

O 13 Solid-liquid interfaces

Time: Monday 15:00–17:45

Room: WIL C207

O 13.1 Mon 15:00 WIL C207

The corrosion behaviour of surface- and heat-treated magnesium alloy WE43 in Simulated Body Fluid — ●PETRA GUNDE, PETER J. UGGOWITZER, and JÖRG F. LÖFFLER — Laboratory of Metal Physics and Technology, ETH Zurich, Switzerland

Due to similar mechanical properties between magnesium and the human bone and due to the biocompatibility and non-toxicity of magnesium, it might be considered as an absorbable implant. In the present work, the corrosion behaviour of the magnesium alloy WE43 in simulated body fluid (SBF) was investigated. The corrosion rate of the samples was worked out using two methods; the conventional weight-loss method and the hydrogen evolution method where magnesium-loss is calculated based on the amount of evolved hydrogen. Different surface and heat treatments were applied to WE43 samples and their influence on the corrosion behaviour was characterised by immersion in SBF, X-ray diffraction and impedance spectroscopy. All methods indicate that the corrosion resistance is significantly increased by these surface treatments. The outstanding corrosion resistance of such treated WE43 samples is assumed to result in a relatively thick and less crack-afflicted protective oxide layer. In conclusion, surface treatments as performed in this work, significantly influence the degradation behaviour of WE43 specimens.

O 13.2 Mon 15:15 WIL C207

Excess non-specific Coulomb ion adsorption at the metal electrode/electrolyte solution interface — ●ALEXANDER M. GABOVICH, YURI A. REZNIKOV, and ALEXANDER I. VOITENKO — Institute of Physics, prospekt Nauki 46, 03028, Kiev, Ukraine

Excess ion adsorption G induced by the polarization image forces in the system of a metal electrode/symmetric electrolyte solution separated by an insulating interlayer have been calculated. The adopted theoretical scheme involves the Coulomb Green's function in a three-layer system with sharp interfaces and specular reflection at them. The influence of the spatial dispersion of the dielectric permittivities $E(k)$ in all the three media on the image force energy $W(x)$ and the adsorption G has been analyzed (k is a transferred wave-vector). A comparison with the classical model, where $E = \text{const}$, has been carried out. It has been shown that both the Debye-Hückel ion screening and the spatial dispersion of the solvent contribution to the overall dielectric function of the electrolyte solution lead to the qualitative difference with the results for the classical model. In particular, in a wide range of ion concentrations n a thin interlayer $L = 10$ Angstroms effectively screens out the attractive influence of the metallic electrode, so that the net Coulomb adsorption becomes repulsive. The approach and the results obtained qualitatively describe two physically different situations. Specifically, the introduced interlayer corresponds either to the dense near-electrode (inner) electrolyte layer or to the intentionally deposited control coating of arbitrary thickness.

O 13.3 Mon 15:30 WIL C207

Modeling electrocatalysis – electro-oxidation of Pt(111) — ●TIMO JACOB and MATTHIAS SCHEFFLER — Fritz-Haber Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

Electrochemical reactions (such as in fuel cells) usually occur under conditions of finite temperature, pressure, and electrode potential, implying a very involved situation, possibly leading to novel surface materials. Especially the presence of an electrode potential, which results in the formation of an electric double-layer, affects the composition and structure of the electrode/electrolyte-interface.

Towards a more realistic treatment of electrocatalysis we developed an appropriate theory in which the electrode of the interface is assumed to be in contact with a *bulk-electrode* reservoir (at chemical potential μ_{el}) while the electrolyte is in contact with a *bulk-electrolyte* reservoir. Although we are in the process of simulating the entire electric-double layer self-consistently, the present approach already allows us to estimate the limites of the expected effects.

As a first application we studied the electro-oxidation of Pt(111) by calculating the $p/T/\phi$ -phase diagram. The obtained behavior, that positive electrode potentials stabilize higher oxygen coverages, is in qualitative agreement with cyclic-voltammetry experiments.

O 13.4 Mon 15:45 WIL C207

ATR-IR spectroscopic measurements of cooperative effects during CO electro-oxidation on Pt film electrodes — ●JOHANNES BOLTEN¹, ANTOINE BONNEFONT², SAURADIP MALKHANDI¹, and KATHARINA KRISCHER¹ — ¹Physik Department E19, Technische Universität München, James Franck Str. 1, 85748 Garching — ²Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France

Attenuated total reflection infrared (ATR-IR) spectroscopy allows the in-situ observation of surface coverages under reaction conditions. When combined with a flow cell, adsorbate coverages under stationary conditions can be monitored. Employing ATR-IR spectroscopy in a flow-cell, we present studies on nonlinear phenomena during CO electro-oxidation on Pt film electrodes. In particular, we investigate the dynamics in the bistable and oscillatory regime of this reaction. The studies allow us to draw conclusions on the physico-chemical mechanism of the oscillations. Moreover, simultaneous measurements of CO and anion coverages make it possible to analyze the adsorption dynamics in the presence of both species, allowing to detect cooperative effects.

O 13.5 Mon 16:00 WIL C207

Ensemble size effects in the electrochemical properties of PtRu/Ru(0001) and PdRu/Ru(0001) surface alloys — ●H.E. HOSTER, A. BERGBREITER, E. FILONENKO, and R.J. BEHM — Abt. Oberflächenchemie und Katalyse, Universität Ulm, 89069 Ulm

Atomically smooth PtRu and PdRu surface alloys can be prepared in UHV by vapor deposition of Pt or Pd on Ru(0001), respectively, followed by heating to 1000-1350 K. This leads to an incorporation of Pt (Pd) mainly into the outermost layer, which then contains fractions of Pt (Pd) immediately determined by the amount deposited initially. The lateral atomic distribution in the 2D alloys, however, is significantly different in PdRu compared to PtRu. As in bulk alloys, Pt and Ru are well miscible also in two dimensions, coming along with a nearly random atomic distribution. Pd and Ru, on the other hand, are bulk immiscible and also show a clear tendency towards phase separation on a low nm-scale in the studied surface alloys. Atomic distribution and surface density of distinct adsorption ensembles are derived from STM images and quantitatively related to certain features in electrochemical adsorption and reaction data, which provides insights into the ensemble size requirements of typical adsorbates and reactants.

O 13.6 Mon 16:15 WIL C207

Potential dependence of the step line tension on vicinal gold surfaces — ●GUILLERMO BELTRAMO, MARGRET GIESEN, and HARALD IBACH — Institut für Schichten und Grenzflächen, ISG4, Forschungszentrum Jülich, Jülich 52425, Germany

The step line tension β per atom plays a crucial role in the electrochemical deposition and dissolution of metals, and in particular, in the creation of nanostructures and their dynamical properties. Recently (1,2) we demonstrated how step energies can be measured in electrolyte by island studies. Now, we introduce a new method to analyze steps energies on metal electrodes.

We present Electrochemical Impedance Spectroscopy studies (EIS) of stepped Au(100) electrodes in electrolyte. Following the model proposed by Schmickler and Ibach (3) one can determine the step line tension, and from the shift of the potential of zero charge (pzc) the dipole moment of the step. Here we will present results obtained in weakly adsorbing electrolytes (sulfuric and perchloric acid). The results will be discussed.

- (1) Farad. Disc. 121 (2002) 27.
- (2) J. Electroanal. Chem. 524-525 (2002) 194.
- (3) Physical Rev. Lett. 91 (2003) 016106.

O 13.7 Mon 16:30 WIL C207

Electrochemistry of Two Dimensional Copper Sulphide Films on Au(111) Studied by in situ STM and Cyclic Voltammetry — ●DANIEL FRIEBEL, CHRISTIAN SCHLAUP, and KLAUS WANDEL — Institut für Physikalische und Theoretische Chemie, Wegelerstr. 12, D-53115 Bonn, Germany

For the electrochemical preparation of ultrathin copper sulphide films on Au(111), Cu underpotential deposition from 1 mM CuSO₄ + 0.1 M H₂SO₄ is followed by two consecutive electrolyte exchanges for (i) *acid*

blank solution (0.1 M H₂SO₄) and (ii) *reactive* solution (0.5 mM Na₂S + 0.1 M NaOH). We can stabilize the first upd layer ($\theta_{\text{Cu}} = 2/3$) with its well-known ($\sqrt{3} \times \sqrt{3}$)R30° structure in the acid blank solution for over 2 hours. In the reactive solution, we observe islands of two ordered Cu_xS phases: a rectangular and, at higher potentials, an incommensurate hexagonal phase. Cu-free, S-covered Au(111) regions are identified by their characteristic ($\sqrt{3} \times \sqrt{3}$)R30° structure. At strongly anodic potentials, Cu_xS is irreversibly dissolved. The latter process cannot be directly observed with STM because HS⁻(aq) is oxidized to S₈(ads) multilayers. Therefore, we have extended our investigations by a third electrolyte exchange, subsequent to Cu_xS formation, for *alkaline blank* solution (0.1 M NaOH), to get further insights into the Cu_xS electrooxidation. Obviously, anodic Cu dissolution in alkaline solutions is enhanced by complexation of Cu(II) with bi- or polysulphides.

O 13.8 Mon 16:45 WIL C207

Exploring the diamond/aqueous electrolyte interface — ●JOSE ANTONIO GARRIDO, STEFAN NOWY, ANDREAS HÄRTL, JORGE HERNANDEZ, and MARTIN STUTZMANN — Walter Schottky Institut, Technische Universität München, Am Coulombwall 3, 85748 Garching

The diamond surface is a unique platform for the investigation of the charged solid/liquid interfaces. Both carbon-hydrogen (C-H) and carbon-oxygen (C-O) surface groups are stable in aqueous solutions, and show a completely different behavior in terms of wetting by water and the resulting charge state. Furthermore, under certain conditions a highly conductive p-type channel is induced at the surface of H-terminated undoped diamond films, which can be used for charge sensing applications. In this contribution, we report on the electrochemical characterization of modified C-H and C-O diamond surfaces in contact with aqueous electrolytes. For this purpose, we have investigated surface conductive single crystalline films as well as boron-doped metal-like polycrystalline and nitrogen-containing ultrananocrystalline diamond films. Using impedance spectroscopy we study the influence of different surface terminations on the interfacial capacitance. Surface charging processes have been investigated as a function of electrolyte pH. The effect of screening and/or specific adsorption of electrolyte ions will be discussed. This work has direct implications for an understanding of the pH and ion sensitivity of diamond surfaces, as well as the physisorption of charged biomolecules on these surfaces.

O 13.9 Mon 17:00 WIL C207

In-plane structure of liquid 8CB layers confined between mica sheets — ●HARALD REICHERT¹, THOMAS BECKER², HELMUT RATHGEN³, and FRIEDER MUGELE³ — ¹MPI for Metal Research, 70569 Stuttgart — ²Universität Ulm, 89081 Ulm — ³University of Twente, 7500 AE Enschede, NL

The ongoing miniaturization of both microelectromechanical and microfluidic devices creates an increasing interest in transport properties of liquids near solid-liquid interfaces and in confinement. For simple liquids confined between atomically smooth solid substrates, it has been shown that the molecules arrange into layers parallel to the surfaces. The question whether the structure of thin confined liquid layers changes from a liquid-like structure (for thicker layers) to a more solid-like structure (monolayer regime) is highly controversial. Direct measurements of the in-plane structure of thin confined liquid layers have not been performed up to now.

We have developed a new x-ray diffraction setup which allows us to study the in-plane structure of liquid layers as a function of temperature. We present the first results of time and temperature dependent measurements of the in-plane structure of liquid crystal 8CB confined between two mica sheets.

O 13.10 Mon 17:15 WIL C207

Probing interfaces of particle suspensions using vibrational sum frequency scattering — ●SYLVIE ROKE — Max-Planck Institute for Metals Research, Heisenbergstr. 3, Stuttgart, Germany

Many important chemical, physical and biological phenomena occur at interfaces of particles in suspension. Most of the tools presently available to study these interfaces use invasive techniques or model systems. Ideally, one would want a non-invasive technique that allows to study interface structure and dynamics with molecular specificity.

We have for the first time used the nonlinear optical technique vibrational sum frequency generation to study the interfaces of sub-micron particles in suspension. As a model system we use a suspension of silica particles covered with alkane (C18) chains [1]. We obtain information

about the molecular structure (molecular order and orientation) as well as particle morphology, by analyzing both the spectra as well as the angle dependent scattered intensity. Finally, we show that the interfacial order and structure is strongly influenced by the solvent [3].

- [1] S. Roke, W. G. Roeterdink, J. E. G. J. Wijnhoven, A. V. Petukhov, A. W. Kleyn and M. Bonn, Phys. Rev. Lett., 91, 258302 (2003)
 [2] S. Roke, M. Bonn, A. V. Petukhov, Phys. Rev. B, 70, 115106 (2004)
 [3] S. Roke, J. Buitenhuis, J. C. van Miltenburg, M. Bonn and A van Blaaderen, J. Phys. Condens. Matter, 17, S3469 (2005)

O 13.11 Mon 17:30 WIL C207

Benzene diffusion measurements using neutron and helium spin-echo — ●PETER FOUQUET¹, HOLLY HEDGELAND², ANDREW P. JARDINE², GIL ALEXANDROWICZ², WILLIAM ALLISON², and JOHN ELLIS² — ¹Institut Laue-Langevin, BP 156, F-38042 Grenoble Cedex, France — ²Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

The accurate description of surface-molecule interaction potentials is crucial for a correct description of molecule dynamics in systems with a large fraction of molecules close to a surface, such as zeolites, mesoporous confinements and real catalysts. Here we present a new approach using two techniques that will allow to extract the surface contribution to the dynamics of molecules in confinements by measuring bulk diffusion (neutron spin-echo, NSE) and surface diffusion (helium spin-echo, HeSE) on the same system on identical length scales. NSE is an established technique for the analysis of dynamics in the ps to 100 ns time window at molecular length scales in bulk samples. Recently, surface sensitivity could be introduced by translating the NSE principle to helium atom scattering [1].

In a prototype experiment we could show the complementarity of NSE and HeSE by studying benzene diffusion on graphite(0001) surfaces. We characterized the specific response by the two techniques in respect of signal, diffusion mechanism and possible excitation of phonons. The measured diffusion mechanisms and constants agree well between the two techniques and also with recent MD calculations.

- [1] A.P. Jardine et al., Science 304 (2004) 1790.