

O 20: Poster Monday: Solid-Liquid Interfaces

Time: Monday 18:00–20:00

Location: P4

O 20.1 Mon 18:00 P4

Pd nanoparticles supported on ordered Co₃O₄(111): Particle size effects in electrochemical environment — ●MAXIMILIAN KASTENMEIER¹, XIN DENG¹, TOMÁŠ SKÁLA², NATALIYA TSUD², LUKÁŠ FUSEK^{1,2}, VIKTOR JOHÁNEK², JOSEF MYSLIVEČEK², YAROSLAVA LYKHACH¹, OLAF BRUMMEL¹, and JÖRG LIBUDA¹ — ¹FAU Erlangen-Nürnberg, Erlangen, Germany — ²Charles University, Prague, Czech Republic

Pd nanoparticles (NPs) are efficient electrocatalysts for oxidation of ethanol in alkaline direct ethanol fuel cells. We investigated the morphology and the oxidation state of Pd NPs supported on well-ordered Co₃O₄(111) films as a function of the particle size after treatment in ultrahigh vacuum and in alkaline electrolyte under potential control. We combined synchrotron radiation photoelectron spectroscopy and scanning tunneling microscopy. Electronic metal support interaction associated with the charge transfer at the Pd/Co₃O₄(111) interface yield partially oxidized ultra-small Pd^{δ+} aggregates and Pd²⁺ species at Pd coverages below 0.1 ML followed by the growth of two-dimensional metallic Pd⁰ NPs at higher coverages. The stabilities of ultra-small and conventionally-sized NPs supported on Co₃O₄(111) and HOPG were compared following an emersion from alkaline electrolyte at potentials between 0.5 and 1.5 VRHE. We observed different oxidation behavior related to two-dimensional and three-dimensional morphologies of supported Pd NPs on Co₃O₄(111) and HOPG, respectively. In sharp contrast, the oxidation state of the ultra-small Pd deposits remains unchanged between 0.5 and 1.5 VRHE.

O 20.2 Mon 18:00 P4

Film growth and stability of the ionic liquid [C₁C₁Im][Tf₂N] on Cu(111) — ●TIMO TALWAR, STEPHEN MASSICOT, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie 2, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Ionic liquids (ILs) are salts with melting points below 100°C and extremely low vapor pressure. These properties made them promising candidates for various new catalytic concepts like solid catalysis with Ionic Liquid Layer (SCILL). In this context, the interplay of ILs with metal surfaces is highly important.

In this study, the growth and thermal behavior of ultrathin films of 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide [C₁C₁Im][Tf₂N] on Cu(111) are investigated under UHV conditions. The films are prepared in vacuum by physical vapor deposition and measured by angle-resolved and temperature-programmed X-ray photoelectron spectroscopy. Different film thicknesses are investigated to identify the underlying growth model, which is 2D growth up to 0.3 ML and 3D growth for higher coverages. Note that 1 ML corresponds to a bilayer of cations and anions irrespective of their arrangement. These films are stable up to 300 K. However above 300 K, the anion partly decomposes, and above 500 K, the remaining IL desorbs leaving a decomposed residual on the surface.

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O 20.3 Mon 18:00 P4

Influence of water in the electrolyte on the electrochromic characteristics of WO₃ — ●SOPHIE GÖBEL, THI HAI QUYEN NGUYEN, and DERCK SCHLETTWEIN — Justus-Liebig-Universität Gießen, Institut für Angewandte Physik

In view of global warming, the reduction of CO₂ emissions in the energy sector, e.g. in private households is urgent. In this case, especially heat flow through windows has a main impact. With the help of so-called smart windows, the irradiation of sunlight can be controlled to decrease the energy consumption by air conditioning or heating systems. A possible approach to such switching is provided by electrochromic layers. One of the best observed materials for such smart windows is tungsten oxide WO₃. In this work, porous WO₃ films were prepared via a sol-gel process and spin-coating on fluorine-doped tin oxide (FTO). In order to achieve the porous structure, polymers (PEG400 and PIB₅₀ - b - PEO₄₅) were added as additives in the precursor solution. To enhance the electrochromic characteristics of the WO₃ films in contact to an electrolyte consisting of LiClO₄ in propylene carbonate, addition of water into the electrolyte was stud-

ied. The amount of added water was varied while the influence on the electrochemical and spectral properties was monitored by cyclic voltammetry and UV/Vis spectroscopy.

O 20.4 Mon 18:00 P4

In situ surface X-ray diffraction studies of Pt(110) — ●JAN OLE FEHR¹, TIMO FUCHS¹, JAKUB DRNEC², MARTA MIROLO², SERHIY CHEREVKO³, VALENTIN BRIEGA³, DAVID HARRINGTON⁴, CHENTIAN YUAN⁴, and OLAF MAGNUSSEN¹ — ¹Christian-Albrechts Universität zu Kiel, Germany — ²European Synchrotron Radiation Facility, Grenoble, France — ³Helmholtz Institute Erlangen-Nürnberg for Renewable Energy, Germany — ⁴University of Victoria, Canada

The surface oxidation of platinum is an important process in the degradation of platinum electrocatalysts in PEM fuel cells. Previously, the oxidation of the (111) and (100) surfaces of platinum was investigated by Fuchs et al. to understand the underlying mechanisms and growth of the oxide structures. In this work the (110) surface was studied by similar in situ high energy surface X-ray diffraction (HESXRD) at the ID31 beamline of the European Synchrotron Radiation Facility. Unreconstructed as well as (1x2)-reconstructed Pt(110) surfaces were prepared and their restructuring upon oxidation was examined. Distinct differences in this restructuring of the unreconstructed and the (1x2)-reconstructed surface were found. The changes in occupancy of the topmost surface layers after one oxidation/reduction cycle are greater for the unreconstructed surface than for the reconstructed surface, suggesting that the latter is more stable upon oxidation. In accordance with this result, it was also found that the missing row reconstruction of the surface was only lifted during the reduction of the surface oxide.

O 20.5 Mon 18:00 P4

Increase of the Spectroelectrochemical Performance of WO₃ Films by Using Additives During Film Growth — ●THI HAI QUYEN NGUYEN¹, FLORIAN EBERHEIM¹, SOPHIE GÖBEL¹, PASCAL COP², MARIUS ECKERT¹, TIM P. SCHNEIDER¹, LUKAS GÜMBEL¹, BERND M. SMARSLY², and DERCK SCHLETTWEIN¹ — ¹Justus-Liebig-Universität Gießen, Institut für Angewandte Physik — ²Justus-Liebig-Universität Gießen, Physikalisch-Chemisches Institut

Tungsten oxide (WO₃) is commonly used as an electrochromic material in smart windows. The electrochromic performance of WO₃ is highly influenced by the mixed electronic and ionic transport in the film and, thus, by the accessibility of the internal film volume. In this work, WO₃ thin films were prepared by spin-coating from a precursor solution based on peroxotungstic acid and different polymer additives such as polyethylene glycol (PEG), a block copolymer (PIB₅₀ - b - PEO₄₅) and a combination thereof. The influence of the additives on the porosity and composition of WO₃ was studied by, e.g., scanning electron microscopy, X-ray photoelectron spectroscopy and atomic emission spectroscopy. Electrochromic characteristics of the films were measured with LiClO₄ in propylene carbonate as electrolyte. The intercalation of Li⁺ ions was analyzed by time-of-flight secondary ion mass spectrometry. The use of PEG provided microporous films leading to improved effective diffusion coefficients, transmittance modulations and response times compared to compact WO₃. Further improved characteristics were obtained for films with interconnected mesopores prepared with PEG and PIB₅₀ - b - PEO₄₅.

O 20.6 Mon 18:00 P4

Visualizing electrochemical interfaces with combined AFM/STM — ●ANDREA AUER, BERNHARD EDER, and FRANZ GIESSIBL — Institute of Experimental and Applied Physics, University of Regensburg, Germany

Atomic force microscopy (AFM) that can be simultaneously performed with scanning tunneling microscopy (STM) modes using metallic tips attached to self-sensing quartz cantilevers (qPlus sensors) has advanced the field of surface science by allowing for unprecedented high spatial resolution under ultrahigh vacuum conditions. Applying a qPlus sensor-based AFM/STM setup to electrochemistry could offer new and groundbreaking possibilities to locally image both the 3D layering of the interfacial water and the lateral structure of the electrochemical double layer. In this work, a home-built AFM/STM instrument equipped with a qPlus sensor for operation under precise potential control in an electrochemical liquid cell is presented. Special care is taken

in the preparation of etched Pt/Ir tips, which are attached to the qPlus sensor and subsequently coated with insulating wax to allow for both AFM and STM measurements in the electrolyte with minimal leak currents. Ongoing work includes investigations of the potential-dependent structural interface organization of the electrochemical double layer on both highly oriented pyrolytic graphite (HOPG) and Au(111) electrodes in acidic media by means of (simultaneous) AFM/STM imaging and force spectroscopy.

O 20.7 Mon 18:00 P4

Phase-shifting electron holography in an environmental TEM — ●ULRICH ROSS¹, JONAS LINDNER², TOBIAS MEYER², MICHAEL SEIBT¹, and CHRISTIAN JOOSS² — ¹IV. Physik Georg-August Universität Göttingen — ²IMP Georg-August Universität Göttingen

Off-axis electron holography is a phase reconstruction technique which enables access to the complex exit-wave of thin samples. Information on the phase and amplitude of the exit wave is useful in order to gain insight on nm-scale electromagnetic fields. In the field of catalyst research electrostatic surface fields are of particular interest, since the potential drop over the surface can be assumed to play a major role in the reaction mechanisms.

Conventional off-axis holography reconstruction operates via the Fourier domain. As a consequence, the accessible range of spatial frequencies is band-limited by the carrier frequency of the hologram. A trade-off is always necessary in order to optimize fringe frequency, visibility, phase-contrast transfer and instrument stability for a certain range of spatial frequencies. In contrast, we demonstrate the implementation of phase-shifting holography at sub-nm resolution combined with an advanced drift correction scheme, and successfully match the results to multislice image simulations as well as conventional defocus series. The method is added to the in-situ capabilities of a third-order aberration-corrected environmental TEM in order to investigate surface effects in catalytic platinum samples under low pressures of oxygen and water.

O 20.8 Mon 18:00 P4

Self-organized structures of peri-arylenes on electrode surfaces — ●KRISTIN GRATZFELD¹, ANNA KNY¹, TOMASZ KOSMALA², RADOSŁAW WASIELEWSKI², MAREK NOWICKI², KLAUS WANDELT^{1,2}, and MORITZ SOKOŁOWSKI² — ¹Institut für Physikalische und Theoretische Chemie der Universität Bonn — ²Institute of Experimental Physics, University of Wrocław, Poland

We investigated self-ordered structures of 3,4,9,10-perylene-tetracarboxylic acid (PTCA) on the Au(111) electrode interface. In recent electrochemical studies, the protonation/ deprotonation process of PTCA was studied, however no structural data information was reported, yet [1]. To investigate the structures of PTCA at the Au(111) electrode interface we used cyclic voltammetry (CV) and electrochemical STM (EC-STM). For negatively charged surfaces, we observed stripe like phases of PTCA with an edge-on orientation of the molecules that transform into a less dense phase at more positive potential with flat-lying molecules. We suppose that this transition is correlated with a partial deprotonation of the PTCA. Acknowledgement: This work was supported by the DFG through the research training group 2591, the DAAD (Deutscher Akademischer Austauschdienst) program Ostpartnerschaften and the NAWA (National Agency for Academic Exchange) program. We thank H. Baltruschat for helpful discussions and experimental support. [1] J. Am. Chem. Soc., 138, 1493, 2016.

O 20.9 Mon 18:00 P4

DFT study of the interaction of Br and S adsorbates on the Ag(100) surface — ●SÖNKE BUTTENSCHÖN and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

Adsorbate-adsorbate interactions on metal surfaces affect the adsorp-

tion and diffusion on surfaces and, in case of self-diffusion, the growth of surfaces. As a model system, the diffusion of S adatoms on halogen-covered Cu and Ag electrodes at electrochemical interfaces has been studied by O. Magnussen and his group [1]. Prerequisite for a theoretical analysis is an accurate quantitative description of the adsorbate-adsorbate interactions of the species involved. To this end we have carried through density-functional total-energy calculations of the Br-Br and S-Br interaction on Ag(100) using the codes PWscf and PWneb from the Quantum ESPRESSO package [2]. We observe that additional contributions to the interaction energy beyond the dipole-dipole interaction [3] need to be included, which are due to electronic and elastic mechanisms [4].

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O 20.10 Mon 18:00 P4

The optical spectroscopy of InP(100) in contact with hydrochloric acid: A first-principles study — ●JONGMIN KIM^{1,2}, MARGOT GUIDAT^{1,2}, MARIO LÖW¹, and MATTHIAS M. MAY^{1,2} — ¹Institute of Physical and Theoretical Chemistry, Universität Tübingen, D-72076 Tübingen, Germany — ²Institute of Theoretical Chemistry, Universität Ulm, Ulm, Germany

The III–V semiconductors, such as indium phosphide (InP), show highest solar energy conversion efficiencies, and are commonly used for a variety of applications, particularly high-performance opto-electronic devices. However, these semiconductors face fundamental challenges since they tend to corrode in aqueous electrolytes [1]. A passivation layer on their surface is the most efficient way to address this drawback. Studies have demonstrated that a system of the InP(100) in contact with hydrochloric acid exhibits high conversion efficiencies and reasonable stability. In this computational work, we investigate the interaction of InP(100) with hydrochloric acid by means of computational optical spectroscopy. Theoretically derived reflection anisotropy spectroscopy (RAS) is employed for the optical spectroscopy. According to our calculations, the RA spectra are significantly changed with probable surface geometries. A comparison of our results with experiment spectra reveals that the fully Cl-covered structure is the most reasonable surface. This verified structure can be used as a starting structure for further investigations of the InP(100)-electrolyte interface.

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O 20.11 Mon 18:00 P4

Imaging and Illumination of Self-Assembled Molecules at Solid and Liquid Interfaces — ●BENSU GÜNAY, ●SHILPA PANCHAMI RAJ, CHRISTOPHE NACCI, and LEONHARD GRILL — University of Graz

Nanotechnological approaches for photochemical on-surface synthesis of covalently-bonded nanostructures have received recent attention at solid/air and solid/liquid interfaces. At the solid/liquid interface, there is in principle always a dynamic equilibrium between the molecules adsorbed on the surface and those still dissolved in the supernatant solution. Additionally, on-surface photochemical activation of chemical reactions provides new reaction pathways and enables the formation of long-range ordered covalent structures. The scanning tunneling microscope (STM) is a powerful tool for observing such structures at surfaces. In this study we present STM measurements under ambient pressure and at room temperature at the solid/liquid interface. In a first step for investigating photoactivated polymerisation under such conditions, 2,5-didodecyl-1,4-di-1-propenyl benzene was introduced onto a highly oriented pyrolytic graphite (HOPG) surface. We report on the self-assembled structures as well as attempts for photochemical activation using various wavelengths at room temperature.