Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2016 October 20; 120(41): 23542–23551. doi:10.1021/acs.jpcc.6b07067.

Electrochemical Oxidation of Hydrogen in Bis(trifluoromethylsulfonyl)imide Ionic Liquids under Anaerobic and Aerobic Conditions

Yongan Tang and Xiangqun Zeng*

Department of Chemistry, Oakland University, Rochester, Michigan 48309, United States

Abstract

The electrochemical behavior of hydrogen oxidation on a platinum electrode in two aprotic room temperature ionic liquids (RTILs)—1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][NTf₂] and 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide [Bmpy][NTf₂]—was investigated in both anaerobic and aerobic conditions. At platinum electrode in the ILs, the first step of hydrogen oxidation is the formation of Pt–H(ad) (the Tafel step), which is similar to those observed in the aqueous electrolytes. However, there are differences in the oxidation steps (the Heyrovsky and Volmer steps). In ILs, the oxidation of Pt–H(ad) forms a hydrogen radical and a proton rather than a proton or a water in aqueous acid or alkaline electrolytes, respectively. This difference is significant as it results in a completely different following reaction pathway in the anaerobic vs aerobic conditions. A coupled chemical reaction between oxygen and hydrogen oxidation intermediates was observed in aerobic conditions which has a correlation with hydrogen concentrations. Furthermore, the overall rate of hydrogen oxidation is shown to be much higher in [Bmpy][NTf₂] than that of [Bmim][NTf₂], which is rationalized as the result of both higher solubility of hydrogen and the unique IL–electrode interface structure which promotes the hydrogen adsorption in [Bmpy][NTf₂] than that of [Bmim][NTf₂]. This study is the first example showing that hydrogen oxidation mechanism in aprotic ILs follows two different oxidation mechanisms in anaerobic and aerobic conditions.

Graphical Abstract

*Corresponding Author: (X.Z.) zeng@oakland.edu, phone 248-370-2881.

Notes

The authors declare no competing financial interest.

INTRODUCTION

The hydrogen oxidation reaction (HOR) is one of the most important reactions in both fundamental and applied chemical science, particularly in connection with the alternative energy research field.¹ In aqueous electrolytes, hydrogen oxidation involves an intermediate adsorption step, and a volcano curve of reaction rate of hydrogen oxidation versus the free energy of adsorption of the intermediate exists.^{2,3} It was shown that the rate of HOR reaction depends on both the solvent and the electrode material, and platinum is found to be the most suitable material for providing appropriate adsorption energy and the best catalyst in hydrogen evolution and HOR.⁴ Electrolytes have been found to affect the HOR with 2 orders of magnitude lower reactivity in alkaline electrolyte than that in acidic electrolytes.^{5,6} Most studies of HOR in the literature are carried out in aqueous electrolytes with platinum electrode under aerobic conditions.⁷ In aqueous electrolytes, the reaction kinetics of HOR is very facile with larger value of the exchange current density (j_0) compared to that of oxygen reduction reaction (ORR).^{8,9} While the aerobic oxidation of hydrogen is of significant importance in developing hydrogen fuel cells, the anaerobic oxidation of hydrogen is essential for understanding microbial metabolism. Although the oxidation of hydrogen is considered to be one of the simplest electrochemical reactions, involving a one-electron transfer process, the mechanism of HOR in nonaqueous solvents is not well studied. A few studies of hydrogen oxidation in nonaqueous solvents were conducted in the anaerobic environment. For example, Sawyer et al. investigated the redox process of hydrogen in four conventional organic solvents in anaerobic conditions—*N,N*-dimethyl-formamide (DMF), dimethyl sulfoxide (DMSO), pyridine (pyr), and acetonitrile (MeCN)—and reported the reproducible process of hydrogen oxidation in these organic solvents.¹⁰ They found that the peak current of cyclic voltammetry was directly proportional to the partial pressure of dissolved hydrogen and can be used for quantitative determination of the hydrogen solubility in these solvents. In addition, several groups have investigated the hydrogen oxidation process in protic ILs at anaerobic conditions (i.e., Ar or N₂) for their potential applications in the hydrogen fuel cells.^{11,12} The protic ionic liquids (PILs) are often formed by the transfer of a proton between a Brønsted acid and a base and display interesting properties due to their “free” available proton (e.g., hydrogen bond).^{13,14} For example, the hydrogen redox reactions in a number of protic ionic liquids (e.g., diethymethylammonium bistrifluoromethanesulfonimide) shows a significant potential gap (0–800 mV) between the potential at which proton reduction occurs and the potential at which facile hydrogen oxidation occurs. This was explained based on the difference in the energy for proton extraction from the anion (acid with the form HA: $\text{HA} + \text{e}^- \leftrightarrow \text{A}^- + \frac{1}{2}\text{H}_2$) and from the cation (acid with the form BH⁺: $\text{BH}^+ + \text{e}^- \leftrightarrow \text{B} + \frac{1}{2}\text{H}_2$).¹¹ In another study of protic ionic liquid diethylmethylammonium trifluoromethanesulfonate,¹⁵ [dema][TfO], at Pt electrodes, the hydrogen oxidation mechanisms were proposed to follow the Tafel–Volmer and Heyrovsky–Volmer pathways, and the under-potential-deposited hydrogen atoms (H_{upd}) can block adsorption and electrooxidation of hydrogen at the Pt surface. It is widely accepted that hydrogen oxidation involves intermediate adsorption during the hydrogen redox processes and the electrode–electrolyte double layer structure is very important for its kinetics.^{11,16} For example, in aqueous electrolytes, the weakly solvated spherical ions, such as SO₄²⁻, Br⁻, and I⁻ were known to form ordered layers at the electrolyte/electrode

interface.¹⁷ We intend to investigate the mechanisms of hydrogen oxidation in aprotic ILs with different cations or anions structures in anaerobic and aerobic conditions to further understand how molecular structure of ILs and environmental condition affect the electron transfer process of hydrogen oxidation in the ILs. In the aprotic ILs, electrostatic interactions are dominant factors for the interfacial structure which are different from those in solvent-based electrolytes where ions are surrounded by a significant amount of solvent molecules.¹⁸ The organic cation or anions of the ILs could adsorb specifically or nonspecifically on the metal surfaces.¹⁹ The nonaromatic ([Bmpy]⁺) and heteroaromatic ([Bmim]⁺) cation in the [NTf₂]-based ILs display uncomplicated electrochemical reactivity and represent unique structural and chemical properties to study their effects on the HOR electrode reaction kinetics. HOR processes are extremely sensitive to the electrode interfacial properties, and they serve as ideal systems to investigate the adsorption dynamics of the ionic liquids at metal electrodes. The [NTf₂]⁻-based ILs were selected since they were proven to form a stabilize protonated product [HNTf₂]^{20,21} and have good electrochemical stability and wide potential window. In our early work, we have demonstrated that IL–electrode interface double layer structure plays a significant role in the selective gas adsorption.²² Hydrogen is the smallest gas molecule, and its oxidation has facile kinetics at platinum electrode. The aromatic 1-butyl-3-methylimidazolium [Bmim]⁺ and heterocyclic 1-butyl-1-methylpyrrolidinium [Bmpy]⁺ will allow us to understand the adsorption of IL ions at the interface and their influence on the adsorption of hydrogen and on the reactivity of hydrogen oxidation process. Thus, these two ILs provide a comparable system to understand the surface structure of the IL–electrode interface and the coverage of the adsorbed ions from the IL electrolytes on the rates of HOR electrode reactions on platinum.^{23–25} The results of this study will allow us to detail the mechanisms of hydrogen oxidation in the ILs in both aerobic and anaerobic environments for many scientific and technological applications.

EXPERIMENTAL SECTION

Chemicals and Reagents

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Bmpy][NTf₂], 99%) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf₂], 99%) were purchased from IOLITEC Inc. and prepared by standard literature procedures.²⁶ Briefly, all ILs were dried before used in the electrochemical experiments in a vacuum oven (70 °C) overnight until no visible sign of the water peak in the IR spectrum was observed. Using this drying process, the water level could be limited to less than 25 ppm in our IL system.^{27,28} The parameters of ILs at 0.101 MPa (1 atm) are listed here for better comparison. The viscosity of [Bmpy][NTf₂] and [Bmim][NTf₂] is 79 and 54 cP, respectively,²⁹ and the solubility of hydrogen in [Bmpy][NTf₂] and [Bmim][NTf₂] is 0.90 and 0.77 mM, respectively.³⁰ High purity gases (nitrogen, hydrogen and air, 99.99% purity) were obtained from Airgas Great Lakes (Independence, OH).

Electrochemical Cell and Instrumentation

A back-flow electrochemical gas cell (i.e., Clark-type electrochemical cell) was used in this study similar to our previous investigation, as shown in Scheme 1.³¹ This design enables the gas analyte to reach the working electrode surface right after passing through the gas

permeable membrane. This electrochemical cell design permits fast response of gaseous analyte redox process and has been widely used for gas sensors using aqueous electrolytes.^{32,33} A platinum gauze (Sigma-Aldrich) was used as a working electrode that was directly contacting gas permeable porous Teflon membrane. The electrochemical active surface area (5.96 cm^2) was calculated by the hydrogen adsorption/ desorption charges ($210 \mu\text{C cm}^{-2}$) of platinum electrode in 0.1 M HClO_4 . The analyte (hydrogen) was purged through gas inlet and diffused onto working electrode without diffusion through thick layers of the IL electrolyte. Counter and reference electrodes (0.5 mm diameter platinum wires) were placed into the ILs for providing electron flow and stable potential and separated by filter papers; an amount of $150 \mu\text{L}$ of IL was added into the electrochemical cell as electrolyte.

Electrochemical Characterization Methods

All electrochemical measurements were performed with a CHI 1000A electrochemical workstation (CH Instrument, Inc.). All of the potentials reported were referenced versus ferrocene unless specifically noted. The total gas flow rate was maintained at 200 sccm (standard cubic centimeter per minute) by digital mass-flow controllers (MKS Instruments, Inc.), and the volume ratio (v/v)% of hydrogen to nitrogen was adjusted by two mass-flow controllers, in which one was used to control the background gas flow (Air or N_2) and the other was used to control the analyte gas flow. Before each experiment, pure nitrogen gas was flowed through the cell overnight as the background gas for removing the oxygen and other residual gas inside the electrochemical cell. Based on our previous oxygen sensing investigation, the overnight nitrogen purging will provide an anaerobic environment for containing less than 0.03% oxygen in the system.³⁴ The cyclic voltammetric measurements were recorded directly in the potential range of -0.50 to 1.00 V . During HOR measurements, potential sweeps were started at 0 V to negative to ensure that no reaction occurred at the initial stage. For the anaerobic condition investigation, the cyclic voltammetry and chronoamperometry results were recorded in sequence with purging nitrogen for 1 hour between experiments for restoring the electrochemical cell into the original condition. For the aerobic experiment, the cell was purged with air for 2 h before the measurement, and the cyclic voltammetry was analyzed at aerobic condition until oxygen reduction peak was observed. Electrochemical experiments were conducted at room temperature ($22 \pm 1^\circ\text{C}$).

RESULTS AND DISCUSSION

Hydrogen Oxidation in Anaerobic Conditions

We select $[\text{NTf}_2]^-$ based aprotic ILs with two different cations $[\text{Bmim}]^+$ and $[\text{Bmpy}]^+$ (also abbreviated as $[\text{C}_4\text{mim}]^+$ and $[\text{C}_4\text{mpy}]^+$) to investigate the mechanism of hydrogen oxidation at platinum electrode in ILs at both aerobic and anaerobic conditions. We performed cyclic voltammetry and constant potential chronoamperometry to quantitatively study the effects of ILs on the hydrogen oxidation processes. Figure 1 presents multiple cycles of the cyclic voltammograms of hydrogen oxidation processes in two ILs in different potential windows under anaerobic conditions. Several reports show that there is a potential dependent hysteresis at the electrified IL–electrode interface.¹⁸ However, Figure 1 shows that the steady state current can be reached and maintained within only a few subsequent cycles,

suggesting that the HOR redox processes does not affect the IL–electrode interface structure and the peak current as well as the peak potential is stable during the HOR redox reactions.

As shown in Figure 1a, the voltammetry of (1%, v/v) hydrogen in [Bmpy][NTf₂] shows a broad oxidation peak at 0.20 V and partially reversible reduction peak at 0.10 V. In [Bmim][NTf₂], the same concentration of hydrogen (1%, v/v) was tested. However, as the data indicate in Figure 1b, the peak current in [Bmim][NTf₂] is only half of that in [Bmpy][NTf₂] IL (Figure 1a). The viscosity of ILs and the solubility of hydrogen in the ILs as well as the surface available adsorption sites of the platinum electrode should all contribute to the current signals in the electrochemical approach. At 0.101 MPa (1 atm), the viscosity of [Bmpy][NTf₂] and [Bmim][NTf₂] is 79 and 54 cP.²⁹ The solubility of hydrogen in [Bmpy][NTf₂] and [Bmim][NTf₂] is 0.90 and 0.77 mM, respectively.³⁰ We use back-flow gas cells, which will allow the diffusion coefficient difference of hydrogen in both ILs to be minimized. Additionally, the diffusion of product H⁺ away from the electrode interface also contributes to the observed currents and the rate of the reactions. Since we use the same anion ([NTf₂]), the ion pairing H[NTf₂] in both IL is the same. Thus, the current signal obtained will be mainly due to the solubility and also the availability of the platinum surface sites for hydrogen adsorption. The electrode surface available sites would affect the adsorption behavior of analyte and serve as an indirect evidence of the IL–Pt electrode interface structures.^{35–37} The electrode material and interface properties often determine the reaction rate of the electrochemical redox processes.^{38,39} Since we use the same electrode material of platinum, we should be able to understand the IL–electrode interface properties on the overall reaction rate of hydrogen oxidation.

Since both ILs have the same anion, the difference of the voltammetric behavior should come from the effect of cations which results in the different solubility of hydrogen (0.90 mM vs 0.77 mM).³⁰ The ratio of solubility of hydrogen in [Bmim][NTf₂] vs [Bmpy][NTf₂] is 0.85, which is much higher than the peak current ratio of two ILs for hydrogen oxidation (0.50). Thus, the difference of the IL–Pt interface properties contributes partially to the smaller current signal in [Bmim][NTf₂]. The observation here provides an opportunity for investigating the cation effect at the IL–Pt interface on hydrogen oxidation in these ILs.

The electrochemical oxidation of the hydrogen on the polycrystalline platinum electrode in acidic aqueous electrolytes is considered to proceed through

- a. dissociative adsorption reaction (Tafel step):

- b. truncated electrodesorption (Volmer step):

- c. combined dissociative/electrosorption (Heyrovsky step):

where M is active adsorption site at the electrode. These three reactions are historically referred to as the Tafel, Volmer, and Heyrovsky reactions, respectively. The HOR can proceed via either the Tafel–Volmer mechanism or the Heyrovsky–Volmer mechanism depending on whether the preceding dissociative adsorption step is a pure chemical process or not. As shown in Figure 2, the voltammetry in the [Bmpy][NTf₂] for hydrogen oxidation present quasi-reversible behavior at all scan rates studied. The linearity between peak current and scan rate indicates a surface process for hydrogen oxidation which is consistent with the Tafel reaction mechanism. The scan rate results in Figures 2b and 2d confirm the same surface process of hydrogen oxidation in [Bmim][NTf₂].

The elementary steps of hydrogen oxidation in the IL should be similar to that of the Tafel–Heyrovsky–Volmer mechanism reported in the aqueous solvents (i.e., as shown in eqs 1–3). However, the oxidation kinetics of atomic H on platinum in the ILs should be facile since it occurred at a less positive potential (Figure 2). In addition, since different solubilities of hydrogen in [Bmpy][NTf₂] and [Bmim][NTf₂] present different current response in hydrogen oxidation, the adsorption process in eq 4 should be the rate-determining step for the hydrogen oxidation in the ILs.

Table 1 summarizes the peak potentials and separations of the oxidation of hydrogen and the reduction of proton. The oxidation potential for hydrogen in [Bmpy][NTf₂] is less positive than that in [Bmim][NTf₂], which represents a higher catalytic activity of hydrogen oxidation in [Bmpy][NTf₂] on the platinum electrode. In addition, the peak separation of hydrogen oxidation and proton reduction in [Bmpy][NTf₂] is much smaller than that in [Bmim][NTf₂] (0.11 V vs 0.21 V), which suggests a more reversible redox process in [Bmpy]-[NTf₂]. Thus, [Bmpy][NTf₂] is a better electrolyte for hydrogen oxidation based on its higher solubility and suitable interface structure of hydrogen adsorption, which results in the higher current at the same concentration of hydrogen and less positive oxidation potential than that of [Bmim][NTf₂].

In a potential sweep experiment, the charging current, i_c , is always present as the baseline for the measurement of faradaic current, i_f , due to the continuously changing potential throughout potential cycling. The charging current relates to the scan rate and can be calculated through the equation of $|i_c| = AC_d v$, where A is the electrochemical active surface area, C_d states for the capacitance of double layer charging, and v is the scan rate. The capacitance of the electrical double layer can provide the information that relates to the IL–electrolyte interface structure. Table 1 also shows the capacitance (C_d) in the two ILs studied that was obtained from the charging current during the oxidation process of hydrogen in Figure 2. The capacitance in [Bmpy][NTf₂] is more than doubled when compared to that of [Bmim][NTf₂]. Since the capacitance ($C_d = \epsilon A/d$) relates to the dielectric and the double layer thickness, the slightly larger dielectric constant (ϵ) of [Bmpy][NTf₂] (11.70) should contribute to the larger value of capacitance compared to the dielectric constant of [Bmim][NTf₂] (11.60).⁴⁰ Another possible contribution is the interaction of hydrogen and [Bmim]⁺ cations, in which aromatic ring of [Bmim] cation will interact with hydrogen which causes a tilted structure due to the small spacing of [Bmim]⁺ cations and the increase the double layer thickness.⁴¹

Hydrogen Oxidation in Aerobic Conditions

For practical applications such as fuel cells, it is important to study HOR in the presence of oxygen in ILs. Figure 3 shows the multiple CVs with and without the presence of 1% (v/v) hydrogen in air environment. The major difference of the CVs between nitrogen and air environment is the appearance of oxygen reduction peak at -1.20 V. The oxygen reduction processes in ILs with the formation of superoxide radicals have been well-studied.^{31,42} As shown in Figure 3, a much smaller anodic peak at 0.40 V was observed for the oxidation of hydrogen in both ILs compared to the value in nitrogen environment. One obvious difference between two ILs is the change of the oxygen reduction current, in which [Bmpy][NTf₂] shows a 2 times increase of the oxygen reduction current in the presence of hydrogen while no obvious change was observed in [Bmim][NTf₂]. A similar increase of oxygen reduction current was observed previously by our group for studying methane oxidation,⁴³ in which the unique double layer structure of [NTf₂][−] anion can facilitate the adsorption and oxidation of methane. In addition, our previous study also shows that the initial oxidation of platinum surface is an important process that determines the reactivity of methane.⁴⁴ The increased current of oxygen reduction in [Bmpy][NTf₂] indicates that a new equilibrium was established when hydrogen was introduced. In the absence of hydrogen, the oxygen reduction current obtained in both ILs in air environment is similar, although the solubility of oxygen is higher in [Bmpy][NTf₂] (7.10 mM) than [Bmim][NTf₂] (4.30 mM).⁴⁵ However, with the presence of hydrogen, the reduction current of oxygen increased in [Bmpy][NTf₂]. As discussed above, the formation of superoxide radical in cyclic voltammetry might lead to the formation of platinum oxide at positive potentials, which in turn increases the reduction current of oxygen at -1.20 V due to the accumulation of oxygen at electrode surface. It is found that the oxidation current for platinum electrode at 0.50 V in [Bmpy][NTf₂] is 2 times higher than that in [Bmim][NTf₂], which indicates easier surface oxide formation in air environment in [Bmpy][NTf₂] compared to that of [Bmim][NTf₂]. The higher affinity of [Bmim]⁺ cation to platinum surface is well explained by the lower oxidation current of electrode and the unchanged reduction current in the present of

hydrogen in [Bmim][NTf₂]. In addition, isopotential points (IP) were observed at (−1.10 V) for oxygen reduction process in both ILs, indicating a coupling reaction of oxygen redox process with the hydrogen oxidation process. Thus, in aerobic conditions, the oxidation of hydrogen shows different oxidation behavior compared to anaerobic condition presented by the smaller oxidation current and higher oxidation potential. The presence of oxygen can alter the reaction pathways of hydrogen oxidation in ILs, and the electrode reaction mechanism is proposed as the following:

In cyclic voltammetry, superoxide radical could be trapped near electrode surface and involved in the oxidation of hydrogen as shown in the proposed redox mechanism above. However, based on the above CV investigation, it still remains unclear for the role of oxygen in hydrogen oxidation when superoxide radicals were not present in the system. Thus, chronoamperometry was employed to further characterize the electrochemical behavior of hydrogen in anaerobic and aerobic conditions to understand the reaction mechanism of hydrogen oxidation in the presence of oxygen.

Potential Step Experiments To Characterize the HOR Reactions in Aerobic Condition

As discussed above, in aerobic conditions, it is possible that the coupling reactions between oxygen and the intermediate of hydrogen oxidation may occur. Thus, we use the potential step experiments at various hydrogen concentration (0.05%–1.00%, v/v) in nitrogen and air environment to further understand the mechanism. We selected the positive oxidation potential (+0.40 V) based on the peak potential of hydrogen oxidation from the cyclic voltammetry results in both anaerobic and aerobic conditions. At this potential, no oxygen reduction process will occur. The current vs time responses in different background gases (nitrogen and air) are presented in Figure 4. The exposure time of hydrogen at various concentrations was chosen as 300 s, which is a standard chronoamperometry parameter in the electrochemical gas sensor study.⁴³ It is found that the background gases (N₂ vs air) have little effect on the hydrogen oxidation process in [Bmim][NTf₂] (red curves in Figures 4a and 4b). However, a significantly different current signal response was observed in [Bmpy][NTf₂] in air or in N₂. The air background affects the current signals both for the initial introduction of hydrogen gas (i.e., the oxidation of hydrogen process) as well as the late

stage of removal of hydrogen in the constant potential chronoamperometry, as shown in Figures 4a and 4b. In the presence of oxygen, hydrogen oxidation chronoamperometry data show a positive current spike with the introduction of hydrogen and a negative current spike with the removal of hydrogen, as shown in Figure 4b. The oxygen in air should involve in the hydrogen oxidation process, in which a reduction process occurred during the oxidation of hydrogen and leads to a negative current. The reduction process was evidenced by the positive current spike observed for the introduction of hydrogen as well as the negative current spike observed during the process of removal of hydrogen. If the hydrogen oxidation process follows the Tafel–Volmer reaction pathways, the oxidation step (eq 6) is not the rate-determining step; the oxidation of hydrogen would be fast enough to not form any intermediates that can react with oxygen. Thus, we proposed the Heyrovsky–Volmer reaction pathways (eqs 4 and 5) for the oxidation of hydrogen in ILs for forming the intermediate of $\text{Pt-H}^\bullet$ that can react with oxygen and contribute to the negative reduction current in $[\text{Bmpy}][\text{NTf}_2]$. In the Heyrovsky–Volmer reaction mechanism, the oxygen interacts with the hydrogen oxidation intermediate ($\text{Pt-H}^\bullet$) forming another product that can be reduced which can contribute to the negative current when hydrogen is introduced and removed from the system. Based on the experimental observation, a new mechanism involving the oxygen molecule in hydrogen oxidation was proposed in eqs 11–13 for explaining the reduction signal response of hydrogen oxidation in $[\text{Bmpy}][\text{NTf}_2]$ IL in air background.

At low hydrogen concentration (0.05%–0.25%), the amount of hydrogen radical intermediate ($\text{Pt-H}^\bullet$) formed and the concentration of proton are relatively small; thus, the oxygen only can interact with a small amount of hydrogen radicals, and no obvious effect for the oxidation signal at low hydrogen concentration is observed which follows the reaction mechanism in eq 6. However, when the hydrogen concentration increases, the interaction of oxygen with $\text{Pt-H}^\bullet$ (eq 11) begins to compete with the direct oxidation of the hydrogen atom, in which the reaction in eq 13 begins to show its effect. It manifests with a different behavior in different stages of hydrogen oxidation processes. First, at constant potential +0.40 V, the initial introduction of hydrogen to the electrochemical cell results in the formation of $\text{Pt-H}^\bullet$, which can subsequently react with oxygen and then follow the reduction processes of eqs 12 and 13. The sum of the positive current due to hydrogen

oxidation (eq 12) and the negative current due to reduction process (eq 13) will lead to a positive current spike at the beginning stage of hydrogen detection, as shown in Figure 4b. Second, when measurement was performed at the time period that hydrogen gas was turned off, the oxygen will consume all the remaining of $\text{Pt-H}^\bullet$ radical formed in eq 11 and lead to the dominant reduction current in chronoamperometry response based on eq 13, shown as the negative current spike observed in Figure 4b. The reaction rate constants K_1 and K_2 for eqs 12 and 13 can be relatively measured by comparing the ratio between positive and negative current in Figure 4b. Based on equation K_1 and K_2 , the concentration of the proton $[\text{H}^+]$ is significant for determining the reaction pathways. At lower hydrogen concentration, the oxygen interacts with the intermediate of hydrogen oxidation, in which the combination of reactions in eqs 11 and 12 is equal to eq 5, which is consistent with the experimental results that at lower concentration of hydrogen, the hydrogen oxidation in air is the same as that in nitrogen, as shown in Figures 4c and 4d. Thus, the current spike of positive and negative current is important to distinguish the pathway of eqs 12 and 13. For the positive current spike, the proton concentration is at the minimal value when hydrogen was just introduced; the current observed should only contribute from eq 12. In contrast, the negative current spike should contribute from eq 13, where the proton concentration is at the maximal value, and the radical intermediate ($\text{Pt-H}^\bullet$) is almost consumed completely due to the removal of hydrogen. The ratio of positive/negative current spike values is 2.47, 1.92, 1.39, 1.18, and 1.02 for 0.35%, 0.50%, 0.75%, and 1.00% (v/v) hydrogen, respectively. The decrease of positive/negative current spike ratio represents a transition in hydrogen oxidation in the air environment, in which the reaction mechanism of eq 13 gradually becomes the dominant reaction pathway with an increase of the hydrogen concentration. Thus, the mechanism presented in eqs 12 and 13 can explain the negative current contribution in the $[\text{Bmpy}][\text{NTf}_2]$ IL based hydrogen oxidation. A similar signal trend was observed in $[\text{Bmim}][\text{NTf}_2]$ in different background gases. The different solubility of hydrogen should be a major factor, in which lower concentration of hydrogen in $[\text{Bmim}][\text{NTf}_2]$ results in a lower concentration of oxidation intermediate ($\text{Pt-H}^\bullet$) and proton. The reaction mechanism of hydrogen in $[\text{Bmim}][\text{NTf}_2]$ in the hydrogen concentration range (0.00%–1.00%, v/v) should follow the reaction mechanism of lower concentration hydrogen in $[\text{Bmpy}][\text{NTf}_2]$, in which eq 12 is dominant for not observing the negative response phenomenon. In addition, as discussed earlier, the steric hindrance effect of $[\text{Bmim}]^+$ due to its adsorption at platinum surface can also cause the lower kinetics of reaction occurring in eq 13. Table 2 summarizes the integrated areas of current response in different time periods when hydrogen was introduced and removed, according to Figure 4. Two different ILs and two different environments (nitrogen and air) were separated as four main columns in Table 2. It is found that at low concentration of hydrogen (0.05%–0.25%) the hydrogen oxidation response is similar in two environments, which is consistent with the mechanism proposed above, in which eq 5 (eqs 11 and 12) is the main reaction pathway of hydrogen oxidation in ILs on the platinum electrode. The increase of hydrogen concentration did not affect the first oxidation process (eq 4), as indicated by the consistent oxidation response in Table 2 in nitrogen and air background gases. In addition, the value of the integrated area for negative current spike in $[\text{Bmpy}][\text{NTf}_2]$ increased with increasing hydrogen concentration and reached a 30% value compared to the positive spike in 1.00% (v/v) hydrogen concentration, which also confirms the domination of eq 13 in high hydrogen concentration.

The current vs hydrogen concentration curves of hydrogen oxidation in aerobic and anaerobic conditions in the two ILs studied are plotted in Figure 5. Equations 14–17 show the linear current density response versus different concentration of hydrogen in two different ILs on platinum electrode. It is found that at low hydrogen concentration (0.05%–0.50%, v/v) the sensitivities of hydrogen in [Bmpy][NTf₂] overlap well with each other, as shown in eq 14 ($3.08 \mu\text{A cm}^{-2} \%^{-1}$) and eq 15a ($3.07 \mu\text{A cm}^{-2} \%^{-1}$). However, the presence of oxygen will affect the sensitivity of hydrogen oxidation in the concentration range of 0.50%–1.00%, v/v, in which lower sensitivity ($1.58 \mu\text{A cm}^{-2} \%^{-1}$) was observed (eq 15b). The sensitivity deviation in higher concentrations of hydrogen in [Bmpy][NTf₂] further confirmed the proposed mechanism, in which oxygen was involved in the oxidation process of hydrogen, especially in the higher concentration of hydrogen (eq 13). The almost identical sensitivities in nitrogen and air environment for hydrogen oxidation in [Bmim][NTf₂] also confirmed with previous observations, where the low solubility of hydrogen force the reaction pathway in air environment went through eqs 11 and 12 due to the lack of enough proton in the electrolyte, which is consistent with the reaction pathway in eq 5 that show identical sensitivity, as shown in eqs 16 and 17 ($0.49 \mu\text{A cm}^{-2} \%^{-1}$).

$$\begin{aligned} j (\mu\text{A cm}^{-2}) &= 3.08 C_{\text{H}_2\%} + 0.12, \\ R^2 &= 0.99 ([\text{Bmpy}][\text{NTf}_2] \text{ nitrogen}) \end{aligned} \quad (14)$$

$$\begin{aligned} j (\mu\text{A cm}^{-2}) &= 3.07 C_{\text{H}_2\%} + 0.10, \\ R^2 &= 0.99 ([\text{Bmpy}][\text{NTf}_2] \text{ air, low concentration hydrogen}) \end{aligned} \quad (15a)$$

$$\begin{aligned} j (\mu\text{A cm}^{-2}) &= 1.58 C_{\text{H}_2\%} + 0.84, \\ R^2 &= 0.99 ([\text{Bmpy}][\text{NTf}_2] \text{ air, high concentration hydrogen}) \end{aligned} \quad (15b)$$

$$\begin{aligned} j (\mu\text{A cm}^{-2}) &= 0.49 C_{\text{H}_2\%} - 0.03, \\ R^2 &= 0.98 ([\text{Bmim}][\text{NTf}_2] \text{ nitrogen}) \end{aligned} \quad (16)$$

$$\begin{aligned} j (\mu\text{A cm}^{-2}) &= 0.49 C_{\text{H}_2\%} - 0.02, \\ R^2 &= 0.98 ([\text{Bmim}][\text{NTf}_2] \text{ air}) \end{aligned} \quad (17)$$

Scheme 2 summarizes the reported hydrogen oxidation mechanisms at Pt electrode in the aqueous electrolytes vs the aprotic ionic liquids we studied. The first step of formation of Pt–H(ad) in the aprotic ILs studied here is similar to those reported in aqueous electrolytes. However, there are difference in the oxidation steps in the aprotic ILs (typically referred as

Heyrovsky and Volmer step) here. The oxidation of Pt-H(ad) will form a hydrogen radical and a proton rather than a proton or a water in aqueous electrolytes. This difference is significant as it results in a complete different pathway for the following reactions in anaerobic and aerobic conditions, and the reactivities of the following reactions are affected by the concentration of hydrogen and the structure of the aprotic ILs. Finally, the high sensitivity and reversible nature of the hydrogen oxidation in the [Bmpy][NTf₂] IL at anaerobic condition suggest that it can be explored as a true reference electrode for IL electrochemistry research and applications.

CONCLUSION

We investigated the oxidation of hydrogen in two different aprotic ILs at both anaerobic and aerobic conditions. Our study in this work shows that the rate of the HOR electrode reactions are affected by the (1) mass transport step which depends on the IL viscosity and the solubility of the hydrogen, (2) heterogeneous step which depends on IL–electrode interface structure since it affects the hydrogen adsorption and desorption at the IL–electrode interface, and (3) homogeneous step (the coupling chemical reactions with oxygen in the ILs at aerobic conditions). The Tafel–Heyrovsky–Volmer HOR reaction mechanism proposed in aqueous electrolytes was valid for the hydrogen oxidation in the ILs but with significant differences in the aerobic conditions as summarized in Scheme 2 and supported by the chronoamperometry results. In aerobic conditions, the coupling of oxygen in the hydrogen oxidation process depends on the hydrogen concentration. At higher concentration of hydrogen in aerobic conditions, a different multiple step reaction pathway occurs in which peroxide was formed through a reduction process that gradually dominates the entire reaction pathway. Our study also shows that the structures of the IL cations affect the IL–electrode interface structure subsequently affecting the rate of hydrogen oxidation processes. Less positive potential and higher hydrogen oxidation current were observed in [Bmpy][NTf₂] than those in [Bmim][NTf₂], suggesting a favorable interface structure for hydrogen adsorption in [Bmpy][NTf₂]. The good reversibility of HOR reaction at Pt electrode in [Bmpy][NTf₂] at the anaerobic condition suggests a facile hydrogen redox reaction occurs at a potential close to the equilibrium potential and can be explored as a true reference electrode for studying IL electrochemistry. In contrast to conventional nonaqueous organic electrolytes that are composed of molecular solvents such as DMSO, DMF, CH₂Cl₂, CHCl₃, or THF, this study shows an example that ILs can be used to control the HOR kinetics under both aerobic and anaerobic conditions. Furthermore, the HOR process can be used as a probe to study the adsorption of IL cations or anions at an IL–electrode interface. This fundamental idea has a much broader scope and can be used in finding new routes of organic electrochemical synthesis, in designing unique interface structures of the electrical double layer, and in developing new electrochemical hydrogen gas sensor and fuel cells.

Acknowledgments

X. Zeng acknowledges the grant support from the National Institute of Environmental Health (R01ES022302) for this research. We also thank Dr. Michael Sevilla for helpful discussions.

References

1. Conway BE, Tilak BV. Interfacial Processes Involving Electrocatalytic Evolution and Oxidation of H₂, and the Role of Chemisorbed H. *Electrochim Acta*. 2002; 47:3571–3594.
2. Quaino P, Juarez F, Santos E, Schmickler W. Volcano Plots in Hydrogen Electrocatalysis - Uses and Abuses. *Beilstein J Nanotechnol*. 2014; 5:846–854. [PubMed: 24991521]
3. Skulason E, Tripkovic V, Bjorketun ME, Gudmundsdottir S, Karlberg G, Rossmeisl J, Bligaard T, Jonsson H, Norskov JK. Modeling the Electrochemical Hydrogen Oxidation and Evolution Reactions on the Basis of Density Functional Theory Calculations. *J Phys Chem C*. 2010; 114:18182–18197.
4. Norskov JK, Bligaard T, Logadottir A, Kitchin JR, Chen JG, Pandalov S. Trends in the Exchange Current for Hydrogen Evolution. *J Electrochem Soc*. 2005; 152:J23–J26.
5. Sheng W, Gasteiger HA, Shao-Horn Y. Hydrogen Oxidation and Evolution Reaction Kinetics on Platinum: Acid Vs Alkaline Electrolytes. *J Electrochem Soc*. 2010; 157:B1529–B1536.
6. Durst J, Siebel A, Simon C, Hasche F, Herranz J, Gasteiger HA. New Insights into the Electrochemical Hydrogen Oxidation and Evolution Reaction Mechanism. *Energy Environ Sci*. 2014; 7:2255–2260.
7. Lin C, Jiao X, Tschulik K, Batchelor-McAuley C, Compton RG. Influence of Adsorption Kinetics Upon the Electrochemically Reversible Hydrogen Oxidation Reaction. *J Phys Chem C*. 2015; 119:16121–16130.
8. Cleghorn SJC, Ren X, Springer TE, Wilson MS, Zawodzinski C, Zawodzinski TA, Gottesfeld S. Pem Fuel Cells for Transportation and Stationary Power Generation Applications. *Int J Hydrogen Energy*. 1997; 22:1137–1144.
9. Springer TE, Zawodzinski TA, Wilson MS, Gottesfeld S. Characterization of Polymer Electrolyte Fuel Cells Using Ac Impedance Spectroscopy. *J Electrochem Soc*. 1996; 143:587–599.
10. Barrette WC, Sawyer DT. Determination of Dissolved Hydrogen and Effects of Media and Electrode Materials on the Electrochemical Oxidation of Molecular-Hydrogen. *Anal Chem*. 1984; 56:653–657.
11. Bautista-Martinez JA, Tang L, Belieres JP, Zeller R, Angell CA, Friesen C. Hydrogen Redox in Protic Ionic Liquids and a Direct Measurement of Proton Thermodynamics. *J Phys Chem C*. 2009; 113:12586–12593.
12. Susan M, Noda A, Mitsushima S, Watanabe M. Bronsted Acid-Base Ionic Liquids and Their Use as New Materials for Anhydrous Proton Conductors. *Chem Commun*. 2003:938–939.
13. Bentley CL, Bond AM, Hollenkamp AF, Mahon PJ, Zhang J. Electrochemical Proton Reduction and Equilibrium Acidity (P_K(a)) in Aprotic Ionic Liquids: Protonated Amines and Sulfonamide Acids. *J Phys Chem C*. 2015; 119:21828–21839.
14. Meng Y, Aldous L, Compton RG. Electrochemistry of Hydrogen in the Room Temperature Ionic Liquid 1-Butyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide: Dissolved Hydrogen “Lubricates” Diffusional Transport. *J Phys Chem C*. 2011; 115:14334–14340.
15. Goodwin SE, Walsh DA. Hydrogen Electrooxidation under Conditions of High Mass Transport in Room-Temperature Ionic Liquids and the Role of Underpotential-Deposited Hydrogen. *J Phys Chem C*. 2016; 120:11498–11507.
16. Buldyrev SV, Malescio G, Angell CA, Giovambattista N, Prestipino S, Saija F, Stanley HE, Xu L. Unusual Phase Behavior of One-Component Systems with Two-Scale Isotropic Interactions. *J Phys : Condens Matter*. 2009; 21:504106. [PubMed: 21836217]
17. Magnussen OM. Ordered Anion Adlayers on Metal Electrode Surfaces. *Chem Rev*. 2002; 102:679–725. [PubMed: 11890754]
18. Uysal A, et al. Structural Origins of Potential Dependent Hysteresis at the Electrified Graphene/Ionic Liquid Interface. *J Phys Chem C*. 2014; 118:569–574.
19. Wang Z, Guo M, Mu XY, Sen S, Insley T, Mason AJ, Kral P, Zeng XQ. Highly Sensitive Capacitive Gas Sensing at Ionic Liquid-Electrode Interfaces. *Anal Chem*. 2016; 88:1959–1964. [PubMed: 26705978]

20. Silvester DS, Aldous L, Hardacre C, Compton RG. An Electrochemical Study of the Oxidation of Hydrogen at Platinum Electrodes in Several Room Temperature Ionic Liquids. *J Phys Chem B*. 2007; 111:5000–5007. [PubMed: 17284067]
21. Silvester DS, Ward KR, Aldous L, Hardacre C, Compton RG. The Electrochemical Oxidation of Hydrogen at Activated Platinum Electrodes in Room Temperature Ionic Liquids as Solvents. *J Electroanal Chem*. 2008; 618:53–60.
22. Tang Y, Wang Z, Chi X, Sevilla MD, Zeng X. In Situ Generated Platinum Catalyst for Methanol Oxidation Via Electrochemical Oxidation of Bis(Trifluoromethylsulfonyl)Imide Anion in Ionic Liquids at Anaerobic Condition. *J Phys Chem C*. 2016; 120:1004–1012.
23. Bak T, Nowotny J, Rekas M, Sorrell CC. Photo-Electrochemical Hydrogen Generation from Water Using Solar Energy. Materials-Related Aspects. *Int J Hydrogen Energy*. 2002; 27:991–1022.
24. Kovalenko A, Hirata F. Self-Consistent Description of a Metal-Water Interface by the Kohn-Sham Density Functional Theory and the Three-Dimensional Reference Interaction Site Model. *J Chem Phys*. 1999; 110:10095–10112.
25. Ataka K, Yotsuyanagi T, Osawa M. Potential-Dependent Reorientation of Water Molecules at an Electrode/Electrolyte Interface Studied by Surface-Enhanced Infrared Absorption Spectroscopy. *J Phys Chem*. 1996; 100:10664–10672.
26. Burrell AK, Del Sesto RE, Baker SN, McCleskey TM, Baker GA. The Large Scale Synthesis of Pure Imidazolium and Pyrrolidinium Ionic Liquids. *Green Chem*. 2007; 9:449–454.
27. Endres F, El Abedin SZ. Air and Water Stable Ionic Liquids in Physical Chemistry. *Phys Chem Chem Phys*. 2006; 8:2101–2116. [PubMed: 16751868]
28. Cammarata L, Kazarian SG, Salter PA, Welton T. Molecular States of Water in Room Temperature Ionic Liquids. *Phys Chem Chem Phys*. 2001; 3:5192–5200.
29. Xiao C, Rehman A, Zeng X. Dynamics of Redox Processes in Ionic Liquids and Their Interplay for Discriminative Electrochemical Sensing. *Anal Chem*. 2012; 84:1416–1424. [PubMed: 22224654]
30. Dyson PJ, Laurenczy G, Ohlin CA, Vallance J, Welton T. Determination of Hydrogen Concentration in Ionic Liquids and the Effect (or Lack of) on Rates of Hydrogenation. *Chem Commun*. 2003:2418–2419.
31. Wang Z, Lin P, Baker GA, Stetter J, Zeng X. Ionic Liquids as Electrolytes for the Development of a Robust Amperometric Oxygen Sensor. *Anal Chem*. 2011; 83:7066–7073. [PubMed: 21848335]
32. Chao YT, Yao S, Buttner WJ, Stetter JR. Amperometric Sensor for Selective and Stable Hydrogen Measurement. *Sens Actuators, B*. 2005; 106:784–790.
33. Stetter JR, Penrose WR, Yao S. Sensors, Chemical Sensors, Electrochemical Sensors, and Ecs. *J Electrochem Soc*. 2003; 150:S11–S16.
34. Tang Y, Chi X, Zou S, Zeng X. Facet Effects of Palladium Nanocrystals for Oxygen Reduction in Ionic Liquids and for Sensing Applications. *Nanoscale*. 2016; 8:5771–5779. [PubMed: 26910528]
35. Tang YA, Yan JW, Zhou XS, Fu YC, Mao BW. An Stm Study on Nonionic Fluorosurfactant Zonyl Fsn Self-Assembly on Au(111): Large Domains, Few Defects, and Good Stability. *Langmuir*. 2008; 24:13245–13249. [PubMed: 18980356]
36. Yan JW, Tang YG, Sun CF, Su YZ, Mao BW. Stm Study on Nonionic Fluorosurfactant Zonyl Fsn Self-Assembly on Au(100): (3/11/1) Molecular Lattice, Corrugations, and Adsorbate-Enhanced Mobility. *Langmuir*. 2010; 26:3829–3834. [PubMed: 20058870]
37. Tang YG, Yan JW, Zhu F, Sun CF, Mao BW. Comparative Electrochemical Scanning Tunneling Microscopy Study of Nonionic Fluorosurfactant Zonyl Fsn Self-Assembled Monolayers on Au(111) and Au(100): A Potential-Induced Structural Transition. *Langmuir*. 2011; 27:943–947. [PubMed: 21214202]
38. Hong ZW, Chen F, Wang YH, Mao JC, Li DF, Tang YA, Shao Y, Niu ZJ, Zhou XS. The Binding Sites of Carboxylic Acid Group Contacting to Cu Electrode. *Electrochem Commun*. 2015; 59:48–51.
39. Yang HZ, Tang YG, Zou SZ. Electrochemical Removal of Surfactants from Pt Nanocubes. *Electrochem Commun*. 2014; 38:134–137.

40. Weingaertner H, Sasisanker P, Daguenet C, Dyson PJ, Krossing I, Slattery JM, Schubert T. The Dielectric Response of Room-Temperature Ionic Liquids: Effect of Cation Variation. *J Phys Chem B*. 2007; 111:4775–4780. [PubMed: 17279790]
41. Xu S, Xing S, Pei SS, Ivanistsev V, Lynden-Bell R, Baldelli S. Molecular Response of 1-Butyl-3-Methylimidazolium Dicyanamide Ionic Liquid at the Graphene Electrode Interface Investigated by Sum Frequency Generation Spectroscopy and Molecular Dynamics Simulations. *J Phys Chem C*. 2015; 119:26009–26019.
42. Wang Z, Zeng X. Bis(Trifluoromethylsulfonyl)Imide (Ntf2)-Based Ionic Liquids for Facile Methane Electro-Oxidation on Pt. *J Electrochem Soc*. 2013; 160:H604–H611.
43. Wang Z, Guo M, Baker GA, Stetter JR, Lin L, Mason AJ, Zeng X. Methane-Oxygen Electrochemical Coupling in an Ionic Liquid: A Robust Sensor for Simultaneous Quantification. *Analyst*. 2014; 139:5140–5147. [PubMed: 25093213]
44. Wang Z, Mu X, Guo M, Huang Y, Mason AJ, Zeng X. Methane Recognition and Quantification by Differential Capacitance at the Hydrophobic Ionic Liquid-Electrified Metal Electrode Interface. *J Electrochem Soc*. 2013; 160:B83–B89.
45. Xiao C, Rehman A, Zeng X. Evaluation of the Dynamic Electrochemical Stability of Ionic Liquid-Metal Interfaces against Reactive Oxygen Species Using an in Situ Electrochemical Quartz Crystal Microbalance. *RSC Adv*. 2015; 5:31826–31836.

Figure 1.

Different potential range of multiple cyclic voltammetry cycles for (1.00%, v/v) hydrogen in (a) [Bmpy][NTf₂] and (b) [Bmim][NTf₂] in a nitrogen environment; scan rate 500 mV/s.

Figure 2.

Multiple cyclic voltammetry of (1.00%, v/v) hydrogen in (a) [Bmpy][NTf₂] and (b) [Bmim][NTf₂] at different scan rates in a nitrogen environment; peak current vs scan rate in (c) [Bmpy][NTf₂] and (d) [Bmim][NTf₂].

Figure 3. Multiple CV cycles of (1.00%, v/v) hydrogen in different in ILs: (a) [Bmpy][NTf₂]; (b) [Bmim][NTf₂] at air background gases; scan rate: 500 mV/s. Dry air was used as background gas for CV scanning with and without the existence of hydrogen.

Figure 4.

Amperometric response of hydrogen oxidation at constant potential of +0.40 V in [Bmpy][NTf₂] and [Bmim][NTf₂] at (a) nitrogen and (b) air background; amperometric response of hydrogen in different background of (c) [Bmpy][NTf₂] and (d) [Bmim][NTf₂] IL.

Figure 5. Four calibration curves obtained for two different IL sensors at nitrogen and air environment in Figure 4.

Scheme 1. Schematic Side Profile of Back-Flow Electrochemical Gas Cell for IL Gas Sensing^a

^aCE: counter electrode, RE: reference electrode, WE: working electrode, GPM: gas permeable membrane.

Scheme 2.
Schematic Mechanisms of Hydrogen Oxidation in Aqueous Solvents and Ionic Liquids

Table 1

Peak Potentials for the Oxidation of H₂ and the Reduction of the Proton “H⁺” and the Double Layer Capacitance of ILs during the Oxidation Process

ionic liquid	Ox H ₂ (V)	red “HA” (V)	E_{pp} (V)	C_d ($\mu\text{F cm}^{-2}$)
[Bmpy][NTf ₂]	0.20	0.09	0.11	5.91
[Bmim][NTf ₂]	0.23	0.02	0.21	2.66

Table 2
Charge in the Time Period of Hydrogen Gas “On” Aand “Off” in Figure 4 Experiments^a

hydrogen concentration											
		0.05%		0.15%		0.25%		0.35%			
		on	off	on	off	on	off	on	off	on	off
[Bmpy]/[NTf ₂]	nitrogen	55.82	27.26	157.33	35.77	243.75	46.48	327.76	60.70		
	air	37.98	22.67	135.55	10.82	261.93	20.41	377.05	71.16		
[Bmim]/[NTf ₂]	nitrogen	1.86	0.79	11.13	1.44	19.86	2.46	29.80	4.09		
	air	1.88	1.06	9.68	3.69	21.17	5.60	37.29	5.84		
hydrogen concentration											
		0.50%		0.75%		1.00%					
		on	off	on	off	on	off	on	off	on	off
[Bmpy]/[NTf ₂]	nitrogen	441.31	86.31	618.29	83.79	826.20		69.74			
	air	530.89	117.55	679.97	179.92	829.76		220.48			
[Bmim]/[NTf ₂]	nitrogen	44.76	7.61	76.54	8.43	116.97		6.13			
	air	64.45	5.02	93.45	4.48	119.85		3.32			

^aIntegrated from the current vs time curves in Figure 4.