



## Properties of Asymmetric Benzyl-Substituted Ammonium Ionic Liquids and Their Electrochemical Properties

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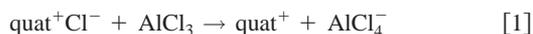
Benzyl-substituted quaternary ammonium ions were used to form room-temperature ionic liquids with chloroaluminate ions. Asymmetric ammonium structures significantly lowered the melting point of the ionic liquid. Asymmetric benzyl-substituted ammonium chlorides were mixed with  $\text{AlCl}_3$  to form acidic room-temperature ionic liquids. It is shown that the melting point and viscosity are a function of the symmetry of the quaternary ammonium ion and its molecular weight. Asymmetry and low molecular weight favor lower viscosity and melting point, and higher conductivity. These liquids were neutralized with  $\text{NaCl}$  and tested as electrolytes for sodium batteries. The neutralized ionic liquid of benzyldimethylammonium chloride had a low self-discharge current ( $3.96 \mu\text{A}/\text{cm}^2$ ) at room temperature on a platinum electrode substrate.

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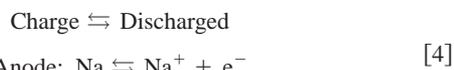
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Imidazolium-based chloroaluminate ionic liquids (ILs) have been investigated for battery<sup>1,2</sup> and electroplating<sup>3-6</sup> applications. Quaternary ammonium-based ILs have drawn attention as an alternative to the imidazolium-based ILs.<sup>7,8</sup> Quaternary ammonium salts (quats) are attractive for use in ILs because they are easy to synthesize and relatively safe. Imidazolium or quat chloroaluminate ILs have been studied as electrolyte materials for over a decade<sup>1,9,10</sup> as a derivative battery of the medium temperature “zebra” cell.<sup>11</sup> Sodium is utilized as the anode material because it does not form dendrites during deposition. Also, sodium is an abundant material in nature.

In this work, a new series of quaternary ammonium chloride salts is introduced as the cationic component of room-temperature ILs for electrochemical applications. Figure 1 shows a series of quats investigated in this study. They are composed of a benzyl group, and three alkyl groups (methyl, ethyl, and/or propyl groups). The ILs were prepared by mixing a quaternary ammonium chloride with aluminum chloride ( $\text{AlCl}_3$ ). The acidity of the melt is defined using the mole fraction of  $\text{AlCl}_3$ ,  $N = n/(n + m)$ , where  $n$  is the number of moles of  $\text{AlCl}_3$  and  $m$  is the number of moles of quat.  $\text{AlCl}_3$  acts as a Lewis acid and  $\text{Cl}^-$  as a base, as shown in Reaction 1. Neutral melts containing equal numbers of moles of  $\text{AlCl}_3$  and quat ( $N = 0.5$ ) contain only the  $\text{AlCl}_4^-$  (Lewis neutral) anions. Acidic melts contain an excess of  $\text{AlCl}_3$ ,  $N > 0.5$ , and form  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  (Lewis acid) anions (Reaction 2). Melts containing an excess of quat,  $N < 0.5$ , are basic and contain  $\text{AlCl}_4^-$  and  $\text{Cl}^-$  anions. Neutralization of the  $\text{Al}_2\text{Cl}_7^-$  occurs by reacting the  $\text{Al}_2\text{Cl}_7^-$  with a Lewis base, e.g.,  $\text{Cl}^-$ , such as from  $\text{NaCl}$ ,<sup>12</sup> to produce neutral  $\text{AlCl}_4^-$  ions (Reaction 3).



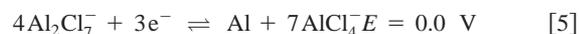
In this paper, the physical properties of the ILs (density, viscosity, and conductivity) were measured. The ILs were also tested as electrolytes for the Na battery. The electrolytes were investigated by plating sodium on Pt and W substrates. The performance of the electrolytes was evaluated by self-discharge currents and coulombic efficiencies for the sodium couple



### Experimental

Quats were prepared by *N*-alkylation through the reaction of amines and alkylchlorides (1:1.1 mole ratio, less than 50 mL scale). Amines and alkylchlorides for each of the quats are: *N*, *N*-dimethylethylamine and benzylchlorides for quat A; *N*, *N*-dimethylbenzylamine and propylchloride for quat B; *N*, *N*-dimethylisopropylamine and benzylchloride for quat C; *N*, *N*-diethylmethylamine and benzylchloride for quat D. All reactions except that for quat A need to be refluxed and require a week reaction. The yield for quat A is nearly 90%, but the others are less than 50%. The salts were filtered and recrystallized in acetonitrile and/or recrystallized with carbon black power to remove unreacted species. This procedure can be repeated until the color of the salt becomes uniform and whiter.  $\text{AlCl}_3$  (99.99%) and thionyl chloride ( $\text{SOCl}_2$ , >99%) were purchased from Aldrich (St. Louis, MO).  $\text{NaCl}$  (99.999%) was purchased from Alfa Aesar (Ward Hill, MA). All salts were dried for 48 h at 70°C prior to use.

An EG&G model 273 potentiostat was used for the electrochemical measurements. The three electrodes were positioned close to each other (within several mm), and no IR compensation was used. All measurements were performed in a Vacuum Atmospheres glove box (Hawthorne, CA) in a nitrogen atmosphere. The oxygen and moisture levels in the dry box were maintained below 10 ppm. Acidic melts were prepared, and neutralized with  $\text{NaCl}$ . A twofold excess of  $\text{NaCl}$  was used to buffer the melt. The addition of thionyl chloride (approximately 1 vol %) was necessary to activate the  $\text{Na}/\text{Na}^+$  redox process. The electrolytes were stirred with a spin bar throughout the potentiostatic measurements. The sample temperature was controlled using an oil-jacketed cell with a recirculating temperature controller (Fisher Scientific). Pt (99.999%) and W (99.95%) wires were purchased from Alfa Aesar. Working electrodes were fabricated from these wires by sealing in glass tubes and cleaning in hot  $\text{HNO}_3$  prior to use. They were polished using 0.3  $\mu\text{m}$  alumina power and thoroughly rinsed with deionized (DI) water prior to use. A twisted platinum wire served as a counter electrode in the electrochemical experiments. The reference electrode was formed by immersing an aluminum wire in an acidic melt (60 mol %  $\text{AlCl}_3$  and 40% quat) in a glass tube separated from the electrolyte by a fine glass frit. The cell equation for the reference electrode is as follows

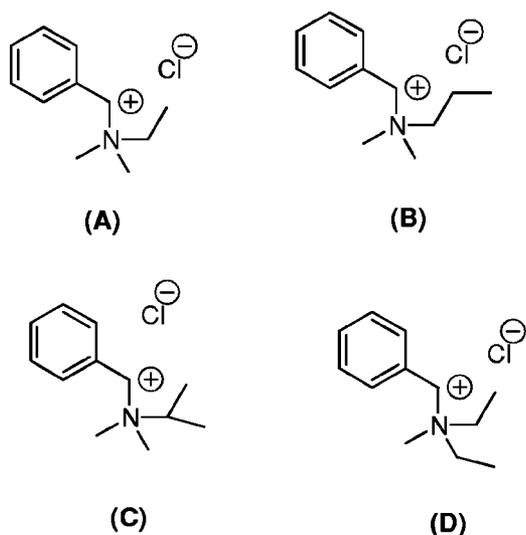


Conductivity measurements were performed using a custom-built probe and a ThermoOrion conductivity meter. Two platinum plates were set a fixed distance apart, the corners sealed in glass to prevent bending or movement of the plates. Platinum leads were connected

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**Figure 1.** Quaternary ammonium cations: (quat A) benzyldimethylammonium chloride, (quat B) benzylpropyldimethylammonium chloride, (quat C) benzylisopropyldimethylammonium chloride, and (quat D) benzylmethyldiethylammonium chloride.

to each plate. Calibration was performed using a standard KCl solution (Fisher Scientific). After each use, the probe was cleaned with nitric acid, rinsed with DI water, and dried.

A Seiko Instruments S II 220C differential scanning calorimeter (DSC) was used to determine the melting points. The ramp rate for the cooling cycle was 1-2°C/min and the heating cycle was 5°C/min. The reactivity of the plated Na with the melt can be quantified by measuring the self-discharge current. An open-circuit period was inserted between the plating and stripping of Na. 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 <sup>1</sup>H-NMR (400 MHz CDCl<sub>3</sub>): benzyldimethylethylammonium chloride (BDMEACl, quat A): δ 1.43 (t, CH<sub>3</sub>), 3.26 (s 2CH<sub>3</sub>), 3.70 (q, N-CH<sub>2</sub>), 5.03 (s, Ar-CH<sub>2</sub>), 7.40 (m, arom CH), 7.65 (m, arom CH); benzyldimethylpropylammonium chloride (BDM-PACl, quat B): 0.96 (t, CH<sub>3</sub>), 1.84 (m, CH<sub>2</sub>), 3.29 (s, 2CH<sub>3</sub>), 3.45 (m, N-CH<sub>2</sub>), 5.04 (s, Ar-CH<sub>2</sub>), 7.40 (m, arom CH), 7.62 (m, arom CH); benzyldimethylisopropylammonium chloride (BDMIPACl, quat C): 1.46 (m, 2CH<sub>3</sub>), 3.07 (br-s, 2N-CH<sub>3</sub>), 4.06 (septet, CH), 4.86 (br-s, Ar-CH<sub>2</sub>), 7.33 (m, arom CH), 7.62 (m, arom CH); benzyldiethylmethylammonium chloride (BDEMACl, quat D): 1.33 (t, 2CH<sub>3</sub>), 3.06 (s, N-CH<sub>3</sub>), 3.46 (m, 2N-CH<sub>2</sub>), 4.86 (s, Ar-CH<sub>2</sub>), 7.30 (m, arom CH), 7.56 (m, arom CH).

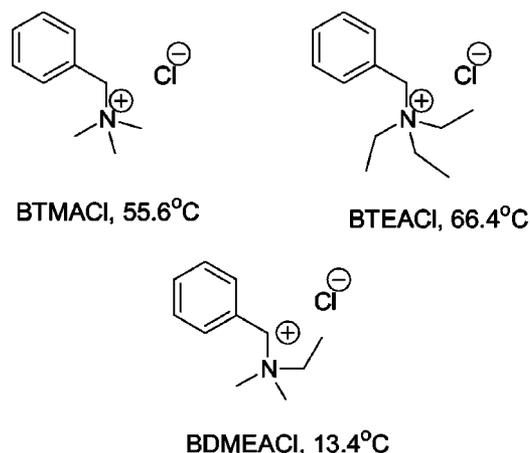
### Results and Discussion

Acidic melts ( $N = 0.55$ ) were created by mixing the quaternary ammonium chloride with aluminum chloride. The mixtures formed ILs at room temperature. The conductivity ( $\kappa$ ), density ( $\rho$ ), melting

**Table I. Properties of acidic ILs formed from 55 mol % AlCl<sub>3</sub> +45 mol % quat.**

Quat	$\eta$ (cP) at 27°C	$\rho$ (g/mL) at 27°C	$\kappa$ (mS/cm) at 27°C	$T_g$ (°C)	MP (°C)
A	278	1.26	0.716	-67.9	13.4
B	364	1.25	0.570	-63.1	-
C	735	1.24	0.333	-57.9	-
D	771	1.25	0.343	-64.1	-

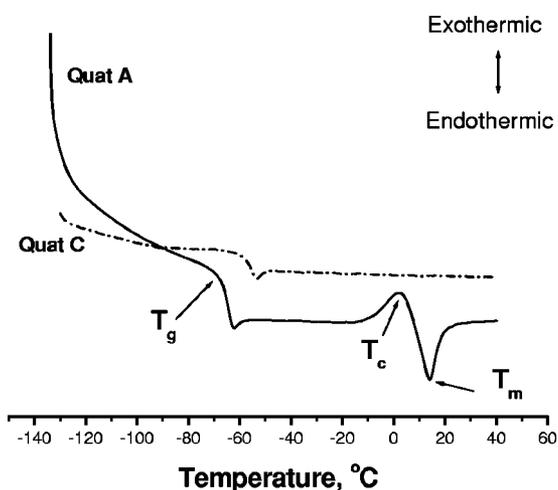
Quat A: BDMEACl, quat B: BDM-PACl, quat C: BDMIPACl, quat D: BDEMACl.



**Figure 2.** Structural comparison of quaternary ammonium chloroaluminate ILs and their MPs ( $N = 0.55$ ) for starting materials BTMACl, BTEACl, and BDMEACl.

point (MP), and viscosity ( $\eta$ ) of the ILs at  $N = 0.55$  are shown in Table I for acidic (55 mol % AlCl<sub>3</sub>) melts. Three of the quats shown in Fig. 1 are structural isomers, and the molecular weight of the nonisomer (Fig. 1A) is close to the others (one less CH<sub>2</sub>). 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 quat C is more compact than the *n*-propyl on quat B, leading to a higher viscosity for quat C.

Previously, we reported the MPs of several benzyltrialkylammonium chloroaluminates.<sup>14</sup> The MPs of ILs with benzyltrimethylammonium chloride (BTMACl) and benzyltriethylammonium chloride (BTEACl) were 55.6 and 66.4°C, respectively. Figure 2 compares the structures of these quats and their MPs. The three quats in Fig. 2 have similar structures and molecular weights. However, the asymmetric component of BDMEACl (mixture of the methyl and ethyl groups vs. all methyl or all ethyl) has a dramatic effect on its MP compared to BTMACl and BTEACl. 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 BDMEACl's IL. 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. Quats B, C, and D in Fig. 1 do not have MPs but glass transition points. Figure 3 shows



**Figure 3.** DSC curves for two acidic melts. The curve shows glass transition ( $T_g$ ), crystallization ( $T_c$ ), and melting point ( $T_m$ ).

Table II. Properties of neutral ILs from Table I.

Quat	$\kappa$ (mS/cm) at 27°C	$T_g$ (°C)	MP (°C)
A	0.324	-56.1	-
B	0.216	-57.1	33.3
C	0.125	-45.9	-
D	0.160	-61.4	-9.57

Quat A: BDMEACl, quat B: BDMPACl, quat C: BDMIPACl, quat D: BDEMACl.

the transitions for two of the ILs. The IL composed of quat A with  $\text{AlCl}_3$  has a glass transition and a melting point; however, the quat C melt has a glass transition only. Sun *et al.* reported a similar DSC thermogram for tributylhexylammonium imide.<sup>7</sup>

Table II shows the properties for the neutral melts ( $N = 0.50$ ).<sup>15</sup> The neutral melts were formed by adding NaCl to the  $N = 0.55$  melts. A twofold excess of NaCl was added to each melt to ensure neutrality. The viscosity was not measured because of the undissolved salt.<sup>16</sup> The glass transition point occurred at a higher temperature for the melts compared to their acidic counterparts. Also, quats B and C had MPs even though none was observed in the acidic melts. The second phase transition points observed in the neutral melts with quats B and D prohibit the electrochemical measurements at low temperature. An acidic melt with quat A at a higher acidity ( $N = 0.67$ ) was previously investigated for aluminum plating.<sup>17</sup> The conductivity of the neutralized melts (excess NaCl added) was lower than those of the acidic ILs. Acidic melts are composed of  $\text{quatAlCl}_4$ , and  $\text{quatAl}_2\text{Cl}_7$ . The neutralization reaction converts the melts into  $\text{quatAlCl}_4$  and  $\text{NaAlCl}_4$ . Due to the smaller radius and higher charge density of the sodium ion, the  $\text{NaAlCl}_4$  in the neutral ILs has higher ionic interaction (*i.e.*, ion pairing) than the  $\text{quatAl}_2\text{Cl}_7$  and  $\text{quatAlCl}_4$  in the acidic melts. The greater ionic attraction causes lower ionization (more ion pairing), resulting in a higher MP and lower conductivity for the neutral ILs.<sup>15</sup>

Figure 4 shows the conductivity *vs.* temperature for the acidic melts ( $N = 0.55$ ). The melt formed with quat A has a higher conductivity than the others. Melts from quats C and D are more viscous than those from quats A and B, possibly due to their denser packing density around the nitrogen. This shows that the conductiv-

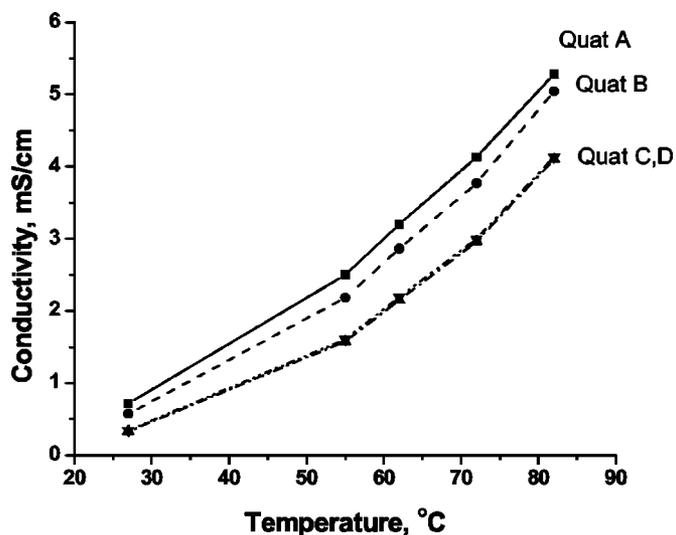


Figure 4. Conductivity *vs.* temperature for acidic ILs using the cations from Fig. 1 ( $N = 0.55$ ).

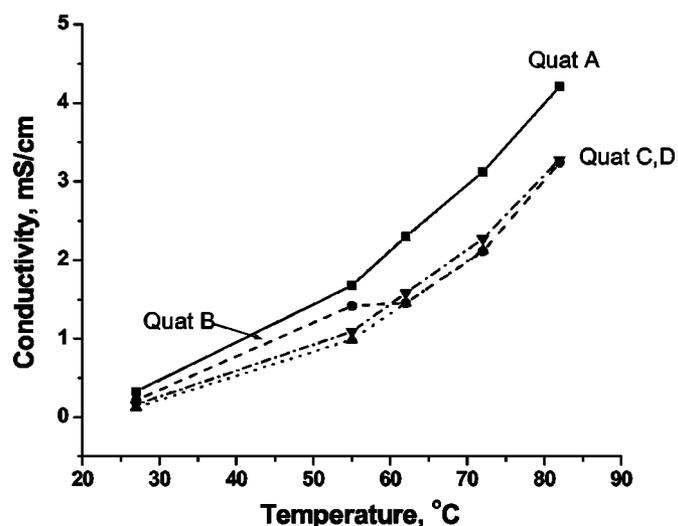


Figure 5. Conductivity *vs.* temperature with the neutral ILs using the cations from Fig. 1.

ity of the ILs (for the same chemical family) is closely tied to the viscosity in the acidic melts. Figure 5 shows the conductivity *vs.* temperature for the neutral melts. Figure 5 shows that the structural isomers have similar conductivity *vs.* temperature. The conductivity difference between the melt of quat A and the others increased as the temperature increased. During the neutralization process, a second cation is introduced (*i.e.*,  $\text{Na}^+$ ). The drop in conductivity with the addition of  $\text{Na}^+$  was discussed previously.<sup>15</sup> The higher charge density of  $\text{Na}^+$  compared to  $\text{quat}^+$  caused ion-pairing, which affects all the melts.

The electrochemical properties of the neutral melts (starting material had  $N = 0.55$ ) were measured. The neutral melts formed with quat A have a wide electrochemical potential window, in excess of 4 V, as shown in Fig. 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.<sup>18</sup> Figure 6 shows current-potential scans at Pt, Au, and tungsten (W) electrodes in the neutral IL. Chloride ion is oxidized at about 2.0 V.<sup>18</sup> We believe that the reduction current near -2.0 V is from the

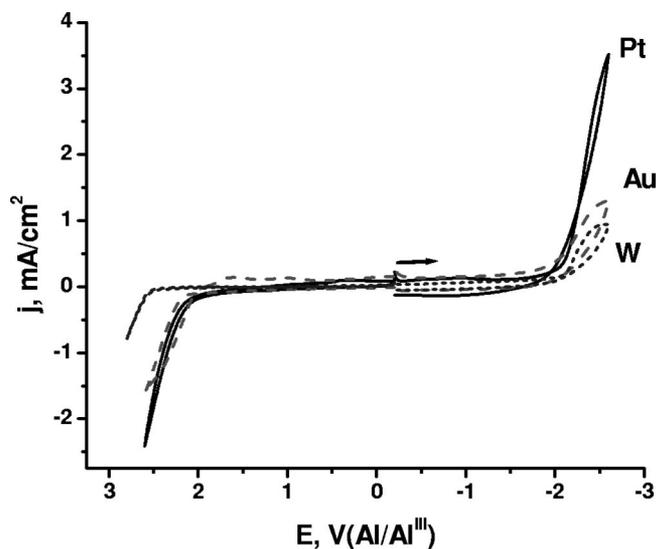


Figure 6. Cyclic voltammetry of the neutral quat A ionic liquid at 27°C. Working electrodes are platinum, gold, and tungsten electrodes, 1 mm diam disks. The scan rate was 100 mV/s.

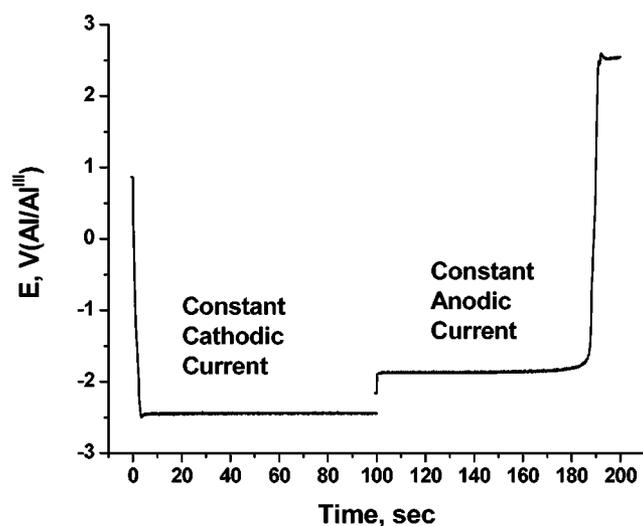


Figure 7. Chronopotentiometry of sodium deposition and reoxidation at 0.68 mA/cm<sup>2</sup>.

reduction of the quat<sup>+</sup> 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<sub>2</sub> (about 1 vol %) was necessary for the reduction of sodium ion and reoxidation of the sodium metal. The role of the additive (*i.e.*, SOCl<sub>2</sub>) was studied and discussed elsewhere.<sup>15</sup> Figure 7 is a typical chronopotentiometry curve for Na<sup>+</sup> reduction and its reoxidation (Reaction 4) in quat A melt at a constant current of 0.68 mA/cm<sup>2</sup> 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 Fig. 7. This indicates that a constant voltage can be provided for a long period of time when a battery using this anode is discharged.

Lower or higher constant-current experiments resulted in a lower coulombic efficiency than that shown in Fig. 7, most likely due to the reduction of impurities or the quat<sup>+</sup> itself.<sup>14</sup> Figure 8 shows the

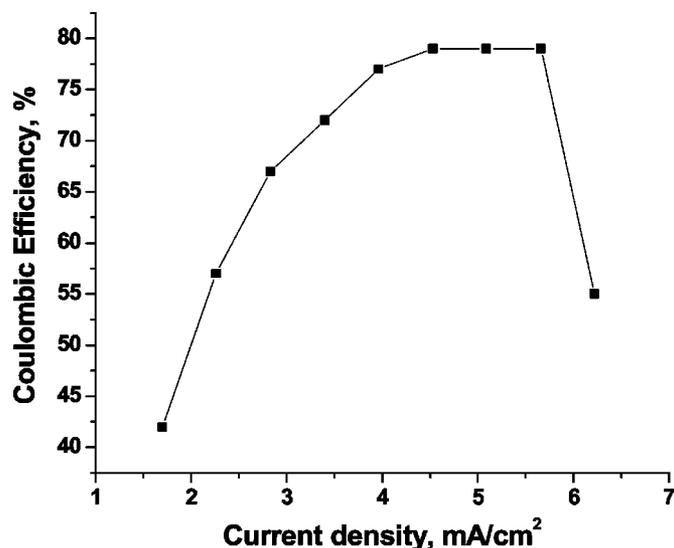


Figure 8. Coulombic efficiency vs. current density obtained through chronopotentiometry at 50°C and Pt electrode.

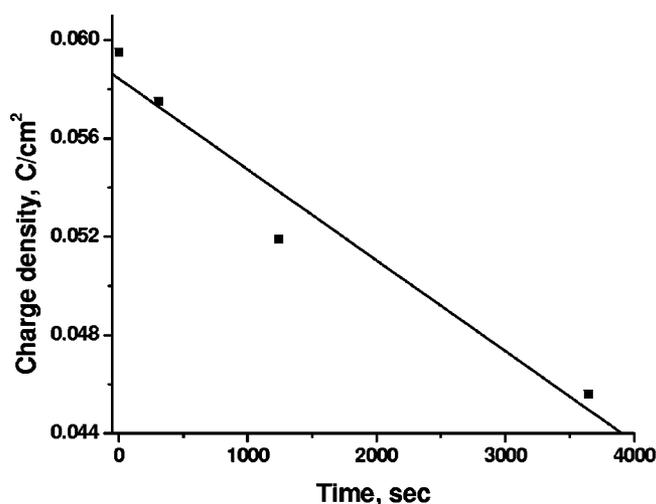


Figure 9. Charge recovered upon reoxidation of sodium (100 s deposition at 0.68 mA/cm<sup>2</sup>) vs. open-circuit time at 25°C on a Pt electrode.

change in coulombic efficiency vs. current density (as applied in a constant-current, chronopotentiometric experiment). In Fig. 8, a reduction current was applied for 10 s and the efficiency for reoxidation 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 Fig. 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.

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<sup>2</sup> 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 9 shows the charge recovered (oxidation of sodium) vs. open-circuit time following the constant-current deposition of sodium at 0.68 mA/cm<sup>2</sup> for 100 s. The values of self-discharge current are reported in Tables III and IV for different ILs and conditions.

Table III shows the comparison of the two electrodes in the same melt (quat A) at two temperatures. The current density for the maximum coulombic efficiency is shown. Table III 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 temperatures. However, the higher temperature also expedites unwanted reactions that are reflected in the self-discharge current. At 50°C, the coulombic efficiency and the self-

Table III. Comparison of chronopotentiometry results (100 s cathodic charging time). The melt was 45 mol % BDMEACl and 55 mol % AlCl<sub>3</sub>, neutralized with NaCl and SOCl<sub>2</sub> added. The coulombic efficiencies are the average values for three measurements.

Temperature	Electrode	Current density (mA/cm <sup>2</sup> )	Coulombic efficiency (%)	Self-discharge current (μA/cm <sup>2</sup> )
25°C	Pt	0.68	87.5	3.96
	W	1.02	88.5	5.25
50°C	Pt	4.24	92.4	15.6
	W	5.09	92.0	15.6

**Table IV. Self-discharge current and coulombic efficiency for 3 ILs. Chronopotentiometry and a Pt electrode were used. The coulombic efficiencies are the average values for three measurements. The working electrode is a Pt electrode.**

Temperature	Quat	Current density (mA/cm <sup>2</sup> )	Coulombic efficiency (%)	Self-discharge current (μA/cm <sup>2</sup> )
50°C	A	4.24	92.4	15.6
	C	1.98	91.2	28.7
71°C	A	4.24	91.5	52.0
	B	3.40	81.7	36.4

discharge current for the two electrodes were nearly identical, *i.e.*, 92% and 15.6 μA/cm<sup>2</sup>, respectively. The sodium deposit is thick enough so that the effect of the base metal substrate was not seen.

Table IV shows a comparison of the electrochemical properties for sodium plating in ILs formed from quats A, B, and C. Quat D was too viscous to obtain electrochemical data. Neutral melts of quats B and C have higher viscosities and melting points than the neutral melt of quat A. Thus, the melts of quats B and C need to be operated at higher temperatures to achieve comparable viscosities to quat A, as reported in Table IV. The coulombic efficiency for IL from quat A at 50°C is the maximum efficiency for that IL and was chosen as a reference. The same current density was used at 50 and 70°C (4.24 mA/cm<sup>2</sup>) so that the self-discharge currents can be compared to ILs from quats B and C. The melt of quat A shows better performance than the melt of quat C in terms of both coulombic efficiency and self-discharge current. The melt of quat A has a higher efficiency than the melt of quat B, but the self-discharge current is larger. The high viscosity of the quat B 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 BDMEACl in Table III, where the higher viscosity (lower temperature) correlated with a lower coulombic efficiency. Also, the longer alkyl group (propyl) of quat B is more electron-releasing to the nitrogen center (positive charge) than the ethyl group of quat A. This electron-releasing action for quat B slows down the self-discharge current at this temperature.<sup>14</sup> The self-discharge current value from the IL composed of 1-methyl-3-propylimidazolium chloride (MPIC)<sup>13</sup> was 22 μA/cm<sup>2</sup> and that of the methanesulfonyl chloride (MSC)<sup>19</sup>-based IL was 3 μA/cm<sup>2</sup>. The IL of quat A has comparable values of self-discharge currents at room temperature.

The IL of quat A showed the best performance among the quats in Fig. 1, because it can be used at room temperature. However, the self-discharge current becomes worse at higher temperatures. The alkyl groups on quat A 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 slight increase of size of alkyl groups increased the viscosity remarkably. Thus, tailoring the size and the structure of the 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 1-ethyl-3-methylimidazolium (EMIC) have been studied. The comparable EMIC IL had a molar conductivity, (κ)/(mol/cm<sup>3</sup>), of ~4 S cm<sup>2</sup>/mol, which is 20 times greater than that of the IL formed from quat A (0.2 S cm<sup>2</sup>/mol) as calculated from the data in Table I.<sup>20</sup> Comparisons can be made between chloroaluminate ILs from EMIC and quat A. First, the number of atoms on the quat A cation is 50% higher than on 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 EMIC and quat A cations. Work is currently underway to optimize the quats to improve the conductivity and lower the MP without sacrificing the electrochemical stability.

### Conclusion

The asymmetric nature of the quat lowered the MP of the chloroaluminate melts and lowered the viscosity. However, the less electron-donating nature of small alkyl substituents lowered the electrochemical stability. Benzylethyldimethylammonium chloroaluminate had a coulombic efficiency and self-discharge current comparable to that of MPIC- and MSC-based ILs.

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