DEVELOPMENT OF QUATERNARY AMMONIUM BASED ELECTROLYTES
FOR RECHARGEABLE BATTERIES AND FUEL CELLS

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LIST OF ABBREVIATIONS

κ – Conductivity

ρ – Density

η – Viscosity

I – Me₃(MeCl)NCl

II – 1-methyl-3-propylimidazolium chloride

III – butylmethylpyrrolidinium chloride

IV – Et₃MeNCl

V – Bu₃MeNCl

VI – BenMe₂NCl

VII – BenEt₃NCl

VIII – BenBu₃NCl

IX – BenEtMe₂NCl

X – BenMe₂ProNCl

XI – BenMe₂i-ProNCl

XII – BenEt₂MeProNCl

XIII – EtMe₂ProNCl

XIV – BuEtMe₂NCl

XV – BuMe₂ProNCl

XVI – [EtOMe]EtMe₂NCl

XVII – [MeOEt]EtMe₂NCl

18C6 – 18-Crown-6
AA – Alfa Aesar
AD – Aldrich
ACN – Acetonitrile
Al – Aluminum
Au – Gold
BMIF – 1-butyl-3-methylimidazolium tetrafluoroborate
CA – Chronoamperometry
CE – Chronopotentiometry
CV – Cyclic Voltammetry
D – Donated
DSC – Differential Scanning Calorimeter
E – EMD Chemicals
EMIC – 1-ethyl-3-methylimidazolium chloride
FL-Fluka
FS-Fisher Scientific
IL – Ionic Liquid
JES – Journal of the Electrochemical Society
K – Potassium
MP – Melting Point
MSC – Methanesulfonyl chloride
PEM – Proton Exchange Membrane
Pt – Platinum
Quat – Quaternary Ammonium
RT – Room Temperature

RTC – Room Temperature Carbonate

S-Sachem, Inc.

SEI – Solid-electrolyte Interface

TFSI – (CF₃SO₂)₂N⁻

V – Volts

W – Tungsten
SUMMARY

In this work, electrolytes for secondary batteries and fuel cells were investigated. Ionic liquids (ILs), for use as battery electrolytes, were formed using quaternary ammonium salts (Quats) and aluminum chloride. The room temperature (RT) carbonate fuel cell was demonstrated by modifying a commercially available anion exchange membrane, utilizing positive quaternary ammonium fixed sites, to transport carbonate.

The charge density on the nitrogen and the symmetry of the Quat were demonstrated to be the dominant factors in determining the IL melting point (MP). Introduction of a benzyl ring both increases the size and disrupts the symmetry of the Quat, lowering the MP of the resulting ILs. The ILs formed from the asymmetric BenzylR’R”NCl salts were found to have lower melting points (below room temperature) than ILs formed when R’ was equal to R”. The additional asymmetry is believed to make crystallization more difficult, significantly lowering the melting point and viscosity. For the ILs with moderate viscosity, upon neutralization with NaCl and addition of an additive (SOCl₂), sodium can be reversibly deposited. The coulombic efficiency of the plating/stripping process, defined as the oxidation current over the reduction current, was found to be comparable to other chloroaluminate ILs.¹

An additive is necessary to disrupt the strong coordination between Na⁺, or Li⁺, and AlCl₄⁻, which makes the ions unavailable for reduction to the metal. Additives, such as HCl or SOCl₂, are effective in disrupting the alkali-chloroaluminate complex freeing the ions for electroreduction to the metal. The bulk conductivity was observed to increase with SOCl₂ content as the ions became available and sodium...
reduction/reoxidation was observed. The chlorinated compounds chloroform-D and carbon tetrachloride were demonstrated to have similar performance to SOCl\textsubscript{2} though a large number of chlorinated compounds could be utilized. The electronegative chlorine atoms found in these solvents are oriented near the positive sodium cation, weakening its attraction to AlCl\textsubscript{4}.

Along with free sodium ions, sufficient reductive stability of the Quat is necessary to deposit sodium. The electrochemical stability is dependent on the ability of the substituent groups to form stable radicals. The benzyl substituted cation (salt IX) was less stable than the alkyl substituted cation (salt XV), due to the benzyl group being a better leaving group than the smaller butyl chain. The 9-carbon salt, XV, was demonstrated to form a RTIL with significantly lower viscosity than the benzyl substituted ILs. This is due to the much smaller size of XV than IX. Utilizing only carbon, nitrogen and hydrogen, 9 carbons appears to be the smallest number of atoms, with which a RTIL can be formed. As with the benzyl substituted ILs, upon the addition of SOCl\textsubscript{2}, sodium can be efficiently reduced and reoxidized.

Based on its placement, the introduction of a rigid ether group, compared to an alkyl group, can result in a lower molecular weight RTIL. The ionic conductivity increased upon neutralization of the ether substituted ILs. However, due to the stability of the quaternary ammonium cation, an additive is still necessary to form an SEI. SOCl\textsubscript{2} was demonstrated to form a more stable SEI than CDCl\textsubscript{3}. The greater availability of sodium in the ether systems results in larger sodium reduction current densities.

The Quat-based RTILs formed have been shown to support the deposition of both lithium and sodium. When neutralized with both lithium and sodium, a mixed state is
developed that results in the electrodeposition of Li-Na alloys at efficiencies similar to those measured with sodium. The Li-Na alloy appears to suppress dendrite formation and could potentially be used as a metal based anode in a rechargeable Li battery.

A technique that is becoming fairly common is the packaging of fuel cell and battery technology together. In this work, a novel room temperature carbonate fuel cell has been constructed by modifying anion exchange membranes so as to transport carbonate. The alkaline environment could eliminate the need for water in the oxidation of methanol. Cells were operated with hydrogen, 1M methanol, and pure methanol fuels using dry O₂ and CO₂ as the cathode gases. CO₂ was produced at the anode and O₂ & CO₂ were necessary at the cathode for operation, indicating that carbonate was the conducting ion.
CHAPTER 1

INTRODUCTION

The automobile and electronics industries continue to require lower cost, higher energy density conversion and storage devices. Based on their high energy and power densities, secondary lithium ion and polymer batteries have gained widespread use in consumer electronics. Fuel cells offer an efficient means of converting chemical energy to electrical energy. Proton exchange membrane (PEM) fuel cells are among the most extensively investigated systems for near room-temperature (RT) operation. However, due to kinetic limitations, the power densities of PEM cells are much lower than rechargeable batteries. Therefore, batteries and fuel cells are typically utilized together. The battery provides higher power, typically for short periods of time, while the fuel cell produces a lower constant power level to power the external device and/or charge the battery. In this work, ionic liquids (ILs) are investigated as a conductive, nonvolatile battery electrolyte. Also, a RT carbonate fuel cell was constructed and demonstrated by modifying anion exchange membranes to transport carbonate.

1.1 Ionic Liquids

ILs are intriguing because of their wide electrochemical window, ionic conductivity, and low vapor pressure. By combining asymmetric organic cations and inorganic anions, room-temperature ILs can be formed and used in the electroplating of
materials that would otherwise react with water, such as lithium or sodium. The wide potential window of ILs allows for the combination of lithium or sodium metal-based anodes with conventional intercalation cathodes. Lithium’s low molecular weight and very negative reduction potential make a lithium metal-based anode attractive, however, lithium typically forms dendrites on deposition that can lead to capacity fading and electrode shorting.\textsuperscript{2,3} A separator can be inserted between the electrodes, though this results in high resistance and low current density. Typically secondary lithium batteries use an intercalation anode reducing the anode capacity. Sodium-based batteries have received attention as an alternative to the lithium-based batteries due to several factors. Sodium forms uniform dendrite free electrodeposits on the electrode surface. Also, sodium has a low atomic weight and cost, due to its relative abundance.

A medium temperature sodium rechargeable battery, the “Zebra” cell, has demonstrated encouraging results. While the specific energy is greater than 130 Wh/kg, operating temperatures of \~250°C are necessary to maintain the molten state of the chloroaluminate inorganic salt, NaCl:AlCl\textsubscript{3}, electrolyte. At this operating temperature, the Zebra cell contains molten sodium (melting point (mp) 98°C) as the anode. As shown in Figure 1.1, a solid-state separator is placed between the liquid Na and the electrolyte as direct contact results in the production of aluminum (Equation 1.1).
3Na + NaAlCl₄ → Al + 4 NaCl \hspace{1cm} (1.1)

An appreciable voltage drop (ca. 350 mV) results from the use of the separator under typical operating conditions.⁴,⁵ The overall cell reaction and half-cell reaction for the “Zebra” cell are given in Equations 1.2 to 1.4.

\[
\begin{align*}
\text{Charged} & \quad \Leftrightarrow \quad \text{Discharged} \\
\text{Anode:} & \quad 2Na \quad \Leftrightarrow \quad 2Na^+ + 2e^- \quad (1.2) \\
\text{Cathode:} & \quad \text{FeCl}_2 + 2e^- \quad \Leftrightarrow \quad \text{Fe} + 2\text{Cl}^- \quad (1.3) \\
\text{Overall:} & \quad \text{FeCl}_2 + 2Na \quad \Leftrightarrow \quad 2\text{NaCl} + \text{Fe} \quad (1.4)
\end{align*}
\]
Ionic liquids can be utilized in place of the sodium tetrachloroaluminate electrolyte allowing for lower temperature operation and elimination of the separator. ILs formed by mixing dialkylimidazolium chloride and aluminum chloride have been investigated widely for both battery and electroplating applications. For example, 1-ethyl-3-methylimidazolium chloride (EMIC) forms a liquid phase at ambient temperature when mixed with aluminum chloride over a wide composition range. Also, ILs using 1-methyl-3-propylimidazolium chloride (salt II in Figure 1.2) and methanesulfonyl chloride (MSC) have demonstrated encouraging results for sodium-based batteries. This work examines Quaternary ammonium (Quat) based ILs as an alternative to the imidazolium-based ILs. Quat-based 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. A main objective of this work is to identify salts that, when mixed with aluminum chloride, give us low operating temperature and viscosity, high stability (especially to reduction), and are applicable to battery utilization.

ILs are formed by mixing a halide salt with aluminum halide. Equations 1.5 and 1.6 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$_2$Cl$_7^-$ (Lewis acid) when mixed with the organic chloride salt, as shown in Equation 1.5 and 1.6. Neutralization of the Al$_2$Cl$_7^-$ occurs by reacting Al$_2$Cl$_7^-$ with a Lewis base (e.g. NaCl or Quat$^+$ Cl$^-$) to produce neutral AlCl$_4^-$ ions (Equation 1.7). 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.
Figure 1.2 Structures of salts investigated in this work.
Quat$^+$Cl$^-$ + AlCl$_3$ → Quat$^+$ + AlCl$_4^-$  

(1.5)

AlCl$_4^-$ + AlCl$_3$ → Al$_2$Cl$_7^-$  

(1.6)

Al$_2$Cl$_7^-$ + NaCl → NaAlCl$_4$ + AlCl$_4^-$  

(1.7)

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$_2$Cl$_7^-$ anions. ILs containing an excess of Quat, N < 0.5, are basic and contain AlCl$_4^-$ and Cl$^-$ anions.

The electrochemical window of the resulting IL is determined by the relative acidity of the chloroaluminate IL. Neutral melts have the widest electrochemical window with the negative potential determined by the reduction of the Quat$^+$ cation and the positive potential by the oxidation of the AlCl$_4^-$ anion. In an acidic melt, the negative potential is limited by reduction of Al$_2$Cl$_7^-$ to elemental aluminum$^{16}$, while Cl$^-$ is easily oxidized to chlorine in basic melts. Previous studies have found that it is necessary to add an acid (such as HCl or SOCl$_2$) to the neutral ionic liquid to activate the Na/Na$^+$ redox process.$^{6,7,17-19}$ Without an additive, Na$^+$ reduction has only been observed at a mercury electrode.$^{20}$ Lithium and potassium were also reduced at a mercury electrode by Scordilis-Kelley et al.$^{16}$

Figure 1.2 shows the structures of the salts investigated throughout this study. The Quats containing three different alkyl groups, IX through XVII, were synthesized by reacting tertiary amines and alkyl chlorides. In Chapter 4, the properties of ILs formed by mixing AlCl$_3$ and R’R$_3”$NCI are reported. The presence of a benzyl group was found...
to delocalize the positive charge on the nitrogen and lower the IL mp. Similar to the imidazolium ILs, sodium could be reversibly deposited upon addition of SOCl$_2$.\textsuperscript{17} In Chapter 5, ILs formed from asymmetric benzyl substituted Quats were investigated. Disrupting the symmetry of the cation lowered the mp of the resulting IL. For example, the IL of BenEtMe$_2$NCl (IX) was liquid at room temperature. The role of the additive in reversibly depositing sodium was evaluated in Chapter 6. The additive was determined to disrupt the coordination between Na$^+$ and AlCl$_4^-$, freeing Na$^+$ ions for reduction to the metal state. Chapter 7 examines the stability of several salts both as the solute in Acetonitrile (ACN) and in the IL form. Quats composed of butyl and propyl groups were found to be more stable than those containing a benzyl group. Also, the IL of BuMe$_2$ProNCl (XV) with aluminum chloride was found to be a more conductive and less viscous liquid than the benzyl substituted ILs. In Chapter 8, new additives are identified that catalyze the efficient reduction and reoxidation of sodium from a neutral IL. The electron pairs found on the chlorides of small hydrocarbons, such as chloroform-D and carbon tetrachloride, disrupt the coordination between Na$^+$ and AlCl$_4^-$. In Chapter 9, ether substituted Quats were synthesized and the impact of placing the oxygen one or two carbons from the nitrogen was determined. Upon neutralization, the conductivity of the ether substituted ILs was found to increase as the electron pairs on the oxygen atom are believed to free Na$^+$ ions. Chapter 10 examines the possibility of a Li-Na alloy anode. The codeposition of lithium and sodium was demonstrated to suppress the dendrite formation observed when depositing lithium alone.
1.2 Fuel Cells

Fuel cells have several potential advantages over other energy conversion and storage devices. High temperature cells, such as solid oxide fuel cells have high power and energy conversion efficiency. Low temperature fuel cells (i.e. near room-temperature), such as PEM fuel cells are more convenient to use, however, the power and conversion efficiency are lower because of kinetic limitations. PEM cells using liquid fuels, such as methanol or formic acid, can have high energy density compared to batteries, if concentrated liquid fuels can be used. Dilute methanol or formic acid are often used to increase the power density at the expense of energy density.

PEM cells use a polymeric membrane to transport protons from the anode to the cathode, converting the fuel (e.g. hydrogen, methanol, formic acid) and oxygen into water. Equation 1.8 shows the half reaction for the oxidation of methanol and water.

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-
\] (1.8)

Expensive, precious metal catalysts, such as platinum, are required at the cathode due to the production of hydrogen peroxide under acidic conditions. Alkaline fuel cells can use nonprecious metal catalysts (e.g. nickel) due to a more facile mechanism for oxygen reduction and the higher operating temperature. However, alkaline cells with hydroxide electrolytes are intolerant to air because of the formation and precipitation of carbonate salts. Molten carbonate cells are tolerant to carbon dioxide and can be operated
in air, although their operating temperature and liquid electrolyte are technologically challenging to deal with.\textsuperscript{21}

Small fuel cells, where high energy density and convenience are at a premium, are generally operated at ambient temperature with little or no auxiliary hardware (such as pumps or water recycling equipment) because of the lack of insulation and need for low cost. The critical aspect of low power fuel cells, such as for low power wireless sensors, is the ability to store and use highly concentrated fuels in the smallest possible form factor.

In Chapter 11, the feasibility of a room temperature carbonate (RTC) fuel cell system is examined. The RTC used a commercial anion exchange membrane, converted to the bicarbonate/carbonate form by soaking in an aqueous solution. Typically these anion exchange membranes are formed by incorporating positive quaternary ammonium sites into a polymeric structure. A RTC cell offers carbon monoxide tolerance, as well as the potential to use nonprecious metal catalysts (e.g. nickel), especially at the air cathode.\textsuperscript{21} Another significant advantage of the carbonate cycle is that when methanol is used as the fuel at the anode, water is not necessary to oxidize methanol (as in PEM cells). Thus, the anode does not consume water and it may not need to be carried with the fuel, which would significantly increase the energy density of the fuel. Equations 1.9 and 1-10 show the proposed half reaction for an ambient temperature carbonate conducting fuel cell using hydrogen or methanol as the fuel.

\begin{align*}
\text{CH}_3\text{OH} + 3\text{CO}_3^{2-} & \rightarrow 2\text{H}_2\text{O} + 4\text{CO}_2 + 6e^- \\
\text{H}_2 + \text{CO}_3^{2-} & \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2e^- 
\end{align*}

\text{(1.9)} \quad \text{(1.10)}
Carbonate fuel cells recycle the carbon dioxide produced at the anode to the cathode, Equation 1.11, so as to increase its concentration and the fuel efficiency.

\[
2\text{CO}_2 + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{CO}_3^{2-}
\]  
(1.11)
CHAPTER 2

IONIC LIQUID LITERATURE REVIEW

Ionic liquids are interesting because of their ionic conductivity and negligible vapor pressure. The low vapor pressure results in virtually nonflammable liquids. Also, when used as a solvent, the IL can easily be separated from volatile reactants or products. A nearly infinite number of organic cations and inorganic anions can be combined together to form molten salts (ILs). Of particular interest are the combinations of ions that result in ILs with melting points near room temperature. The useful electrochemical window of such an IL is determined by the oxidative and reductive stability of the composite ions.

Considerable attention has been focused on chloroaluminate systems in which AlCl₄⁻ or Cl⁻ determine the oxidative limit of the electrochemical window. Researchers have found that some combinations of 1-alkylpyridinium chlorides with aluminum chloride result in liquids at or near room temperature. For example, the butylpyridinium/aluminum chloride system has been widely studied.³⁰⁻³³ Gale and Osteryoung characterized the wide range of Lewis acidities obtainable in these systems.³⁴ However, the negative potential of the electrochemical window is limited to −1.16 V vs. SCE by the reduction of the pyridinium cation.³⁵ Substitution of the 1-alkylpyridinium with a dimethylamino group was found to shift the entire potential window approximately −700 mV.³⁶
In an attempt to increase the negative limit of the electrochemical window, Wilkes et al. synthesized several dialkylimidazolium chlorides and formed chloroaluminate ILs. These liquids demonstrated a similar wide Lewis acidity range with increased stability. Also, they reported that these systems were able to solvate several compounds including ferrocene, CuCl$_2$ and TiCl$_4$. Further the aromatic structure of the imidazolium ring resulted in room temperature ILs over a wide range of compositions. Gifford and Palmisano showed the stability of the imidazolium cation could be increased further by replacing the hydrogen at the C-2 position with a methyl group. This however will increase the viscosity of the resulting IL.

The increased potential window of the imidazolium chloroaluminate ILs allows for the study of a wide range of oxidation and reduction reactions, including materials that would otherwise react with water, such as sodium or lithium. The 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. Lithium and potassium were also reduced at a mercury electrode by Scordilis-Kelly et al. It was later demonstrated that the presence of protons stabilized the plated metal and promoted the reduction of metallic lithium. Gray et al. measured the coulombic efficiency of the sodium couple as a function of the HCl partial pressure and found that a minimum of approximately 6 Torr HCl partial pressure was necessary to observe sodium plating and stripping. Fuller, Osteryoung and Carlin established that both lithium and sodium could be deposited when SOCl$_2$ was added to a neutral IL.
With a medium from which to deposit lithium and sodium at room temperature, researchers focused on the solubility of metal chlorides in the imidazolium chloroaluminate ILs. However, in acidic EMIC:AlCl$_3$ ILs, Co, Fe, Mn, and Ni were found to be soluble and complexes of the form M(AlCl$_4$)$_3$ were suggested.$^{40-42}$ In a NaCl buffered melt Pye et. al found that nickel chloride was insoluble, but the low charge density would require a very large active area.$^{43}$ Methanesulfonyl chloride (MSC) was demonstrated to form a “Quasi-Molten Salt” with aluminum chloride at room temperature that allowed for the deposition of lithium and in which copper chloride was insoluble.$^{1,44,45}$

Along with modification of the cation, there has been an emphasis on identifying new anions that form RTILs with imidazolium and quaternary ammonium salts. In particular hydrophobic, asymmetric, water stable molecules have been targeted. For example, anions such as PF$_6^-$, BF$_4^-$, CF$_3$SO$_3^-$, and (CF$_3$SO$_2$)$_2$N$^-$ (TFSI), have been combined with imidazolium cations.$^{46-48}$ Many mixtures of imidazolium/TFSI mixtures melt well below room temperature and have large electrochemical windows (> 4 V).$^{46}$ Similarly, a wide range of Quat/TFSI mixtures have been reported. Many of these systems have glass transition and melting points below 0°C.$^{14,49}$ Recently, Zhou et. al released a series of papers examining a wide variety of cations and perfluoroalkyltrifluoroborate (R$_F$BF$_3^-$, where R$_F$ = CF$_3$, C$_2$F$_5$, n-C$_3$F$_7$, or n-C$_4$F$_9$) anions, several of which formed RTILs.$^{50-52}$

A number of research groups have examined the introduction of nonalkyl groups to Quats and imidazolium salts. For example, Shirota and Castner, Jr. examined the impact effect of replacing –CH$_2$C(CH$_3$)$_3$ with –CH$_2$Si(CH$_3$)$_3$ in an imidazolium salt. For
ILs with both BF$_4^-$ and TFSI, the viscosity was decreased with the addition of silicon.$^{53}$ Several groups have also demonstrated that the inclusion of an ether group in the cation lowers the melting point of the resulting IL.$^{46,50,51,54-57}$ For example, Matsumoto et. al showed that, with TFSI as the anion, replacement of an alkyl group with an ether group can result in very low melting ILs.$^{13,58,59}$

These results indicate the wide range of anions and cations that result in liquids at or near room temperature. Similarly, ILs have been utilized in a variety of different applications. Along with both battery$^6,7$ and electroplating$^8-11$ applications, ILs have been used as a medium for organic reactions$^{60,61}$ and biocatalytic transformations.$^{62,63}$ Proton exchange membranes$^6$, numerical displays$^6$, solar cells$^{66,67}$, and supercapacitors$^{68,69}$ have all been designed utilizing ILs.
CHAPTER 3

EXPERIMENTAL

All experiments involving moisture-sensitive materials were carried out under nitrogen in a Vacuum Atmosphere (Hawthorne, CA) glove box. 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.

Table 3.1 and 3.2 list the purity and source of the liquid and solid materials utilized in this work. Unless noted, all materials were used as received. The source of purchased quaternized salts and ionic liquids is given in Table 3.3. Each of the salts was dried under vacuum at ~70°C for at least 2 days before use in the dry box. Ten Quats were synthesized by N-alkylation of 1:1 ratio of amines and alkyl chlorides while refluxing. The salts produced and reagents and solvents used are given in Table 3.4. Unless noted all reactions were carried out at room temperature for a week. The salts were then filtered and re-crystallized in acetonitrile. As necessary, the salts were dissolved in ACN and spun with activated carbon powder to remove unreacted species. The salts were then filtered and dried under vacuum at 70°C for a minimum of 48 hrs before use in the glove box.
Table 3.1 Liquid materials used throughout this work.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity</th>
<th>Supplier</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>99.5%</td>
<td>AD</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>1-Chloropropane</td>
<td>98%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>1M Boron trichloride</td>
<td>--</td>
<td>AD</td>
<td>In dichloromethane</td>
</tr>
<tr>
<td>1-Methyl-2-Pyrrolidinone</td>
<td>99.5%</td>
<td>AD</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>2-Chloroethyl methyl ether</td>
<td>98%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>99.8%</td>
<td>AD,FS</td>
<td>ACN,Anhydrous</td>
</tr>
<tr>
<td>Benzyl chloride</td>
<td>99%</td>
<td>AD</td>
<td>Reagent Plus</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>99.5%</td>
<td>AD</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>Chloroform-D</td>
<td>99.9% atom%</td>
<td>AD</td>
<td>Stirred over fresh sodium metal in the dry box to remove any traces of water.</td>
</tr>
<tr>
<td>Chloromethyl ethyl ether</td>
<td>95%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>Ethylene carbonate</td>
<td>99%</td>
<td>AD</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>Heptane</td>
<td>99%</td>
<td>AD</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>Methanol</td>
<td>99.9%</td>
<td>FS</td>
<td></td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>99.9%</td>
<td>FS</td>
<td>Spun over dry P₂O₅ while performing vapor distillation under vacuum before use in the dry box.</td>
</tr>
<tr>
<td>N,N-Diethylmethylamine</td>
<td>97%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>N,N-Dimethylbenzylamine</td>
<td>98%</td>
<td>AA</td>
<td></td>
</tr>
<tr>
<td>N,N-Dimethylbutylamine</td>
<td>99%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>N,N-Dimethylethylamine</td>
<td>99%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>N,N-Dimethylisopropylamine</td>
<td>≥99%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>99.7%</td>
<td>AD</td>
<td>Anhydrous</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>≥99.9%</td>
<td>AD</td>
<td>THF, Chromasolv Plus for HPLC</td>
</tr>
<tr>
<td>Thionyl chloride</td>
<td>&gt;99%</td>
<td>AD</td>
<td>SOCl₂</td>
</tr>
</tbody>
</table>
Table 3.2 Solid chemicals used in research.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity</th>
<th>Supplier</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-Crown-6</td>
<td>99.95%</td>
<td>AD</td>
<td>Melted, dried under vacuum and recrystallized.</td>
</tr>
<tr>
<td>Aluminum chloride</td>
<td>99.99%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>Aluminum Wire</td>
<td>99.9995%</td>
<td>AA</td>
<td>0.5 mm Diameter</td>
</tr>
<tr>
<td>Calcium Hydroxide</td>
<td>99.5%</td>
<td>FS</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>--</td>
<td>FS</td>
<td>Activated</td>
</tr>
<tr>
<td>Lithium chloride</td>
<td>99.999%</td>
<td>AA</td>
<td>Dried under vacuum at ~70°C for 2 days.</td>
</tr>
<tr>
<td>Lithium perchlorate</td>
<td>99.99%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>Nickel Wire</td>
<td>--</td>
<td>AA</td>
<td>0.5 mm Diameter</td>
</tr>
<tr>
<td>Phosphorous pentachloride</td>
<td>95%</td>
<td>AD</td>
<td></td>
</tr>
<tr>
<td>Platinum Foil</td>
<td>99.99%</td>
<td>AA</td>
<td>Thickness 0.05 mm</td>
</tr>
<tr>
<td>Platinum Wire</td>
<td>99.999%</td>
<td>AA</td>
<td>0.5 mm Diameter</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>&gt;99.9%</td>
<td>FS</td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>99.50%</td>
<td>E</td>
<td></td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>99.999%</td>
<td>AA</td>
<td>Dried under vacuum at ~70°C for 2 days.</td>
</tr>
<tr>
<td>Sodium cubes</td>
<td>99.5%</td>
<td>AD</td>
<td>In mineral oil</td>
</tr>
<tr>
<td>Sodium perchlorate</td>
<td>--</td>
<td>AA</td>
<td></td>
</tr>
<tr>
<td>Tungsten Foil</td>
<td>99.95%</td>
<td>AA</td>
<td>Thickness 0.05 mm</td>
</tr>
<tr>
<td>Tungsten Wire</td>
<td>99.95%</td>
<td>AA</td>
<td>0.5 mm Diameter</td>
</tr>
</tbody>
</table>
Table 3.3 Source and purity of purchased Quats and ILs.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity</th>
<th>Supplier</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butyl-3-Methylimidazolium tetrafluoroborate</td>
<td>&gt;97.0%</td>
<td>FL</td>
<td>BMIBF$_4$</td>
</tr>
<tr>
<td>1-Methyl-3-Propylimidazolium chloride</td>
<td></td>
<td>N/A</td>
<td>Salt II, synthesized and purified previously following published procedures.</td>
</tr>
<tr>
<td>Benzyltributylammonium chloride</td>
<td>98%</td>
<td>AA</td>
<td>Salt VIII</td>
</tr>
<tr>
<td>Benzyltriethylammonium chloride</td>
<td>98%</td>
<td>AA</td>
<td>Salt VII</td>
</tr>
<tr>
<td>Benzyltrimethylammonium chloride</td>
<td>97%</td>
<td>AA</td>
<td>Salt VI</td>
</tr>
<tr>
<td>Butylmethylpyrrolidinium chloride</td>
<td></td>
<td>D-S</td>
<td>Salt III, purified before use.</td>
</tr>
<tr>
<td>Chloromethyltrimethylammonium chloride</td>
<td></td>
<td>D-S</td>
<td>Salt I, purified before use.</td>
</tr>
<tr>
<td>Tributylmethylammonium chloride</td>
<td></td>
<td>D-S</td>
<td>Salt V, purified before use.</td>
</tr>
<tr>
<td>Triethylmethylammonium chloride</td>
<td></td>
<td>D-S</td>
<td>Salt IV, purified before use.</td>
</tr>
</tbody>
</table>
Table 3.4 Synthesis steps and Quats produced via N-alkylation of tertiary amine.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Reagents</th>
<th>Solvent</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyldiethylmethylammonium chloride</td>
<td>Benzyl chloride, N,N-Diethylmethylamine</td>
<td>ACN</td>
<td>Salt IX, went to completion in &lt; 4 hours</td>
</tr>
<tr>
<td>Benzyldimethylisopropylammonium chloride</td>
<td>Benzyl chloride, N,N-Dimethylisopropylamine</td>
<td>ACN</td>
<td>Salt XI</td>
</tr>
<tr>
<td>Benzyldimethylpropylammonium chloride</td>
<td>1-Chloropropane, N,N-Dimethylbenzylamine</td>
<td>ACN</td>
<td>Salt X</td>
</tr>
<tr>
<td>Benzyldimethylammonium chloride</td>
<td>Benzyl chloride, N,N-Dimethylethylamine</td>
<td>ACN</td>
<td>Salt XII</td>
</tr>
<tr>
<td>Butyldimethylpropylammonium chloride</td>
<td>1-Chlorobutane, N,N-Dimethylbutylamine</td>
<td>ACN</td>
<td>Salt XV, reacted at ~45°C for 5-7 days</td>
</tr>
<tr>
<td>Butylethyldimethylammonium chloride</td>
<td>1-Chlorobutane, N,N-Dimethylethylamine</td>
<td>ACN</td>
<td>Salt XIV</td>
</tr>
<tr>
<td>Ethyldimethylmethyl-etherammonium chloride</td>
<td>2-Chloroethyl methyl ether, N,N-Dimethylethylamine</td>
<td>ACN</td>
<td>Salt XVII, reacted at ~40°C for 5-7 days</td>
</tr>
<tr>
<td>Ethyldimethylmethyl-ethyletherammonium chloride</td>
<td>Chloromethyl ethyl ether, N,N-Dimethylethylamine</td>
<td>THF</td>
<td>Salt XVI, reacted at ~3°C for 3 hours and overnight at room temperature.</td>
</tr>
<tr>
<td>Ethyldimethylpropylammonium chloride</td>
<td>1-Chloropropane, N,N-Dimethylethylamine</td>
<td>ACN</td>
<td>Salt XIII</td>
</tr>
</tbody>
</table>
Conductivity measurements were performed using a custom-built probe and ThermoOrion conductivity meter.\textsuperscript{70} 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 in the dry box. Pt and W wires were fabricated into working electrodes by sealing them inside glass tubes. Prior to use, the electrodes were cleaned in hot HNO\textsubscript{3}, polished using 0.3 μm alumina powder and thoroughly rinsed with de-ionized water. The counter electrode was a twisted Pt wire or platinum foil sealed in glass on the corners. For the IL tests, the reference electrode was formed by immersing an aluminum wire in an acidic melt (N = 0.6) in a glass tube separated from the electrolyte by a fine glass frit. Equation 3.1 shows the half reaction for the reference electrode.

\[4 \text{Al}_2\text{Cl}_7^- + 3e^- \leftrightarrow \text{Al} + 7 \text{AlCl}_4^- \quad E = 0.0 \text{ V} (-0.03 \text{ V vs. NHE})^{16} \]  

The reference electrode for the acetonitrile tests was formed by immersing a silver wire coated with AgCl in the 0.1 M Quat: acetonitrile solution in a glass tube separated from the electrolyte by a fine glass frit. In all measurements, the three electrodes were positioned as close as possible to one another. IR compensation was not performed for the IL tests, but was performed for the measurements in acetonitrile solutions.
For the Li-Na alloy tests, various ratios of LiCl/NaCl were added to the acidic melt at a 20% excess to ensure that neutrality was achieved while maintaining a consistent Li\(^{+}/Na^{+}\) relation. The electrolytes were then stirred for at least 10 hours to make certain that neutrality was reached. In order to maintain neutrality of the electrolyte, it was important to perform thorough mixing immediately prior to experimentation. Approximately 0.5 mol% thionyl chloride was added using a micro-pipette and the melt was stirred for 15 minutes immediately before running the experiments. Before running the tests, the three electrodes (working, counter, and reference) were placed as close as possible to each other.

The deposits were observed with a custom built glass cell with an internal cavity less than 1 mm deep. A rectangle Pt foil electrode (~0.75 cm\(^2\) area and 0.5 mm thick) was sealed inside the cell on one end. On the opposite end of the cell from the Pt electrode, a small vacuum joint allowed liquid to be pipetted into the cell. The working electrode was formed by sealing a 0.5 mm diameter Ni wire in epoxy and polishing the exposed end smooth. The working electrode was then fitted into the joint such that it was in the IL and the liquid was completely sealed from the external environment. CE tests were performed under a nitrogen environment with the reference and counter electrodes. An optical microscope and video camera were used to capture images of the electrode surface after deposition.

Melting points were determined using a Seiko Instruments S II 220C differential scanning calorimeter (DSC). The ramp rate of the cooling cycle was 1-2°C/min and the heating cycle was 5°C/min. In the electrochemical experiments involving the electrodeposition and reoxidation of sodium, the chemical reactivity of the sodium metal
with the melt 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.\textsuperscript{19}

For the fuel cell tests, carbon dioxide, hydrogen, oxygen, and nitrogen gases were obtained from Air Products. Carbonate anion exchange membranes were prepared by soaking chloride containing AFN anion exchange membranes (received from AFN in Somerset, New Jersey) in aqueous solutions of sodium bicarbonate and sodium carbonate. Upon soaking in 1M sodium carbonate, the membranes darkened from a light brown to near black and were found to be unusable as carbonate exchange membranes due to the high pH. The aqueous solution also changed from clear to yellow. In an attempt to prevent damage to the membranes, sodium bicarbonate was added to lower the pH of the solution (resulting in green transparent membranes). The resulting membrane was measured to be 150\mu m thick. Fuel cells were constructed in two ways. The cells used for the hydrogen tests were formed by sandwiching the carbonate anion exchange membrane between two carbon electrodes coated on one side with platinum (20 wt\% Pt/Vulcan XC-72 [1 mg/cm\textsuperscript{2} Pt], ElectroChem, Inc.) and hot-pressed together. The cells used in the methanol tests were constructed using epoxy to attach a rubber gasket (with a hole of known area punched out) to the electrode and membrane. An EG&G Princeton Applied Research model 263A potentiostat was used for the electrochemical measurements.
CHAPTER 4

PROPERTIES OF TRIALKYL QUATERNARY AMMONIUM-BASED IONIC LIQUIDS

4.1 Objective

This chapter discusses the characteristics of ILs formed by mixing R’R_3”NCl salts with AlCl_3. The structures of the five chloride salts investigated are shown in Figure 4.1. These Quats were selected because of their different substituents (e.g. short chain, long chain, a benzyl (aromatic resonance)). Also, the salts are all commercially available avoiding the need to synthesize them. ILs were formed with each salt and characterized. Following neutralization with sodium chloride and the addition of thionyl chloride, sodium was electrodeposited from the benzyl substituted ILs. The stability of the metal in the IL was evaluated. The work presented in this chapter has been published in the Journal of the Electrochemical Society (JES).^71
Figure 4.1 Quaternary ammonium salts (Quats): (A) methyltriethylammonium chloride, (IV); (B) methyltributylammonium chloride, (V); (C) benzyltrimethylammonium chloride (VI); (D) benzyltriethylammonium chloride (VII); (E) benzyltributylammonium chloride (VIII).

4.2 Results

The melting points of the ionic liquids formed from the Quats in Figure 4.1 and AlCl$_3$ are shown in Table 4.1. The positive charge on the ammonium ion is delocalized by alkyl substituents. Longer alkyl chains release more electron density to the positive center than shorter alkyl chains. However, the charge delocalizing ability of the benzyl group is greater than the alkyl branches. Thus, BenMe$_3$N$^+$ has weaker ionic strength with chloride ions than salts IV and V (Table 4.1). Even though the melting point of the IL of VI and AlCl$_3$ is above room temperature, the melting point is lower than the melting
point of Na (98°C) making it potentially interesting for battery usage. In an attempt to lower the melting point, longer alkyl chains were used on the Quat to increase the charge delocalization.

Table 4.1 Melting point of ionic liquids (55 mole % of AlCl$_3$ and 45 mole % Quat).

<table>
<thead>
<tr>
<th></th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (°C) of Acidic Melt</td>
<td>278.2</td>
<td>105.2</td>
<td>55.6</td>
<td>66.4</td>
<td>40.6</td>
</tr>
<tr>
<td>Melting Point (°C) of Neutralized Melt</td>
<td>--</td>
<td>--</td>
<td>65.3</td>
<td>66</td>
<td>42.7</td>
</tr>
</tbody>
</table>

The melting point of benzyltriethylammonium chloride (VII) was greater than benzyltributylammonium chloride (VIII). However, the melting point of the melt of VII is higher than that of the IL of VI due to charge delocalization. This result implies that there are other contributions to the melting point, such as, the symmetry of the ions. A higher degree of symmetry increases the melting points of salts because of the ease of crystallization. Also, when compared to the ethyl and butyl groups found in IV and V, the benzyl group is more effective in disrupting symmetry.

The addition of sodium chloride to neutralize the three acidic melts in Table 4.1, does not greatly impact the melting points. In this case the chloride ions from NaCl convert Al$_2$Cl$_7^-$ to AlCl$_4^-$ (Equation 4.3). While Quat$^+$Al$_2$Cl$_7^-$ is replaced by Na$^+$AlCl$_4^-$, the IL remains predominately composed of Quat$^+$AlCl$_4^-$ ions (roughly 78% in the acidic
liquid versus 82% in the neutral liquid). This is believed to be the reason for the small change in the melting points.

Figure 4.2 shows the temperature dependence of the conductivity for the VI:AlCl₃ ionic liquid. For operating temperatures of 65°C to 82°C, the values range from 2.5 to 5 mS/cm, which is lower than that of EMIC (35 mS/cm at room temperature). The conductivity increases with the acidity of the melts. The fraction of Al₂Cl₇⁻ ions also increases with the acidity of the melts as more aluminum chloride molecules are forced to share the chloride atoms from QuatCl. The higher conductivity is attributed to a reduction in the viscosity of the melt and the increased percentage of Al₂Cl₇⁻ ions and possibly a lower degree of ion pairing between the Al₂Cl₇⁻ and Quat⁺ ions as compared to the AlCl₄⁻ and Quat⁺ ions. Melting points of 55.6 and 57.7°C were measured for the N=0.55 and N=0.53 melts, respectively. These results are consistent with previously reported findings.

Figure 4.3 shows a CV for VI:AlCl₃ (N = 0.55) neutralized with excess NaCl and a trace amount of SOCl₂, at 71°C on a tungsten electrode. The coulombic efficiency of 86% will vary depending on the switching potentials and the measurement conditions. Switching the potential significantly before or after the peak current is reached will result in lower efficiencies as a substantial portion of the current will go to irreversible reduction of impurities or of the electrolyte itself. The shape of the reduction and oxidation peak are very sharp, indicating a rapid redox process. The sharp rise in the reduction current and hysteresis loop shows that the nucleation of the first layers of sodium requires a small overpotential related to the nucleation and crystallization of the sodium metal on a non-sodium surface. This current-voltage shape is typical of the
sodium couple in dialkylimidazolium ionic liquids.\textsuperscript{6,19} Figure 4.3 shows a wide potential window with low background current, which indicates the presence of few impurities. Therefore, further purification of the starting materials may not result in appreciable improvements in the coulombic efficiency.

![Figure 4.2 Conductivity vs. temperature for three ILs of VI and AlCl₃.](image)

Figure 4.2 Conductivity vs. temperature for three ILs of VI and AlCl₃.
Figure 4.3 CV of the VI:AlCl$_3$ melt (N = 0.55) neutralized with excess NaCl and a trace of SOCl$_2$.

The efficiency of reduction and re-oxidation can also be measured by utilizing chronoamperometry (CA). Using this technique the reduction of sodium is initiated by applying the appropriate voltage for a fixed period of time. The voltage is then switched to that corresponding to the re-oxidation of sodium for a set period of time. The efficiency can be found by comparing the areas under each of the curves (which corresponds to the total charge deposited and removed). In Figure 4.4, the discharge time is 2 seconds longer than the charge time. The average current for the reduction process is higher than that for the re-oxidation process. As the oxidation rate is a function of the oxidation potential, modifying the switching potential and the time, will result in different efficiencies. The efficiency for Figure 4.4 is 87%.
Figure 4.4 Chronoamperometry of the VI:AlCl$_3$ melt (N = 0.55) neutralized with excess NaCl and SOCl$_2$ added.

A critical question in the study of ionic liquids is the optimum current for reduction and oxidation of sodium. This value is dependent on the melt composition, the electrode utilized and the operating temperature. Table 4.2 summarizes the resulting coulombic efficiency when the current density (for a CE test) and reduction/re-oxidation time is varied. From this table it can be seen that the maximum efficiency can be achieved at currents of 5.7 to 6.3 mA/cm$^2$, with very low efficiencies when the current density approaches low (1.3 mA/cm$^2$) or high (10 mA/cm$^2$) values.
Table 4.2 Coulombic efficiencies of a buffered VI:AlCl₃ melt (N = 0.55) with trace SOCl₂ at a tungsten electrode at 71°C.

<table>
<thead>
<tr>
<th>Current Density (mA/cm²)</th>
<th>Charge/Discharge Time (sec)</th>
<th>Efficiency (%) [+/- 1%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td>2.5</td>
<td>10</td>
<td>52</td>
</tr>
<tr>
<td>3.8</td>
<td>60</td>
<td>85</td>
</tr>
<tr>
<td>4.4</td>
<td>50</td>
<td>86</td>
</tr>
<tr>
<td>4.4</td>
<td>60</td>
<td>88</td>
</tr>
<tr>
<td>5.1</td>
<td>30</td>
<td>82</td>
</tr>
<tr>
<td>5.1</td>
<td>60</td>
<td>88</td>
</tr>
<tr>
<td>5.7</td>
<td>60</td>
<td>89</td>
</tr>
<tr>
<td>6.3</td>
<td>60</td>
<td>89</td>
</tr>
<tr>
<td>6.3</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>6.3</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>7.6</td>
<td>60</td>
<td>84</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>16</td>
</tr>
</tbody>
</table>

Figures 4.5 and 4.6 illustrate why low efficiencies were obtained with the high and low currents. Figures 4.5A and 4.5B are examples of low and high current densities, respectively. Figure 4.5 shows the reduction current with time for sodium plating. Though the background current is low, there are species present that can be reduced more easily than the Na⁺ ions in the melt. In Panel A the current density (0.63 mA/cm²) is low enough that it takes a significant amount of time (4 out of 10 seconds) and charge to reduce these species before the sodium ions can be reduced at approximately −2.4 V. In Panel B, the time prior to sodium deposition was negligible due to the high current density (10 mA/cm²). However, the current density exceeds the maximum value for sodium ion reduction resulting in the reduction of some other species, probably Quat⁺ (and a slight shift of the potential to more negative values) after ~3 seconds. The CE curves for the optimum case are shown in Figure 4.6. In Panel A the current was high...
enough (6.3 mA/cm²) that the voltage for the reduction of sodium ions rapidly reached –2.4 V, but still low enough that the voltage remained relatively constant for the entire deposition process. Following the reduction of sodium, the re-oxidation portion of the process is carried out at the same current (6.3 mA/cm²) and is shown in Panel B. During the re-oxidation, the potential remained fixed at –2.0 V until the rapid increase near 70 sec. The plateau at 2.3 V represents Cl₂ gas evolution. The efficiency for the process shown in Figure 4.6 is ~90%.

To quantify the parasitic reactions on the plated sodium in the melt, the self-discharge current, I_{self-discharge}, was calculated by measuring the efficiency as a function of the open circuit time. Using CE the self-discharge current was measured at a tungsten electrode with reduction and oxidation current densities of 6.3 mA/cm² for 100 seconds and an operating temperature of 71°C. Under these conditions, with no open circuit time, the average efficiency was 88.8%. As the measurement was repeated several times, the efficiency of the process is more precisely defined than for the CV in Figure 4.6. Figure 4.7 shows the self-discharge current using a linear-fit of the data points for the neutralized IL of VI (N = 0.55) with SOCl₂ added. The self-discharge current was 76.6 μA/cm², which is higher than that of the 1-methyl-3-propylimidazolium chloride (II) melt (22 μA/cm²).¹⁹ It suggests that the parasitic reactions in the melt with VI are more active than those in the melt with II. The higher operating temperature of the VI melt could account for the increase in the activity of the parasitic reactions.
Figure 4.5 Chronopotentiometry of a buffered VI:AlCl₃ melt (N = 0.55) with trace SOCl₂ added. The oxidation currents, not shown here, were applied after the reduction measurements.
Figure 4.6 Chronopotentiometry on a W electrode at 71°C. The buffered VI:AlCl₃ melt (N = 0.55) has SOCl₂ added. The current density was 6.3 mA/cm².
Figure 4.7 Charge density vs. open circuit time in a buffered VI:AlCl$_3$ melt (N = 0.55) with SOCl$_2$ added.

The most likely candidate to scavenge electrons from the plated sodium is the Quat$^+$ ion. The reduction potential of the Quat$^+$ depends on the electron withdrawing (or releasing) nature of the constituents groups. As discussed earlier, the ionic strength is related to the ability of the constituent groups to delocalize the charge on the nitrogen. In this regard, the aromatic ring of II has a higher level of positive ion delocalization than the benzyl and methyl groups in VI, resulting in the lower self-discharge current for the IL of II. The addition of more electron releasing groups on the cation should help in reducing the self-discharge current.
The self-discharge tests were performed using a buffered VII:AlCl$_3$ (N = 0.55) melt. Utilizing the CE test procedure outlined previously, an average baseline efficiency of 91.0% was determined using a current density of 6.37 mA/cm$^2$ on a tungsten electrode at 82°C. Under these conditions the self-discharge current was 32.7 μA/cm$^2$, which is approximately half that measured for the melt with VI. Ethyl groups release more electron density on the positive center than methyl groups. This result is very encouraging since the operating temperature (82°C) for the tests with the IL of VII was higher than that (71°C) used for the tests with the IL of VI. The increased temperature should result in more active parasitic reactions for the ethyl substituted case.

To see if the thickness of the sodium deposit affects the self-discharge current, self-discharge tests were carried out using the same conditions for the melt of VII but a lower current density (2.55 mA/cm$^2$). With these conditions, the average baseline efficiency was 92.0% and the self-discharge current was 18.0 μA/cm$^2$. The decrease in the self-discharge current with a lower current density may be due to the deposit of a thinner film.

While the results for the melts of VI and VII were encouraging, the plating of sodium in an IL of VIII was poor. Both platinum and gold electrodes showed reduction/re-oxidation cycle efficiencies of less than ~20%. The efficiency on a tungsten electrode was the highest. Efficiencies for the CV tests ran at 100 mV/sec and 74°C varied from 38 to 59%. The maximum efficiency (75.3%) was achieved using chronopotentiometry by applying a current density of 2.55 mA/cm$^2$ at 74°C. Due to the low efficiency the self-discharge current was not measured. The long butyl chains
increase the viscosity of the melt, which is believed to be, at least in part, responsible for the low efficiencies.

4.3 Discussion

In this chapter, the modification of the cation and its effect on melting points was investigated. Introduction of the benzyl group was seen to disrupt the symmetry of the cation and distribute a portion of the charge from the nitrogen. While this does not result in a room temperature ionic liquid, it provides a path to the ultimate goal of this work, the development of a room temperature ionic liquid for use in sodium batteries. Having a moderate operating condition will reduce the overall energy necessary to run the battery and therefore lead to higher overall system efficiencies. Due to the size of the benzyl group, when the Quat pairs with chloroaluminate, the viscosity is higher than desired. The extreme case is the melt of VIII, where the long alkyl chains lead to a liquid with a viscosity that is high enough to prevent the efficient reduction and re-oxidation of sodium. In contrast, both VI and VII form ionic liquids near room temperature (70 to 85°C) that support the efficient plating and stripping of sodium. The improved performance of the VII IL, when compared with the IL of VI, is attributed to the increased electron releasing ability of the ethyl groups over the methyl groups.

Modifying the anion can also impact the melting point of an ionic liquid. In other studies, larger, asymmetric anions have been shown to lower the melting points of ionic liquids. In order to achieve a room temperature ionic liquid, the symmetry of both the cation and the anion must be reduced.
4.4 Summary

Benzyl(trialkyl)ammonium chlorides were found to be good quaternary ammonium chlorides to make ionic liquids with chloroaluminate at slightly above room temperatures (70 to 85°C). The benzyl ring serves two functions: it greatly increases the size of the cation, lowering the charge density of the Quat\(^+\), while also disrupting the symmetry of the Quat\(^+\). These effects both contribute to the melting points of the ILs. As compared with the melt of VI, the IL of Quat VII had better reduction/re-oxidation efficiencies and a lower self-discharge current. The longer alkyl groups (ethyl groups) release more electron density toward the positive center than the shorter ones (methyl groups).
5.1 Objective

In the previous chapter benzyl substituted Quats were shown to result in lower melting ILs. This chapter examines ILs formed with asymmetric BenzylR’R2”NCl salts and aluminum chloride. To minimize the molecular weight and size of the cation, methyl, ethyl, isopropyl, and/or propyl groups were chosen for R’ and R”. The Quats studied were each synthesized by N-alkylation through the reaction of amines and alkyl chlorides. Increased yields (typical yields <50%) may be obtained by using an alkyl bromide or alkyl iodide and performing an ion exchange to obtain the chloride salt. The results contained within this chapter were published in JES.72

Figure 5.1 shows the structures of the four Quats examined. The physical properties (density, viscosity, and conductivity) of the resulting ILs were measured at room temperature. The ILs were also tested as electrolytes for a Na battery. The electrolytes were investigated by plating sodium on Pt and W substrates. The performance of the electrolytes was evaluated by self-discharge currents and coulombic efficiencies for the sodium couple.
5.2 Results and Discussion

Each of the Quats formed ILs at room temperature. The conductivity ($\kappa$), density ($\rho$), melting point (MP), and viscosity ($\eta$) of the ILs at $N=0.55$ are shown in Table 5.1. The densities and viscosities reported are the average values measured at room temperature using precalibrated volumetric flasks and viscometers. Three of the Quats shown in Figure 5.1 are structural isomers, and the molecular weight of the non-isomer (Figure 5.1A) is close to the others. The density for each acidic IL is nearly the same. However, the viscosity and conductivity of the Quats are different. It appears that the
packing density around the nitrogen is important. For example, the isopropyl substituent on XI is more compact than the n-propyl on X leading to a higher viscosity for XI.

Table 5.1 Properties of acidic RTILs composed of 55 mole % AlCl₃ + 45 mole % Quat.

<table>
<thead>
<tr>
<th>Quat</th>
<th>η (cP) at 27°C</th>
<th>ρ (g/ml) at 27°C</th>
<th>κ (mS/cm) at 27°C</th>
<th>T_g(°C)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td>278</td>
<td>1.26</td>
<td>0.716</td>
<td>-67.9</td>
<td>13.4</td>
</tr>
<tr>
<td>X</td>
<td>364</td>
<td>1.25</td>
<td>0.57</td>
<td>-63.1</td>
<td>-</td>
</tr>
<tr>
<td>XI</td>
<td>735</td>
<td>1.24</td>
<td>0.333</td>
<td>-57.9</td>
<td>-</td>
</tr>
<tr>
<td>XII</td>
<td>771</td>
<td>1.25</td>
<td>0.343</td>
<td>-64.1</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5.2 compares the structures and MPs for the ILs of VI, VII and IX. The three Quats have similar structures and molecular weights. However, the asymmetric component of IX (mixture of the methyl and ethyl groups vs. all methyl or all ethyl) has a dramatic effect on its MP compared to VI and VII. It is believed that the higher symmetry of the Quat permits easier crystallization resulting in a higher MP. There are two phase transitions for the IL of IX. The transition at -67.9°C is the glass transition point and the secondary transition at 13.4°C is the MP of the IL. The other Quats in Figure 5.1 only have glass transition points. Figure 5.3 shows the transitions for two of the ILs. The IL composed of IX with AlCl₃ has a glass transition and a melting point, however the XI melt has a glass transition only. Sun et. al. reported a similar DSC thermogram for tributylhexylammonium imide.¹⁴
Figure 5.2 Structural comparison and IL MPs of VI, VII and IX.

Figure 5.3 DSC curves for two acidic melts. The curve shows glass transition ($T_g$), crystallization ($T_c$), and melting point ($T_m$).
Table 5.2 shows the properties for the neutral melts (N=0.50). The neutral melts were formed by adding NaCl to the N=0.55 melts. A two-fold excess of NaCl was added to each melt to ensure neutrality. The viscosity was not measured because of the undissolved salt.\textsuperscript{73} The glass transition point occurred at a higher temperature for the melts compared to their acidic counterparts. Also, X and XI had MPs even though none were observed in the acidic melts. The second phase-transition points observed in the neutral melts with X and XII prohibit the electrochemical measurements at low temperature. An acidic melt with IX at a higher acidity (N=0.67) was previously investigated for aluminum plating.\textsuperscript{74} The conductivity of the neutralized melts (excess NaCl added) was lower than those of acidic ILs.

Table 5.2 Properties of neutral RTILs formed by neutralizing acidic melts in Table 5.1 with two-fold excess of NaCl.

<table>
<thead>
<tr>
<th>Quat</th>
<th>$\kappa$ (mS/cm) at 27°C</th>
<th>$T_g$(°C)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td>0.324</td>
<td>-56.1</td>
<td>-</td>
</tr>
<tr>
<td>X</td>
<td>0.216</td>
<td>-57.1</td>
<td>33.3</td>
</tr>
<tr>
<td>XI</td>
<td>0.125</td>
<td>-45.9</td>
<td>-</td>
</tr>
<tr>
<td>XII</td>
<td>0.16</td>
<td>-61.4</td>
<td>-9.57</td>
</tr>
</tbody>
</table>

Figure 5.4 shows the conductivity vs. temperature for the acidic melts (N= 0.55). The melt formed with IX has a higher conductivity than the others. Melts formed with XI and XII are more viscous than those of IX and X, possibly due to their denser packing density around the nitrogen. This shows that the conductivity of the ILs (for the same chemical family) is closely tied to the viscosity in the acidic melts. Figure 5.5 shows the
conductivity vs. temperature for the neutral melts. Figure 5.5 shows that the structural isomers have similar conductivity vs. temperature. The conductivity difference between the melt of IX and the others increased as the temperature increased. During the neutralization process, a second cation is introduced (i.e., Na$^+\$). The drop in conductivity with the addition of Na$^+$ will be discussed in the following chapter.

Figure 5.4 Conductivity vs. temperature for acidic ILs using the cations from Fig. 5.1 (N=0.55).
Figure 5.5 Conductivity vs. temperature with the neutral ILs using the cations from Figure 5.1.

The electrochemical properties of the neutral melts (starting material had N=0.55) were measured. The neutral melts formed with IX have a wide electrochemical potential window, in excess of 4 V, as shown in Figure 5.6. The acidic melt has a relatively narrow potential window because the \( \text{Al}_2\text{Cl}_7^- \) ion can be reduced near 0 V.\(^{39}\) Figure 5.6 shows current-potential scans at Pt, Au, and tungsten (W) electrodes in the neutral IL. Chloride ions are oxidized at about 2.0 V.\(^{39}\) We believe that the reduction near -2.0 V is from the reduction of the Quat\(^+\) ion. The current density at Pt is the highest, probably due to its catalytic activity and lack of a native oxide. Chronopotentiometry was used to evaluate the coulombic efficiency and the self-discharge current for the sodium/sodium ion couple. Addition of SOCl\(_2\) (about 1 vol. \%) was necessary for the reduction of
sodium ion and reoxidation of the sodium metal. The role of the additive (i.e., \(\text{SOCl}_2\)) was studied and will be discussed in the next chapter. Figure 5.7 is a typical chronopotentiometry curve for \(\text{Na}^+\) reduction and its re-oxidation in the IL of IX at a constant current of 0.68 mA/cm\(^2\) and 25°C. The maximum coulombic efficiency for the sodium redox couple (ratio of reoxidation charge to reduction charge) was 87.7%. For most of the constant-current measurements, both the reduction and the oxidation potentials were constant while sodium was being reduced or oxidized, such as those shown in Figure 5.7. This indicates that a constant voltage can be provided for a long period of time when a battery using this anode is discharged.

Figure 5.6 Cyclic voltammetry of the neutral IL of IX at 27°C. Working electrodes are platinum, gold and tungsten electrodes.
Figure 5.7 Chronopotentiometry of sodium deposition and reoxidation at 0.68 mA/cm².

Lower or higher constant-current experiments resulted in a lower coulombic efficiency than that shown in Figure 5.7, most likely due to the reduction of impurities or the Quat⁺ itself. Figure 5.8 shows the change in coulombic efficiency vs. current density (as applied in a constant-current, chronopotentiometric experiment). In Figure 5.8, a reduction current was applied for 10 s and the efficiency for re-oxidation of the sodium was measured (coulombic efficiency). Several current densities near the peak efficiency were selected for the extended time (100 s) to obtain the maximum coulombic efficiency. The coulombic efficiency (shown in Figure 5.8) changes with the total amount of sodium plated on the electrode. Deposition of larger amounts of sodium resulted in higher
efficiency because the reduction of impurities occurred during the first seconds of sodium reduction.

Figure 5.8 Coulombic efficiency vs. current density obtained by CE at 50°C on Pt.
The reactivity of sodium in contact with the ILs was evaluated by measuring the effective self-discharge current. Sodium ions were reduced at a constant-current of 0.68 mA/cm^2 for 100 s followed by an open-circuit period of time. The amount of sodium metal remaining after the open-circuit period was evaluated by oxidizing the sodium in a chronopotentiometric experiment. The loss of sodium as a function of open-circuit time was expressed as a current (self-discharge current). Figure 5.9 shows the charge recovered (oxidation of sodium) vs. open-circuit time following the constant-current deposition of sodium at 0.68 mA/cm^2 for 100 s. The values of self-discharge current are reported in Tables 5.3 and 5.4 for different ILs and conditions.

![Linear Fit of Data](chart.png)

Figure 5.9 Charge recovered upon reoxidation of sodium (100 s deposition at 0.68 mA/cm^2) vs. open-circuit time at 25°C on a Pt electrode.
Table 5.3 Comparison between Pt and W electrodes for coulombic efficiency and self-discharge current. The measurements were performed by chronopotentiometry for 100 s. The melt is composed of 45 mole % IX and 55 mole % AlCl$_3$ and neutralized with 100% excess NaCl. SOCl$_2$ has been added to initiate sodium deposition.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Electrode</th>
<th>Current Density (mA/cm$^2$)</th>
<th>Coulombic efficiency (%)</th>
<th>Self-discharge current (μA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25ºC</td>
<td>Pt</td>
<td>0.68</td>
<td>87.5</td>
<td>3.96</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>1.02</td>
<td>88.5</td>
<td>5.25</td>
</tr>
<tr>
<td>50ºC</td>
<td>Pt</td>
<td>4.09</td>
<td>92.4</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>5.09</td>
<td>92.0</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Table 5.4 Self-discharge current vs. Quats. Chronopotentiometry measurements were performed for 100 s with the IL of IX. The charge was matched for all melts by adjusting the time, because each melt has a different optimum current density.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Quat</th>
<th>Current Density (mA/cm$^2$)</th>
<th>Coulombic efficiency (%)</th>
<th>Self-discharge current (μA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50ºC</td>
<td>IX</td>
<td>4.09</td>
<td>92.4</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td>XI</td>
<td>1.98</td>
<td>91.2</td>
<td>28.7</td>
</tr>
<tr>
<td>71ºC</td>
<td>IX</td>
<td>4.09</td>
<td>91.5</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>3.4</td>
<td>81.7</td>
<td>36.4</td>
</tr>
</tbody>
</table>

Table 5.3 shows the comparison of the two electrodes in the same melt (IX) at two temperatures. The current density for the maximum coulombic efficiency is shown. Table 5.3 shows that at a higher temperature, higher currents and efficiencies can be achieved. The higher efficiencies may be the result of increased mobility of the reactant at higher temperature. However, the higher temperature also expedites unwanted reactions that are reflected in the self-discharge current. At 50ºC, the coulombic
efficiency and the self-discharge current for the two electrodes were nearly identical, \(i.e., 92\%\) and \(15.6\ \mu A/cm^2\), respectively. The thickness of the sodium deposit is thick enough that the effect of the base metal substrate was not seen.

Table 5.4 shows a comparison of the electrochemical properties for sodium plating in IL’s formed from salts IX, X and XI. The IL of XII was too viscous to obtain electrochemical data. Neutral melts of X and XI have higher viscosities and melting points than the neutral melt of IX. Thus, the melts of X and XI need to be operated at higher temperatures to achieve comparable viscosities to the IL of IX, as reported in Table 5.4. The coulombic efficiency for the IL of IX at 50°C is the maximum efficiency for that IL and was chosen as a reference. The same current density was used at 50°C and 70°C (4.24 mA/cm\(^2\)) so that the self-discharge currents can be compared to ILs from X and XI. The melt of IX shows better performance than the melt of XI in terms of both coulombic efficiency and self-discharge current. The melt of IX has a higher efficiency than the melt of X, but the self-discharge current is larger. The high viscosity of the X melt could be the cause of the low efficiency and the low self-discharge current due to the limited ability of reactants and impurities to reach the electrode. A similar trend was observed with IX in Table 5.3, where the higher viscosity (lower temperature) correlated with a lower coulombic efficiency. Also, the longer alkyl group (propyl) of X is more electron-releasing to the nitrogen-center (positive charge) than the ethyl group of IX. This electron releasing action for the IL of X slows down the self-discharge current at this temperature. The self-discharge current value from the IL composed of II was 22 \(\mu A/cm^2\) and methanesulfonyl chloride (MSC) based IL was 3 \(\mu A/cm^2\). The IL of IX has comparable values of self-discharge currents at room temperature.
The IL of IX showed the best performance among the Quats in Figure 5.1, because it can be used at room temperature. However, the self-discharge current becomes worse at higher temperature. The alkyl groups on IX give it the lowest viscosity and highest conductivity; however, they are also the least electron-donating groups resulting in the most easily reduced nitrogen center. The bigger alkyl groups for the Quats shared electron clouds more than the smaller alkyl groups, which can reduce the self-discharge current. On the contrary, the little increase of size of alkyl groups increased the viscosity remarkably. Thus, tailoring the size and the structure of Quat is the key element to balancing the physical properties (MP, viscosity, and conductivity) and the electrochemical performance (Quat stability) for the battery.

Previously, ILs of EMIC have been studied. The comparable EMIC IL had a molar conductivity, \( (\kappa)/(\text{mole/cm}^3) \), of ~ 4 S cm\(^2\)/mol which is 20 times greater than the IL formed from IX (0.2 S cm\(^2\)/mol) as calculated from the data in Table 5.1.\(^1\) Comparisons can be made between chloroaluminate ILs from EMIC and IX. First, the number of atoms on the cation of salt IX is 50 % higher than the EMIC cation (12 vs. 8). Second, the EMIC is a ring structure, which can reduce entanglement of the Quat substituents. EMIC’s compact structure (lower molecular weight and ring structure) helps increase its conductivity. Third, the EMIC cation is aromatic, which delocalizes the positive charge. The delocalized charge can reduce electrostatic interactions (\(i.e.,\) ion pairing) between the positive and the negative ions. These three factors contribute to the conductivity differences between the cations of EMIC and salt IX.
5.3 Summary

When mixed with aluminum chloride, asymmetric benzyl-substituted ammonium chlorides were found to form RTILs. The melting point and viscosity were measured and shown to be functions of the symmetry and molecular weight of the Quat. The acidic ILs were neutralized with NaCl and tested as electrolytes for sodium batteries. The neutralized ionic liquid of benzylethylidimethylammonium chloride (IX) has a low self-discharge current (3.96 μA/cm$^2$) at room temperature on a platinum electrode substrate. The best coulombic efficiency with this IL was 92.4 % at 50ºC. These values are comparable to the ILs of salt II and MSC. The substrate material was found to not affect the efficiency and the self-discharge current as long as they are inert in the system.
6.1 Objective

The necessity of an additive, such as HCl or SOCl₂, to electrodeposit sodium from chloroaluminate ILs has been known for more than 10 years. However, the role of the additive is not fully understood. Comments have been made that the additives may affect the electrochemical stability of the cation (reduction potential) or may form an insulating layer on the sodium. However, the comments do not explain all the data. Only very small amounts of 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. In this chapter the role of the additive in the electrodeposition of sodium is investigated. This work was previously published in JES.

In a neutral melt, sodium ions can precipitate as NaAlCl₄ or NaCl. In this study, IX-based ILs (characterized previously) were utilized. Because the solubility of NaCl in the melt is very low, NaAlCl₄ is the primary source of Na⁺ for deposition of the larger anion due to its higher solubility. Without the addition of a trace of acid, no sodium deposition is observed. It is believed that 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 here for the first time.

6.2 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 ionic liquid by altering the mole fraction of Al\(_2\)Cl\(_7^\) and AlCl\(_4^-\). Table 6.1 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 approaches neutrality (N approaches 0.5).

Table 6.1 Properties of acidic melts of IX: AlCl\(_3\). *Ref.\(^{77}\)

<table>
<thead>
<tr>
<th>Mole Fraction</th>
<th>Mole fraction (^a)</th>
<th>Measurement at 27 ± 1°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl(_3)</td>
<td>IX</td>
<td>AlCl(_4^-)</td>
</tr>
<tr>
<td>0.51</td>
<td>0.49</td>
<td>0.479</td>
</tr>
<tr>
<td>0.53</td>
<td>0.47</td>
<td>0.436</td>
</tr>
<tr>
<td>0.55</td>
<td>0.45</td>
<td>0.389</td>
</tr>
<tr>
<td>0.59</td>
<td>0.41</td>
<td>0.279</td>
</tr>
</tbody>
</table>

\(^a\) Due to equilibrium constant*, the fraction of Cl\(^-\) is of the order of 10\(^{-17}\).

\(^b\) Kinematic viscosity.
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, BenEtMe$_2$N$^+$, was kept constant, so that the relative contributions of the Al$_2$Cl$_7^-$ 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 4.46x10$^{21}$, 4.18x10$^{21}$, and 3.96x10$^{21}$ 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$_2$Cl$_7^-$ decreases, the potential number of anions increases, however, the conductivity decreases. The potential number of ions increases because Al$_2$Cl$_7^-$ 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$_2$Cl$_7^-$ ion than for the AlCl$_4^-$ ion. On a per mole basis, the equivalent conductance of Al$_2$Cl$_7^-$ 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$_2$Cl$_7^-$ is larger than AlCl$_4^-$ (Al$_2$Cl$_7^-$ ion has a bridging chloride between two AlCl$_3$ units). Thus, the electrostatic interaction between Al$_2$Cl$_7^-$ 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$_2$Cl$_7^-$ (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 6.1 shows the decrease in
conductivity as the mole fraction of AlCl$_4^-$ is increased. At higher temperatures, one would expect higher conductivity due to greater disassociation of the ion pairs and higher mobility (lower viscosity) of the IL.

![Conductivity vs. AlCl$_4^-$ mole fraction for mixtures of AlCl$_3$ and IX at 27°C.](image)

Figure 6.1 Conductivity vs. AlCl$_4^-$ mole fraction for mixtures of AlCl$_3$ and IX at 27°C.
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 mS/cm 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\(_2\)Cl\(_7^-\) were the same as in the acidic melts then, the conductivity of the N = 0.5 melt could be estimated from extrapolation of Table 6.1 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, 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
would be 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 versus temperature for each of the aforementioned melts was measured and plotted in Figure 6.2. At 27°C the sample partially neutralized to N = 0.51 (Figure 6.2D) 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°C to 82°C the conductivity values for the N = 0.51 mixtures rose from 2.18 to 5.12 for the acidic case (Figure 6.2C) and 1.647 to 4.65 mS/cm for the partially neutralized sample (Figure 6.2D). For the N = 0.53 mixture, the difference in conductivity between the acidic (Figure 6.2A) and partially neutralized (Figure 6.2B) samples increased with temperature from 0.092 mS/cm at 27°C to 0.58 mS/cm at 82°C. At each temperature, for the two acidities, 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.
Figure 6.2 Conductivity versus temperature for: (A) Mixture of 53% AlCl$_3$ and 47% IX; (B) Mixture of 53% AlCl$_3$, 43.3% IX, and 3.7% NaCl; (C) Mixture of 51% AlCl$_3$ and 49% IX; (D) Mixture of 51% AlCl$_3$, 35.3% IX, and 13.7% NaCl.

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 since the fraction of ions present (Quat$^+$, AlCl$_4^-$, and Al$_2$Cl$_7^-$) is known. The conductivity vs. mole % NaAlCl$_4$ is shown in Figure 6.3. Upon addition of 1.76 mole % 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 mole %. 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 just by 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.

Figure 6.3 Conductivity vs. mol % NaAlCl$_4$ for an initial mixture of 53% AlCl$_3$ and 47% IX at 27°C.
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.\textsuperscript{6,17,19,39,75,76} 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\textsubscript{2} were added to a NaCl-neutralized IL. An IL composed of IX and AlCl\textsubscript{3} (N = 0.55) was prepared and neutralized with two-fold excess NaCl. SOCl\textsubscript{2} was added with a micropipette and the conductivity was measured after one hour of stirring for each addition of SOCl\textsubscript{2}. Long mixing times were avoided because SOCl\textsubscript{2} could evaporate. The results of the conductivity tests after each addition are shown in Figure 6.4. The addition of 1 wt % SOCl\textsubscript{2} results in nearly a 10% increase in the conductivity even though SOCl\textsubscript{2} itself is not expected to be ionized in the melt.
Figure 6.4 Conductivity at 30°C vs. wt % SOCl₂ for an initial mixture of 50% AlCl₃, 40.9% IX, and 9.1% NaCl.

The remarkable ability of SOCl₂ (and other additives) to facilitate the deposition of sodium can be shown electrochemically. A CV of a Pt electrode in a neutralized IX: AlCl₃ melt (starting material N = 0.55) results in no electroreduction of sodium ions, only the irreversible reduction of salt IX. Similar results were obtained for mixtures tested with less than 0.025 mol % SOCl₂. However, the CV results for the same melt with 0.18 mol % SOCl₂ is shown in Figure 6.5. The reduction and re-oxidation of sodium at ca. -2 V is observed. The reduction current is far in excess of the flux that could be provided by the SOCl₂. This result suggests that the SOCl₂ 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 re-oxidation rather than changes in the potential at which reduction occurred.

Figure 6.5 CV scan for a N=0.55 AlCl$_3$:IX IL neutralized with 100% excess NaCl and 0.18 mol % SOCl$_2$ added.
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 ionic liquid cell requires an additive to electrodeposit sodium even though the melt is liquid. The conductivity data showed that exchange of $\text{Quat}^+$ for $\text{Na}^+$ resulted in a drastic drop in conductivity to a level where it appears that the $\text{Na}^+$ is contributing nothing toward the overall melt conductivity. The addition of $\text{NaAlCl}_4$ also lowers the melt conductivity, even though it appears to dissolve. Finally, the addition of trace amounts of $\text{HCl}$ (previous results) or $\text{SOCl}_2$ appear to activate the sodium ions 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 conductivity (Figure 6.4) with $\text{SOCl}_2$ addition, shows that $\text{SOCl}_2$ dramatically increases the melt conductivity. This behavior is consistent with the concept that the $\text{SOCl}_2$ serves to release $\text{Na}^+$ ions from ion-pairs enabling them to contribute to the conductivity and be reduced to sodium metal. Figure 6.6 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 $\text{Na}^+$ and $\text{AlCl}_4^-$ ions. $\text{Na}^+$ is thus available for conduction and electrodeposition. $\text{HCl}$ acts in a similar way to provide more freedom to the $\text{Na}^+$ ion. Thus, $\text{SOCl}_2$ and $\text{HCl}$ act as Lewis acids$^{78-80}$ and compete with $\text{AlCl}_3$ for $\text{Cl}^-$. 
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 6.7 shows the sodium deposition without an additive, by oxidizing the melt just prior to sodium ion reduction. A 55 mol % AlCl₃ + 45 mol % VI melt was neutralized with excess NaCl. The melting point of the neutral melt was 65°C. The temperature for the experiment was 61°C, which is below the freezing point producing a slushy melt. Before the measurement, a constant current (1.2 mA/cm²) was applied for 10 s to oxidize the chloride-containing species to chlorine. The potential scan shown in Figure 6.7A occurred immediately after the oxidation current where a chloride-containing species (e.g., AlCl₄⁻) was oxidized to chlorine. The reduction of sodium ions and subsequent reoxidation of the metal is clearly seen in Figure 6.7A. 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, Equation 6.1.

$$2\text{NaAlCl}_4^- + 2e^- \rightarrow 2\text{Na}^+ + 2\text{AlCl}_3 + \text{Cl}_2$$  \hspace{1cm} (6.1)

This behavior was not observed at higher temperatures most likely because the melt can re-equilibrate faster in the less viscous state. Figure 6.7B 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 Figure 6.7B was performed) by scanning the potential to the oxidative limit at 2.5 V. Figure 6.7C is the eleventh scan to -2.5 V, immediately following the oxidation cycle. Clearly, the oxidative current, Equation 6.1, 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 can enable the sodium ion reduction process.
Figure 6.7 CV scans at 61°C for a mixture of 55% AlCl₃ and 45% VI neutralized with 100% excess NaCl and no additives added: (A) first scan, (B) tenth scan, and (C) eleventh scan immediately after oxidation current.
6.3 Summary

The degree of ionization of the ions in an IL depends on the charge density of the ions with significant ion pairing possible. When present in a chloroaluminate IL, Na\(^+\) is coordinated strongly with AlCl\(_4^-\), making the ions unavailable for reduction to sodium metal. The sodium ions can be made available for electroreduction either by weakening the bond strength between Cl and Al atoms (Figure 6.6) of the chloroaluminate complex or by removing the chloride ion from the NaAlCl\(_4\) (Equation 6.1 and Figure 6.7). The use of additives, such as HCl or SOCl\(_2\), is consistent with this approach. The observed increase in ionic conductivity provided by the SOCl\(_2\) supports this proposed mechanism. In very viscous conditions, sufficient time is necessary to reestablish equilibrium that removal of a chlorine from NaAlCl\(_4\) results in an ability to electrodeposit sodium metal without the use of an additive.
CHAPTER 7

CATION ELECTROCHEMICAL STABILITY IN CHLOROALUMINATE IONIC LIQUIDS

7.1 Introduction

In this chapter the electrochemical stability of ten organic cations, shown in Figure 7.1, was examined as the solute in acetonitrile. Previously, similar cations were investigated in ACN by Gifford and Palmisano to investigate the impact of replacing the beta hydrogen in an imidazolium cation with a methyl group.\textsuperscript{38} For salts III, IX, and XV, the reduction mechanism was studied using mass spectroscopy. Also, the stability in the chloroaluminate IL was evaluated. This work was published in the Journal of Physical Chemistry B.\textsuperscript{81}
7.2 Results

Cyclic Voltammetry in Acetonitrile

Room-temperature ILs can be formed by mixing an imidazolium or quaternary ammonium salt with aluminum trichloride. Upon formation of an IL, the reduction potential of the cation will determine the negative potential limit of the electrochemical window. In this work, the stability of the salts was evaluated by dissolving the organic chloride salts (shown in Figure 7.1) in acetonitrile to form 0.1M solutions. The chloride
salts were used so that only the cation was changed between the samples. CV was performed scanning from the open circuit voltage toward the negative potential direction until a significant reduction current was observed. The reduction potentials reported in this text correspond to the potential at which the current exceeded 1 mA/cm² at a scan rate of 100 mV/s.

Figure 7.2 shows a comparison of three salts: salt I (Me₃(MeCl)NCl), salt II (1-methyl-3-propylimidazolium chloride) and salt IX. Sodium metal can be electrodeposited from salts II and IX when they are used in chloroaluminate ILs.¹,² Salt I is most easily reduced as shown in Figure 7.2 where a reduction current of 1 mA/cm² was observed at –1.35 volts. The chloromethyl group is easily reduced due to the electron withdrawing nature of the halogen. The imidazolium, salt II, is more difficult to reduce than I, 1 mA/cm² at –1.53 volts, and salt IX is the most difficult to reduce with 1 mA/cm² at –1.74 volts. Finkelstein et al. found that during reduction the leaving group is the benzyl radical.³,⁴ The benzyl radical is the most likely product from the reduction of salt IX. However, the hydrogen at the beta position of the imidazolium ring of salt II is more easily reduced resulting in the lower reduction potential (1.53 vs. 1.74 volts) for salt II compared to salt IX.⁵
Alkyl substituents on the quaternary ammonium cation are more difficult to reduce than benzyl groups because they form less stable radicals (i.e. poorer leaving groups). A comparison of two alkyl-substituted quaternary ammonium cations to the benzyl-substituted quaternary ammonium salt is shown in Figure 7.3. The benzyl-substituted quaternary ammonium cation is the most easily reduced among the three, -1.74 V. The reduction potential of the cation becomes more negative (more difficult to reduce) when an alkyl group is used in place of the aromatic benzyl substituent. Further, the shorter the alkyl chain length, the more negative its reduction potential due to stability of the resulting product. The smallest cation, salt XIII, is the most difficult to reduce at -1.89 V, with salt IV at -1.87 V. The difference between salts IX and XIV (benzyl to...
alkyl) is more significant than the difference between salts XIV and XIII (both are alkyl substituted).

Figure 7.3 CV scans for 0.1M solutions of salts IX, XIII and XIV in ACN.

Figure 7.4 shows the stability of the pyrrolidinium-substituted quaternary ammonium cation (III), to the benzyl-substituted (IX) and tetra alkyl-substituted cation in ACN. Salts III and XV both have nine total carbons, however, salt III, the pyrrolidinium cation, is different in that a heterocyclic ring is formed by four of the carbons. Salt III is significantly more stable than salt IX (1 mA/cm² at -2.09 V vs. -1.74 V) and more stable than salt XV (1 mA/cm² at –1.78 V). The heterocyclic ring structure of salt III makes for a very poor leaving group. If this increased stability translates to a wider electrochemical
window when the cation is used in an IL, this cation would be an attractive candidate at negative potentials (e.g. stable in the presence of sodium or lithium for metal anode batteries).

![Figure 7.4 CV scans for 0.1M solutions of salts III, IX and XV in acetonitrile.](image)

Figure 7.4 CV scans for 0.1M solutions of salts III, IX and XV in acetonitrile.
Along with the previous 7 salts, the reduction potential of three additional quaternary ammonium cations (IV, V, and X) in acetonitrile were investigated. Table 7.1 summarizes the reduction potentials measured utilizing CV tests for these three salts, as well as salts IX, XIV and XIII. The potential reported is the potential at which the reduction current exceeded 1 mA/cm$^2$. The seven carbon salts, salts XIII and IV, are structural isomers that both had a reduction potential of -1.89 V. The best stability measured for a quaternary ammonium cation was for the salt with the largest molecular weight, salt V, which reduced at –1.95 V. The two salts with benzyl groups, salt IX and X, reduced at similar potentials, -1.74 and –1.75 V, respectively. The similarity in reduction potential indicates that the aromatic benzyl group is the primary substituent determining the stability of the cation.

Table 7.1 Reduction potentials of 0.1M salt solutions in ACN.

<table>
<thead>
<tr>
<th>Name</th>
<th>MW (g/mol)</th>
<th>Carbon #</th>
<th>Reduction Potential (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_3$MeNCl (Salt IV)</td>
<td>151.68</td>
<td>7</td>
<td>-1.89</td>
</tr>
<tr>
<td>ProEtMe$_2$NCl (Salt XIII)</td>
<td>151.68</td>
<td>7</td>
<td>-1.89</td>
</tr>
<tr>
<td>BuEtMe$_2$NCl (Salt XIV)</td>
<td>165.71</td>
<td>8</td>
<td>-1.87</td>
</tr>
<tr>
<td>BenEtMe$_2$NCl (Salt IX)</td>
<td>199.73</td>
<td>11</td>
<td>-1.74</td>
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<tr>
<td>BenProMe$_2$NCl (Salt X)</td>
<td>213.75</td>
<td>12</td>
<td>-1.75</td>
</tr>
<tr>
<td>Bu$_3$MeNCl (Salt V)</td>
<td>235.84</td>
<td>13</td>
<td>-1.95</td>
</tr>
</tbody>
</table>
For the structural isomers, the propyl group in salt XIII is a better leaving group than the ethyl groups of salt IV. However, this effect appears to be offset by replacing a methyl group with the larger ethyl group. The presence of three ethyl groups is believed to sterically hinder reduction of the nitrogen. This would explain the increased stability when the three ethyl groups are replaced with butyl groups, going from salt IV to V. Though the butyl groups are better leaving groups, their size more effectively blocks the reduction of the nitrogen. The longer alkyl chains are also beneficial as they release more electron density to the positive nitrogen center.  

Mass Spectroscopy of Acetonitrile Solutions

Mass spectroscopy was used to help identify the reaction products from electroreduction of the cations in ACN. A 0.1M solution of salt IX in ACN was electrolyzed and the results are shown in Figure 7.5. The mass spectrum of an electrolyzed solution, where charge corresponding to 12.5% of the cations being reduced, is compared to a control solution, which was not electrolyzed. The electrolysis was carried out at 0°C to slow the evaporation of acetonitrile and volatiles produced during the electrolysis period. The dominant peak observed for both the electrolyzed salt IX solution and the control was mass 165, which corresponds to the mass of the salt IX cation alone. The intensity of the other masses was normalized to the 165 peak for comparative purposes. Both the control and the electrolyzed solution show mass peaks at 58.9, 100 and 363.2. The peak at 363.2 was produced in the spectrometer and corresponds to two cations bridged by a chloride anion. The electrolyzed solution shows
new peaks at 42.1, 74.1, 114.9, 135.9, 141.9, 150.1, 273.1 and 335.2. The peak at 42.1 is most likely due to addition of a proton to acetonitrile.

Figure 7.5 Mass spectroscopy results for 0.1M acetonitrile solution of salt IX before and after 12.5% reduction.
Several of the new peaks correspond to decomposition products from the cation. The peak at 74.1 corresponds to the loss of the benzene. Similarly, the peak at 114.9 could be the loss of benzene and the additional presence of acetonitrile. Loss of the ethyl group matches with the peak seen at 135.9. The loss of a methyl group corresponds to the peak seen at 150.1. Finally, the loss of the benzene and the ethyl groups from the dication with bridging chloride are seen at masses 273.1 and 335.2, respectively.

The mass spectrometry results for the electrolysis of a 0.1M ACN solution (charge corresponding to 10% electrolysis of the cations present) of salt III is shown in Figure 7.6. The results from the electrolyzed solution are compared to a control sample. The spectra are normalized to the dominant peak at 142, which corresponds to the cation, BuMePyr\textsuperscript{+}. Both the electrolyzed and control solution show peaks at mass 58.9, 100, 116.9, and 319.2. No new significant peaks were observed from the electrolyzed solution. The peak at 319.2 appears to be due to two cations bridged by a chloride anion, similar to the results for salt IX. There are two potential explanations for the absence of daughter peaks resulting from the reduction of butyl methyl pyrrolidinium cation. First, the loss of a butyl group results in a small molecule that evaporates prior to mass analysis, however, no quaternary ammonium fragment was found. Second, and more likely, is that the reduction of the salt III cation resulted in breaking the carbon-nitrogen bond within the heterocyclic ring. If this were the case, the reduced form would result in one fragment with the same mass as the parent cation. That is, reduction of the non-cyclic alkyl results in an alkyl leaving group, but the cyclic structure does not because it remains bonded to the nitrogen.
Figure 7.6 Mass spectroscopy results for 0.1M acetonitrile solution of salt III before and after 10% reduction.

Figure 7.7 shows the spectrometry results before and after a 20% reduction for a 0.1M acetonitrile solution of salt XV. Salt XV has the same number of carbons as salt III, however, the four carbon, one nitrogen heterocyclic ring has not been formed between the propyl and methyl substituents. The dominant peak in both electrolyzed and control sample is mass 144, which corresponds to the cation, BuMe₂ProN⁺. Both solutions showed peaks at 129.9, 158, 323.2, and 333.3. The peak at 323.2 corresponds to two cations bridged by a chloride anion. New peaks due to electrolysis of the solution are seen at mass 59, 75.9, 100, 116.8, 123.9, 164.1 and 375.3. The peak at 129.9 corresponds to the loss of a single methyl group, while the peak at 116.8 corresponds to
the loss of two methyl groups. The absence of additional daughter peaks is believed to be due to the formation of a lower molecular weight, more volatile species, such as when butyl and/or propyl are the leaving groups.

Figure 7.7 Mass spectroscopy results for 0.1M acetonitrile solution of salt XV before and after 20% reduction.
Ionic Liquid Properties

ILs were formed by mixing salts III, IX and XV with aluminum chloride. While the properties of the IL formed with salt IX were examined in Chapter V\textsuperscript{72}, this is the first report of ILs formed by mixing salts III or XV with AlCl\textsubscript{3}. MacFarlane et al. reported the formation of a room-temperature IL when salt III was mixed with the bis-(trifluoromethanesulfonyl) imide ion.\textsuperscript{84} ILs of salt III and its isomer, salt XV, were studied due to the increased stability in ACN. Salt IX was chosen as a reference based on its ability to form a room temperature IL and support the reduction/reoxidation of sodium.\textsuperscript{72} When mixed with AlCl\textsubscript{3}, salts I, IV and V did not form room temperature ILs. Though salt X formed an IL it was not studied due to its increased viscosity, relative to the salt IX IL. ILs formed utilizing salt II have been widely investigated in the literature, for example by Gray et al.\textsuperscript{19}

Acidic, N=0.55, mixtures were first prepared followed by neutralization with 100 mole% excess of NaCl. Previously, we showed that the acidic and neutral mixtures formed from salt IX were liquid at temperatures slightly below room temperature.\textsuperscript{72} For mixtures formed with salt XV, melting points of 0.3°C and 3.7°C for the acidic and neutral mixtures, respectively, were measured. The acidic mixture with salt III was also fluid at room temperature. However, the DSC analysis showed two endothermic phase transitions. The first was a sharp, repeatable peak at -49.2°C. The other was a broad peak, with a base at 50°C to 55°C. Upon neutralization the mixture was not liquid at room temperature and a melting point of 43.2°C was measured. It is believed that the -49.2°C phase transition for the acidic melt could be due to the presence of the larger
Al₂Cl₇⁻ anion. Upon addition of NaCl, Al₂Cl₇⁻ was converted to the smaller, more symmetric AlCl₄⁻ anion, resulting in the higher melting point, 43.2°C.

For the acidic melt of salt XV the conductivity and viscosity were measured to be 2.86 mS/cm and 61 mm²/s, respectively. This conductivity is almost four times greater than that measured for the acidic melt of salt IX. This kinematic viscosity is nearly one-quarter of that measured for the IL of salt IX, 222 mm²/s. The higher conductivity and lower kinematic viscosity is a result of the smaller size of salt XV versus salt IX.

The electrochemical window for the neutralized ILs of salt III, IX and XV are shown in Figure 7.8. The reference electrode was an N = 0.60 mixture of the corresponding salt and AlCl₃. Due to the higher melting point, tests with the salt III IL were performed at 71°C, versus 25°C for the ILs of salts IX and XV. The reduction for the IL from salt IX starts at -2 V with a peak at –2.65 V. The current was irreversible with no oxidation current observed upon scan reversal. This is typical of Lewis neutral ILs containing sodium ions and no ‘additive’ where the IL itself is reduced in favor of sodium metal deposition. For the IL of salt XV, Figure 7.8b, the reduction begins at –2.2 V with a peak at -2.6 V. Again the cathodic current was irreversible with no oxidation current, as from sodium metal or other species, upon scan reversal. For the IL of salt III the initial reduction peak is observed at –1.73 V with a maximum at –2.14 V, Figure 7.8c. A precipitous drop in current was observed after the initial cathodic peak. On repeat scans, the sharp decline in the current at –2.36 V also occurred, but at slightly different potentials. A black deposit was observed on the electrode surface after the reduction process. The drop in current and presence of a black film are consistent with the formation of a passivating film during reduction. The peak current was directly
proportional to the square root of the scan rate, indicating diffusion-limited behavior during the reduction process. A second reduction peak was observed at –2.82 V, as shown in Figure 7.8c. Repetitive scans between 0 V and -3 V for the IL of salt III showed a progressive decrease in the reduction current. The black deposit remained on the surface when the voltage was restricted to the 0 to -3 V range. The black deposit was removed when the voltage was scanned to +2 V where the \( \text{AlCl}_4^- \) was oxidized to \( \text{Cl}_2 \).

The presence of an insoluble reduction product is consistent with the mass spectrometry data presented previously in this paper. Reduction of the heterocyclic cation, salt III, does not lead to low molecular weight products whereas reduction of salts IX or XV do produce low molecular weight products which apparently do not precipitate on the electrode surface.
Figure 7.8 CV scans with 100% excess sodium and: (A) N=0.55 Mixture of Salt IX; (B) N=0.55 Mixture of Salt XV; (C) N=0.554 Mixture of Salt III.
The addition of a small amount of an acidic ‘additive’, such as SOCl₂ to a sodium-containing neutral IL facilitates the electrodeposition of sodium metal. The electrodeposition and reoxidation of sodium from the neutralized IL of salt III with SOCl₂ is shown in Figure 7.9. The reduction of sodium ions on the initial scan to negative potentials occurs at –2.3 V with a peak current of 33.2 mA/cm² at –2.4 V. However, a precipitous drop in current occurred at more negative potentials, just as in the previous figure, Figure 7.8c, when no SOCl₂ was present. On scan reversal, an oxidation current corresponding to sodium oxidation was observed. The oxidation peak current was 30.6 mA/cm² and occurred at –1.96 V. The columbic efficiency for reduction and reoxidation of sodium (charge due to oxidation divided by the charge due to reduction) was 79.2%. Thus, about 21% of the reduction current did not result in recoverable sodium deposition. The precipitous drop in current, indicating reduction of the IL is consistent with the non-sodium related current.
Figure 7.9 CV scan at 71°C for a mixture of 55.4% AlCl₃ and Salt III neutralized with 100% excess NaCl and SOCl₂ added.

If the reduction current were restricted to the less negative potentials during the reduction of sodium metal, the coulombic efficiency for reduction of sodium improved. The reduction potential was stepped to -2.3 V and held, CA, and then stepped to -1.8 V to oxidize the deposited sodium, as shown in Figure 7.10. The resulting coulombic efficiency for the neutral IL of salt III was 87.2%. No precipitous drop in current was observed at -2.3 V showing that the reduction of the salt III cation was less a factor at these potentials.
Figure 7.10 CA scan at 71°C for a mixture of 55.4% AlCl$_3$ and Salt III neutralized with 100% excess NaCl and SOCl$_2$ added.

The long-term stability of sodium in the IL formed from salt III was measured by use of CE. Sodium was electrodeposited at a current of 3.82 mA/cm$^2$ for 100 sec. An open circuit delay was inserted prior to applying an oxidation current. The average coulombic efficiency for 23 CE tests with open circuit times of 7-9 seconds was 80.3%. The loss in recoverable sodium was converted to a self-discharge rate. The effective self-discharge current over a one-hour open circuit time was 57.9 μA/cm$^2$ using a platinum electrode. On tungsten, the average coulombic efficiency from CE experiments was 79.3% and the effective self-discharge current was 86.9 μA/cm$^2$.

The voltammogram for the neutralized IL of salt XV with SOCl$_2$ is shown in Figure 7.11. Although salt XV is a quaternary ammonium cation with the same number
of carbon atoms as III, the absence of the heterocyclic ring yields lower molecular weight reductive products, as discussed previously. The voltammogram in Figure 7.11 shows a reduction current without the presence of a passivating film. The reduction of Na\(^+\) ions was observed starting at –2.35 V. Oxidation of the sodium occurred after scan reversal with a maximum current of 6.29 mA/cm\(^2\) at –1.74 V. The coulombic efficiency for the reduction and reoxidation process in Figure 7.11 was 76.2\%. A higher coulombic efficiency, 90.8\%, was observed in a CE experiment. The cathodic current was 1.13 mA/cm\(^2\) for 200 seconds at a platinum electrode. On tungsten, a slightly higher efficiency (CE experiment) was observed, 91.3\%, where the cathodic current was held at 1.53 mA/cm\(^2\) for 200 seconds. The self-discharge current was 8.5 and 9.8 \(\mu\)A/cm\(^2\) for tests at the platinum and tungsten conditions, respectively.

In each of these previous tests with the salt XV melt no agitation of the sample was performed. When a CE test was performed while stirring the sample, the current using a tungsten electrode increased to 3.56 mA/cm\(^2\). Though the baseline efficiency also increased, from 91.3 to 94.1\%, the self-discharge current increased by a factor of 10 to 101 \(\mu\)A/cm\(^2\). This indicates a greater increase in parasitic reaction rate.

The self-discharge values for the ILs of salts III and XV can be compared with the previously reported results for the salt IX IL. At 25°C, the self-discharge rate for salt XV is double the rate for salt IX, 3.96 \(\mu\)A/cm\(^2\). The discharge rate for salt III though is similar to the value, 52.0 \(\mu\)A/cm\(^2\), observed for a salt IX IL at 71°C.\(^{72}\) The increased self-discharge rate for salt XV is attributed to the reduced IL viscosity relative to the IL of salt IX.
Figure 7.11 CV scan at 25°C for a mixture of 55% AlCl₃ and Salt XV neutralized with 100% excess NaCl and SOCl₂ added.

7.3 Summary

The electrochemical stability of ten organic cations as solutes in ACN was investigated. For salts III, IX, and XV the stability in ACN was compared to that measured in the chloroaluminate IL. Both salts were liquid at elevated temperatures, but only the IL for salt XV was a liquid at room temperature and is the smallest Quat to form an RTIL with aluminum chloride. Due to its small size, the resulting IL is more conductive and less viscous than the benzyl substituted ILs. In both medium, the benzyl substituted cation (salt IX) was less stable than the alkyl substituted cation (salt XV), due to the benzyl group being a better leaving group than the smaller butyl chain. Mass
spectroscopy measurements before and after electrolysis on the salt IX samples, confirmed that reduction involves the loss of the various alkyl groups. In ACN, salt III was the most stable molecule due to its cyclic structure. However, in the IL form, salt III was the most easily reduced, resulting in an insoluble black deposit. This is consistent with the mass spectrometry data, which did not show formation of low molecular weight products, as in the reduction of salts IX and XV. The ILs of salts IX and XV demonstrate a greater ability to support the efficient reduction and reoxidation of sodium than the IL of salt III. The formation of insoluble products through the reduction of the salt III cation, leads to the inferior performance compared to salts IX and XV, even though the I-V behavior in ACN is better.
8.1 Objective

In this chapter 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. This work was recently published in Electrochimica Acta.$^{85}$

8.2 Results

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.$^{17,71,72}$ 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.$^{70}$ In this work, PCl$_5$, a weaker Lewis acid than aluminum chloride, was added to a
neutralized \( N = 0.55 \) IX 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 Figure 8.1. The scan shown in Figure 8.1 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.\(^{71}\) The reduction peak at 0.4 V was only observed when \( \text{PCl}_5 \) was added to the IL and is believed to be due to the reduction of \( \text{P} (\text{V}) \). Fuller et al. observed a similar reduction peak after the addition of \( \text{SOCl}_2 \) and attributed it to the irreversible reduction of \( \text{SOCl}_2 \).\(^{17}\) Figure 8.1 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 \( \text{PCl}_5 \) is sufficiently soluble in the IL to catalytically promote sodium reduction, but the conversion to \( \text{PCl}_6^- \) is very slow. By increasing the temperature, the time to reach equilibrium in the IL is shortened.
Figure 8.1 CV curves for neutralized N=0.55 IX IL with 5 mole % PCl\textsubscript{5} added.

The maximum columbic efficiency measured for a CV test was 21%. CA experiments produced efficiencies greater than 60% for the reoxidation of sodium metal. Figure 8.2 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\textsubscript{5} in the IL as PCl\textsubscript{6}\textsuperscript{-} produces sodium ions that are reducible at the working electrode. The lower charge density of PCl\textsubscript{6}\textsuperscript{-}, compared to
AlCl$_4^-$, lowers the degree of ion pairing between the Na$^+$ and the counter anion, enabling the deposition of sodium metal.

![Graph showing CA test results for neutralized N=0.55 IX IL with 5.8 mole % PCl$_5$.](image)

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 hours and more than 20 hours. 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.

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 IL. Figure 8.3 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 mole % 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 mole %) and additional crown ether remained undissolved. Figure 8.4 shows the voltammogram of the IL containing 1.8 mole % of 18C6. The crown ether provided a solvent shell for the sodium ions so that they were reducible. The reduction and reoxidation peaks in Figure 8.4 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$_4^-$.
Figure 8.3 Conductivity versus temperature for neutralized N=0.55 IX IL with 0, 0.66, 1 and 1.5 mole % 18-Crown-6 added.

Figure 8.4 CV results for neutralized N=0.55 IX IL with 1.8 mole % 18-Crown-6.
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 neutralized $N = 0.55$ IX IL. The reduction of sodium ions to the metal was observed after the addition of 4 mole % dichloromethane, as shown in the voltammogram, Figure 8.5. 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$_2$.\(^{71}\) 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 AlCl$_4^-$ anion.\(^{70}\)
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 sec reduction current 0.64 mA/cm$^2$, followed by a 25 sec 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 coulombic 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 potentials. However, at a reduction current of 0.32 mA/cm$^2$ for 50 seconds, followed by an oxidation current of 1.27 mA/cm$^2$ for 12.5 seconds, the measured efficiency was 47%. An additional aliquot of dichloromethane, about 4 mole %, 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 sec.

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%).

To investigate the general nature of chlorocarbons as additives, chloroform-D and carbon tetrachloride were tested as additives in fresh, 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 mole %) and CCl$_4$ (6.1 mole %) from open circuit voltage to –2.6 volts are shown in Figure 8.6. Both chloroform and carbon tetrachloride 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 current coincides with greater coulombic efficiency for chloroform-D (79.3%) versus carbon tetrachloride (55.2%).
Figure 8.6 CV test results with carbon tetrachloride and chloroform-D added to a neutral N=0.55 IX IL.

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 8.1. The maximum efficiency for the two additives is essentially the same: 90.5% for CDCl$_3$ and 88.2% for CCl$_4$. 
Table 8.1 CA test results for CDCl$_3$ and CCl$_4$ added to a neutral N = 0.55 IX IL.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Reduction Voltage</th>
<th>Oxidation Voltage</th>
<th>Step Time (s)</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDCl$_3$</td>
<td>-2.35</td>
<td>-1.96</td>
<td>300</td>
<td>90.5</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>-3.15*</td>
<td>-2.7*</td>
<td>300</td>
<td>88.2</td>
</tr>
</tbody>
</table>

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

* Pt reference, estimated potential vs acidic reference: 700 mV.

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.$^{19}$ The test conditions and results are summarized in Table 8.2. The self-discharge rates, 5.62 and 5.47 $\mu$A/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 $\mu$A/cm$^2$.\(^72\)

Table 8.2 Self-discharge test results for CDCl$_3$ and CCl$_4$ added to a neutralized N = 0.55 IX IL.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Reduction/Oxidation Current (mA/cm$^2$)</th>
<th>Step Time (s)</th>
<th>Open-Circuit Time (s)</th>
<th>Self-Discharge Rate ($\mu$A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDCl$_3$</td>
<td>1.02</td>
<td>50</td>
<td>3600</td>
<td>5.62</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>0.76</td>
<td>50</td>
<td>3600</td>
<td>5.47</td>
</tr>
</tbody>
</table>

Unless noted all tests performed using 0.5 mm diameter Pt working electrode and N=0.6 acidic reference.
Following the initial series of tests, the ILs were allowed to sit exposed to the dry box atmosphere. Figure 8.7 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.

Figure 8.7 CV results 0 days, 2 weeks and 4 weeks after addition of chloroform-D to neutral N=0.55 IX IL.
The minimum chloroform-D concentration was experimentally determined, as shown in Figure 8.8. The addition of 0.34 mole % was adequate to provide a low level of reducible sodium ions. The sodium reduction and reoxidation currents were similar for the addition of 0.96 and 1.79 mole % chloroform-D. The addition of 0.34 mole % 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 mole % (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 mole %). Increasing the concentration to 1.79 mole % (5 Na$^+$ per chloroform-D) did not produce significant improvements and resulted in a coulombic efficiency of 66%.

![Figure 8.8 CV test results after addition of 0.34, 0.96 and 1.79 mole % chloroform-D.](image-url)
CA tests were performed at three additive concentrations (Figure 8.9) where the potential was set at –2.4 V for 100 sec, followed by a potential step to –1.95 V for 100 sec. The efficiency was lowest (39.2%) at 0.34 mole % chloroform-D and highest (78.8%) at 1.79 mole % 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 sec) 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.

Figure 8.9 Results of chronoamperometry tests with 0.34, 0.96 and 1.79 mole % chloroform-D added.
A similar test was carried out to determine the effect of chloroform-D concentration on conductivity, Figure 8.10. There was little change in the conductivity when the additive was 0 to 0.5 mole %. There was a sharp increase in the conductivity when the additive concentration was increased above 1 mole %. The conductivity with 3.1 mole % CDCl$_3$ is nearly 35% greater than the IL without the CDCl$_3$ additive. The samples with greater than 1 mole % 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$_2$, 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.
To investigate the impact of reducing the chloride density of the additive, 1,1,1-Trichloroethane was added to a fresh, neutral IL. The methyl group replaces the deuterium and chloride found in chloroform-D and carbon tetrachloride, respectively. Following the addition of 1.2 mole% Cl\textsubscript{3}CCH\textsubscript{3} no sodium reduction was observed. While increasing the additive to 3.5 mole% resulted in deposition and recovery of sodium, the process was very inefficient. At 5.5 mole% additive, efficiencies greater than 60% were achievable. Figure 8.11 shows a CV scan under these conditions. The efficiency for this scan was ~63%. Using CA, efficiencies between 72 and 73% were achievable with 7.7 mole% additive.
Figure 8.11 CV results with 5.5 mole% 1,1,1-Trichloroethane added.

These results demonstrate a decreased ability of Cl$_3$CCH$_3$ to facilitate the reduction of sodium, as compared to chloroform-D and carbon tetrachloride. Introducing the methyl group increases the size and viscosity of the solvent. Also, the methyl group is not anticipated to interact with the other species in the IL potentially reducing the solubility in the IL. Further, a small degree of steric hindrance will be introduced reducing the interactions between chlorine and sodium molecules.
8.3 Summary

The ability of six different compounds to facilitate reduction of sodium from a chloroaluminate IL was investigated. PCl₆⁻ and 18-Crown-6 act to disrupt the Na⁺ and AlCl₄⁻ ion pairs producing reducible sodium ions. The addition of the small chlorinated compounds, CH₂Cl₂, Cl₃CCH₃, CDCl₃ or CCl₄, resulted in the efficient reduction and reoxidation of sodium. Addition of chloroform-D and carbon tetrachloride resulted in coulombic efficiencies greater than 88% with self-discharge currents similar to SOCl₂. It is believed that the electronegative chlorine atoms found in these solvents are oriented near the positive sodium cation, weakening its attraction to AlCl₄⁻.
CHAPTER 9

INVESTIGATION OF ETHER SUBSTITUTED QUATERNARY AMMONIUM IONIC LIQUIDS

9.1 Objective

In this chapter, two 8-atom (7 carbons, 1 oxygen) ether-containing Quats were investigated (Figure 9.1). The two ether containing Quats are isomers and the only difference between the two cations is the position of the oxygen along the ether chain. This allows investigation of the impact of the electronegative oxygen on the properties of the IL. For comparison, results for the 8-carbon salt butylethylidimethylammonium chloride (XIV) and 9-carbon salt butyldimethylpropylammonium chloride (XV) are also included. The electrochemical stability in acetonitrile (ACN) was first investigated. Then, ILs were formed with AlCl₃ and the physical and electrochemical properties were measured. For the [MeOEt]EtMe₂NCl (XVII) IL, the deposition and stability of sodium was investigated. This work has been submitted to JES for publication.
9.2 Results and Discussion

The reductive stability of the Quat is extremely important because it determines the negative potential limit of the electrochemical window. The stability of Quats can be investigated as solutes in other solvents, such as ACN. Figure 9.2 shows the cyclic voltammetry (CV) scans for 0.1M acetonitrile solutions of Quats XIV to XVII. Quat XVII (-1.78 V at 1 mA/cm$^2$) showed similar stability to Quats XIV (-1.87 V) and XV (-1.78 V). However, shifting the oxygen one atom closer to the nitrogen, to form Quat XVI, reduced the stability by 1.2 V to about -0.6 V. The reduction potential is a function of the stability of the radicals formed on reduction of the Quat. The decreased stability of Quat XVI, suggests that ACN has a greater ability to stabilize the reduction intermediates formed in the reduction of XVI than those formed with the other Quats.
To examine the impact of the ether substituent, ionic liquids were formed by mixing together 55 mole% AlCl$_3$ and 45 mole% QuatCl (N = 0.55). Particular care was taken in forming the IL of Quat XVI as the reaction is extremely exothermic and can result in the thermal degradation of the Quat if the reactants are not mixed very slowly. While previous reports indicated that formation of the acidic melt was not possible, due to a continued reaction with the excess AlCl$_3$ forming ethyl chloride, a stable IL was formed here.$^{87}$ When mixed with AlCl$_3$, Quat XV has been shown to form a room-temperature IL.$^{81}$ Reducing the size of the Quat by one carbon, to form Quat XIV, results in a solid at room temperature (minor endothermic phase transitions at -41.4 and -3.8°C, bulk mp of 51.3°C). Replacement of the butyl group with an ethyl methyl ether, resulting

Figure 9.2 CV results for 0.1M Quat in ACN.
in a similar MW 8-atom (7 carbons, 1 oxygen) cation, produces a RTIL (Tg ~ -56.6°C, endothermic phase transition at -43.1°C, mp -2.2°C). The RTIL was found to have a higher density, 1.27 g/ml, and viscosity, 118 mm²/s, than that measured for the IL of XV, 1.18 g/ml and 61 mm²/s. When neutralized with 100% excess NaCl, the resulting IL had a Tg of -66.2°C, phase transition at -29.4°C and melting point of 3.2°C. However, similar to Quat XIV, the acidic (melting point 58-62°C) and neutral (melting point 61-64°C) ILs of Quat XVI were solid at ambient temperature. The results from these two isomers show the direct impact of placing the oxygen atom closer to the nitrogen. It is believed that for Quat XVI the more electronegative oxygen draws electron density from the nitrogen atom resulting in a greater amount of positive charge localized on the nitrogen. The result is an increased coordination between the Quat and anions. In Quat XVII, 2 carbons atoms separate the oxygen from the nitrogen, reducing the positive charge on the nitrogen. The rigid ether linkage reduces the MP by making it more difficult for the cation to reorient and form a crystalline structure.

Figure 9.3a shows the electrochemical windows for the acidic ILs of Quats XVI and XVII. In both electrolytes the reduction and recovery of aluminum can clearly be seen, though the onset of aluminum reduction is shifted negative of where it typically occurs, between –0.3 and –0.4 V. For the IL of XVII, the oxidation of the electrolyte occurs at significantly more positive voltages providing a much larger electrochemical window. Figure 9.3B shows the electrochemical windows following neutralization with 100% excess sodium chloride. To ensure that an equilibrium had been reached, CVs were performed after mixing for 2 to 3 days at 60 to 70°C and then repeated after mixing for several additional days. In each case, the aluminum peak is reduced but still present.
A similar inability to completely neutralize ILs, was seen for other quaternary ammonium ILs at acidities greater than 0.6.\textsuperscript{71} Though the reduction of AlCl\textsubscript{4}\textsuperscript{-} thermodynamically occurs before sodium, the kinetics are typically slow allowing for the observation of sodium reduction. However, for Quats XVI and XVII, the ether groups appear to improve the kinetics of AlCl\textsubscript{4}\textsuperscript{-} reduction resulting in the aluminum reduction peaks observed in the CVs of the neutral ILs. While there are several potential interactions that could account for this behavior, considerable additional work is necessary to fully isolate the interaction responsible for the increase in AlCl\textsubscript{4}\textsuperscript{-} reduction kinetics.

The ILs show similar reductive limits, with the oxidative limit for each IL remaining unchanged from the acidic case. This results in electrochemical windows of approximately 4 and 4.5 V for the ILs of XVI and XVII, respectively. For Quat XVI, this is similar to the previously reported potential region.\textsuperscript{87} The similar stability of Quat XVI and XVII in the ionic form indicates that ACN facilitates the reduction process, resulting in the reduced stability observed for XVI in ACN. The results using gold and tungsten substrates were similar to those on Pt for both the acidic and neutral ILs.
Figure 9.3 (a) Electrochemical windows for acidic ILs of XVI and XVII. (b) Electrochemical windows for neutral ILs of XVI and XVII.
Figure 9.4 shows the conductivity vs. temperature relationship for the acidic and neutral ILs of Quats XVI, XVII and XV. Previously, we have shown that the neutralization results in reduction of the conductivity due to conversion of the more conductive $\text{Al}_2\text{Cl}_7^-$ ion to $\text{AlCl}_4^-$ and the coordination between $\text{Na}^+$ and $\text{AlCl}_4^-$.\textsuperscript{70} The $\sim$50% drop in conductivity upon neutralization of the IL of XV is representative of the results previously observed, where although the total number of ions increased (due to $\text{Na}^+$) ion pairing decreased the conductivity. However, for each of the ether systems, the conductivity increased upon neutralization. This indicates that the sodium ions are more free and available to act as conductors. While the acidic IL of XVII has a lower room temperature conductivity than the IL of XV, due to an increased viscosity, the neutral IL is about 40% more conductive than its Quat XV counterpart. At higher temperature, this gap widens further with the neutral IL of XVII and acidic IL of XV having similar conductivities at 82°C. Due to its increased melting point, the Quat XVI IL has very low conductivity although an increase in conductivity was observed at all measured temperatures upon neutralization. It is believed that the oxygen atom plays a similar role in freeing sodium ions as previously identified for the chlorinated additives.\textsuperscript{70,85} In both cases, the dense, positive charge is attracted to the lone electron pairs found on the chlorine or oxygen atoms, thereby weakening the interaction between $\text{Na}^+$ and $\text{AlCl}_4^-$.\textsuperscript{70}
Figure 9.4 Conductivity vs. temperature for acidic and neutral ILs of XV, XVI and XVII.

Unfortunately, while the sodium ions are available for reduction, Quat XVI and XVII are reduced more easily than sodium ions. CDCl$_3$ were added in an attempt to form a solid-electrolyte interphase (SEI) and allow for the reduction of sodium. Following the addition of 0.2 wt% CDCl$_3$, no significant change was observed in the CV behavior. With the addition of ~0.9 wt% CDCl$_3$ a slight re-oxidation was observed follow reduction (i.e. sodium metal was formed). The coulombic efficiency (ratio of the oxidative to reductive charge) was 36%. Upon increasing the CDCl$_3$ to 2 wt%, the efficiency increased to 61% recorded via CA. Figure 9.5 shows a CV curve following the addition of ~4.3 wt% CDCl$_3$. The coulombic efficiency for the scan was 67.4%.
Figure 9.5 CV results following the addition of CDCl$_3$ and/or SOCl$_2$ to the neutral XV and XVII ILs.

In the Quat XVII IL, the primary role of the additive is the formation of a stable SEI. As such, the ability of an additive to form a SEI can be readily evaluated. Thionyl chloride was added to the IL and its performance compared with that of chloroform-D. Figure 9.5 shows the impact of ~3.7 wt% SOCl$_2$ is very similar to that of CDCl$_3$ with the reduction peaks falling nearly on top of one another. However, the maximum oxidation current is about 40% greater when using SOCl$_2$, which results in a 7% improvement in the coulombic efficiency. For comparison, a CV for the neutral IL of IV with SOCl$_2$ added is also shown in Figure 9.5. The maximum current is only about 1/3 of that for Quat XVII IL, though the conductivity for the Quat XV IL is 70% of the Quat XVII IL. In the case of the IL of XV, only the Quat and AlCl$_4^-$ anion contribute to the conductivity.
until the addition of the additive.\textsuperscript{70} In the neutral Quat XVII IL, however, a significant contribution comes from the Na\textsuperscript{+} ions. The result is a more significant increase in the concentration of available sodium ions than indicated by a comparison of bulk conductivities. For both systems an overpotential of 150 to 170 mV is observed, though the potential for sodium reduction is shifted more than 300 mV positive in the IL of XVII.

The increased concentration allows for the utilization of much larger currents when performing CE experiments. For both CDCl\textsubscript{3} and SOCl\textsubscript{2} added, the maximum reduction current that could be sustained for 100 seconds was 4.07 mA/cm\textsuperscript{2}. This is nearly 4 times the 1.13 mA/cm\textsuperscript{2} achievable with the Quat XV IL. For SOCl\textsubscript{2}, CE experiments for reduction/oxidation currents of between 3 and 5 mA/cm\textsuperscript{2} for 50 to 100 seconds resulted in efficiencies between 77.4 and 81.3\%. Maximum efficiencies of \textasciitilde 83\% were achieved using CA, indicating that SOCl\textsubscript{2} forms a more stable SEI than CDCl\textsubscript{3} in the IL of XVII.

The stability of the metal deposit is important for utilization of the electrolyte in a practical device. To measure the stability, the self-discharge current was measured by first determining the average efficiency (79.2\%) for a given reduction/oxidation process, 4.07 mA/cm\textsuperscript{2} for 100 s, using a minimal amount of time between reduction and oxidation. The test was then repeated with an hour open-circuit period inserted between the reduction and re-oxidation processes. The difference between the recovered charge for the average cycles and after the open-circuit hour was then converted to an equivalent current density.\textsuperscript{19} For the IL of XVII, the self-discharge rate was nearly 76 \(\mu\)A/cm\textsuperscript{2} or more than 8 times the value of the Quat XV IL without agitation. This value is less than
the 101 μA/cm\(^2\) measured on tungsten when agitation was provided and the current was increased to 3.56 mA/cm\(^2\). However, in both tests with the IL of XV the efficiency was greater than 90\%.\(^8\) It is anticipated that the residual acidity of the Quat XVII IL has a small impact on both the cycling efficiency and self-discharge rate of the system, though the stability of the SEI and Quat are believed to be the dominating factors.

9.3 Summary

Quat XVI and XVII, both 8-atom (7 carbons, 1 oxygen) ether substituted Quats, were synthesized and investigated. In ACN, Quat XVI, with only one carbon between the nitrogen and oxygen, showed significantly less reductive stability (1 mA/cm\(^2\) at -0.6 V vs. Ag/AgCl) than Quat XVII (-1.78 V). However, the chloroaluminate IL form showed similar stability for the two systems, though the methyl ethyl ether group appears to localize a greater portion of the positive charge on the nitrogen. This results in an IL with a higher melting point (58-62°C) than the similar IL of XIV (51.3°C). In contrast, the ethyl methyl ether delocalizes the positive charge from the nitrogen producing a RTIL (mp of –2.2°C for the acidic form). Due to the oxygen atoms found in the ether substituted ILs, neutralization with sodium chloride resulted in an increase in the bulk conductivity. For example, after neutralization the conductivity of the IL of XVII increased from 1.73 mS/cm to 2.22 mS/cm at 25°C, while at 27°C neutralization of the similar Quat XV IL lowered the conductivity from 2.86 to 1.58 mS/cm. This result indicates a greater availability of sodium in these systems than other comparable Quat chloroaluminate ILs. To reduce sodium, CDCl\(_3\) and SOCl\(_2\), which both form a SEI on
the substrate surface, were added to the IL. The increased sodium concentration allowed for reduction and oxidation currents greater than 4 mA/cm$^2$ at room temperature. However, the maximum achievable cycling efficiency for the sodium reduction/oxidation process was only 83%, as compared to more than 91% for Quat XV.$^{81}$ The self-discharge rate, 76 $\mu$A/cm$^2$, was much higher than the other Quat based ILs studied.
CHAPTER 10

ELECTROCHEMICAL DEPOSITION OF LI-NA ALLOYS FROM AN IONIC LIQUID ELECTROLYTE

10.1 Objective

In this chapter, we investigate a lithium metal anode for use in a secondary battery. However, anodes using lithium metal are prone to forming dendrites when recharged leading to capacity fading and electrode shorting. The formation of dendrites also occurs with other metals, such as in the electrodeposition of tin, silver, and zinc. Electronic-system failures have been attributed to short circuits caused by metallic dendrites. The silver and tin whiskers observed in electronic components grow slowly over time when the circuit elements are maintained at different potentials. In general, dendrite suppression has been achieved by alloying the metal with a small amount of a second metal, ca. >1%. For example tin-lead and zinc-nickel are reliable metal systems for solderability and corrosion resistance. The deposition potential and melting point of the alloy are often lower due to the alloy effect.

In this chapter, the lithium-alloy has been investigated as a means to producing a dendrite-free anode for lithium batteries. Sodium has been chosen as the alloying metal, although other elements can also be considered, such as potassium. The formation of dendrites for lithium, sodium, and their alloys were investigated in an IL electrolyte. The deposition potential, coulombic efficiency for the re-oxidation of the deposited metal, and composition of the deposit are reported. These findings were published in JES.
10.2 Results

The IL was formed by mixing 45 mole % benzylethyldimethylammonium (IX) and 55 mole % aluminum chloride. NaCl and/or LiCl were then used to neutralize the IL with excess salt added to maintain neutrality. The conductivity of the neutral IL containing sodium and/or lithium is of interest because of the degree of ion pairing that occurs between the alkali cation and AlCl$_4^-$.

The conductivity of the ILs was measured as a function of the concentration of the dissolved lithium and sodium cations at 25°C. The mole fraction of BenEtMe$_2$N$^+$, AlCl$_4^-$, and SOCl$_2$ was held constant in all the experiments. The conductivity values for five, neutral ILs with and without SOCl$_2$ are shown in Table 10.1. The mole fraction of the alkali cation in the liquid phase was 9 mol% in each IL. The conductivity of the IL increased as the lithium-to-sodium ion ratio increased. The lithium-only ion IL had a conductivity of 549 $\mu$S/cm while the sodium-only IL had a conductivity of 321 $\mu$S/cm. Previously, it was shown that replacement of the organic cations with sodium ions results in a lower conductivity melt due to ion-pairing of Na$^+$ with AlCl$_4^-$. The improvement in conductivity by replacement of lithium ions for sodium ions may be due to the smaller size of the lithium ion. A smaller ion could result in a higher packing density along with a greater mobility resulting in an increase in conductivity. The conductivity of the LiCl-neutralized melt may also be higher than that of the NaCl melt due to a higher molar saturation for Li$^+$ than Na$^+$ (i.e. some of the excess LiCl could dissolve). To ensure neutrality of the melt, excess LiCl and/or NaCl was added (depending on the desired melt composition). If a higher
percentage of the excess LiCl was dissolved, relative to that of the NaCl, a higher conductivity would be observed due to the greater ion density of the melt.

Table 10.1 IL conductivity at room temperature at various LiCl:NaCl ratios before and after adding SOCl₂.

<table>
<thead>
<tr>
<th>LiCl (%)</th>
<th>NaCl (%)</th>
<th>Before Adding SOCl₂ Conductivity (μS/cm)</th>
<th>After Adding SOCl₂ Conductivity (μS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>549</td>
<td>542</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>466</td>
<td>469</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>428</td>
<td>466</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>364</td>
<td>371</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>321</td>
<td>363</td>
</tr>
</tbody>
</table>

Additives also affect the conductivity of the melts. Thionyl chloride (SOCl₂) has been shown to increase the conductivity by increasing the degree of dissociation of the Li⁺ and Na⁺ from their counter ions, allowing electrodeposition to occur. The ~10% increase in the conductivity of the Na-only melt (and little change in the Li-only melt) implies that the SOCl₂ increases the free Na⁺ concentration more than for Li⁺. The mixed melts show a small increase in conductivity after SOCl₂ was added. Since the SOCl₂ is neutral and its molar fraction is small, the liquid itself has little influence on the overall conductivity.
CV was used to characterize the electrodeposition and reoxidation of sodium and lithium. Figure 10.1 shows CVs for five ILs with different sodium-to-lithium ratios. In each case, the IL had an acidity of $N = 0.55$ before neutralization.

The reduction potential of the IL neutralized with only NaCl has previously been reported to be -2.3 V.\textsuperscript{71} The sodium-containing IL reduction potential is more negative than that of the IL neutralized with LiCl, which begins to reduce at -1.8 V. In each case, a hysteresis was observed where an overpotential for nucleation of the metal was present on the first scan to negative potentials. The 90\% Li\textsuperscript{+}/10\% Na\textsuperscript{+} IL has a similar current-
voltage (I-V) behavior to that of the lithium-only IL, and the 10% Li<sup>+</sup>/90% Na<sup>+</sup> IL is similar to the sodium-only IL.

The reoxidation of the metal is different for each mixture in Figure 10.1. The pure sodium and pure lithium ILs have one large oxidation peak, while the mixed sodium-lithium deposits have two or three oxidation peaks. This is possibly due to the presence of different Li-Na alloys (different ratios of metal), or the selective oxidation of one metal from the alloy at a more negative potential than the other metal. For example, the oxidation potential of pure sodium is different from pure lithium metal. A less negative oxidation potential will prevent any reaction between the metal and the organic cation (IX) that is reduced at -2.8 V.

The CV curve for the 50% Li<sup>+</sup>/50% Na<sup>+</sup> is shown in Figure 10.1. The slope of the I-V curve is more gradual than the other melts, indicating possible kinetic effects. The re-oxidation of the metal shows the most distinct double oxidation peaks of all the alloys studied here. A significant oxidation current is observed at potentials negative of the initial reduction values, indicating that both lithium and sodium are reduced, with lithium at a more positive potential. The sodium is expected to be oxidized first (having a more negative reduction potential) from the alloy.

The coulombic efficiencies for the deposition-stripping of the metal was obtained from the CV curves by integrating the total charge on reduction and oxidation, as reported in Table 10.2. The coulombic efficiency is the total oxidation charge divided by the reduction charge. The first column of results in Table 10.2 shows the coulombic efficiencies from the CV experiments when a -2.6 V switching potential was used. The 90% LiCl/10% NaCl IL had the highest efficiency, 84%, and the 50% LiCl/50% NaCl
melt had an efficiency of 83%. This is consistent with the previous observation that alloy deposition occurs at more positive potentials, where there is a lower probability of IL reduction. A survey of conditions was performed to find the highest coulombic efficiency in each IL of IX. In these experiments, the scan rate was held constant at 100 mV/sec, while the switching potential was varied. The second column of Table 10.2 shows the highest efficiency obtained from the survey experiments along with its corresponding switching potential. The 90% LiCl/10% NaCl melt had the highest efficiency at 88% (switching potential of -2.3 V). The pure lithium IL had an efficiency of 74% (switching potential -2.4 V) while the pure sodium melt had an efficiency of 78% (switching potential -2.6 V). This is consistent with the observation that lithium is deposited at more positive potentials than sodium. The optimal switching potential for the 90% LiCl/10% NaCl melt is similar to that of the 100% LiCl melt. This is consistent with the data in Figure 10.1 that shows a similar I-V behavior for the two ILs.

Table 10.2 Coulombic efficiencies at room temperature for 5 different LiCl:NaCl ratios.

| LiCl (%) | NaCl (%) | Cyclic Voltammetry | | Chronoamperometry | | Chronopotentiometry | |
|----------|----------|-------------------|---|-------------------|---|-------------------|
|          |          | Max Efficiency    | |                |    | Max Efficiency    | |                |    | Max Efficiency    | |                |    |
| Efficiency | Switching Potential | (%) | | Efficiency | Potential Steps | (%) | | Efficiency | Current Steps | (%) | |
| 100 | 0 | 72 | 74, -2.4 | N/A | 62, -2.35/-1.2 | 50 | 75, 1.02/-1.02 | |
| 90 | 10 | 84 | 88, -2.3 | 31 | 91, -2.3/-1.3 | 40 | 80, 1.02/-1.02 | |
| 50 | 50 | 83 | 87, -2.4 | 46 | 68, -2.4/-1.3 | 62 | 65, 0.41/-0.41 | |
| 10 | 90 | 74 | 74, -2.6 | 63 | 72, -2.45/-1.3 | 65 | 65, 0.51/-0.51 | |
| 0 | 100 | 78 | 78, -2.6 | 71 | 71, -2.5/-1.8 | 85 | 85, 0.51/-0.51 | |

* Switching potential was -2.6 V

b Voltage step to -2.5 V and -1.2 V

c Potential steps of +0.51 and -0.51 mA/cm²
CA was also used to measure the coulombic efficiency, as shown in Table 10.2. When the efficiency is measured by CV, the potential varies throughout the experiment. The current corresponding to metal deposition vs. that corresponding to IL reduction is a function of potential, especially at the extremes of the potential scans. In CA, potential steps are used which correspond more closely to that of a battery’s operation. The reduction and oxidation potential steps used in the experiments were varied to find the optimal setting for deposition in each of the ILs. The 90% LiCl/10% NaCl melt had the highest efficiency, 91%, with potential steps of -2.3 V followed by -1.3 V (each step was for 100 s). The 90% LiCl/10% NaCl melt also gave the highest efficiency from CV measurements. The CA curve for the 90% LiCl/10% NaCl melt can be seen in Figure 10.2.

Constant potential steps and step times were applied to each melt to compare the melt efficiencies directly. The efficiency should increase as the amount of metal plated was increased. This was previously shown to be true in other IL’s and was attributed to an initial parasitic current due to the reduction of impurities. Potential steps of -2.5 V and -1.2 V (100 s per run) were applied to each melt. The efficiency values of each IL subjected to the same potential steps (-2.5 V/-1.2 V) can be seen in Table 10.2 in the first chronoamperometry efficiency column. The 100% LiCl IL efficiency is not reported because the potential step to -2.5 V is beyond the stable range of the mixture. The general trend in the maximum efficiencies follows a trend similar to the CV data.
Figure 10.2 CA curve at room temperature for the 90% LiCl/10% NaCl IL. Potential steps of -2.3 V followed by -1.3 V were applied.

CE was also used to measure the coulombic efficiency. The maximum efficiency was measured by optimizing conditions to maximize the efficiency for each IL. These results are shown in Table 10.2. The values of efficiency are similar to those observed by the other techniques. The 90% LiCl/10% NaCl, which gave the highest efficiency values with CV and CA, had a coulombic efficiency of 80% when the current steps were 1.0 mA/cm$^2$ for 100 s. The current steps for maximum efficiency were higher in the ILs with high lithium concentration. This can be seen in the CVs in Figure 10.1 during deposition where at lower overpotentials there is less competition from reduction of the IL. The current steps required for maximum efficiency for a CE measurement, depending on the melt, ranged from 0.41 mA/cm$^2$ to 1.22 mA/cm$^2$, as seen in Table 10.2. Each melt was
then directly compared by subjecting each IL to current steps of 0.51 mA/cm$^2$ for 100 s per step. These results are seen in Table 10.2 and show that at a relatively low current, like 0.51 mA/cm$^2$, ILs with higher sodium concentrations have a higher efficiency.

Elemental analysis was performed on the metal deposits for each of the melts in order to determine if both lithium and sodium were present. Atomic absorption spectroscopy and a qualitative flame test were used to determine the presence of lithium and sodium in the deposits. The metal from the electrochemical depositions was initially dissolved in DI water. A platinum wire was immersed in the metal-containing solution and then placed into a blue flame. Sodium and lithium ions produce yellow and red flames, respectively. The pure sodium IL produced a deposit which resulted in a yellow flame and the lithium IL produced a deposit which resulted in a red flame. When the Li$^+/\text{Na}^+$ alloy deposits were tested, the flame color was clearly a mixed yellow and red flame. This qualitative analysis confirmed the presence of lithium and sodium deposit from the mixed Li$^+/\text{Na}^+$ IL. Atomic absorption was used to quantify the alloy ratio deposited from the 90% Li/10% Na IL. Standard solutions of LiCl and NaCl were prepared and used to calibrate the atomic absorption spectrometer. The electrodeposited metal was dissolved in DI water and the concentration of the two ions was measured. The Na-to-Li ratio obtained by atomic absorption was compared to that in the melt. A Na/Li molar ratio of 50:1 was found from metal deposited from the IL of IX. This ratio is not consistent with the composition of the melt, indicating that the deposit was sodium-rich; however, quantitative dissolution of the metal deposit may not have occurred. This result clearly shows that Li/Na alloys are present during deposition, resulting in the changes of the electrochemical properties discussed earlier.
Visual examination of the deposits for dendrite formation was performed using a custom-built optical cell. This cell was thin so that visual observations could be made through the IL without disturbing the working electrode. CE tests were performed using a nickel electrode (0.5 mm diameter) and IL of XV, which was found to be more transparent than the IL of IX. Initially, a constant reduction current of 1.53 mA/cm\(^2\) was applied for 2.5 min. Following deposition, the open circuit voltage of the working electrode (relative to the counter electrode) was between –3.3 and –4 V. A constant oxidation current of 1 mA/cm\(^2\) was then applied until a sharp increase in the voltage was observed, indicating the oxidative removal of the alkali metal. Reduction (1.53 mA/cm\(^2\)) was performed for 30 min followed by examination under a microscope.

Figure 10.3 shows the dendrite formation from an IL containing only LiCl (no sodium ions present). Dendrites are clearly visible in all depositions from lithium-only ILs. This is consistent with previous findings where dendrites were seen at currents as low as 0.5 mA/cm\(^2\) in as short as 1 min.\(^9^4\) When the tests were repeated with a 50/50 wt% mixture of LiCl and NaCl neutral ILs, no dendritic growth was observed. The Li-Na alloy deposit was thin and smooth on the surface of the electrode. The electrodes were thoroughly examined for dendrites. The potential of the working electrode was –3.65 V vs. the counter electrode at open circuit. This shows that alkali deposit was present on the surface. The application of an oxidation current of 1 mA/cm\(^2\) for 1 min resulted in a voltage consistent with the oxidation of alkali metal from the surface. The open circuit voltage was –3.55 V following this test. Finally, immersion of the alkali metal electrode in water resulted in a visible reaction and formation of gas bubbles, consistent with the reaction of elemental lithium or sodium with water.
Extending the deposition time to 4 h resulted in a thicker, rough deposit in each IL. While the Li/Na deposit had a rougher but non-dendritic surface, the lithium-only IL showed the preferential growth of dendrites.

The ability of codeposited sodium to suppress the growth of dendrites was also investigated by dissolving LiClO\textsubscript{4} and NaClO\textsubscript{4} (1M) in ethylene carbonate/propylene carbonate (50:50 vol.%). When only 1M LiClO\textsubscript{4} was used in the electrolyte, dendritic growth was observed upon deposition for 5 h. When a 50:50 vol.% mixture of 1M LiClO\textsubscript{4} and 1M NaClO\textsubscript{4} was used, a spongy, porous deposit was formed.
10.3 Discussion

The goal of this work is to deposit a Li-Na alloy which could be used as the anode in an alkali metal battery without the formation of dendrites during deposition. Shifts in reduction potentials and oxidation peaks are consistent with alloy deposition. A reduction potential shift occurred during deposition for all the mixed Na\(^+/\)Li\(^+\) ILs, indicating alloy deposition. Studies have shown that the deposition of two or more metals (in this case, lithium and sodium) is possible as long as the reduction potentials are similar.\(^9\) Figure 10.1 shows that the pure lithium and pure sodium I-V curves are similar in shape and potential from -2.15 V to -2.32 V. The 90% Li/10% Na IL clearly exhibits reduction in this potential range. Chemical analysis confirms the presence of sodium and lithium in the deposit.

The overpotential exhibited during oxidation of the 90% LiCl and 10% NaCl melt deposit is consistent with the existence of an alloy. On positive-going sweeps, oxidation begins at -2.0 V, which is 0.2 V more negative than the point of initial reduction (-1.8 V). This could be due to the presence of an alloy or selective oxidation of one metal from the alloy at a more negative potential. Other studies have shown that two-phase alloys can codeposit on a polarized electrode surface even if a system is capable of forming a continuous solid deposit.\(^9\) Multi-phase alloys can produce the multiple oxidation peaks, as seen in our results.

Like lithium, both silver and tin form dendrites in the presence of a potential gradient. Dendritic growth with silver and tin is suppressed by alloy formation. Similarly, dendrite formation was observed when the deposition was carried out at 1.5
mA/cm² for 30 minutes in a LiCl neutral IL. When a mixed (LiCl and NaCl) neutral IL was used under the same conditions, dendrite formation was not observed. Further studies are necessary to determine the optimal conditions and composition for preventing dendritic growth. Parameters such as concentration and current density must be examined for use as a Li-Na alloy anode.

A rechargeable Li-ion battery consists of a lithium anode and a metal oxide cathode such as lithium cobalt oxide. To maximize the specific capacity of the battery, the minimum sodium concentration at which a nondendritic deposit is formed should be used. Also, the amount of sodium should be minimized as the cathode works on the lithium-only cycle, making it necessary for the electrolyte to hold the entire Na⁺ content when the battery is discharged. For example, the minimum sodium content to suppress dendrites needs to be understood to operate in a battery with a metal-anode and oxide cathode (e.g. MnO₂/LiₓMnO₂). The sodium would participate in the anode reaction but not with the cathode (to an appreciable extent). During charging, the majority of the sodium would reside in the metallic state on the anode and maintain a minimum content so as to suppress dendrite growth. During discharge, the lithium would reside in the metal oxide (e.g. LiₓMnO₂) and a majority of the sodium ions would remain dissolved in the electrolyte. Thus, the volume of electrolyte, solubility of sodium ions, and minimum sodium content in the alloy to suppress dendritic growth are intimately related.
10.4 Summary

The deposition of Li-Na alloys from an ionic liquid medium has been demonstrated and evaluated. The conductivity of the IL increased with increasing lithium content, from 364 $\mu$S/cm$^2$ for a sodium neutral melt to 466 $\mu$S/cm$^2$ for a lithium neutral melt. The maximum coulombic efficiency for the re-oxidation of the Li-Na alloy was found to be 91%. Lithium dendrites were visually observed when electrodepositing from a lithium neutral IL. However, from the mixed lithium-sodium IL a Li-Na alloy was deposited (mA/cm$^2$ current density range) that appears to suppress dendrite formation. Such an alloy system could allow for the safe use of a metal based anode in a rechargeable Li battery. This would eliminate the need for carbon which adds to the mass but not the capacity of the battery.
CHAPTER 11

HIGH ENERGY DENSITY, ROOM TEMPERATURE CARBONATE FUEL CELL

11.1 Objective

In this chapter, the viability of a high energy density, low power, room temperature carbonate fuel cell has been investigated. A solid carbonate conducting electrolyte based anion exchange membrane was used. The pH sensitivity of the membrane was addressed by converting it to the bicarbonate/carbonate form. The resistivity of the membranes was measured and chemical stability in methanol evaluated. Hydrogen, 1M and pure methanol have been shown to be viable anode fuels operating according to Equations 11.1 to 11.3. Carbon dioxide was observed at the anode exhaust when operating on hydrogen. This work has been published in Electrochemical and Solid-State Letters.96

\[
\text{CH}_3\text{OH} + 3\text{CO}_3^{2-} \rightarrow 2\text{H}_2\text{O} + 4\text{CO}_2 + 6\text{e}^- \quad (11.1)
\]

\[
\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^- \quad (11.2)
\]
11.2 Results and Discussion

Hydrogen provides the more facile electrochemical fuel for testing the operation of the carbonate fuel cell and was first used in the anode compartment. Carbon dioxide and oxygen, roughly 2-to-1 ratio, were used as the feed to the cathode. Figure 11.1 shows the polarization curve for a cell operated at four temperatures. The maximum power and current increased from 0.54 mW/cm$^2$ and 5.4 mA/cm$^2$ to 0.68 mW/cm$^2$ and 6.2 mA/cm$^2$, as the temperature increased from 26 to 44°C. However, when the temperature was increased to 55°C the performance deteriorated significantly with the maximum current, 4.8 mA/cm$^2$, falling below that measured at 26°C. When discharged across a 74.4 ohm resistor, a stable 0.3 V (+/- 2mV) was measured for more than 6.5 hours, after which the experiment was terminated.
Figure 11.1 (a) Polarization curve for RTC fuel cell operating on hydrogen, and (b) power curve for RTC fuel cell operating on hydrogen.
The performance drop at 55°C is likely due to drying of the polymer membrane. The effect of humidification was tested by soaking two membranes in the same 0.5 M sodium bicarbonate/0.5 M sodium carbonate (0.5B/O.5C) solution. One membrane was then removed from the solution and used while the other was dried under vacuum at ambient temperature for 18 hours. The resistivity of each membrane was measured in a 0.5B/0.5C solution. The ‘area resistivity’ of the dried membrane was found to be 101.4 ohm-cm$^2$, which was nearly 3 times higher than the measured 36.2 ohm-cm$^2$ for the membrane that was not dried. It is known that the membranes swell when exposed to moisture resulting in an increase in conductivity. The dried membrane was then resoaked in a 0.5B/0.5C solution for 48 hours. After soaking, the area resistivity dropped below 5 ohm-cm$^2$. It is believed that this reduction in resistivity is related to the contraction and swelling that occurs on drying and wetting of the membranes. Upon drying, the membrane contracts potentially forming larger pores or pinholes that allow carbonate ions to more easily pass from one side of the cell to the other. As the treatment with carbonate solution impacts the structure of the membrane, these defects are more likely to occur in the treated membranes than the untreated membranes. Also, upon drying, the membrane contracts and pulls away from the Pt on the carbon electrode resulting in poorer interfacial contact between the electrode and membrane, reducing the performance of the system.

In an attempt to retain moisture in the membrane, a new fuel cell was constructed and characterized. BMIBF$_4$, a hydrophobic ionic liquid (IL), was applied first to the surface of the anode and then to the surface of the cathode. The polarization and power curves from the initial test and after the addition of IL to the surfaces are shown in Figure
11.2a and b. Application of the IL to one side of the cell increased the current nearly 30%. However, when the cell was retested 3 days later (Figure 11.2a and 2b) with IL on both electrodes, the performance returned to the initial level. It is believed that the hydrophobic IL will slow water loss from the surface of the membrane and impact the diffusion of CO$_2$, H$_2$, and O$_2$ to the surface of the membrane. Also, the IL may trap the gases, retaining them at the surface for reaction while improving the wetting between the electrode and electrolyte.
Figure 11.2 (a) Polarization curve for RTC fuel cell modified with IL operating on hydrogen, and (b) power curve for RTC fuel cell modified with IL operating on hydrogen.
Verification of carbonate ion transport is an important issue. This involves consumption of carbon dioxide at the cathode, transport of carbonate ions in the membrane, and production of carbon dioxide at the anode. To verify carbonate transport and carbon dioxide consumption and production, two tests were carried out. Each of the inlets and outlets was properly sealed and/or purged to prevent atmospheric CO\textsubscript{2} from interfering. In the first test, hydrogen was used as the fuel and the anode exhaust was first passed through a gas trap cooled with liquid nitrogen and then bubbled through an oil bubbler to prevent air from back diffusing into the cell. The cell was operated under a 50ohm load for approximately 10 hours (potential 0.190± 10 mV) and a thick white solid accumulated at the bottom of the trap during the run. After completion of the run, the stopcocks at the inlet and outlet of the gas trap were closed. A tube was then connected to one side, with the other side immersed in a calcium hydroxide solution. If the precipitate were carbon dioxide, produced at the anode according to Equation 11.2, calcium carbonate would participate. When the stopcock was opened the solution immediately turned milky due to reaction between CaOH and CO\textsubscript{2}. As the white solid warmed, it evaporated increasing the pressure in the gas trap. When directly injected into the gas trap, the CaOH solution became white. These tests indicate that a large amount of carbon dioxide was present in the anode exhaust during the operation of the cell, consistent with the production of CO\textsubscript{2} at the anode, which could only occur if carbonate/bicarbonate were the conductive ions.

In the second test we examined the impact of interrupting the flow of carbon dioxide feed to the cathode, to see if CO\textsubscript{2} is consumed at the cathode. Figure 11.3 shows that immediately after the CO\textsubscript{2} flow was stopped, there was a substantial drop in cell
voltage across the load resistor. The voltage then continued to decay more slowly over the next four hours. However, the system did not reach 0 V by the end of the test indicating the continued presence or introduction of CO$_2$. The most likely source of CO$_2$ is permeation of CO$_2$ from the anode to the cathode through the membrane. As CO$_2$ is produced at the anode, it can cross back across the membrane to the anode. The permeation coefficient of CO$_2$ through a 0.5B/0.5C treated membrane was found to be 35.4 Barrer, which could account for the trickle charge measured after 5 and 6 hours.

While the permeation of neutral CO$_2$ through the membrane from the anode to the cathode is desirable for cell operations, it does make it difficult to eliminate CO$_2$ from the cathode compartment for test purposes. In addition, it is difficult to completely purge and seal out all air from the cathode compartment.
While hydrogen provides an efficient method of testing the carbonate conduction mechanism, liquid fuels are of interest for atmospheric pressure operation and fuel storage. Methanol was tested as a fuel in the carbonate fuel cell under a variety of conditions. Figure 11.4 shows a polarization curve for 1M methanol fuel after 2 hours of operation using dry air and carbon dioxide as the cathode feed. From the current-voltage curve, the maximum power and current were ~2 μW/cm² and ~16.2 μA/cm², respectively. After 1 hr of operation, the power of the fuel cell increased to 2.5 μW/cm² when operating with a 15 kohm load. After 24 hr, the open circuit voltage (OCV) had increased to 750 mV. Purging the cathode chamber with nitrogen for several hours.
resulted in the steady reduction of the cell voltage. When O\textsubscript{2} was bled back into the cell, the cell voltage increased rapidly as O\textsubscript{2} and CO\textsubscript{2} were available at the cathode for reduction. Cycling the CO\textsubscript{2} flow on and off effected the performance of the cell. For example, when operating near OCV (current < 1 nA/cm\textsuperscript{2}) the voltage increased more than 40 mV (from 763 to 804 mV) when the CO\textsubscript{2} flow was turned on. The increase in voltage, from 750 mV to 804 mV, was due to the use of O\textsubscript{2} rather than air along with CO\textsubscript{2}. Stopping the flow would lead to a gradual decline in the voltage of the cell and not a full loss of voltage because CO\textsubscript{2} was also supplied from the anode side by permeation through the membrane.

![Figure 11.4 Polarization and power curves for RTC fuel cell operated on 1M methanol](image)

Figure 11.4 Polarization and power curves for RTC fuel cell operated on 1M methanol
A critical test for the carbonate cell is the ability to operate with pure methanol, according to Equation 11.1, maximizing the energy density of the system. In contrast, as shown in Equation 11.3, a proton exchange membrane requires water and methanol at the anode for oxidation to CO$_2$. The addition of water lowers the energy density of the system. Measurements were taken while the cell was operated with pure methanol. The polarization curve taken after 5 hours of operation under load is shown in Figure 11.5. The current under load was higher than with 1M methanol, however, OCV was less, ca. 440 mV. The maximum current, ~74μA/cm$^2$, and power, ~8.8μW/cm$^2$, are more than 4 times the values measured for the 1M methanol system. The higher current is due to the increased methanol concentration, from 1M to 24.7M in pure methanol. The decrease in OCV, from 750mV to 440mV, is likely due to cross over from the anode to the cathode.

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \] \hspace{1cm} (11.3)
Figure 11.5 Polarization and power curves for RTC fuel cell operated on pure methanol.

The effective diffusion coefficient of pure methanol through the 0.5B/0.5C treated membranes was evaluated by measuring the rate of transport through the membrane. A reservoir of methanol was sealed in a glass container with the membrane as the top enclosure. Based on the weight change with time, the effective diffusion coefficient was found to be $2.26 \times 10^{-7}$ cm$^2$/s. While this value is an order of magnitude lower than that measured for Nafion® 117 ($2.38 \times 10^{-6}$ cm$^2$/s), it is sufficient for methanol to pass through the membrane and wet the cathode electrode resulting in a lower cell voltage. In the case of 1M methanol, the concentration of methanol is only 4% of pure methanol,
substantially lowering the methanol diffusion through the membrane and its effect on OCV.

11.3 Summary

A room temperature carbonate fuel cell has been constructed by modifying anion exchange membranes to transport carbonate. The cells were operated with hydrogen, 1M methanol, and pure methanol fuels using dry O₂ and CO₂ as the cathode gases. CO₂ was produced at the anode and O₂ & CO₂ were necessary at the cathode for operation, indicating that carbonate was the conducting ion. Though the initial performance was poor, the feasibility of a RTC fuel cell has been demonstrated. As no water is required for oxidation, this system could be utilized with pure methanol, maximizing the energy density of the system. The system performance could be improved by improving the carbonate membrane, its sensitivity to high pH values, and the interface between the electrodes and membranes.
CHAPTER 12

CONCLUSIONS AND FUTURE WORK

12.1 Conclusions

This work focused on the development of RTILs for use in electrochemical devices, including batteries, and advancement of the fundamental understanding of the electrochemical processes involving ILs and battery technology. New ionic liquids have been synthesized and investigated for the purpose of optimizing the following properties: low-cost (simple and high yield synthetic route), safe, low operating temperature, low viscosity, high stability (especially to reduction), and excellent battery performance. These ionic liquids were formed using quaternary ammonium salts and aluminum chloride. Quats were investigated because of the ease in which a large number of structures can be produced. The room temperature carbonate fuel cell was demonstrated by modifying a commercially available anion exchange membrane, utilizing positive quaternary ammonium fixed sites, to transport carbonate.

The charge density on the nitrogen and the symmetry of the Quat were demonstrated to be the dominant factors in determining the MP of the resulting ILs. Introduction of a benzyl ring both increases the overall size of the quaternary ammonium cation and disrupts the symmetry of the Quat. While the melting point of benzyl(trialkyl)ammonium-based ILs is above room temperature, sodium can be reversibly deposited from ILs with moderate viscosity. The ethyl substituted Quat, VII,
was found to have better reduction/re-oxidation efficiencies and a lower self-discharge current than the methyl substituted Quat, VI. The longer alkyl groups (ethyl groups) release more electron density toward the positive center than the shorter ones (methyl groups).

Introducing a third alkyl group can disrupt the symmetry of the Quat further. These asymmetric benzyl-substituted ammonium chlorides were found to form RTILs, though all were larger in size than BenMe$_3$NCl (VI). The additional asymmetry is believed to make crystallization more difficult, significantly lowering the melting point and viscosity. Upon neutralization with NaCl, and addition of an additive, sodium could be reversibly deposited at room temperature. The IL of IX had comparable coulombic efficiency and self-discharge properties as the ILs of salt II and MSC.$^1$

RTILs can be formed by delocalizing the charge on the nitrogen, decreasing the charge density and disrupting the symmetry of the Quat. However, these steps cannot be taken with Li$^+$ and Na$^+$ ions. Therefore when present in a chloroaluminate IL, Li$^+$ and Na$^+$ are coordinated strongly with AlCl$_4^-$, making the ions unavailable for reduction to the metal. Additives, such as HCl or SOCl$_2$, are effective in disrupting the alkali-chloroaluminate complex freeing the ions for electroreduction to the metal. Conductivity measurements can be utilized to observe this phenomenon, as the bulk conductivity will increase as ions become available. Compounds that attract one or both of the species should be effective as additives for the deposition of sodium.

Along with free sodium ions, sufficient reductive stability of the Quat is necessary to deposit sodium. The electrochemical stability for several salts was evaluated in both ACN and the IL. In both medium, the benzyl substituted cation (salt IX) was less stable
than the alkyl substituted cation (salt XV), due to the benzyl group being a better leaving group than the smaller butyl chain. Along with being among the most stable Quats, the 9-carbon salt, XV, was demonstrated to form a RTIL with significantly higher conductivity (lower viscosity) than the benzyl substituted ILs. Utilizing only carbon, nitrogen and hydrogen, 9 carbons appears to be the smallest number of atoms, with which a RTIL can be formed. As with the benzyl substituted ILs, upon the addition of SOCl₂, sodium can be efficiently reduced and reoxidized.

In an attempt to expand the number of available additives, several new compounds were tested. The small chlorinated compounds chloroform-D and carbon tetrachloride were demonstrated to have similar performance to SOCl₂ though a large number of chlorinated compounds could be utilized. The electronegative chlorine atoms found in these solvents are oriented near the positive sodium cation, weakening its attraction to AlCl₄⁻. Similarly, PCl₆⁻ and 18-Crown-6 act to disrupt the Na⁺ and AlCl₄⁻ ion pairs producing reducible sodium ions.

An electronegative atom, such as chlorine, oxygen or fluorine, can be directly incorporated into the structure of the Quat. When ILs were formed with 8-atom (7 carbons, 1 oxygen) ether substituted Quats (XVI and XVII) the conductivity was found to increase upon neutralization. This indicates that the oxygen atom is able to disrupt the sodium ion: tetrachloroaluminate coordination. However, placement of the oxygen is crucial in determining MP. When placed near the nitrogen, only one CH₂ group away, the oxygen localizes a greater portion of the positive charge on the nitrogen. Placement of the oxygen two CH₂ groups away from the nitrogen results in a RTIL, even utilizing only an 8-atom structure. Due to the stability of the Quat, an additive is still necessary to
form an SEI. SOCl$_2$ was demonstrated to form a more stable SEI than CDCl$_3$. The greater availability of sodium in the ether systems results in larger sodium reduction current densities. Potentially due to the residual acidity, the maximum achievable cycling efficiency for the ether system was less than for the other Quat-based ILs.

The Quat-based RTILs formed have been shown to support the deposition of both lithium and sodium. Due to its size, the lithium neutral IL is slightly more conductive than its sodium counterpart. When neutralized with both lithium and sodium, a mixed state is developed that results in the electrodeposition of Li-Na alloys at efficiencies similar to those measured with sodium. The deposition of a Li-Na alloy appears to suppress dendrite formation. Such an alloy system could allow for the safe use of a metal based anode in a rechargeable Li battery, eliminating the need for the currently utilized intercalation anode.

A technique that is becoming fairly common is the packaging of fuel cell and battery technology together. The fuel cell constantly charges the system, with the battery providing short bursts of high current/power. Utilizing pure methanol as the fuel can maximize the energy density of a fuel cell. In this work, a novel room temperature carbonate fuel cell has been constructed by modifying anion exchange membranes to transport carbonate. The alkaline environment could allow for the use of nonprecious metal catalysts and eliminate the need for water in the oxidation of methanol. Cells were operated with hydrogen, 1M methanol, and pure methanol fuels using dry O$_2$ and CO$_2$ as the cathode gases. CO$_2$ was produced at the anode and O$_2$ & CO$_2$ were necessary at the cathode for operation, indicating that carbonate was the conducting ion. While the initial performance was poor, the feasibility of a RTC fuel cell has been demonstrated.
12.2 Recommendations for Future Work

While there are a number of directions for future work, three seem likely to make the most impact. The first is to systematically study the impact of introducing atoms containing lone pairs of electrons, such as oxygen. The second is to fully characterize the Li-Na and Li-K alloys in both half-cell and full-cell configurations. The third is to more fully develop the concept of the room temperature carbonate fuel cell.

Introduction of an ether linkage was shown to not only reduce the necessary atom size for an IL (from 9 carbons to 7 carbons, 1 oxygen), but also increase the available number of sodium ions for reduction. Evaluating the ability to deposit lithium and potassium, as well as neutralize differing acidity levels may elucidate the apparent impact on the aluminum deposition observed in this system. Changing one of the methyl groups to an ethyl, or an even bigger group, may result in a more stable Quat providing a sufficient window to deposit lithium and sodium. Shifting the oxygen one atom further from the nitrogen, may also positively affect stability, conductivity and viscosity. Introduction of chlorine, fluorine, and silicon are anticipated to have a similar positive impact.

The higher currents observed with the ether-substituted system could be particularly helpful in developing a practical Li alloy anode. Any additional increases in current would help overcome the high viscosities and low conductivities of the current systems. Prior to use in a battery, the suppression of lithium dendrites needs to be evaluated as a function of Na or K concentration and deposition current. Full cells could then be assembled, matching the alloy anode and an intercalation cathode, and lifetime
performance and reliability tests performed. Based on the ability to reversibly cycle the battery, the alloy system may result in a secondary battery with greater energy and power density.

The final concept that I believe can result in a noteworthy impact is the room temperature carbonate fuel cell. This idea was only demonstrated in this work and significant work remains to improve the performance level of the system. However, as this system offers the potential to carry only methanol, this fuel cell could provide a maximum energy density. One area in which significant improvement can be made is in the interface between the electrodes and membrane. Reducing the triple phase boundary that exists between the electrolyte, catalyst and reactants could improve the fuel cell performance substantially. Also, identification and implementation of membranes with greater sensitivity to the alkaline conditions are necessary for reliable performance.
CHAPTER 13

REFERENCES


(13) Matsumoto, H.; Kageyama, H.; Miyazaki, Y. Chemical Communications (Cambridge, United Kingdom) 2002, 1726.


(82) Ross, S.; Finkelstein, M.; Petersen, R. Journal of the American Chemical Society 1960, 82, 1582.

(83) Finkelstein, M.; Petersen, R.; Ross, S. Journal of the American Chemical Society 1959, 81, 2361.


