An Ultra-high Vacuum Electrochemical/Mass Spectrometry Study of Anodic Decomposition of a Protic Ionic Liquid

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Abstract

Protic ionic liquids (PILs) are ionic liquids that are formed by proton transfer from Brønsted acids to Brønsted bases, and which are being proposed for use in a wide range of electrochemical devices. In this contribution, we describe electrolysis of the PIL diethylmethylammonium trifluoromethanesulfonate at Pd, Pt, and Au electrodes in an ultra-high vacuum chamber connected to a mass spectrometer. At potentials negative of about -0.8 V *vs.* Pd/H, reduction of the PIL cations occurs, liberating H₂. Positive of about 2.2 V *vs.* Pd/H, electrooxidation of the PIL anions occurs, resulting in the detection of a number of fragments of the trifluoromethanesulfonate ions using the mass spectrometer. Notably, electrooxidation of the PIL anions occurs at the same potential, regardless of whether Pt, Au, or Pd is used as the electrode. In contrast, electrooxidation of water in the PIL occurs at different potentials in the PIL as the electrode composition changes. These results show that the electrochemical window of the PIL is independent of the electrode composition, but if water is present in the liquid, this independence is masked by the electrolysis of water.

Keywords: ionic liquids; electrochemical window; mass spectrometry; ultra-high vacuum

1. Introduction

Room temperature ionic liquids (RTILs) are commonly defined as liquids that comprise ions and which are liquid below 100 °C. Due to the inherent conductivity, wide electrochemical window, and chemical and thermal inertness of many RTILs, these materials are being used in a wide range of electrochemical applications [1-3]. The wide electrochemical window of many RTILs, in particular, makes them particularly useful in applications such as batteries [4-7], electroreduction of CO₂ [8,9], and electrodeposition, [10-13]. It has been reported that the most important parameter in determining the widths of electrochemical windows of the RTILs (which can often exceed 3 V) is the electrode material [14]. It is also known that both the presence of impurities and ionic composition of the RTIL also affect the electrochemical window [15-18]. Typically, the cathodic limit of RTILs is defined by reduction of the cations, while the anodic limit is defined by oxidation of the anions (although exceptions have been noted [19]), and electrochemical windows usually increase as the electrode material changes in the order Pt < Au < GC [1,20-23].

A number of experimental [19,24-27] and computational [7,28,29] methods have been used to study the electrochemical windows of (usually aprotic) RTILs, and identify RTIL-decomposition pathways. For example, Luhmer and co-workers used 1D and 2D NMR spectroscopy to identify the products of reduction of the cations of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [BMIm][NTf₂], at Au electrodes [25]. Two decomposition pathways were observed yielding, among other products, the N-heterocyclic carbene imidazolin-2-ylidene. Behm and co-workers electrolysed 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, [BMP][NTf₂], and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [EMIm][NTf₂] using Au electrodes, and identified decomposition products using mass spectrometry [24]. The influence of

impurities on the behaviour of RTILs has also been reported. For example, Compton and co-workers showed that oxidation of Cl^- ions to Cl_3^- and Cl_2 occurs within the electrochemical window of some RTILs [30]. Water (an extremely common impurity in RTILs) reduces the electrochemical window of RTILs [2], a phenomenon that has been attributed to electrolysis of water [17,18]. A catalytic role for water in RTIL electrolysis has also been proposed by Howlett and co-workers, who attributed a reduction wave during electroanalysis of *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide $[\text{PYR}_{13}][\text{NTf}_2]$ to water-catalysed decomposition of $[\text{NTf}_2]^-$ anions [19].

In this contribution, we describe electrolysis of diethylmethylammonium trifluoromethanesulfonate, $[\text{dema}][\text{TfO}]$. This particular RTIL is a protic ionic liquid (PIL), an RTIL synthesised by the addition Brønsted acids to Brønsted bases [1]. PILs have attracted a lot of attention in recent years, particularly for their potential applications in energy storage and conversion devices [31-33], as well as solvents for organic syntheses and biocatalysis [1]. In comparison to the wealth of information available on the electrochemical windows and electrolysis of aprotic RTILs, relatively little is known about the electrolysis of PILs. It is known that reduction of PIL cations at negative potentials reforms the parent base and liberates H_2 [34,35]. However, while some efforts have been made to rank anions in order of electrochemical stability [1], to the best of our knowledge no detailed investigations of the anodic decomposition of $[\text{dema}][\text{TfO}]$ (or any PILs) have been reported. Using an electrochemical cell inserted directly into an ultra-high vacuum (UHV) chamber and connected to a mass spectrometer, we describe decomposition of $[\text{dema}][\text{TfO}]$ at positive potentials. We show that, unlike for other RTILs, electrooxidation of the PIL anions occurs at the same potential, when Pt, Pd, and Au electrodes are used and the PIL contains negligible amounts of water. However, water electrolysis in the PIL occurs at different potentials at the various electrodes, following the order $\text{Pt} < \text{Pd} < \text{Au}$.

2. Materials and Methods

2.1 *Synthesis and characterisation of protic ionic liquids*

Diethylmethanamine (dema, 98%, Sigma Aldrich) and trifluoromethanesulfonic acid (TfOH, 99%, Alfa Aesar) were used as received. [dema][TfO] was prepared by adding neat TfOH to neat dema to a mol ratio of 1:1.05. The PIL was dried and excess base was removed by heating the PIL for 2 days at 70 °C and 2×10^{-2} mbar prior to use. After purification, the PIL was characterised using ^1H NMR spectroscopy and Karl Fischer analysis, and the residual water content was < 200 ppm.

2.2 *Voltammetry in vacuo*

A glass electrochemical cell that could be inserted into a UHV chamber with a base pressure of 2×10^{-8} mbar was fabricated in house. The cell contained electrodes made from 0.5-mm diameter Pt (99.997%), Au (99.999%), or Pd (99.9%) wire (all from Alfa Aesar), which were connected to an external CHI1140 potentiostat (CH Instruments, Austin, TX). A Pd/H reference electrode, which was made by bubbling H_2 gas over a length of Pd wire for 1 hr, was used for all measurements. The Pd/H reference electrode provides a stable reference potential based on the equilibrium between protons in the PIL and hydrogen in the Pd [34]. 100 mM TfOH was added to the PIL to ensure the reference electrode stayed at a stable potential.

Volatile species emanating from the electrochemical cell passed into a silicone-rubber tubing shroud that was held over the working electrode or the counter electrode (to collect species from that electrode) and which was separated from the mass spectrometer (Vacuum Generator SX200, 1-200 amu quadrupole mass spectrometer, operated with an ESS European

Spectrometry Systems power supply and software) by a valve. This setup is similar to that described by Behm and co-workers who developed a cell that exploited the extremely low vapour pressures of ionic liquids [24], and allows analysis of the liquid *in situ*, without the need for the membrane commonly found in differential electrochemical mass spectrometry setups [36].

3. Results and Discussion

Figure 1A shows a cyclic voltammogram (CV) of pure [dema][TfO] recorded using a Pt electrode. Reduction of [dema]⁺ cations to H₂ and dema occurred negative of about -0.8 V during the negative sweep. Oxidation of the electrogenerated H₂ occurred during the positive sweep, giving the anodic peak at about -0.8 V. During the positive sweep, bulk oxidation of [TfO]⁻ anions occurred positive of about 2.3 V. Very similar voltammograms were recorded when Au and Pd were used as working electrodes. The inset of Figure 1A shows a mass spectrum (in the $m/z \sim 60$ -75 range) when 2.65 V was applied to an Au electrode immersed in [dema][TfO]. A number of signals were detected, the largest of which were (in decreasing order of magnitude), $m/z = 2, 69, 64, 44, 48, 50, 82$ and 133 (note that signals in quadrupole mass spectrometers decrease as m/z increases and only those observed between $m/z \sim 60$ -75 are shown in Figure 1A for clarity). Similar responses were observed when Pt and Pd were used as the working electrode. By using the valve system described in Section 2.2 to isolate various electrodes from the mass spectrometer, we found that H₂ ($m/z = 2$) was evolved from the electrodes at negative potentials, in agreement with previous reports of the cathodic behaviour of PILs [34]. All other species detected using the mass spectrometer resulted from anodic oxidation of the PIL. The peak assignments are as follows: $m/z = 69$ is due to CF₃⁺, m/z

= 64 is due to SO_2^+ , $m/z = 48$ is due to SO^+ , $m/z = 50$ is due to CF_2^+ , and $m/z = 133$ is due to CF_3SO_2^+ , all of which arise from oxidation of the $[\text{TfO}]^-$ anions.

We examined the mass spectrometer traces in pairs (the mass spectrometer could record two m/z signals simultaneously). A single volatile species emanating from the electrode will yield ions at a fixed ratio of intensities, characteristic of the parent molecule. If two or more different chemical species are evolved under the same electrochemical conditions, but sharing common ion fragments, then each molecule will give rise to its own cracking pattern. In either case, the ratio of intensities will remain fixed, but for two or more molecules the cracking pattern will not correspond to simply one molecule. Regardless of the number of different molecules formed, by comparing the changes in signals as the potential was varied, we could ascertain whether two signals increased at the same time and in the same ratio, indicating that they resulted from the same process. For example, Figure 1B shows normalised (to the maximum intensity) $m/z = 69$ and $m/z = 64$ traces recorded as the potential of an Au electrode was swept positive at 5 mV s^{-1} . The traces overlap extremely well, indicating that the species with $m/z = 64$ (SO_2^+) and $m/z = 69$ (CF_3^+) entered the mass spectrometer at the same time (either individually, or as part of a larger species that fragmented inside the detector). This comparison was repeated for $m/z = 69$ and 50 (Figure 1C), and then for $m/z = 64$ and 48 (Figure 1D). In each case, good overlap between the signal intensities was observed and the species were observed as the potential increased above 2.3 V . Unfortunately, because of the very significant difference in signal intensity between $m/z = 69, 64, 48, 50$, and 133 , it was difficult to determine if the species with $m/z = 133$ was evolved at the same potential as the other species. Nonetheless, the appearance of the majority of the signals at the same potential indicates that oxidation of $[\text{dema}][\text{TfO}]$ occurred by oxidation of $[\text{TfO}]^-$ ions and was a single process (as opposed to multiple processes occurring at different potentials).

Figure 2 shows a comparison of the detected $m/z = 69, 64, 50$ and 48 traces (parts A, B, C and D respectively) recorded when using Au, Pd, and Pt as the working electrode. In each case, the traces overlap extremely well, showing that the onset of $[\text{TfO}]^-$ oxidation at each electrode occurred at the same potential. This observation contrasts with many literature reports of variations in the electrochemical stability of RTILs as electrode materials are changed [1,14,22,23,37]. To examine the effect of the environment on the behaviour of the PIL, it was held under vacuum for 40 days and linear sweep voltammograms (LSVs) were recorded using Au, Pd, and Pt electrodes. The LSVs (solid lines) in Figure 3A-C show that electrooxidation of the PIL anions began at about 2.3 V and increased exponentially as the applied potential increased. Dry N_2 was then leaked into the vacuum chamber, and the pressure increased to ambient pressure. LSVs recorded in the presence of dry N_2 overlapped very well with those recorded under vacuum (dashed lines in Figure 3A-C), demonstrating that the electrochemical stability of the PIL was unaffected by the presence of N_2 . Ambient air was then leaked into the chamber and waves due to oxidation of water, with onset potentials of about 1.6 V, 1.4 V, and 1.3 V at Au, Pd, and Pt, respectively, appeared (dotted lines in Figure 3A-C). Notably, the potential at which oxidation of the $[\text{TfO}]^-$ anions occurred was the same under all conditions. Therefore, the anodic stability of the PIL was independent to the composition of the electrode. On the other hand, if any water was present in the PIL, the electrochemical window of the PIL is narrowed by electrolysis of water. These results show that the possible effects of water on measurements of the electrochemical windows must be considered when such measurements are carried out. While some researchers have shown that water can “affect” the electrochemical windows of RTILs, it may in fact be that the electrochemical windows of some RTILs are insensitive to the composition of the electrode used to carry out the measurement, and that simple differences in rates of water electrolysis at various electrodes are being observed.

4. Conclusions

Anodic decomposition of the protic ionic liquid [dema][TfO] was studied using Pd, Pt, and Au electrodes in an ultra-high vacuum chamber, allowing us to carefully control the environment during electrolysis. In each case, oxidation of [TfO]⁻ ions occurred at the positive-potential limit of the liquid, which was insensitive to the composition of the electrode. In contrast, the potential at which water was oxidised in the liquid changed as the electrode was changed. It is commonly reported that the addition of water, and changing the electrode material, affect the widths of RTIL electrochemical windows. This study shows that changing the electrode material and adding water had no effect on the electrolysis of [dema][TfO]. Oxidation of water did, however, occur at different potentials in the ionic liquid, demonstrating the crucial role that water plays during ionic liquid electrochemistry. It is important that such effects are considered when studying the electrochemical behaviour of ionic liquids (under conditions that will almost certainly be much “wetter” than in our UHV chamber). What may be interpreted and reported as the effects of changing the electrode material on the “electrochemical window” of the ionic liquids may in fact simply and solely be observation of changes in the rate of water electrolysis at different electrodes.

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Figure Legends

Figure 1. (A) CV of Ar-saturated [dema][TfO] recorded using 2-mm diameter Pt disk working electrode, an Au counter electrode, and a Pd/H reference electrode. The potential was swept from 1.0 V to -0.9 V, then to 4.0 V, and back to 1.0 V at 5 mV s^{-1} . (Inset) Background-subtracted mass spectrum, with signals normalised to the $m/z = 69$ peak, recorded when an Au electrode immersed in [dema][TfO] was held at 2.65 V. (B-D) Normalised, background-subtracted mass spectrometer signal intensities versus applied potential of an Au-wire electrode. The potential was swept positive from the negative potential limit at 5 mV s^{-1} . The intensities of the two traces in each figure were monitored simultaneously. The $m/z = 69$ signal was much more intense than the other signals.

Figure 2. Normalised, background-subtracted mass spectrometer signal intensities versus applied potential of Pt (grey), Pd (red) and Au (yellow) electrodes immersed in [dema][TfO]. In each case, the potential was swept positive from the negative potential limit at 5 mV s^{-1} . The signals are (A) $m/z = 69$, (B) $m/z = 64$, (C) $m/z = 50$, and (D) $m/z = 48$.

Figure 3. Linear sweep voltammograms of [dema][TfO] recorded using (A) Au, (B) Pd, and (C) Pt electrodes under vacuum (solid lines), N_2 (dashed lines), and air (dotted lines). Applied potentials were swept from the negative limit to the positive limit at 50 mV s^{-1} .

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Figure 1

Figure 2

Figure 3