



**Experiment title:**

Ion Distribution near Electrodes - The Transition from Ionic Liquids to Solvated Ions

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**Report:**

Ionic Liquids (ILs) are organic salts with outstanding electrochemical properties. In many applications, such as double layer capacitors and dye-sensitised solar cells, the performance of possible devices strongly depends on processes at the IL-electrode interface. Previous experiments (SI 2361) focused on pure ILs revealed an oscillatory structure at interfaces comprised of alternating cation and anion enriched layers. In this study we investigated the structure, dynamics and substrate dependence of ILs-solvent mixtures at an electrode interface.

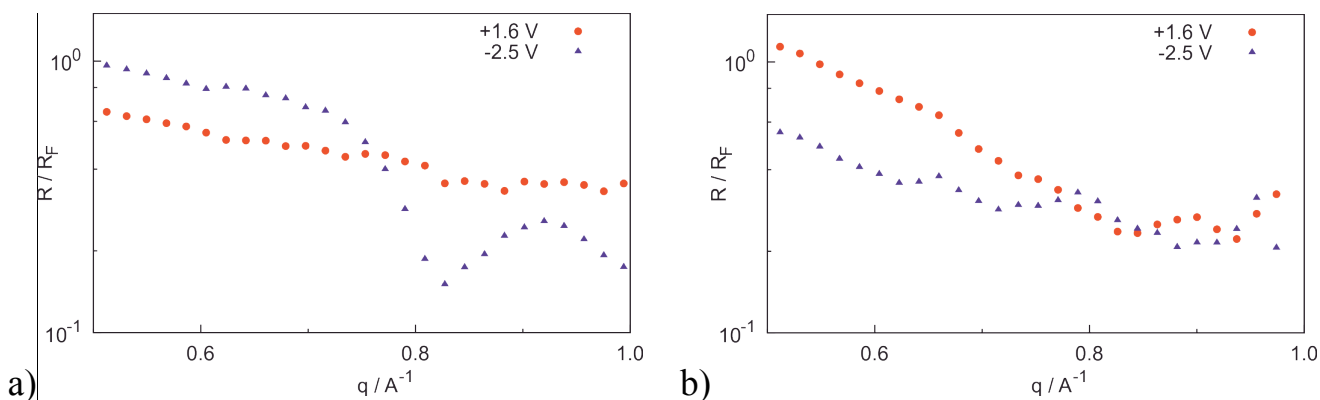


Figure 1: X-ray reflectivity data at cathodic and anodic potential of pure  $[\text{bmpy}]^+[\text{FAP}]^-$  (a) and  $[\text{bmpy}]^+[\text{FAP}]^-$  - Propylene Carbonate solution (1:1) (b)

X-ray reflectivity (XRR) data was collected for pure IL  $[\text{bmpy}]^+[\text{FAP}]^-$  (1-butyl-1-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate) and for a solution of  $[\text{bmpy}]^+[\text{FAP}]^-$  and propylene carbonate (PC) in a 1:1 volume ratio at a single crystalline

boron doped diamond (BDD) electrode (figure 1; for details see report for SI 2361). At cathodic potential the XRR intensity of the pure IL shows a kink at  $0.8 \text{ \AA}^{-1}$  which is related to the electron density oscillations from the interfacial layering structure. At anodic potential the kink vanishes, indicating a much weaker layering. The XRR data of the  $[\text{bmpy}]^+[\text{FAP}]^-$  PC solution shows a much weaker kink which is now more pronounced at anodic potential. Further, the intensity at low angles is higher at anodic potential opposite to the pure IL data. These findings indicate a different rearrangement of the interfacial structure of the IL in presence of PC.

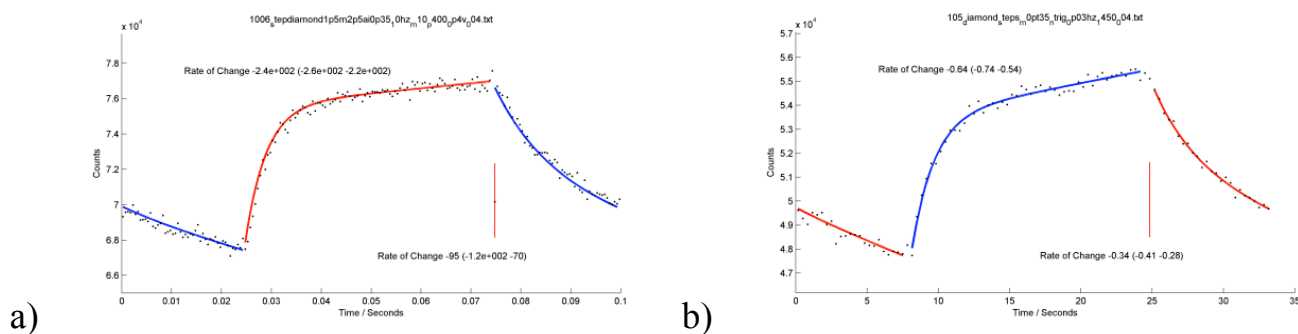


Figure 2: X-ray reflectivity data while switching from negative (blue) to positive (red) potential from pure  $[\text{bmpy}]^+[\text{FAP}]^-$  at 10 Hz (a) and  $[\text{bmpy}]^+[\text{FAP}]^-$  propylene carbonate solution (1:1) at 30 mHz (b)

Time resolved XRR shows a slowing down of the interfacial dynamics of  $[\text{bmpy}]^+[\text{FAP}]^-$  when adding PC by three orders of magnitude (figure 2). The intensities at anodic and cathodic potential are inverted as observed in the steady state XRR before. The deceleration is remarkable as the relaxation time is expected to decrease with the lower viscosity of the solution. A possible explanation could be an interfacial process which is not governed by bulk diffusion but by a more complicated adsorption process involving both ions and solvent molecules.

In the second part of the experiment we examined the influence of the electrode material on the dynamics of the interfacial structure. We discovered an intriguing dynamic behaviour of the  $[\text{tba}]^+[\text{FAP}]^-$  (tetrabutylammonium tris(pentafluoroethyl)trifluoro-phosphate) platinum interface. When switching from anodic to cathodic potential the intensity first increases and then decreases again after the first few milliseconds (figure 3). This effect might be related to specific adsorption states on the platinum surface which are also visible in cyclic voltammetry as distinct adsorption peaks.

For further investigation of the interfacial dynamics, we plan to do supplementary impedance spectroscopy. This might allow us to separate interfacial and bulk processes occurring on different time scales.

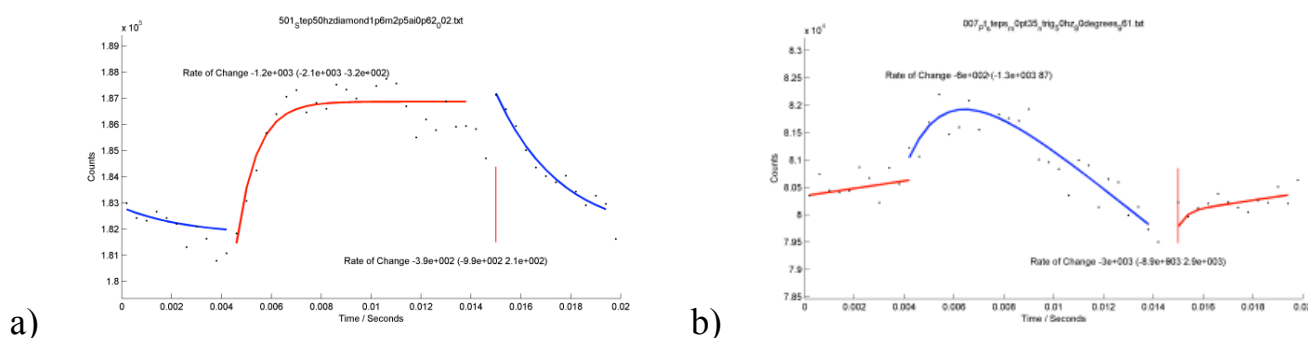


Figure 3: X-ray reflectivity data while switching from negative (blue) to positive (red) potential at 50 Hz from  $[\text{tba}]^+[\text{FAP}]^-$  BDD interface (a) and  $[\text{tba}]^+[\text{FAP}]^-$  Pt interface (b)