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Study of the interface Pt(111)/ [Emmim][NTf₂] using laser-induced temperature jump experiments.

Paula Sebastián¹, Andrea P. Sandoval^{1,2}, Victor Climent¹, Juan M. Feliu¹

1 Departamento de Química Física e Instituto Universitario de Electroquímica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

2 Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Cra. 30# 45-03, Edificio 451, Bogotá, Colombia

ABSTRACT:

The interface between a Pt(111) electrode and a room temperature ionic liquid, 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, was investigated with the laser-induced temperature jump method. In this technique, the temperature of the interface is suddenly increased by applying short laser pulses. The change of the electrode potential caused by the thermal perturbation is measured under coulstatic conditions during the subsequent temperature relaxation. This change is mainly related to the reorganization of the solvent components near the electrode surface. The sign of the potential transient depends on the potential of the experiment. At high potential values, positive transients indicate a higher density of anions than cations close the surface, contributing negatively to the potential of the electrode. Decreasing the applied potential to sufficiently low values, the transient becomes negative, meaning that the density of cations becomes then higher at the surface of the electrode. The potential dependence of the interfacial response shows a marked hysteresis depending on the direction in which the applied potential is changed.

Keywords: Ionic liquid, platinum single crystal, potential of zero charge, potential of maximum entropy, laser induced temperature jump, imidazolium

INTRODUCTION:

Room temperature ionic liquids (RTILs) have attained special attention in the last years due to their singular properties as solvents, such as wide electrochemical window, high thermal stability and enough conductivity. Their benefits for electrochemical devices make RTILs promising electrolytes in many applications such as metal electrodeposition, electrocapacitors and electrocatalysis [1-3]. Despite the increasing research focused in RTILs, there is still a lack of knowledge about the structure and properties that characterize the interfacial region between a RTIL and a metal surface [4], especially for well-defined electrode surfaces.

The nature of the interfacial region between a RTIL in contact with a solid electrode cannot be compared with that formed when the electrode is in contact with an aqueous solution. Since a RTIL is a high viscous liquid composed entirely by its ions, the Gouy-Chapman-Stern theory (or other mean field theories), which are valid to study diluted aqueous solutions, fail when are applied to the study of the interface RTILs/electrode [5, 6]. Several works using AFM and STM microscopies [7-13] and others employing spectroscopic techniques [14, 15] show that the RTIL is structured in multilayers on the metal electrode, forming a compact lattice. This result reflects the strong ion-ion interactions between the species of the ionic liquid in addition to the ion-electrode interactions.

Despite the big efforts focused on the study of the interfacial region between an ionic liquid and a metal electrode, the number of studies for Pt group metals is very limited [4, 16-20], especially in the case of Pt single crystals [21, 22]. Platinum surfaces are in general very reactive and have a strong tendency to adsorb the different components of the electrolyte. For that reason, the study of the interface between Pt electrodes and RTIL is expected to be challenging.

The laser induced temperature jump method is a valuable technique for the identification of the sign and magnitude of the contribution to the potential drop due to solvent orientation [23-26]. By using short laser pulses, the temperature of the interface is suddenly raised (in the submicrosecond time scale) and the displacement of the electrode potential is measured at coulstatic conditions during the temperature relaxation [23-31]. The response of the interface through the thermal perturbation is

mainly dominated by the reorganization of the different ionic and dipolar components of the interphase. The increase of the temperature will increase the thermal movement of the different components of the liquid part of the interphase therefore decreasing the potential drop associated to their organization/polarization. The potential at which the transient is zero is the potential of maximum entropy (pme). The pme in water solution is close to the potential of zero charge [26, 27, 32-34].

In the present work the interface Pt(111) / 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([Emmim][NTf₂]) will be analyzed by using laser jump temperature measurements. A clear potential dependence of the potential transients has been observed.

EXPERIMENTAL SECTION:

Before each experiment, the Pt(111) electrode was flame annealed and cooled down to room temperature in a reductive atmosphere composed of a H₂/Ar mixture. The Pt(111) electrode was transferred to the working cell by protecting it with a drop of the same ionic liquid in equilibrium with the H₂/Ar gas mixture. A Ag wire was used as a reference electrode whereas a Pt wire was used as counter electrode. The experiments were carried out with the Pt(111) in the meniscus configuration.

Cyclic voltammograms were recorded using a μ -Autolab III potentiostat (Eco-Chemie, Utrecht, The Netherlands) under the current integration mode.

The [Emmim][NTf₂], (N99% purity), was purchased from IoLiTec. The ionic liquid was purified as reported elsewhere [35].

The laser induced temperature jump experiment was performed as described previously [36]. Pulses of 5 ns of the second harmonic of a Nd-YAG laser (532 nm) were used as laser source, with an energy density around 15-20 mJ/cm² (beam diameter ca. 4 mm), small enough to prevent the damage of the electrode. The only effect from laser irradiation is the increase of the temperature of the interface. The laser energy was measured with a piroelectric sensor head (Model M-935-10). To measure the potential transient, a home-made differential amplifier was used. This amplifier measures the potential difference between the working electrode and another platinum electrode initially polarized at the same potential of the working. Approximately 200 μ s before

the laser pulse, both electrodes are disconnected to ensure true coulostatic conditions. During this time, the drift of the open circuit potential is negligible.

RESULTS AND DISCUSSION:

Figure 1 shows the cyclic voltammogram of the Pt(111) in [Emmim][NTf₂]. The voltammetric profile is free of reversible peaks or redox signals and only shows a small capacitive current. This result evidences that the purification process works successfully [21]. Scanning from positive to negative potentials, the decomposition of the ionic liquid starts around -1.5V, whereas in the opposite direction the decomposition starts around 1.2V. Therefore, the electrochemical window of this ionic liquid for a Pt(111) electrode extends to 2.5 – 3 V which is considerably wide taking into account the high reactivity of this electrode.

Laser pulsed transients were recorded in the potential range between 0.80V and -1.00V to avoid the decomposition of the ionic liquid which could influence the measurement. Cyclic voltammograms were recorded before and after the laser temperature jump experiment. Both voltammograms are essentially identical as shown in the inset of figure 1, assuring the stability of the system during the experiment. The small peak at 0.0 V was always observed in the first cycle and slowly disappeared after a few cycles of the electrode potential. Therefore, its disappearance is not related with the laser irradiation.

Laser pulsed transients were recorded at different applied potential values. Figure 2A shows the results when the potential was changed towards decreasing values. At sufficiently positive potential values, the laser induced transients are positive, indicating that the contribution from the ionic network to the potential of the electrode is negative. Increasing the temperature decreases this negative contribution, therefore resulting in a positive potential shift. This suggests a higher density of anions than cations near the electrode surface. As the applied potential is decreased, the magnitude of the transients also decreases, suggesting a diminution of the potential contribution due to the layering of the ions at the interphase. The potential where the transient is zero is the potential of maximum entropy (pme) [26, 27]. At this potential, the same density of anions and cations should be present close to the surface. This potential value is ca. -650 mV. At potentials more negative than the pme the transient becomes negative. Under those

applied potentials the contribution from the ionic network to the potential of the electrode is positive, indicating that the cation density is now higher than the anion density. This proves that the interchange between the cation and the anion have taken place.

Figure 2B shows the laser induced transients recorded when the potential is varied towards increasing values. These transients were recorded just after recording those shown in figure 2A. In this case, higher values of the potential are needed to restore the positive sign of the transient, indicating a hysteresis in the behavior of the interphase. While the pme appears around -650mV when the potential is changed from positive to negative values, it appears around 0.0V when the applied potential is varied from negative to positive values. These results evidence that the restructuring of the interface in the RTILs is more complex than that observed in classical aqueous solutions [25], where the response is reversible. By using a simple heat transport model it has been shown that the relaxation of the temperature after the laser pulse follows the equation [26, 27]:

$$\Delta T(t) = \frac{1}{2} \Delta T_0 \sqrt{\frac{t_0}{t}} \quad t \geq t_0 \quad (1)$$

Where ΔT_0 is the maximum temperature achieved at the end of the laser pulse and t_0 is the pulse duration.

If the reorganization of the interphase is faster than the time scale of the temperature perturbation and the change of the temperature is sufficiently small, the change of the potential will be given by:

$$\Delta E = \left(\frac{\partial \Delta_M^s \phi}{\partial T} \right)_q \frac{1}{2} \Delta T_0 \sqrt{\frac{t_0}{t}} \quad t \geq t_0 \quad (2)$$

Therefore, a plot of ΔE as a function of $t^{-1/2}$ will give straight lines, with slope proportional to the thermal coefficient $\left(\frac{\partial \Delta_M^s \phi}{\partial T} \right)_q$. Figure 2C and 2D show such plots.

Good linearity was obtained for times longer than 200 ns, demonstrating that the reorganization of the interphase is very fast. Figure 3 shows a plot of the slopes vs. the

applied potential for both scan directions. A clear hysteresis is observed in this plot, demonstrating that a significant overpotential is required to change the layered structure of the ionic liquid next to the electrode, resulting in significantly different values of the pme depending on the scan direction.

These results are in agreement with theoretical studies that demonstrate that negative polarization causes a substitution of anions by imidazolium cations. The cations remain at the first layer even for small positive electrode polarization [37, 38], suggesting that there is a strong adsorption of the cation due to van der Waals interaction with the electrode.

CONCLUSIONS:

The result of the application of the laser induced temperature jump method to the investigation of the Pt(111) / ionic liquid interphase demonstrate a change in the organization of ions at the interphase as a function of the electrode potential. At sufficiently high potentials, positive values of $\left(\frac{\partial \Delta_M^s \phi}{\partial T}\right)_q$ indicate a higher concentration of anions closer to the surface. By decreasing the applied potential, the magnitude of the coefficient $\left(\frac{\partial \Delta_M^s \phi}{\partial T}\right)_q$ decreases, suggesting a progressive replacement of the cation by the anion in the first layer in contact with the electrode. At sufficiently negative potentials, the coefficient $\left(\frac{\partial \Delta_M^s \phi}{\partial T}\right)_q$ becomes negative, indicating that the contribution to the potential from the ionic network has been inverted.

The structure of the interface Pt(111)/RTIL is complex and the response to the thermal perturbation shows marked hysteresis with the applied potential. The high viscosity of the medium due to the strong ion-ion interactions could explain this behavior as well as the interaction ion-electrode. More work is in progress to elucidate the role of electrode structure and chemical nature on these interactions.

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FIGURE CAPTIONS:

Figure1) cyclic voltammogram for Pt(111) in [Emmim][NTf₂]. Scan rate 50 mV s⁻¹. Inset: Comparison of voltammograms before (black) and after (red line) the laser pulsed transients.

Figure2) Laser-induced coulostatic potential transients measured for a Pt(111) in [Emmim][NTf₂] at different applied potentials A) from positive to negative applied potentials B) from negative to positive applied potentials. C) and D) are plots of the potentials transients in A and B), respectively, as a function of $t^{-0.5}$.

Figure3) Plot of the slope of the potential transients in Figures 2C and D as a function of the applied potential, when the potential applied is changed from positive to negative values (red circles) and from negative to positive values (black squares).

Figure 1

Figure 2

Figure 3

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Highlights

- The temperature jump method is used to investigate the Pt(111)/ionic liquid interface.
- A change of polarity is detected as a function of potential
- A potential of maximum entropy is identified.
- The potential dependence of the interfacial response shows significant hysteresis