

O 72: Solid-Liquid Interfaces: Reactions and Electrochemistry

Time: Wednesday 18:15–20:30

Location: Poster A

O 72.1 Wed 18:15 Poster A

Measurement of surface diffusion at solid-liquid interfaces using in situ linear optical diffraction — ●LASSE KATTWINKEL, CHRISTOPH LEMKE, and OLAF MAGNUSSEN — Insitut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel

Surface diffusion at solids in liquid environment is a fundamental process in many interface reactions, but much less understood than surface diffusion under vacuum conditions. We develop a novel method to measure the surface diffusion rates in such systems using optical diffraction. In this method a density grating in an adsorbate layer is created by thermal desorption induced by the two interfering beams of a nanosecond Nd:YAG laser. The evolution of the grating is then probed by linear optical diffraction of a HeNe laser beam at the grating. From the exponential decrease of the diffraction intensity the surface diffusion coefficient can be extracted. We describe the setup for this novel in situ technique and first experimental results.

O 72.2 Wed 18:15 Poster A

Laterally varying electrochemical deposition of solid copper on magnetically patterned exchange bias templates — ●IRIS KOCH¹, FLORIAN AHREND¹, TIMO UELTZHÖFFER¹, SVETLANA IVANOVNA SHEVTSOVA², PHILIPP MARTIN REINTANZ¹, ULRICH SIEMELING¹, and ARNO EHRESMANN¹ — ¹Institute of Physics and Center for Interdisciplinary Nanostructure Science and Technology (CINaT), University of Kassel, Heinrich-Plett-Str. 40, D-34132 Kassel — ²Research Institute of Physics, Southern Federal University, Stachki Ave. 194, RUS-344090 Rostov-on-Don

The inhomogeneous magnetic field landscape above magnetically patterned exchange bias (EB) systems [1] was utilized to influence the electrochemical reaction between a copper sulfate solution and a tantalum layer in a laterally anisotropic way. Thus, a local change of the copper deposition rate due to the specially designed magnetic stray fields acting on the paramagnetic Cu²⁺ ions is initiated. For process optimization, parameters like ion concentration, deposition time, and tantalum layer thickness were varied and analyzed by optical microscopy and energy dispersive x-ray spectroscopy. In all of the performed experiments, a significant influence of the EB system's magnetic pattern and, therefore, surface properties on the electrochemical reaction could be observed. This novel concept appears to be a promising method for the controlled growth of metallic nanowires.

[1] F. Ahrend et al., J. Magn. Magn. Mater. 381, 292 (2015)

O 72.3 Wed 18:15 Poster A

Achieving selective electrocatalytic activity for CO₂ reduction using highly porous Cu black catalysts — ●ABHIJIT DUTTA, MOTIAR RAHAMAN, MIKLOS MOHOS, NICOLA CHRISTIAN LUDI, and PETER BROEKMANN — Department of Chemistry and Biochemistry, University of Bern Freiestrasse 3 CH 3012 Bern Switzerland

The selective electroreduction of carbon dioxide to ethane and carbon monoxide on porous Cu-black catalysts has been investigated at various electrochemical potentials in aqueous 0.5 M NaHCO₃ solution. The evolution of hydrogen gas at an electrode surface plays a significant role to form this novel porous architecture during the electrodeposition of copper, particularly when a high current density is maintained. The hydrogen gas evolution inhibits electrodeposition of copper directly onto the cathode by temporarily preventing contact between the copper cathode and the electrolyte. Ultimately, a thin film of electrolyte surrounding hydrogen bubble comes into contact with the cathode, which completes the EC circuit and permits for electrodeposition of copper black. This porous morphology remains alike even after 1 h electrolysis at -1.0 V vs RHE. The Cu black catalyst exhibited the best selectivity for CO and ethane at -0.50V and -0.70V vs RHE with faradaic efficiencies of 40% and 37% respectively. Furthermore, the total FE of these two products is almost 75 to 80% at moderately cathodic potential range. Understanding the structural morphology of Cu black and the selectivity of products distribution could be valuable for the further development of advanced electro-catalytic materials for carbon di-oxide reduction.

O 72.4 Wed 18:15 Poster A

Sustainable sarcosine inhibitors for corrosion reduction

on DC01 steel — ●SAAD KASKAH¹, PAULO FERREIRA², GITTA EHREHAFT², JÖRG GOLLNICK², and CHRISTIAN B. FISCHER¹ — ¹Department of Physics, University Koblenz-Landau, 56070 Koblenz, Germany — ²Institute of mechanics and material science, TH Mittelhessen University of Applied Sciences, 35390 Giessen, Germany

Sustainable corrosion inhibitors are considered for good efficiencies without any environmental limitations in steel protection. In this work four N-acyl sarcosine derivatives are investigated via direct surface adsorption on cold rolled steel DC01 as potential corrosion inhibitors. Potentiodynamic polarization measurements were conducted in an aqueous solution buffered with potassium phosphate. Furthermore, for a realistic test a spray corrosion chamber with fresh water was used in long term. The short-term electrochemical tests were performed for one hour and the spray corrosion chamber for 24 hours. For the chamber test, each metallic sample was digitalized with a scanner at specific times and the corrosion process evaluated by corroded area. The results showed an improved corrosion reduction for the tested inhibitors on DC01 steel. Their efficiencies show a direct correlation according to their molecular weight. The worst inhibitor is the natural mixture of coconut derived sarcosines with 20 % efficiency. The best one with the highest molecular weight and longest carbon chain is Oleylsarcosine with 96 % efficiency.

O 72.5 Wed 18:15 Poster A

In situ Surface X-ray Diffraction Study of Ultrathin Epitaxial Co Films on Au(111)/H-Si(111) in Transmission Geometry — ●JONATHAN LAUFER¹, FINN REIKOWSKI¹, TIM WIEGMAN¹, FOUAD MAROUN², PHILIPPE ALLONGUE², JAKUB DRNEC³, JOCHIM STETTNER¹, and OLAF M. MAGNUSSEN¹ — ¹IEAP, CAU Kiel, Germany — ²Ecole Polytechnique, CNRS, Palaiseau, France — ³ESRF, Grenoble, France

Grating incidence diffraction in reflection geometry belongs to the standard repertoire for the in situ characterization of single crystal surfaces and adsorbate structures. Although being commonly used for measurements of crystal truncation rods, mapping in-plane structures proves to be tedious with this method. Here we present surface diffraction studies in transmission geometry, in which a large portion of the in-plane structure can be seen on a single detector frame. To flatten the curvature of the Ewald sphere, high energies in the range 25 keV to 70 keV were used. This means that the out-of-plane wavevector transfer changes only slightly over the range of reciprocal space covered by the detector. Furthermore, the high energies result in low absorption which is necessary since the beam has to travel through the entire sample in this configuration. Using this novel approach, we investigated samples consisting of 30 monolayers Au(111) deposited on H-Si(111) with a thickness of 600 μm. 10 - 20 monolayers of Co were electrochemically deposited on these substrates and analyzed by surface sensitive in situ transmission X-ray scattering. With this method the Co deposition and dissolution could be monitored under reaction conditions.

O 72.6 Wed 18:15 Poster A

Trends in catalytic activity of Ni-based electrodes for the hydrogen evolution reaction — ●HANNAH SCHLOTT¹, MARC LEDENDECKER², MENNY SHALOM², MARKUS ANTONIETTI², and BERND MEYER¹ — ¹Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg — ²Max-Planck-Institute of Colloids and Interfaces, Potsdam

Using density-functional theory (DFT) we investigated the hydrogen adsorption on (0001) surface terminations of different Ni-based compounds, which are promising new electrode materials for the hydrogen evolution reaction (HER). While pure Ni is known to be not a good electrode material for the HER since it binds hydrogen too strongly [1,2], electrochemical experiments indicate an improved performance for the binary compounds Ni₃N, Ni₃S₂ and Ni₅P₄. In our DFT calculations we find decreased hydrogen adsorption energies for the Ni compounds, placing them closer to the activity maximum in a volcano plot relation than pure Ni [1,2]. However, experiment and theory suggest a different order of the performance for the investigated compounds. Reasons for this discrepancy will be discussed and consequences of these findings will be presented.

[1] J.K. Nørkov, T. Bligaard, A. Logadottir, J.R. Kitchin, J.G. Chen,

S. Pandelov, U. Stimming, J. Electrochem. Soc. **152**, J23 (2005).
 [2] P. Quaino, F. Juarez, E. Santos, W. Schmickler, Beilstein J. Nanotechnol. **5**, 846, (2014).

O 72.7 Wed 18:15 Poster A

Cu surface reactions in hydrochloric solution probed on the atomic scale by polarization optical methods and STM — ●CHRISTOPH COBET, GHOLAMREZA BARATI, VLADYSLAV SOLOKHA, and KURT HINGERL — Center for Surface- and Nanoanalytics (ZONA), Johannes Kepler Universität, Altenbergerstr 69, A-4040, Linz, Austria
 Electrochemical reactions on metal electrodes have been in the focus of many scientific studies and Cu is probably the most investigated example. The interest on Cu is motivated by questions concerning e.g. corrosion, electro-polishing, and catalytic processes. It is evident that a fundamental understanding requires knowledge about the microscopic occurrence of the surface in electrolyte. But unfortunately, most of the classical surface sensitive techniques as used in UHV cannot be applied in liquid environments and thus many details about surface structures are still under discussion. In the presented work we combine reflection anisotropy spectroscopy and a homemade electrochemical scanning tunneling microscope in order to study Cu(110) single crystals in hydrochloric solutions. With this approach we could monitor the local appearance as well as the dynamics of interface transformations/reactions on atomic scale. In particular it was possible to correlate anodic Faraday-current maxima with structural transformation. Accordingly, the Cl adsorption minimizes the surface energy by a formation of monoatomic steps parallel to the [001] direction which finally ends in a faceting of the surface. These surface modifications may influence also the rate of the known Cu dissolution at increasing anodic potentials.

O 72.8 Wed 18:15 Poster A

Directional Movement of Third Generation Light-Driven Molecular Motors on Surfaces — ●HENRIEKE HEIDEMAN¹, JOHAN VISSER¹, JOS KISTEMAKER¹, PETER STACKO¹, MEIKE STÖHR², and BEN FERINGA¹ — ¹Stratingh Institute for Chemistry, Groningen, The Netherlands — ²Zernike Institute for Advanced Materials, Groningen, The Netherlands

Third generation molecular motors are equipped with two rotor units, which can rotate unidirectionally when powered by light. Although the solution behavior of these molecules has recently been studied, integrating them into useful nanodevices represents a major challenge. One key requirement is that these molecular motors are functional under ambient conditions. Moreover, it is crucial to have the achiral unidirectional rotary motion of these molecular motors happening on surfaces in order to get out of the Brownian regime. In the present study, the behavior of third generation molecular motors on modified HOPG surfaces was studied with STM under ambient conditions.

O 72.9 Wed 18:15 Poster A

Towards understanding the mechanism of water splitting on TiO₂ — ●SIMON J. SCHMITT, SAMAN HOSSEINPOUR, and ELLEN H.G. BACKUS — Max-Planck-Institute for Polymer Research, Ackermannweg 10, Mainz, Germany

Finding a clean and renewable energy source to replace fossil fuels has attracted much attention, the past few decades, as a requirement for the sustainable development of societies. Direct hydrogen generation on TiO₂ by photocatalytic dissociation of water using sunlight was already proposed more than 40 years ago. However, despite extensive work in this area, the fundamentals of the process remain ill-understood, mainly due to the lack of a proper tool to specifically explore the interface between water and TiO₂. Sum frequency generation spectroscopy (SFG), is an inherently surface sensitive tool, allowing the study of specifically the water molecules at the TiO₂ surface. We present data on water in contact with TiO₂ thin films at various pH values and isotopic dilution and correlate the spectral observations with surface species. Moreover, we show first UV-pump-SFG-probe data, illustrating the first steps towards following the photo-induced dissociation of water at the TiO₂ interface in real-time.

O 72.10 Wed 18:15 Poster A

Experimental Approach for Determining Semiconductor/Liquid Junction Energetics by Operando Ambient-Pressure X-ray Photoelectron Spectroscopy — ●MATTHIAS H. RICHTER^{1,2,7}, MICHAEL F. LICHTERMAN^{1,2}, SHU HU^{1,2}, ETHAN J. CRUMLIN³, STEPHANUS AXNANDA³, MARCO FAVARO^{3,4}, WALTER DRISDELL^{3,4}, ZAHID HUSSAIN³, BRUCE S. BRUNSCHWIG¹, ZHI LIU^{3,5,6}, NATHAN S. LEWIS^{1,2}, and HANS-JOACHIM LEWERENZ^{1,2} — ¹Caltech, Pasadena, USA. — ²JCAP, Pasadena, USA. — ³LBNL, Berkeley, USA. — ⁴JCAP, Berkeley, USA. — ⁵Chinese Academy of Sciences, China. — ⁶ShanghaiTech University, China. — ⁷BTU C-S, Cottbus, Germany.

The performance of a photoelectrochemical solar cell depends strongly on the electrochemical nature of the semiconductor/electrolyte junction [1]. Operando Ambient Pressure X-ray photoelectron spectroscopy investigation of semiconductor/liquid junctions provides quantitative understanding of the energy bands in these photoelectrochemical solar cells [2, 3, 4]. We demonstrate how OAP-XPS may be used to determine these relationships for semiconductor/liquid systems. The data can be analyzed to determine the energy relationship between the electronic energy bands in the semiconductor electrode and the redox levels in the solution. The major conditions for semiconductor-electrolyte contacts including accumulation, depletion, and Fermi-level pinning are observed, and the so-called flat-band energy can be determined. [1] Science 344 (2014) 1005; [2] Sci Rep 5 (2015) 9788; [3] Ener & Env Sci 8 (2015) 2409; [4] J Electrochem Soc 162 (2016) H1