

O 121: Solid-Liquid Interface IV: Structure and Spectroscopy

Time: Friday 10:30–13:30

Location: TRE Phy

O 121.1 Fri 10:30 TRE Phy
Implementation of a high-pressure cell in a UHV setup — ●JIRI PAVELEC, FLORIAN KRAUSHOFER, FRANCESCA MIRABELLA, JIAN XU, MANUEL ULREICH, MICHAEL SCHMID, ULRIKE DIEBOLD, and GARETH S. PARKINSON — Institut of Applied Physics, Vienna University of Technology, Austria

The importance of bridging the pressure gap in studies of model catalysts has been recognized for decades. Here we will discuss a novel design for a high-pressure cell that allows us to study reactions occurring on UHV-prepared metal-oxide single-crystal samples at pressures up to 1 bar and temperatures up to 500 °C. In our setup, only the sample surface and the inner surface of a quartz tube are exposed to the gas at elevated temperature, which minimizes contamination. The maximum operational temperature is currently limited by quartz purity. Case studies of the Fe₃O₄(001) surface exposed to water vapour [1] and the oxidation of reduced rutile TiO₂ will be presented.

[1] Kraushofer, Mirabella, Xu, Pavelec, Balajka, Müllner, Resch, Jakub, Hulva, Meier, Schmid, Diebold, and Parkinson; "Self-limited growth of an oxyhydroxide phase at the Fe₃O₄(001) surface in liquid and ambient pressure water." *Chem. Phys.* 151: 154702 (2019)

O 121.2 Fri 10:45 TRE Phy
Wet-chemically prepared porphyrin-layers on rutile TiO₂(110) — ●DANIEL WECHSLER¹, CYNTHIA CAROLINA FERNÁNDEZ², JULIA KÖBL¹, HANS-PETER STEINRÜCK¹, FEDERICO JOSÉ WILLIAMS², and OLE LYTKEN¹ — ¹Chair of Physical Chemistry II, University Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany — ²Department of Inorganic, Analytical and Physical Chemistry, University of Buenos Aires, Buenos Aires C1428EHA, Argentina

Porphyrins are large organic molecules that are interesting for different applications like photovoltaic cells, gas sensors or in catalysis. For many of these applications the interactions between adsorbed molecules and surfaces play a crucial role.

Recent surface science publications focused mainly on systems that were prepared by standard ultra-high vacuum (UHV) procedures, like sputtering, annealing and physical vapor deposition. This results in well-defined and impurity-free samples but neglects effects arising from the interaction with solutions or air occurring during a preparation process outside of UHV.

In this study, we present a way to wet-chemically prepare porphyrin layers on rutile TiO₂(110) surfaces in a reproducible way while keeping the amount of impurities at a minimum. X-ray photoelectron spectroscopy measurements show the differences between in-solution and pure UHV prepared samples.

The project is supported by the DFG through FOR 1878 (funCOS).

Invited Talk O 121.3 Fri 11:00 TRE Phy
Photoelectron spectroscopy at liquid/solid interfaces — ●HENDRIK BLUHM — Fritz Haber Institute of the Max Planck Society, Berlin

Solid/liquid interfaces are ubiquitous in technological applications and the environment and govern numerous important phenomena, including corrosion, electroplating, and weathering of rocks. A detailed understanding of these processes requires the investigation of solid/liquid interfaces with chemical sensitivity and interface specificity under operating conditions. Ambient pressure X-ray photoelectron spectroscopy is an excellent method to probe the heterogeneous chemistry of these interfaces, and provides in addition the opportunity to measure the local potentials simultaneously with the chemical composition through the observation of shifts in the kinetic energy of the photoelectrons, which serve as a non-contact probe. The challenge for photoelectron experiments on solid/liquid interfaces under ambient conditions is not only the elevated pressure at which these experiments have to be carried out, but equally so the preparation of well controlled samples with high cleanliness and reproducibility. This talk shows examples of the application of APXPS to solid/liquid interfaces and discusses some of the remaining challenges that still need to be overcome in these investigations.

O 121.4 Fri 11:30 TRE Phy

Spectroscopic Insights into Liquid Metal Solutions for Catalysis — ●HAIKO WITTKÄMPER¹, MATHIAS GRABAU¹, SVEN MEISEL², MINGJIAN WU³, ANDREAS GÖRLING², ERDMANN SPIKER³, HANS-PETER STEINRÜCK¹, and CHRISTIAN PAPP¹ — ¹Chair of Physical Chemistry 2, FAU Erlangen-Nürnberg — ²Chair of Theoretical Chemistry, FAU Erlangen-Nürnberg — ³Chair of Micro- and Nanostructure Research, FAU Erlangen-Nürnberg

Supported catalytically active liquid metal solutions (SCALMS) are deactivation resilient and highly active dehydrogenation catalysts, based on binary transition metal Gallium alloys. The remarkable properties of these catalysts, especially their good resiliency towards deactivation, are attested to the atomic dispersion of the active transition metal in liquid Gallium nano-droplets and the dynamics at the liquid metal/gas interface. The concept was pioneered at FAU and over the recent years we published findings on PdGa, PtGa and most recently RhGa alloys. Herein we present XPS studies on macroscopic alloy droplets and model catalyst particles, including in situ heating and comparative near ambient pressure oxidation studies for Pd-, Pt- and RhGa alloys. In all cases transition metal enrichment at the surface is observed, the development during the oxidation however suggests that despite their similarity the chemical origin of the enrichment effects differ for the transition metals.

O 121.5 Fri 11:45 TRE Phy
Understanding metal dissolution at Mg/H₂O interfaces from first-principles modelling — ●SUDARSAN SURENDRALAL, MIRA TODOROVA, and JÖRG NEUGEBAUER — Department of Computational Materials Design, Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, Düsseldorf-40237, Germany

The fundamental reaction that governs the corrosion of metals in an aqueous environment is the electrochemical dissolution reaction. Using our recently developed ab initio potentiostat scheme [1], we study the atomistic mechanism of metal dissolution at the vicinal Mg(1 2 -3 15)/water interface using density functional theory based molecular dynamics simulations under conditions of anodic polarization. Our results show water dissociation and the subsequent adsorption of OH groups at low coordinated kink sites of the electrode. This adsorption process is found to make these sites prone to dissolution. Analysis of our calculated trajectories confirms that a kink Mg atom dissolves as a divalent cation with a six-fold solvation shell. In addition, the anomalous hydrogen evolution reaction reported for anodically polarized Mg/H₂O interfaces is also observed. Based on our observations, we propose a reaction mechanism of Mg dissolution involving water dissociation.

[1] S. Surendralal, M. Todorova, M. W. Finnis, J. Neugebauer, *Phys. Rev. Lett.* **120**, 246801 (2018)

O 121.6 Fri 12:00 TRE Phy
Investigation of ion mobility and material transport on KBr surfaces in air in dependence of the relative humidity. — ●DOMINIK KIRPAL, KORBINIAN PÜRCKHAUER, and FRANZ J. GIESSBL — University of Regensburg

On every surface exposed to humid air a thin film of water molecules forms. The presence of water plays an important role for chemical reactions, material exchange and movement. The effect of condensed water layer, present in ambient conditions plays a significant role especially on surfaces that dissolve easily in water [1]. Surface atoms can easily diffuse into the thin water layer and, when surface conditions are favourable, they can re-attach to the surface. We collected FM-AFM images of the KBr surface in a climate-controlled glove box at various values of relative humidity. By scratching the surface with the AFM tip, we construct energetically unfavourable hills and scratch sites. We observed an exponential decay of the size of the defects and material accumulations, and from this data we determined energy barriers to dissolution and aggregation of approximately 0.9 eV [2].

[1] M. Luna, et al., *Journal of Physical Chemistry A*, 102.34 (1998) 6793-6800.

[2] D. Kirpal, et al. *Beilstein Journal of Nanotechnology*, 10.1 (2019): 2084-2093.

O 121.7 Fri 12:15 TRE Phy
Comparative AFM and STM study of the ionic liquid

[C1C1Im][Tf2N] on Au(111) from 110 K to Room Temperature — ●MANUEL MEUSEL, MATTHIAS LEXOW, AFRA GEZMIS, ANDREAS BAYER, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Ionic liquids (IL) have raised increased interest in surface science due to their low vapour pressure and the unique possibility to investigate liquid systems using UHV methods. For catalytic concepts involving thin layers of ionic liquids (SCILL and SILP), the understanding of the IL/solid and IL/gas interface is crucial. Therefore, we investigated the adsorption behaviour of [C1C1Im][Tf2N] deposited on Au(111) via AFM and STM from 110 K to room temperature (RT). While it was easier to obtain high sub-molecular resolution images with STM, AFM provided a more stable imaging, especially over the micrometer scale. At 110 K, we observe a closed wetting layer (WL) of anions and cations, showing up two different appearances: a striped and a hexagonal pattern. We assign these two patterns to different molecular orientations resulting in different superstructures. Around 200 K, transitions between both superstructures occur but none of them is dominant after further annealing. Even at RT the molecular ordering of the WL is still present, however the superstructures have vanished.

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O 121.8 Fri 12:30 TRE Phy

Potential and distance dependent measurements of tunneling barrier-heights at the interface of gold(111) in ionic liquids — ●MARCEL LANG and ROLF SCHUSTER — Karlsruher Institut für Technologie, Deutschland

The structure of the solid-liquid interface of ionic liquids on charged surfaces depends on the cell potential. E.g. multi-layered structures are found at polarization negative of the pzc.

To investigate these structures perpendicular to an Au(111) electrode we measured the distance dependence of the tunneling current, from which we calculated the local tunneling barrier-heights in four different ionic liquids ([BMP][TFSI], [BMP][FSI], [EMIM][TFSI], [EMIM][FSI]). The measurements were performed using a STM under inert gas atmosphere operating at room temperature.

The measured tunneling barrier-heights are very low at positive potentials. At positive to moderately negative potentials we observed an almost linear increase in tunneling barrier-height with increasing distance. At more negative potentials (< -0.9 V vs Pt) strong variations of the tunneling barrier-heights were observed. These variations of the tunneling barrier-heights can be correlated to the local electron density, indicating the formation of up to 3 layers, consisting of alternating cation and anion enriched layers.

O 121.9 Fri 12:45 TRE Phy

Bulk ion conductivity and near surface composition of Ionic Liquid and Zwitterion Ionic Liquid based electrolyte for lithium battery applications — ●FABIAN ULLMANN, ANNA DIMITROVA, and STEFAN KRISCHOK — Institut für Physik & IMN Macro-Nano, Technische Universität Ilmenau, Germany

In this contribution we focus on the bulk conductivity and the near surface composition of several tertiary electrolytes, which consist of Ionic Liquid (IL), Zwitterion Ionic Liquid (ZwIL) and a Li salt. Two ILs and ZwIL are chosen: IL: 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide - [EMIm][Tf2N] and 1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl)imide - [Py1,4][Tf2N]; ZwIL: 3-(3-methylimidazolium-1-yl)Propane-1-sulfonate and 3-(3-vinylimidazolium-1-yl)Propane-1-sulfonate. As lithium precursor - bis(trifluoromethylsulfonyl)imide - Li[Tf2N] was

used. Different Li[Tf2N]/ZwIL ratios are considered and studied. Electrochemical Impedance Spectroscopy (EIS) enables us to determine the ion conductivity of the electrolyte. The results reveal that the presence of ZwILs enhances the ion conductivity, although they itself are not ion conductive. Further, by using X-Ray Photoelectron Spectroscopy (XPS) we analyze the near surface chemical composition at UHV-conditions. The XPS analysis displays a cation/anion/ZwIL distribution as depended on the concentration of Na[Tf2N] and the type of IL and ZwIL used. The spectroscopic results revealed solute-solvent interactions which modify the ion mobility.

O 121.10 Fri 13:00 TRE Phy

Bulk ion conductivity and near surface composition of Ionic Liquid and Zwitterion Ionic Liquid based electrolyte for sodium battery applications — ●THIMO BRENDL, ANNA DIMITROVA, and STEFAN KRISCHOK — Institut für Physik & IMN Macro-Nano, Technische Universität Ilmenau, Germany

With this contribution we discuss the bulk ion conductivity, as well as the near surface chemical composition of ternary electrolytes containing Ionic Liquid (IL), sodium salt and Zwitterion Ionic Liquids (ZwIL). Two ILs and ZwIL are chosen: IL: 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide - [EMIm][Tf2N] and 1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl)imide - [Py1,4][Tf2N]; ZwIL: 3-(3-methylimidazolium-1-yl)Propane-1-sulfonate and 3-(3-vinylimidazolium-1-yl)Propane-1-sulfonate. As sodium precursor - bis(trifluoromethylsulfonyl) imide ([Na][Tf2N]) was used. Different Na[Tf2N]/ZwIL ratios are considered and studied. By using Electrochemical Impedance Spectroscopy (EIS) and X-Ray Photoelectron Spectroscopy (XPS) we were able to measure the ion conductivity of the electrolytes in the temperature range 263K-323K and to determine the near surface chemical composition at UHV-conditions. The EIS results reveal that the presence of ZwILs enhances the ion conductivity, although they itself are not ion conductive. This implies to an ion decoupling in the other two electrolyte components. The XPS analysis displays a cation/anion/ZwIL (cation: [Py1,4]⁺, [EMIm]⁺, Na⁺; anion: [Tf2N]⁻) distribution as depended on both: the concentration of Na[Tf2N] and the type of IL and ZwIL used.

O 121.11 Fri 13:15 TRE Phy

Temperature-dependent sticking coefficient measurements of hydrocarbons on ionic liquid surfaces using molecular beam techniques — ●LEONHARD WINTER, RADHA G. BHUIN, MATTHIAS LEXOW, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Ionic Liquids (ILs) are a class of compounds consisting only of cations and anions, which are usually liquid already below room temperature. Besides numerous other applications, IL thin films are the key components in the catalytic concepts Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). These catalysts show improved behavior e.g. in hydrogenation and hydroformylation reactions. In these processes, the phase transfer of hydrocarbons through the ionic liquid/gas interface plays a crucial role.

We have built a new ultra-high vacuum apparatus dedicated for the investigations of ILs with molecular beam techniques. It was used to study the interaction of *n*-butane with alkyylimidazolium ionic liquids with varying chain length ([C_nC₁Im][Tf₂N]). Based on the temperature-dependent behavior of the initial sticking coefficient at low temperatures, measured by the direct method of King and Wells, we discuss the adsorption dynamics on the different surfaces and their correlation with the molecular structure of the ILs.

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