

O 45: Nonaqueous Liquid/Solid Interfaces

Time: Wednesday 11:30–13:00

Location: HE 101

O 45.1 Wed 11:30 HE 101

Formation of double layers in ionic cells and their relevance for cell voltage and charge transfer — ●RENÉ HAUSBRAND — Darmstadt University of Technology, Materials Science Department, Darmstadt, Germany

Double layers at electrode-electrolyte interfaces in ionic devices determine charge transfer kinetics and cell voltage. Lately, interest to understand the double layer formation of Li-ion electrode - electrolyte interfaces has increased due to the future use of Li-ion cells for energy storage. Under equilibrium conditions, the electric potential gradient at an ion electrode - electrolyte interface is determined by the difference of ion chemical potential between electrode and electrolyte, contributing to the electrode potential. For ion transfer, the formation of diffuse double layers (space charge layers) is relevant. This contribution focuses on the impact of the interfacial electrical potential gradients on cell voltage using the example of an all-solid Li-ion cell. First, the fundamentals regarding the origin of cell voltage are briefly introduced. Then, results of surface science investigations on thin film LiCoO₂ electrodes and LiPON solid state electrolytes are presented, and evaluated to yield the energy level diagram of the LiCoO₂|LiPON|Li cell. The results demonstrate the formation of space charge layers and indicate that the ionic contribution to the cell voltage remains low.

O 45.2 Wed 11:45 HE 101

Complementary Theoretical and Experimental Study of Ionic Liquid-Solid Interfaces — ●ZLATKO BRKLJAČA¹, MICHAEL KLIMCZAK², ANDREAS MAGERL², DAVID M. SMITH^{3,4}, and ANA-SUNČANA SMITH^{1,3} — ¹Institut für Theoretische Physik, FAU Erlangen-Nürnberg, Erlangen, Germany — ²Crystallography and Structural Physics, FAU Erlangen-Nürnberg, Erlangen, Germany — ³Ruder Bošković Institute, Zagreb, Croatia — ⁴Computer Chemie Centrum, FAU Erlangen-Nürnberg, Erlangen, Germany

Understanding the molecular-level behavior of ionic liquids (ILs) at IL-solid interfaces is of fundamental importance with respect to their application in electrochemical systems and electronic devices. Using a model system consisting of an imidazolium-based IL ([C₂Mim][NTf₂]) in contact with sapphire substrate, we have approached this problem using complementary experimental and theoretical methodologies. We employed high-resolution X-ray reflectivity measurements, capable of probing buried IL-solid interfaces, and atomistic molecular dynamics (MD) simulations, which can be used to interpret experimental data in atomistic detail. Our strategy enabled us to compare experimental and theoretically calculated reflectivities in a direct manner, thereby critically assessing the applicability of force-field variants we implemented. In turn, using the best-matching MD description, we were able to describe the nature of the model IL-solid interface in appreciable detail, finding that the hydrogen bonding between the imidazolium rings and the surface hydroxyl groups has a dominant role in inducing a bilayering cation/anion profile close to the surface.

O 45.3 Wed 12:00 HE 101

Alternating Ion Monolayering in Alkylimidazolium Ionic Liquids at the Solid-Liquid Interface — ●MICHAEL KLIMCZAK¹, NICOLA TACCARDI², JOHANNES WILL¹, MATTHIAS WEISSER¹, PETER WASSERSCHIED² und ANDREAS MAGERL¹ — ¹Lehrstuhl für Kristallographie und Strukturphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — ²Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Room temperature ionic liquids (RTILs) in general – and molten alkylimidazolium-bis(trifluoromethylsulfonyl)imide ([C_nMim][NTf₂]) salts in particular – are promising chemicals in electrochemical application. With the current trend of downsizing technology, interfacial effects take over a dominant role in these systems.

Using specular X-ray reflectivity (XRR) we have therefore systematically studied the solid-ionic liquid interface of [C_nMim][NTf₂] RTILs and sapphire (0001) in dependence of the alkyl chainlength and temperature. We observe alternating cation/anion monolayers with an enrichment of [C_nMim]⁺ cations close to the interface in all cases. However, the definition and extent of the observed structures varies with chainlength which can be attributed to a size match/mismatch between the anion and cation, leading to more/less compact packing of

the molecules.

O 45.4 Wed 12:15 HE 101

Lithium Ion Transport in LiMn₂O₄ Nanowire Cathode of Lithium Ion Battery — ●SOYEON LEE^{1,3}, YOSHIFUMI OSHIMA^{2,3}, and KUNIO TAKAYANAGI^{1,3} — ¹Tokyo Tech., Tokyo, Japan — ²JAIST, Ishikawa, Japan — ³JST-CREST, Tokyo, Japan

Structural phase transition of electrode materials in lithium ion batteries causes capacity decrease. In order to avoid capacity decrease, it is essential to understand mechanism of transport of lithium ions and phase transition in the electrode. In the present work, a lithium ion battery with the LiMn₂O₄ nanowire, as a positive electrode, was developed specially for in-situ observation by a sub-50pm resolution electron microscope. The LiMn₂O₄ (LMO) electrode consists of a single nanowire or of a bundle of nanowires, which contacts with ionic liquid electrolyte (ILE) on a Li₄Ti₅O₁₂ negative electrode. The nanowire electrode is free standing, being suspended between Pt and ILE; little manganese (Mn) ions can dissolve from LMO into the electrolyte to cause capacity decrease. The nanowire battery was proved after in-situ observation to work without capacity degradation at high charge/discharge rate (fully charged within 24 minutes), and structure of LMO transformed reversibly while the cyclic voltammetry between 3.5-5.5 V (vs Li/Li⁺). The structure of the nanowire at the area of ILE/LMO contact showed cubic to tetragonal phase transformation, while the other area, non-equilibrium structure change has occurred by high charge/discharge rate. Our developed nanowire battery and in-situ study have revealed the nanowire battery can work reversibly without capacity decrease for high-rate charge/discharge operation

O 45.5 Wed 12:30 HE 101

Temperature-induced different patterns in the self-assembled network of Benzene-1,3,5-triphosphonic acid observed by scanning tunneling microscopy at the liquid-solid interface. — ●DOAN CHAU YEN NGUYEN¹, THI NGOC HA NGUYEN¹, MICHAEL MEHRING², and MICHAEL HIETSCHOLD¹ — ¹Solid Surfaces Analysis Group, Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany — ²Coordination Chemistry Group, Institute of Chemistry, Chemnitz University of Technology, Chemnitz, Germany

Benzene-1,3,5-triphosphonic acid (BTP), which is the phosphonic acid analogue of trimesic acid (TMA), forms a columnar packing in the crystalline solid state that is characterized by strong hydrogen bonds and π-stacking involving the aromatic rings. Therefore, BTP is an interesting intermediate to design both three-dimension (3D) supramolecular hydrogen-bonded architectures and organic-inorganic hybrid frameworks. Supramolecular self-assembly at liquid solid interfaces is a thermodynamically complex process producing a variety of structures. The formation of multiple network morphologies from the same molecular building blocks is a common occurrence. We use Scanning Tunneling Microscopy (STM) to investigate the self-assembly of BTP in different kind of solvents (undecanol, octanoic acid) adsorbed on highly oriented pyrolytic graphite (HOPG (0001)). The influence of substrate temperature is studied and the STM results reveal that with every kind of solvents, the influence of substrate temperature is strong enough to induce different self-assembled structures of BTP on the substrate.

O 45.6 Wed 12:45 HE 101

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