Electrochemistry Communications 34 (2013) 331–334

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

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

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ARTICLE INFO

Article history:
Received 21 June 2013
Accepted 4 July 2013
Available online 11 July 2013

Keywords:
Cyclic voltammetry
Chloride
Oxychloride
Water content
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
Acetate

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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http://dx.doi.org/10.1016/j.elecom.2013.07.006

(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];

$$2Cl^- + 2e^- \rightarrow Cl_2 \quad (1)$$

$$Cl_2 + Cl^- \leftrightarrow Cl_3^- \quad (2)$$

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].

$$Cl_2 + H_2O \rightarrow ClOH + HCl \quad (3)$$

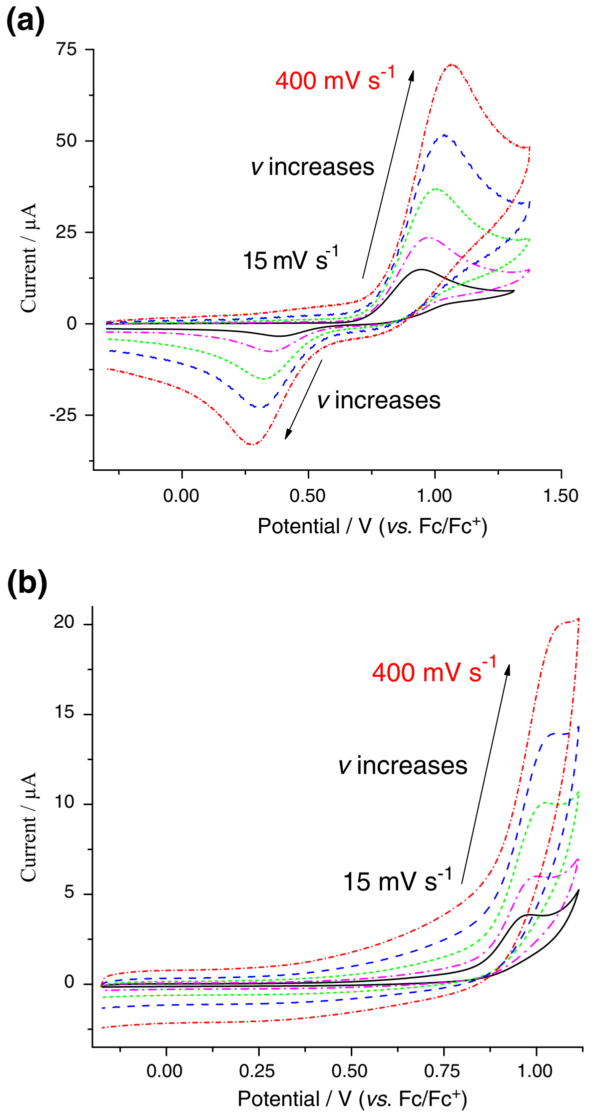

Fig. 1. CVs of 10 mM [Emim]Cl in ambient (a) [Emim][NTf_2] and (b) [Emim][OAc] (GC, ν = 15, 40, 100, 200, 400 mVs^{-1}).

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)

$$Cl_2 + [OH]^- \rightarrow ClOH + Cl^- \quad (4)$$

$$ClOH + [OH]^- \rightarrow [ClO]^- + H_2O \quad (5)$$

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

$$2Cl^- + 2[OH]^- \rightarrow [ClO]^- + Cl^- + H_2O + 2e^- \quad (6)$$

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

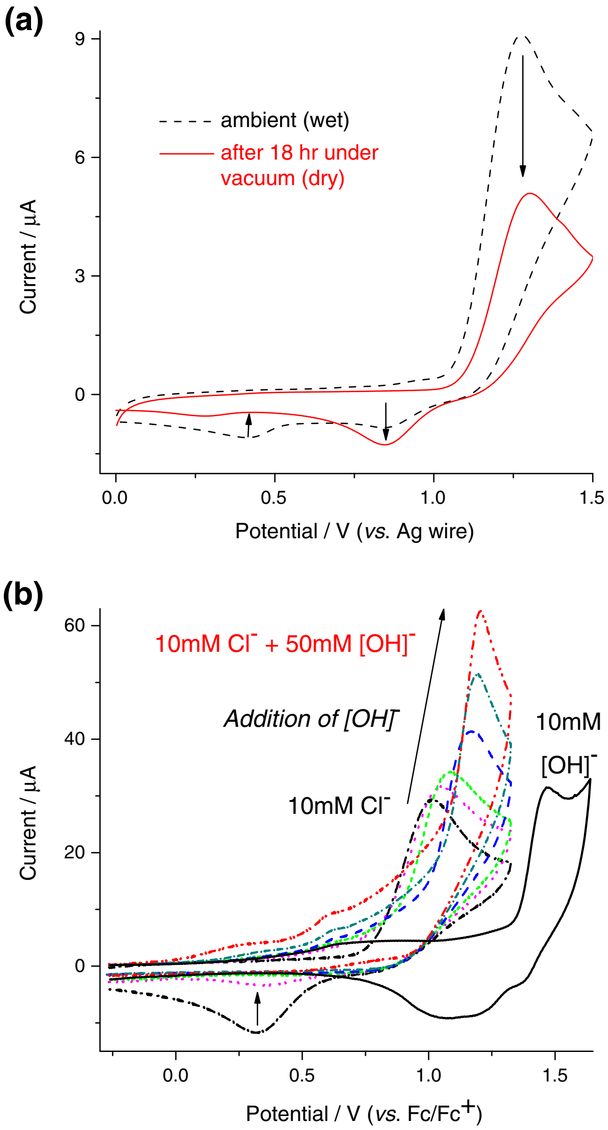

Fig. 2. (a) CVs of 10 mM [Emim]Cl in [Emim][NTf$_2$] before (– – –) and after (—) 18 h vacuum drying (GC, $\nu = 5$ mVs^{-1}), and (b) CVs for 10 mM [TMA][OH] (—) and 10 mM [Emim]Cl (–·–) in [Emim][NTf$_2$], with successive addition of 15, 20, 28, 36 and 50 mM [TMA][OH] to the latter (GC, $\nu = 100$ mVs^{-1}).

tetramethylammonium hydroxide ([TMA][OH]). Also shown is the oxidation of 10 mM [TMA][OH] in the absence of Cl$^-$. Upon addition of the [OH]$^-$, the Cl$^-$ oxidation peak increased in a manner consistent with a change from a 2e$^-$ to 4e$^-$ oxidation, with the concurrent loss of the Cl$_2$ reduction peak indicating its consumption. The peak also shifted anodically, whereas a cathodic shift with addition of [TMA][OH] might initially be expected due to the shift in equilibrium [21]; this is believed to relate to the [OH]$^-$ preferentially adsorbing at the GC surface over Cl$^-$ at lower potentials, with an increasing concentration of [OH]$^-$ displacing more Cl$^-$.

3.4. Electrochemistry of various oxychloride species in [Emim][NTf$_2$]

[ClO]$^-$ is the logical product of Cl$_2$ reacting with [OH]$^-$ in an IL, and [ClO]$^-$ could be phase transferred from a commercial hypochlorite solution into [Emim][NTf$_2$] providing the IL contained [TMA][OH]. The characteristic UV–vis spectra of [ClO]$^-$ in [Emim][NTf$_2$] was observed, with λ_{max} at 293 nm (*c.f.* $\lambda_{max} = 292$ nm for [ClO]$^-$ in 1 M Na[ClO$_4$] aqueous solution [19]). However, extended bulk electrolysis of Cl$^-$ in the presence of [OH]$^-$ in [Emim][NTf$_2$] resulted in consumption of Cl$^-$ but did not produce [ClO]$^-$, nor any other UV–vis active species. Therefore phase-transferred [ClO]$^-$ and the higher oxidation species [ClO$_2$]$^-$, [ClO$_3$]$^-$ and [ClO$_4$]$^-$ (introduced as Na$^+$ salts) were investigated electrochemically.

Fig. 3(a) displays the CV for 10 mM [TMA][OH] before and after the introduction of 20 mM [ClO]$^-$ (as an aqueous Na[ClO]/Na[OH] solution). The increase in the [OH]$^-$ oxidation feature is attributed to additional [OH]$^-$ present in the aqueous [ClO]$^-$ solution, while the broad new oxidation feature between +0.9 to +1.3 V corresponds to the oxidation of [ClO]$^-$ to a higher valence state of chlorine; [ClO]$^-$ is known to be easily over-oxidised to [ClO$_3$]$^-$ in aqueous systems (Eq. (6)) [18,22]. An associated reduction feature at +0.20 V (*vs.* Fc/Fc$^+$) is qualitatively similar to the reduction feature observed at +0.42 V (*vs.* Ag) after the reaction of Cl$_2$ and water in Fig. 2(a).

$$6[\mathrm{ClO}]^- + 3\mathrm{H_2O} \rightarrow 2[\mathrm{ClO_3}]^- + 4\mathrm{Cl}^- + 6\mathrm{H}^+ + \frac{3}{2}\mathrm{O_2} + 6e^- \qquad (7)$$

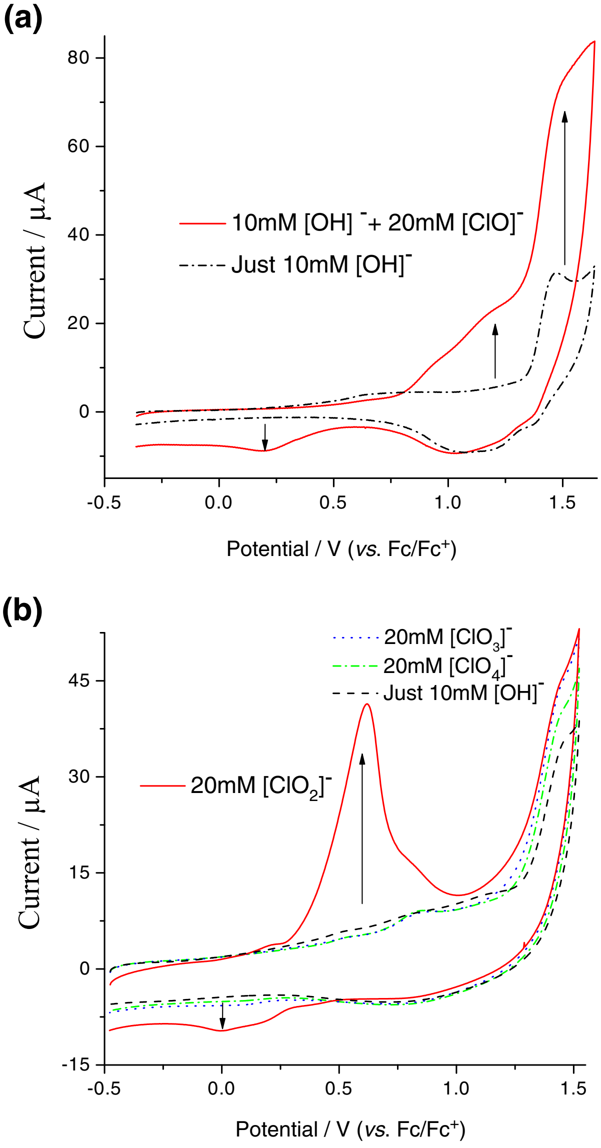

Fig. 3. CVs in [Emim][NTf$_2$] containing 10 mM [TMA][OH] (GC, $\nu = 100$mVs^{-1}) with the addition of (a) 20 mM [ClO]$^-$, (b) 20 mM [ClO$_2$]$^-$, 20 mM [ClO$_3$]$^-$ and 20 mM [ClO$_4$]$^-$.

CVs of $[ClO_2]^-$ demonstrated it could not be a final product. Fig. 3(b) displays a representative CV of 20 mM $[ClO_2]^-$ in the presence of 10 mM [TMA][OH] *ca.* 14 min after $[ClO_2]^-$ addition. The oxidative feature at +0.62 V highlights that if any $[ClO_2]^-$ were electrochemically formed it would be rapidly oxidised further. In both the presence and absence of $[OH]^-$, the $[ClO_2]^-$ voltammetry was unstable and changed over a period of an hour; eventually only voltammetric features consistent with [TMA][OH] and a lower concentration of Cl^- remained. No electrochemical activity was observed for $[ClO_3]^-$ and $[ClO_4]^-$ (also shown in Fig. 3(b)) in the presence and absence of [TMA][OH].

The oxidation of chloride in ILs leads to Cl_2 or $[Cl_3]^-$ [3,7,9]; in ambient (wet) ILs these react further, likely to ClOH which is known to disproportionate in aqueous solution to $[ClO_3]^-$ and Cl^- [20]. In the presence of added hydroxide, subsequent follow-up chemical and electrochemical reactions are much more rapid, passing through at least the $[ClO]^-$ oxidation product which can be slowly oxidised further, likely resulting in the formation of the $[ClO_3]^-$ species in a similar manner to aqueous systems.

4. Conclusions

The electrochemistry of Cl^- has been investigated in ambient (wet) hydrophobic and hydrophilic ILs. Water is highly reactive in the hydrophilic [Emim][OAc], with a slower reaction in [Emim][NTf_2] and [Bmpyrr][NTf_2]. This is of significance to the numerous prior works on the electroanalysis of Cl^-, electrolytic removal of Cl^-, application of ILs for Cl_2 gas sensors, and physiochemical investigation of Cl^-/Cl_2 interactions in ILs, all of which have hitherto excluded water from the system. Introduction of hydroxide accelerates and facilitates the electrochemical formation of oxychloride species in ILs, with $[ClO]^-$ and $[ClO_3]^-$ as likely intermediate and product, respectively. The rich electrochemistry of oxychloride species (chlorine oxidation states −1, +1, +3, +5 and +7) has been probed for the first time in ILs.

Acknowledgements

LA acknowledges the Australian Research Council (ARC DECRA DE130100770) for research funding.

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