

## O 56: Symposium: The Solid-Liquid Interface: A Challenge for Theoreticians I

Time: Thursday 15:45–19:00

Location: H36

**Invited Talk** O 56.1 Thu 15:45 H36  
**Computer Simulation of Electrochemical Reactions at the Water / Metal Interface** — ●ECKHARD SPOHR — IWV-3, Forschungszentrum Jülich, D-52425 Jülich

The interface between an (aqueous) electrolyte solution and a (noble) metal is the microscopic structural and dynamical heart of many electrochemical phenomena and has over the last 20 years attracted significant efforts in pure theory, electronic structure calculations and atomistic computer simulations. Recently, significant progress has been reached by merging concepts of electronic structure theory with dynamical simulations. At the same time, force field-based simulations will continue to be important, in view of the many-body nature of the interface.

Two topics from recent work in our group will be discussed. (i) A density functional theory / molecular dynamics study of methanol oxidation at the water / platinum interface unambiguously showed that interfacial water on a platinum surface is not only a spectator but actively participates in the oxidation process [1]. (ii) The chemical reaction dynamics was studied during the primary steps of the hydrogen evolution reaction in aqueous environment. The objective, to gain insight into the potential and metal dependence of this reaction, mandated the use of an empirical valence bond force field [2].

[1] C. Hartnig, J. Grimminger and E. Spohr, *Electrochim. Acta* 52, in press.

[2] F. Wilhelm, W. Schmickler, R. Nazmutdinov and E. Spohr, in preparation.

**Invited Talk** O 56.2 Thu 16:15 H36  
**Electric field effects at metal surfaces** — ●ALI ALAVI<sup>1</sup> and ALEXANDER LOZOVOI<sup>2</sup> — <sup>1</sup>Department of Chemistry, Cambridge CB2 1EW — <sup>2</sup>School of Mathematics and Physics, Queen's University, Belfast Bt7 1NN

We review our recent work on electric field effects at metal surfaces, concentrating on (a) the relation between first-principles theory and the thermodynamics of charged surfaces [1] (held either at constant charge or constant potential), (b) a practical implementation of suitable for periodic slabs, and (c) new results on the stark effect for CO on Pt(111)[2]. Regarding (a), by generalising Koopman's theorem, we derive expressions for the surface (excess) free energy as a function of charge (or potential) in terms of the neutral surface energy, the work-function and the position of the image plane. This is used to investigate potential-induced surface reconstructions. We show that a remarkable type of phase-coexistence in which charge-separation occurs. If time permits, we will show results on field effects on surface-relaxation, and adatom diffusion.

[1] A.Y. Lozovoi and A. Alavi, *Phys. Rev. B* 68, 245416, (2003).

[2] A.Y. Lozovoi and A. Alavi, *J. Electroanalytical. Chem.*, to appear.

O 56.3 Thu 16:45 H36  
**Sum-Frequency Vibrational Spectroscopy of Al<sub>2</sub>O<sub>3</sub>(0001)/Water Interfaces** — ●BJÖRN BRAUNSCHWEIG, STEPHAN EISSLER, and WINFRIED DAUM — Institut für Physik und Physikalische Technologien, TU Clausthal, Leibnizstrasse 4, D-38678 Clausthal-Zellerfeld

Sum-frequency generation (SFG) has been applied to study O-H stretching vibrations of water molecules and hydroxyl groups at Al<sub>2</sub>O<sub>3</sub>(0001)/water interfaces. The vibrational spectra of these interfaces strongly depend on the roughness of the Al<sub>2</sub>O<sub>3</sub> surface which was characterized by AFM. O-H stretching bands at 3140 cm<sup>-1</sup> and 3450 cm<sup>-1</sup> are assigned to hydrogen-bonded water molecules at the interface with tetrahedral and non-tetrahedral coordination, respectively. A strong pH dependence observed for the intensity of the 3140 cm<sup>-1</sup> band can be attributed to the interfacial electric field caused by protonation or deprotonation of surface hydroxyl groups. A marked minimum in the pH dependence of this band is related to the isoelectric point of the Al<sub>2</sub>O<sub>3</sub>(0001) surface. On rough Al<sub>2</sub>O<sub>3</sub>(0001) surfaces we observe an additional narrow band at 3700 cm<sup>-1</sup> originating from O-H stretching vibrations of free surface hydroxyl groups (aluminol, AlOH). This band is completely absent on smooth Al<sub>2</sub>O<sub>3</sub>(0001) surfaces which have been prepared by annealing at 1100 °C and which exhibit atomically flat terraces. The 3700 cm<sup>-1</sup> band is assigned to hydroxyl groups, presumably adsorbed at defect or step sites, that do

not couple to the hydrogen-bonded network of the interfacial water molecules.

**30 min. Break**

**Invited Talk** O 56.4 Thu 17:30 H36  
**Computer simulation of solution/electrode interfaces** — ●FERNANDO FERNANDES — Department of Chemistry and Biochemistry, Faculty of Sciences, University of Lisboa, Campo Grande, Bloco C8, 1749-016 Lisboa Portugal

In the last few years we have carried out some work on the adsorption and self-assembly of organic molecules (e.g. phenol and alkythiols solvated by water and ethanol, respectively) on gold electrodes, in collaboration with two experimental groups of interfacial electrochemistry.

Our contributions have been focused towards the atomistic description of structures and processes at the solid-liquid interface. To this end, DFT force fields for the interactions water-Au and ethanol-Au have been proposed and applied to simulations by Monte Carlo techniques. Additionally, we have done preliminary ab initio calculations for the prediction of reactive sites and mechanisms concerned with electropolymerisation processes.

In this talk, we shall review some recent results obtained in our laboratory, from the standpoint of fundamental issues, challenges and possible future developments.

**Invited Talk** O 56.5 Thu 18:00 H36  
**Proton Conductors for Fuel Cells: The Role of Interfacial Structure and Dynamics** — ●MICHAEL EIKERLING, ATA ROUDGAR, and SUDHA NARASIMACHARY — Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada

Polymer electrolyte membranes (PEM) are the key components in polymer electrolyte fuel cells. Our work focuses on mechanisms of proton transport in the interfacial region between polymer fibrils and aqueous pathways in PEM. Understanding structure and dynamics at these ion-lined interfaces is of fundamental interest and it could facilitate the rational design of advanced PEM. As a basic model for performing ab-initio quantum mechanical calculations we consider a dense 2D array of ionized surface groups under conditions of minimal hydration. In optimization studies we found a critical separation 7Å of surface groups for the transition between highly ordered and clustered interfacial conformations. The transition from weak to strong binding of additional water molecules occurs also at 7Å. We systematically explore effects of density and chemical architecture of surface groups on conformations, strength of water binding, and interfacial dynamics. Our calculations have identified tilting of surface groups, rotation of acid head groups, and lateral shift of hydronium ions as relevant collective coordinates that control proton motion at the hydrated interface. Currently, we utilize ab-initio molecular dynamics and transition path sampling methods to systematically study free energy profiles along reaction paths and determine relevant transition rates.

O 56.6 Thu 18:30 H36  
**New aspects of the sulfur electrooxidation on Au(111) - An in situ STM study** — ●CHRISTIAN SCHLAUP, DANIEL FRIEBEL, PETER BROEKMANN, and KLAUS WANDEL — Institut für Physikalische und Theoretische Chemie, Wegelerstr. 12, D-53115 Bonn

We have reinvestigated the nature of the ring-like structure of the S-covered Au(111) surface, which appears both under electrochemical conditions as well as in UHV, respectively. In contrast to previous electrochemical studies, the HS<sup>-</sup> containing alkaline electrolyte was exchanged, after deposition of 0.33 ML sulfur, for a blank 0.01 M NaOH solution, in order to prevent the formation of amorphous bulk overlayers at higher potentials. Subsequently, the structural and morphological changes of the ( $\sqrt{3} \times \sqrt{3}$ )R30° S layer upon potential increase were studied in situ with STM. Significant Au mass transport perpendicular to the surface with the formation of vacancies and new islands could be observed. The new islands have an ordered rhombic lattice which consists of the known ring-like units. This observation strongly suggests the formation of an Au<sub>x</sub>S compound in contrast to the traditional view of the formation of S<sub>8</sub> species. During the growth of Au<sub>x</sub>S islands, S atoms are consumed from the ( $\sqrt{3} \times \sqrt{3}$ )R30° struc-

ture. Due to the high electrode potential, S atoms are rather immobile, in particular at upper step edges, which enabled us for the first time to image S-covered  $(\sqrt{3} \times \sqrt{3})R30^\circ$  islands along with uncovered  $(1 \times 1)$  regions simultaneously.

O 56.7 Thu 18:45 H36

**Step Bunching Instability on Stepped Au(1 1 17) Electrodes in Sulfuric Acid Solution** — •MARGRET GIESEN, ERNESTO PICHARDO PEDRERO, and GUILLERMO BELTRAMO — Institute for Bio- and Nanosystems, IBN 4, Research Centre Juelich, D 52425 Juelich, Germany

We present scanning tunneling microscopy data on the stability of stepped Au(1 1 17) electrodes (vicinal to the Au(001) surface) in sulfuric acid solution. We have analyzed the step-step distance proba-

bility distribution as a function of the electrode potential. The width of the probability distribution increases with the (absolute) difference between the electrode potential and the potential of zero charge. Our findings are in agreement with a recent theoretical model [1] showing that all electrode surfaces in contact with an electrolyte are unstable against step bunching in a certain potential regime with respect to the potential of zero charge. This is the first quantitative experimental confirmation of the step bunching instability model for metal electrodes. Furthermore, we can deduce an estimate for the step-step interaction constant of  $120 \pm 25$  meVÅ. This value is more than an order of magnitude larger than typical values for metal surfaces in vacuum. The reason may lie in the specific adsorption of sulfate ions at the step edges. [1] Surf. Sci. 573 (2004) 24