



	Experiment title: Surface x-ray diffraction of ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluorosulfonylmethyl)imide on gold single crystals in a novel electrochemical cell	Experiment number: CH5500
Beamline: ID03	Date of experiment: from: 01/11/18 to: 06/11/18	Date of report: 07/05/19
Shifts: 18	Local contact(s): Martini Santroni	<i>Received at ESRF:</i>
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Report:

The aim of this experiment was to elucidate the interactions of ions of an ionic liquid (IL) with metal single crystal electrodes by surface X-ray diffraction and measure any potential dependent structural changes observed at the surface. The experiment involved using a new setup which was previously successfully tested and validated during experiment CH-5134 at the ESRF, 2017. Au(111) and Pt(111) surfaces were investigated in neat purified [BMPyr] [TFSI] IL, along with a protonated system containing 0.1M HTFSI/[BMPyr] [TFSI]. During the later stages of the experiment the effects of CO was measured by saturating the experimental chamber with purified CO gas. By using CO as a test molecule it was possible to probe the influence of the electrolyte ordering on surface restructuring and electrochemical reactivity of the systems.

The electrode | IL interface has been shown to form structured multilayers in certain ILs¹ and displaying potential dependent structural behaviour². X-ray reflectivity measurements have shown varying IL to demonstrate different surface layering dependent on cation size³.

In this experiment crystal truncation rod (CTR) profiles alongside X-ray voltammogram were performed, a full data set of the (1 0 L), (0 1 L) and the (1 1 L) rods were recorded between in an extended potential range to our previous experiment between -2400 -1500 mV in 200 mV increments vs a Ag wire reference electrode. XRV measurements were recorded at the (1 0 4.7) and the (1 0 0.5) and (1 0 3.5) positions in reciprocal space to measure any relaxations or structural changes.

Contrary to other studies there is no evidence of a reconstructed surface in either the Au or Pt surfaces in the typical potential regime for aqueous systems, or even those reported in STM for IL⁴. CTR profiles for the Au(111) system are in line with that of a smoothly terminated gold surface at potentials close the OCP and PZC.

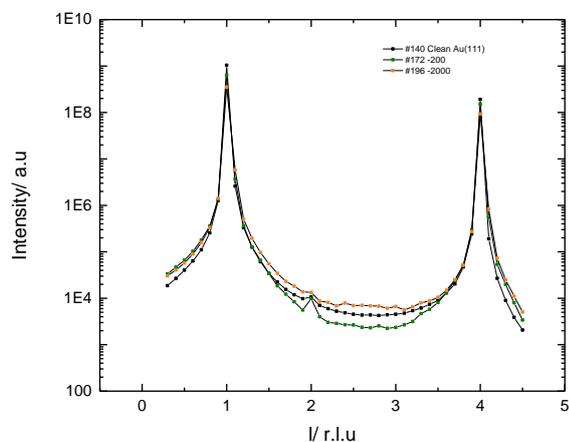


Figure 2 CTR profiles recorded on a Au(111) surface, clean (black curve), in ionic liquid at 200mV (orange) and in ionic liquid at -2000 mV (green)

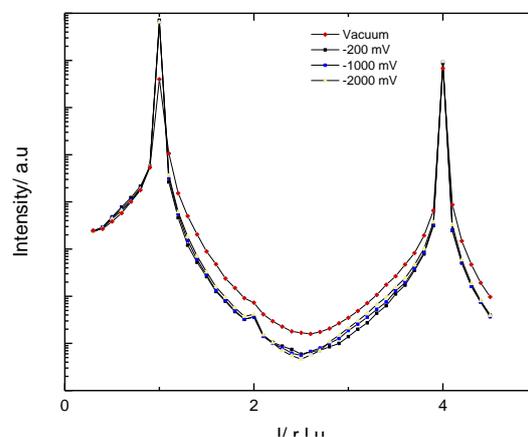


Figure 1 CTR profiles recorded on the Pt(111) surface showing potential dependence recorded at 3 varying potentials

Potentially dependant behaviour can be observed however with relaxation or absorption processes being visible from a change in the intensity at the anti-Bragg position. Upon driving the potential more negative a loss in intensity. This process is reversible as the intensity recovers again at positive potentials.

XRV measurements have shown no alteration of the intensity in the negative regime with only a reversible relaxation seen in the positive regime. This process coincides with voltametric features.

The Au protonated system shows similar behaviour to the clean gold with a larger roughening at potentials negative of -1000 mV.

The Pt acid system shows interesting electrochemical behaviour with a double nucleation loop being visible in the negative regime at potentials indicative of surface restructuring/reordering (-100 mV) just negative of the PZC. This indicates there could be a process blocking the surface, which could be due to the catalytic absorption H⁺ from solution at negative potentials. Preliminary data analysis shows again the presence of relaxation processes. Data analysis for Pt/CO system is underway.

References:

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2. Atkin, R. *et al.* Structure and dynamics of the interfacial layer between ionic liquids and electrode materials. *J. Mol. Liq.* 44–54 (2014). doi:10.1016/j.molliq.2013.08.006
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