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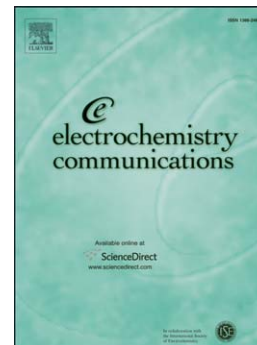
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Hydrogen redox reactions in 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide on platinum single crystal electrodes

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Abstract

Hydrogen oxidation and the subsequent proton reduction are studied on platinum single crystal electrodes in purified 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid. The hydrogen redox reaction shows some dependence of the surface orientation. The highest reversibility is observed with Pt(111) whereas the reaction in electrodes with {100} sites is less reversible and with a slow kinetics. Adsorption states are observed in presence of hydrogen along with the main oxidation reaction. Also, it is possible to detect protons after oxidation of water and H₂O₂.

Keywords: Hydrogen redox reactions, ionic liquid, platinum single crystals

1. Introduction

The interest on the electrochemical properties of Ionic Liquids (ILs) has grown mainly because they exhibit good electrical conductivities and wide potential windows. These properties make them interesting materials for a variety of applications such as rechargeable lithium batteries, electrochemical double-layer capacitors, electrochemical mechanical actuators, fuel cells and gas sensors [1-4].

Hydrogen oxidation and evolution are among the most important reactions in electrochemistry. Their study in non-aqueous media, such as ILs, is growing since these electrolytes offer high chemical and thermal stability [1].

In this work the hydrogen redox reactions were studied at Pt single crystal electrodes and using purified 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([Emmim][NTf₂]).

2. Experimental

Platinum single crystals prepared following standard procedures [5] were used as working electrodes. The electrodes were heated in a gas-oxygen flame, cooled down in reductive atmosphere (H₂ + Ar) and protected with a droplet of the IL at low enough temperatures to avoid decomposition. The electrodes contacted the deaerated IL (Ar ≥ 99.995% Alphagaz) in a meniscus configuration. The quasireference and counter electrodes were silver and platinum wires, respectively.

[Emmim][NTf₂], (>99% purity), was purchased from Io-li-tec. The purification procedure was a modification of the one reported in reference [6]. In summary, 2 mL of the IL were vacuum-dried in the presence of molecular sieve of 0.3nm (Merck) (400mg/mL) during 24 hours. The first 6 hours the IL was heated at 80°C. The molecular sieve was heated in a microwave during 5 minutes at 800 W. Solutions were prepared with hydrogen peroxide (≥30% Fluka) and ultrapure water (18.2 MΩ·cm, Elga Vivendi).

The experiments to study hydrogen oxidation were performed as follow: (a) before and during the experiment the cell was kept in an argon atmosphere; (b) after flame annealing, the electrode was transferred to the cell and meniscus was made to contact with the IL; (c) then the cyclic voltammetry between -1.0 V and 1.0 V was registered; (d) at the beginning of the second cycle, a hydrogen flux (≥ 99.995% Alphagaz) was allowed to pass through the cell and, finally, it was stopped when the third scan was about to begin. After that, the five subsequent scans were recorded.

3. Results and Discussion

3.1 Purification of the IL

Gnahm and Kolb [6] reported that vacuum treatments are unable to eliminate the impurities of 1-butyl-3-methyl-imidazolium hexafluorophosphate, coming from either “omnipresent humidity” or IL synthesis. They proposed the use of molecular sieves with pore size of 0.3 nm to eliminate the impurities without introducing other contaminants. In the case of platinum single crystals, a quasireversible couple around -0.6 V is observed in the as received IL (Figure 1). After the purification process, this redox signal disappears and a wide potential window with only capacitive currents is observed. The small currents between 0.0 and 0.5 V (arrow) are related to redox reactions of products of the IL oxidation at the upper limit potential value. Also, the yellowish color of the initial reagent disappears after purification.

3.2 Hydrogen oxidation in the IL

Usually, hydrogen oxidation has been studied in saturated solutions [7]. In order to observe interfacial features it is convenient to use more diluted solutions. Under our experimental conditions a H₂ flux of about 40 s in the cell atmosphere is enough to record its oxidation, the reverse process (Figure 2) and also the behavior within the double layer zone (Figure 3).

The use of platinum single crystal electrodes and the flame annealing procedure lead to highly reactive surfaces. The voltammetric profile is similar to that obtained with oxidized microelectrodes [8]. Also, it has a similar behavior observed for hydrogen oxidation in aqueous solution in meniscus configuration [9]: the high currents above 0.5 V observed in the first scan, not present in the subsequent scans, are due to the enhanced diffusion in the meniscus, produced by the gas phase.

The oxidation of hydrogen is slightly surface sensitive (Figure 2). The peak separation and the ratio between oxidation and reduction currents show quasireversible behavior, depending on the electrode structure. The mean potential (0.34 ± 0.005 V vs Ag in electrodes containing {111} and {110} sites) is similar to that obtained on electrochemically activated Pt microelectrodes in related [NTf₂]⁻ imidazolium ILs [7,8]. However, the peak to peak potential difference is almost 100 mV lower, revealing

higher reversibility. Table 1 shows that ΔE increases in the order Pt(111)<Pt(110)<Pt(100). The highest reversibility was obtained with Pt(111). On the other hand, the kinetics of the hydrogen redox reaction is slower at Pt(100) and Pt(210), especially proton reduction. This could be due to particular adsorption of the IL at {100} sites, likely related to the nitrogen atoms [10].

The electrochemical behavior of the H^+/H_2 redox system (Figure 2a) suggests that both solution and adsorbed species are electroactive. Indeed, the peaks current at 0.3 V in presence of hydrogen gas have a linear dependence with the square root of the scan rate. This is why the shape of the voltammograms changes upon redox cycling from the expected one for diffusion controlled kinetics, to the expected one for adsorbed species that are quite symmetrical (Figure 3). In this way, the shape of the voltammogram and the peak separation are better explained in terms of electron transfer from/to adsorbed species. These surface processes appear to be clearly dependent of the surface structure. More work is in progress to elucidate this point.

Comparing the last cycle with the blank (Figure 3), it is observed that the presence of hydrogen and protons generates also a pre-peak around 0.0 V. This peak shows a linear relationship with the scan rate which indicates an adsorption behavior. The fact that protons can be reduced in a wide potential range could be explained if protons are not free but bonded to electronegative anions. This interaction could modify the formal potential of the reaction [11]. Another possibility is that the structure of the adsorbed species changes in this potential range, thus changing the kinetic of the reaction.

The mass transport and the change of H^+ concentration upon cycling break the symmetry between cathodic and anodic peaks as it is observed in Figure 3. These effects are also observed in neutral or alkaline media [12].

3.3 Water and H_2O_2 oxidation

It is also possible to study the hydrogen redox reaction using protons from molecules containing hydrogen, as it can be observed during redox cycling in the presence of water and H_2O_2 (Figure 4). As expected, the oxidation of H_2O_2 begins at lower potentials than the oxidation of water. In both cases, a clear hydrogen oxidation peak at

about 0.4 V is observed. The oxidation of the IL also takes place at potentials higher than 1.0 V because new broad signals were seen after the excursion up to potentials where water is being oxidized (Figure 4a). Comparing the hydrogen redox signals using a dry (Figure 3a) and wet IL (Figure 4), it is clear that the hydrogen redox reaction is more reversible in the dry IL.

The reduction signal between 0.5 V and 1.5 V seems to be related to oxygen reduction to soluble species because this signal disappears when a rotating disk electrode is used. Figure 4b also shows that the oxidation of H_2O_2 does not change the nature of the electrode surface because the background currents are almost constant in the absence or in the presence of H_2O_2 . These results suggest that it is possible to develop electrochemical sensors for hydrogen and H_2O_2 using IL as electrolytes.

4. Conclusions

It was proved that the main hydrogen redox process is slightly structure sensitive in [Emmim][NTf₂]. This observation was possible due to use of low concentrations of hydrogen in a dry IL. It was seen that reversibility of the hydrogen redox reaction decrease in the following order Pt(111)>Pt(110)>Pt(100). The reaction in electrodes with {100} sites showed less reversibility and slower kinetics. In addition, small signals indicate clear structure sensitive reactions associated to adsorbed species. It was possible to detect proton formation from the oxidation of water and H_2O_2 .

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Figure captions

Figure 1 Voltammogram of [Emmim][NTf₂] on Pt(111) before (dashed line) and after purification (solid line). Scan rate 50mVs⁻¹.

Figure 2 a) Voltammogram of [Emmim][NTf₂] on Pt(111) (black line) in the presence of a hydrogen flux through the cell (red line) and when the flux is stopped (blue line). b) Voltammogram for the hydrogen redox reaction (with a flux of H₂) using Pt(111) (solid line), Pt(100) (dashed line) or Pt(110) (dotted line) electrodes. Scan rate 50 mV s⁻¹.

Figure 3 Voltammogram of [Emmim][NTf₂] in absence (dashed line), and presence of hydrogen (solid line) using Pt(hkl) electrodes. It is shown the fifth cycle after the hydrogen flux was suspended. Scan rate 50 mV s⁻¹.

Figure 4 Voltammogram of [Emmim][NTf₂] on Pt(111) in absence (dashed line) and presence (solid line) of a) 6.3 mM H₂O₂, and b) 0.024 mM of H₂O₂ and 0.1 mM H₂O. The second scan is shown. Scan rate 50 mV s⁻¹.

Table caption

Table 1 Peak potentials, peak separation and mean peak values of hydrogen oxidation. Peak potentials were obtained from voltammograms recorded after the flux of H₂ was stopped.

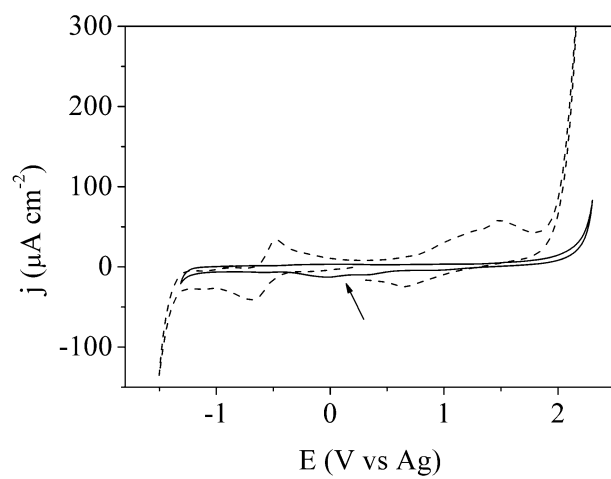


Figure 1

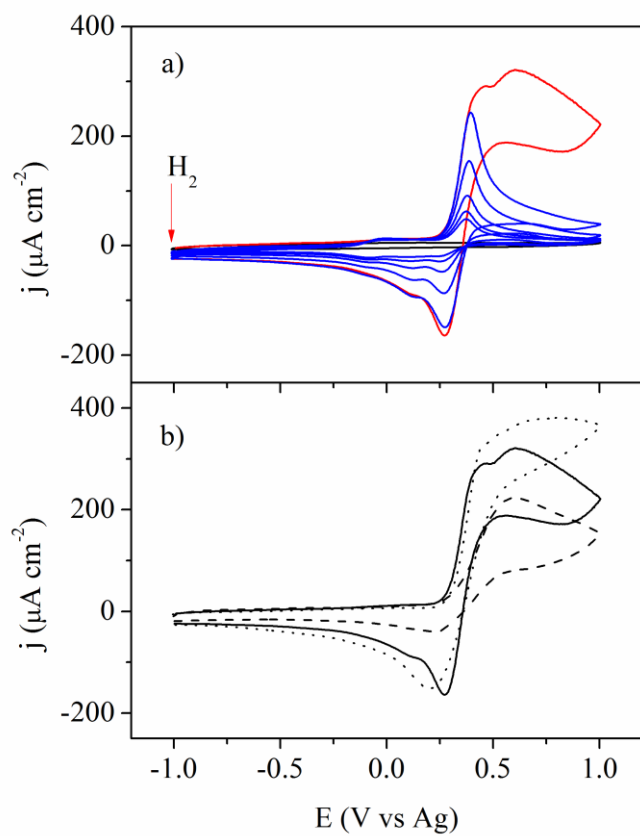


Figure 2

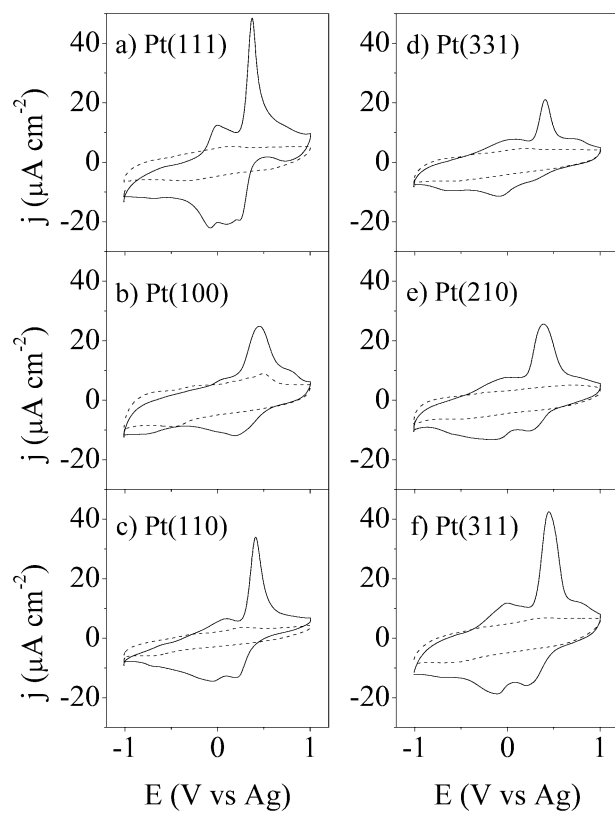


Figure 3

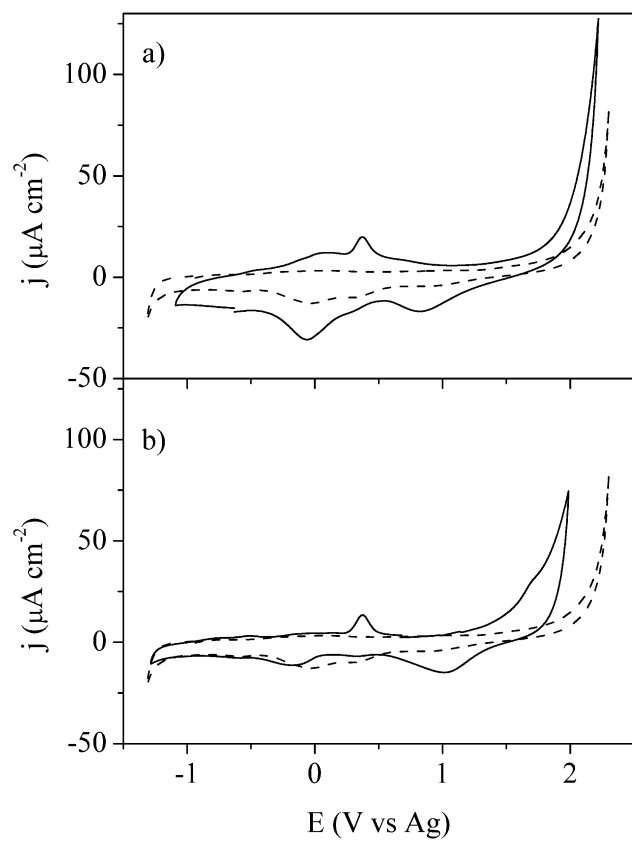


Figure 4

Electrode	Ep oxidation (V)	Ep reduction(V)	ΔE (V)	$E^*_{H^+/H_2}$
Pt(111)	0.426	0.243	0.183	0.335
Pt(311)	0.407	0.252	0.155	0.330
Pt(100)	0.462	0.264	0.198	0.363
Pt(210)	0.478	0.287	0.191	0.383
Pt(110)	0.424	0.225	0.199	0.325
Pt(331)	0.453	0.209	0.244	0.331

Table 1

Highlights

- Hydrogen oxidation was studied on platinum single crystals in [Emmim][NTf₂].
- Hydrogen oxidation was observed even at low concentrations.
- The reversibility and kinetic of the reaction depends on purity of ionic liquid.
- Hydrogen redox reaction in pure [Emmim][NTf₂] is surface sensitive.
- The highest reversibility of hydrogen redox reaction was observed on Pt(111).

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