



Investigation of Ether-Substituted Quaternary Ammonium Ionic Liquids

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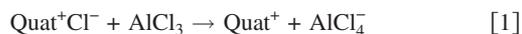
The effect of structural rigidity in quaternary ammonium-based ionic liquids (ILs) was investigated. [EtOMe]EtMe₂NCl(I) and [MeOEt]EtMe₂NCl(II), both 8 atom (7 carbons, 1 oxygen) ether-substituted quaternary ammonium chlorides (Quats), were synthesized and investigated. In acetonitrile, placement of the oxygen one atom from the nitrogen (Quat I) resulted in a significant decrease in the reductive stability. While the IL form showed similar stability for the two systems, placing the oxygen close to the nitrogen (methyl ethyl ether) 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 nonether analog, BuEtMe₂NCl (III, 51.3°C) IL. In contrast, placing two carbon atoms between the nitrogen and ether group, ethyl methyl ether (Quat II), delocalizes the positive charge from the nitrogen and produces a room-temperature IL. Neutralization of the acidic IL with sodium chloride resulted in an increase in the bulk conductivity, due to the polar ether group. Upon addition of CDCl₃ or SOCl₂, which both form a solid-electrolyte interphase on the substrate surface, the increased free sodium ion concentration allowed sodium reduction and oxidation currents greater than 4 mA/cm² at room temperature.

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Ionic liquids (ILs) are interesting 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 sodium or lithium. For example, imidazolium-based chloroaluminate ILs have been investigated for both battery^{1,2} and electroplating^{3,6} applications. ILs based on quaternary ammonium salts (Quats) are attractive because a large variety of structures can be readily synthesized through *n*-alkylation of the appropriate tertiary amine.^{7–9} Both imidazolium and quaternary ammonium ILs have been studied^{2,10,11} as electrolytes in a derivative of the medium-temperature battery, the “zebra” cell.¹² A sodium-based battery is appealing due to the relative abundance of sodium, its low atomic weight and cost, and absence of dendrites for metallic anodes.

ILs can be formed by mixing quaternary ammonium chloride and aluminum chloride. Equations 1 and 2 show the acid-base reactions that occur when the Quat and AlCl₃ are mixed. AlCl₃, a Lewis acid, forms AlCl₄⁻ (Lewis neutral) and Al₂Cl₇⁻ (Lewis acid) when mixed with the Quat. Neutralization of the Al₂Cl₇⁻ occurs by reacting Al₂Cl₇⁻ with a Lewis base (e.g., NaCl or Quat⁺Cl⁻) to produce neutral AlCl₄⁻ ions (Eq. 3)¹³



The composition of the melts is given in terms of the mole fraction of AlCl₃, *N*. Neutral melts containing equal moles of AlCl₃ and salt (*N* = 0.5) contain only the Quat⁺ and AlCl₄⁻ ions. Acidic melts contain an excess of AlCl₃, *N* > 0.5, and form AlCl₄⁻ and Al₂Cl₇⁻ anions. Melts containing an excess of chloride salt, *N* < 0.5, are basic and contain AlCl₄⁻ and Cl⁻ anions. Neutralization of the acidic melts with sodium chloride provides the IL with a source of sodium ions for electrodeposition to the metallic state. Typically 100% excess sodium chloride is added to buffer the melt.

Previously, we demonstrated that by utilizing asymmetric Quats, room temperature chloroaluminate ILs (RTILs) could be formed.^{14,15} However, RTILs could only be formed with Quats of

nine or more carbon atoms. A number of research groups have examined the inclusion of an ether group in the cation to lower the melting point of the resulting IL.^{16–22} For example, Matsumoto et al. showed that with bis(trifluoromethylsulfonyl)imide replacement of an alkyl group with an ether group can result in very low melting ILs.^{7,8,23}

In this work, two 8-atom (7 carbons, 1 oxygen) ether-containing Quats were investigated (Fig. 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 butylethyltrimethyl-

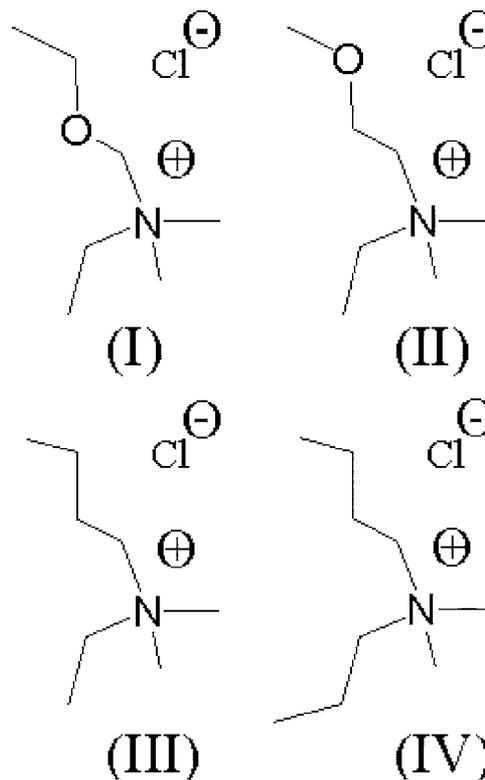


Figure 1. Quat structures investigated: (a) [EtOMe]EtMe₂NCl(I), (b) [MeOEt]EtMe₂NCl(II), (c) BuEtMe₂NCl(III), and (d) BuMe₂ProNCl(IV).

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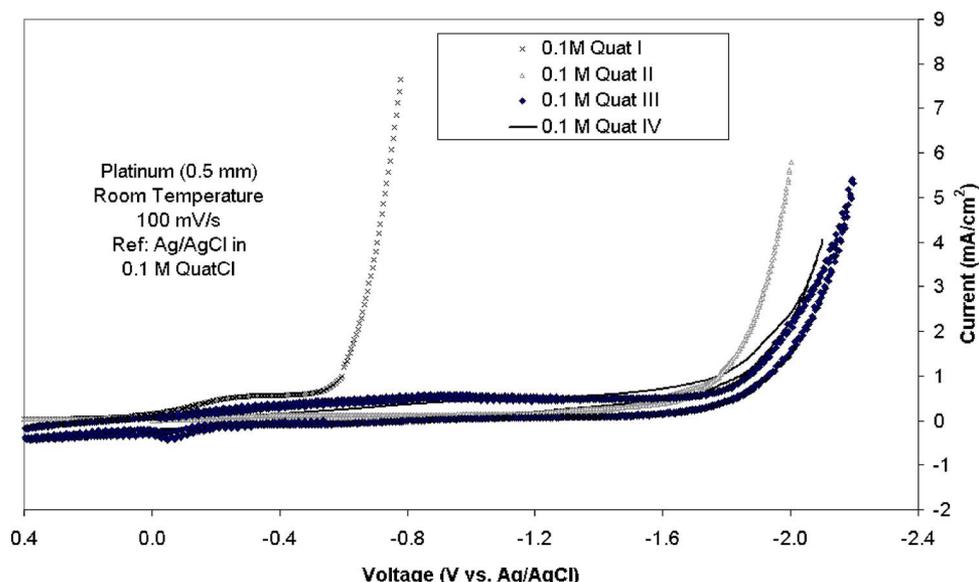


Figure 2. CV results for 0.1 M Quat in ACN.

ammonium chloride(III) and 9-carbon salt butyldimethylpropylammonium chloride(IV) are also included. The electrochemical stability in acetonitrile (ACN) was first investigated. Then, ILs were formed with AlCl_3 and the physical and electrochemical properties were measured. For the $[\text{MeOEt}]\text{EtMe}_2\text{NCl}(\text{II})$ IL, the deposition and stability of sodium was investigated.

Experimental

All experiments were carried out in a Vacuum Atmospheres glove box under dry nitrogen due to the sensitivity of the ILs and salts to moisture. 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. Aluminum trichloride, AlCl_3 , (99.99%), chloroform-D (99.9 atom %), and thionyl chloride, SOCl_2 , (99+%) were obtained from Aldrich and used as received. Quats III and IV were synthesized by reacting the appropriate trialkyl-substituted amine with an alkyl chloride at elevated temperatures (40–50°C).¹⁴ $[\text{MeOEt}]\text{EtMe}_2\text{NCl}(\text{II})$ was synthesized by reacting *N,N*-dimethylethylamine (99%, Aldrich) with 2-chloroethyl methyl ether (98%, Aldrich) at 35–40°C in ACN while refluxing for 1 week.¹⁷ $[\text{EtOMe}]\text{EtMe}_2\text{NCl}(\text{I})$ was prepared by reacting *N,N*-dimethylethylamine and chloromethyl ethyl ether (95%, Aldrich) in tetrahydrofuran (THF) at 3–4°C for 3 h and then overnight at room temperature.²⁰ The salts were then purified using activated carbon prior to electrochemical study. All of the salts and NaCl (99.999%, Alfa Aesar) were dried under vacuum for 48 h at 70°C before use in the glove box. The structures of all the Quats was verified by H-NMR. For Quat I, mass spectrometry was performed to verify that it was the predominant species.

Conductivity measurements were performed using a custom-built probe and ThermoOrion conductivity meter.²⁴ Two platinum plates were set a fixed distance apart and the corners were sealed in glass to prevent bending or movement of the plates. Platinum leads were connected to each plate. Calibration was performed using a standard (Orion) NaCl solution before use in the glove box. After each use the probe was cleaned with nitric acid, rinsed with deionized 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 HNO_3 , polished using 0.3 μm 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 at 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 given by Eq. 4



The reference electrode for the ACN tests was formed by immersing a silver wire coated with AgCl in the 0.1 M Quat 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.

The melting points were determined using a Seiko Instruments S II 220C differential scanning calorimeter (DSC). The ramp rate of the cooling cycle was 2°C/min and the heating cycle was 5°C/min.

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.^{15,25} Figure 2 shows the cyclic voltammetry (CV) scans for 0.1 M acetonitrile solutions of Quats I–IV. Quat II (–1.78 V at 1 mA/cm²) showed similar stability to Quats III (–1.87 V) and IV (–1.78 V).¹⁵ However, shifting the oxygen one atom closer to the nitrogen, to form Quat I, 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.¹⁵ The decreased stability of Quat I suggests that ACN has a greater ability to stabilize the reduction intermediates formed in the reduction of I than those formed with the other Quats.

To examine the impact of the ether substituent, ionic liquids were formed by mixing together 55 mol % AlCl_3 and 45 mol % Quat Cl ($N = 0.55$). Particular care was taken in forming the IL of Quat I, 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.²⁶ When mixed with AlCl_3 , Quat IV has been shown to form a room-temperature IL.¹⁵ Reducing the size of the Quat by one carbon, to form Quat III, 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 in a similar Mw 8-atom (7 carbons, 1 oxygen) cation, produces a RTIL ($T_g \approx$

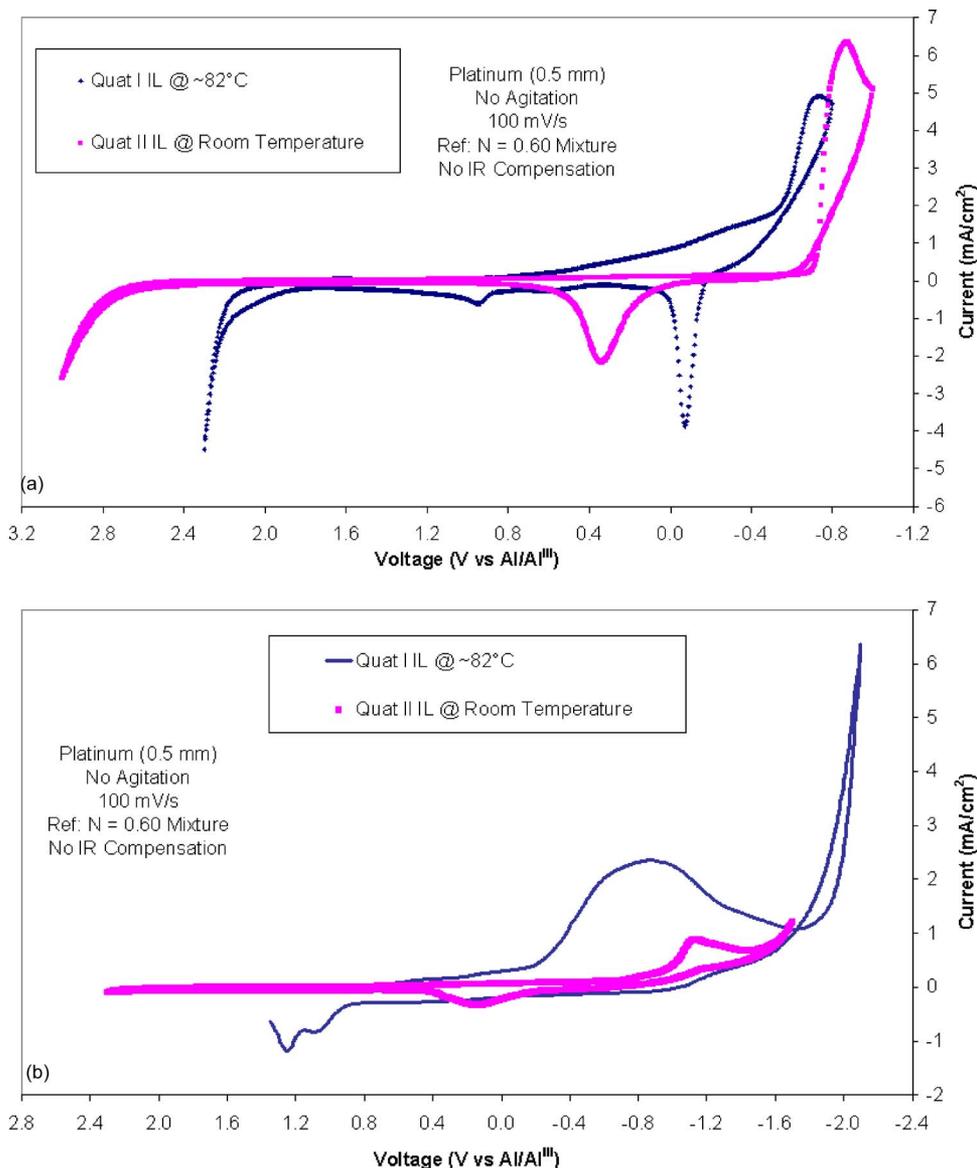


Figure 3. (Color online) (a) Electrochemical windows for acidic ILs of Quats I and II. (b) Electrochemical windows for neutral ILs of Quats I and II.

−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 IV, 1.18 g/mL and 61 mm²/s.¹⁵ When neutralized with 100% excess NaCl, the resulting IL had a T_g of −66.2°C, phase transition at −29.4°C, and melting point of 3.2°C. However, similar to Quat III, the acidic (melting point 58–62°C) and neutral (melting point 61–64°C) ILs of Quat I 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 I 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 II, 2 carbon atoms separate the oxygen from the nitrogen, reducing the positive charge on the nitrogen. The flexible ether linkage reduces the MP by making it easier for the cation to reorient and therefore maintain a fluid state.

Figure 3a shows the electrochemical windows for the acidic ILs of Quats I and II. 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 II, the oxidation of the electrolyte occurs at significantly more positive voltages, providing a much larger elec-

trochemical window. Figure 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 60–70°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 0.6.²⁷ Though the reduction of AlCl₄ thermodynamically occurs before sodium, the kinetics are typically slow, allowing for the observation of sodium reduction.

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 I and II, respectively. For Quat I, this is similar to the previously reported potential region.²⁶ The similar stability of Quats I and II in the ionic form indicates that ACN facilitates the reduction process, resulting in the reduced stability observed for I in ACN. The results using gold and tungsten substrates were similar to those on Pt for both the acidic and neutral ILs.

Figure 4 shows the conductivity vs temperature relationship for the acidic and neutral ILs of Quats I, II, and IV. Previously, we have shown that the neutralization results in reduction of the conductivity

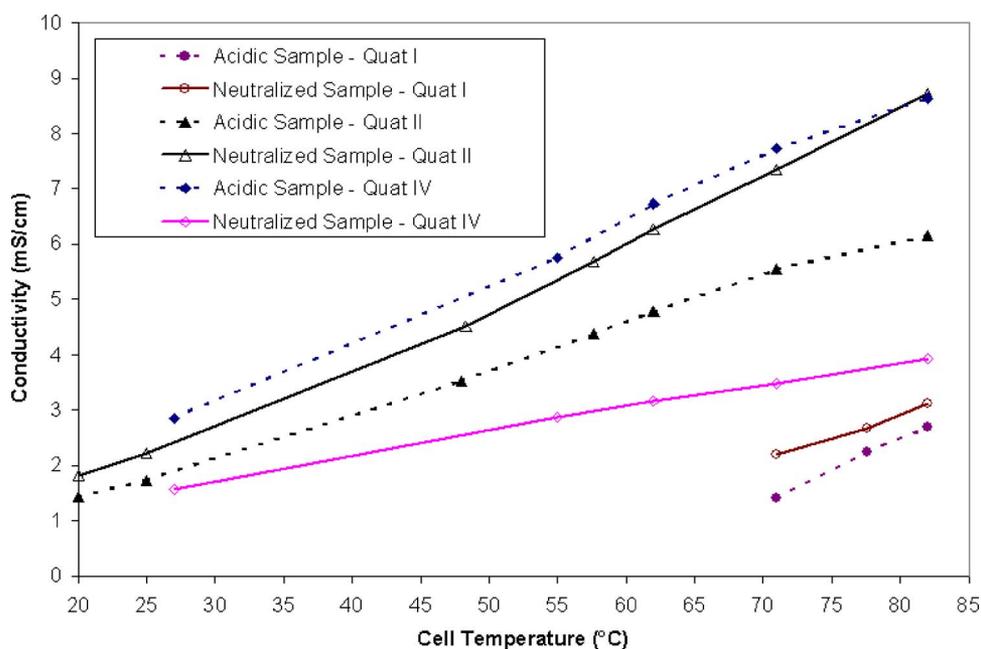


Figure 4. (Color online) Conductivity vs temperature for acidic and neutral ILs of Quats I, II, and IV.

due to conversion of the more conductive Al_2Cl_7^- ion to AlCl_4^- and the coordination between Na^+ and AlCl_4^- .²⁴ The $\sim 50\%$ drop in conductivity upon neutralization of the IL of IV is representative of the results previously observed, where although the total number of ions increased (due to Na^+), ion pairing decreased the conductivity. However, for each of the other 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 II has a lower room-temperature conductivity than the IL of IV, due to an increased viscosity, the neutral IL is about 40% more conductive than its Quat IV counterpart. At higher temperature, this gap widens further, with the neutral IL of II and acidic IL of IV having similar conductivities at 82°C. Due to its increased melting point, the Quat I 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.^{24,28} 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 Na^+ and AlCl_4^- .

Unfortunately, while the sodium ions are available for reduction, Quats I and II are reduced more easily than sodium ions. Previously, CDCl_3 was found to be an effective additive for the reduction of sodium in quaternary ammonium chloride ILs.²⁸ 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 reoxidation was observed following 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 chronoamperometry (CA). Figure 5 shows a CV curve following the addition of ~ 4.3 wt % CDCl_3 . The Coulombic efficiency for the scan was 67.4%. It is believed that the chloroform is reduced forming an SEI similar to those observed in lithium systems. The SEI film helps to protect the

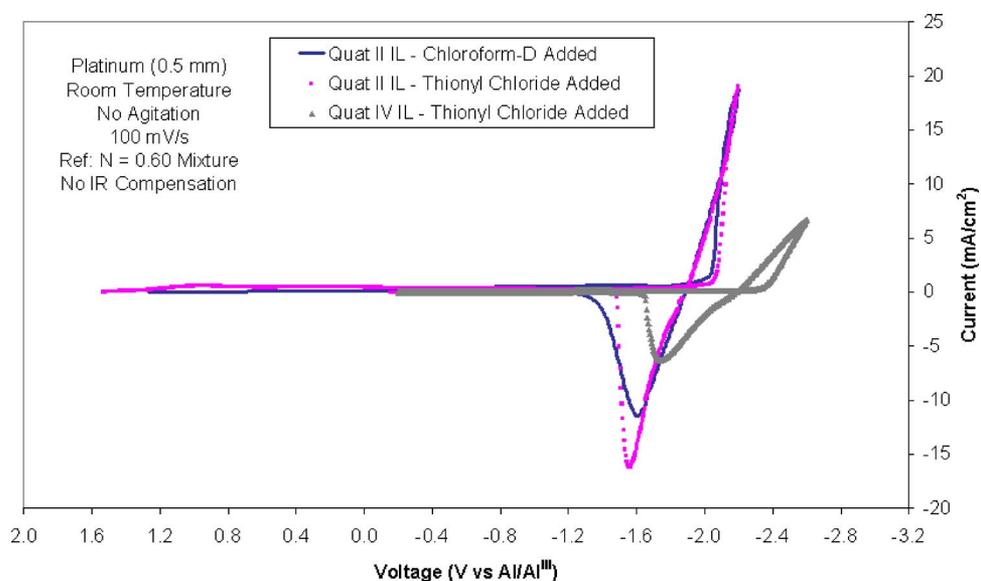


Figure 5. (Color online) CV results following the addition of CDCl_3 and/or SOCl_2 to the neutral Quats II and IV.

sodium deposited from reduction, allowing for a recovery of charge. However, the film does not completely protect the surface, resulting in a partial oxidation of the sodium surface and loss of Coulombic efficiency. This oxidation is counterbalanced by the reduction of the IL.

As sodium ions are available for reduction in the Quat II IL, the primary role of an additive is the formation of a stable SEI; therefore, 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. Previously, SOCl_2 has been demonstrated to form an SEI film in lithium systems.²⁹ Figure 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 Fig. 5. The maximum current is only about 1/3 of that for Quat II IL, though the conductivity for the Quat IV IL is 70% of the Quat II IL. In the case of the IL of IV, only the Quat and AlCl_4^- anion contribute to the conductivity until the addition of the additive.²⁴ In the neutral Quat II IL, however, a significant contribution comes from the Na^+ 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 150–170 mV is observed, though the potential for sodium reduction is shifted more than 300 mV positive in the IL of II.

The increased concentration allows for the utilization of much larger currents when performing chronopotentiometry (CE) experiments. For both CDCl_3 and SOCl_2 added, the maximum reduction current that could be sustained for 100 s was 4.07 mA/cm^2 . This is nearly 4 times the 1.13 mA/cm^2 achievable with the Quat IV IL. For SOCl_2 , CE experiments for reduction/oxidation currents of between 3 and 5 mA/cm^2 for 50–100 s resulted in efficiencies between 77.4 and 81.3%. Maximum efficiencies of $\sim 83\%$ were achieved using CA, indicating that SOCl_2 forms a more stable SEI than CDCl_3 in the IL of II.

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^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 reoxidation 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.³⁰ For the IL of II, the self-discharge rate was nearly $76 \mu\text{A/cm}^2$, or more than 8 times the value of the Quat IV IL without agitation. This value is less than the $101 \mu\text{A/cm}^2$ 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 IV the efficiency was greater than 90%.¹⁵ It is anticipated that the residual acidity of the Quat II 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.

Conclusion

Quats I and II, both 8-atom (7 carbons, 1 oxygen) ether-substituted Quats, were synthesized and investigated. In ACN, Quat

I, 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 II (-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 ($58\text{--}62^\circ\text{C}$) than the similar IL of III (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 II increased from 1.73 to 2.22 mS/cm at 25°C , while at 27°C neutralization of the similar Quat IV 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 IV. The self-discharge rate was approximately $76 \mu\text{A/cm}^2$.

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