Catalytic additives for the reversible reduction of sodium in chloroaluminate ionic liquids

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Abstract

The ability of five different compounds to facilitate reduction of sodium from a chloroaluminate IL was investigated. $PCl_6{}^-$ and 18-Crown-6 act to disrupt the Na^+ and $AlCl_4{}^-$ ion pairs producing reducible sodium ions. The addition of the small chlorinated compounds, CH_2Cl_2, $CDCl_3$ or CCl_4, resulted in the efficient reduction and reoxidation of sodium. It is believed that the electronegative chlorine atoms are oriented near the positive sodium cation, weakening its attraction to $AlCl_4{}^-$. For the five compounds tested, the highest coulombic efficiencies were measured after the addition of $CDCl_3$ (90.5%) and CCl_4 (88.2%). The addition of $CDCl_3$ was found to substantially increase the conductivity of the IL.
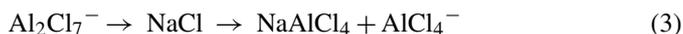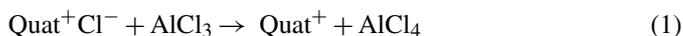© 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Imidazolium-based chloroaluminate ionic liquids (ILs) have been investigated for both battery [1,2] and electroplating [3–6] applications. Quaternary ammonium-based (Quat) ILs are an attractive alternative to the imidazolium ILs, because they are easy to synthesize, relatively safe, and a large number exist with a variety of properties [7,8]. Both imidazolium and quaternary ammonium ILs have been studied [2,9,10] as electrolytes in a derivative of the medium temperature battery, the 'zebra cell' [11]. A sodium-based battery is appealing due to the relative abundance of sodium, its low cost, and absence of dendrites for metallic anodes. The low atomic weight of sodium also leads to a system with high-energy density.

ILs are formed by mixing a halide salt with aluminum halide. Eqs. (1) and (2) show the acid-base reactions that occur when the Quat and $AlCl_3$ are mixed. The Lewis acid, $AlCl_3$, forms $AlCl_4{}^-$ (Lewis neutral) and $Al_2Cl_7{}^-$ (Lewis acid) when mixed with the organic chloride salt, as shown in Eqs. (1) and (2). Neutralization of the $Al_2Cl_7{}^-$ occurs by reacting $Al_2Cl_7{}^-$ with a Lewis base (e.g. NaCl or $Quat^+Cl^-$) to produce neutral $AlCl_4{}^-$

ions (Eq. (3)) [12]. The neutralization of the acidic ILs with sodium chloride provides the IL with a source of sodium ions for electrodeposition to the metallic state. Excess sodium chloride is added to buffer the IL, which is important at the anode and cathode where electron transfer results in acidity changes

$$Quat^+Cl^- + AlCl_3 \rightarrow Quat^+ + AlCl_4 \tag{1}$$

$$AlCl_4{}^- + AlCl_3 \rightarrow Al_2Cl_7{}^- \tag{2}$$

$$Al_2Cl_7{}^- \rightarrow NaCl \rightarrow NaAlCl_4 + AlCl_4{}^- \tag{3}$$

The composition of the ILs is given in terms of the mole fraction of $AlCl_3$, N. Neutral ILs containing equal moles of $AlCl_3$ and Quat ($N = 0.5$) contain only the $Quat^+$ and $AlCl_4{}^-$ ions. Acidic ILs contain an excess of $AlCl_3$, $N > 0.5$, and form $AlCl_4{}^-$ and $Al_2Cl_7{}^-$ anions. ILs containing an excess of Quat, $N < 0.5$, are basic and contain $AlCl_4{}^-$ and Cl^- anions.

Deposition of alkali metals has been extensively studied in a variety of neutralized chloroaluminate ILs. Yu et al. demonstrated that sodium could be electro-deposited onto a mercury electrode from an imidazolium-based chloroaluminate IL [10]. Lithium and potassium were also reduced at a mercury electrode by Scordilis-Kelley et al. [13]. It was later demonstrated that the presence of protons stabilized the plated metal and promoted the reduction of metallic lithium [2,14]. Gray et al. measured the coulombic efficiency of the sodium couple as a function of

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the HCl partial pressure and found that a minimum of approximately 6 Torr HCl partial pressure was necessary to observe sodium plating and stripping [15]. Fuller et al. established that both lithium and sodium could be deposited when $SOCl_2$ was added to a neutral IL [16].

In earlier articles we showed that the addition of $SOCl_2$ to Quat-based ILs results in the efficient reduction/reoxidation of sodium [17,18]. However, the effect of HCl, a gas, and $SOCl_2$, a volatile liquid, decreases over time as they evaporate from the IL [15]. Also, $SOCl_2$ is reduced at a potential positive of that for sodium [16]. We previously demonstrated that the additive coordinates with chloride in the IL to provide free sodium ions for plating [19].

In this study we investigate the ability of several compounds to catalytically facilitate the electrodeposition of sodium. Our initial work focused on determining the effect of Lewis acids (e.g. PCl_5) and Na^+ complexing species (e.g. 18-Crown-6, 18C6). However, it was discovered that small amounts of low molecular weight chlorocarbons produce the same catalytic effect.

2. Experimental

All experiments were carried out in a vacuum atmosphere glove box under dry nitrogen due to the sensitivity of the ILs to moisture. The glove box was maintained at oxygen and moisture levels below 10 ppm. Experiments above room temperature were performed in an oil-jacketed cell connected to a Fisher Scientific IsoTemp 3016 for temperature control. Aluminum trichloride, $AlCl_3$ (99.99%), anhydrous carbon tetrachloride (99.5+%), and thionyl chloride, $SOCl_2$ (99+%), were obtained from Aldrich and used as received. Chloroform-D (99.9 atom%) was purchased from Aldrich and stirred over fresh sodium metal in the dry box to remove any traces of water. 18-Crown-6 (99.95%) was obtained from Aldrich melted, dried under vacuum and recrystallized. To dry dichloromethane, dry P_2O_5 was added and spun while performing vapor distillation under vacuum. Benzyldimethylethylammonium chloride, BME, was synthesized by reaction of dimethylethylamine and benzyl chloride [17]. BME, 1-butyl-3-methylimidazolium tetrafluoroborate (>97.0%, Fluka), and NaCl (99.999%, Alfa Aesar) were dried under vacuum for 48 h at 70 °C before use in the glove box.

Conductivity measurements were performed using a custombuilt probe and ThermoOrion conductivity meter [19]. Two platinum plates were set a fixed distance apart and the corners were sealed in glass to prevent bending or movement of the plates. Platinum leads were connected to each plate. Calibration was performed using a standard (Orion) NaCl solution before use in the glove box. After each use the probe was cleaned with nitric acid, rinsed with de-ionized water and dried.

An EG&G model 273 potentiostat was used for the electrochemical measurements. Pt (99.999%) and W (99.95%) wires were obtained from Alfa Aesar and fabricated into working electrodes by sealing them inside glass tubes. The electrodes were cleaned in hot HNO_3, polished using 0.3 μm alumina powder and thoroughly rinsed with de-ionized water prior to use. The counter electrode was a twisted Pt wire or platinum foil sealed

in glass on the corners. The reference electrode was formed by immersing an aluminum wire (99.9995%) in an acidic IL ($N = 0.6$) in a glass tube separated from the electrolyte by a fine glass frit. The half reaction for the reference electrode is as follows:

$$4Al_2Cl_7^- + 3e^- \leftrightarrow Al + 7AlCl_4^-, \quad E = 0.0\,V \qquad (4)$$

The three electrodes were positioned as close as possible to one another and IR compensation was not performed.

For several of the additives the chemical reactivity of the sodium metal with the IL was quantified by measuring the self-discharge current. An open-circuit period was inserted between the plating and stripping of the sodium. The amount of charge recovered upon electrochemical stripping of the sodium was measured as a function of open-circuit time and expressed as an equivalent current density [20].

3. Results

3.1. Effect of Lewis acid addition

The Lewis acid $SOCl_2$ has been demonstrated to be effective in promoting the reduction and reoxidation of sodium. In both imidazolium and quaternary ammonium chloroaluminate ILs, coulombic efficiencies of greater than 90% have been repeatedly measured [16–18]. It was proposed that Na^+ ions coordinate with $AlCl_4^-$ in the ILs and the $SOCl_2$ serves to weaken this coordination, freeing Na^+ ions for reduction to the metal [19].

Since water can react with $AlCl_3$ to form HCl, care was taken to dry each of the additives and eliminate the possibility that water was responsible for the electro deposition enhancement [2,14,15]. First, neutral ILs were formed by making the acidic $N = 0.55$ BME IL and then neutralizing with 100% excess NaCl. CV scans were then performed to verify that only the irreversible reduction of the cation was observed, and no sodium was deposited. CV scans were then performed following the addition of the 'additive' to determine its effect. Solid additives were dried on a vacuum pump, while liquid additives were either obtained in the anhydrous form or stirred over sodium prior to use in a dry box. Exposure of the liquid additives to pure sodium metal resulted in no observable reaction. Thus, it is believed that water is not the source of the chemical effects described here.

In this work, PCl_5, a weaker Lewis acid than aluminum chloride, was added to a neutralized $N = 0.55$ BME IL. Initially, the liquid was stirred at room temperature for a day prior to performing CV tests and only the irreversible reduction of the cation was observed, similar to when no additive was present. However, the deposition and reoxidation of sodium were observed after the sample was stirred for a second day at 45–50 °C, as shown in Fig. 1. The scan shown in Fig. 1 is at a tungsten electrode, but similar results were obtained with a platinum electrode. The reduction and oxidation peaks are both steep with a reduction overpotential due to nucleation and crystallization of the metallic sodium on a nonsodium surface [18]. The reduction peak at 0.4 V was only observed when PCl_5 was added to the IL and is believed
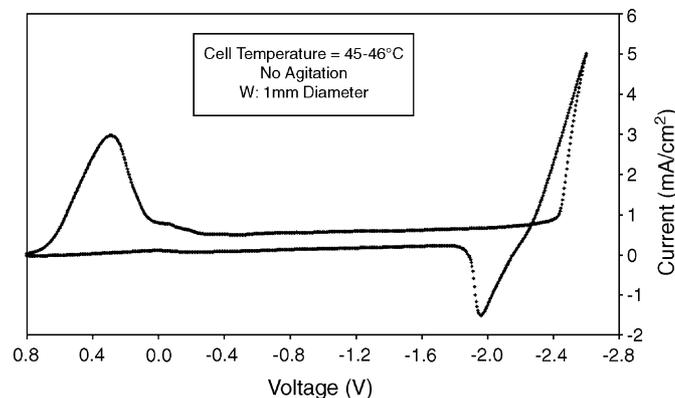
Fig. 1. CV curves for neutralized $N = 0.55$ BME IL with 5 mol% PCl$_5$ added.

Fig. 3. Conductivity vs. temperature for neutralized $N = 0.55$ BME IL with 0, 0.66, 1 and 1.5 mol% 18-Crown-6 added.

to be due to the reduction of P(V). Fuller et al. observed a similar reduction peak after the addition of SOCl$_2$ and attributed it to the irreversible reduction of SOCl$_2$ [16]. Fig. 1 shows a CV scan at 45–46 °C, but the reoxidation of sodium was also observed when a CV was performed at room temperature. This indicates that at room temperature PCl$_5$ is sufficiently soluble in the IL to catalytically promote sodium reduction, but the conversion to PCl$_6^-$ is very slow. By increasing the temperature, the time to reach equilibrium in the IL is shortened.

The maximum columbic efficiency measured for a CV test was 21%. Chronoamperometry (CA) experiments produced efficiencies greater than 60% for the reoxidation of sodium metal. Fig. 2 shows the highest efficiency CA experiment where the reduction was carried out at −2.6 V. Holding the potential minimized the time spent at potentials that were less efficient for depositing sodium metal. At more negative potentials, the IL is reduced and at more positive potentials the reduction of impurities can account for a majority of the current. The dissolution of PCl$_5$ in the IL as PCl$_6^-$ produces sodium ions that are reducible at the working electrode. The lower charge density of PCl$_6^-$, compared to AlCl$_4^-$, lowers the degree of ion pairing between the Na$^+$ and the counter anion, enabling the deposition of sodium metal.

Based on the results with PCl$_6^-$ and AlCl$_4^-$, halogenated anions with a higher charge density than AlCl$_4^-$ are not expected
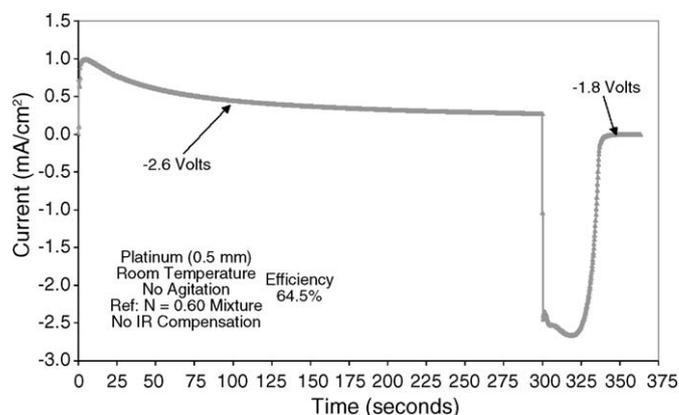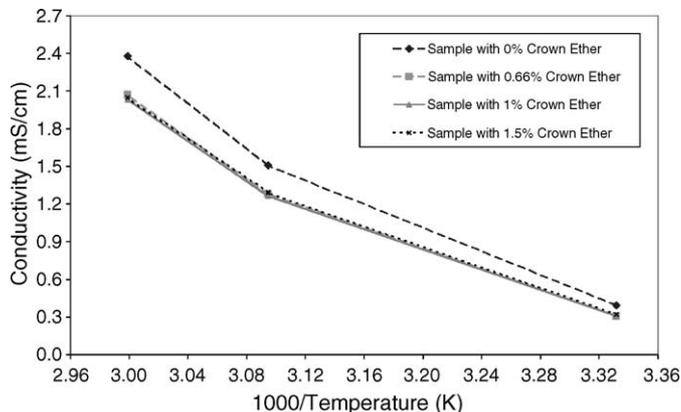
to provide sodium ions with sufficient freedom to be electrodeposited due to ion pairing. This was tested by using BF$_4^-$ as an additive in the chloroaluminate IL. The IL was made by adding 1-butyl-3-methylimidazolium tetrafluoroborate (BMIF), which is a liquid at room temperature, to a neutral IL. CV tests were performed after stirring the sample for 3 h and more than 20 h. However, all the CV tests performed with the BF$_4^-$ additive showed no Na deposition/recovery whereas the larger anion, PCl$_6^-$, was effective in enabling the deposition of sodium. The smaller BF$_4^-$ anion pairs more strongly with Na$^+$ than AlCl$_4^-$ resulting in an IL with no reducible sodium ions.

3.2. Effect of Na$^+$ complexing species

Based on the need for weak sodium ion complexes, 18-Crown-6 (18C6) was tested as an additive because of its ability to capture Na$^+$. A higher mixing temperature was used to increase the solubility and dissolution rate of 18C6 in the NaCl neutral IL. Fig. 3 shows IL conductivity as a function of temperature and mole fraction of 18C6 in the IL. The conductivity decreased upon addition of the initial aliquot of 0.66 mol% 18C6. Additional aliquots of crown ether had no effect on the conductivity. The solubility limit of 18C6 in the IL was low (less than 0.66 mol%) and additional crown ether remained undissolved. Fig. 4 shows the voltammogram of the IL containing 1.8 mol% of 18C6. The
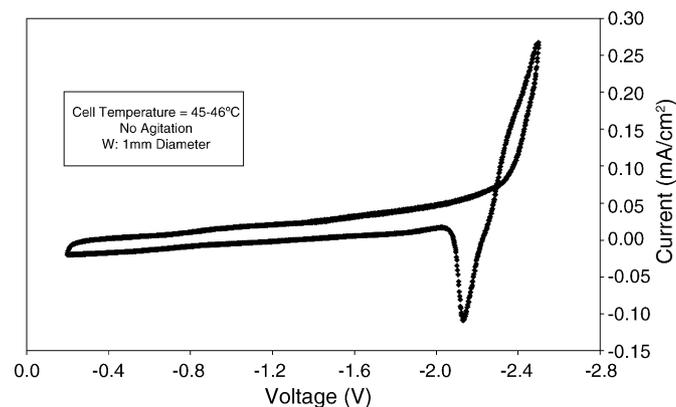

Fig. 2. CA test results for neutralized $N = 0.55$ BME IL with 5.8 mol% PCl5 added.

Fig. 4. CV results for neutralized $N = 0.55$ BME IL with 1.8 mol% 18-Crown-6.

crown ether provided a solvent shell for the sodium ions so that they were reducible. The reduction and reoxidation peaks in Fig. 4 were very sharp. The reduction process showed a slight overpotential due to nucleation of the metal in the foreign surface. In the coordinated state, the Na^+ ion is held within the cyclic ring of the crown ether. The additive specifically targets the cation, Na^+, disrupting the ion pair between the sodium ion and $AlCl_4^-$.

3.3. Effect of chlorocarbons

Solvation of the sodium ions disrupts the anion-sodium ion pair so that the sodium ions can be reduced to the metal, as in the case of 18C6. The use of low molecular weight chlorocarbons was investigated as a solvating species for the sodium ions. It is desirable to have an additive more soluble than 18C6 and more difficult to reduce than PCl_6^-. The effect of dichloromethane on the deposition of sodium was investigated using a NaCl neutralized IL. Prior to additive addition only the irreversible reduction of the cation was observed. The reduction of sodium ions to the metal was observed after the addition of 4 mol% dichloromethane, as shown in the voltammogram, Fig. 5. The coulombic efficiency was improved by adjusting the temperature, switching potential in the potential scan, and other conditions. The reduction and reoxidation peaks for sodium are very steep, indicating a rapid redox process, similar to the results obtained for $SOCl_2$ [18]. Dichloromethane can orient such that the negative dipole of the chloride atoms are in close proximity to the Na^+ cations. The attraction between the partial negative charge on the chloride and the sodium cation weakens the interaction between the sodium cation and the $AlCl_4^-$ anion [19].

The coulombic efficiency for the reduction and reoxidation of sodium was measured using chronopotentiometry (CE) at a tungsten electrode at room temperature following the addition of dichloromethane. The initial experiments produced a coulombic efficiency of 63% for a 50 s reduction current 0.64 mA/cm^2, followed by a 25 s oxidation current at 1.27 mA/cm^2. After letting the sample sit for six days in an open vessel in the dry box, the same test resulted in a columbic efficiency of 52%. After an additional five days, it was not possible to obtain 0.64 mA/cm^2 without the voltage going to very negative poten-

tials. However, at a reduction current of 0.32 mA/cm^2 for 50 s, followed by an oxidation current of 1.27 mA/cm^2 for 12.5 s, the measured efficiency was 47%. An additional aliquot of dichloromethane, about 4 mol%, then improved the efficiency to 79% using 0.64 and 1.27 mA/cm^2 for the reduction and oxidation currents, respectively. The average coulombic efficiency was 77% (average of seven repetitions) when reduction and oxidation currents of 0.64 mA/cm^2 were applied for 50 s.

The decrease in efficiency over time is consistent with the evaporation of the dichloromethane from the IL. The lower dichloromethane concentration results in fewer solvated sodium ions available for reduction. The coulombic efficiencies were less than when $SOCl_2$ was used as an additive under similar conditions (coulombic efficiency of 88.5%) [17].

To investigate the general nature of chlorocarbons as additives, chloroform-D and carbon tetrachloride were tested as additives in fresh, NaCl neutral ILs. Carbon tetrachloride provides an interesting comparison to dichloromethane and chloroform because of its symmetry (lack of dipole) and absence of a C–H bond. The first CV scans with $CDCl_3$ (6.5 mol%) and CCl_4 (6.1 mol%) from open-circuit voltage to -2.6 V are shown in Fig. 6. Both chloroform and carbontetrachloride are effective in providing reducible sodium ions. While the reduction and oxidation currents observed with each of the two additives are very steep, the reduction and reoxidation current for $CDCl_3$ are nearly double that for CCl_4. The higher oxidation currents coincides with greater coulombic efficiency for chloroform-D (79.3%) versus carbon tetrachloride (55.2%).

CA tests were performed to quantify the efficiency of the sodium reduction/reoxidation process with chloroform-D and carbon tetrachloride. The conditions at which the highest efficiencies were obtained are summarized in Table 1. The maximum efficiency for the two additives is essentially the same: 90.5% for $CDCl_3$ and 88.2% for CCl_4.

CE tests were used to measure the long-term stability of sodium in the IL with each additive. Sodium was first deposited at a constant current followed by an open-circuit delay before reoxidation at the same current. The loss of recoverable sodium was then converted to a self-discharge rate [20]. The test conditions and results are summarized in Table 2. The self-discharge
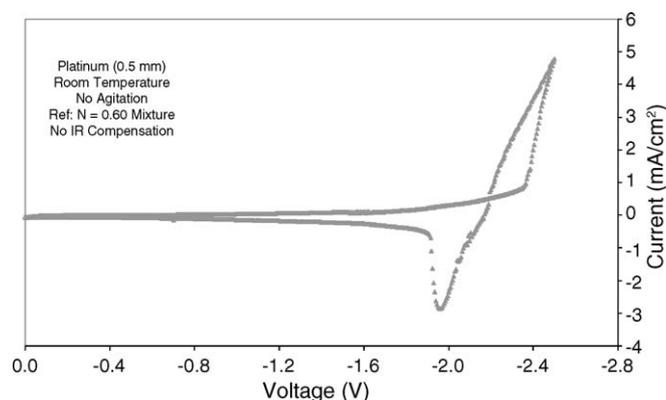

Fig. 5. CV scan following the addition of dichloromethane to the $N = 0.55$ BME IL.
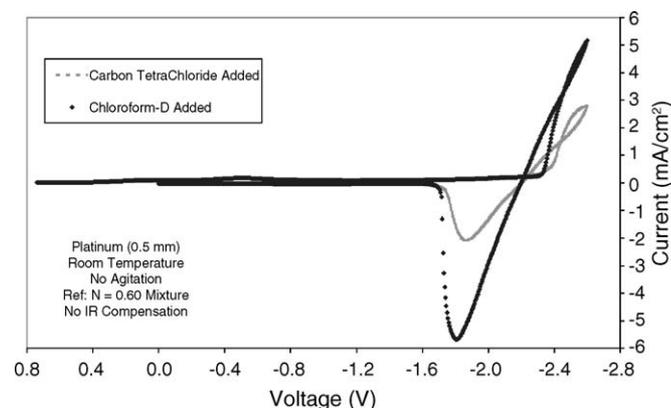

Fig. 6. CV test results with carbon tetrachloride and chloroform-D added to a neutral $N = 0.55$ BME IL.

Table 1
CA test results for $CDCl_3$ and CCl_4 added to a neutralized $N = 0.55$ BME IL

Additive	CA test results			
	Reduction (V)	Oxidation (V)	Step (time, s)	Coulombic (efficiency)
$CDCl_3$	−2.35	−1.96	300	90.5
CCl_4	−3.15[a]	−2.7[a]	300	88.2

Unless noted all tests performed at room temperature using 0.5 mm diameter Pt working electrode and $N = 0.6$ acidic reference.

[a] Pt reference, estimated potential vs. acidic reference: 700 mV.

Table 2
Self-discharge test results for $CDCl_3$ and CCl_4 added to a neutralized $N = 0.55$ BME IL

Additive	Self-discharge test results			
	Reduction/oxidation (current, mA/cm^2)	Step (time, s)	Open-circuit (time, s)	Self-discharge (rate, μA/cm^2)
$CDCl_3$	1.02	50	3600	5.62
CCl_4	0.76	50	3600	5.47

All tests performed using 0.5 mm diameter Pt working electrode.

rates, 5.62 and 5.47 μA/cm^2, for chloroform-D and carbon tetrachloride respectively, are within 3% of one another. These values are comparable to the self-discharge rate measured using $SOCl_2$ as the additive, 3.96 μA/cm^2 [17].

Following the initial series of tests, the ILs were allowed to sit exposed to the dry box atmosphere. Fig. 7 shows the results of CV tests performed on the day chloroform-D was added, 2 weeks later, and finally 4 weeks later. The results after 2 weeks show a substantial decrease in both the reduction and oxidation currents. After 4 weeks, no sodium deposition was observed. Similarly, when carbon tetrachloride was used as the additive, no sodium reduction was observed after 3 weeks. These results are consistent with those obtained using dichloromethane where the evaporation of the solvent resulted in a decrease in the reducible sodium ions.

The minimum chloroform-D concentration was experimentally determined, as shown in Fig. 8. The addition of 0.34 mol% was adequate to provide a low level of reducible sodium ions.
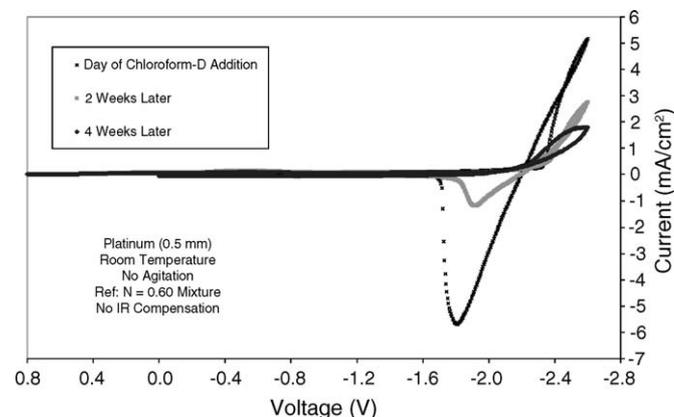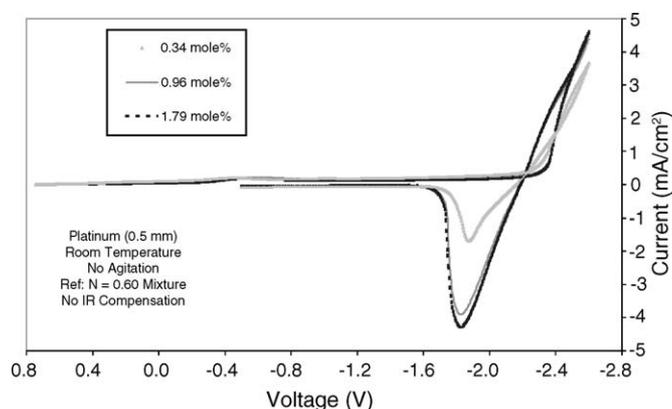

Fig. 8. CV test results after addition of 0.34, 0.96 and 1.79 mol% chloroform-D.

The addition of 0.34 mol% corresponds to 26 Na ions for each $CDCl_3$ molecule, however, the efficiency is only 25.1%. When the concentration of $CDCl_3$ was increased to 0.96 mol% (9 Na$^+$ per chloroform-D molecule), both the reduction and oxidation currents increased and the reduction current became much steeper. The coulombic efficiency increased to 60.8% with the higher additive concentration (0.96 mol%). Increasing the concentration to 1.79 mol% (5 Na$^+$ per chloroform-D) did not produce significant improvements and resulted in a coulombic efficiency of 66%.

CA tests were performed at three additive concentrations (Fig. 9) where the potential was set at −2.4 V for 100 s, followed by a potential step to −1.95 V for 100 s. The efficiency was lowest (39.2%) at 0.34 mol% chloroform-D and highest (78.8%) at 1.79 mol% $CDCl_3$, which is in line with the CV tests. For the two higher concentrations, the peak current and overall behavior were similar to each other showing that additional additive, above a critical level, does not result in additional benefits. In all three cases, the current at longer times (>40 s) was the same indicating that it is independent of the chloroform-D concentration. The higher peak oxidation current at higher additive concentrations is due to a higher concentration of reducible sodium ions.

A similar test was carried out to determine the effect of chloroform-D concentration on conductivity, Fig. 10. There was little change in the conductivity when the additive was

Fig. 7. CV results 0 days, 2 weeks and 4 weeks after addition of chloroform-D to neutral $N = 0.55$ BME IL.
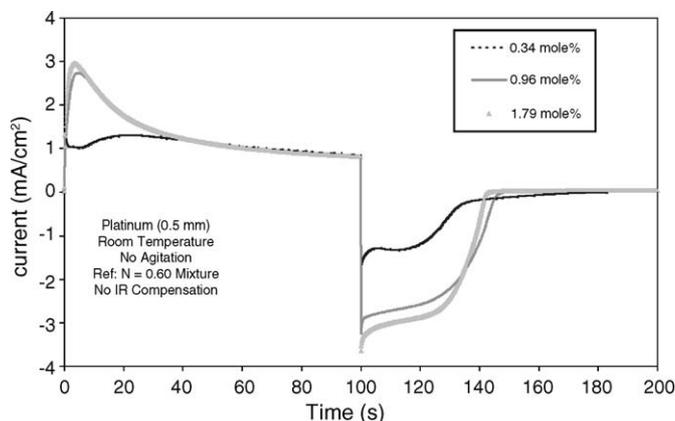

Fig. 9. Results of chronoamperometry tests with 0.34, 0.96 and 1.79 mol% chloroform-D added.
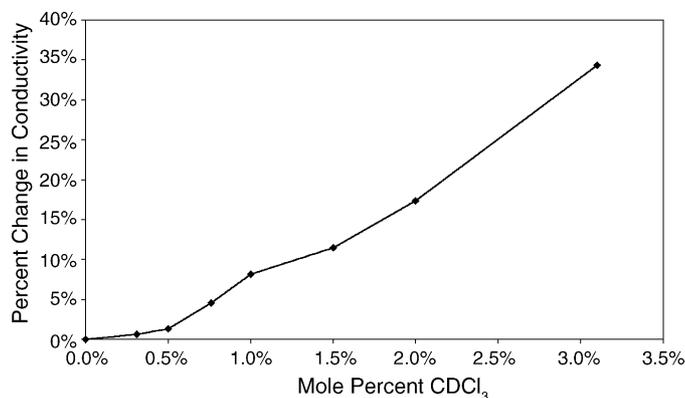
Fig. 10. Conductivity vs. mol% chloroform-D in a neutral IL.

0–0.5 mol%. There was a sharp increase in the conductivity when the additive concentration was increased above 1 mol%. The conductivity with 3.1 mol% $CDCl_3$ is nearly 35% greater than the IL without the $CDCl_3$ additive. The samples with greater than 1 mol% chloroform-D were less viscous than the initial sample. The increase in conductivity is due to two effects: less ion pairing of the sodium ions and lower viscosity. As with $SOCl_2$ [19], chloroform-D is a neutral molecule that does not directly contribute to the conductivity. The CV and CA test results confirm that the concentration of free sodium ions is greater, as shown by the reduction current. The lower viscosity of the IL is because the hydrocarbon acts as a solvent, similar to that demonstrated by Liao et al. in the plating of aluminum from a chloroaluminate IL with benzene added [21].

4. Summary

The ability of five different compounds to facilitate reduction of sodium from a chloroaluminate IL was investigated. PCl_6^- and 18-Crown-6 act to disrupt the Na^+ and $AlCl_4^-$ ion pairs producing reducible sodium ions. The addition of the small chlorinated compounds, CH_2Cl_2, $CDCl_3$ or CCl_4, resulted in the efficient reduction and reoxidation of sodium. It is believed that the electronegative chlorine atoms are oriented near the positive sodium cation, weakening its attraction to $AlCl_4^-$.

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