

O 67: Poster Wednesday: Solid-Liquid Interfaces

Time: Wednesday 17:45–20:00

Location: Poster B2

O 67.1 Wed 17:45 Poster B2

Structure of electric double layer at the graphene/ionic liquid interface probed by X-ray photoelectron spectroscopy —

•SUNGHWAN SHIN¹, FRANCESCO GRECO¹, ELMAR KATAEV¹, OLESYA KAPITANOVA², FLORIAN MAIER¹, and HANS-PETER STEINRÜCK¹ — ¹Friedrich-Alexander University Erlangen-Nürnberg, 91058, Erlangen, Germany — ²Lomonosov Moscow State University, Leninskie gory, 119991 Moscow, Russia

Ionic liquids (ILs) electrochemical interfaces find applications in fuel cells, supercapacitors, and dye-sensitized solar cells. However, in situ analysis of these interfaces is difficult because of their inaccessibility to the surface science tools. Here, we report a photoemission study of electric double layer (EDL) formation on the graphene/IL electrolyte (1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) using a two-electrode electrochemical cell with graphene-covered porous silicon nitride membrane as a working electrode and a platinum wire as a counter electrode.

Cathodic and anodic polarization of graphene electrode up to 2V resulted in an asymmetric broadening of the peak in F 1s photoemission spectrum towards lower or higher binding energies correspondingly. For explaining this data, we developed a model consisting of EDL at the graphene/IL interface and a confined layer of IL situated between the graphene layer and the silicon nitride support and assign these shifts to the voltage drop at the working electrode.

Supported by the European Research Council (ERC) through an Advanced Investigator Grant to HPS (No. 693398*ILID).

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Asymmetric Potential Screening at Electrode/Ionic Liquid Interfaces —

•SUNGHWAN SHIN, FRANCESCO GRECO, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie 2, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

Ionic liquids (ILs) have received considerable attention as unique candidates to perform electrochemistry due to their larger electrochemical windows and high ion densities. To understand and control an electrochemical reaction in ILs, it is essential to understand the interface between ILs and metal electrodes playing a crucial role in capacitance charging and redox reactions. For ILs, potential screening (PS) at the anode and cathode interface can be dramatically different due to the asymmetric shape of the IL ions and their specific interactions with the charged electrodes. We studied PS effects by use of X-ray photoelectron spectroscopy (XPS) with an in situ two-electrode-cell. The amount of PS at the anode/cathode was determined using XPS binding energy shifts of the IL signals. In the case of symmetric Pt-Pt electrodes, the potential screening at the cathode was smaller than that at the anode for imidazolium-based ILs, which indicates a specific adsorption of imidazolium on platinum. For the Au-Au-setup, weak specific adsorption of imidazolium on gold leads to different PS effects that are related to the size of ions. Supported by the European Research Council (ERC) through an Advanced Investigator Grant to HPS (No. 693398*ILID)

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First Principles Modeling of the Hydrogen Evolution Reaction in Mg Corrosion —

•TIM WÜRGER^{1,2}, MIKHAIL ZHELUDKEVICH¹, and ROBERT HORST MEISSNER^{1,2} — ¹Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research GmbH, Institute of Materials Research, Geesthacht, Germany — ²Hamburg University of Technology, Institute of Polymer and Composites, Hamburg, Germany

Magnesium is a material with a high potential for a variety of applications in areas such as transport, energy and medicine. However, the corrosion properties of magnesium restrict its practical application and are still not fully understood. One unresolved phenomenon is the anodic hydrogen evolution, also called negative difference effect. High corrosion rates and corresponding hydrogen evolution are observed under anodic polarization, whereas fundamental corrosion concepts indicate hydrogen evolution to occur at the cathodic site. Iron replating is proposed to be a possible reason for the observed negative difference effect. In the corrosion process, embedded iron impurities are set free and replate on the magnesium surface where they promote

the hydrogen evolution. As there is still no consensus about the preferred reaction site and mechanism of the hydrogen evolution, further investigations on an atomistic level in Mg as well as Fe systems are supposed to bring clarity. Obtaining further knowledge about the reaction energetics is crucial to find the favored hydrogen evolution site and mechanism, leading to a deeper understanding of magnesium corrosion and thus opening up new perspectives in magnesium corrosion engineering.

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Study on femtosecond laser surface alloys for an improved catalytic activity —

•LUISE F. HOFFMANN¹, VIKTOR HOFFMANN¹, MATTHIAS KOJ², ANDREAS GABLER¹, MIA BÖRNER³, ANDERS NILSSON³, THOMAS TUREK², WOLFGANG SCHADE^{1,4}, and THOMAS GIMPEL¹ — ¹EST, Clausthal University of Technology, Goslar, Germany — ²ICVT, Clausthal University of Technology, Clausthal-Zellerfeld, Germany — ³Chemical Physics Division, Stockholm University, Sweden — ⁴Fraunhofer Heinrich Hertz Institute, Goslar, Germany

Femtosecond laser material processing is used to alloy the surface structure of many materials. Chemical compositions are achieved far beyond conventional, thermal or metallurgical methods. Foreign substances in the substrate matrix help to tailor important material properties, such as the catalytic activity, the wettability, the heat transfer and fluid transport mechanisms. This is beneficial in order to functionalise electro catalysts e.g. for the electrochemical CO₂ reduction reaction or the alkaline water electrolysis. However, the distribution of the additional elements is of main interest in order to evaluate the changed properties adequately. Therefore, energy dispersive x-ray spectroscopy as well as Auger electron spectroscopy is used to analyse the alloyed foreign substances in the structured substrate surface. We present studies on sulphur incorporated into copper and iron incorporated into nickel substrates. The composition is determined via cross-section images in spatial and depth resolution. This allows an extended understanding of the femtosecond laser material interaction.

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Femtosecond laser iron incorporation of nickel electrodes for the alkaline water electrolysis —

•VIKTOR HOFFMANN¹, LUISE F. HOFFMANN¹, MATTHIAS KOJ², THOMAS TUREK², WOLFGANG SCHADE^{1,3}, and THOMAS GIMPEL¹ — ¹EST, Clausthal University of Technology, Goslar, Germany — ²ICVT, Clausthal University of Technology, Clausthal-Zellerfeld, Germany — ³Fraunhofer Heinrich Hertz Institute, Goslar, Germany

The hydrogen production via alkaline water electrolysis is one of the key technologies for the energy transition. This technique will be used to store energy from fluctuating renewable sources. The chemical activity and microstructure are crucial factors determining the overpotential of an electrode within the electrolysis. Previous works show the enhanced efficiency of femtosecond laser structured electrodes in alkaline water electrolysis. In this work, iron is additionally incorporated into a nickel mesh electrode during the femtosecond laser treatment in order to improve the catalytic activity. Therefore, iron is provided from a liquid or a solid element source during the laser process. The influence of this treatment is analysed electrochemically. Furthermore, a scanning electron microscope with an energy dispersive x-ray spectroscope is used to characterise morphology and chemical composition of the electrode.

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X-Ray photoelectron spectroscopic study of the near surface composition of [TfO] and [Tf2N] based Ionic Liquids at different electrode surfaces —

ALEKSANDR BARANOV, •FABIAN ULLMANN, ANNA DIMITROVA, and STEFAN KRISCHOK — Institut für Physik und IMN MacroNano, Technische Universität Ilmenau, Deutschland

With this contribution we will discuss the electronic structure and the ion assembly of four Ionic Liquids (ILs): 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMim]TfO), 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([BMP]TfO), 1-ethyl-3-methylimidazolium-bis-(trifluoromethylsulfonyl) imide ([EMim][Tf2N]) and 1-butyl-1-methyl pyrrolidinium-bis-

(trifluoromethyl-sulfonyl)imide ([BMP][Tf2N]).

By using spin-coating technique and X-Ray Photoelectron spectroscopy we were able to prepare an IL*layers in *m and nm * range and to elucidate the chemical composition at the near surface and at the interface with three metal substrate: Ni, Ti and Au.

The results reveal that the cation/anion distribution depends on both: the IL used and the metal substrate. Moreover, a spectroscopic evidence demonstrate an existence of an anion*cation interaction, when TfO is present in the molecular structure.

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Impact of the Electrolyte Salt Anion on the Solid Electrolyte Interphase (SEI) Formation at the Hard Carbon Electrodes of Sodium Ion Batteries — GEBREKIDAN GEBRESILASSIE ESHETU^{1,2,3}, ●THOMAS DIEMANT⁴, MARAL HEKMATFAR^{1,2}, SYLVIE GRUGEON⁵, R. JÜRGEN BEHM^{1,4}, STÉPHANE LARUELLE⁵, MICHEL ARMAND³, and STEFANO PASSERINI^{1,2} — ¹Helmholtz Institute Ulm (HIU), Helmholtzstr. 11, D-89081 Ulm, Germany — ²Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany — ³CIC EnergiGUNE, Parque Tecnológico de Álava, Albert Einstein 48, E-01510 Miñano, Spain — ⁴Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany — ⁵Laboratoire de Réactivité et Chimie des Solides (LRCS) CNRS UMR 7314, Réseau Français sur le Stockage Electrochimique de l'Énergie (RS2E) FR CNRS 3459, F-80039 Amiens, France

Aiming at a more comprehensive understanding of the solid electrolyte interphase (SEI) in sodium ion batteries, we performed a detailed X-ray photoelectron spectroscopic (XPS) investigation of the few-nanometer thick passivation film formed on hard carbon (HC) in contact with various Na-ion conducting electrolytes (1M solutions of NaPF₆, NaClO₄, NaTFSI, NaFSI, or NaFTFSI in a 1/1 mixture of diethylcarbonate/ethylcarbonate). For comparison, analogous studies were carried out using LiPF₆ and LiFSI as electrolyte salt. Taken together, the anion and cation of the electrolyte salt appear to play a key role for the overall SEI layer composition, including its depth evolution and thickness.

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Electrolyte structure at Gallium Arsenide - KOH solution interfaces — ●ALRIK STEGMAIER and HANS HOFSSÄSS — 2. Physikalis-

ches Institut, Georg-August Universität Göttingen

The electrolyte-semiconductor interface is a very active area of research. While the electrolyte structure near ideal surfaces in weak electrolytes are reasonably well understood, non-ideal conditions, such as surface and near surface defects or strong electrolytes, are more difficult to understand. However, these conditions are important in many applications.

Here we present our latest results in modeling KOH solution structure near GaAs <100> surfaces with defects using molecular dynamics. For this we parameterize a polarizable force field against experimental, DFT, MP2 and CCSD(T) data. The electrolyte structure at different KOH concentrations and applied voltages is reconstructed. These results are compared against experimental data (such as impedance spectra) and continuum models.

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Polarimetric angle-resolved second harmonic scattering on colloidal TiO₂ nanoparticles in aqueous environments — ●MARIE BISCHOFF, ARIANNA MARCHIORO, and SYLVIE ROKE — Laboratory for fundamental BioPhotonics (LBP), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne

Titanium dioxide TiO₂ is a semiconductor material with a high physical and chemical stability. Therefore it is extensively studied for the use in environmental and energy applications, such as for example photocatalytic water splitting. Despite its highly promising characteristics, the underlying performance of TiO₂ is still limited. In order to enhance surface-mediated processes and photochemical reactions, it is crucial to understand the microscopic structure of the TiO₂/electrolyte interface.

Nonlinear optical techniques are powerful tools to study processes at surfaces and interfaces as they are sensitive to surface molecular orientation and interfacial electric fields. In this work we investigate TiO₂ nanoparticles in aqueous environments with nonlinear optical techniques, more specifically polarimetric angle-resolved second harmonic scattering (AR-SHS). We apply AR-SHS in order to extract information on the TiO₂/electrolyte interface and determine parameters such as surface potential and surface molecular orientation, which are difficult to obtain by other techniques.