

## Cation Electrochemical Stability in Chloroaluminate Ionic Liquids

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The electrochemical stability of 10 organic cations, which can be used in ionic liquids (IL), was investigated as solutes in acetonitrile (ACN). The stability of three of the salts, BenMe<sub>2</sub>EtNCl (salt III), 1-butyl-2-methyl pyrrolidinium chloride (salt VI), and its structural isomer, BuMe<sub>2</sub>ProNCl (salt VII), were also compared in chloroaluminate ILs. The chloroaluminate ILs of salts VI and VII are investigated for the first time. The NaCl-neutralized ILs of salts VI and VII have melting points of 43.2 and 3.7 °C, respectively. The benzyl-substituted cation, salt III, was more easily reduced in ACN or as the neutral chloroaluminate IL than the alkyl-substituted cation, salt VII, due to the better leaving ability of the benzyl group. Mass spectroscopy measurements before and after electrolysis on the benzyl-substituted solutions confirmed that reduction involves the loss of an alkyl group. In ACN, salt VI was found to be the most difficult to reduce (1 mA/cm<sup>2</sup> at −2.09 V) due to its cyclic structure. However, in the chloroaluminate IL, the pyrrolidinium cation was more easily reduced than salt III or its isomer, salt VII, resulting in an insoluble black deposit. This is consistent with the mass spectrometry data, which do not show formation of low-molecular-weight products, as in the reduction of salts III and VII. The IL of salt VII was the most stable in the presence of sodium. Sodium ions could be reduced and reoxidized with a maximum Coulombic efficiency of 94.1% versus 87.2% for salt VI. Reduction of the pyrrolidinium cation produces insoluble products, most likely through opening of the cyclic ring, and an inferior medium for sodium ion reduction compared to the benzyl- and butyl-substituted cations, even though reduction of the cation occurs at a more negative potential in acetonitrile.

### Introduction

Ionic liquids (ILs) with melting points less than 100 °C have drawn interest in the study of a wide range of oxidation and reduction reactions due to their wide electrochemical window and low vapor pressure. Organic ILs can be used in the electroplating of materials that would otherwise react with water, such as sodium or lithium. For example, imidazolium-based chloroaluminate ILs have been investigated for both battery<sup>1,2</sup> and electroplating<sup>3–6</sup> applications. Quaternary ammonium-based ILs are attractive alternatives to imidazolium-based ILs because they are easy to synthesize, are relatively safe, and a large number exist with a variety of properties.<sup>7,8</sup> Both imidazolium and quaternary ammonium ILs have been studied<sup>2,9,10</sup> as electrolytes in a derivative of the medium-temperature battery, the “zebra cell”.<sup>11</sup> A sodium-based battery is appealing due to the relative abundance of sodium, its low cost, and absence of dendrites for metallic anodes. The low atomic weight of sodium also leads to a system with high energy density. A room-temperature IL for use as the electrolyte in a sodium metal battery is of interest.

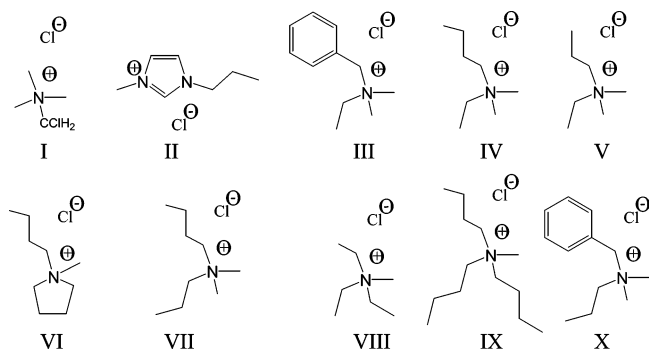
ILs are formed by mixing a halide salt, either imidazolium or quaternary ammonium chloride, with aluminum halide. Equations 1 and 2 show the acid–base reactions that occur when the salt and AlCl<sub>3</sub> are mixed. The Lewis acid, AlCl<sub>3</sub>, forms AlCl<sub>4</sub><sup>−</sup> (Lewis neutral) and Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> (Lewis acid) when mixed with the organic chloride salt, as shown in eqs 1 and 2. Neutralization of the Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> occurs by reacting Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> with a Lewis base (e.g., NaCl or salt<sup>+</sup>Cl<sup>−</sup>) to produce neutral AlCl<sub>4</sub><sup>−</sup> ions (eq 3).<sup>12</sup>



The composition of the melts is given in terms of the mole fraction of AlCl<sub>3</sub> (*N*). Neutral melts containing equal moles of AlCl<sub>3</sub> and salt (*N* = 0.5) contain only the salt<sup>+</sup> and AlCl<sub>4</sub><sup>−</sup> ions. Acidic melts contain an excess of AlCl<sub>3</sub>, *N* > 0.5, and form AlCl<sub>4</sub><sup>−</sup> and Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> anions. Melts containing an excess of salt, *N* < 0.5, are basic and contain AlCl<sub>4</sub><sup>−</sup> and Cl<sup>−</sup> anions.

The neutralization of the acidic melts 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 melt, which is important at the anode and cathode where electron-transfer results in acidity changes. The acidic window is limited at negative potentials by the reduction of chloroaluminate. Under Lewis base conditions, the electrochemical window is limited at positive potentials by the oxidation of chlorine. The neutral melt has a much wider potential window limited by sodium plating (or IL reduction) at negative potential and AlCl<sub>4</sub><sup>−</sup> oxidation at positive potentials. It has been demonstrated that the electrodeposition of sodium requires an additive such as HCl or SOCl<sub>2</sub>.<sup>1,13</sup> We previously investigated the role of the additive, showing that the additive coordinates with chloride in the IL to provide free sodium ions for plating.<sup>14</sup> A critical parameter in achieving a sodium metal anode is the stability of sodium metal in the presence of the organic cation, without electroreducing the organic cation itself.

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**Figure 1.** I:  $\text{Me}_3\text{MeCINCl}$ ; II: 1-methyl-3-propylimidazolium chloride; III: benzylethyldimethylammonium chloride; IV: butylethyldimethylammonium chloride; V: ethyldimethylpropylammonium chloride; VI: butylmethylpyrrolidinium chloride; VII: butyldimethylpropylammonium chloride; VIII: triethylmethylammonium chloride; IX: tributylmethylammonium chloride; X: benzyltrimethylpropylammonium chloride.

In this paper, the electrochemical stability of 10 organic cations is investigated. The structures of the salts are shown in Figure 1. The stability of the 10 cations was investigated as the solute in acetonitrile (ACN). 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.<sup>15</sup> For salts III, VI, and VII, the stability in the chloroaluminate IL was also evaluated. The reduction mechanism of salts III, VI, and VII was studied using mass spectroscopy. Also, the performance of the ILs of salts VI and VII as electrolytes for the reduction/reoxidation of sodium are reported here for the first time.

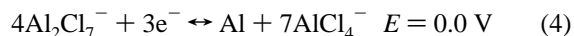
## Experimental Section

All experiments were carried out in a vacuum atmosphere glovebox under dry nitrogen due to the sensitivity of the ILs and salts to moisture. The glovebox was maintained at oxygen and moisture levels below 10 ppm. Experiments above room temperature were performed in an oil-jacketed cell connected to a Fisher Scientific IsoTemp 3016 for temperature control. Aluminum trichloride,  $\text{AlCl}_3$  (99.99%), and thionyl chloride,  $\text{SOCl}_2$  (99+%), were obtained from Aldrich and used as received. Salts I, II, VI, VIII, and IX were obtained from Sachem, Inc. (Austin, TX) and purified before use. Methyl propyl imidazolium chloride (MPLICI) was synthesized and purified following previously published procedures.<sup>1</sup> Salts III, IV, V, VII, and X were synthesized by reacting the appropriate trialkyl-substituted amine with an alkyl chloride.<sup>16</sup> The salts were then purified using activated carbon prior to electrochemical study. All of the salts and  $\text{NaCl}$  (99.999%, Alfa Aesar) were dried under vacuum for 48 h at 70 °C before use in the glovebox.

Conductivity measurements were performed using a custom-built probe and ThermoOrion conductivity meter.<sup>14</sup> 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)  $\text{NaCl}$  solution before use in the glovebox. After each use, the probe was cleaned with nitric acid, rinsed with deionized water, and dried.

An EG&G model 273 potentiostat was used for the electrochemical measurements. Pt (99.999%) and W (99.95%) wires were obtained from Alfa Aesar and fabricated into working electrodes by sealing them inside glass tubes. The electrodes were cleaned in hot  $\text{HNO}_3$  prior to use. They were polished using 0.3- $\mu\text{m}$  alumina powder and thoroughly rinsed with

deionized water prior to use. 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 (99.9995%) in an acidic melt ( $N = 0.6$ ) in a glass tube separated from the electrolyte by a fine glass frit. The half reaction for the reference electrode is as follows:



The reference electrode for the acetonitrile tests was formed by immersing a silver wire coated with  $\text{AgCl}$  in the 0.1 M 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 it was performed for the measurements in acetonitrile solutions.

The 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.<sup>13</sup>

Results of  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ): salt IV:  $\delta$  0.98 (t,  $\text{CH}_3$ ), 1.38 (m,  $\text{CH}_2 + \text{CH}_3$ ), 1.68 (m,  $\text{CH}_2$ ), 3.41 (s,  $2\text{N}-\text{CH}_3$ ), 3.49 (t,  $\text{N}-\text{CH}_2$ ), 3.72 (q,  $\text{N}-\text{CH}_2$ ); salt V: 0.99 (t,  $\text{CH}_3$ ), 1.35 (t,  $\text{CH}_3$ ), 1.74 (m,  $\text{CH}_2$ ), 3.35 (s,  $2\text{N}-\text{CH}_3$ ), 3.43 (t,  $2\text{N}-\text{CH}_2$ ), 3.68 (q,  $2\text{N}-\text{CH}_2$ ); salt VII: 0.76 (m,  $2\text{CH}_3$ ), 1.18 (m,  $\text{CH}_2$ ), 1.46 (m,  $\text{CH}_2$ ), 1.55 (m,  $\text{CH}_2$ ), 3.14 (s,  $2\text{N}-\text{CH}_3$ ), 3.30 (m,  $2\text{N}-\text{CH}_2$ ).

## 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 (compounds I to X shown in Figure 1) in acetonitrile to form 0.1 M solutions. The chloride salts were used so that only the cation was changed between the samples. Cyclic voltammetry (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  $\text{mA}/\text{cm}^2$  at a scan rate of 100  $\text{mV}/\text{s}$ .

Figure 2 shows a comparison of three salts: salt I ( $\text{Me}_3(\text{MeCl})\text{NCl}$ ), salt II (1-methyl-3-propylimidazolium chloride), and salt III (benzylethyldimethylammonium chloride). Sodium metal can be electrodeposited from salts II and III when they are used in chloroaluminate ILs.<sup>16,17</sup> Salt I is most easily reduced, as shown in Figure 2, where a reduction current of 1  $\text{mA}/\text{cm}^2$  was observed at  $-1.35$  V. 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 salt I, 1  $\text{mA}/\text{cm}^2$  at  $-1.53$  V, and salt III is the most difficult to reduce with 1  $\text{mA}/\text{cm}^2$  at  $-1.74$  V. Finkelstein et al. found that during reduction the leaving group is the benzyl radical.<sup>18,19</sup> The benzyl radical is the most likely product from the reduction

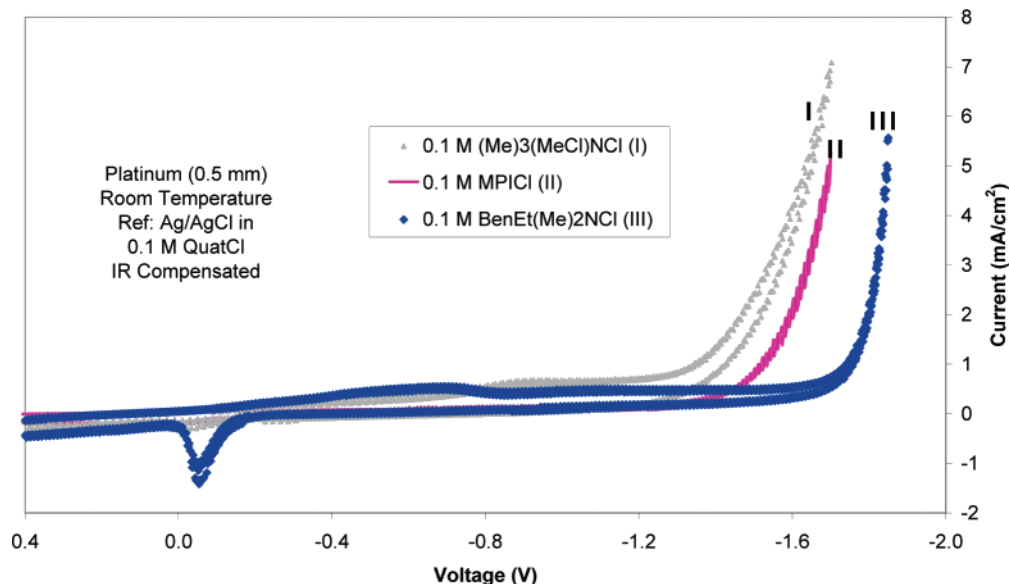


Figure 2. CV scans for 0.1 M solutions of salts I, II, and III in acetonitrile.

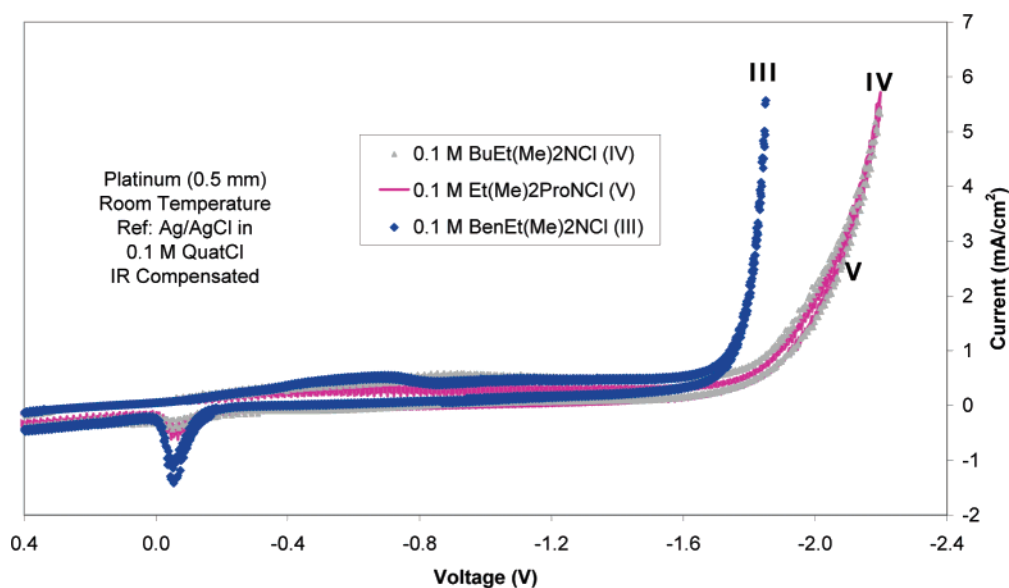


Figure 3. CV scans for 0.1 M solutions of salts III, IV, and V in acetonitrile.

of salt III. 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 V) for salt II compared to salt III.<sup>15</sup>

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 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 V, is the most difficult to reduce at  $-1.89$  V, with salt IV at  $-1.87$  V. The difference between salts III and IV (benzyl to alkyl) is more significant than the difference between salts IV and V (both are alkyl-substituted).

Figure 4 shows the stability of the pyrrolidinium-substituted quaternary ammonium cation (VI) to the benzyl-substituted (III) and tetraalkyl-substituted cation in ACN. Salts VI and VII both have nine total carbons; however, salt VI, the pyrrolidinium cation, is different in that a heterocyclic ring is formed by four of the carbons. Salt VI is significantly more stable than salt III ( $1 \text{ mA/cm}^2$  at  $-2.09$  V vs  $-1.74$  V) and more stable than salt VII ( $1 \text{ mA/cm}^2$  at  $-1.78$  V). The heterocyclic ring structure of salt VI 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).

Along with the previous 7 salts, the reduction potential of three additional quaternary ammonium cations (VIII, IX, and X) in acetonitrile were investigated. Table 1 summarizes the reduction potentials measured utilizing CV tests for these three salts as well as for salts III, IV, and V. The seven-carbon salts, salts V and VIII, are structural isomers that both had a reduction potential of  $-1.89$  V. The best stability measured for a

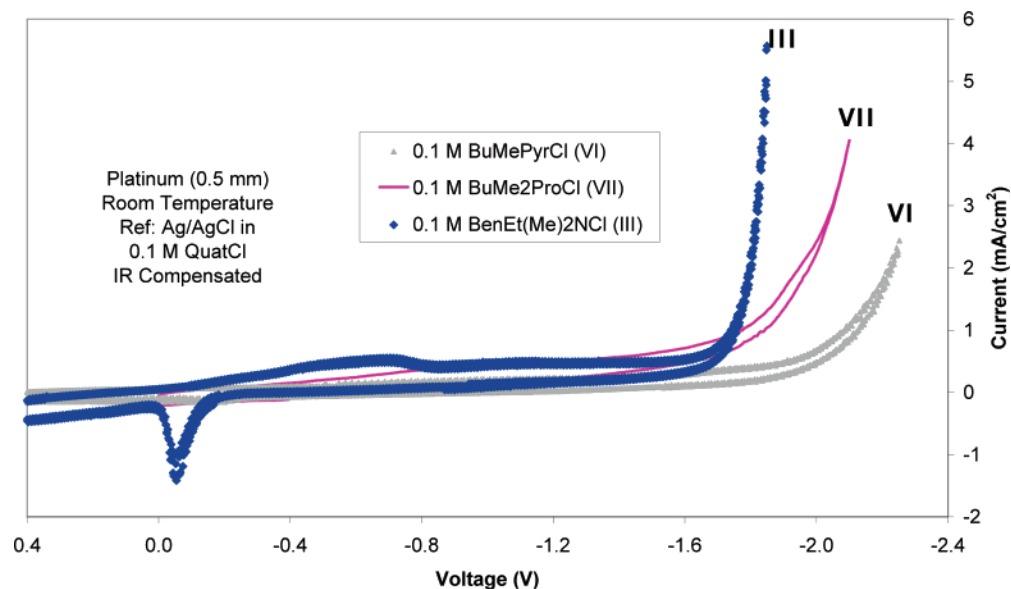


Figure 4. CV scans for 0.1 M solutions of salts III, V, and VI in acetonitrile.

TABLE 1: Reduction Potentials of 0.1 M Salt Solutions in Acetonitrile

name	MW (g/mol)	carbon no.	reduction potential (volts)
Et <sub>3</sub> MeNCl (salt VIII)	151.68	7	-1.89
ProEtMe <sub>2</sub> NCl (salt V)	151.68	7	-1.89
BuEtMe <sub>2</sub> NCl (salt IV)	165.71	8	-1.87
BenEtMe <sub>2</sub> NCl (salt III)	199.73	11	-1.74
Ben ProMe <sub>2</sub> NCl (salt X)	213.75	12	-1.75
Bu <sub>3</sub> MeNCl (salt IX)	235.84	13	-1.95

quaternary ammonium cation was for the salt with the largest molecular weight, salt IX, which reduced at  $-1.95$  V. The two salts with benzyl groups, salts III 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.

For the structural isomers, the propyl group in salt V is a better leaving group than the ethyl groups of salt VIII. 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 VIII to salt IX. 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.<sup>20</sup>

**Mass Spectroscopy of Acetonitrile Solutions.** Mass spectroscopy was used to help identify the reaction products from electroreduction of the cations in ACN. A 0.1 M solution of salt III in ACN was electrolyzed, and the results are shown in Figure 5. The mass spectrum of an electrolyzed solution, where charge corresponding to 12.5% of the cations being reduced, is compared to that of 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 III solution and the control was mass 165, which corresponds to the mass of the salt III cation alone. The intensity of the other masses was normalized to the 165 peak for comparative purposes. Both the control and the electrolyzed solutions show mass peaks at 58.9, 100, and 363.2. The peak at 363.2 was produced in the spectrometer; it 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.

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 corresponds to 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 0.1 M ACN solution (charge corresponding to 10% electrolysis of the cations present) of salt VI is shown in Figure 6. The results from the electrolyzed solution are compared to those from a control sample. The spectra are normalized to the dominant peak at 142, which corresponds to the cation BuMPyr<sup>+</sup>. 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 III. 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 VI cation resulted in breaking the carbon–nitrogen bond within the heterocyclic ring. If this were the case, the reduced form would result in still one fragment with the same mass as the parent cation. That is, reduction of the noncyclic alkyl results in an alkyl leaving group, but the cyclic structure does not because it remains bonded to the nitrogen.

Figure 7 shows the spectrometry results before and after a 20% reduction for a 0.1 M acetonitrile solution of salt VII. Salt VII has the same number of carbons as salt VI; 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 samples is mass 144, which corresponds to the cation BuMe<sub>2</sub>ProN<sup>+</sup>. Both solutions showed



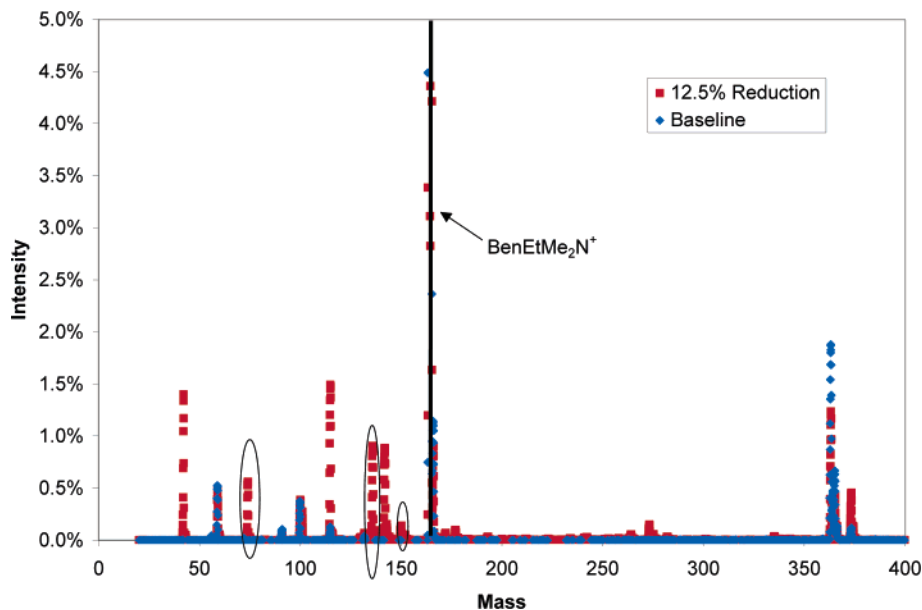


Figure 5. Mass spectroscopy results for a 0.1 M acetonitrile solution of salt III before and after 12.5% reduction.

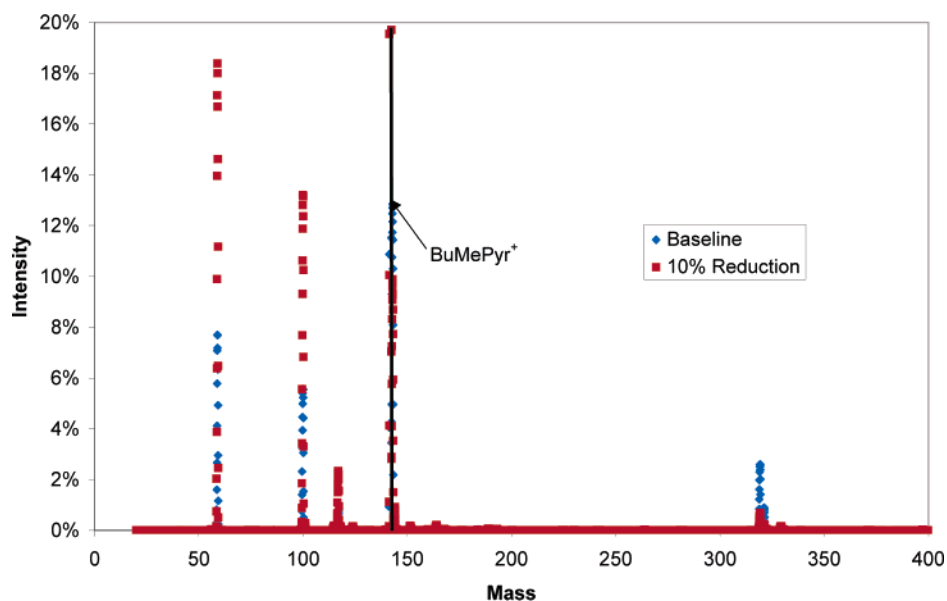


Figure 6. Mass spectroscopy results for a 0.1 M acetonitrile solution of salt VI before and after 10% reduction.

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.

**Ionic Liquid Properties.** Ionic liquids, mixtures that contain only ions and are liquids at or near room temperature ( $T < 100$  °C), were formed from salts III, VI, and VII by mixing them with aluminum chloride. While we previously reported on the IL formed with salt III,<sup>16</sup> this is the first report of ILs formed by mixing salts VI or VII with AlCl<sub>3</sub>. MacFarlane et al. reported the formation of a room-temperature IL when salt VI was mixed with the bis(trifluoromethane sulfonyl) imide ion.<sup>21</sup> ILs of salt VI and its isomer, salt VII, were studied due to the increased stability in ACN. Salt III was chosen as a reference on the basis of its ability to form a room-temperature

IL and support the reduction/reoxidation of sodium.<sup>16</sup> When mixed with AlCl<sub>3</sub>, salts I, VIII, and IX did not form room-temperature ILs. Though salt X formed an IL, it was not studied due to its increased viscosity relative to that of the salt III IL. ILs formed utilizing salt II have been widely investigated in the literature, for example, by Gray et al.<sup>13</sup>

Acidic,  $N = 0.55$ , mixtures were first prepared and then followed by neutralization with 100 mol % excess of NaCl. Previously, we showed that the acidic and neutral mixtures formed from salt III were liquid at temperatures slightly below room temperature.<sup>16</sup> For mixtures formed with salt VII, melting points of 0.3 and 3.7 °C for the acidic and neutral mixtures, respectively, were measured. The acidic mixture with salt VI 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 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 Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>

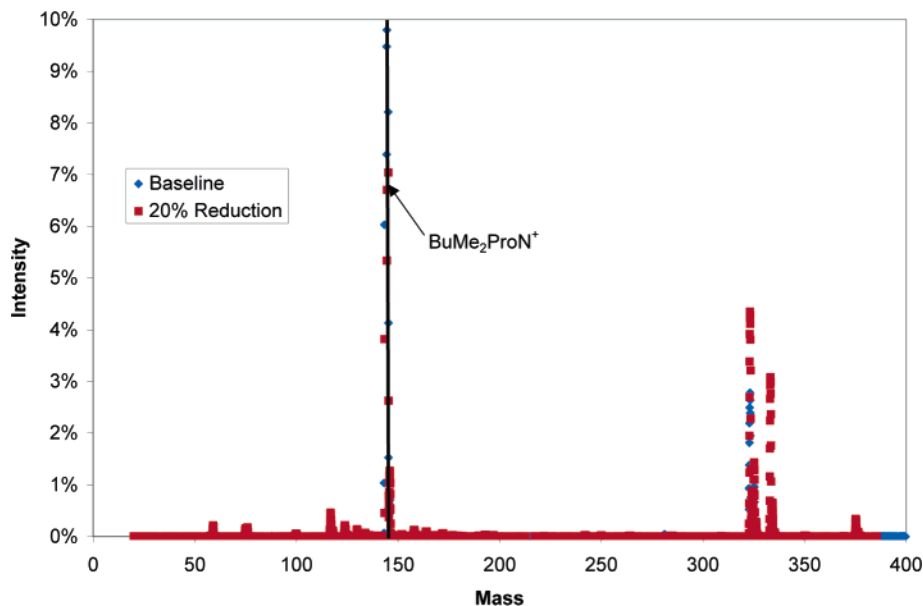


Figure 7. Mass spectroscopy results for a 0.1 M acetonitrile solution of salt VII before and after 20% reduction.

anion. Upon addition of NaCl,  $\text{Al}_2\text{Cl}_7^-$  was converted to the smaller, more symmetric  $\text{AlCl}_4^-$  anion, resulting in the higher melting point, 43.2 °C.

For the acidic melt of salt VII, the conductivity and viscosity were measured to be 2.86 mS/cm and 61  $\text{mm}^2/\text{s}$ , respectively. This conductivity is almost four times greater than that measured for the acidic melt of salt III. This kinematic viscosity is nearly one-quarter of that measured for the IL of salt III, 222  $\text{mm}^2/\text{s}$ .<sup>16</sup> The higher conductivity and lower kinematic viscosity are a result of the smaller size of salt VII versus salt III.

The electrochemical window for the neutralized ILs of salts III, VI, and VII are shown in Figure 8. The reference electrode was an  $N = 0.60$  mixture of the corresponding salt and  $\text{AlCl}_3$ . Due to the higher melting point, tests with the salt VI IL were performed at 71 °C, versus 25 °C for the ILs of salts III and VII. The reduction for the IL from salt III 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.<sup>14</sup> For the IL of salt VII, Figure 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 VI, the initial reduction peak is observed at -1.73 V with a maximum at -2.14 V, Figure 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 8c. Repetitive scans between 0 and -3 V for the IL of salt VI 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  $\text{Cl}_2$ .

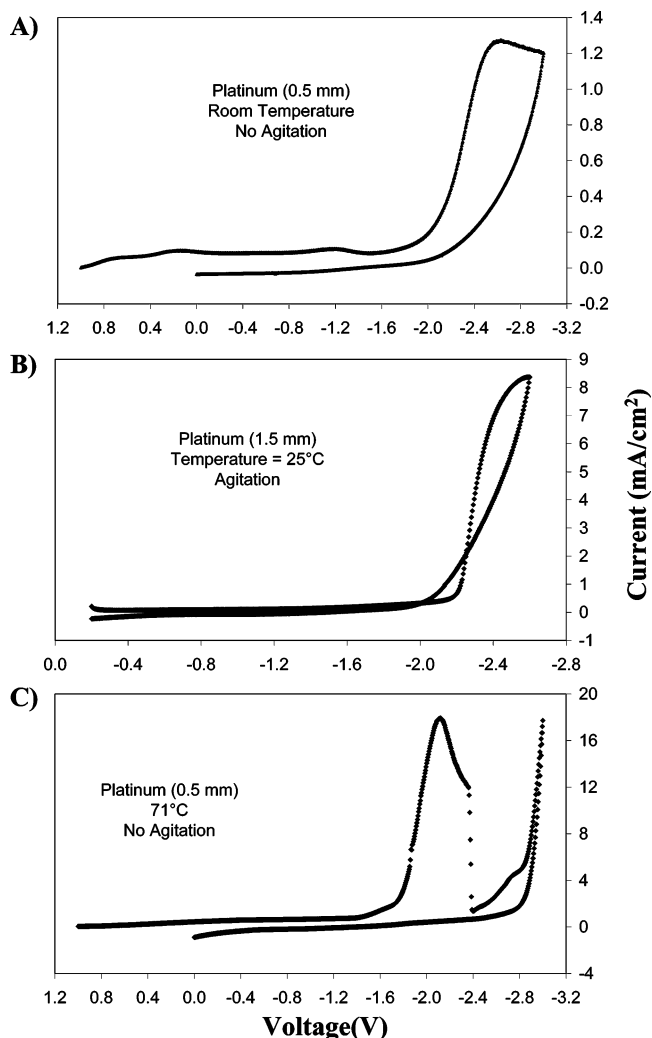
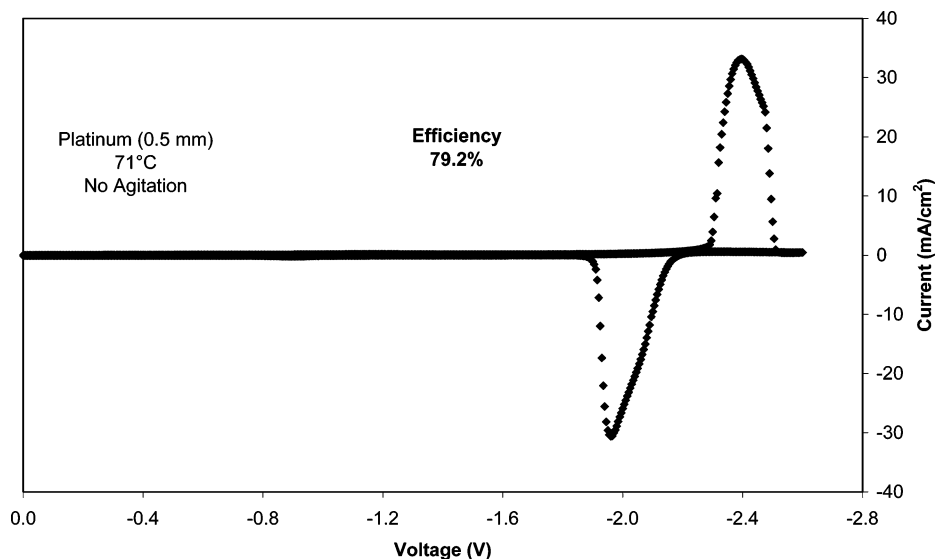
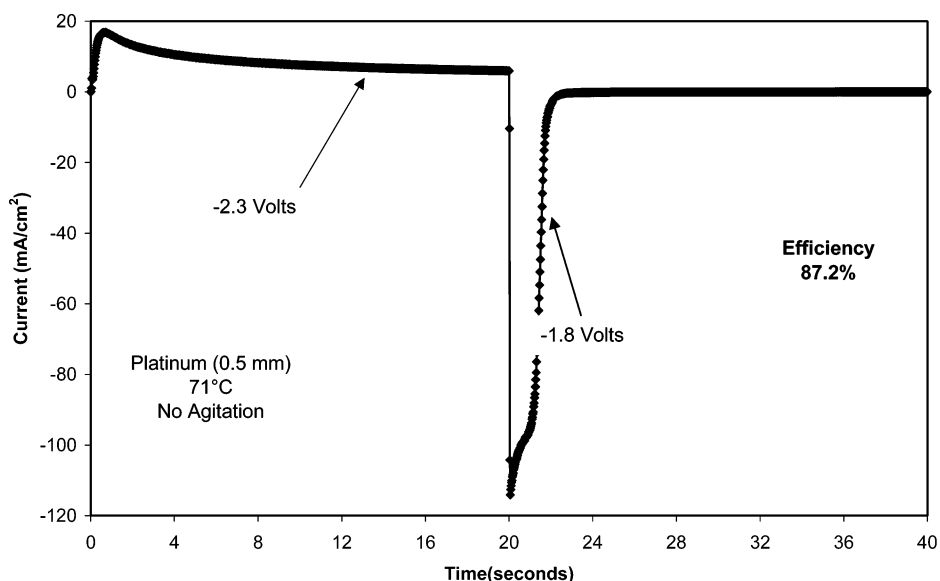


Figure 8. CV scans with 100% excess sodium and (A)  $N = 0.55$  mixture of salt III; (B)  $N = 0.55$  mixture of salt VII; and (C)  $N = 0.554$  mixture of salt VI.

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 VI, does not



**Figure 9.** CV scan at 71 °C for a mixture of 55.4%  $\text{AlCl}_3$  and salt VI neutralized with 100% excess  $\text{NaCl}$  and  $\text{SOCl}_2$  added.



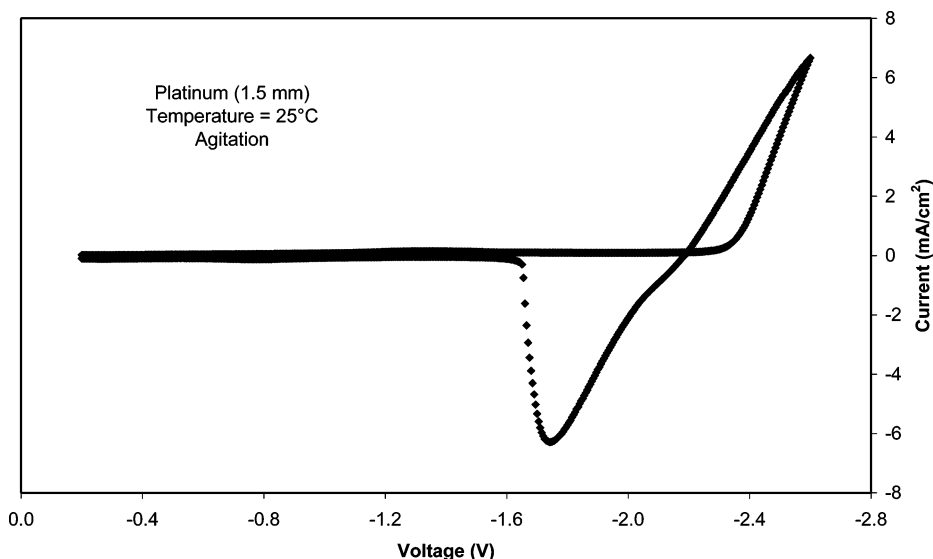
**Figure 10.** CA scan at 71 °C for a mixture of 55.4%  $\text{AlCl}_3$  and salt VI neutralized with 100% excess  $\text{NaCl}$  and  $\text{SOCl}_2$  added.

lead to low-molecular-weight products, whereas reduction of salts III or VII do produce low-molecular-weight products which apparently do not precipitate on the electrode surface.

The addition of a small amount of an acidic “additive”, such as  $\text{SOCl}_2$ , to a sodium-containing neutral IL facilitates the electrodeposition of sodium metal. The electrodeposition and reoxidation of sodium from the neutralized IL of salt VI  $\text{SOCl}_2$  is shown in Figure 9. The reduction of sodium ions on the initial scan to negative potentials occurs at  $-2.3$  V with a peak current of  $33.2$   $\text{mA}/\text{cm}^2$  at  $-2.4$  V. However, a precipitous drop in current occurred at more negative potentials, just as in the previous figure, Figure 8c, when no  $\text{SOCl}_2$  was present. On scan reversal, an oxidation current corresponding to sodium oxidation was observed. The oxidation peak current was  $30.6$   $\text{mA}/\text{cm}^2$  and occurred at  $-1.96$  V. The Coulombic 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.

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, chronoamperometry (CA), and then stepped to  $-1.8$  V to oxidize the deposited sodium, as shown in Figure 10. The resulting Coulombic efficiency for the neutral IL of salt VI was 87.2%. No precipitous drop in current was observed at  $-2.3$  V, showing that the reduction of the salt VI cation was less a factor at these potentials.

The long-term stability of sodium in the IL formed from salt VI was measured by use of chronopotentiometry (CE). Sodium was electrodeposited at a current of  $3.82$   $\text{mA}/\text{cm}^2$  for 100 s. 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 s was 80.3%. The loss in recoverable sodium was converted to a self-discharge rate. The effective self-discharge current over a 1-h open-circuit time was  $57.9$   $\mu\text{A}/\text{cm}^2$  using a platinum electrode. On tungsten, the average Coulombic efficiency from CE experiments was 79.3%, and the effective self-discharge current was  $86.9$   $\mu\text{A}/\text{cm}^2$ .



**Figure 11.** CV scan at 25 °C for a mixture of 55%  $\text{AlCl}_3$  and salt VII neutralized with 100% excess  $\text{NaCl}$  and  $\text{SOCl}_2$  added.

The voltammogram for the neutralized IL of salt VII with  $\text{SOCl}_2$  is shown in Figure 11. Although salt VII is a quaternary ammonium cation with the same number of carbon atoms as VI, the absence of the heterocyclic ring yields lower molecular reductive products, as discussed previously. The voltammogram in Figure 11 shows a reduction current without the presence of a passivating film. The reduction of  $\text{Na}^+$  ions was observed starting at  $-2.35$  V. Oxidation of the sodium occurred after scan reversal with a maximum current of  $6.29$   $\text{mA}/\text{cm}^2$  at  $-1.74$  V. The Coulombic efficiency for the reduction and reoxidation process in Figure 11 was 76.2%. A higher Coulombic efficiency, 90.8%, was observed in a CE experiment. The cathodic current was  $1.13$   $\text{mA}/\text{cm}^2$  for 200 s at a platinum electrode. On tungsten, a slightly higher efficiency (CE experiment) was observed, 91.3%, where the cathodic current was held at  $1.53$   $\text{mA}/\text{cm}^2$  for 200 s. The self-discharge current was 8.5 and 9.8  $\mu\text{A}/\text{cm}^2$  for tests at the platinum and tungsten conditions, respectively.

In each of these previous tests with the salt VII 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  $3.56$   $\text{mA}/\text{cm}^2$ . Though the baseline efficiency also increased, from 91.3 to 94.1%, the self-discharge current increased by a factor of 10 to  $101$   $\mu\text{A}/\text{cm}^2$ . This indicates a greater increase in parasitic reaction rate.

The self-discharge values for the ILs of salts VI and VII can be compared with the previously reported results for the salt III IL. At 25 °C, the self-discharge rate for salt VII is double the rate for salt III,  $3.96$   $\mu\text{A}/\text{cm}^2$ . The discharge rate for salt VI, though, is similar to the value  $52.0$   $\mu\text{A}/\text{cm}^2$  observed for a salt III IL at 71 °C.<sup>16</sup> The increased self-discharge rate for salt VII is attributed to the reduced IL viscosity relative to the IL of salt III.

## Summary

The electrochemical stability of 10 organic cations as solutes in ACN was investigated. For salts III, VI, and VII, the stability in ACN was compared to that measured in the chloroaluminate IL, with the performance of the chloroaluminate ILs of salts VI and VII presented for the first time. Both salts were liquid at elevated temperatures, but only the IL for salt VII was a liquid at room temperature. In both mediums, the benzyl-substituted cation (salt III) was less stable than the alkyl-substituted cation

(salt VII), 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 III samples confirmed that reduction involves the loss of the various alkyl groups. In ACN, salt VI was the most stable molecule due to its cyclic structure. However, in the IL form, salt VI 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 III and VII. The ILs of salts III and VII demonstrate a greater ability to support the efficient reduction and reoxidation of sodium than the IL of salt VI. The formation of insoluble products through the reduction of the salt VI cation leads to an inferior performance compared to salts III and VII, even though the I–V behavior in ACN is better.

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