

## O 67: Symposium: The Solid-Liquid Interface: A Challenge for Theoreticians II

Time: Friday 10:15–13:00

Location: H38

## Invited Talk

O 67.1 Fri 10:15 H38

**Interfacial Properties of Transition Metal Oxides** — •ELISABET AHLBERG, ZAREEN ABBAS, and STURE NORDHOLM — Department of Chemistry, Göteborg University, 412 96 Göteborg, Sweden

Catalytic and electrocatalytic ability of transition metal oxides is commonly related to the nature of the metal cation and its coordination. However, in aqueous solution the pH rather than potential determines their interfacial chemistry and surface complexation models have been successfully used to describe interfacial properties by including specific chemical surface interactions besides electrostatic effects. We have used corrected Debye-Hückel (CDH) analysis to clarify the mechanisms at work in surface complexation. Ion size in the ion-ion interactions is accounted for in the diffuse screening and a layer of condensed counterions are introduced to treat nonlinear electrostatic response close to the surface. In the CDH theory the particle is considered to be a sphere which can have any size.

Recently, the effect of particle size on the surface charge density was investigated. The results show an increase in surface charge density as the size decreases. This sharp rise in the surface charge density may be explained by the increasing curvature of the double layer as the particle size decreases. The screening becomes more efficient as the size of the particles decreases due to accumulation of ions around the small particles.

In my talk surface complexation at oxide surfaces will be treated from both theoretical and experimental point of view. The implication on electrocatalytic properties will also be discussed.

## Invited Talk

O 67.2 Fri 10:45 H38

**Modeling the Electrochemical Potential of the Aqueous-Electrode Interface within Periodic Density Functional Theory** — •SALLY WASILESKI<sup>1</sup>, CHRISTOPHER TAYLOR<sup>2</sup>, MICHAEL JANIK<sup>2</sup>, and MATTHEW NEUROCK<sup>2</sup> — <sup>1</sup>Department of Chemistry, University of North Carolina at Asheville, Asheville, NC 28804 USA — <sup>2</sup>Departments of Chemical Engineering and Chemistry, University of Virginia, Charlottesville, VA 22904 USA

Ab-initio methods such as density functional theory (DFT), used extensively in modeling the structure and reactivity of adsorbates at vacuum interfaces, are now capable of probing energies and pathways for complex metal/solution environments and are proving to be a good complement to experimental efforts. A model has been developed to include the influence of the tunable electrochemical potential at the aqueous-electrode interface within the periodic density functional theory methodology [Taylor, CD, Wasileski, SA, Filhol, J-S, Neurock, M, "First principles reaction modeling of the electrochemical interface: Consideration and calculation of a tunable surface potential from atomic and electronic structure" Phys. Rev. B (2006) 73, 165402/1-165402/16]. Specific aspects of the model will be addressed in detail along with examples of using the methodology to investigate electrocatalytic reactions such as potential-dependent water dissociation at VIII and IB surfaces and potential-dependent methanol dehydrogenation and carbon monoxide oxidation (relevant chemistry to direct methanol fuel cells).

O 67.3 Fri 11:15 H38

**Structural stability and OH adsorption properties of Au/Pt(111) surfaces** — •YOSHIHIRO GOHDA and AXEL GROSS — Institute of Theor. Chemistry, Ulm Univ., 89069 Ulm/Germany

Platinum-based bimetallic electrodes are of current interest for electrochemical and electrocatalytic applications to fuel cells for example. The structural stability of such electrodes is one of the most important prerequisites. Furthermore, OH groups adsorbed on the electrode surface are produced in the initial stage of the oxygen reduction at the cathode. The OH adsorption could also be of importance during the consumption of water in the electro-oxidation of methanol at the anode. A fundamental understanding of OH adsorption properties should thus be helpful for a better description of such reactions on the atomic scale.

Here we report first-principles calculations on the structural stability of Au/Pt(111) surfaces and the OH adsorption on them. We have found that 1-monolayer (ML) thick surface alloys on Pt(111) are energetically preferred compared to the decomposition into the clean Pt(111) surface and Au droplets. They are also more stable than 2-ML

thick alloys with the same Au concentration, too, because Au atoms that are larger than Pt atoms prefer to be located in the uppermost layer where they reduce the surface stress which is in general tensile. This bimetallic surface system favors separating into two phases at 0 K: the clean Pt(111) surface and the Au/Pt(111) overlayer. In contrast, stable surface alloy formation due to entropy effects is seen for the Au<sub>0.5</sub>Pt<sub>0.5</sub> composition at 800 K. Calculations for the OH adsorption will also be reported.

O 67.4 Fri 11:30 H38

**d-Band Catalysis in Electrochemistry** — •SONJA BARTENSCHLAGER<sup>1</sup>, WOLFGANG SCHMICKLER<sup>1</sup>, and ELIZABETH SANTOS<sup>2</sup> — <sup>1</sup>Universität Ulm, Institut für Theoretische Chemie, Albert-Einstein-Allee 11, 89069 Ulm — <sup>2</sup>Zentrum für Sonnenenergie und Wasserstoff-Forschung, Helmholtzstr. 8, 89081 Ulm

Understanding the mechanism of electrocatalysis is of primary importance for the development of efficient fuel cells. We present the first theory for electrochemical electron transfer reaction that can account for specific catalytic effects caused by the interaction of the reactants with the d-band of a metal electrode. It is based on a model Hamiltonian that combines elements of the Anderson-Newns theory with tight binding and with the Marcus theory.

We have applied this model to the breaking of a bond in a diatomic molecule; this is a particularly important case, since generally bond breaking requires a strong catalytic effect of the electrode. Specifically, we have performed calculations based on a simple, semi-elliptical form of the d-band. In this way, we were able to demonstrate and understand a number of qualitative effects: the change in the density of states as the reaction proceeds and the system passes the saddle point; the importance of a high density of d-band states near the Fermi level, which interact with the anti-bonding orbital as it passes the Fermi level; the loss of symmetry between the anodic and cathodic direction; the decrease in the energy of activation with increasing interaction, which in extreme cases can result in dissociative adsorption without barrier.

O 67.5 Fri 11:45 H38

**Theoretical study of the dynamics of gold islands on Au(100)** — •KAY PÖTTING<sup>1</sup>, PAOLA QUAINO<sup>1</sup>, WOLFGANG SCHMICKLER<sup>1</sup>, and TIMO JACOB<sup>2</sup> — <sup>1</sup>Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin-Dahlem, Germany

Nanostructures on metal electrodes are presently the subject of intensive investigations because they are expected to play an important role in future nanotechnologies. Their stability and dynamics has been found to depend exponentially on the electrode potential, an effect which we ascribe to the interaction of local dipole moments with the electric field of the double layer. In order to verify the validity of this conjecture, and to clarify the details of the underlying mechanism, we have investigated the dynamics of gold island on Au(100), which has been the subject of intense experimental investigations, by a combination of DFT calculations and kinetic Monte Carlo simulations. For this purpose, we have calculated the diffusion barriers and associated dipole moments for several important elementary processes by DFT. These results were combined with embedded atom potentials in order to generate the rates for all possible steps, which were then used as the basis for kinetic Monte Carlo simulations. In this way we have investigated both the dynamics of single islands and the Ostwald ripening of two islands of different sizes. Preliminary results indicate a strong effect of the field on energetic parameters like the step line tension and the kink energy, and on the rate of particle exchange and Ostwald ripening.

O 67.6 Fri 12:00 H38

**DFT-Studies on the Potential-Induced Lifting of the Au(100) Surface Reconstruction** — •SUDHA VENKATACHALAM, TIMO JACOB, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, D-14195 Berlin, Germany

The study of potential-induced changes of single crystal surface morphologies is of great interest because of its diverse application in electrocatalysis and nanostructuring. In case of Au(100), different surface sensitive techniques show the lifting of stable hexagonal-reconstructed

Au(100)-hex to the regular Au(100)-(1×1) structure at electrode potentials >0.55V in 0.01M HClO<sub>4</sub> and at >0.32V in 0.1M H<sub>2</sub>SO<sub>4</sub> [1]. Although various theoretical and experimental investigations have hitherto been carried out, the rationale behind the lifting of reconstruction is still not clear. In order to study this effect, we performed DFT calculations on Au(100)-hex and Au(100)-(1×1), first neglecting the electrolyte and studying the influence of the electrode potential by applying an external electric field. For both electrolytes (HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>) we were able to reproduce the experimentally measured transition potentials after correlating the applied electric field to the electrode potential using experimental capacity curves. While this already implies a major role of surface charging, we are now in the process of investigating the influence of ion adsorption. [1] D. M. Kolb, *Prog. Surf. Sci.*, **51**, 109 (1996).

O 67.7 Fri 12:15 H38

**Theoretical Studies on the Electro-Oxidation of Pt-electrodes** — ●TIMO JACOB and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, D-14195 Berlin, Germany

Using an extension of the *ab initio* atomistic thermodynamics approach to electrochemical systems the interfacial structure and composition of Pt-electrodes in aqueous electrochemical environments was studied. Focusing on positive electrode potentials, at which first electro-oxidation and then oxide-formation occurs, we evaluated the full ( $p, T, \phi$ )-surface phase diagram. Assuming experimental temperature and pressure conditions, we find that after forming a (2×2) structure at 0.95 V, the bulk-oxide is thermodynamically stable above 1.20 V. Consequently, the assumption of a plain Pt-electrode, often used in the modeling of electrochemistry, is clearly incomplete. Instead, the surface structure and composition is significantly modified. To further investigate the oxide-formation, we focused on bulk-oxide systems and calculated the stability of the low-index surfaces of  $\alpha$ -PtO<sub>2</sub>,  $\beta$ -PtO<sub>2</sub>, and PtO bulk-oxides. On the basis of formation energies we first deduced the stability ranges at which the bulk-oxides are the thermodynamically stable phase. Afterwards for each of the considered bulk-oxides the corresponding ( $p, T, \phi$ )-phase diagram of surface structures was obtained, showing a preference for  $\alpha$ -PtO<sub>2</sub>(001),  $\beta$ -PtO<sub>2</sub>(110), and PtO(100) respectively, which all have PtO<sub>2</sub> bulk-like compositions even on their surfaces. However, in case of thin oxide layers a PtO composition might also be relevant.

O 67.8 Fri 12:30 H38

**Surface stress and surface tension at charged solid-liquid interfaces** — ●DOMINIK KRAMER<sup>1</sup> and JÖRG WEISSMÜLLER<sup>1,2</sup> — <sup>1</sup>Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Postfach

3640, 76021 Karlsruhe, Germany — <sup>2</sup>Technische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany

Most experimental and theoretical results of surface stress changes of electrodes support either the view that the variations of surface stress are identical or similar of that of surface tension, i.e. have essentially a quadratic dependence on the potential, or that the basic dependence is a linear function of the charge. By using a simple model of the solid surface and using both the Lippmann equation (which describes the potential dependence of surface tension) and Shuttleworth's equation (which relates stress and tension) we demonstrate that the surface stress can be considered as a sum of two terms. The first one is a linear function of the surface tension; the second one is a linear function of the surface charge density. This comprehensive description allows explaining of the different results and their seeming discrepancies without assuming experimental errors or fundamental thermodynamic problems.

O 67.9 Fri 12:45 H38

**Räumlich aufgelöste IR Spektroskopie und elektrochemische Messungen zur nichtlinearen Dynamik der Elektrooxidation von H<sub>2</sub>,CO Gemischen an Pt-Elektroden** — ●PHILIPP BAUER, NILÜFER BABA, JOHANNES BOLTEN, JAN SIEGMEIER und KATHARINA KRISCHER — Technische Universität München, Physik-Department E19, James Franck Str.1, 85748 Garching

Bei Niedertemperaturbrennstoffzellen vermindert die herstellungsbedingte Kohlenmonoxidverunreinigung des Wasserstoffgases den Wirkungsgrad erheblich. Wir verfolgen den Ansatz, mit Hilfe von Methoden der nichtlinearen Dynamik diesen negativen Effekt zu minimieren.

Berechnungen mit einem System von gekoppelten Differentialgleichungen [1], das die Oxidation von H<sub>2</sub>,CO an einer Platinelektrode beschreibt, sagen von monostabilem Verhalten über Oszillationen und Domänenbildung bis hin zu komplexer Dynamik, eine Vielzahl von zeitlichen und räumlichen Mustern voraus. Wir stellen experimentell ermittelte Bifurkationsdiagramme, die aus globalen potentiostatischen Messungen gewonnen wurden vor und zeigen erste Ergebnisse zur räumlichen Musterbildung. Hierfür findet ein Infrarotspektrometer mit Focal-Plane-Array in ATR-Konfiguration (abgeschwächte Totalreflexion) Verwendung, mit dem raumzeitliche Muster in der CO Bedeckung abgebildet werden können.

Wir diskutieren, inwiefern durch Kontrolle der Parameter ausgewählte Muster eingestellt werden können, die auch in Gegenwart von CO eine hohe Effizienz der Wasserstoffoxidation erlauben.

[1] J. Siegmeier, Diplomarbeit, Physik Department, TU-München, München (2005)