



	<b>Experiment title:</b> Structure of Ionic Liquids near Electrode Interfaces Probed by High-Energy X-Ray Reflectivity.	<b>Experiment number:</b> SI-2361
<b>Beamline:</b> ID15A HEMD	<b>Date of experiment:</b> from: 12-10-2011                      to: 25-10-2011	<b>Date of report:</b> 08-03-2012
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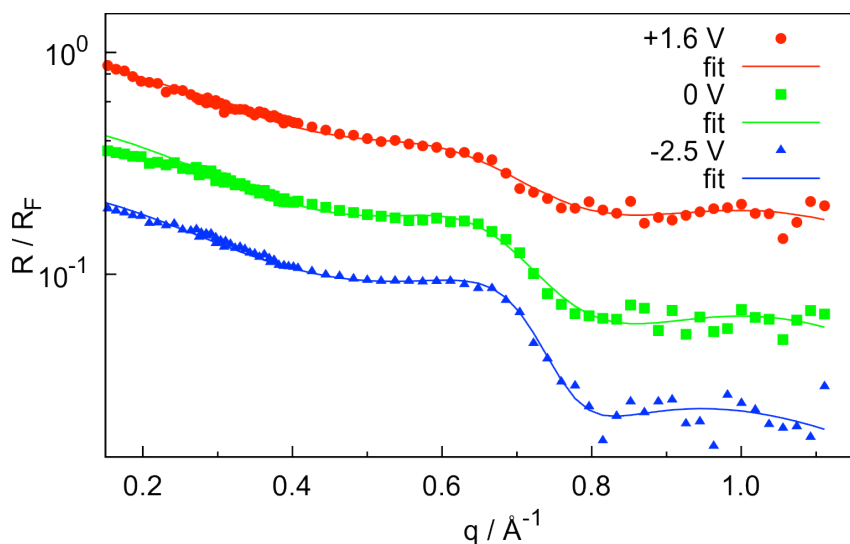
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**Report:**

Ionic liquids (ILs) are organic salts with a melting point below 100 °C. Their properties can be tuned by different combinations of anions and cations. So far a huge variety of ILs were synthesized which have superior properties such as high electrochemical window and low vapor pressure.

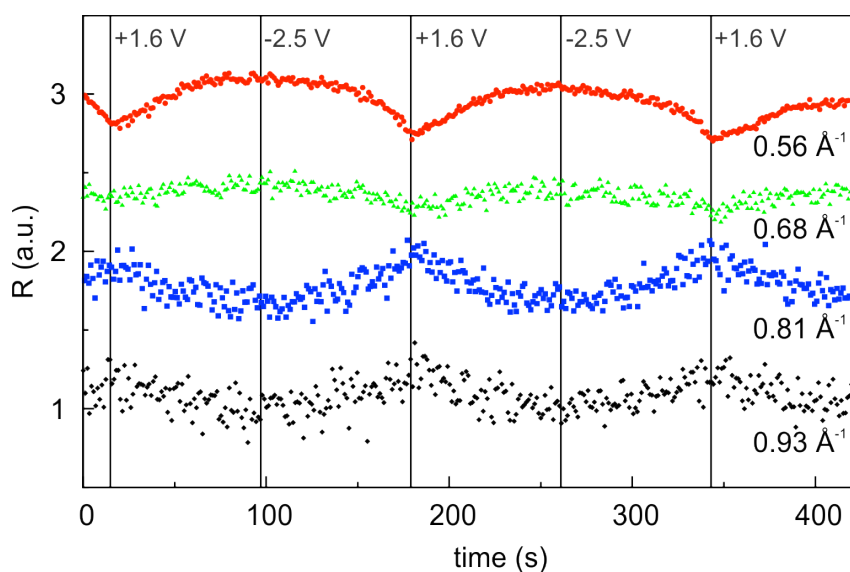
During our beamtime at ID15A we used the HEMD instrument to study the potential dependence interfacial structure between two ILs ( (tetrabutylammonium tris(pentafluoroethyl)trifluorophosphate)  $[tba]^+[FAP]^-$  and 1-butyl-1-methylimidazolium tris(pentafluoroethyl)trifluorophosphate  $[bmpy]^+[FAP]^-$ ) and a single crystalline boron doped diamond (BDD). The experimental chamber, based on a setup that was successfully used previously (SI-2147), was extensively modified for improved temperature control and increased electrical stability to allow quantitative electrochemical in-situ measurements during XRR. The working electrode is immersed from the top in a PTFE trough filled with the IL. The sample can be cooled by a closed cycle refrigerator and the temperature is controlled by 4 heating cartridges with 200W each. For precise measurements an external aluminum frame that decouples the sample mount from the liquid trough achieved a high mechanical stability of the setup. To remove dissolved gases and impurities such as water, oxygen and CO<sub>2</sub> from the ILs the chamber can be evacuated. During the experiments the cell was filled with 100 mbar of helium to achieve a homogeneous temperature across the sample. For potential control the setup was connected to a potentiostat in 3-electrode

configuration using a 10 mm x 10 mm poly crystalline boron doped diamond plate as counter electrode and a platinum wire as quasi reference electrode. The high purity ILs were bought from Merck and degassed for several hours in a vacuum oven at 70 °C prior to the experiment. Additionally, the  $[tba]^+[FAP]^-$  was cleaned by zone melting, which was repeated eight times. The single crystalline BDD was polished to a surface roughness  $< 3 \text{ \AA}$ . The electron density of the BDD substrate is extremely low compared to other conducting and chemical inert materials such as gold or platinum. This provides a balanced contrast between the IL and the substrate on the one hand and the modulations caused by interfacial layering on the other side. Therefore, the reflectivity curves showed pronounced features originating from the interfacial structure in the region of  $0.4 \text{ \AA}^{-1}$  to  $1.0 \text{ \AA}^{-1}$  (figure 1).



In the first part of SI-2361 we studied the interfacial layering structure of the ILs by reflectivity scans vs. angle at different constant potentials. Before each measurement we applied 50 Hz step-functions between  $-2.5 \text{ V}$  and  $+1.6 \text{ V}$  to reset the surface to the same initial state. Figure 1 shows the reflectivity curves of the  $[tba]^+[FAP]^-/BDD$  interface for anodic, cathodic and zero potential. The data was fitted via the Parratt

formalism to the electron density profile described by the distorted crystal model. The distorted crystal model consists of the sum of alternating Gaussian distributions representing anion and cation enriched regions. Preliminary results show that the cation is adsorbed at the electrode surface at anodic potential up to  $1.6 \text{ V}$  and that there is no exchange of cation to anion in the very first layer. At the moment we are working on a more refined model taking effects into account such as crowding.



To ensure the reproducibility of the experiment and to investigate the evolution of the interfacial structure we recorded the reflectivity signal while doing cyclic voltammetry between  $-2.5 \text{ V}$  and  $+1.6 \text{ V}$  at a speed of  $0.05 \text{ V/s}$ . Figure 2 shows the recorded signal at various angles around the layering feature. The amplitude inversion between  $0.68 \text{ \AA}^{-1}$  and  $0.81 \text{ \AA}^{-1}$  is in accordance with the observations in the total reflectivity curves. The periodic signal confirms the

reproducibility of the measurement and proves the stability of this IL against radiation damage.