

**Experiment title:**

Arrangement of metal ions in the interfacial layering structure of ionic liquids

**Experiment number:**

SI-2147

**Beamline:**

ID15A

**Date of experiment:**

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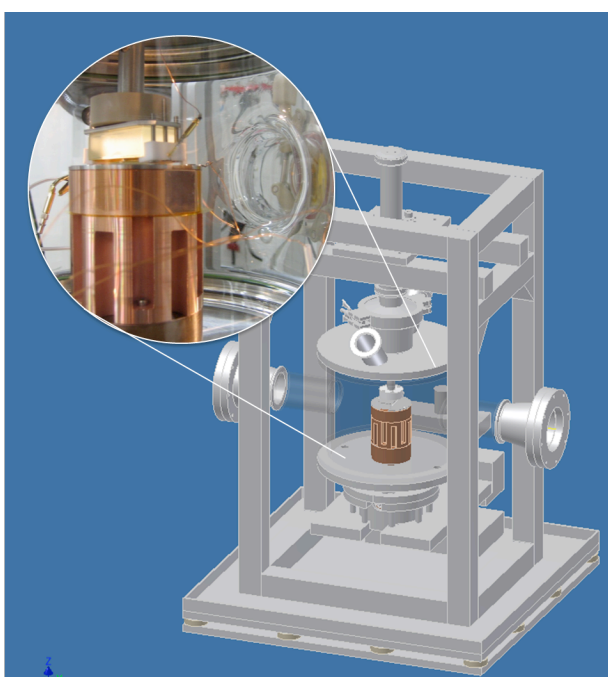
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Room temperature ionic liquids (ILs) are promising candidates in a variety of technological applications ranging from special solvents in green chemistry to electrodeposition of corrosion and wear protection layers. Although crucial for the understanding of solvent properties, only little is known about the structural rearrangement of the anions and cations at solid interfaces. While our previous x-ray reflectivity studies<sup>1, 2</sup> concentrated on the structure of ILs on isolation dielectric substrates (SI-1610) in this experiment we focused on the interface between ILs and conductive metallic substrates under potential control.



In this project we have used high-energy x-ray reflectivity to get precise and direct information on the structure of ILs at metal electrodes under the influence of electric fields. For this purpose we constructed a new sample cell that can be used at ID15A (see Fig. 1). The working electrode is immersed from the top in a PTFE trough filled with the IL. The sample can be cooled by liquid nitrogen 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 or filled with an inert gas such as helium. For potential control the setup was connected to a potentiostat in 3-electrode configuration using a 10 mm x 16 mm glassy carbon plate as counter electrode and a platinum wire as quasi reference electrode.

For the working electrode, polycrystalline gold substrates were prepared by template stripping. Glass substrates were bonded with epoxy resin on gold-coated (approx. 130 nm thickness) silicon wafers and cleaved at the gold/SiO<sub>2</sub> interface prior to the transfer of the substrate into the sample chamber. Profile scans of the bare gold surface using an alpha stepper showed a waviness of less than 1 nm on a length scale of 500 microns. XRR confirmed that our procedure yields smooth gold films with a surface roughness of 2 Å – 3 Å.

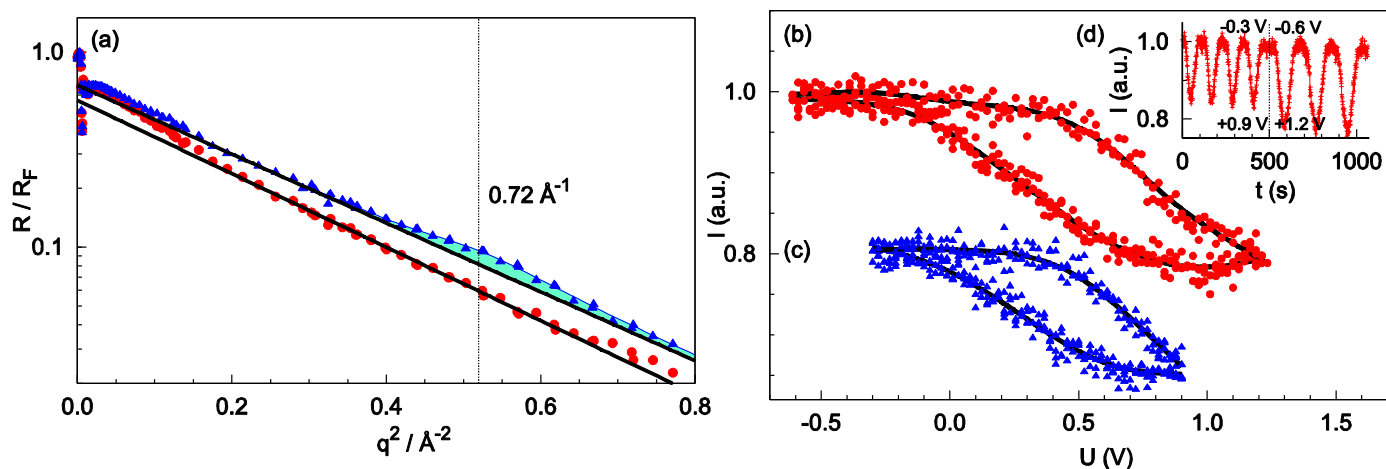


FIG 2. (a) Fresnel normalized X-ray reflectivity from the liquid-solid interface with [bmpy]<sup>+</sup>[FAP]<sup>-</sup> at -25 °C at a potential of -0.8 V (blue triangle, upper curve) and 1.0 V vs. a platinum quasi reference electrode (red circles, lower curve). The blue shaded area represents a Lorentzian peak at 0.72 Å<sup>-1</sup> fitted to the experimental data. (b-c) Reflectivity vs. applied potential on [tba]<sup>+</sup>[FAP]<sup>-</sup> at 2θ = 1.2° corresponding to a vertical momentum transfer  $q_z$  of 0.74 Å<sup>-1</sup>. The data was collected during cyclic voltammetry measurements between -0.6 V and +1.2 V (b) and between -0.3 V and +0.9 V (c). Curves are vertically offset for clarity. Lines are guides for the eye. The inset (d) shows the reflectivity vs. time while performing cyclic voltammetry between the two sets of potential limits.

We chose a selection of tris(pentafluoroethyl)trifluorophosphate ([FAP]<sup>-</sup>) based ILs for which in our previous studies on sapphire we observed pronounced interfacial layering. In the first experiments we studied the solid-liquid interface between gold substrates and [bmpy]<sup>+</sup>[FAP]<sup>-</sup> and [tba]<sup>+</sup>[FAP]<sup>-</sup> ([bmpy]<sup>+</sup> = 1-butyl-1-methylimidazolium, [tba]<sup>+</sup> = tetrabutylammonium) under potential control in the range between -0.8 V and +1.0 V vs. the platinum quasi reference electrode i.e. within the electrochemical window of 6.6 V for [bmpy]<sup>+</sup> and 7.0 V for [tba]<sup>+</sup> respectively. Figure 2a shows the Fresnel normalized reflectivity data of the gold substrate in contact with [bmpy]<sup>+</sup>[FAP]<sup>-</sup>. Data at positive and negative potentials was collected under identical conditions on the same sample. The  $q$ -range between 0.55 Å<sup>-1</sup> and 0.90 Å<sup>-1</sup> was measured alternately by multiple scans to confirm that the differences are reproducible and not caused by sample degradation such as beam damage. In contrast to our earlier work on the same ILs in contact with sapphire where interfacial layering manifested itself in pronounced modulations of the reflectivity curve, the data on the gold films showed rather weak features. However, switching the polarity clearly affected the measured reflectivity. While for a negative potential of -0.8 V a peak that can be attributed to interfacial layering was observed around 0.8 Å<sup>-1</sup> (blue shaded area), the reflection pattern at +1.0 V is readily explained by a single smooth interface (Fresnel curve) plus an exponential damping factor  $\exp(-\sigma^2 q^2)$  taking into account interfacial roughness (straight lines in Fig. 2a). Interestingly, the overall slope of the intensity decay depends on the applied potential. Figure 2b-d shows that in a cyclic voltammetry type experiment where the reflected intensity was monitored at a fixed incident angle of 0.6°, switching is reproducible and stable over multiple periods. While for negative polarity an increase in the voltage has only a minor influence on the reflected intensity in the positive region no saturation was reached up to the maximum applied potential of +1.2 V.

These experimental findings are tentatively explained by a combination of gold surface reconstruction<sup>3</sup> and an alternated near interface structure of the ILs. A more detailed quantitative analysis and interpretation of the extensive experimental data including the extraction of interfacial profile by parameter refinement is currently underway.

## References:

- <sup>1</sup> M. Mezger, et al., *Science* **322**, 424 (2008).
- <sup>2</sup> M. Mezger, et al., *J Chem Phys* **131** (2009).
- <sup>3</sup> J. Wang, A. J. Davenport, H. S. Isaacs, and B. M. Ocko, *Science* **255**, 1416 (1992).