The Role of Additives in the Electroreduction of Sodium Ions in Chloroaluminate-Based Ionic Liquids

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Ionic liquids are an ionically conductive medium that can provide a wide potential window for the study of electrochemical processes. We have observed that the degree of ionization of the ions depends on the charge density of the ions with significant ion pairing possible. Previously, it was shown that sodium ions can be reduced only to sodium metal if an acidic additive (*e.g.*, $SOCl_2$) is added to the liquid. It is shown here that the additive increases the degree of dissociation of the Na^+ from its counterion in the liquid, making it available for electrodeposition. The observed increase in ionic conductivity provided by the $SOCl_2$ supports this proposed mechanism. It is believed that the additive coordinates with chloride in the liquid, to provide greater freedom for the Na^+ ion. In addition, conditions were found for the reduction of sodium ions to sodium metal without the use of an additive.
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Ionic liquids (ILs) with a wide stability range (wide electrochemical window) allow for the study of a range of oxidation and reduction reactions. Organic ILs can be used in the electroplating of materials that would otherwise react with water, such as sodium or lithium. This fact along with the appreciable conductivity of ionic liquids makes them an appealing candidate for use as an electrolyte in batteries.

The investigation of new electrolytes and materials for use in batteries is driven by the need for high-energy density, durable, low-cost batteries. To meet these goals, an IL must provide a conductive environment in which the reduction and oxidation reactions at the anode and cathode can occur with high efficiency over a wide potential window. Considerable work has been done in the investigation of sodium and lithium for use as the anode in batteries.[1-3] Lithium-based anodes have been particularly successful, leading to the widespread implementation of lithium and lithium-ion batteries. Sodium is an appealing material for use in batteries due to its relative abundance, low cost, and absence of dendrites, especially if the metallic anode is compared to an intercalation one. The low atomic weight of sodium may also lead to a system with a high-energy density. The Zebra cell, which utilizes sodium as an anode material, has demonstrated encouraging results.[4] However, the Zebra cell operates at a high temperature that causes the sodium anode to be molten. A room-temperature sodium battery analogous to the Zebra cell is of interest.

Quaternary ammonium chloroaluminates ($AlCl_4^-$) have been investigated in place of $NaAlCl_4$ used in the Zebra cell. Equation 1 and 2 show the acid-base reactions with quaternary ammonium salts (Quats) and $AlCl_3$. The Lewis acid, $AlCl_3$, forms $AlCl_4^-$ (Lewis neutral) and $Al_2Cl_7^-$ (Lewis acid) when mixed with quaternary ammonium chloride, as shown in Eq. 1 and 2. Neutralization of $Al_2Cl_7^-$ occurs by reacting $Al_2Cl_7^-$ with a Lewis base (*e.g.*, Cl^- from NaCl or $Quat^+Cl^-$) to produce neutral $AlCl_4^-$ ions[5] (Eq. 3)

$$Quat^+Cl^- + AlCl_3 \rightarrow Quat^+ + AlCl_4^- \qquad [1]$$

$$AlCl_4^- + AlCl_3 \rightarrow Al_2Cl_7^- \qquad [2]$$

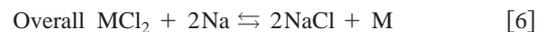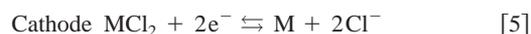$$Al_2Cl_7^- + NaCl \rightarrow NaAlCl_4 + AlCl_4^- \qquad [3]$$

The make-up of the melts is shown in terms of the mole fraction of $AlCl_3$, *N*. For example, neutral melts containing equal moles of $AlCl_3$ and Quat ($N = 0.5$) contain only $AlCl_4^-$ ions. Acidic melts contain an excess of $AlCl_3$, $N > 0.5$, and form $AlCl_4^-$ and $Al_2Cl_7^-$ anions. Melts containing a excess of Quat, $N < 0.5$, are basic and contain $AlCl_4^-$ and Cl^- anions.

Sodium chloride has been used to neutralize acidic melts and provide a source of sodium ions for electrodeposition of sodium metal. Excess sodium chloride is added to buffer the melt. The neutral melt has a wide potential window allowing sodium plating and stripping to occur.

The overall cell reaction and the half-cell reactions for sodium batteries are as follows

$$Charge \leftrightarrows Discharged$$

$$Anode \quad 2Na \leftrightarrows 2Na^+ + 2e^- \qquad [4]$$

$$Cathode \quad MCl_2 + 2e^- \leftrightarrows M + 2Cl^- \qquad [5]$$

$$Overall \quad MCl_2 + 2Na \leftrightarrows 2NaCl + M \qquad [6]$$

Where M may be a transition metal, such as Fe,[2] Ni,[6] or Cu.[7] These cathodes gave cell potentials from 2.3 to 3.3 V in an ethylmethylimidazolium chloride (EMIC): $AlCl_3$ melt. However, to electrodeposit sodium, an additive is required, such as, HCl or $SOCl_2$.[3,8] The role of the additive is not fully understood. Comments have been made that the additives may effect the electrochemical stability of the cation (reduction potential) or may form an insulating layer on the sodium.[8-12] However, the comments do not explain all the data. Only very small amounts of the additive are needed which cannot account for a shift in the reduction potential of a major melt constituent (*i.e.*, the cation). Further, the general nature of the additive effect (various acids can be used) and small concentration does not explain the formation of an insulating layer because not all the additives form insulating layers, and they would be consumed during the process, which does not seem to happen.[8-12] The aim of this work is to investigate the role of the additive in the electrodeposition of sodium.

In a neutral melt, sodium ions can precipitate as $NaAlCl_4$ or NaCl. In this study, we used benzyldimethylethylammonium chloride. The properties and comparison with imidazolium salts are discussed elsewhere.[13] Because the solubility of NaCl in the melt is very low,[14] $NaAlCl_4$ is the primary source of Na^+ for deposition. Without the addition of a trace of additive, no sodium deposition is observed. In this paper we suggest the added acid interacts with the Na^+-anion complex freeing the Na^+ for electroreduction. Without the acid additive, no sodium ions are available for deposition due to ion pairing. However, sodium ions can be made available, producing sodium metal without an additive, by oxidation of chloride just prior to sodium ion reduction, as demonstrated in here for the first time.

Table I. Properties of acidic melts of BDMEACl:AlCl₃.[a]

Mole fraction		Mole fraction[b]		Measurement at $27 \pm 1°C$		
$AlCl_3$	BDMEACl	$AlCl_4^-$	$Al_2Cl_7^-$	Density (mmol/ml)	Viscosity (mm²/s)	Conductivity (mS/cm)
0.51	0.49	0.479	0.021	7.40	370	0.512
0.53	0.47	0.436	0.064	-	-	0.617
0.55	0.45	0.389	0.111	6.95	222	0.715
0.59	0.41	0.279	0.221	6.59	123	1.010

[a] The viscosity is kinematic viscosity.
[b] Due to the equilibrium constant,[15] the fraction of Cl^- is of the order of 10^{-17}.

Experimental

All experiments were carried out in a Vacuum Atmospheres glove box due to the sensitivity to moisture. The glove box maintained the oxygen and moisture levels below 10 ppm. All experiments were performed in oil-jacketed cells connected to a Fisher Scientific IsoTemp 3016 for temperature control. Benzyltrimethylammonium chloride (98%) (BTMAC) was purchased from Acros (Belgium). Aluminum chloride ($AlCl_3$) (99.99%) and thionyl chloride ($SOCl_2$, 99+%) were obtained from Aldrich and used as received. The Quat, benzyldimethylethylammonium chloride, was synthesized with dimethylethylamine and benzyl chloride.[13] Both the Quat 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 custom-built probe and ThermoOrion conductivity meter. 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 deionized (DI) 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. Working electrodes were fabricated from these wires by sealing them inside glass tubes. The electrodes were cleaned in hot HNO_3 prior to use. They were polished using 0.3 μm alumina powder and thoroughly rinsed with DI water prior to use. The counter electrode was a twisted Pt wire. The reference electrode was formed by immersing an aluminum wire (99.9995%) in an acidic melt ($N = 0.6$) in a glass tube separated from the electrolyte by a fine glass frit. The cell equation for the reference electrode is as follows

$$4Al_2Cl_7^- + 3e^- \leftrightarrows Al + 7AlCl_4^- \quad E = 0.0 \text{ V} \quad [7]$$

Due to the high viscosity of the liquids, the electrolytes were kept stirred with a spin bar throughout the electrochemical experiments. The three electrodes were positioned as close as possible to one another and IR compensation was not performed.

Results and Discussion

Acidic mixtures were prepared by mixing excess aluminum chloride with the Quat. Varying the mole fraction of $AlCl_3$ changed the acidity of the IL by altering the mole fraction of $Al_2Cl_7^-$ and $AlCl_4^-$. Table I shows the density, viscosity, and conductivity for mixtures, $N = 0.51$, 0.53, 0.55, and 0.59. A significant increase in viscosity was observed as the melt approached neutrality (N approaches 0.5).

The conductivity of a liquid is a function of the concentration (or density) of the ions and their interaction (mobility). For each of the acidic IL mixtures, the cation mole fraction, $BDMEA^+$, was kept constant, so that the relative contributions of the $Al_2Cl_7^-$ and $AlCl_4^-$ ions to the conductivity could be evaluated. A significant drop in conductivity is observed as the liquid approaches neutrality (N approaches 0.5) with the lowest conductivity, 0.512 mS/cm, observed

for the $N = 0.51$ melt. The maximum number of anions possible in 1 mL was obtained from the density (mmol/mL) and the molecular weight. The maximum number of anions are 4.46×10^{21}, 4.18×10^{21}, and 3.96×10^{21} anions/mL for $N = 0.51$, 0.55, and 0.59 melts, respectively. As the acidity decreases (from $N = 0.59$ to $N = 0.51$) and the mole fraction of $Al_2Cl_7^-$ decreases, the potential number of anions increases, however, the conductivity decreases. The potential number of ions increases because $Al_2Cl_7^-$ converts to two $AlCl_4^-$ species as the melt approaches the neutral point (N approaches 0.5). However, the increased number of $AlCl_4^-$ anions does not provide higher conductivity. These results indicate a higher individual contribution to the conductance for the $Al_2Cl_7^-$ ion than for the $AlCl_4^-$ ion. On a per mole basis, the equivalent conductance of $Al_2Cl_7^-$ is about 4.4 times that of $AlCl_4^-$. This value was obtained from the number of ions and the conductivity of the IL. The size of $Al_2Cl_7^-$ is larger than $AlCl_4^-$ ($Al_2Cl_7^-$ ion has a bridging chloride between two $AlCl_3$ units). Thus, the electrostatic interaction between $Al_2Cl_7^-$ and $Quat^+$ is weaker than between $AlCl_4^-$ and $Quat^+$ at this temperature. Although the mobility of an unassociated $AlCl_4^-$ ion would be higher than that of $Al_2Cl_7^-$ (because of its size), the degree of association between $AlCl_4^-$ and $Quat^+$ (*i.e.*, ion pairing) is apparently responsible for the low contribution of $AlCl_4^-$ to the conductivity. Figure 1 shows the decrease in conductivity as the mole fraction of $AlCl_4^-$ is increased. At higher temperatures, one expects higher conductivity due to greater disassociation of the ion pairs and higher mobility (lower viscosity) of the IL.

Neutralization of the $N = 0.55$ acidic melt with excess NaCl results in a mixture with 41% $Quat^+$, 9% Na^+, and 50% $AlCl_4^-$ ions on a molar basis. The conductivity dropped from 0.715 to 0.324 mS/cm even though the total number of potential ions per volume increased. If the conductivity of the cations ($Quat^+$ and Na^+) were the same and the equivalent conductances of $AlCl_4^-$ and $Al_2Cl_7^-$
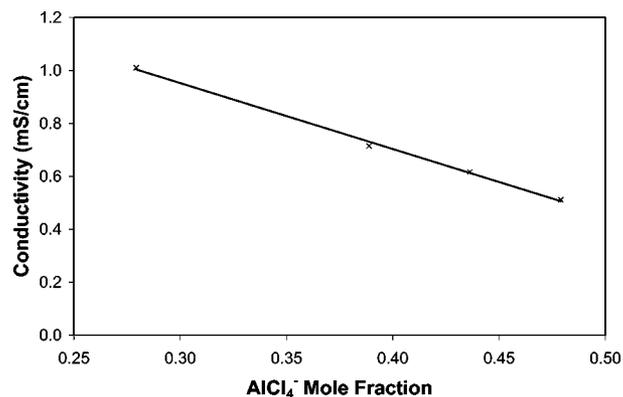

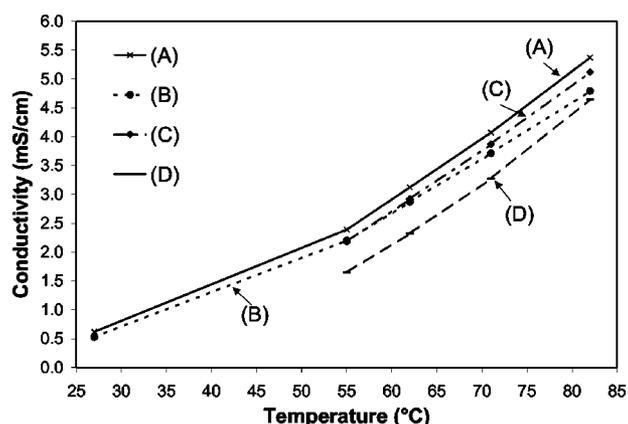**Figure 1.** Conductivity *vs.* $AlCl_4^-$ mole fraction for a mixture of $AlCl_3$ and BDMEACl at 27°C.

Figure 2. Conductivity *vs.* temperature for (A) mixture of 53% AlCl$_3$ and 47% BDMEACl; (B) mixture of 53% AlCl$_3$, 43.3% BDMEACl, and 3.7% NaCl.; (C) mixture of 51% AlCl$_3$ and 49% BDMEACl; and (D) mixture of 51% AlCl$_3$, 35.3% BDMEACl, and 13.7% NaCl.

Figure 3. Conductivity *vs.* mol % NaAlCl$_4$ for an initial mixture of 53% AlCl$_3$ and 47% BDMEACl at 27°C.

were the same as in the acidic melts then, the conductivity of the $N = 0.5$ melt could be estimated from extrapolation of Table I to $N = 0.5$. The expected value would be 0.455 mS/cm. The actual value (0.324 mS/cm) is 0.130 mS/cm lower than the extrapolated value. This result indicates that the individual conductivity of Na$^+$ is actually lower than that of Quat$^+$. That is, there is little contribution from Al$_2$Cl$_7^-$ in the $N = 0.51$ melt and the most significant change caused by neutralization is the addition of Na$^+$ in place of Quat$^+$. If we assume NaAlCl$_4$ has no contribution to conductivity, the Quat$^+$:AlCl$_4^-$ pair comprises roughly 82% of the mixture. The expected conductivity from Quat$^+$:AlCl$_4^-$ in $N = 0.5$ melt is 0.372 mS/cm (0.455 mS/cm $\times$ 0.82), which is 0.05 mS/cm higher than the observed value. These results indicate that the addition of excess NaCl to the liquid is responsible for the 0.05 mS/cm shortfall. That is, the NaCl has a negative impact on the solution conductivity.

In each case, the ion fractions were calculated assuming that the solubility of NaCl is sufficiently low so as not to affect the final mole fractions of the other ions. When excess NaCl is added, a solid powder is observed at the bottom of the liquid supporting this assumption. The salt that is dissolved could either stay as NaCl or disassociate into its respective ions, Na$^+$ and Cl$^-$. In both cases the salt will impact the solution conductivity. If the salt disassociates, the small Na$^+$ and Cl$^-$ ions in the melt are expected to increase the conductivity. Salt present as NaCl would hinder conductivity by introducing a neutral, nonconductive species to the liquid.

The relative contribution of Na$^+$ in comparison to Quat$^+$ was investigated by comparing the conductivity of the melts with the same acidity but different Na$^+$-to-Quat$^+$ ratios. An $N = 0.55$ melt was partially neutralized to $N = 0.53$ by the addition of NaCl and compared to a $N = 0.53$ melt with no NaCl. Also an $N = 0.59$ melt was converted to $N = 0.51$ with NaCl and compared to an $N = 0.51$ melt with no NaCl. The conductivity *vs.* temperature for each of the aforementioned melts was measured and plotted in Fig. 2. At 27°C the sample partially neutralized to $N = 0.51$ (Fig. 2D) formed a slurry comprised of liquid and very thick gel that prevented the measurement of its conductivity. The other mixtures each formed liquids that were a single homogeneous phase at 27°C. When the temperature was increased from 55 to 82°C the conductivity values for the $N = 0.51$ mixtures rose from 2.18 to 5.12 for the acidic case (Fig. 2C) and 1.647 to 4.65 mS/cm for the partially neutralized sample (Fig. 2D). For the $N = 0.53$ mixture, the difference in conductivity between the acidic (Fig. 2A) and partially neutralized (Fig. 2B) samples increased with temperature from 0.092 mS/cm at 27°C to 0.58 mS/cm at 82°C. In each of the two acidities, at each temperature, the exchange of Na$^+$ for Quat$^+$ (as a result of
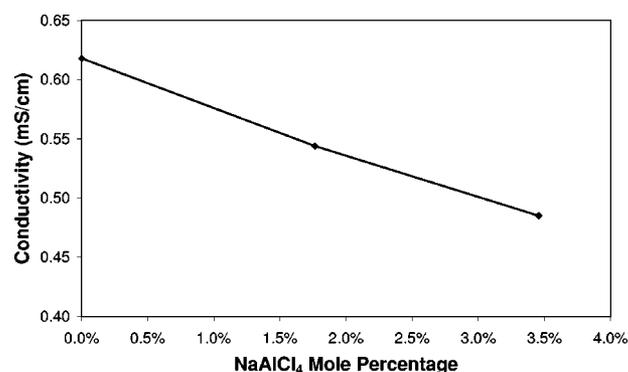
partial neutralization) lowered the conductivity. Once again, this shows that the presence of Na$^+$ in the melts contributes little or nothing to the melt conductivity, and the Na$^+$ contribution is less than that of Quat$^+$ even though Na$^+$ is a smaller ion.

The conductivity contribution of NaAlCl$_4$ may be evaluated by addition of NaAlCl$_4$ fine powder to the melt. If NaAlCl$_4$ is completely insoluble in the liquid, the addition will have no positive effect on the conductivity. An acidic melt ($N = 0.53$) with an initial conductivity of 0.618 mS/cm at 27°C was used as the starting liquid. An acidic mixture was chosen because the fraction of ions present (Quat$^+$, AlCl$_4^-$, and Al$_2$Cl$_7^-$) is known. The conductivity *vs.* mol % NaAlCl$_4$ is shown in Fig. 3. Upon addition of 1.76 mol % NaAlCl$_4$, the conductivity decreased 12% to 0.544 mS/cm. No solid precipitate was observed after mixing for two days. After two days, NaAlCl$_4$ was again added bringing the NaAlCl$_4$ content of the liquid to its final value, 3.46 mol %. As a result of the addition, the conductivity dropped further to 0.485 mS/cm (an additional 9.5%). After the second addition, a solid precipitate was observed indicating that the liquid was saturated with NaAlCl$_4$. The results show a reduction in conductivity greater than can be accounted for by only a change in the fraction of ions (*i.e.*, addition of an inert substance to an ionic liquid). The drop in conductivity indicates a decrease in the individual conductances of the ions present, as occurs with increased ion association.

Previously, it has been shown that sodium metal cannot be electrodeposited from a neutralized ionic liquid (*e.g.*, imidazolium-based melts) even though sodium ions are in the melt.[3,8-12] A trace amount of an acidic additive activates the electrodeposition process producing sodium metal. These previous results are consistent with a lack of free sodium ions in the IL (ions available for deposition). To test this hypothesis, very small amounts of SOCl$_2$ were added to a NaCl-neutralized IL. An IL composed of BDMEACl and AlCl$_3$ ($N = 0.55$) was prepared and neutralized with twofold excess NaCl. SOCl$_2$ was added with a micropipette and the conductivity was measured after 1 h of stirring for each addition of SOCl$_2$. Long mixing times were avoided because SOCl$_2$ could evaporate. The results of the conductivity tests after each addition are shown in Fig. 4. The addition of 1 wt % SOCl$_2$ results in nearly a 10% increase in the conductivity even though SOCl$_2$ itself is not expected to be ionized in the melt.

The remarkable ability of SOCl$_2$ (and another additive such as HCl) to facilitate the deposition of sodium can be shown electrochemically. A cyclic voltammogram (CV) of a Pt electrode in a neutralized BDMEACl:AlCl$_3$ melt (starting material $N = 0.55$) results in no electroreduction of sodium ions, only the irreversible reduction of the BDMEA$^+$. Similar results were obtained for mixtures tested with less than 0.025 mol % SOCl$_2$. However, the CV results for the same melt with 0.18 mol % SOCl$_2$ is shown in Fig. 5. The reduction and reoxidation of sodium at *ca.* -2 V is observed.
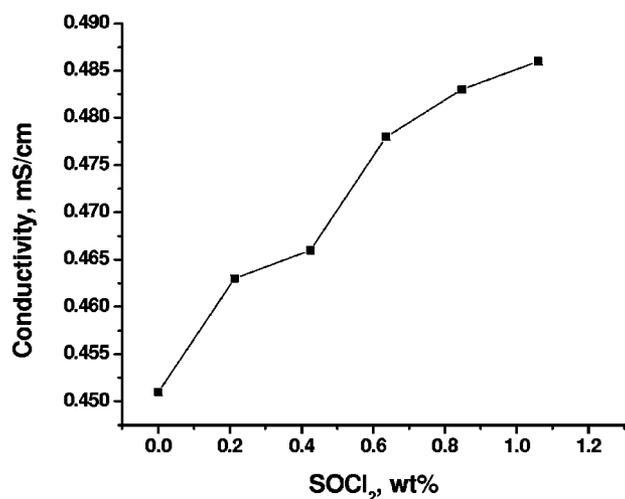
Figure 4. Conductivity at 30°C *vs.* weight % $SOCl_2$ for an initial mixture of 50% $AlCl_3$, 40.9% BDMEACl, and 9.1% NaCl.

The reduction current is far in excess of the flux that could be provided by the $SOCl_2$. This result suggests that the $SOCl_2$ additive is working to increase the concentration of sodium ions in a catalytic way and is not being consumed. As the concentration of sodium ions in the solution increases, the reduction potential shifts to more positive potentials. Increasing the $SOCl_2$ level also led to higher current densities for the reduction and reoxidation rather than changes in the potential at which reduction occurred.

The Zebra cell that operates at a high temperature does not require the addition of an additive because all components are molten and ionized. However, the low-temperature IL cell requires an additive to electrodeposit sodium even though the melt is liquid. The conductivity data showed that exchange of $Quat^+$ for Na^+ resulted in a drastic drop in conductivity to a level where it appears that the Na^+ is contributing nothing toward the overall melt conductivity. The addition of $NaAlCl_4$ also lowers the melt conductivity, even though it appears to dissolve. Finally, the addition of trace amounts of HCl (previous results) or $SOCl_2$ appears to dissociate the sodium salt in the melt so that they can be electrodeposited at rates far in excess of the flux of the additive. The increase in the melt conduc-
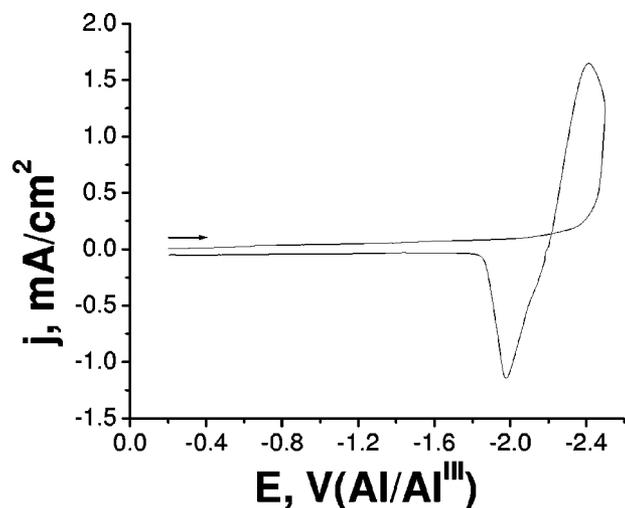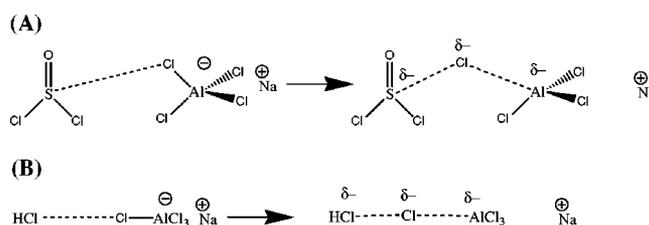

Figure 6. Interaction between additives and $NaAlCl_4$ ion.

tivity (Fig. 4) with $SOCl_2$ addition, shows that $SOCl_2$ dramatically increases the melt conductivity. This behavior is consistent with the concept that the $SOCl_2$ serves to release Na^+ ions from ion-pairs enabling them to contribute to the conductivity and be reduced to sodium metal. Figure 6 shows the proposed interaction between the additives and sodium ions in the melt. As the acid is added to the melt the interaction between the additive and the chloride becomes stronger. This interaction weakens the interaction between Na^+ and $AlCl_4^-$ ions. Na^+ is thus available for conduction and electrodeposition. HCl acts similarly to provide more freedom to the Na^+ ion. Thus, $SOCl_2$ and HCl act as a Lewis acids[16-18] and compete with $AlCl_3$ for Cl^-.

Na^+ dissociation (as measured by conductivity and deposition of Na metal) may also be achieved in these melts without the addition of a new chemical by carrying out the oxidation of the melt producing chlorine from the chloride-containing species. Figure 7 shows the sodium deposition without an additive, by oxidizing the melt just prior to sodium ion reduction. A 55 mol % $AlCl_3$ + 45 mol % BTMACl melt was neutralized with excess NaCl. The melting point of the neutral melt was 65°C.[19] The temperature for the experiment was 61°C which is below freezing point producing a slushly melt. Before the measurement, a constant current (1.2
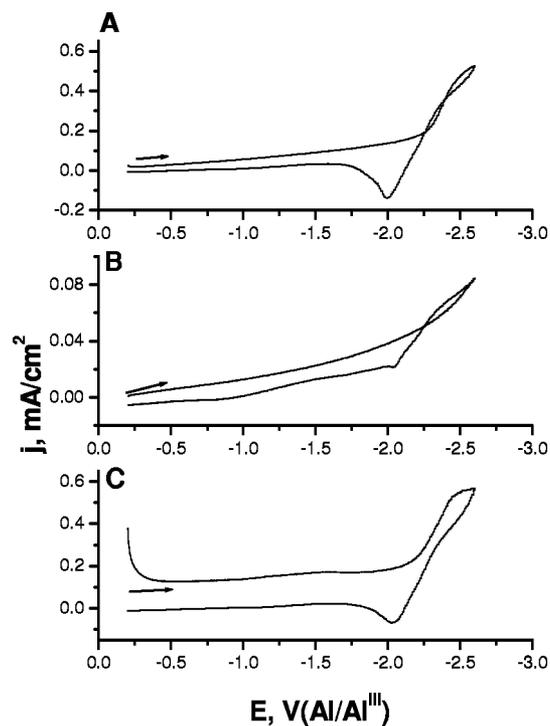

Figure 5. CV scan at 27°C for a mixture of 55% $AlCl_3$ and 45% BDMEACl neutralized with 100% excess NaCl and 0.18 mol % $SOCl_2$ added.

Figure 7. CV scans at 61°C for a mixture of 55% $AlCl_3$ and 45% BTMACl neutralized with 100% excess NaCl and no additives added: (A) first scan, (B) tenth scan, and (C) eleventh scan immediately after oxidation current.

mA/cm^2) was applied for 10 s to oxidize the chloride-containing species to chlorine. The potential scan shown in Fig. 7A occurred immediately after the oxidation current where a chloride-containing species (*e.g.*, AlCl$_4^-$) was oxidized to chlorine. The reduction of sodium ions and subsequent reoxidation of the metal is clearly seen in Fig. 7A. Oxidation of the chloride-containing species (*e.g.*, AlCl$_4^-$) disrupts the ion pair with sodium ions making sodium ions available for reduction to the metal, Eq. 8

$$2NaAlCl_4 - 2e^- \rightarrow 2Na^+ + 2AlCl_3 + Cl_2 \qquad [8]$$
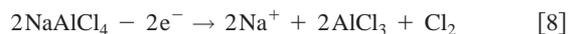
This behavior was not observed at higher temperatures most likely because the melt can re-equilibrate faster in the less viscous state. Figure 7B shows the tenth voltammetry scan to −2.5 V following the oxidation current at positive potentials. The slow equilibration of the melt appears to restore the original neutral condition (recall excess sodium chloride is present to buffer the melt). The condition needed for the reduction of sodium ions to sodium metal could be restored again (after Fig. 7B was performed) by scanning the potential to the oxidative limit at 2.5 V. Figure 7C is the eleventh scan to −2.5 V, immediately following the oxidation cycle. Clearly, the oxidative current, Eq. 8, is responsible for providing the conditions where sodium ions can be reduced. This shows that any appropriate means of dissociating the sodium ion pairs in the melt at the electrode surface may enable the sodium ion reduction process.

In summary, sodium ions can be made available for electroreduction to sodium metal either by weakening the bond strength between Cl and Al atoms (Fig. 6) of the chloroaluminate complex or by removing the chloride ion from the NaAlCl$_4$ (Eq. 8 and Fig. 7). The use of additives, such as HCl or SOCl$_2$, is consistent with this approach.

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