



Electrochemical Investigation of Quaternary Ammonium/Aluminum Chloride Ionic Liquids

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Quaternary ammonium salts have been studied as ionic liquids for electrochemical applications, including sodium batteries. Mixtures of benzyltrialkylammonium chlorides with chloroaluminate formed ionic liquids near room temperature. The maximum coulombic efficiency for the reduction and re-oxidation of sodium ions with benzyltriethylammonium chloride ionic liquid was over 91%. The self-discharge current for a sodium electrode in this ionic liquid was 32.7 and 18 $\mu\text{A}/\text{cm}^2$ by chronopotentiometry at tungsten electrodes at 6.37 and 2.55 mA/cm^2 , respectively. These are comparable to values in 1-methyl-3-propylimidazolium chloride melt. Issues with the coulombic efficiencies and the self-discharge currents are discussed.

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The need for low-cost, high-energy density, durable, secondary batteries continues to rise with the demands of the electronics and automobile industries. Sodium-based batteries have received attention as an alternative to lithium-based batteries due to several factors. Formation of lithium dendrites during deposition has required the use of a separator that lowers the coulombic efficiency.^{1,2} A wide separation between the electrodes results in high resistance and low current density. On the other hand, sodium forms uniform electrodeposits on the electrode surface without dendrites. Furthermore, sodium is an abundant element in nature.

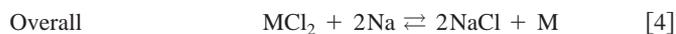
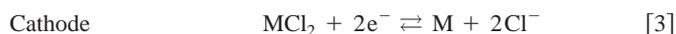
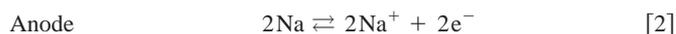
One of the current sodium rechargeable batteries, the “Zebra” cell, has a specific energy greater than 130 $\text{Wh}/(\text{kg})^{-1}$. This secondary cell operates at $\sim 250^\circ\text{C}$ and uses a molten chloroaluminate inorganic salt, $\text{NaCl}:\text{AlCl}_3$ (melting point (m.p.) 185°C), as the electrolyte. At this operating temperature, the Zebra cell contains molten sodium (m.p. 98°C) as the anode and a solid-state separator between the liquid Na and the electrolyte; direct contact results in a chemical reaction producing Al.



An appreciable voltage drop (*ca.* 350 mV) results from the use of the separator under typical operating conditions.³

The separator and high operating temperature are disadvantages of the “Zebra” cell that can be addressed by using a low m.p. ionic liquid in place of NaAlCl_4 . Dialkylimidazolium chloride: aluminum chloride has been electrochemically investigated. 1-ethyl-3-methylimidazolium chloride (EMIC) forms a liquid phase when mixed with aluminum chloride at ambient temperature covering a wide composition range.⁴ 1-methyl-3-propylimidazolium chloride (MPIC) and methanesulfonyl chloride (MSC) show encouraging results for sodium-based batteries.⁵ In this study, we have investigated nonimidazolium ionic liquids because of their low cost and versatility. The purpose of this study is to discover salts that have a low operating temperature, low viscosity, high stability (especially to reduction), and are applicable to battery applications.

The overall cell reaction and the half-cell reactions for a sodium battery are as Charge \rightleftharpoons Discharged



where M could be a transition metal, such as Fe,⁶ Ni,⁷ or Cu.⁸ These cathodes gave cell potentials from 2.3 to 3.3 V in an EMIC: AlCl_3

melts. It has been shown that the substrate for the anode reaction (Na/Na^+) can play an important role because the sodium deposit must nucleate on the surface (desired reaction) and the melt can be electrodecomposed (undesired reaction).

In this paper, we report the results for several quaternary ammonium salts (Quats), which form near room temperature ionic liquids with aluminum chloride. The melt characterization includes melting point, conductivity vs. temperature, coulombic efficiency for the deposition/stripping of sodium, and Na/Na^+ (anode) self-discharge current. The coulombic efficiency of the Na/Na^+ couple has been measured by cyclic voltammetry (CV), chronopotentiometry (CE), and chronoamperometry (CA) and is defined as the ratio of oxidation charge to reduction charge.

Coulombic efficiency of (Na/Na^+)

$$= (\text{oxidation charge}/\text{reduction charge}) \quad [5]$$

Quaternary ammonium salts.—The ionic liquids were prepared by mixing Quat with aluminum chloride. The acidity of the melt is defined using the mole fraction of AlCl_3 , $N = n\text{AlCl}_3 / (n\text{AlCl}_3 + m\text{Quat})$ where n is the moles of AlCl_3 and m is the moles of Quat. AlCl_3 acts as a Lewis acid and Cl^- as a base. Neutral melts containing equal moles of AlCl_3 and Quat ($N = 0.5$) contain (essentially) only AlCl_4^- anions. Acidic melts contain an excess of AlCl_3 , $N > 0.5$, and form AlCl_4^- and Al_2Cl_7^- anions. Al_2Cl_7^- is a Lewis acid that can accept Cl^- to produce 2 AlCl_4^- . Melts containing an excess of Quat, $N < 0.5$, are basic and contain AlCl_4^- and Cl^- anions. Cl^- anions can react with a Lewis acid in the melt.



The constituents of the melts at various acidities is as follows. Basic melts:Neutral melts:Acidic melts⁹



Equation 8 shows the major anions in each acid state. Basic melts can be converted to acidic melt by the addition of AlCl_3 . In acidic condition, there is excess Al_2Cl_7^- ions rather than Cl^- ions that exist in basic melts. AlCl_4^- ions (Lewis neutral) are present in all melts regardless of acidity.

Neutral melts have the widest electrochemical window (~ 4.5 V). The Al_2Cl_7^- anion, as would exist in acidic melts, is easily reduced to Al, and Cl^- is easily oxidized to chlorine in basic melts. Alkali chlorides (*e.g.*, NaCl) can be used to buffer acidic melts and establish buffered, neutral conditions.¹⁰ Excess NaCl converts Al_2Cl_7^- to AlCl_4^- while providing the sodium ion source for the battery. Ex-

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cess NaCl buffers the melt by providing a reservoir of chloride. The reduction potential of the organic cation is very close to the Na/Na⁺ redox couple.

Previous studies have shown that it is necessary to add an acid (such as HCl or SOCl₂) to the neutral, buffered ionic liquid to facilitate the Na/Na⁺ redox process.^{11,12} Without an additive, Na⁺ reduction has only been observed at a mercury electrode.⁶ The role of the additives has not been described.

Experimental

Quaternary ammonium salts were dried under vacuum for 48 h at ~70°C. Methyltriethylammonium chloride (MTEACl) and methyltributylammonium chloride (MTBACl) were obtained from Sachem, Inc (Austin, TX). Benzyltrimethylammonium chloride (98%) (BTMACl), benzyltriethylammonium chloride (98%) (BTEACl), and benzyltributylammonium chloride (98%) (BTBACl) were purchased from Acros (Belgium). AlCl₃ (99.99%) and thionyl chloride (SOCl₂, > 99%) were purchased from Aldrich (St. Louis, MO). NaCl (99.999%) was purchased from Alfa Aesar (Ward Hill, MA). All chemicals were used as received without further purification. Pt (99.999%) and W (99.95%) wires were purchased from Alfa Aesar. Working electrodes were fabricated from these wires in sealed glass tubes. Working electrodes were treated in hot HNO₃, and polished with 0.3 μm alumina powder and thoroughly rinsed with de-ionized water prior to use. The diameter of the working electrodes was 1 mm. The counter electrode was a twisted Pt wire. The reference electrode was formed by immersing an aluminum wire (99.9995%) in an acidic melt (60 mol% AlCl₃ and 40% Quat) in a glass tube separated from the electrolyte by a fine glass frit. The half equation for the reference electrode is



An EG&G model 273 potentiostat was used for the electrochemical measurements. All measurements were performed in a Vacuum Atmosphere glove box (Hawthorne, CA). The oxygen and moisture level in the dry box was maintained below 10 ppm. Acidic melts were prepared, and buffered with NaCl. The scale of electrochemical measurements was about 10 g of the acidic melts. A twofold excess of sodium chloride needed to neutralize the acidic melt was added. Once the melt is neutralized, the reduction of Al₂Cl₇⁻ to Al at 0 volt and the melt provides a wider potential window to -2 V or higher.¹³

The addition of thionyl chloride (~1 vol %) was necessary to reduce Na⁺ to Na. The electrolytes were stirred with a spin bar throughout the potentiostatic measurements. The sample tempera-

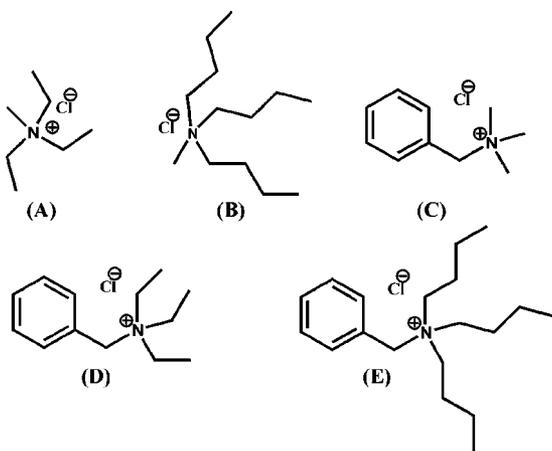


Figure 1. Quaternary ammonium salts (Quats): (A) methyltriethylammonium chloride, MTEACl, (B) methyltributylammonium chloride, MTBACl, (C) benzyltrimethylammonium chloride, BTMACl, (D) benzyltriethylammonium chloride (BTEACl), (E) benzyltributylammonium chloride, BTBACl.

Table I. Melting point of ionic liquids (55 mole % of AlCl₃ and 45 mole % Quat).

	MTEACl	MTBACl	BTMACl	BTEACl	BTBACl
Melting point (°C) of acidic melt	278.2	105.2	55.6	66.4	40.6
Melting point (°C) of neutralized melt	--	--	65.3	66.0	42.7

ture was controlled using an oil-jacketed cell with a recirculating temperature controller (Fisher scientific). The three electrodes were positioned as close as possible to each other. The IR drop was not compensated. An Orion conductivity meter (model 115 A plus) was used for conductivity measurements. It was calibrated with a NaCl calibration standard solution (Orion) outside the dry box before measurements. A Seiko Instruments S II 220C differential scanning calorimeter (DSC) was used to determine the melting points. Each sample was sealed in the dry box for eventual melting point measurements, which were performed under a nitrogen purge. The reactivity of the deposited 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.^{5,12}

Results

Figure 1 shows the structure of the Quats used in this study. These Quats were selected because of their unique aliphatic alkyl chains (*e.g.*, short chain, long chain, (aromatic nature). Acidic melts were formed and later neutralized with NaCl to form the buffered, neutral melt. Acidic melts higher than N = 0.6 were difficult to buffer. In many cases, acidic melts higher than N = 0.6 were not able to be buffered, even though excess NaCl was added. Thus, N = 0.55 was chosen as a moderate composition used as the starting composition for the melting point studies. The melting points of the ionic liquids formed from the Quats in Fig. 1 and AlCl₃ are shown in Table I.

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 that of the alkyl branches. Thus, BTMA⁺ has weaker ionic strength with chloride ions compared to the MTEACl and MTBACl in Table I. Even though the BTMACl:AlCl₃ melting point is above room temperature, the melting point of the BTMACl melt is lower than the melt-

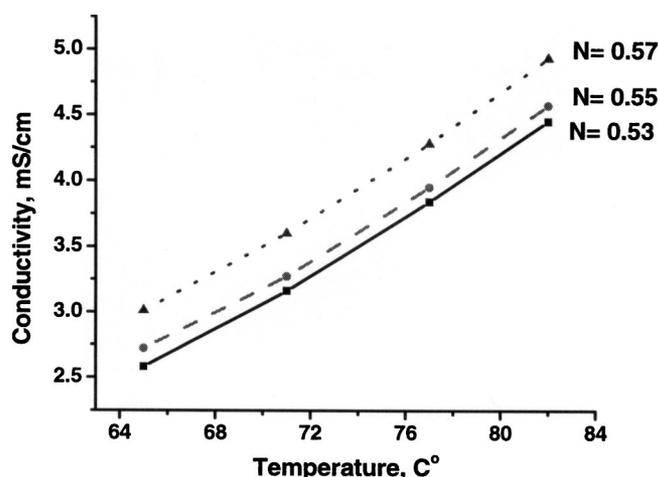


Figure 2. Conductivity vs. temperature for three BTMACl:AlCl₃ melts.

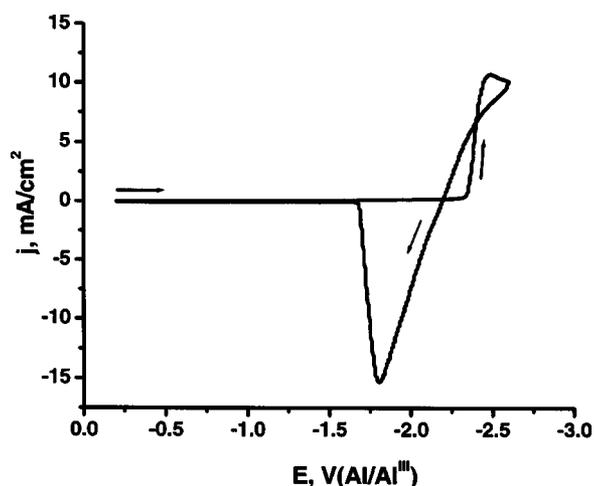


Figure 3. CV of the BTMACl:AlCl₃ melt (N = 0.55) neutralized with excess NaCl and a trace of SOCl₂ at 71°C on a tungsten electrode.

ing 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.

The melting point of benzyltriethylammonium chloride (BTEACl) was greater than benzyltributylammonium chloride (BTBACl). However, the melting point of the BTEACl melt is higher than that of the BTMACl melt. This result implies that there are other contributions to the melting point, such as, the symmetry of the ions.¹⁴ 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 MTEACl and MTBACl, the benzyl group is more effective in disrupting symmetry.

The addition of sodium chloride to neutralize the three acidic melts in Table I, does not greatly impact the melting points. Melting points of neutralized melts were within a few degrees (higher or lower) of those in Table I. In this case the chloride ions from NaCl convert Al₂Cl₇⁻ to AlCl₄⁻. The NaCl concentration was not sufficient to effect the melting points.

Figure 2 shows the temperature dependence of the conductivity for the BTMACl:AlCl₃ ionic liquid. For operating temperatures of 65 to 82°C, the values range from 2.5 to 5 mS/cm, which is lower than that of 1-methyl-3-ethylimidazolium chloride (35 mS/cm at room temperature).¹¹ The conductivity increased with acidity of the melts. As shown in Eq. 8, the fraction of Al₂Cl₇⁻ ions also increases with the acidity of the melts. 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 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.¹⁵

Figure 3 shows a CV for BTMACl: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 the figure was 86%. The efficiencies vary with switching potential and other measurement conditions. The shape of the reduction and oxidation peak are very sharp, indicating a rapid redox process. The sharp rise in the

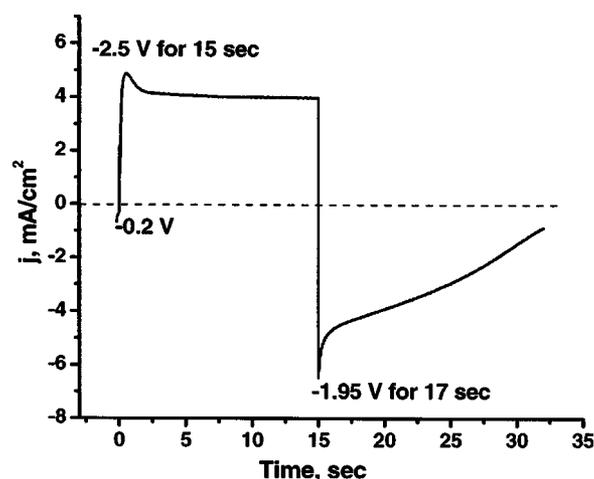


Figure 4. Chronoamperometry of the BTMACl:AlCl₃ melt (N = 0.55) neutralized with excess NaCl on a W electrode at 65°C with SOCl₂ added.

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 nonsodium surface. This current-voltage shape is typical of the sodium couple in dialkylimidazolium ionic liquids. Figure 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.

The efficiency of reduction and re-oxidation can also be measured by utilizing CA methods. 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 Fig. 4, the discharge time was 2 s longer than the charge time. The coulombic efficiency was obtained based on the allotted time, even though the oxidation current did not decay to zero. The average current for the reduction process was higher than that for the re-oxidation process, indicating a slower oxidation rate (when compared to the reduction rate). The efficiency for Fig. 4 is 87%.

The optimum current for reduction and oxidation of sodium is dependent on the melt composition, the electrode utilized and the operating temperature. Table II summarizes the resulting coulombic efficiency when the current density (for the CE experiment) and reduction/re-oxidation time was varied. From this table it can be seen that the maximum efficiency can be achieved at currents of 5.7 to 6.3 mA/cm², with very low efficiencies when the current density approached low (1.3 mA/cm²) or high (10 mA/cm²) values.

Figures 5 and 6 illustrate why low efficiencies were obtained with the high and low currents. Figures 5A and B are examples of low and high current densities, respectively. Figure 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 Fig. 5A, the current

Table II. Coulombic efficiencies of a buffered BTMACl:AlCl₃ melt (N = 0.55) with trace SOCl₂ at a tungsten electrode at 71°C.

Current density (mA/cm ²)	1.3	2.5	3.8	4.4	4.4	5.1	5.1	5.7	6.3	6.3	6.3	7.6	10
Charge/discharge Time (s)	10	10	60	50	60	30	60	60	60	80	100	60	10
Efficiency (%)	31	52	85	86	88	82	88	89	89	90	88	84	16

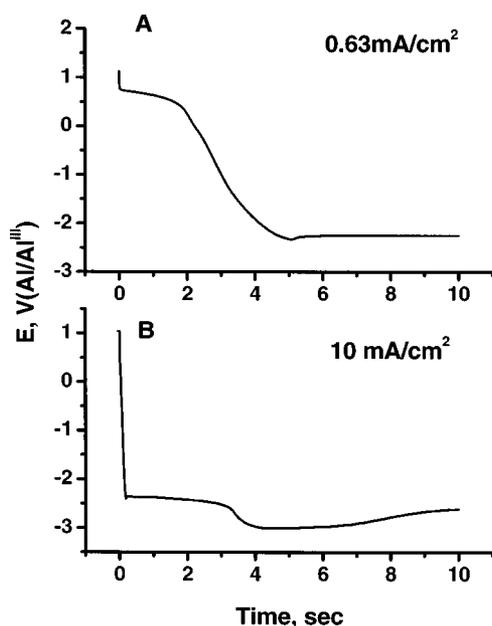


Figure 5. Chronopotentiometry of a buffered BTMACl:AlCl₃ melt ($N = 0.55$) with trace SOCl₂ added on a W electrode at 71°C. The oxidation currents, not shown here, were applied after the reduction measurements.

density (0.63 mA/cm²) is low enough that it takes a significant amount of time (4 of the 10 s) and charge to reduce these species before the sodium ions can be reduced at approximately -2.4 V. In Fig. 5B, 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 other species, probably Quat⁺ (and slight shift of the potential to more negative values) after ~ 3 s. The CE curves for the optimum case are shown in Fig. 6. In Fig. 6A 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 was carried out at the same current (6.3 mA/cm²) and is shown in Fig. 6B. During the re-oxidation, the potential remained fixed at -2.0 V until the rapid increase near 70 s. The plateau at 2.3 V represents Cl₂ gas evolution. The efficiency for the process shown in Fig. 6 is 90%.

To quantify the parasitic reactions, the self-discharge current, $I_{\text{self-discharge}}$, 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 s and an operating temperature of 71°C. Under these conditions (no open circuit time between reduction and re-oxidation) the average efficiency was 88.8%. Figure 7 shows the self-discharge current using a linear-fit of the data points for the neutralized BTMACl:AlCl₃ ($N = 0.55$) melt with SOCl₂ added. The self-discharge current was 76.6 $\mu\text{A}/\text{cm}^2$, which is higher than that of the 1-methyl-3-propylimidazolium chloride melt (22 $\mu\text{A}/\text{cm}^2$).¹² It suggests that the parasitic reactions in the BTMACl melt are more active than those in the MPIC melt. The higher operating temperature of the BTMACl melt could account for the increase in the activity of the parasitic reactions.

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 MPIC has a higher level of positive ion delocalization than the benzyl and methyl groups in

the BTMACl melt resulting in the lower self-discharge current for MPIC. 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 BTEACl:AlCl₃ ($N = 0.55$) 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/cm² on a tungsten electrode at 82°C. Under these conditions the self-discharge current was 32.7 $\mu\text{A}/\text{cm}^2$, which is approximately half that measured for the BTMACl melt. 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 BTEACl tests was higher than that used for the BTMACl tests (71°C), which should result in more active parasitic reactions for the BTEACl 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 BTEACl melt but at a lower current density (2.55 mA/cm²). With these conditions, the average baseline efficiency was 92.0% and the self-discharge current was 18.0 $\mu\text{A}/\text{cm}^2$. The decrease in the self-discharge current with a lower current density may be due to the thinner film.

While the results for the BTMACl melt and the BTEACl melt were encouraging, the deposition of sodium from the BTBACl melt was poor. Both platinum and gold electrodes showed reduction/re-oxidation efficiencies of less than 20%. The efficiency on a tungsten electrode was the highest. Efficiencies for the CV tests (100 mV/s scan rate 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/cm² 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.

Discussion

The ultimate goal of this work is to develop 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 BTBACl melt where the long alkyl chains lead to a liquid with a viscosity that is high enough to prevent the efficient reduction and

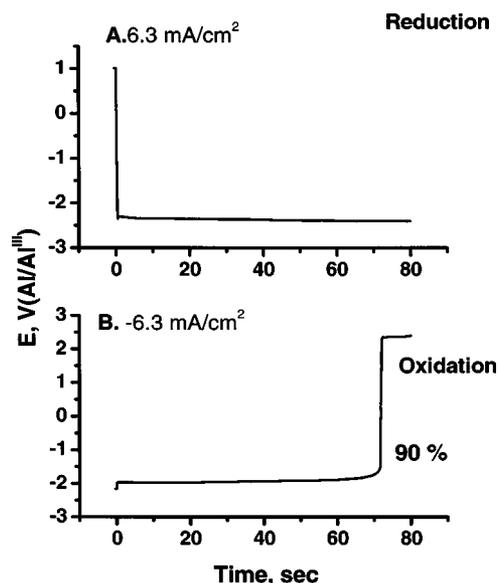


Figure 6. Chronopotentiometry on a W electrode at 71°C. The buffered BTMACl:AlCl₃ melt ($N = 0.55$) has SOCl₂ added. The current density was 6.3 mA/cm².

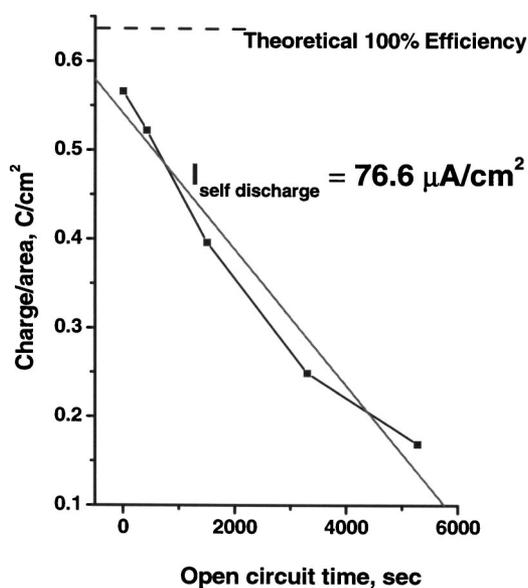


Figure 7. Charge density vs. open-circuit time on a W electrode at 71°C in a buffered BTMACl:AlCl₃ melt (N = 0.55) with SOCl₂ added.

re-oxidation of sodium. In contrast, both BTMACl and BTEACl form ionic liquids near room temperature (70 to 85°C) that support the efficient plating and stripping of sodium. The improved performance of the BTEACl melt when compared with the BTMACl melt is attributed to the increased electron releasing ability of the ethyl groups over the methyl groups.

In this study, we investigated the modification of the cation and its effect on melting points. However, 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.¹⁴ To achieve a room-temperature ionic liquid, the symmetry of both the cation and the anion must be reduced. Though effective in lowering the melting point, it may become necessary to substitute an alternative alkyl or aromatic groups for the benzyl group. Regardless, the data collected using the melts discussed in this report will be useful in determining the structures of the salts to be synthesized and examined in future studies.

Conclusion

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: the ring de-localizes the positive charge well around the Quat⁺, while also disrupting the symmetry of the Quat⁺. These effects both contribute to the melting points of the melts. As compared with the BTMACl melt, the BTEACl melt 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).

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