subsurface OH moving to the surface. Accompanying Raman peaks at 240 and 1200 cm^{-1} , complemented with in-situ IR absorption experiments, indicate that the adsorption of SO_4^{2-} starts only after initial AuOx reduction.

Our potential-jump experiments on AuOx surfaces reinforce the role of OH species for the reduction process even in acidic media and represent an interesting approach to gain quasi-atomistic insights into surface reactions under realistic working conditions.