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Short communication

Electrochemistry of chloride in ambient room temperature ionic liquids: Formation of oxychloride species

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ABSTRACT

The electrochemistry of chloride in water-containing hydrophobic ([Emim][NTf_2] and [BmPyrr][NTf_2]) and hydrophilic ([Emim][OAc]) ionic liquids (ILs) has been described in detail for the first time. Cyclic voltammetric studies at a glassy carbon electrode note the significant effect of ambient water on the electrochemistry of chloride, with different outcomes based upon the hydrophilicity (*c.f.* water content) of the hygroscopic ILs. Added hydroxide highlighted this as a reactive species. Evaluation of chloride, hypochlorite, chlorite, chlorate and perchlorate electrochemistry (chlorine oxidation states −1, +1, +3, +5 and +7) was performed. Ultimately, the electrochemically formed chlorine (Cl_2) was determined to react with water or hydroxide to yield higher oxidation state species via oxychloride intermediates (*e.g.* hypochlorite) through multiple EC steps, likely resulting in chlorate as the final product.

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1. Introduction

Ionic liquids (ILs) have numerous applications due to their various electrochemical and physical properties, as well as solvating and catalytic abilities [1]. The quantification and electrochemical properties of halides in ILs (and particularly chloride) have attracted significant interest with, as many ILs are synthesised from chloride precursors. Chloride can therefore be present as an impurity in the final IL post-metathesis [2], and these impurities can exert a significant influence upon the ILs' physiochemical properties such as viscosity, melting point, electrochemical window and even catalytic activity [2,3].

Electroanalytical methodologies have been developed to quantify trace chloride in ILs [2,4] and bulk electrolysis suggested as a method of chloride removal from ILs [5]. The reported high solubility and stability of chlorine gas (Cl_2) in ILs suggest potential application of ILs for Cl_2 gas sensing [6]. Chloride-based ILs are widely used to solubilise biomass [1]. Simulation [3] and experiment [3,7–9] have demonstrated the formation of $[Cl_3]^-$ by addition of Cl_2 to Cl^- [3,8] or electrolysis of Cl^- [2,7]. HCl gas is highly soluble in ILs [10] and leads to the $[HCl_2]^-$ in the presence of Cl^- [10–12].

Almost exclusively, the studies noted above were performed using virtually *anhydrous* ILs. Water is ubiquitous in IL studies unless extensive efforts are made to exclude it, due to the hygroscopic nature of ILs, and water is known to significantly change the physiochemical properties of ILs, such as viscosity, conductivity, electrochemical window, *etc.* [13] Murugappan *et al.* have recently investigated ambient ILs under 'real conditions' for ammonia gas sensing (*e.g.* wet ILs which are equilibrated with the ambient atmosphere), with resulting interferences on Au from oxide formation [14].

In this study we report the electrochemistry of chloride in three ILs under *ambient conditions* (*i.e.* containing a significant molar ratio of ambient water) for the first time. Ultimately, electrochemically-generated chlorine reacts with water or hydroxide to form various oxychloride compounds, indicating water content needs to be considered for all electrochemical processes involving Cl^- and Cl_2 in ILs (*c.f.* [2–11]), and reported simulations [3,11] therefore only apply to anhydrous ILs.

2. Experimental

1-Ethyl-3-methylimidazolium chloride ([Emim]Cl), 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) and 1-butyl-1-methylpyrridinium bis(trifluoromethanesulfonyl)imide ([Bmpyrr][NTf_2]) (IoLiTec, Germany) were used as received. 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Emim][NTf_2]) was synthesized in-house via the bromide salt, according to previously reported methods [15]. Sodium hypochlorite (12.5%w/v, Ajax Finechem Pty Ltd.), sodium chlorite, sodium chlorate and sodium perchlorate (Sigma–Aldrich, Australia) were used as received. A solution of tetramethylammonium hydroxide in methanol ([TMA][OH], Sigma–Aldrich, Australia) was evaporated to dryness under vacuum before use.

Ambient experiments were performed using an Autolab PGSTAT101 (Ecochemie, the Netherlands) and a conventional three-electrode system, consisting of a glassy carbon (GC, 3 mm diameter) working electrode, a coiled Pt counter and non-aqueous reference electrode kit

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(BASI Analytical, USA) containing an Ag wire immersed in 0.01 M $AgNO_3$ in [Emim][NTf_2]. The potential of the latter was determined daily against Fc/Fc^+ in [Emim][NTf_2], and the data shifted such that $E°(Fc/Fc^+) = 0$ V. Experiments under vacuum were performed using an Ag quasi-reference, as described previously [16]. Water content was measured by Karl Fischer titration using an 831 KF Coulometer (Metrohm, Switzerland).

3. Result and discussion

3.1. Oxidation of chloride in wet ILs

The hydrophobic IL [Emim][NTf_2] and hydrophilic IL [Emim][OAc] were equilibrated with the ambient atmosphere for 4 h, resulting in respective water contents of 0.521 ± 0.082w/w% and 22.49 ± 0.75w/w%. At inert electrodes the oxidation of chloride anions in ILs may generate two species; chlorine (Cl_2) and the tri-chloride anion (Cl_3^-) [2];

$$2Cl^- + 2e^- \rightarrow Cl_2 \tag{1}$$

$$Cl_2 + Cl^- \leftrightarrow Cl_3^- \tag{2}$$

Fig. 1(a) displays cyclic voltammograms (CVs) for 10 mM [Emim]Cl in ambient [Emim][NTf_2] at a GC electrode as a function of scan rate. The CVs display one oxidation peak for Cl^- at *ca.* +1.0 V and a reverse peak for Cl_2 reduction at *ca.* −0.3 V. The diffusion co-efficient (*D*) of Cl^- was calculated using the Randle–Sevcik equation to be $4.35 \times 10^{-7} cm^2 s^{-1}$ in ambient [Emim][NTf_2] at room temperature. Such redox features are consistent with prior investigations in various (dried) ILs [2,9]. However, at slower scan rates the Cl_2 reduction feature was lost (discussed below). In order to exclude reaction between the imidazolium cation and Cl_2, the experiment was repeated in the pyrrolidinium-based IL [Bmpyrr][NTf_2] which exhibited qualitatively identical responses (not shown).

In contrast, Cl^- oxidation was completely irreversible in ambient [Emim][OAc] (Fig. 1(b)). The oxidation peak was observed at *ca.* +1.0 V (same as [Emim][NTf_2]) and increased as a function of root-square of scan rate, although an associated reduction feature was entirely absent.

3.2. Investigation of the influence of water on chloride oxidation in ILs

Water was found to influence the Cl^-/Cl_2 redox couple in the ILs. Fig. 2(a) displays $5 mVs^{-1}$ scans recorded for 10 mM [Emim]Cl in [Emim][NTf_2] before and after vacuum drying at room temperature for 18 h. Before drying the Cl_2 reduction feature at +0.85 V (*vs.* Ag) was virtually absent at this slow scan rate, while an additional reduction feature is clearly present at +0.42 V (*vs.* Ag). After 18 h vacuum drying, the peak current for Cl^- oxidation decreased by *ca.* 45%, consistent with an increase in viscosity with water removal [16]. However, the Cl_2 reduction peak increased indicating more Cl_2 remains by the time the scan is reversed, with a decrease in the peak at +0.42 V.

A Cl_2 reduction peak 555 mV cathodic of the Cl^- oxidation peak (not shown) appeared in [Emim][OAc] only after 18 h vacuum drying at 70 °C. These observations indicates that the water present in ambient [Emim][NTf_2] and [Emim][OAc] reacts with Cl_2, likely along similar routes to those identified in aqueous media [17,18] which forms hypochlorous acid (ClOH) (Eq. (3)). ClOH is unstable in (aqueous) solution and known to disproportionate to form $[ClO_3]^-$ and 2HCl [19].

$$Cl_2 + H_2O \rightarrow ClOH + HCl \tag{3}$$

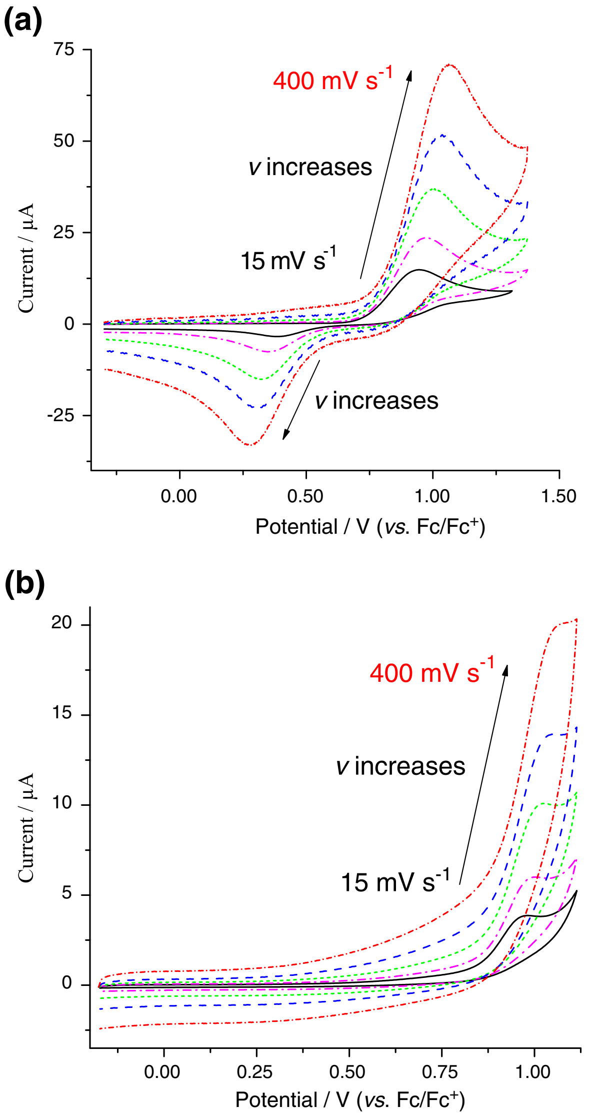

Fig. 1. CVs of 10 mM [Emim]Cl in ambient (a) [Emim][NTf_2] and (b) [Emim][OAc] (GC, $\nu = 15, 40, 100, 200, 400 \ mVs^{-1}$).

3.3. Chloride oxidation in ILs containing hydroxide anions

Basic pHs encourage the formation of the more stable anionic hypochlorite ($[ClO]^-$) species instead of the unstable hypochlorous acid [20], *c.f.* Eqs. (5) and (6)

$$Cl_2 + [OH]^- \rightarrow ClOH + Cl^- \tag{4}$$

$$ClOH + [OH]^- \rightarrow [ClO]^- + H_2O \tag{5}$$

Therefore the electrochemical oxidation of Cl^- in the presence of $[OH]^-$ can lead to the process shown in Eq. (6).

$$2Cl^- + 2[OH]^- \rightarrow [ClO]^- + Cl^- + H_2O + 2e^- \tag{6}$$

One half of Cl^- is consumed via an EC mechanism, while the other half is regenerated by an EC` mechanism. Further oxidation and consumption of Cl^- results in a *ca.* $4e^-$ oxidation process with respect to the initial Cl^-, when $[ClO]^-$ is the final product.

Fig. 2(b) displays CVs of 10 mM [Emim]Cl in ambient [Emim][NTf_2] in the absence and then with the gradual addition of

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