

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231647541>

Electrochemical Oxidation of Hydrogen on Basal Plane Platinum Electrodes in Imidazolium Ionic Liquids

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · MAY 2011

Impact Factor: 4.77 · DOI: 10.1021/jp201886m

CITATIONS

17

READS

82

5 AUTHORS, INCLUDING:



Adriana M. Navarro-Suarez

CIC Energigune

3 PUBLICATIONS 21 CITATIONS

SEE PROFILE



J.M. Feliu

University of Alicante

488 PUBLICATIONS 11,593 CITATIONS

SEE PROFILE



Marco F. Suárez

National University of Colombia

41 PUBLICATIONS 571 CITATIONS

SEE PROFILE

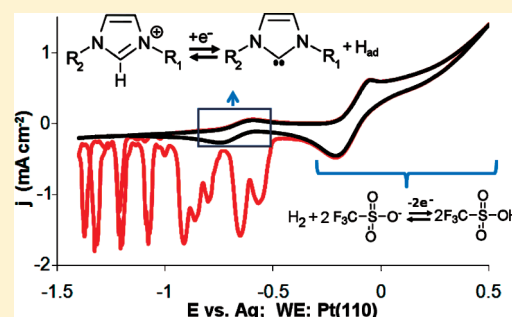
Electrochemical Oxidation of Hydrogen on Basal Plane Platinum Electrodes in Imidazolium Ionic Liquids

Adriana M. Navarro-Suárez,[†] Jonnathan C. Hidalgo-Acosta,[†] Luca Fadini,[‡] Juan M. Feliu,[‡] and Marco F. Suárez-Herrera^{*,†}

[†]Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Cra 30 # 45-03, Edificio 451, Bogotá, Colombia

[‡]Instituto de Electroquímica, Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain

ABSTRACT: In this paper, the electrochemical oxidation of hydrogen at the interface between single-crystal platinum electrodes and imidazolium-type room-temperature ionic liquids (RTILs) is studied. This is the first report about the electrochemical properties of single-crystal platinum electrodes in contact with ionic liquids. It was found that the imidazolium cation can be reduced to 1-alkyl-3-methylimidazol-2-ylidene species on the basal plane platinum electrodes and that the presence of hydrogen increases the reversibility of this process, suggesting that it is a proton-coupled electron-transfer reaction. On the other hand, it was found that the oxidation of H₂ is a surface structure-sensitive process on RTIL/Pt interfaces. The activity toward H₂ oxidation was found to increase in the order of Pt(100) < Pt(110) < Pt(111) in [C₄mim][OTf], [C₂mim][EtSO₄], and [C₄mim][BF₄]. However, in [C₂mim][NTf₂], Pt(100) is the best electrocatalytic electrode for this reaction. Finally, a complex kinetic behavior was observed upon potential cycling of [C₄mim][OTf] saturated with H₂ in contact with Pt(110) as a working electrode. This is the first experimental example of an electrochemical oscillator in RTILs. The competitive adsorption of H₂ and carbenes and the electrode reconstruction, modulated by the adsorbates, can be at the origin of this electrochemical oscillatory behavior. The results presented here are expected to be useful for clarifying the complex nature of the platinum electrode/RTIL interface and to be of practical use for its possible applications in the electrosynthesis of carbenes, electrochemical sensors, and fuel cells.



INTRODUCTION

Because most energy devices can accidentally explode or ignite, there is plenty of incentive to seek safe materials for this kind of applications. Room-temperature ionic liquids (RTILs) show very high ionic conductivity, nonvolatility, and nonflammability.^{1–3} This is why they are being developed for energy devices. It is, therefore, important to have an understanding of the basic electrochemical properties of these interesting materials.^{1–6} Despite the extensive research work on the electrochemical properties of the electrode/RTIL interface, only few electrochemical studies have been done on truly clean and structurally well-defined surfaces^{7,8} and no work has been done using platinum single-crystal electrodes cleaned by flame annealing. To understand the electrochemical processes that take place at this interface, such as the electric double layer, the electrochemical synthesis of carbenes from imidazolium cations and the kinetics and mechanism of redox reactions, such as hydrogen oxidation and oxygen reduction (which are used in batteries, fuel cells, and sensing devices), the use of electrodes with a well-defined surface state is compulsory. In this report, we show our attempts to explore some points of the above subjects using crystalline platinum electrodes.

RTILs can be defined as salts with a melting temperature below the boiling point of water. That is an arbitrary definition, based on temperature, that says little about the composition of the materials themselves, except that they are completely ionic.

RTILs, in general, are salts of nitrogen-containing organic cations and inorganic anions that are fluid over a wide temperature range, including room temperature, with higher viscosities than either aqueous or organic electrolytes at room temperature. RTILs are nonvolatile, nonflammable, and relatively inexpensive to manufacture. RTILs have high ionic conductivities, broad electrochemical windows (about 5 V), and thermal stability. When compared with other electrolytes, some RTILs also have the advantage that they can be obtained in a very dry state, making them especially suitable for applications in electrochemical systems from which moisture must be excluded over long periods of operation. The broad electrochemical window of RTILs allows the study of redox reactions at potentials that cannot be obtained in aqueous, or organic molecular solvents, electrolyte solutions. The intrinsic conductivity of RTILs usually means that the addition of a supporting electrolyte to them may be avoided because they have the role of solvent and electrolyte at the same time.^{1–3}

Despite the great importance of RTILs for new electrochemical processes, relatively little is known about the structure of the metal/RTIL interface.^{4,5} Only a few theoretical studies that dealt with metal/RTIL interfaces have been compared with

Received: February 26, 2011

Revised: May 4, 2011

Published: May 17, 2011

experimental data.⁶ On the other hand, electrochemical studies have rarely been done on truly clean and structurally well-defined surfaces;^{7,8} this, together with the often questionable purity of the RTILs, accounts for the widely differing quality of the reports.

It is of general interest to explore the oxidation of hydrogen (H_2) at the platinum/RTIL interface due to its major importance in fuel cells and sensor applications. The nonvolatility of RTILs means that the sensor does not “dry out”, and their high thermal stability allows gas sensing at high temperatures. The catalytic properties of platinum for this reaction makes this research subject especially important for fuel cell development. Silvester et al.^{9,10} have studied the oxidation of hydrogen on polycrystalline platinum electrodes. The main focus of this work was to study how platinum surface orientation affects the oxidation of H_2 in some ionic liquids. This reaction was studied using as an electrolyte four RTILs incorporating different imidazolium cations and anions, namely, 1-butyl-3-methylimidazolium tetrafluoroborate $[C_4mim][BF_4]$, 1-butyl-3-methylimidazolium trifluoromethylsulfonate $[C_4mim][OTf]$, 1-ethyl-3-methylimidazolium-bis (trifluoromethylsulfonyl) imide $[C_2mim][NTf_2]$, and 1-ethyl-3-methylimidazolium ethylsulfate $[C_2mim][EtSO_4]$.

EXPERIMENTAL SECTION

The RTILs were purchased from Solvent Innovation GmbH. The ionic liquids were vacuum-dried for 4 h at room temperature before each experiment. All experiments, including handling of the RTILs, were performed in a nitrogen atmosphere.

The electrochemical experiments were carried out using a one-compartment electrochemical cell including a platinum counter electrode and a silver wire pseudoreference electrode. Single-crystal platinum surfaces with basal orientations (approximately 2 mm diameter) were used as working electrodes. The platinum electrodes were prepared from small single-crystal beads following the method developed by Clavilier et al.^{11–13} The electrochemical measurements were performed using a computer-controlled potentiostat/galvanostat μ -Autolab II (EcoChemie, The Netherlands).

Prior to any experiment, working electrodes were heated around 180 s in a gas–oxygen flame and cooled in a reductive atmosphere¹⁴ ($H_2 + Ar$ or N_2) inside the electrochemical cell in order to avoid excessive manipulation of the electrodes and contamination with water. The low volatility of ionic liquids makes the latter procedure safe because there is no risk of ignition. The hydrogen flux was then stopped, keeping the flux of Ar or N_2 , and after 120 s, the single-crystal electrode was positioned in contact with the ionic liquid using a meniscus configuration. The scan (cyclic or ac voltammetry) was then initiated. The voltammograms were recorded until no hydrogen electrochemical signals were observed. The electrochemical experiments were repeated until the main characteristics of the voltammograms were constant in different day experiments.

The oxidation of hydrogen, H_2 , was studied in a series of RTILs on single-crystal platinum electrodes with basal orientations. Hydrogen gas was allowed to bubble through the ionic liquids for at least 10 min in order to allow complete saturation at atmospheric pressure (75.06 kPa), as evidenced by stable voltamperograms.

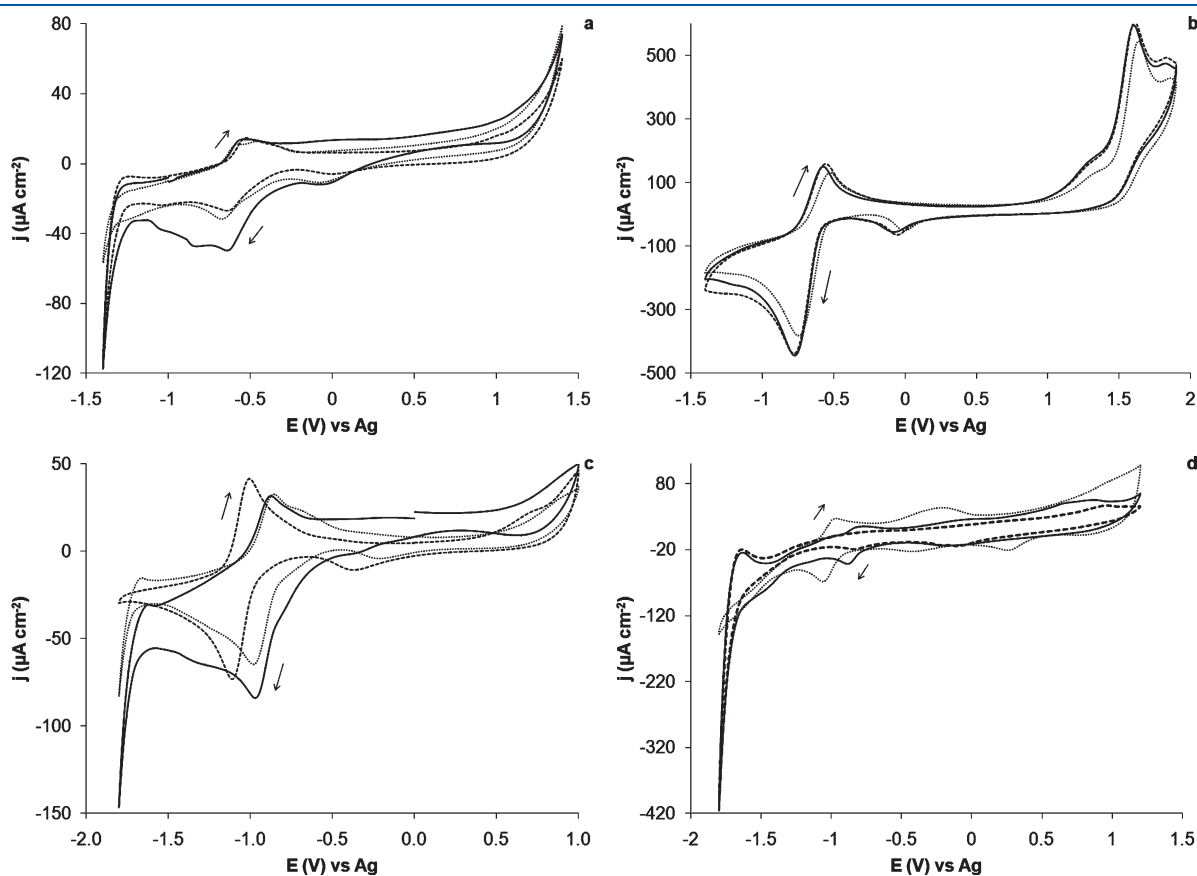
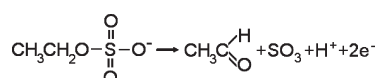


Figure 1. Voltammograms of single-crystal platinum electrodes (100) (dotted line), (110) (dashed line), and (111) (solid line) using as electrolytes the following ionic liquids: (a) $[C_4mim][OTf]$, (b) $[C_2mim][EtSO_4]$, (c) $[C_4mim][BF_4]$, and (d) $[C_2mim][NTf_2]$. Scan rate = $0.01 V s^{-1}$.

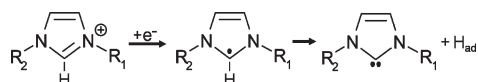
RESULTS AND DISCUSSION

Electrochemical Behavior of Imidazolium RTILs on Single-Crystal Platinum Electrodes. There are many reports^{5,15–17} of cyclic voltammograms of imidazolium RTILs on polycrystalline platinum electrodes that show a flat, “double-layer”-type, behavior over a range between 2 and 4 V. Employing single-crystal platinum electrodes cleaned by flame annealing, the CVs of RTILs are anything but flat. This is demonstrated in Figure 1, which shows a 10 mV/s CV for basal plane platinum electrodes in four imidazolium RTILs. All voltammograms show quasi-reversible waves between -0.4 and -1.2 V. The cyclic voltammogram of $[\text{C}_2\text{mim}][\text{EtSO}_4]$ (Figure 1b) also shows a complex irreversible process at 1.6 V corresponding to the oxidation of $[\text{EtSO}_4]^-$

Scheme 1. Oxidation of Ethyl Sulfate Anion



Scheme 2. Reduction of Imidazolium Cation



(Scheme 1) and/or the oxidation of a new chemical species that is generated from the reduction of $[\text{C}_2\text{mim}]^+$, leading to carbenes, as it is going to be explained later (Scheme 2). The lower homologues of alkylsulfate anions are known for their sensitivity toward hydrolysis.¹⁸ In the presence of water, these anions form the corresponding alcohol, which can be oxidized on the electrode, and hydrogen sulfate. Obviously, this process is undesired for most applications because the ionic liquid system changes dramatically in its properties and an acidic proton is formed that may be a reactive species in many applications.

Redox Behavior of Oxygen and Water in Imidazolium RTILs on Single-Crystal Platinum Electrodes. At this point, it is important to study the effect of oxygen and water on the cyclic voltammograms shown in Figure 1 because those species are likely to be present as contaminants inside the electrochemical cell. Figure 2 shows that, when oxygen is present, the voltammetric profiles for all RTILs studied are completely different. It is clear that the oxygen gives an irreversible reduction signal in $[\text{C}_4\text{mim}][\text{OTf}]$, $[\text{C}_2\text{mim}][\text{EtSO}_4]$, and $[\text{C}_2\text{mim}][\text{NTf}_2]$. On the other hand, a well-defined reduction and oxidation response is observed in $[\text{C}_4\text{mim}][\text{BF}_4]$. Further, the quasi-reversible signal observed between -0.4 and -1.2 V in the absence of oxygen disappears in the presence of oxygen for all RTILs. Finally, no significant difference on the voltammetric profile, for oxygen reduction, was observed when different basal plane platinum electrodes were used; for this reason, only the behavior on Pt(111) is reported.

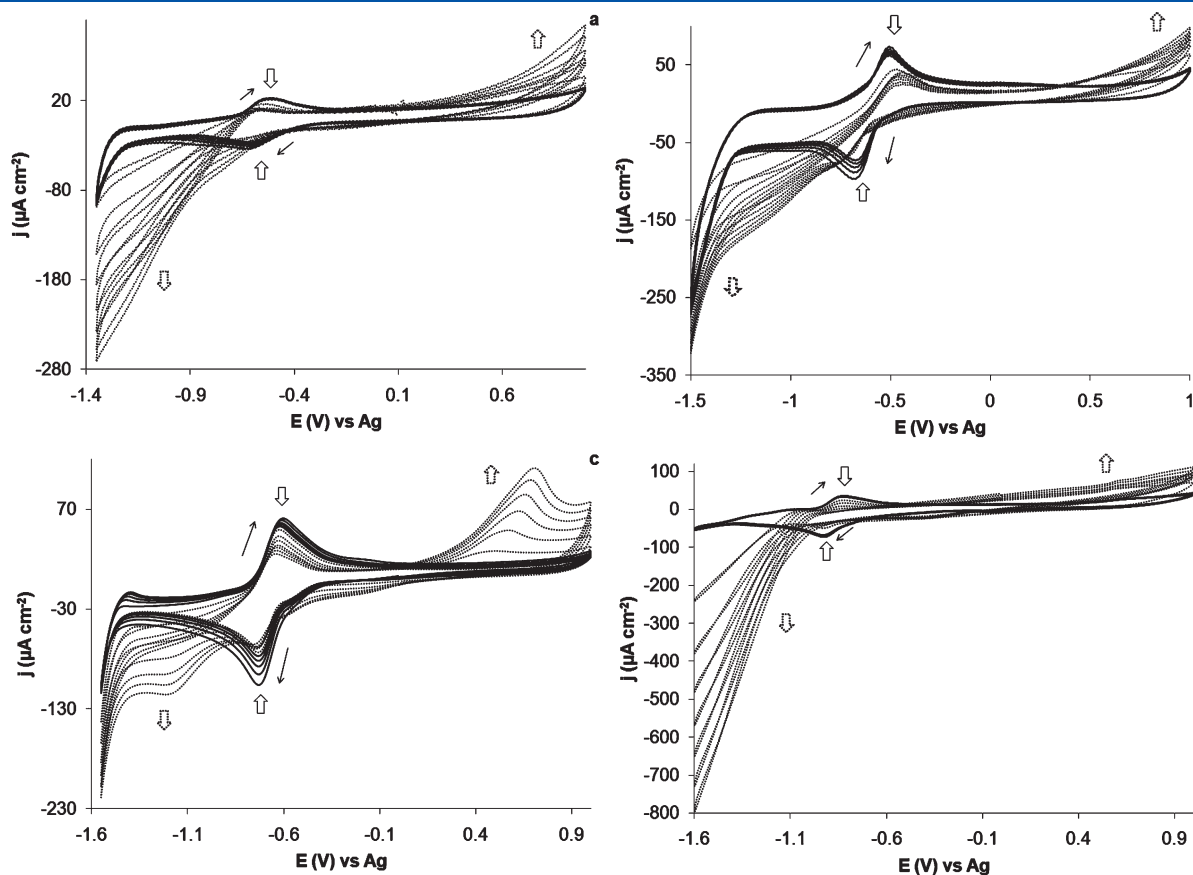


Figure 2. Evolution of the voltammetric profile of the Pt(111) electrode in contact with (a) $[\text{C}_4\text{mim}][\text{OTf}]$, (b) $[\text{C}_2\text{mim}][\text{EtSO}_4]$, (c) $[\text{C}_4\text{mim}][\text{BF}_4]$, and (d) $[\text{C}_2\text{mim}][\text{NTf}_2]$ in a N_2 atmosphere (solid line), and when oxygen diffuses inside the electrochemical cell (dotted line) after stopping the flux of N_2 . Scan rate = 0.025 V s^{-1} .

If the results shown in Figure 2 are compared to the previous reports from other authors using polycrystalline platinum electrodes,^{19,20} it is observed that the onset of the oxygen reduction signal on single-crystal platinum electrodes is at lower overpotentials; the electrochemical signal shifts to positive potentials between 0.3 and 0.5 V. The current loops, observed when $[C_2mim][NTf_2]$ is used, are highly characteristic of processes involving adsorbed species that can poison and/or passivate the electrode surface.

Despite the fact that all researchers agree that $O_2^{\bullet-}$ is the electrogenerated species upon oxygen reduction,^{19,21,22} the stability of this radical anion in the media under consideration is still being investigated. For example, it has been reported that the superoxide ion, electrochemically generated by reduction of oxygen, reacts with the alkyl imidazolium cations of the corresponding ionic liquids at room temperature and atmospheric pressure to give the corresponding 2-imidazolones.²³ Compton et al.¹⁹ have proposed that a strong association between the electrogenerated superoxide anion and the solvent cation is the cause of the positive shift in the back peak potential observed in the CV of the oxygen in $[C_2mim][NTf_2]$. The data shown in this communication suggest that the reduction product of the imidazolium cation, a carbene, affects the kinetics of oxygen reduction. Figure 2 shows that both reactions occur in almost the same potential range and that the oxygen reduction is highly irreversible, possibly due to coupled homogeneous chemical reactions and to the adsorption of poisoning species.

Islam et al.²¹ reported that a catalytic two-electron quasi-reversible process is observed for the oxygen reduction reaction on mercury electrodes, in comparison to Au and Pt electrodes, in $[C_4mim][BF_4]$ and that the adsorption of the 1-ethyl-3-methylimidazolium ion on the surface of mercury plays a crucial role in this reaction. It is well known that proton-coupled electron-transfer reactions, such as the reduction of imidazolium ion (Scheme 2), are favored kinetically and thermodynamically on Pt electrodes in comparison to Hg electrodes.²¹ Taking the latter fact into account, it seems that carbenes are not formed at the same potentials where oxygen is reduced on the Hg electrode. This can explain the higher activity of the Hg electrode because there is no formation of carbenes during oxygen reduction that can poison the electrode surface, as it seems to happen on Pt electrodes.

RTILs, whether they are hydrophobic or hydrophilic in nature, can absorb considerable amounts of water, which changes their physical and chemical properties. The uptake of water from any source reduces the electrochemical window of RTILs and increases its conductivity, and finally, it can be involved in both chemical and electrochemical reactions.²⁴ Figure 3 shows the effect of the addition of water on the voltammetric profile of the three basal plane platinum electrodes in $[C_4mim][OTf]$. It can be seen that the processes observed between -0.4 and -1.0 V become less reversible, the reduction currents increase, and new reduction (with some shoulders) and oxidation peaks appear at about -0.1 and 1.3 V, respectively. The cathodic peak at -0.1 V is due to the reduction of protons, as it will be explained below (Figure 5). It seems that the oxidation peak at about 1.3 V is due to the splitting of water molecules into adsorbed OH and H^+ . The associated reduction peak of this reaction can be hidden by the strong reduction signals of protons and imidazolium cation. In fact, the origin of protons does not matter, either from water (Figure 3) or from H_2 oxidation (Figure 5); the reduction signal associated with proton reduction is at the same position. This suggests that water is completely dissociated in $[C_4mim][OTf]$ at the experimental conditions of Figure 3.

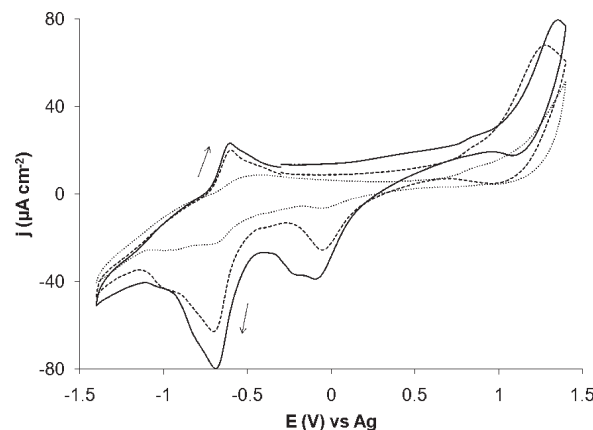


Figure 3. Effect of the presence of water on the voltammograms of single-crystal platinum electrodes (100) (dotted line), (110) (dashed line), and (111) (solid line) using as an electrolyte $[C_4mim][OTf]$. Scan rate = 0.025 V s^{-1} ; $[H_2O] = 0.5\%$.

The presence of a quasi-reversible signal between -0.4 and -1.2 V versus Ag observed for all RTILs studied (Figures 2, solid lines, and 1), which is not due to the presence of oxygen (Figure 2, dotted lines) or water (Figure 3), suggests the formation of free uncomplexed nucleophilic carbenes in ionic liquids at those potentials. It seems that the imidazolium ion can be reduced quasi-reversibly to 1-alkyl-3-methylimidazol-2-ylidene (Scheme 2).²⁵ On the other hand, the same onset potential observed for oxygen and imidazolium ion reduction suggests that oxygen can oxidize the electrochemically formed carbenes. The differences in the shape of the redox signal observed between -0.4 and -1.2 V in Figures 2 and 1 are due to the different potential ranges used. Higher limiting potential (Figure 1) can induce restructuring of the electrodes and the formation of new species that can be adsorbed or to passivate the electrode, affecting in this way the kinetics of the redox processes.

ac Voltammograms of Imidazolium RTILs on Single-Crystal Platinum Electrodes. ac voltammetry is a good technique to study the reversibility of electrochemical processes and the changes of the electric double layer with the applied potential without interference of the IR drop. Figure 4 shows the ac voltammograms of the basal plane platinum electrodes in the RTILs. The shape and height of the peaks change with the direction of the scan, the initial potential, and the electrochemical pretreatment of the electrodes. For this reason, the ac voltammograms reported are those obtained after performing five cycles in the same experimental conditions of Figure 1. For all cases studied, a well-defined peak is observed between -0.2 and -1.2 V vs Ag, which is due to the reduction of the imidazolium cation (Scheme 2). The middle or right side zone of about 1.5 V, where the ac currents are almost constant, represents a potential window within which the current seems to be non-Faradaic in nature; hence, it might be considered as the double-layer charging region.

When $[C_2mim][EtSO_4]$ was used, no significant differences between the ac voltammograms of the platinum single-crystal electrodes were observed (Figure 4). It seems that the electrochemical properties of this ionic liquid are not significantly sensitive to the electrode surface state. On the other hand, on Pt(110), the reduction process of the imidazolium ion is less reversible, for example, the electron-transfer rate is lower, than on Pt(111) and Pt(100) in the other three RTILs studied. Pt(111)

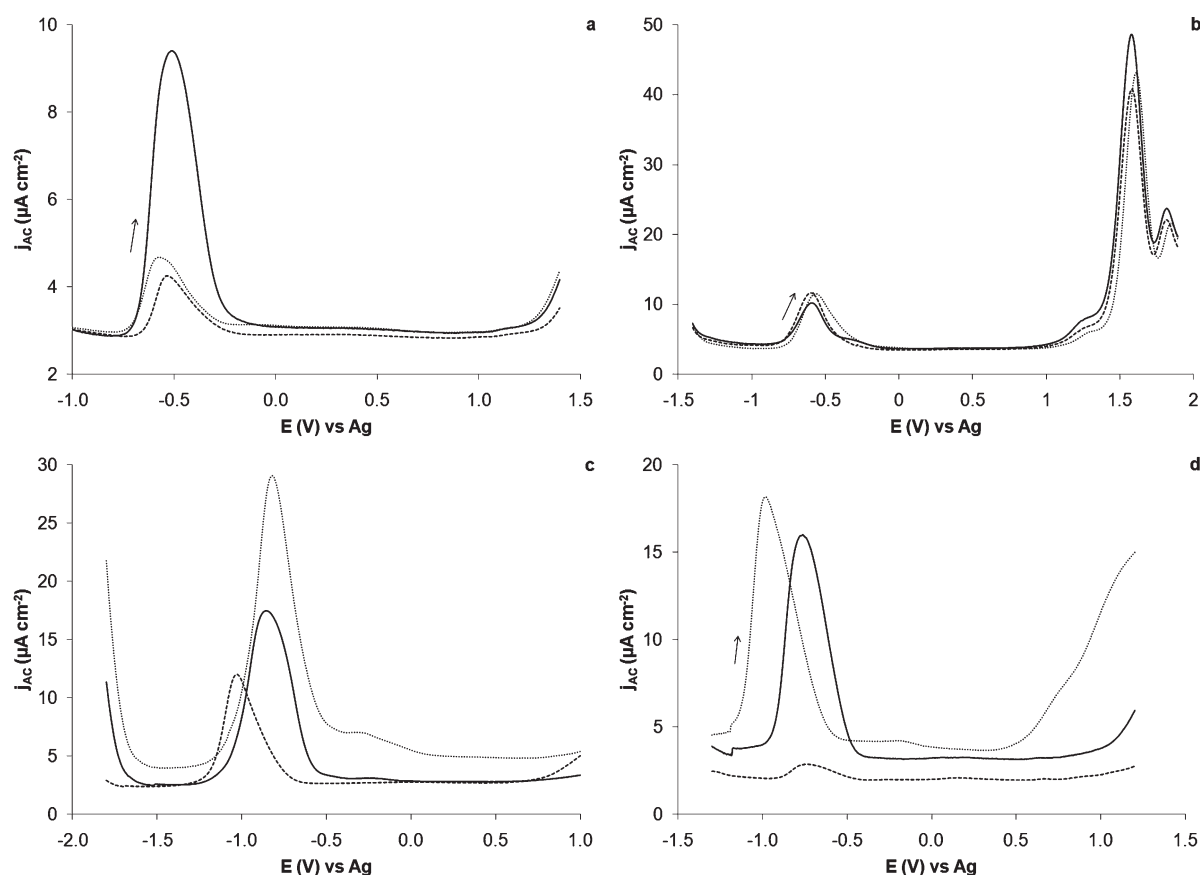


Figure 4. ac voltammograms of single-crystal platinum electrodes (100) (dotted line), (110) (dashed line), and (111) (solid line) using as electrolytes the following ionic liquids: (a) $[\text{C}_4\text{mim}][\text{OTf}]$, (b) $[\text{C}_2\text{mim}][\text{EtSO}_4]$, (c) $[\text{C}_4\text{mim}][\text{BF}_4]$, and (d) $[\text{C}_2\text{mim}][\text{NTf}_2]$. Frequency = 5 Hz; step width = 5 mV.

in $[\text{C}_4\text{mim}][\text{OTf}]$ and Pt(100) in $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_2\text{mim}][\text{NTf}_2]$ have kinetic advantages for the reaction shown in Scheme 2. Finally, the Pt(100) electrode shows the highest currents in the double-layer charging region for all RTILs and it seems that it starts to oxidize at lower potentials.

Redox Behavior of H_2 in Imidazolium RTILs on Single-Crystal Pt Electrodes. After studying the electrochemical properties of basal plane platinum electrodes in RTILs, the oxidation of H_2 in this media was studied. Figures 5 and 6 show the cyclic and ac voltammograms, respectively, of H_2 -saturated RTILs solutions in contact with single-crystal Pt electrodes. The redox processes of H_2 are seen at potentials higher than -0.5 V, whereas the redox reaction of the imidazolium cation (Scheme 1) is seen between -0.4 and -1.2 V. These voltammograms are different from the ones reported by Silvester^{9,10} using polycrystalline platinum electrodes. The first difference is that the onsets of H_2 oxidation currents shift to negative potentials for flame-annealed single-crystal platinum electrodes in comparison with polycrystalline Pt electrodes. For example, in $[\text{C}_2\text{mim}][\text{NTf}_2]$, the onset of H_2 oxidation on single-crystal Pt electrodes is about 0.7 V less negative than that reported for the polycrystalline Pt electrode.⁹ It is unclear why the single-crystal Pt electrodes should be more electrocatalytic than the polycrystalline ones for H_2 oxidation. It might be related to the fact that crystalline electrodes were cleaner than polycrystalline electrodes.

In the second place, the polycrystalline electrode is strongly passivated at higher potentials in $[\text{C}_2\text{mim}][\text{NTf}_2]$ and $[\text{C}_4\text{mim}][\text{BF}_4]$.¹⁰

On the other hand, single-crystal Pt electrodes behave very differently in $[\text{C}_2\text{mim}][\text{NTf}_2]$ during H_2 oxidation: Pt(111) is strongly passivated, Pt(110) is slightly passivated, and Pt(100) is not passivated at all. The highly unusual shape of the voltammograms, in which the current abruptly falls (in $[\text{C}_4\text{mim}][\text{BF}_4]$ and $[\text{C}_2\text{mim}][\text{NTf}_2]$) or increases (in $[\text{C}_4\text{mim}][\text{OTf}]$ and $[\text{C}_2\text{mim}][\text{EtSO}_4]$) at about 0.7 V vs Ag with increasing potential, might indicate that the structure of the adsorbed anions on the surface changes at those potentials, modifying the electron-transfer kinetics (Figure 5). The formation of platinum oxides at those potentials is unlike in the absence of water (Figure 3), and these oxides must inhibit the oxidation reaction and not to promote it, as it is observed in some RTILs (Figure 5a).

Barrette and Sawyer studied the oxidation of H_2 on polycrystalline platinum electrodes in dimethylformamide, dimethyl sulfoxide, pyridine, and acetonitrile.²⁶ They found a passivation region between 0.4 and 1.2 V vs SCE for the electrochemical oxidation of H_2 that is independent of solvent, H_2 partial pressure, scan rate, scan direction, and the use of a preanodization treatment. The authors suggested two mechanisms to explain the electrode passivation: the interaction between platinum and some solution species common to all solvents, such as water or O_2 , and the formation of Pt oxides. From our point of view, it seems that, in RTILs and organic solvents, the adsorption of anions plays an important role on the kinetics of H_2 oxidation. The strong adsorption of anions can passivate the electrode, and the formation of H^+ can help anion desorption through the

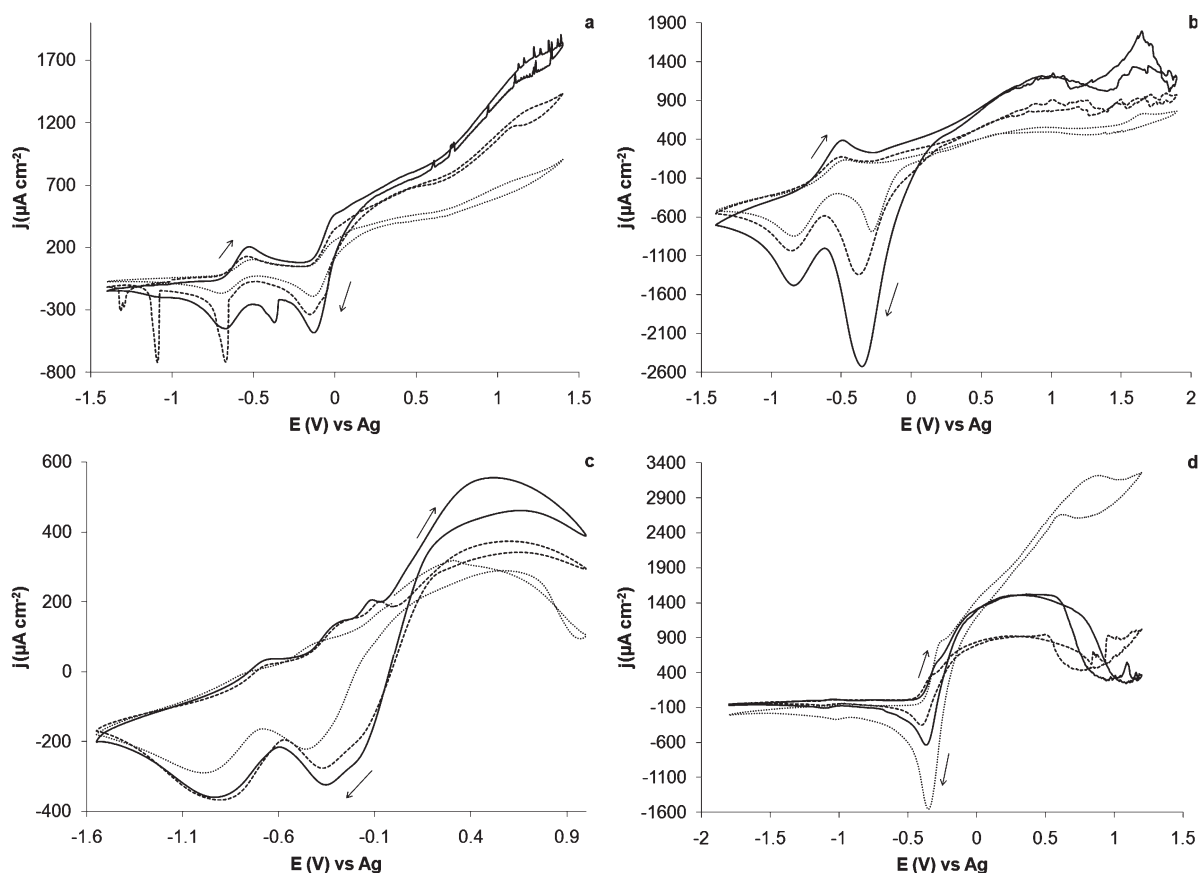


Figure 5. Cyclic voltammograms for the oxidation of a saturated solution of H_2 on single-crystal platinum electrodes (100) (dotted line), (110) (dashed line), and (111) (solid line) using as electrolytes the following ionic liquids: (a) $[\text{C}_4\text{mim}][\text{OTf}]$, (b) $[\text{C}_2\text{mim}][\text{EtSO}_4]$, (c) $[\text{C}_4\text{mim}][\text{BF}_4]$, and (d) $[\text{C}_2\text{mim}][\text{NTf}_2]$. Scan rate = 0.01 V s^{-1} ; atmospheric pressure = 75.06 kPa.

formation of the ionic pair. Those processes have to be surface-sensitive, and it can explain the differences in reactivity between the single-crystal platinum electrodes observed in Figures 5 and 6.

The potential of zero total charge (pztc) in $[\text{C}_4\text{mim}][\text{BF}_4]$ was reported to be approximately -0.5 V vs Ag , and it was also suggested that the ions of a neat ionic liquid are organized in a Helmholtz layer at the electrified metal electrode interface.²⁷ The fact that the pztc is between the electric potential range where imidazolium cation can be reduced (Figures 2 and 1) suggests that there might be an error in this value and on the interpretation of the experimental data. Measuring the pztc of Pt electrodes in contact with RTILs is a challenging problem because both the Pt electrodes and the RTILs are highly reactive, the electrode surface cleanliness cannot be assured, and high-purity RTILs are not available in most cases.

Figures 5 and 6, at potentials higher than 0.7 V , show spikes and/or high-frequency noise-like signals with randomly varying amplitudes. These irregularities occurred only in this region, strongly suggesting that they are intrinsic to the dynamics rather than are caused by instrumental or other types of “external” noise. This behavior is observed when an instable passivating film is formed on the electrodes.²⁸ As explained before, the formation of platinum oxides is unlikely, so it seems that a passivation layer, of species, such as ionic pairs between H^+ and the anions, is formed at the electrode interface.

Silvester et al.¹⁰ reported that the oxidation of H_2 on polycrystalline Pt electrodes is a quasi-reversible process in RTILs

with the anions $[\text{NTf}_2]^-$ and $[\text{OTf}]^-$. Our results show a similar behavior on single-crystal platinum electrodes and in the presence of the anion $[\text{NTf}_2]^-$ (Figures 5 and 6). In the case of $[\text{EtSO}_4]^-$ and $[\text{BF}_4]^-$, this reaction is more irreversible, perhaps indicating the scope for dissociation of the anion. The same authors suggested that the ion BF_4^- is hydrolytically unstable, because it has the tendency to decompose and release highly corrosive species like HF.

The most important observation from Figures 5 and 6 is that the oxidation of H_2 is a surface structure-sensitive process on Pt electrodes. Among the low-index Pt single-crystal surfaces, the activity toward H_2 oxidation was found to increase in the order of $\text{Pt}(100) < \text{Pt}(110) < \text{Pt}(111)$ in $[\text{C}_4\text{mim}][\text{OTf}]$, $[\text{C}_2\text{mim}][\text{EtSO}_4]$, and $[\text{C}_4\text{mim}][\text{BF}_4]$. The increased activity of the more compact surfaces toward H_2 oxidation can be related to weaker anion adsorption at lower overpotentials compared with the less densely packed crystalline planes. In $[\text{C}_2\text{mim}][\text{NTf}_2]$, Pt(100) is the best electrocatalytic electrode. It might be due to a particular reconstruction of the Pt (100) surface in the presence of NTf_2^- anion or to a particularly strong adsorption on four coordinated sites.

On Pt(110) in $[\text{C}_4\text{mim}][\text{OTf}]$ saturated with H_2 (Figures 5a and 7), several current spikes are seen in the negative electrode potential region (ca. -0.5 to -1.4 V) of the voltammograms. Those oscillations were seen only on Pt(110) in $[\text{C}_4\text{mim}][\text{OTf}]$ saturated with H_2 , when the scan rate was between 10 mV s^{-1} (Figure 5a, trace for Pt(110)) and 25 mV s^{-1} (Figure 7) and

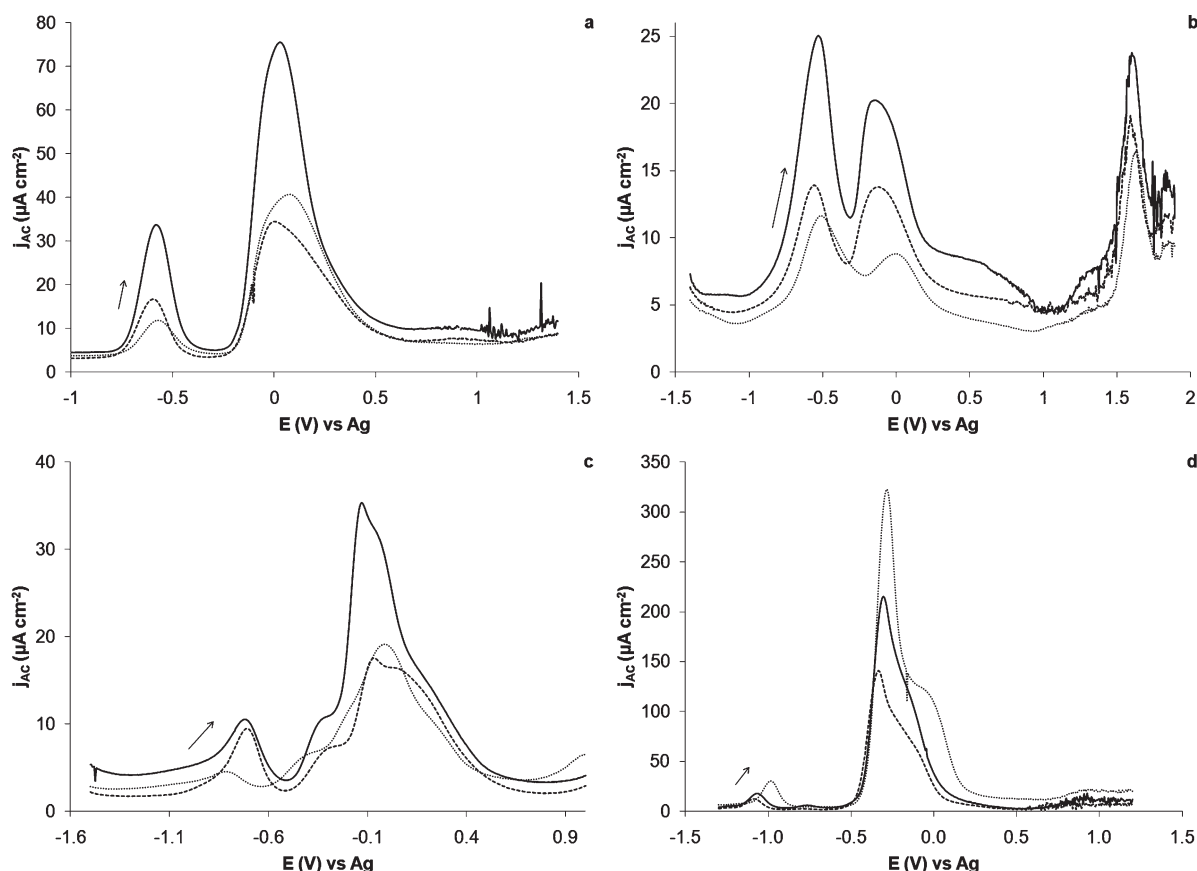


Figure 6. ac voltammograms for the oxidation of a saturated solution of H_2 on single-crystal platinum electrodes (100) (dotted line), (110) (dashed line), and (111) (solid line) using as electrolytes the following ionic liquids: (a) $[\text{C}_4\text{mim}][\text{OTf}]$, (b) $[\text{C}_2\text{mim}][\text{EtSO}_4]$, (c) $[\text{C}_4\text{mim}][\text{BF}_4]$, and (d) $[\text{C}_2\text{mim}][\text{NTf}_2]$. Frequency = 5 Hz; step width = 5 mV; atmospheric pressure = 75.06 kPa.

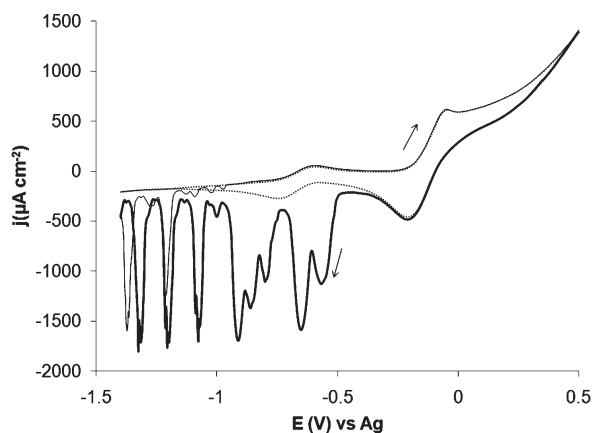


Figure 7. Cyclic voltammograms for the oxidation of a saturated solution of H_2 on a (110) single-crystal platinum electrode in $[\text{C}_4\text{mim}][\text{OTf}]$: when no current oscillations were observed (dotted line) and when they are seen (solid line). The thick line is the negative-going scan, and the thin line is the positive-going scan. Scan rate = 0.025 V s^{-1} ; atmospheric pressure = 75.06 kPa.

when the upper limit potential was higher than 0.5 V vs Ag. It is clear that the shape and frequency of the oscillations change with the experimental conditions. Figure 7 shows two characteristic oscillatory zones: the first one between -0.4 and -1 V vs Ag and the second one between -1 and -1.4 V vs Ag . In the first region,

the oscillations are broad and chaotic, but in the second region, the oscillations are sharp, periodic, and their height remains constant. When low scan rates are used, the oscillations are sharp and they have low frequencies (Figure 5a, trace for Pt(110)).

Either current or potential oscillatory behavior in electrochemical systems is well-known.^{29–31} The spikes of Figures 5a and 7 are seen more frequently in the negative-going scan but sometimes are also seen in the positive-going scan. Voltammograms, such as those in Figures 5a and 7, were no longer obtained when the RTILs are wet or after about 2 h of performing electrochemical experiments using the same sample of RTIL. This suggests that the absorption of water might inhibit the oscillatory behavior and, therefore, the dryness is of great importance to observe the oscillations.

It can be seen that the presence of hydrogen increases the voltammetric currents as well as the reversibility of the signals between -0.5 and -1.2 V (Figures 5 and 6), which are related to the electrochemical reduction of the imidazolium cations (Scheme 2). The latter fact suggests that hydrogen decreases the passivation of the electrode caused by the adsorption of carbenes. It seems that hydrogen competes for the same adsorption sites with the electrogenerated carbenes and, during the positive-going scan, it makes the formation of the imidazolium cation from its carbene form (Scheme 2) easy. The competitive adsorption of H_2 and carbenes can be the cause of the oscillatory instability in the range of potential between -0.4 and -1.4 V (Figure 7).

Electrochemical oscillations are usually observed when the interfacial electrode potential has a certain freedom to choose its own value, either by the presence of an uncompensated series resistance or by driving the cell at a constant applied current.³⁰ Truly potentiostatic oscillations, where the electrode potential is a parameter rather than a variable, are less frequently observed.^{29–31} In this sense, the high resistance of the RTILs and the associated IR drop can be one of the causes of the observed oscillation, but the fact that oscillations were observed only on Pt(110) in [C₄mim][OTf] saturated with H₂ suggests that the oscillations are chemical in nature, and they are the first experimental example of a so-called strictly potentiostatic oscillator in RTILs. Even so, more experiments have to be done in order to clarify this point.

The oscillation observed in Figure 7 can be also explained by considering a reconstruction model.³¹ The key observation leading to the reconstruction model for oscillations on Pt surfaces is that the only orientations displaying oscillatory behavior are those that are structurally unstable, whereas the stable Pt(111) surface merely exhibited bistability in catalytic reactions.³² Of the three low-index planes, only the close-packed Pt(111) surface is stable in its bulklike 1 × 1 termination, whereas the more open (100) and (110) surfaces reconstruct into a quasi hexagonal and a (1 × 2) “missing row” geometry, respectively. The reconstruction of both Pt(100) and Pt(110) can reversibly be lifted by adsorbates. This constitutes an adsorbate-induced phase transition, which is controlled by critical adsorbate coverages.

CONCLUSIONS

To the best of our knowledge, this is the first report about the electrochemical properties of flame-annealed single-crystal platinum electrodes in contact with ionic liquids. The voltammograms show a quasi-reversible signal between −0.4 and −1.2 V versus Ag for all imidazolium-type RTILs studied on the three basal plane platinum electrodes, which is not due to the presence of oxygen or water. This signal has not been observed on polycrystalline platinum electrodes, and it can be due to the reduction of the imidazolium ion to 1-alkyl-3-methylimidazol-2-ylidene. The presence of hydrogen increases the current and reversibility of this process, suggesting that it is a proton-coupled electron-transfer reaction.

One of the most important observations of this study is that the oxidation of H₂ is a surface structure-sensitive process on Pt electrodes and in RTILs. Among the low-index Pt single-crystal surfaces, the activity toward H₂ oxidation was found to increase in the order of Pt(100) < Pt(110) < Pt(111) in [C₄mim][OTf], [C₂mim][EtSO₄], and [C₄mim][BF₄]. In [C₂mim][NTf₂], Pt(100) is the best electrocatalytic electrode for this reaction.

Electric current oscillations, which seem to be chemical in nature, were observed in the voltammograms of [C₄mim][OTf] saturated with H₂ in contact with Pt(110) as a working electrode. They are the first experimental example of an electrochemical oscillator in ionic liquids. The competitive adsorption of H₂ and carbenes and the electrode reconstruction, modulated by the adsorbates, can be the cause of the electrochemical oscillatory behavior.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mfsuarezh@unal.edu.co. Fax: +571 3165220. Telephone: +571 3165000, ext. 14459.

ACKNOWLEDGMENT

This work has been done in the framework of the project DIB-11809, Universidad Nacional de Colombia. J.C.H.-A. acknowledges the scholarship for young researchers “Virginia Gutiérrez de Pineda” (2009) from COLCIENCIAS, M.F.S.-H. acknowledges the Universidad Nacional de Colombia, which supported this research, and J.M.F. thanks MICINN (Spain) for support through project CTQ2010-16271 (Feder).

REFERENCES

- (1) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8*, 621–629.
- (2) Endres, F.; El Abedinw, S. Z. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101–2116.
- (3) Galiński, M.; Lewandowski, A.; Stepniak, I. *Electrochim. Acta* **2006**, *51*, 5567–5580.
- (4) Kornyshev, A. A. *J. Phys. Chem. B* **2007**, *111*, 5545–5557.
- (5) Liu, H.; Liu, Y.; Li, J. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1685–1697.
- (6) Fedorov, M. V.; Georgi, N.; Kornyshev, A. A. *Electrochem. Commun.* **2010**, *12*, 296–299.
- (7) Gnahn, M.; Pajkossy, T.; Kolb, D. M. *Electrochim. Acta* **2010**, *55*, 6212–6217.
- (8) Su, Y. Z.; Fu, Y. C.; Yan, J. W.; Chen, Z. B.; Mao, B. W. *Angew. Chem., Int. Ed.* **2009**, *48*, 5148–5151.
- (9) Silvester, D. S.; Ward, K. R.; Aldous, L.; Hardacre, C.; Compton, R. G. *J. Electroanal. Chem.* **2008**, *618*, 53–60.
- (10) Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G. *J. Phys. Chem. B* **2007**, *111*, 5000–5007.
- (11) Clavilier, J.; Armand, D.; Sun, S. G.; Petit, M. *J. Electroanal. Chem.* **1986**, *205*, 267–277.
- (12) Clavilier, J.; Faure, R.; Guinet, G.; Durand, R. *J. Electroanal. Chem.* **1979**, *107*, 205–209.
- (13) Clavilier, J. *J. Electroanal. Chem.* **1979**, *107*, 211–216.
- (14) Clavilier, J.; El Achi, K.; Petit, M.; Rodes, A.; Zamakhchari, M. A. *J. Electroanal. Chem.* **1990**, *295*, 333–356.
- (15) Silva, F.; Gomes, C.; Figueiredo, M.; Costa, R.; Martins, A.; Pereira, C. M. *J. Electroanal. Chem.* **2008**, *622*, 153–160.
- (16) Migliorini, M. V.; Donato, R. K.; Benvegnia, M. A.; Dupont, J.; Gonçalves, R. S.; Schrekker, H. S. *Catal. Commun.* **2008**, *9*, 971–975.
- (17) Zhang, J.; Bond, A. M. *Analyst* **2005**, *130*, 1132–1147.
- (18) Sowmiah, S.; Srinivasadesikan, V.; Tseng, M. C.; Chu, Y. H. *Molecules* **2009**, *14*, 3780–3813.
- (19) Barnes, A. S.; Rogers, E. I.; Streeter, I.; Aldous, L.; Hardacre, C.; Wildgoose, G. G.; Compton, R. G. *J. Phys. Chem. C* **2008**, *112*, 13709–13715.
- (20) Buzzeo, M. C.; Klymenko, O. V.; Wadhawan, J. D.; Hardacre, C.; Seddon, K. R.; Compton, R. G. *J. Phys. Chem. A* **2003**, *107*, 8872–8878.
- (21) Islam, M. M.; Ferdousi, B. N.; Okajima, T.; Ohsaka, T. *Electrochem. Commun.* **2005**, *7*, 789–795.
- (22) AlNashef, I. M.; Leonard, M. L.; Matthews, M. A.; Weidner, J. W. *Ind. Eng. Chem. Res.* **2002**, *41*, 4475–4478.
- (23) AlNashef, I. M.; Hashim, M. A.; Mjalli, F. S.; Ali, M. Q. A.; Hayyan, M. *Tetrahedron Lett.* **2010**, *51*, 1976–1978.
- (24) O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G. *J. Chem. Eng. Data* **2008**, *53*, 2884–2891.
- (25) Gorodetsky, B.; Ramnial, T.; Branda, N. R.; Clyburne, J. A. C. *Chem. Commun.* **2004**, 1972–1973.
- (26) Barrette, W. C.; Sawyer, D. T. *Anal. Chem.* **1984**, *56*, 653–657.
- (27) Baldelli, S. *J. Phys. Chem. B* **2005**, *109*, 13049–13051.
- (28) Ilevbare, G. O.; Burstein, G. T. *Corros. Sci.* **2003**, *45*, 1545–1569.
- (29) Malkhandi, S.; Bonnefont, A.; Krischer, K. *Surf. Sci.* **2009**, *603*, 1646–1651.

- (30) Koper, M. T. M. *J. Chem. Soc., Faraday Trans.* **1998**, 94, 1369–1378.
- (31) Honda, Y.; Song, M. B.; Ito, M. *Chem. Phys. Lett.* **1997**, 273, 141–146.
- (32) Imbihl, R.; Ertl, G. *Chem. Rev.* **1995**, 95, 697–733.