

## O 15: Solid-Liquid Interfaces: Structure, Spectroscopy II

Time: Monday 15:00–16:15

Location: WIL B321

O 15.1 Mon 15:00 WIL B321

**Traceable chemical analyses of new liquid and solid battery components by X-ray spectrometry in UHV environment** — ●CLAUDIA ZECH<sup>1</sup>, OLGA GRÄTZ<sup>2</sup>, IVAN RAGUZIN<sup>2</sup>, SVETLOZAR IVANOV<sup>3</sup>, MARKUS BÖRNER<sup>4</sup>, MARCO EVERTZ<sup>4</sup>, MARCELINA PYSCHIK<sup>4</sup>, DANIEL GRÖTZSCH<sup>5</sup>, WOLFGANG MALZER<sup>5</sup>, MANFRED STAMM<sup>2</sup>, SASCHA NOWAK<sup>4</sup>, and BURKHARD BECKHOFF<sup>1</sup> — <sup>1</sup>Physikalisch-Technische Bundesanstalt, Berlin, Germany, — <sup>2</sup>Leibniz-Institut für Polymerforschung, Dresden, Germany — <sup>3</sup>Technische Universität Ilmenau, Germany — <sup>4</sup>Münster Electrochemical Energy Technology, Germany — <sup>5</sup>Technische Universität Berlin, Germany

The decomposition of the electrolyte solution, the degradation of the active material and the deposition of impurities are among the main aspects that worsen the performance of a battery so that the elemental composition and the species of the single components need to be studied. The determination of these properties is the challenge for most analytical methods due to a lack of reference materials. With reference-free X-ray fluorescence spectrometry (XRF) we can determine the mass deposition of elements and with X-ray absorption spectrometry (XAS) we get access to the oxidation state of single elements. With these techniques we investigated the cathodes of lithium-sulfur batteries, the anodes of NCM based Li-Ion batteries and Ionic Liquids. All measurements are done with synchrotron radiation under UHV environment at BESSY II in Berlin.

O 15.2 Mon 15:15 WIL B321

**Unraveling water structuring on Nafion-like sulfonate-based model surfaces with increasingly hydrophobic character using force spectroscopy** — ●LAILA MORENO OSTERTAG<sup>1</sup>, XIAO LING<sup>2</sup>, THOMAS UTZIG<sup>1</sup>, PHILIPP STOCK<sup>1</sup>, SAPUN PAREKH<sup>2</sup>, KATRIN DOMKE<sup>2</sup>, and MARKUS VALTINER<sup>1,3</sup> — <sup>1</sup>Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf - Germany — <sup>2</sup>Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz - Germany — <sup>3</sup>Institut für Physikalische Chemie der TU Bergakademie Freiberg, 09599 Freiberg - Germany

Nafion membranes are an essential component of fuel cells, providing an effective medium to separate cathode and anode while facilitating proton conduction. Specifically, Nafion is a porous material with 1-2 nm pore diameters. The way water is structured across a pore is essential to understand the mechanism of proton transport. Here, we used atomic force microscopy to measure interaction forces between Nafion-like model surfaces emulated via self-assembled monolayers (SAM) where SO<sub>3</sub>- groups were gradually substituted by hydrophobic groups. The resulting interaction force profiles can be fitted to extended DLVO models depending on hydrophobic or charged content, in order to gain insight into the molecular surface structure that gives rise to the measured forces. Our data indicates a non-linear trend of the solvent structure at the surface as a function of the hydrophobic-to-sulfonate group ratio, indicating that small changes in stoichiometry can significantly alter water layering. We will discuss how our results relate to proton conductivity and how they may help to optimize membrane properties.

O 15.3 Mon 15:30 WIL B321

**STM investigation on the adsorption of water on Ru(0001) - Influence of temperature and coadsorbed CO** — ●MARTIN SCHILLING, LAURA FRIEDRICH, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, 89069 Ulm, Germany

The interaction of water with metal surfaces is of particular interest as model for the solid-liquid interface, and has therefore been studied intensely [1]. Besides adsorbate-metal interactions, also intermolecular interactions were found to play an important role. The situation becomes even more complex for the coadsorption of two adsorbing species.

Here we present results of a low temperature scanning tunnelling mi-

croscopy (STM) study on the structure of adsorbed water and water co-adsorbed with CO on Ru(0001), which was performed under ultra-high vacuum (UHV) conditions. For the adsorption of water we found distinctly different adsorbate arrangements, depending on the adsorption temperature (100 - 150 K). For deposition temperatures of 120 - 150 K, well-ordered stripe structures can be formed.

Post-exposure of such surfaces to CO revealed that only little CO was adsorbed in the areas between the stripes formed by adsorbed water, indicating that these areas are not bare Ru(0001) but (partly) covered by a dilute adsorbate layer that is not resolved in STM images. Different possibilities are discussed. Finally we investigated the influence of the dosing sequence on the structure of the resulting adlayer.

[1] J. Carrasco *et al.*, *Nat. Mater.* **11** (2012) 667

O 15.4 Mon 15:45 WIL B321

**In-situ tracking of the dynamic structure evolution in nanometer confined liquids by combining X-Ray Reflectivity and white light interferometry in a surface forces apparatus** — ●SADHANAA BUVANESWARAN<sup>1</sup>, HENNING WEISS<sup>2</sup>, HSIU-WEI CHENG<sup>1</sup>, CLAUDIA MEROLA<sup>1</sup>, JULIAN MARS<sup>2</sup>, MARKUS MEZGER<sup>2</sup>, and MARKUS VALTINER<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Eisenforschung GmbH — <sup>2</sup>Max-Planck-Institut für Polymerforschung

Nanometer confined liquids between solids exhibit molecular ordering and find importance in friction and energy conversion. How this structuring reacts to external triggers such as sliding of surfaces against each other, or changing applied stresses is notoriously hard to measure in experiment. Here, we experimentally obtain the structural information under precisely controlled liquid confinement with dynamically changing conditions. For this, we combine the Surface Force Apparatus which allows quantification of applied forces between two opposing surfaces based on optical interference and XRR that determines crystallographic structure on a molecular scale. A pore(mm<sup>2</sup> area) with controlled height of only 100s of nm of a model liquid crystal 8CB could be realized. When no force is applied, X-Ray scattering (probed horizontal direction) showed a sharp peak at  $q=2\text{nm}^{-1}$  which agreed well with the calculated molecular length established in previous literature. In XRR (investigated vertical liquid layering) similar intensities at identical  $q$  indicated isotropic behavior. However, during dynamic straining, the scattering intensities were 180 degree out-of-phase to the reflectivity intensity pointing towards anisotropic behavior.

O 15.5 Mon 16:00 WIL B321

**Self-Assembly of Imidazolium Based Ionic Liquids at Mica Interfaces is Induced by Confinement and the Presence of Water** — ●HSIU-WEI CHENG, JAN-NIKLAS DIENEMANN, PHILIPP STOCK, CLAUDIA MEROLA, YING-JU CHEN, and MARKUS VALTINER — Max-Planck Instut für Eisenforschung

Tuning chemical structure and molecular layering of ionic liquids (IL) at solid interfaces offers leverage to tailor performance of ILs in applications such as super-capacitors, catalysis or lubrication. Recent experimental interpretations suggest that ILs containing cations with long hydrophobic tails form well-ordered bilayers at interfaces. Here we demonstrate that interfacial bilayer formation is not an intrinsic quality of hydrophobic ILs. In contrast, bilayer formation is triggered by boundary conditions including confinement, surface charging and humidity present in the IL. Therefore, we performed force versus distance profiles using atomic force microscopy and the surface forces apparatus. Our results support models of disperse low-density bilayer formation in confined situations, at high surface charging and/or in the presence of water. Conversely, interfacial structuring of long-chain ILs in dry environments and at low surface charging is disordered and dominated by bulk structuring. Our results demonstrate that boundary conditions such as charging, confinement and doping by impurities have decisive influence on structure formation of ILs at interfaces. As such, these results have important implications for understanding the behavior of solid/IL interfaces as they significantly extend previous interpretations.