O 8: Solid-liquid interfaces: Structure, Spectroscopy I

Time: Monday 10:30–13:00 Location: MA 144

O 8.1 Mon 10:30 MA 144

Structural changes of water islands due to kosmotropes vs. chaotropes imaged in real space — •Irene Weber and Karina Morgenstern — Chair of Physical Chemistry I, Ruhr-Universität Bochum, Germany

Solvation effects of ions near the liquid-solid interface are of tremendous importance for the understanding of electrochemical processes, i.e. in electrocatalysis or in corrosion. Although studying these solvation effects has a long tradition, the understanding of the microscopic influence of alkali metal ions onto water structure and dynamics near metal surfaces on the atomic scale is still at its infancy. In our study, crystalline water is used to mimic ordered water close to an electrode and lithium or cesium ions to represent circular cations. Lithium with its high charge density is a kosmotrope and cesium with its low charge density a chaotrope. Already, the adsorption of lithium and cesium ions on the Au(111) surface differs at around 215 K. Both ions change the water structure. The lithium ions change the distribution of water islands on Au(111) as compared to water islands on pristine Au(111) and alter their structure. The cesium ions reduce the height of the islands and change the structure of water islands in a different way. Depending on the water-to-ion-ratio, the subtle balance of interactions between water, ions and the substrate is changed. In this contribution, we will present our variable-temperature Scanning Tunneling Microscopy (STM) studies of these differences induced by lithium and cesium ion co-adsorption on crystalline ice structures on Au(111).

O 8.2 Mon 10:45 MA 144

In-situ and operando near sulfur K-edge X-ray absorption spectrometry of Li-S battery coin cells — •Claudia Zech[1], Olga Grätz[2], Svetlozar Ivanov[3], Daniel Grötzsch[4], Philipp Hönicke[1], Yves Kayser[1], Manfred Stamm[2] und Burkhard Beckhoff[1] — [1]Physikalisch-Technische Bundesanstalt, Berlin, Germany — [2]Leibniz-Institut für Polymerforschung, Dresden, Germany — [3]Technische Universität, Ilmenau, Germany — [4]Technische Universität, Berlin, Germany

Lithium Sulfur (Li-S) batteries are promising candidates for improved batteries offering up to 5 times higher capacity than conventional lithium ion batteries. For a better understanding of battery degradation processes in-situ and in-operando characterization techniques are required. By means of in-operando near sulfur K-edge X-ray absorption spectrometry recorded during galvanostatic cycling with potential limitation (GCPL) measurements we could determine the different sulfur species for 8 cycles of a Li-S battery with DOL/DME (1:1 wt.%) 1 Mol TFSI electrolyte. In particular, the formation of polysulfides could be revealed. We used CR-2032 coin cell formed Li-S batteries modified with thin windows enabling the transmission of excitation and fluorescence radiation. Traceable X-ray spectrometric measurements were performed using radiometrically calibrated instrumentation in the PTB laboratory at BESSY II synchrotron radiation facility. While for the first cycles the polysulfides convert almost entirely we see for further cycles a permanent appearance.

O 8.3 Mon 11:00 MA 144

Structure of electrochemical electrode-electrolyte interfaces — •Florian Gossenberger and Axel Gross — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

In electrochemistry, the atomistic structure at the solid-liquid interface has a strong influence on electrocatalytic reactions. Therefore it is of fundamental importance to understand surface properties like adsorbate structures at particular thermodynamic conditions e.g. pH, electrolyte-concentration and electrode potential first, before looking at any reaction at this interface. We adressed the structure of a Pt(111) electrode in a the presence of protons and halides in the electrolytes based on density functional theory calculations [1] using the concept of the computational hydrogen electrode (CHE). This represents an efficient method to combine total energy calculations from density functional theory with thermodynamic properties of electrochemistry. We have now extended these studies to analyze the co-adsorption of (bi)sulfate and hydrogen. We will discuss the important role of water molecules in stabilizing the resulting adsorbate structures.

[1] F. Gossenberger, T. Roman and A. Groß, Electrochim. Acta **216**, 152 (2016).

O 8.4 Mon 11:15 MA 144

Determination of the surface charge of the water-rutile (110) surface at low and high pH — •Shumei Sun, Mischa Bonn, and Ellen Backus — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

We have used visible-infrared sum-frequency generation spectroscopy (SFG) to reveal the surface charge of the rutile (110) surface in contact with water of different pH. The surface is positively and negatively charged at pH3 and pH11, respectively, through protonation and deprotonation reactions. Phase-resolved SFG experiments show that under influence of the charged surface water molecules orient themselves with the hydrogen atoms towards (basic solution) or away from (acidic solution) the TiO2 surface. By combining a recently developed theoretical framework and salt concentration-dependent SFG measurements, we are able to near quantitatively evaluate the surface charge density at pH3 and pH11. The results reveal that the surface charge density of TiO2/pH11 is one order of magnitude smaller than that of TiO2/pH3. Moreover, by increasing the pH above 11, the surface charge is not increasing anymore.

O 8.5 Mon 11:30 MA 144

***Ab initio* description of semiconductor-water interfaces at finite electrode potential** — •Lei Yang[1], Fang Niu[1], Stefanie Tecklenburg[1], Simantini Nayak[1], Andreas Erbe[1], Francois Gygi[2], Giulia Galli[3], and Stefan Wippermann[1] — [1]MPI Eisenforschung — [2]UC Davis — [3]U Chicago

Despite the importance of understanding the structural and bonding properties of solid-liquid interfaces for a wide range of (photo-)electrochemical applications, there are presently no experimental techniques available to directly probe the microscopic structure of solid-liquid interfaces. To develop robust strategies to interpret experiments and validate theory, we carried out attenuated total internal reflection (ATR-IR) spectroscopy measurements and *ab initio* molecular dynamics (AIMD) simulations of the vibrational properties of interfaces between liquid water and well-controlled prototypical semiconductor substrates. We show the Ge(100)/H_2O interface to feature a reversible potential-dependent surface phase transition from a hydrophilic to a hydrophobic surface. The Si(100)/H_2O interface is proposed as a model system for corrosion and oxidation processes. We performed *ab initio* time-resolved spectroscopy, providing a molecular-level explanation for the difference between the vibrational properties of the H_2O molecules on surfaces with different hydrophobicities on the basis of hydrogen bonding. Funding from DOE-BES Grant No. DE-SS0008939, Deutsche Forschungsgemeinschaft (RESOLV, EXC 1069) and BMBF NanoMatFutur Grant No. 13N12972 is gratefully acknowledged.

O 8.6 Mon 11:45 MA 144

GaP(100) in contact with water: Reflection anisotropy spectroscopy from first principles — •Matthias M. May and Michiel Sprik — Univeristy of Cambridge, Department of Chemistry

Surfaces of III-V semiconductors in contact with an electrolyte are not only relevant for applications such as solar water splitting, but also offer the opportunity to correlate experiments on well-defined surfaces with theory. Here, we study the P-rich surface of GaP(100), which shows an extraordinary stability against oxidation from gas-phase water. While its surface ordering is modified by exposure to water as evidenced by *in situ* reflection anisotropy spectroscopy (RAS), no traces of oxygen could be found by experiment.[1] Modelling the surface with density functional theory and deriving RAS, we find evidence for a water-induced hydrogen-rich surface phase. [2] We furthermore extend this work towards RAS in a bulk electrolyte by investigating the influence of finite electric fields and potentials [3] on the optical anisotropy in the Helmholtz layer.

[1] May et al, NJP 15:103003 (2013). [2] May and Sprik, arXiv:1710.08194. [3] Zhang and Sprik, PRB 94:245309 (2016).

O 8.7 Mon 12:00 MA 144

Molecular Dynamics of the Water-gold Interface including Metal Polarizability Effects in the Classical Force Field — •Victor G. Ruiz[1], Matej Kanduč[1], Won Kyu Kim[1], Rafael Roa[1], and Joachim Dzubiella[1,2] — [1]Helmholtz-Zentrum Berlin,

Berlin, Germany — [2]Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany

Solid-liquid interfaces are of growing interest to basic science and technology. The water-gold interface has received much attention due to its applications in catalysis and biotechnology. The need of including biomolecular and ionic species in the aqueous environment within atomistic simulations necessitates the accurate inclusion of charge and fluctuations effects of the liquids [Small 12, 2395 (2016)]. The formed interfaces are complex due to the interplay of van der Waals (vdW) interactions, covalent bonds, and image-charge effects due to the highly polarizable surface. Using a classical Drude-oscillator model [JCP 119, 3025 (2003)], we present a force field for the gold-water interface which includes image-charge effects induced in the metal surface. Our parametrization is based on calculations of a single molecule/monolayer of water using vdW-corrected density-functional theory [PRL 108, 146103 (2012)] that includes the many-body collective response of the substrate electrons in the vdW interaction coefficients. We show that this methodology yields a consistent connection between the induced polarizability effects in the surface and the vdW interaction between water molecules and the surface when compared to available literature.

O 8.8 Mon 12:15 MA 144

Growth and dynamics of ultrathin ionic liquid layers on metal surfaces

— •Matthias Lexow, Bettina Heller, Benjamin May, Radha G. Bhuin, Florian Maier, and Hans-Peter Steinrück — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Ionic liquids (IL) are ionic compounds with a relatively low melting point, often even below room temperature. In addition to numerous applications as a solvent or electrolyte, the extremely low vapour pressure of ILs also led to the development of completely new concepts for catalytically active systems. Thin layers of ILs on solid materials are applied e.g. in SCILL (Solid Catalyst with Ionic Liquid Layer) catalysis.

In this context, the structure and composition of the IL/solid interface is studied by our group combining in vacuo deposition of ultrathin IL films and angle-resolved X-ray photoelectron spectroscopy. The investigations show how the IL/solid interface forms and how to control the process by modifying the IL or substrate properties on the molecular scale.

Aiming to understand and predict the behaviour of applied catalyst systems, we discuss on the example of imidazolium based ionic liquids the role of the molecular structure in the mechanisms of initial film formation.

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O 8.9 Mon 12:30 MA 144

Decisive Role of Nuclear Quantum Effects on Surface Mediated Water Dissociation at Finite Temperature

— •Yair Litman[1], Davide Donadio[2], Michele Ceriotti[3], and Mariana Rossi[1] — [1]Fritz Haber Insitute of the Max Planck Society, Berlin, Germany — [2]University of California, Davis — [3]EPFL, Switzerland

Water molecules adsorbed on inorganic substrates play an important role in several technological applications. In the presence of light atoms in adsorbates, nuclear quantum effects (NQE) influence the structural stability and the dynamical properties of these systems. In this work [1], we explore NQE on the water dissociation of water wires on stepped Pt(221) surfaces. We note that there are several competing minima, calling for the inclusion of anharmonic effects in simulations at finite temperatures. We thus perform *ab initio* path integral molecular dynamics (PIMD) in order to calculate NQE contributions to free energies and their interplay with the electronic structure, making use of an acceleration technique that we propose, based on a spatially-localised ring-polymer contraction. We find that the dissociation process is dominated by ZPE, which can enhance the rate of dissociation by three orders of magnitude and that the inclusion of anharmonicities increase the nuclear quantum contribution to the dissociation free energy by 20 % compared to harmonic estimates. Interestingly, we report how the redistribution of electronic density caused by temperature and NQE can induce work function changes of up to 0.4 eV with respect to static estimates.

[1] Y. Litman *et. al.* JCP **148**, 102320 (2018).

O 8.10 Mon 12:45 MA 144

Surface plasmon resonance at electrified interfaces

— •Ulmas E. Zhumaev and Katrin F. Domke — Max Planck Institute for Polymer Research, Mainz

Operating low-temperature fuel cells in the oscillatory regime is a promising approach to avoid the deactivation of platinum (Pt) catalyst by adsorbed carbon monoxide (CO). However, it remains an open question how to controllably activate the oscillatory regime. In the oscillatory regime, the Pt electrocatalyst undergoes spontaneous switching between the removal of adsorbed CO and the main reaction of the fuel cell. Such oscillations are accompanied by the formation of oscillatory CO concentration patterns on the Pt surface. Accessing these patterns with millisecond temporal and micrometer spatial resolutions using surface plasmon resonance (SPR) spectroscopy will help to gain insight into the oscillatory regime. To do so, the relationship between the SPR signal and the CO coverage under electrochemical (ec) conditions should be revealed. Our strategy is to define the contribution of different interfacial regions to the ecSPR signal by exploring well-known ec systems, e.g. Au(111) and Pt in $H_2SO_4/Cl^-/CO$, with SPR spectroscopy. Our first results on Au(111) and Pt/Au(111) in 0.1 M H_2SO_4 suggest a predominant contribution of specific adsorption to the SPR signal, whereas non-specific adsorption and diffusion processes seem to have almost no contribution. The contribution of the surface charge seems to be rather complex and we present experimental approaches towards its understanding.