



Short communication

Characterization of the interfaces between Au(hkl) single crystal basal plane electrodes and [Emmim][Tf₂N] ionic liquid☆



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ABSTRACT

The interface between Au(hkl) basal planes and the ionic liquid 1-Ethyl-2,3-dimethyl imidazolium bis(trifluoromethyl)sulfonyl imide was investigated by using both cyclic voltammetry and laser-induced temperature jump. Cyclic voltammetry showed characteristic features, revealing surface sensitive processes at the interfaces Au(hkl)/[Emmim][Tf₂N]. From laser-induced heating the potential of maximum entropy (pme) is determined. Pme is close to the potential of zero charge (pzc) and, therefore, the technique provides relevant interfacial information. The following order for the pme values has been found: Au(111) > Au(100) > Au(110). This order correlates well with work function data and values of pzc in aqueous solutions.

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1. Introduction

There has recently been considerable interest in the use of room temperature ionic liquids (RTILs) as solvent in a broad range of chemical applications, including organic synthesis, transition-metal catalyzed reactions, synthesis of macromolecules and nanoparticles, separation processes and spectroscopic measurements [1,2]. Such applications take advantage of its ability to perform processes that could not be possible in aqueous solutions thanks to its increased thermal stability, particular interaction with some reactants and low vapor pressure. Being composed entirely of ions, RTILs have many electrochemical applications in electrocatalysis, electrodeposition or as solvent in energy devices (batteries and supercapacitors) [3,4,5,6].

Despite numerous contributions in the field, the information about the electrochemical interphase between RTILs and well-defined surfaces is scarce. Due to the ionic nature of the RTIL, rationalization of capacitance data using Gouy–Chapman–Stern model is not possible [7] and indirect information techniques are needed [8,9,10,11,12,13,14,15,16,17,18,19,20]. The laser temperature jump (LTJ) method has proved valuable in this context. In Au(hkl)/water [21] and Pt(hkl)/water solution [22,23] interfaces, this experiment supplies the value of the potential of maximum interfacial entropy (pme), which has been shown to be close to the potential of zero charge (pzc). This technique has recently been successfully applied to the Pt(111)/[Emmim][Tf₂N] interface [24].

In this ion-crowded environment, coulombic interactions are certainly the most important in the electrolyte side of the interface. Still, other interaction such as hydrogen bonding between anions and cations must also be considered [25]. In the IL chosen in this study, this latter interaction has been decreased because the hydrogen position in C2 is methylated. Combination of voltammetric and LTJ data performed on well-defined Au(hkl) flame annealed electrodes in contact with purified [Emmim][Tf₂N] have been used to characterize these different interfaces. Results are compared with classical data in aqueous solutions.

2. Experimental

The [Emmim][Tf₂N] was purchased from IoLiTec (>99% purity, halides < 100 ppm, water < 60 ppm). It was purified following Kolb's procedure [26], namely, dried under vacuum (P < 0.002 mbar) more than 24 h at 80 °C, followed by treatment with a molecular sieve not larger than 3A. The latter is a key step in the purification process [26,27,28,29].

A waveform generator (EG&G PARC 175) together with a potentiostat (eDAQ EA161) and a digital recorder (eDAQ ED401) was employed for cyclic voltammetry experiments. As a quasi-reference electrode, a silver wire was used, but potentials were further referred to Cobaltocenium scale [30]. A Au wire was used as counter electrode. Experiments were carried out with Au(hkl) in the meniscus configuration. A thermostatted cell was used in order to keep the temperature at 25 °C. Before each experiment, each Au(hkl) electrode was flame-annealed and cooled down to room temperature under Ar atmosphere.

☆ Dedicated to Toni Aldaz.

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The LTJ experiment was described elsewhere [21,24]. In this experiment, a Nd:YAG pulsed laser is used to cause a sudden change of the temperature of the interphase while the open circuit potential of the working electrode is measured during the temperature relaxation. A system of switches is used to connect/disconnect the potentiostat allowing the polarization of the electrode at the desired potential. In this way, the potentiostat is disconnected just before firing the laser, to ensure true coulostatic conditions. The measured change of the potential contains contributions from the response of the double layer to the temperature change, the spillover of electrons and the thermodiffusion potential. However, it has been demonstrated before [21,24] that the main contribution comes from the effect of the temperature on the polarization of solvent molecules.

3. Results

3.1. Voltammetric experiments

Characteristic voltammetric profiles of Au(100) and Au(110) electrodes in contact with [Emmim][Tf₂N] are shown in Fig. 1. In both cases, a broad capacitive current signal, which increases linearly with the sweep rate, is superimposed to different couples of sharp peaks. These sharp peaks are similar to those observed during adsorption of organic adlayers on Au(hkl) single crystals corresponding to 2D phase transitions between different ordered structures [31]. Similar sharp peaks are also observed during anion adsorption on Pt(hkl) and Au(hkl) single crystals [32,33,34]. Interestingly, the characteristic voltammograms are structure sensitive. Starting with Au(110), the most open structure, Fig. 1A, three peaks are seen at 1.34, 1.40 and 1.51 V in the positive going sweep. The peaks in the negative going sweep are located at slightly lower potentials, between 10 and 20 mV less positive than the corresponding anodic counterpart. The interface Au(100)/[Emmim][Tf₂N], Fig. 1B, features only two couples of peaks, at 1.41 and 1.99 V in the positive-going sweep, with counterparts only 10 mV

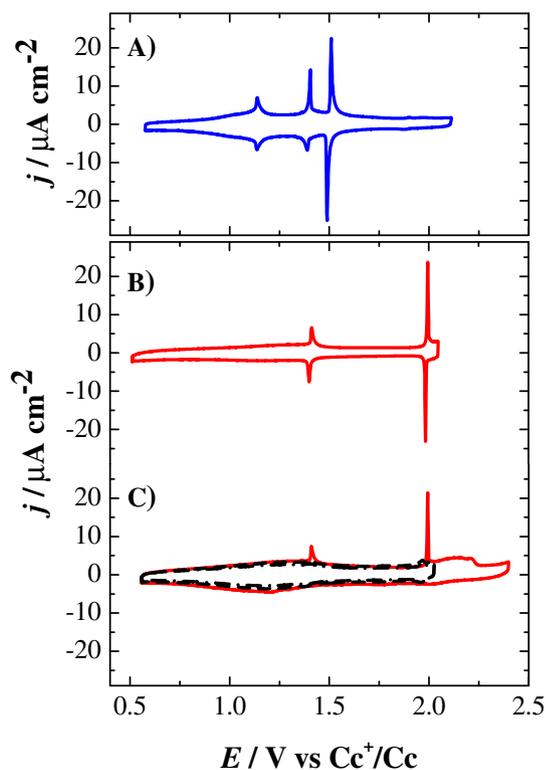


Fig. 1. Cyclic voltammograms for A) Au(110) and B) Au(100) in [Emmim][Tf₂N]. C) For Au(100), effect of the increase of the upper potential limit up to 2.40 V. Scan rate 50 mV s⁻¹.

less positive. The voltammogram is quite stable within this potential range. However, if the upper potential limit is increased, a broad feature starts appearing that modifies the overall profile and both peaks disappear from the voltammogram (Fig. 1C). One tentative explanation for this behavior would be that some decomposition product remains adsorbed on the surface. Another possible explanation would be that a reconstruction formed after flame annealing has been lifted during the excursion to high potentials. Additional STM information would be required to discriminate both possibilities.

The most complex voltammetric profile corresponds to Au(111) electrodes (Fig. 2A). There are numerous couples of spikes superimposed to two broad capacitive processes that grow below and over 1.7 V, respectively. The reversibility of the peaks is similar to the previous cases, with a peak to peak separation around 10–20 mV. This profile is extremely dependent on the scanned potential window. If the upper potential limit is decreased to 1.6 V (curve a), only a doublet of peaks is observed around 1.44 V (a₁). Increasing the upper limit to 2.1 V (curve b) reveals a sharp peak at 2.0 V (b₁). Further increasing the upper limit to 2.7 V (curve c), causes the disappearance of the doublet at 1.44 V, with the development of a new couple at 1.34 V (a₂) and the transformation of the peak at 2.00 V into a new sharper peak at 1.89 V (b₂). This peak, centered at 1.89 V, can be used to identify the presence

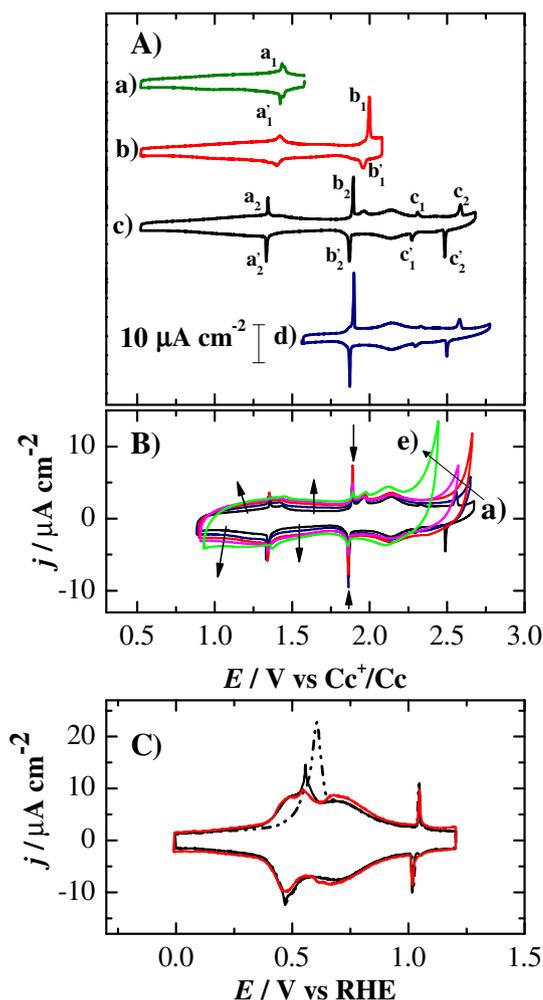


Fig. 2. Cyclic voltammograms for: A) Au(111)/[Emmim][Tf₂N], different potential limits; B) Au(111)/[Emmim][Tf₂N] after adding small amounts of water: a) 0 ppm b) 56.5 ppm, c) 112.5 ppm, d) 544.3 ppm and e) 3125 ppm; C) flame annealed Au(111)/0.5 M H₂SO₄ first (black dashed line) and second (black solid line) cycle, and after cycling the electrode in the IL (red solid line). Scan rate: 50 mV s⁻¹. Arrows in B) indicate the increase of water content.

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