

O 40: Solid-Liquid Interfaces

Time: Tuesday 18:15–21:00

Location: Poster A

O 40.1 Tue 18:15 Poster A

Towards the Simulation of the Water-Zinc Oxide Interface Employing Neural Network Potentials — ●VANESSA QUARANTA, TOBIAS MORAWIETZ, and JOERG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

The reliability of molecular dynamics and Monte Carlo simulations crucially depends on the quality of the underlying potential-energy surface (PES). In recent years, artificial neural networks (NNs) have emerged as a new method to provide accurate PESs for a variety of systems. NNs are flexible functions able to learn the topology of a PES from a set of reference electronic structure calculations. Here, we report first results for a NN potential based on density-functional theory constructed to describe the water-ZnO interface. We find that the NN potential is able to provide a wide range of structural and energetic properties of water, ZnO as well as of interface structures with close to first-principles accuracy.

O 40.2 Tue 18:15 Poster A

Interaction of ionic liquids with alkali metal films — ●MARK OLSCHIEWSKI¹, RENÉ GUSTUS¹, MARCEL MARSCHEWSKI², OLIVER HÖFFER¹, and FRANK ENDRES¹ — ¹Institut für Elektrochemie, Technische Universität Clausthal, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld, Germany — ²Institut für Energieforschung und Physikalische Technologien, Technische Universität Clausthal, Leibnizstr. 4, 38678 Clausthal-Zellerfeld, Germany

As RT-ILs exhibit good ion conductivities, high temperature stability and large electrochemical windows together with a good solubility for lithium salts, they are of potential interest as electrolyte for non flammable Li based batteries, like e.g. lithium/air batteries. To enable good cycle stabilities the interaction of electrolyte and lithium on electrode surfaces has to be investigated carefully. Here thin films of [C1C4Pyr][Tf₂N (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide)] and [OMIm][Tf₂N (1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide)] were evaporated on lithium and sodium surfaces, interactions subsequently were analyzed by XPS (x-ray photoelectron spectroscopy) and UPS (ultraviolet photoelectron spectroscopy). Both the cation and the anion react with the alkali metals, giving a series of decomposition products. The results exhibit instability of ionic liquids in presence of alkali metal and give a first insight in the differences of the reaction chemistry of pyrrolidinium cations and imidazolium ones.

O 40.3 Tue 18:15 Poster A

Electrochemistry of natural polycrystalline vs natural single crystal magnetite — ●DIANA HÖTGER¹, SANTIAGO HERRERA^{1,2}, DORIS GRUMELLI¹, BENJAMIN WURSTER¹, PETER JACOBSON¹, RICO GUTZLER¹, ERNESTO CALVO², and KLAUS KERN^{1,3} — ¹Max Planck Institute for Solid State Research, Stuttgart, Germany — ²Departamento de Química inorgánica, analítica y fisicoquímica, INQUIMAE, Universidad de Buenos Aires, Argentina — ³Institute de Physique de la Matière Condensée, EPFL, Lausanne, Switzerland

Metal oxides have attracted a lot of interest in catalytic research as a cheap alternative to noble metal devices used in present applications. The electrochemistry of natural polycrystalline magnetite (Fe₃O₄) and their reactivity towards oxygen reduction reaction (ORR) has been widely studied [1,2]. Electrocatalysis is a surface dependent process, as surface composition, structure, and defects govern the electrochemical response. For a better understanding of the mechanisms and to improve the efficiency of electrocatalysts, it is crucial to work with very well defined surfaces. Electrochemistry of Fe₃O₄(001) single crystal surfaces prepared under ultra-high vacuum (UHV) conditions has previously been reported [3]. Here we expand this research and compare the electrochemistry of UHV prepared Fe₃O₄(001) single crystals with polycrystalline Fe₃O₄ by using a specially designed transfer system between UHV and electrochemical environment.

[1] P. A. Castro et al., J. Chem. Soc. Faraday Trans. 1996, 92, 3371.

[2] E. J. Calvo, Mater. Corros. 2014, 65, 345–350.

[3] R. Blum et al., 2014, doi: 10.1126/science.1260556.

O 40.4 Tue 18:15 Poster A

First-principles study of structures and growth processes at

metalelectrodes — ●XIAOHANG LIN and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Recently, the operation of an atomic-scale quantum switch has been demonstrated, which is controlled by an external electrochemical voltage applied to an independent gate electric field [1]. Pb, Au and Ag are used as candidate materials for the quantum switches. Still, the atomic processes and principles underlying the operation of the switch are not clear yet. Structural changes of the metal-water interface and deposition/diffusion on the metal electrodes in the presence of an electric field might be the elementary processes that are most likely involved in the switching process.

Hence, the self-diffusion and surface structures at the metal-water interface of Pb (Au and Ag) stepped surfaces have been studied using first-principles electronic structure calculations [2]. These studies show that diffusion across the steps is facilitated by the exchange mechanism. Furthermore, the influence of the presence of water on the properties of the metal electrodes will be discussed.

[1] F.-Q. Xie, L. Nittler, Ch. Obermair, Th. Schimmel, Phys. Rev. Lett. **93**, 128303 (2004).

[2] X. Lin *et al.*, Electrochim. Acta **140**, 505-510 (2014).

O 40.5 Tue 18:15 Poster A

Model Studies on the Electrochemical Decomposition of [BMP][TFSA] on Au electrodes — ●DOROTHEA ALWAST^{1,2}, JOHANNES SCHNAIDT^{1,2}, YEUK TING LAW¹, and R. JÜRGEN BEHM^{1,2} — ¹Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89069 Ulm, Germany

Metal-air batteries like Li-air or Mg-air batteries offer high specific energies and are therefore studied intensively at present. Due to their special physical and chemical properties, the use of ionic liquids (IL) as electrolyte is of great interest. Therefore, the electrochemical stability of these ILs plays a key role for the use in batteries. To gain a better understanding of the stability of the IL n-butyl-n-methylpyrrolidinium-bis(trifluoromethylsulfonyl) imide ([BMP][TFSA]), its decomposition on Au electrodes is studied using a novel differential electrochemical mass spectrometry (DEMS) set-up. Using cyclic voltammetry, decomposition products of the TFSA anion ($m/z = 69$, CF₃⁺; $m/z = 64$, SO₂⁺) are detected at positive (oxidative) potentials. In contrast, the decomposition products of the cation occur when applying negative (reductive) potentials. The implications of these findings on the mechanism of the IL's electrochemical decomposition as well as the influence of adding Li[TFSA], Mg[TFSA]₂ and O₂ to the system as model system for Li-air and Mg-air batteries, will be discussed.

O 40.6 Tue 18:15 Poster A

Preparation, Characterization and Electroanalytic Reactivity of Bimetallic Pt_xAg_y and Pd_xAg_y Nanocrystals — ●ISABELLA WEBER¹, SYLVAIN BRIMAUD¹, JOSÉ SOLLA GULLÓN², JUAN M. FELIU², and R. JÜRGEN BEHM¹ — ¹Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ²University of Alicante, Institute of Electrochemistry, 03080 Alicante, Spain

Bimetallic Pt_xAg_y and Pd_xAg_y nanoparticles with silver contents between 0-35 at% were prepared using water-in-oil microemulsion and seed-mediated growth synthesis, and characterized electrochemically by CO_{ad} electrooxidation. The decrease of CO_{ad} oxidation reactivity of the as-received samples with increasing nominal Ag content indicates an up-shift of the Pt (Pd) d-band center. In order to disentangle contributions from silver dissolution and CO_{ad} oxidation, a combination of in-situ attenuated total reflectance Fourier-transform infra-red spectroscopy (ATR-FTIRS) and on-line differential electrochemical mass spectrometry (DEMS) was employed. Ensemble effects are held responsible for the change of the preferential adsorption configuration from bridge-bonded to linearly bonded CO_{ad} for Pd_xAg_y nanoparticles with Ag >20 at%. After electrochemical dealloying, the samples exhibit the reactivity of pure Pt (Pd) towards CO_{ad} oxidation. An increase in the CO_{ad} saturation coverage with increasing nominal silver content, however, additionally indicates a subtle electronic effect induced by Ag atoms within the bimetallic core of the dealloyed particles.

O 40.7 Tue 18:15 Poster A

Interplay of Different Reaction Pathways in the Pulsed Galvanostatic Deposition of ZnO — ●MARTINA STUMPP, CHRISTIAN LUPO, and DERCK SCHLETTWEIN — Institut für Angewandte Physik, Justus-Liebig-Universität Gießen, D-35390 Gießen

Zinc oxide (ZnO) is a promising electrode material for dye-sensitized solar cells (DSCs) and transparent electronics. Electrochemical deposition serves as a low-temperature and an environmentally-friendly technique to prepare crystalline ZnO films even on temperature-sensitive substrates. Aqueous solutions of $Zn(NO_3)_2$ were used for electrodeposition of ZnO on Au microelectrodes of different shape under pulses of controlled current. Three significant stages were observed in potential-time curves. SEM revealed a correlation between a successively completed coverage of Au by ZnO and an abrupt transition of the deposition and rest potential to less negative values. The deposition time at which such a transition was detected depended not only on the amount of deposited ZnO but also on the current density during electrodeposition and on the electrode geometry, pointing at the influence of different diffusion profiles of the reacting ions. In order to elucidate the role of different redox reactions in the course of electrodepositions of ZnO , measurements were also carried out in various reference electrolytes. The three stages in the potential were only seen for pauses which were equal or longer than the current pulse. The significance of each stage and the corresponding reactions is discussed.

O 40.8 Tue 18:15 Poster A

Polymeric Phthalocyanine Sheets as Electrocatalytic Electrodes for Water-Splitting-Reactions — ●CLEMENS GEIS, SIMON SCHNEIDER, FRIEDER MÜNTZE, and DERCK SCHLETTWEIN — Institute of Applied Physics, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 16, D-35392 Gießen, Germany

Water splitting is an attractive way to convert alternating renewable energy sources to storable chemical fuels. Efficient electrocatalytic materials from abundant sources are needed for widespread applications. Aside from metals or metal oxides as electrode materials, molecular metal complexes are a promising approach for the oxygen evolution reaction. In this work, phthalocyanine metal complexes (Mn, Fe, Co, Ni, Cu) with polymerized ligands were synthesized via a CVD process on conductive substrates and used as electrocatalysts in an alkaline solution. Cyclic voltammetry with optical absorption spectroscopy performed *in operando* was applied to characterize the films. Chronoamperometry at positive potentials was used to study the performance of the films as electrocatalysts in the oxygen evolution reaction. Photoelectron spectroscopy was employed to analyze the elemental composition of the films and details of the atomic environment of the metal atoms.

O 40.9 Tue 18:15 Poster A

The hydrophobic gap under high hydrostatic pressure conditions — FLORIAN WIRKERT¹, ●MICHAEL PAULUS¹, JULIA NASE¹, JOHANNES MÖLLER², PAUL SALMEN¹, IRENA KIESEL³, BENEDIKT NOWAK¹, CHRISTIAN STERNEMANN¹, and METIN TOLAN¹ — ¹Fakultät Physik/DELTA, TU Dortmund, 44221 Dortmund, Germany — ²ESRF - The European Synchrotron, 71 Avenue des Martyrs, F-38043 Grenoble, France — ³Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France

We present an x-ray reflectivity (XRR) study on the influence of high hydrostatic pressure (HHP) on the structure of the so-called hydrophobic gap, a small electron depleted region at the interface between a hydrophobic surface and water. The structure of this gap has been discussed controversially throughout the last few years. In order to obtain a deeper insight into the gap's structural composition, we investigated the interface between a hydrophobic silicon wafer and ultrapure water at HHP conditions using XRR measurements. This technique is known to reliably resolve the shape (thickness, roughness, electron density) of thin layered structures on a molecular length scale.

The experiments have been performed at the synchrotron radiation facilities DELTA (Dortmund, Germany), Diamond Light Source (Didcot, UK) and ESRF (Grenoble, France). It is shown that only a small fraction of the hydrophobic gap is compressed under HHP. The main compression occurs between 1 bar and 1 kbar.

O 40.10 Tue 18:15 Poster A

COMPARING THE INFLUENCE OF CONCENTRATION CONTROL BY STIRRING OR SONICATING ON THE SELF-ASSEMBLY AT THE LIQUID-SOLID INTERFACE — ●NGUYEN THI NGOC HA¹, NGUYEN DOAN CHAU YEN¹, KATHRIN

ALLMAIER¹, THIRUVANCHERIL G. GOPAKUMAR², and MICHAEL HIETSCHOLD¹ — ¹Institute of Physics, Solid Surfaces Analysis Group, Technische Universität Chemnitz, Germany — ²Indian Institute of Technology, Kanpur 208016, India

Sonication has been successfully applied to change concentrations in organic solutions and this way to engineer different self-assembled molecular structures. We have demonstrated this using trimesic acid solved in different solvents: phenyloctane, [1] alkanolic acids [2,3] and alcohols [3]. Nevertheless there raised some fears that sonication might also chemically influence on these solutions. Therefore we compare here sonication and stirring as two different methods to increase concentration. We demonstrate here that stirring leads to the same series of adsorption pattern as obtained using sonication. The only difference seems to be that stirring times are much larger than corresponding sonication times to obtain the same structures. The corresponding self-assembled structures of TMA in those solvents (phenyloctane, octanoic acids and undecanol solvents) have been monitored by the ambient STM. The study demonstrates the key role of the external control parameter concentration via very simple methods: sonication or stir in the self-assembly.

O 40.11 Tue 18:15 Poster A

Dynamics of water adsorption on Pt(111): ab initio molecular dynamics study — ●MARYAM NADERIAN and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Ab initio molecular dynamics (AIMD) simulations based on periodic density functional theory (DFT) calculations using the dispersion-corrected RPBE-D3 functional [1] have been performed to study the dynamics of adsorption and sticking probability of water molecules on Pt(111). As typical for molecular adsorption, the sticking probability has been found to decrease as a function of the initial kinetic energy (IKE) of the impinging water molecules. Special attention has been paid to the role of the internal degrees of freedom of the water molecules upon impinging on the Pt substrate. Most of the IKE of the water molecule is initially transferred into the internal molecular degrees of freedom (vibrations and rotations) and later to the kinetic energy of the substrate atoms [2]. This energy redistribution leads to an efficient dissipation of the initial energy of water molecule which is crucial for understanding molecular adsorption dynamics.

To shed some light on the dynamics of the initial water structure formation on metal electrodes, we have performed AIMD simulations of water molecules impinging on Pt(111) that is already precovered by water. Again analysing the energy redistribution upon adsorption, the physical factors which are responsible for the water structure formation on a Pt surface are identified.

[1] S. Grimme *et al.*, *J. Comput. Chem.* **32**, 1456 (2011).[2] Axel Groß *et al.*, *J. Electrochem. Soc.* **161**, E3015-E3020 (2014).

O 40.12 Tue 18:15 Poster A

The Cu(110) Surface in Hydrochloric Acid Solution: Potential Dependent Surface Restructuring — ●CLAUDIO GOLETTI¹, GIANLORENZO BUSSETTI^{1,2}, ADRIANO VIOLANTE^{1,3}, BEATRICE BONANNI¹, MARCO DI GIOVANNANTONIO¹, GIULIA SERRANO¹, STEPHAN BREUER⁴, KNUD GENTZ⁴, and KLAUS WANDEL⁴ — ¹Dipartimento di Fisica, Università di Roma Tor Vergata, Via della ricerca scientifica 1, 00133 Roma, Italy — ²Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy — ³Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7 D-10117, Berlin, Germany — ⁴Institut für Physikalische und Theoretische Chemie, Wegeler Str. 12, 53115 Bonn, Germany

Using Cyclic Voltammetry (CV), Reflectance Anisotropy Spectroscopy (RAS) and in situ Electrochemical Scanning Tunneling Microscopy (EC-STM) we have studied the structure and structural transitions at a Cu(110) electrode surface in 10 mM HCl solution as a function of the applied electrode potential. At potentials ≥ -550 mV (vs. Ag/AgCl) chloride adsorption first leads to the formation of grooves followed by the growth of added stripes, both being aligned in the [001] direction as shown by EC-STM. This "faceting" is accompanied by a clear optical anisotropy peak in RAS centered at about 500 nm (2.48 eV) when the linearly polarized light is aligned along the [001] direction. Continuous monitoring of the RAS signal through a full CV cycle yields a hysteresis-like curve which supports a (reversible) two-step kinetics of the restructuring process in agreement with the CV- and STM-data.

O 40.13 Tue 18:15 Poster A

Surface-Confined Polymerization on Au(111) in solution by pH control — MARCO DI GIOVANNANTONIO¹, TOMASZ KOSMALA^{1,2},

GIULIA SERRANO¹, BEATRICE BONANNI¹, NICOLA ZEMA³, DANIELE CATONE³, STEFANO TURCHINI³, DARIO PASINI⁴, KLAUS WANDELT², GIORGIO CONTINI³, and •CLAUDIO GOLETTI¹ — ¹Physics Department, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, I-00133 Roma, Italy — ²Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstraße 12, D-53115 Bonn, Germany — ³Istituto di Struttura della Materia, CNR, Via Fosso del Cavaliere 100, 00133 Roma, Italy — ⁴Chemistry Department, University of Pavia, Via Taramelli 10 27100 Pavia, Italy

Surface-confined polymerization is a promising strategy to produce organic conjugated networks via a bottom-up approach. We have explored the Schiff-base reaction to produce polymers at a solid-liquid interface by changing the pH of an aqueous solution. Here, 4,4'-diaminostilbene dihydrochloride and terephthalaldehyde have been studied to create 1D conjugated polymers on an iodide-modified Au(111) surface from solution. The formation of the molecular superstructure as a function of pH was analyzed in situ by scanning tunneling microscopy (STM), and ex situ by x-ray photoelectron spectroscopy (XPS) using synchrotron radiation at Elettra (Trieste). We found clear differences between the polymerization being confined to the surface compared to that proceeding in bulk solution. Insights into the catalytic effect of the substrate on the reaction steps will be shown and discussed.

O 40.14 Tue 18:15 Poster A

Investigating the Water-Titanium Dioxide Interface using SFG Spectroscopy — •SIMON JOHANNES SCHMITT, SAMAN HOSSEINPOUR, and ELLEN H.G. BACKUS — Max-Planck-Institut für Polymerforschung Ackermannweg 10, 55128 Mainz, Germany,

Since the world's fossil fuel supply will run out in a few decades, it is crucial to find cheap and environmentally friendly alternatives. Hydrogen is a good candidate, since it is obtainable by photocatalytic dissociation of water, when in contact with titanium dioxide surfaces, as has been discovered over 40 years ago. However, the fundamentals of the process are still not fully understood. To start, we measured Sum Frequency Generation (SFG) spectra of the water-TiO₂ interface. By overlapping a visible and an infrared laser beam in space and time on the sample the vibrational spectrum of the molecules at the interface can be obtained. We present data on TiO₂ single crystals with different facets and on sputtered thin films of various thicknesses. Moreover we will outline how we plan to use 2D-SFG to investigate the heterogeneity of the water molecules at the interface and time resolved measurements to follow the photo-induced dissociation of water at the interface in real-time.

O 40.15 Tue 18:15 Poster A

Ab-initio molecular dynamics simulations on wet alumina/isopropanol solid/liquid interfaces — •PAUL SCHWARZ and

BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

The solid/liquid interface of wet and hydroxylated α -alumina/isopropanol is studied using ab-initio Car-Parrinello molecular dynamics (CPMD) simulations. The proper description of liquid isopropanol by our PBE+D2 setup was benchmarked by comparing molecular interaction energies with basis set extrapolated coupled-cluster CCSD(T) results. Furthermore, pair correlation functions and diffusion coefficients from CPMD simulations at different temperatures were compared to experiment. The liquid isopropanol was pre-equilibrated by MD runs with a classical force field. For the alumina slab three different surface models were taken into account: a termination with a full hydroxyl layer (**hyd**), an aluminum termination with dissociated water molecules to saturate undercoordinated surface sites (**w1**) and a third model with adsorbed water molecules between the OH groups of the **w1** structure (**w2**). In the CPMD simulations of the combined system of solid and liquid phase the recombination of dissociated water molecules is observed, especially in the case of **w2**. The mechanism and rate of these proton transfer processes is analyzed and we will discuss the influence of the surface model on the structure of the isopropanol liquid.

O 40.16 Tue 18:15 Poster A

Influence of halide ions on the anisotropic growth of gold nanoparticles: Insight from molecular dynamics simulations

— •SANTOSH MEENA¹, ANDREAS HENKEL², and MARIALORE SULPIZI¹ — ¹Institute of Physics, Johannes Gutenberg University Mainz, Germany — ²Physical Chemistry Department, Johannes Gutenberg University Mainz, Germany

Halides ions play a fundamental role in controlling the anisotropic growth of gold nanorods [1]. In particular while Br⁻ is able to promote anisotropic growth in seed mediated synthesis, Cl⁻ is known to induce a faster isotropic growth. We studied the adsorption mechanism of CTAB/CTAC surfactant mixtures at different concentration ratio, namely 1:0, 1:1 1:2 and 0:1 on different gold surfaces, namely the (110), (100) and (111). We use molecular dynamics simulations in order to provide a detailed description of the gold/surfactant/electrolyte solution in the growing solution [2]. We found that Br⁻ is not only responsible for surface passivation, but also acts as the driving force for the CTAB micelle adsorption and stabilization on the gold surface. When Br⁻ is partially replaced by Cl⁻, the surfactant layer become less and less dense. Finally when all the CTAB is replaced by CTAC no halides or micellar structure protect the gold surface and further gold reduction is possible uniformly on all the facets resulting a isotropic faster growth.

[1] S. E. Lohse, N. D. Burrows, L. Scarabelli, L. M. Liz-Marzan, C. J. Murphy, Chem. Mater. 2014, 26(1), 34 [2] S. K. Meena, M. Sulpizi, Langmuir 2013, 29(48), 14954