

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**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:**  
**CH-5134**

<b>Beamline:</b> <b>ID03</b>	<b>Date of experiment:</b> from: 08/11/17 to: 14/11/17	<b>Date of report:</b> 30/01/18
<b>Shifts:</b> 18	<b>Local contact(s):</b> Raja Znaiguia	<i>Received at ESRF:</i>

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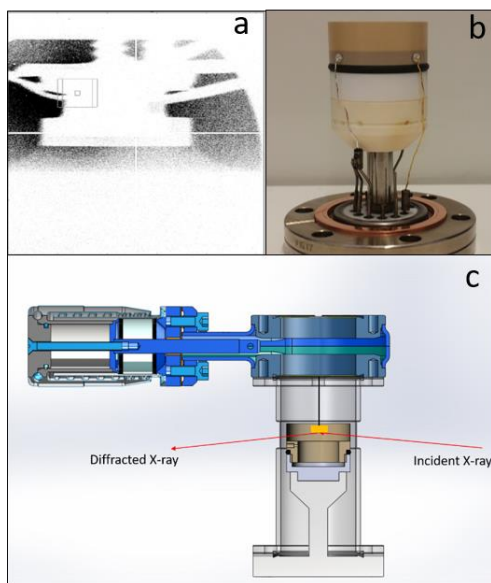
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**Report:**

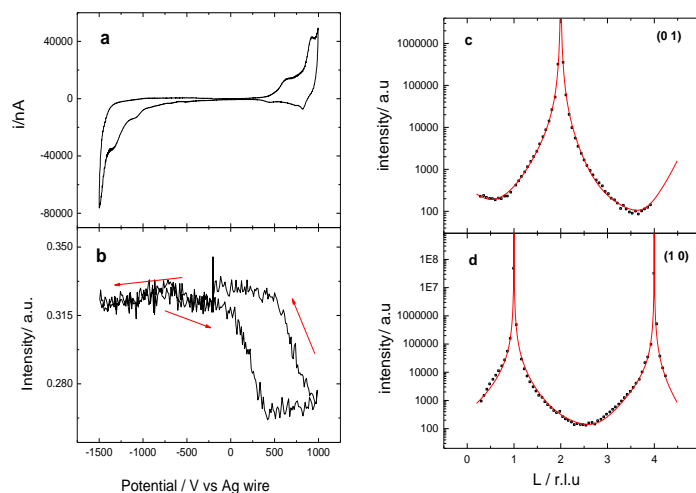
The aim of this experiment was to elucidate the interactions of ions of an ionic liquid (IL) with a solid electrode by surface X-ray diffraction. An electrochemical cell for in-situ electrochemical and structural characterisations of a metal-ionic liquid interface was developed and was tested for the first time successfully. Here we present a setup where-by an ionic liquid is prepared and handled inside a glove box and then assembled in an electrochemical cell under inert conditions before being transferred to the diffractometer.

The electrode | IL interface has been shown to form structured multilayers in certain ILs[1] and displaying potential dependent structural behaviour[2]. X-ray reflectivity measurements have shown varying IL to demonstrate different surface layering dependent on cation size[3].

In this experiment crystal truncation rod (CTR) profiles alongside X-ray voltamograms were performed to measure the potential dependant structural change at the Au(111) interface. A full data set of the (1 0 l), (0 1 l) and the (1 1 l) rods were recorded between -1500 mV and 1000 mV at 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.



**Figure 1:** a) Transmission image of the crystal inside the cell, showing the crystal forming the meniscus in the IL, b) a photo of the electrochemical cell, c) schematic of the complete set up as employed on the ID03 beamline.



**Figure 2:** a) A cyclic voltammogram recorded with the cell, the potential was varied at 10 mV/s. b) Scattered x-ray intensity at the (1, 0, 4.7) position in reciprocal space while scanning the potential at 10 mV/s. And b) and c) show two crystal truncation rod profiles measured at -200mV along the (0 1 l) and (1 0 l) rods respectively.

Figure 1 shows the successful set up used. Figure 2 shows the electrochemical and X-ray results. In Figure 1a a cyclic voltammogram of Au(111) in [BMP][TFSI], recorded at 10 mV s<sup>-1</sup> between 1000 mV and -1500 mV is shown. Electrochemical features can be directly compared to structural changes observed at the surface as eluded to in b) an XRV measurement of the scattered intensity on scanning the potential. The anodic features seen at positive potentials in a) coincide with a decrease in intensity and following increase at (1 0 4.7) position. This suggests that a structural change could be occurring. No structural surface processes have yet been identified for the negative potential region associated with the reconstruction of the Au(111) surface. Crystal truncation rod profiles recorded at -200 mV along the [0 1 l], [1 1 l], direction can be seen in Figure 2c and 2d respectively. The solid red line is a fit to the data and indicates a smoothly terminated gold surface. The origin of these exact structural changes still remains unclear and an additional experiment is required for the full structural characterisation of the entire electrochemical window.

A new electrochemical cell specifically designed for the study of IL in-situ with SXR methods has been presented. The set-up and implementation of the cell has been altered following the experiment, to account for problems which occurred during the experiment. This set-up builds on the already extensive list of setups available for the in-situ study of aqueous systems. Additional structural data was obtained for intermediate potentials which is currently under analysis.

#### Ref:

- [1] M. V. Fedorov and A. A. Kornyshev, "Ionic liquids at electrified interfaces," *Chem. Rev.*, vol. 114, no. 5, pp. 2978–3036, 2014.
- [2] R. Atkin, N. Borisenko, M. Drüscher, F. Endres, R. Hayes, B. Huber, and B. Roling, "Structure and dynamics of the interfacial layer between ionic liquids and electrode materials," *J. Mol. Liq.*, no. 192, pp. 44–54, 2014.
- [3] Y. Su, J. Yan, M. Li, M. Zhang, and B. Mao, "Electric Double Layer of Au(100)/Imidazolium-Based Ionic Liquids Interface: Effect of Cation Size," *J. Phys. Chem. C*, vol. 117, no. 1, pp. 205–212, Jan. 2013.