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Group 15 quaternary alkyl bistriflimides: ionic liquids with potential application in electropositive metal deposition and as supporting electrolytes

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We report the electrochemical properties of Group 15 quaternary alkyl bistriflimide salts, which have very wide electrochemical windows (between +2.6 and −3.4 V *vs.* Fc^+/Fc for $[(Me)_4As][N(SO_2CF_3)_2]$) when used as supporting electrolytes in MeCN and which can be used for the electrodeposition of very electropositive metals, including Eu, in the molten state.

There is much current research effort focused on the use of low temperature ionic liquids in synthesis, catalysis and separations, because of their properties of negligible vapour pressure and high thermal stability.[1] We are currently interested in developing ionic liquid technology for the electrodeposition of actinides of relevance to nuclear fuel processing (U and Pu). High temperature inorganic melts are currently being used for this process,[2] but the extremely high temperatures of operation (>500 °C), and corrosive nature of the molten solvent, makes the switch to lower temperature melts appear advantageous. However, the actinides are very electropositive metals and to achieve electrodeposition requires the use of melts with large electrochemical windows.

Chloroaluminate based ionic liquids have been studied for aluminium electroplating[3] and for U and Pu electrochemical processing,[4] but the hygroscopic nature of these ionic liquids means that they are unsuitable for the bulk electrodeposition of electropositive metals. More recently, attention has focused on tetraalkyl ammonium and pyrrolidinium bis[(trifluoromethyl)-sulfonyl]amide (bistriflimide) salts, which are air and moisture stable and also possess wide electrochemical windows.[5–7] These salts would appear to have wide enough electrochemical windows to allow the deposition of both U and Pu and a preliminary report has indicated that both Na and K (both more electropositive than Pu) can be electrochemically deposited from $[Me_2(i\text{-Pr})(n\text{-Pr})N][N(SO_2CF_3)_2]$.[8] However, despite the ongoing interest in the electrochemical processing of nuclear waste in ionic liquids[9,10] there have been no reports of f-element electrodeposition in air and moisture stable melts. In addition, there have been no investigations into the use of these ionic liquids as supporting electrolytes in organic solvent based electrochemistry.

As tetraalkyl ammonium salts appeared to have the greatest cathodic stability we decided to synthesise a range of Group 15 salts of general formula $[(Me)_4X][N(SO_2CF_3)_2]$ where X = N, P or As and study their electrochemical properties. These salts were prepared by standard synthetic techniques (methylation and/or metathesis reactions) and characterised by a range of analytical and spectroscopic techniques.† All of these salts are air and moisture stable and are thus suitable for industrial electrochemical application. They are also all immiscible with water. Melting points, onset of decomposition point and electrochemical window ranges as 0.2 mol L^{-1} electrolytes in MeCN (*vs.* ferrocinium/ferrocene—Fc^+/Fc) for all three salts are given in Table 1.

Table 1 Physical properties and electrochemical windows of Group 15 salts of general formula $[(Me)_4X][N(SO_2CF_3)_2]$ where X = N, P or As

$[(Me)_4X]^+$	T_{melt}/°C	T_{dec}/°C	E_{window}/V
$[(Me)_4N]^+$	135.5–137.1	380	−2.9 – +2.7
$[(Me)_4P]^+$	149.3–150.3	420	−3.2 – +2.6
$[(Me)_4As]^+$	138.7–142.1	360	−3.4 – +2.6

All three salts have very high thermal stability, but melt at comparatively high temperatures for ionic liquids (the distinction between ionic liquid and molten salt is arbitrary but ionic liquids are usually assumed to melt below 100 °C). This is due to the high symmetry of the cations, which can be lowered by varying the organic substituents and thus lowering the symmetry.[5–8] In addition, a recent paper by Matsumoto *et al.* has shown that the melting point can be lowered further by the use of an unsymmetric anion such as $[CF_3SO_2\text{–N–C–OCF}_3]^-$.[11] However, for the case of this study (and for nuclear fuel processing applications) the comparatively high melting points do not cause any significant problems.

Cyclic voltammograms (CVs) of these new Group 15 salts as 0.2 mol L^{-1} electrolytes in pure MeCN at 25 °C and as pure melts at 170 °C were recorded using standard electrochemical techniques.‡ Selected CVs from both the low temperature electrolyte experiments and the high temperature melt studies are shown in Figs. 1 and 2 respectively.

In all the supporting electrolyte measurements the CVs were initially recorded to measure the size of the electrochemical window before ferrocene was added and the Fc^+/Fc reversible couple used as an internal standard.[12] Cobaltocene was also added during some experiments and the difference observed in Volts between the cobaltocinium/cobaltocene and the Fc^+/Fc couple is in good agreement with the literature.[12] All three salts have very large electrochemical windows in MeCN, between 5.6–6.0 V, with a cathodic limit of −3.4 V for $[(Me)_4As][N(SO_2CF_3)_2]$. It is the cation which dictates the cathodic limit, which increases down the series N > P > As, probably due to the decrease in electronegativity of the central Group 15 element. Preliminary investigations with the Sb analogue indicate that this trend is not continued, possibly due to the decreased chemical stability of the $[(Me)_4Sb]^+$ cation. As these salts consist of weakly-interacting cations and anions and have far wider

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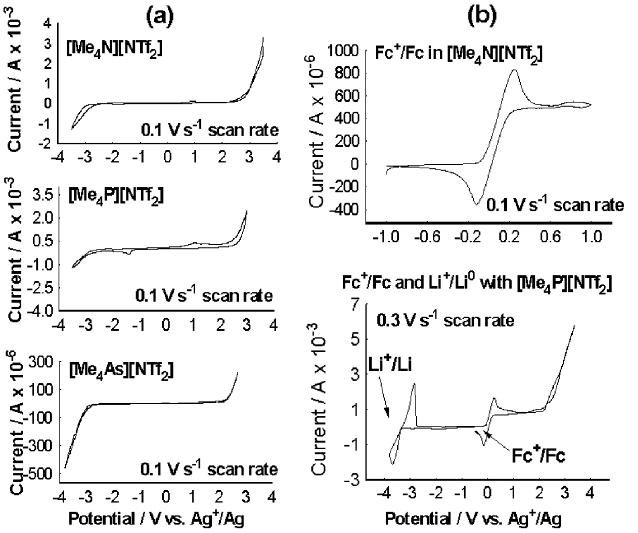

Fig. 1 (a) Cyclic voltammograms of 0.2 mol L^{-1} $[(Me)_4X][N(SO_2CF_3)_2]$ salts in MeCN and (b) cyclic voltammograms of ferrocene and $Li[N(SO_2CF_3)_2]$ in MeCN with 0.2 mol L^{-1} $[(Me)_4X][N(SO_2CF_3)_2]$ salts as supporting electrolyte. Note: $[NTf_2] = [N(SO_2CF_3)_2]$.

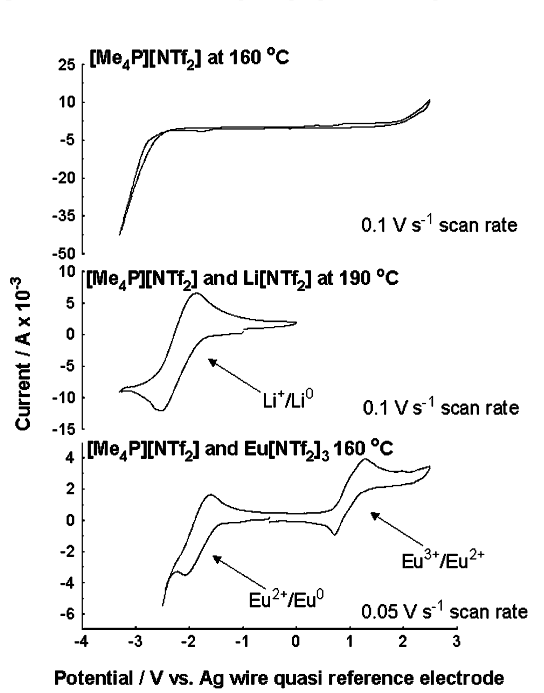

Fig. 2 Cyclic voltammograms of pure $[(Me)_4X][N(SO_2CF_3)_2]$ melts.

windows than common supporting electrolytes (*e.g.* $[Et_4N][BF_4]$ where the window is −2.8 to +2.2 V *vs.* Fc^+/Fc)[13] then they could have great potential for use in the study of a whole range of electrochemical processes in MeCN. Finally, as a link with the pure melt electrochemistry, $Li[N(SO_2CF_3)_2]$ was dissolved in the supporting electrolyte solutions and lithium metal electroplating and stripping was observed just inside the window at −3.2 V *vs.* Fc^+/Fc in $[(Me)_4P][N(SO_2CF_3)_2]$.

The electrochemical measurements made on the pure melts at higher temperatures indicate that the electrochemical windows are slightly smaller (by around 0.2 V at both the cathodic and anodic end) than for the corresponding low temperature electrolyte measurements (Fig. 1). In addition, as ferrocene readily volatilises at these temperatures it was possible to undertake only one internal reference scan before complete loss of ferrocene, making internal calibration of the window less accurate. Nevertheless, by dissolving $Li[N(SO_2CF_3)_2]$ into the melt it was still possible to see Li reduction, although in these operating temperatures Li metal is a liquid and thus electroplating was not observed. Instead we observe diffusion controlled Li reduction and non-diffusion controlled Li oxidation. This reoxidation behaviour is expected for suspended droplets of Li metal at the electrode surface.

Although Li is more electropositive than the most electropositive actinide of interest (Pu) a more direct comparison with the lanthanide ions was also undertaken. The CV of $Eu[N(SO_2CF_3)_2]_3$† in $[(Me)_4P][N(SO_2CF_3)_2]$ is also shown in Fig. 2. The $Eu^{3+/2+}$ and the $Eu^{2+/0}$ electrochemical couples are clearly observed. The (III)/(II) couple is reversible while the (II)/0 couple shows clear evidence for electroreduction down to the zero-valent state. Similar Eu electrochemistry has been observed in higher temperature molten salts (*e.g.* the NaCl/KCl equimolar melt).[14] The standard potential of the $Eu^{2+/0}$ couple is −2.81 V *vs.* −2.03 V for the $Pu^{3+/0}$ "couple" and thus it is almost certain that Pu metal deposition would also be observable in these melts. We have undertaken preliminary studies with other Ln(III) ions and have also observed La and Sm electrodeposition.

The three Group 15 based ionic liquids that we have prepared have extremely large electrochemical windows and can be used for electrochemistry in both the pure melt and as electrolytes in MeCN. By reducing Li to the metallic state and electroplating Eu in these melts we have also shown the potential for the electrodeposition of very electropositive elements, including the actinides of relevance to irradiated nuclear fuel processing. Our future research efforts will focus on the synthesis of Group 15 based ionic liquids with lower melting points, but with comparable electrochemical windows, and a study of U and Pu electrochemistry and speciation in a range of bistriflimide based melts.

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Notes and references

† Additional experimental information:

Example preparation of novel salts—$[(CH_3)_4N][N(SO_2CF_3)_2]$: $(CH_3)_4NCl$ was mixed with $Li(N(SO_2CF_3)_2)$ (in a 1 : 1 molar ratio) in H_2O followed by recrystallisation from CH_2Cl_2. Yield = 78.9%. Elemental analysis: C calc. 20.34%, found 20.21%; H calc. 3.42%, found 3.40%; N calc. 7.91%, found 7.82%; S calc. 18.10%, found 17.95%. ^{19}F NMR: −80.65 ppm (referenced to external $CFCl_3$).

$Eu[N(SO_2CF_3)_2]_3$ was prepared by the addition of Eu_2O_3 to $HN(SO_2CF_3)_2$ in aqueous solution in a 1 : 6 molar ratio with the subsequent removal of H_2O *in vacuo*.

‡ HPLC grade MeCN was purified by refluxing with $AlCl_3$ then distillation, followed by refluxing with $KMnO_4/Li_2CO_3$ then distillation, followed by refluxing with $KHSO_4$ then distillation, followed by three reflux/distillation steps over CaH_2. Purification and handling of MeCN was carried out under an Ar atmosphere at all times.

All the electrochemical measurements were undertaken under an Ar atmosphere using a glassy carbon working electrode (6.3×10^{-3} cm^2 for MeCN or 3.76×10^{-3} cm^2 for high temperature melt experiments), Pt counter electrode (0.063 cm^2 for MeCN or 1.20×10^{-3} cm^2 for high temperature experiments) and a $Ag/^{+}Ag$ reference electrode (MeCN) or a Ag wire pseudo reference electrode (high temperature melt). Cyclic voltammetry was used to measure the electrochemical window of the selected ionic liquid with the Fc^+/Fc couple (0.0 V) used as an internal standard. All of the MeCN measurements were made with 0.2 mol L^{-1} of one of the new salts as the supporting electrolyte.

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