

O 39: Metal substrates: Solid-liquid interfaces

Time: Wednesday 15:00–17:30

Location: SCH A315

O 39.1 Wed 15:00 SCH A315

First-principles characterization of water structures at the metal-water interface — ●SEBASTIAN SCHNUR and AXEL GROSS — Institute für Theoretische Chemie, Universität Ulm, D-89069 Ulm, Germany

A molecular level understanding of the structural arrangement of water molecules at a metal-water interface is one of the most important issues in electrochemistry. Despite numerous studies, the exact microscopic structure of water at a metal-water interface is not fully understood and is still subject of debate between state-of-the-art theory and in-situ surface science techniques. On a number of metal surfaces, deposition of water usually leads to well-ordered structures. In particular, ice-like water bilayers with a $\sqrt{3} \times \sqrt{3}$ hexagonal pattern have been investigated most intensively. The crucial question is whether such an ice-like water pattern remains intact even at room temperature or whether it transforms to a liquid-like structure.

We used ab initio molecular dynamics simulations based on density functional theory to study the water bilayer on different closed packed metal surfaces. Vibrational spectra were obtained from the velocity autocorrelation function recorded in the MD simulation to characterize the water structure. Furthermore, we examined details of the metal-water interaction by considering charge density and work function changes to elucidate the nature of the metal-water interaction. Our results contribute to bridge the gap between theory and experiment by giving a direct molecular level explanation for results obtained in finite-temperature in-situ spectroscopy experiments.

O 39.2 Wed 15:15 SCH A315

Role of anharmonic contributions for the elasticity of ice — ●MIRA TODOROVA, LARS ISMER, and JÖRG NEUGEBAUER — Max-Planck Insitut für Eisenforschung GmbH, Düsseldorf

Water, one of the simplest molecules in chemistry, forms a liquid and solid phase with features essential to life and environment. Many of these can be attributed to hydrogen bonding, but that does not mean that they are fully understood. Ice should be an easier material to understand, because its molecules are arranged on a regular lattice. Yet even the determination of such basic properties as the bulk modulus and the elastic constants proves to be a challenge.

Using first principles calculations we investigate the bulk properties of hexagonal ice. Our initial density-functional theory calculations (GGA-PBE level) yield values, which are much too high when compared to experiment. Even though the consideration of thermal effects within the quasi-harmonic approximation leads to a qualitative agreement between measured and calculated quantities, such as the linear expansion coefficient, ice remains much too hard. The large overestimation of the ice' softness demonstrates the importance of anharmonic contributions, which will be shown to be crucial and lead to a dramatic reduction of the bulk modulus and the elastic constants.

O 39.3 Wed 15:30 SCH A315

Theoretical Studies on the Inner Potential Drop in Pt/Electrolyte-Interfaces — ●JOCHEN BANDLOW, JOSEF ANTON, and TIMO JACOB — Institut für Elektrochemie, Universität Ulm, 89081 Ulm

Understanding the processes occurring at solid/liquid interfaces is of great importance not only for basic electrochemistry, but also for various applications such as fuel cells. However, these interfaces (i.e., the so-called electric double-layers) are rather complex involving different aspects as surface dipoles, a potential drop, specific and non-specific adsorption, or modified surface structures. Since many experimental techniques that are well-established in surface science are not applicable for systems under "wet" conditions, theoretical modeling might help understanding the double-layer on the microscopic level.

In order to evaluate the drop of the electrostatic potential within the electric double-layer first we performed molecular dynamics studies on pure water under different pressure and temperature conditions. We found that many commonly used interaction potentials reported in literature are only valid for a rather limited part of the phase-space. Afterwards, we studied the molecular structure of charged platinum electrodes in contact with an aqueous solution containing various concentrations of NaCl. This allowed us to evaluate the peak and also the averaged potential distribution.

O 39.4 Wed 15:45 SCH A315

Optimizing a bimetallic surface - electrochemical oxygen reduction at $Pt_xRu_{1-x}/Ru(0001)$ surface alloys — ●OTAVIO ALVES, HARRY E. HOSTER, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, 89069 Ulm, Germany

We report on the activity of $Pt_xRu_{1-x}/Ru(0001)$ surface alloys [1] prepared in ultrahigh vacuum (UHV) towards the electrochemical oxygen reduction reaction (ORR). The potential-dependent reaction currents are measured in a wall-jet type flow cell sited in an electrochemical pre-chamber attached to the main UHV system. The kinetically controlled currents depend on the Pt:Ru ratio and exhibit an optimum close to a Pt content of 100%. The high activity of the $Pt_xRu_{1-x}/Ru(0001)$ surface alloys can be rationalized by the versatility of mixed adsorption sites whose reactivity is between that of Ru(0001) on the one hand, which binds reactive intermediates too strongly, and Pt monolayer islands ($Pt_{xML}/Ru(0001)$, $x = 0..1$) on the other hand, whose lower activities are attributed to the sluggish O_2 dissociation as predicted from strain and vertical ligand effects [2,3]. We discuss in how far the high optimum Pt content can be rationalized in an atomic-scale picture of the reaction process.

[1] H. E. Hoster *et al.*; Phys. Chem. Chem. Phys. 2008, 10, 3812.[2] M. Mavrikakis *et al.*; Phys. Rev. Lett. 1998, 81, 2819.[3] M. Lischka *et al.*; Electrochim. Acta 2007, 52, 2219.

O 39.5 Wed 16:00 SCH A315

CO electrooxidation at $Pt_xRu_{1-x}/Ru(0001)$ surface alloys and Pt modified Ru(0001) — ●HARRY E. HOSTER, OTAVIO ALVES, ANDREAS BERGBREITER, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

We report on the activity of $Pt_xRu_{1-x}/Ru(0001)$ surface alloys [1] and Ru(0001) with and without Pt islands [2] towards continuous electrochemical oxidation of CO. The samples were prepared in ultrahigh vacuum (UHV) but the potential dependent CO oxidation currents were recorded under enhanced mass transport conditions in a flow cell attached to the UHV system. On bare Ru(0001), measurable CO oxidation only takes place at $E > 0.55$ V. Whereas modification by Pt islands does not change this threshold, the attainable oxidation currents become much higher, which we explain by a catalytic effect where Pt helps maintaining high local coverage of CO+O(H) adlayer at the Ru areas. Atomically dispersed $Pt_xRu_{1-x}/Ru(0001)$ surface alloys show an even higher activity, which results from the higher versatility of mixed or electronically varied adsorption sites with intermediate bonding power. The role of the lateral atom distribution of PtRu surfaces for their local adsorption properties and the reactivity of mixed adlayers under reaction conditions are discussed and compared to previous experimental and theoretical findings.

[1] H.E. Hoster *et al.*, Phys.Chem.Chem.Phys. 10 (2008) 3812.[2] H.E. Hoster *et al.*, J. Phys. Chem. B 108 (2004) 14780.

O 39.6 Wed 16:15 SCH A315

Anomalous Helmholtz-Capacitance on Stepped Surfaces of Silver and Gold — ●GUILLERMO BELTRAMO, HARALD IBACH, and MARGRET GIESEN — Institute for Bio- und Nano-Systems (IBN), Jülich Forschungszentrum, D-52425 Jülich, Germany

Interest in generation and functionalization of nanoscale structures on solid templates has grown tremendously because of their eminent role in many areas of technology. In vicinal surfaces, the presence of arrays of atomic steps separated by flat terraces creates regions of varying local atomic coordination, which renders unique properties to these surfaces, quite distinct from those of flat surfaces. [1]. We have studied the capacitance of the solid/electrolyte interface on Ag(11n) and Au(11n) surfaces in $KClO_4$ and $HClO_4$ as function of the electrolyte concentration and the step density. We find that the inner layer capacitance (Helmholtz-capacitance) is dramatically reduced on stepped surfaces [2]. Standard theories which describe the Helmholtz-capacitance by properties of the liquid, a hard wall boundary condition and the polarizability of the electron gas at the metal surface fail to describe this behavior. We propose that the different polarizability of water bonded to the surface need be taken into account and attribute the reduced capacitance at steps to the lower polarizability of water molecules bonded to step edges. The results will be discussed. [1]

H. Ibach, M. Giesen and W. Schmickler, *J. Electroanal. Chem.* 544 (2003) 13. [2] G.L. Beltramo, H. Ibach and M. Giesen, *Surf. Sci.* 601 (2007) 1876.

O 39.7 Wed 16:30 SCH A315

Dependency of the Vibrational Stark-Effect on the pre-adsorbed Anion-Species on a Cu(100) Electrode Surface — ●MELANIE RÖEFZAAD, DUC THAN PHAM, PETER BROEKMANN, and KLAUS WANDEL — Institute for Physical and Theoretical Chemistry, University of Bonn

Fourier transform infrared reflection absorption spectroscopy (FT IR-RAS), combined with electrochemical STM, has been used to monitor the vibrational frequency shifting as a function of the electrode potential and the pre-adsorbed anion-species. As probe-molecule served the redoxactive 1,1'-diphenyl-4,4'-bipyridinium (DPV). Halogenide anions are pre-covering the electrode surface by specific adsorption in a wide potential range.^[1] These highly ordered anion-layers are able to serve as a template for the adsorption of DPV. EC-STM studies revealed no structural changes in the adsorbed monolayer while changing the anion or the potential. Excluding changes in IRRA-spectra through reorientation, shifts induced by changing the applied potential are nicely visible. The expected effect was missing in the case of pre-adsorbed Cl⁻ and Br⁻. Only with I⁻ significant changes in the IRRA-spectra could be observed. Specific bands show a clear shift to higher frequencies. Those shifts indicate a strengthening of the bonds between the adsorbed molecules formed through charge-transfer-complexation. This gives a clue to a higher electrostatic effect on the organic adlayer with pre-adsorbed iodide due to its reduced partial charge and as a consequence, a more covalent bonding to the copper surface.

^[1] Broekmann et al., *Surf. Sci.* 517 (2002) 123

O 39.8 Wed 16:45 SCH A315

The influence of additives on the Cu(001)/electrolyte interface — YVONNE GRÜNDER, ●ARNE DRÜNKLER, FREDERIK GOLKS, DANIEL KAMINSKI, KLAUS KRUG, JOCHIM STETTNER, and OLAF M. MAGNUSSEN — Christian-Albrechts-Universität Kiel, Germany

Copper electrodeposition from multicomponent electrolytes containing organic additives is an important process for the defect-free filling of trenches on ultra large scale integrated (ULSI) microchips [1]. In these electrolytes, polyethers, usually polyethylene glycol (PEG), in combination with chloride ions form an overlayer on Cu that inhibits the electrodeposition reaction [2]. Despite the numerous studies on Cu superconformal electrodeposition the precise influence of the additive on the elementary steps of this deposition reaction is largely not understood, mostly due to the difficulty in making direct experimental observations of the growth mechanisms on the atomic scale. In-situ Surface X-Ray Diffraction (SXRD) offers unique possibilities to study the electrochemical processes under the film and could provide first direct data on the atomic-scale growth mechanism under these conditions. SXRD experiments revealed on Cu(001) in PEG containing electrolyte the existence of an ordered Cl⁻ adlayer underneath the inhibiting film. Moreover we found evidence for a pronounced kinetic limitation for the formation of this adlayer structure.

References: [1] P.C. Andricacos, et al., *Electroch. Microf.* 42, 567 (1998) [2] P.M. Vereecken, R.A. Binstead, H Deligianni, P.C. Andricacos, *IBM J. Res. Develop.* 49, 3 (2005)

O 39.9 Wed 17:00 SCH A315

Variation of the electrode potential with elastic strain — ●MAXIM SMETANIN¹, DOMINIK KRAMER¹, SENTHILNATHAN MOHANAN², ULRICH HERR², and JOERG WEISSMUELLER^{1,3} — ¹Forschungszentrum Karlsruhe, Institut für Nanotechnologie, Karlsruhe — ²Universität Ulm, Institut für Mikro- und Nanomaterialien, Ulm — ³Universität des Saarlandes, Technische Physik, Saarbrücken

A fundamental parameter in electrochemistry, the electrode potential, E , is intricately related to the solids Fermi energy and to its work function in vacuum. How does E at the metal-electrolyte interface vary when the electrode is subjected to an elastic tangential deformation with strain ϵ ? This is of interest in relation to strain effects on the metals band structure, which can affect catalytic processes, to corrosion science, and to recent attempts to understand the response of the surface stress, f , of metals to changes in the superficial charge density, q . The connection to surface stress rests on a Maxwell relation, $df/dq = dE/de$. While the left-hand-side has been studied in several experiments, we know of no quantitative experiment exploring the right-hand side. Our approach is to use a small cyclic strain of a thin-film gold electrode along with sensitive potential monitoring. We found that the potential varies linearly with the strain; the response parameter is negative. In 10 mM HClO₄, for quasi-static straining $dE/de = -1$ V, whereas the value converges to -1.8 V at frequencies around 100 Hz. The sign agrees with early predictions, the magnitude is in good agreement with recent results from density functional theory for Au(111) in vacuum and with experimental results for df/dq in electrolyte.

O 39.10 Wed 17:15 SCH A315

Influence of anions on dealloying of Cu₃Au (111): An in-situ x-ray study — ●APARNA PAREEK, GENESIS ANKAH, SASCHA HÜMANN, MICHAEL ROHWERDER, and FRANK RENNER — Max-Planck Institut für Eisenforschung, Max-Planck Strasse 1, 40237 Düsseldorf

Dealloying is a well-known process occurring at the alloy surfaces, which are composed of elements with widely different Nernst potentials. The dealloying behaviour of Cu₃Au in 0.1M H₂SO₄ was previously investigated using electrochemical measurements combined with in-situ X-ray diffraction. We reported the formation of an ultra-thin epitaxial passive Au layer at lower overpotentials with a reversed stacking sequence, which transforms to thicker Au islands at higher overpotentials. Here we investigated the influence of various anionic species (Br, I) dissolved in 0.1M H₂SO₄ on the above electrochemical corrosion process. Presence of these anionic additives influences the potential where the ultra-thin passive layer transforms to the thicker Au islands. To corroborate the results obtained from X-ray measurements, ex-situ AFM measurements were performed, where the topographical changes with the potential change were recorded. In addition, we present first results of high resolution TEM studies.