Behavior of Oxide Containing Chloroaluminate Molten Salts

Robert A. Mantz, Jack Summers, and Robert A. Osteryoung

Air Force Research Laboratory, Fuels Branch
1790 Loop Road North
AFRL/PRSF
WPAFB OH 45433-7103

North Carolina State University
Department of Chemistry
Dabney Hall
Raleigh NC 27695

ABSTRACT

The role of the oxide and hydroxide species play in AlCl₃ / 1-ethyl-3-methylimidazolium chloride (EMIC) melts has been investigated. The oxide and hydroxide species are formed when water is introduced into the melt. Water is an ubiquitous impurity. Melts will be exposed to small amounts of water even when extreme precautions are taken. Both electrochemical and ¹⁷O NMR experiments were conducted in order to characterize the effect of oxides and hydroxides on melt properties. The presence of an aluminum hydroxide species causes the melt to behave as a neutral buffered melt. The degree of buffering increases as the hydroxide concentration increases.

INTRODUCTION

Ambient-temperature chloroaluminate ionic liquids are an important class of non-aqueous solvents; they have been used for a wide variety of chemical and electrochemical studies (1-4). In addition, they show promise as electroplating baths for industrial aluminum electroplating as well as electrolytes in high energy density batteries (5-7).

The chloroaluminate ionic liquids we are studying are comprised of mixtures of 1-ethyl-3-methylimidazolium chloride (EMIC) and aluminum chloride (AlCl₃). The two solids react over a wide range of stoichiometries to yield room-temperature molten salts (5).

Room temperature chloroaluminate molten salts are very hygroscopic and water reactive. In fact, both the AlCl₃ and the 1-ethyl-3-methylimidazolium chloride (EMIC) are hygroscopic. Because water is an ubiquitous impurity it is essential to know how water changes the melt characteristics. When a melt is exposed to water it reacts with the water to generate an aluminum oxide and/or an aluminum hydroxide species and hydrochloric acid. Several studies have been conducted in which either the oxide or the proton (hydrochloric acid) acted as an interference with the chemistry of interest (9-13).

In order to remove the complications caused by the presence of either proton or oxide several removal procedures have been developed (14-16). Proton can be removed in
two ways. The first removal method for proton is treatment of the melt with ethylaluminum sesquichloride (EtAlCl$_2$) (14). One difficulty in using ethylaluminum sesquichloride was the difficulty in adding the exact amount needed to remove all the proton. Not adding enough ethylaluminum sesquichloride leaves residual protons while adding too much leaves ethylaluminum sesquichloride in solution (15). In addition, ethylaluminum sesquichloride changes the melt composition. Its addition makes a melt more acidic while it removes proton. Proton can also be removed simply by applying high vacuum (16). The beauty of this technique is that the melt composition is not changed and nothing has to be added to the melt. This eliminates tedious titrations. One limitation of the vacuum technique is that it cannot be applied to acidic melts above $a_{\text{HCl}} = 1.3:1.0$ mole ratio. At higher acidities the vapor pressure of AlCl$_3$ over the melt increases. The application of vacuum to these melts will remove AlCl$_3$ thereby changing the melt composition (16).

Oxide can also be removed from the melts. Phosgene has been utilized to remove oxide from basic melts (10,17). In practice a basic melt is exposed to an excess of phosgene. The phosgene reacts with the oxide to generate carbon dioxide. Carbon dioxide and excess phosgene are then easily removed using vacuum.

The ability to remove proton and oxide from the melts is important because it allows species to be studied in the melts with and without these potential interferences. If the roles these two impurities play are known then the chemistry of species in the melts can be better predicted.

The study of oxide in the room temperature melts using electrochemistry has been conducted by several groups. Linga et al. found that Ti(IV) exhibited two reduction waves but only a single reoxidation in basic melts. The two waves were assigned to TiCl$_6^{2-}$ and TiOCl$_4^{2-}$ (8). Based on these results an analytical method for the determination of oxide concentration is the melts was developed (13). This study concluded that for the melts studied, the oxide concentration was generally about 2 mM. Sun et al. used NbCl$_6^{7-}$ instead of TiCl$_6^{2-}$ (10). Niobium chloride appears to react to completion with oxide added to basic melts (12). Using this probe molecule an analytical method was developed to determine oxide concentration in the melts (15).

Electrochemistry has not been the only method utilized to characterize oxide in the melts. Mass spectrometry (MS) has been used to determine the ionic make-up of the melts. Fast atom bombardment MS (FAB-MS) and secondary ion MS (SIMS) have both been utilized (18-22). These studies identified a variety of oxide and hydroxide containing melt species including: AlCl$_3$OH$^-$, Al$_2$OCl$_5$, Al$_3$Cl$_6$OH$^-$, Al$_4$Cl$_8$O$_2^-$, Al$_5$Cl$_9$O$^-$, and Al$_6$Cl$_{10}$O$_2^-$. In the basic melts they detected one oxide species, AlOCl$_2$. Zawodzinski et al conducted several $^{17}$O NMR studies of the melts (15,23,24). These studies provide great insight to the speciation of oxide and hydroxide in both acidic and basic melts. In basic melts a single peak is observed in the $^{17}$O NMR spectrum. However, the peak position is dependent on the HCl concentration. When HCl was bubbled through an oxide containing basic melt the chemical shift would move upfield (smaller ppm). Because only a single peak is observed, the exchange between oxide and hydroxide species must be rapid on the NMR timescale.

In acidic melts the $^{17}$O NMR spectrum consists of three lines at 49.7 ppm, 73.8 ppm and 91.8 ppm. The peak positions are not dependent on melt composition. The peak at 49.7 ppm was assigned to an aluminum hydroxide species while the other two peaks
were assigned to aluminum oxide species (15,23,24). This was done based upon the changes in the NMR spectrum when HCl was added to the melt. In this case the peak at 49.7 ppm grew in size while the other two peaks decreased in size at the same rate. When ethylaluminum sesquichloride, which removes proton form the melt, was added to the melt the exact opposite occurred and the peak at 49.7 ppm decreased in size.

Preliminary studies by Summers suggested that oxide present in melts acts as a neutral buffering agent (25). In the presence of oxide, neither a chloride wave nor aluminum deposition was observed electrochemically for slightly acidic melts. In studies where the melt composition is close to neutrality it is important to know if some buffering agent is present altering the melt behavior.

EXPERIMENTAL

Materials

H$_{17}$O (19% isotopic enrichment, Cambridge Isotopes) was used as received. Niobium(V)chloride (99.9+ %, Aldrich) was used without further purification.

Electrochemical Measurements

Electrochemical measurements were conducted in a nitrogen-filled dry box using a PAR EG&G 273 potentiostat, a Pentium personal computer, and Wotan, an in-house data-acquisition program. During the quantification of oxide concentration in a melt a Cypress Systems glassy carbon working electrode was used. For all other portions of the study a single 250 µm diameter tungsten working electrode was used. The reference electrode consisted of an aluminum wire in a 1.5:1.0 melt and the counter electrode was a loop of 1 mm platinum wire. The working electrode was mechanically polished with diamond suspension prior to use. Prior to the acquisition of electrochemical data the working electrode was electrochemically cleaned by cycling into the AlCl$_4^-$ oxidation wave using cyclic staircase voltammetry. Three scans were performed with a scan rate of 500 mV / sec from 1 to 3 volts versus the Al(0) / Al (III) reference (26).

Before electrochemical data were acquired using oxide containing samples, the optimum normal pulse voltammetry conditions to quantitate the AlCl$_4^-$ and Cl$^-$ concentrations were determined (Table I). In addition, square wave voltammetry was utilized with Nb(V)Cl to quantitate the oxide level in a stock melt.

Once the electrochemical data had been acquired it was analyzed using FSQPLT, an in-house data-analysis program. The analysis for the square wave voltammograms consisted of measuring the peak net current. The analysis of the normal pulse data consisted of an applied 15 point moving average smoothing routine followed by a three line graphical analysis to determine the limiting current.
$^{12}$O NMR Experiments

10 mm nuclear magnetic resonance (NMR) tubes were prepared by soaking in 80% HNO$_3$, rinsing with deionized water, soaking in a solution of the tetrasodium salt of EDTA for 12 hours, and again rinsing with deionized water. NMR samples were prepared by combining the stock solutions to prepare a melt with a known acidity and oxide concentration. The resulting melt was then stirred for several hours. After sufficient time had elapsed the melt was transferred into a 9 inch long 10 mm Wilmad NMR tube that had been constricted at 8 inches. A tip-off manifold was placed on the tube, and the sealed assembly was removed from the dry box and flame sealed under vacuum ($\approx 1 \times 10^{-2}$ torr).

$^{17}$O NMR experiments were acquired with the probe temperature set to 85 °C, and each sample was allowed to equilibrate for at least 10 minute prior to spectral acquisition. $^{17}$O NMR spectra consisted of 32769 scans of 4096 points with a sweep width of 250 ppm, and a relaxation delay of 0.5 seconds. An exponential multiplication with a line broadening factor of 40 Hz was applied to the acquired free induction decay (FID) prior to Fourier transformation. The 90° pulse width was calibrated using D$_2$O containing natural abundance $^{17}$O and set to 22 msec throughout the experiments. The chemical shift was externally referenced to D$_2$O containing natural abundance $^{17}$O (0 ppm) whose spectrum was obtained using identical acquisition and processing parameters.

Sample Preparation

In order to minimize error due to the uncertainty of melt composition a single 315 g 0.988:1.0 melt was prepared. The oxide and proton impurities were removed from the melt using phosgene and vacuum as described previously. From this melt, three stock solutions were prepared (Figure I). The first stock solution was simply 175 g of the initial melt. This melt should be oxide and proton free and have a mole ratio of 0.988:1.0. This corresponds to a Cl' concentration of 56.2 mM.

The second stock solution was obtained by titrating 53 g of the first solution using AlCl$_3$ and monitoring the Cl' and Al$_2$Cl$_7^-$ concentrations using electrochemistry (Figure II). The titration of this melt using AlCl$_3$ served three purposes. First, it allowed testing of the experimental parameters used to ensure that the response of the experiment was linear with respect to Cl' and Al$_2$Cl$_7^-$ concentrations. Second, the exact acidity of the melt was now known because the titration goes through a zero point at neutrality. Neutrality is a precise melt condition and any AlCl$_3$ added after this point simply increases the Al$_2$Cl$_7^-$ concentration. Thirdly, the titration allowed the exact determination of the original melt composition. Based on this experiment the initial melt composition was determined to be 0.990:1.0 rather than 0.988:1.0. This seemingly minor difference has consequences because a 0.988:1.0 melt has a Cl' concentration of 56.2 mM while the Cl' concentration of a 0.990:1.0 melt is 44.5 mM. This is approximately a 20% difference. The melt composition of stock solution two is 1.090:1.0 which corresponds to a Al$_2$Cl$_7^-$ concentration of 400 mM.

The third stock solution is the stock solution that contained the oxide. This melt was prepared by taking 88 g of the original melt and adding 203 ml of H$_2^{17}$O (19%
isotopic enrichment). The resultant melt should contain 145 mM oxide. The resulting crust on the melt was allowed to dissolve while the solution was stirred. After the melt had stirred 48 hours the melt was deprotonated using vacuum as described above. After deprotonation procedure the melt was returned to the dry box and a 200 ml aliquot was added to a 0.9:1.0 melt containing 249 mM of Nb(V)Cl. Nb(V)Cl has been shown to react quantitatively with oxide in the melts and has been suggested as a means to determine oxide concentrations in basic melts (5). A problem that arose was the oxide added in each aliquot took days to fully react with the niobium. An explanation for the discrepancy between these results and those just mentioned is that Hussey and coworkers added oxide as lithium carbonate to a melt that already contained Nb(V)Cl. What they measured was the ability of niobium to compete with the melt in order to react with the free oxide. In this case the niobium must abstract the oxide from the melt species. It seems this abstraction process is much slower. Titrating the oxide using Nb(V)Cl resulted in the determination of the oxide concentration as 121 mM. The difference in the oxide concentration from that expected from the addition of the H2O, 146 mM, and that from the titration, 121 mM, is not entirely surprising because of the difficulty of the niobium titration. However the niobium titration is reasonably close to the predicted value. The oxide containing stock solution was taken to have an oxide concentration of 146 mM.

Four series of samples were prepared from the three stock solutions. Within each set of samples the oxide concentration is held constant while the melt composition is incremented from basic to acidic. The four oxide concentrations studied were: 0 mM, 25 mM, 50 mM and 75 mM. In the case of the 75 mM set, larger samples were prepared to allow a portion of the sample to be examined using 170 NMR.

RESULTS AND DISCUSSION

Electrochemical Results

The electrochemical window available in AlCl3/EMIC melts is strongly dependent on melt composition. When the mole ratio of AlCl3:EMIC is greater than one, the melt is acidic and aluminum deposition is possible. When the mole ratio is less than one the chloride species is present and its oxidation is observable. Both the oxidation of chloride and the reduction of Al(III) to Al(0) are absent in neutral melts and alkali metal chloride neutral buffered melts. The presence of an aluminum oxychloride or an aluminum hydroxychloride species also seems to buffer the melts (Figure III). This study evaluates which species, aluminum oxide or aluminum hydroxide is buffering the melt.

Each sample was examined using normal pulse voltammetry. Samples that were close to neutrality were examined for both chloride oxidation and aluminum deposition. Under no conditions were both the chloride oxidation and the aluminum deposition present in the same sample. The melt composition was calculated from the compositions of the stock solutions. Two details were obvious during the preliminary analysis of the data. First, as the concentration of oxide and hydroxide species in the melt was increased the buffering capability of the melt increased. This manifests itself as an increase in the amount of aluminum chloride that must be added to the melt before an aluminum deposition is observed.
Second, the plots were offset from zero on the X axis. The melt composition predicted by the compositions of the stock melts does not agree with experiment. In all cases the samples were more basic than the calculated value. Something caused the X axis to shift. This was very surprising considering the various calibrations that were performed on the stock solutions. The offset is most likely due to one of two possibilities. The first possibility is simply that there was an error in preparing the melt and that the melt composition differed from that used to calculate the expected melt composition. This is not entirely unlikely due to the sensitivity of these measurements. For example, in the preparation of a 25 g melt a weighing error of 0.29 g results in a 100 mM change in either Cl\(^-\) or Al\(_2\)Cl\(_7\) concentration. Given that the balance is in a dry box, static electricity as well as changes in box pressure are a problem. The second possibility is that not all the aluminum hydroxychloride species were removed using vacuum. For every aluminum hydroxychloride there is an extra chloride in solution that was assumed to be removed by vacuum as HCl.

In order to determine if the oxide containing melt was causing the X axis displacement, the offset on the X axis was determined for oxide concentration in each series of melts (Table II). The least squared fit of this data is 0.336 mM of Al\(_2\)Cl\(_7\) for every 1 mM of oxide in the melt. The oxide stock solution contains 146 mM oxide and had a calculated chloride concentration of 57 mM. Calculating the chloride concentration from the slope of the least squared fit results in an actual chloride concentration of 106 mM. In order for this effect to have been caused by residual aluminum hydroxychloride species roughly 33% of the oxide species in the melt would have to be hydroxide.

Using this new chloride concentration for the oxide stock solution Figure IV can be plotted with the X axis corrected to within a few mM. Using a series of these plots with different oxide concentrations the buffering capacity of the oxide containing melts and how it varies with oxide concentration can be determined. The buffering capacity vs. the oxide concentration is contained in Table III. The slope of the linear least squared fit to the data is 0.2. This means to buffer the melt against 1 millimole of the Lewis acid AlCl\(_3\) takes 5 millimoles of oxide/hydroxide in the melt.

\(^{17}\)O NMR Results

\(^{17}\)O NMR provides unique insight about oxide speciation in the melts. The NMR data coupled with the electrochemical results was able to offer a reasonable explanation for the limited buffering capacity of the oxide containing melts. As mentioned previously the NMR samples were portions of the same 75 mM oxide containing samples which were examined electrochemically. This was done so the samples could be directly compared without having to correct for oxide concentration changes or melt composition differences. Ten sample spectra were obtained. These samples varied in melt composition from 93 mM Al\(_2\)Cl\(_7\) to 24 mM Cl\(^-\) using the corrected stock solution composition (Figures V to VIII). Each spectrum was run under identical conditions and the scaling of the Y axis has not been modified. This allows the intensities of peaks to be directly compared.

In the basic melts a single peak is observed. This is in agreement with Zawodzinski et al (15,23,24). In the acidic melts three lines are observed. The peaks have the intensities expected for a near neutral acidic melt (15). Although the melt had been placed under vacuum to remove all proton and aluminum hydroxychloride species the \(^{17}\)O NMR
spectrum shows the presence of a substantial amount of aluminum hydroxychloride. Two equilibria have been proposed for the removal of proton from acidic melts (16):

\[
\text{Al}_2\text{OCl}_4^- + \text{HCl} + \text{AlCl}_4^- \leftrightarrow \text{Al}_2\text{Cl}_6\text{OH}^- + \text{Al}_2\text{Cl}_7^- \tag{1}
\]

\[
\text{Al}_2\text{OCl}_5^- + \text{HCl} \leftrightarrow \text{Al}_2\text{Cl}_6\text{OH}^- \tag{2}
\]

for basic melts. The equilibrium constants have not been measured for either reaction. At high oxide concentrations it may not be possible to remove all hydroxide from the melts.

As the \(\text{Al}_2\text{Cl}_7^-\) concentration is decreased the \(^{17}\text{O}\) NMR peak at 87 ppm becomes smaller. At the same time the peaks associated with the other oxide species and the hydroxide species remain essentially constant in size. The downfield peak disappears at the same time the aluminum deposition current goes to zero. After the 87 ppm peak has disappeared, further reduction in the \(\text{Al}_2\text{Cl}_7^-\) concentration causes both the 71 ppm and the 45 ppm peaks to decrease in size. As the melt becomes basic the remaining two peaks broaden until they are replaced by the single peak associated with basic melts. When the peak associated with basic melts appears, the chloride oxidation becomes possible.

**CONCLUSIONS**

It appears that the buffering of room temperature molten salts with oxide is not actually due to an aluminum oxychloride species but to an aluminum hydroxychloride species. The parallel electrochemical and NMR experiments show that aluminum is not deposited until the aluminum oxide species associated with the 87 ppm peak is present. Aluminum is not deposited when only the hydroxide peak at 45 ppm or the oxide species associated with the 71 ppm peak are present. The buffering capacity measured using normal pulse voltammetry is incorrect because the buffering capacity was based upon the total concentration of oxide and hydroxide species present. It appears the both the aluminum oxide species associated with the peak at 71 ppm and the aluminum hydroxide species associated the peak at 45 ppm are not electroactive. Zawodzinski's results indicate the peak at 87 ppm should be present in acidic melts (15). A rough estimate of the area under the \(^{17}\text{O}\) NMR peak at 71 ppm is approximately 1/5 of the total. This would explain the buffering capacity slope of 1/5 from the electrochemical experiments. It appears that the aluminum hydroxide species somehow interferes with the formation of the electroactive aluminum oxide species until enough aluminum chloride has been added to exceed the concentration of the aluminum hydroxide species. This result is qualitative and further studies are necessary to test this premise.

The NMR experiments also offer an explanation for the offset in melt composition experienced with the electrochemical experiments. The inability to remove all the aluminum hydroxychloride as HCl leads to a melt that has more chloride than would be expected. The additional chloride causes the melt to be more basic.

**ACKNOWLEDGMENT**
This work was supported in part by the Air Force Office of Scientific Research.

Table I. Normal pulse voltammetry parameters for the detection of oxidation of chloride and deposition of aluminum used throughout the study.

| Normal Pulse Experimental Parameters | Parameters to Detect Cl\(^-\) | Parameters to Detect Al\(_2\)Cl\(_7^-\) |
|-------------------------------------|-----------------------------|-----------------------------|
| Initial Potential 0.50 V            | Initial Potential 0.25 V    |                                            |
| Final Potential 2.30 V              | Final Potential -1.10 V     |                                            |
| Step Height 10 mV                   | Step Height 10 mV           |                                            |
| Potential Width 1 msec              | Potential Width 8 msec      |                                            |
| Time Between Pulses 3 seconds       | Time between Pulses 15 seconds |                                    |
| Number of Scans 1                   | Number of Scans 1           |                                            |
| Temperature 25 °C                   | Temperature 25 °C           |                                            |

Table II. The displacement of Al\(_2\)Cl\(_7^-\) concentration and the oxide concentration for each set of samples.

| Displacement of Al\(_2\)Cl\(_7^-\) Concentration (mM) | Oxide Concentration for Set of Samples (mM) |
|-------------------------------------------------------|---------------------------------------------|
| 5                                                     | 0                                           |
| 13                                                    | 25                                          |
| 22                                                    | 50                                          |
| 30                                                    | 75                                          |

Table III. Melt oxide concentration and melt buffering capacity. This is an indicator of how much oxide is needed to buffer against a given concentration of Lewis acid or base. For example, a melt that contains 80 mM oxide can have 25 mM AlCl\(_3\) added before the melt is no longer buffered.

| Oxide Concentration (mM) | Melt Buffering (mM) |
|--------------------------|---------------------|
| 75                       | 25.0                |
| 50                       | 19.4                |
| 25                       | 12.6                |
| 0                        | 10.7                |

REFERENCES

1. R. J. Gale and R. A. Osteryoung, in *Molten Salt Techniques*, Vol 1, D. G. Lovering and R. J. Gale, Editors, p. 55, Plenum: New York (1983).

2. C. L. Hussey, in *Advances in Molten Salt Chemistry*, Vol 5, G. Mamantov, Editor,
3. R. A. Osteryoung, in Molten Salt Techniques, Vol 202, G. Mamantov and R. Marassi, Editors, p. 329, NATO ASI Series C; Reidel: Dordrecht, The Netherlands (1986).

4. C. L. Hussey, Pure Appl. Chem., 60, 1763 (1988).

5. J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, Inorg. Chem., 21, 1263 (1982).

6. A. A. Fannin, Jr., D. A. Floreani, L. A. King, J. S. Sanders, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes and J. L. Williams, J. Phys. Chem., 88, 2614 (1984).

7. D. Floreani, D. Stech, J. Wilkes, J. Williams, B. Piersma, L. King and R. Vaughn, in Proc. 30th Power Sources Symp., p. 84, The Electrochemical Society: Pennington NJ (1982).

8. H. Linga, Z. Stojek, and R. A. Osteryoung, J. Am. Chem. Soc., 103, 3754 (1981).

9. Z. J. Karpinski, C. Nanjundiah, and R. A. Osteryoung, Inorg. Chem., 23, 3358 (1984).

10. I. W. Sun, E. H. Ward, and C. L. Hussey, Inorg. Chem., 26, 4309 (1987).

11. T. B. Scheffler, C. L. Hussey, K. R. Seddon, C. M. Kear, and P. D. Armitage, Inorg. Chem., 22, 2099 (1983).

12. I. W. Sun and C. L. Hussey, Inorg. Chem., 28, 2731 (1989).

13. Z. Stojek, H. Linga, and R. A. Osteryoung, J. Electroanal. Chem., 119, 365 (1981).

14. T. A. Zawodzinski, Jr., R. T. Carlin, and R. A. Osteryoung, Anal. Chem., 59, 2639 (1987).

15. T. A. Zawodzinski, Jr. and R. A. Osteryoung, Inorg. Chem., 29, 2842 (1990).

16. M. A. Noël, P. C. Trulove and R. A. Osteryoung, Anal. Chem., 63, 2892 (1991).

17. A. K. Abdul-Sada, A. G. Avent, M. J. Parkington, T. A. Ryan, K. R. Seddon, and T. Welton, J. Chem. Soc., Chem. Commun., 1643 (1987).

18. B. L. Ackerman, A. Tsarbopoulos, and J. Allison, Anal. Chem., 57, 1766 (1985).

19. G. Franzen, B. P. Gilbert, G. Pelzer, and E. DePauw, Org. Mass Spectrom., 21, 443 (1986).

20. S. P. Wicelinski, R. J. Gale, K. M. Pamidimukkala, and R A. Laine, Anal. Chem., 60, 2228 (1988).
21. A. K. Abdul-Sada, A. M. Greenway, K. R. Seddon, and T. Welton, Org. Mass Spectrom., 24, 917 (1989).

22. A. K. Abdul-Sada, A. M. Greenway, K. R. Seddon, and T. Welton, Org. Mass Spectrom., 28, 759 (1993).

23. T. A. Zawodzinski, Jr., and R. A. Osteryoung, Inorg. Chem., 26, 2920 (1987).

24. T. A. Zawodzinski, Jr., and R. A. Osteryoung, in Proceedings of the Joint International Symposium on Molten Salts/1987, PV 87-7, p. 406, The Electrochemical Society Proceedings Series, Pennington, NJ (1987).

25. J. Summers, R. A. Osteryoung, North Carolina State University, unpublished results.

26. R. T. Carlin, W. Crawford, and M. Bersch, J. Electrochem. Soc., 139, 2720 (1992).

Figure I. Experimental flow chart for the generation of proton free melts with known composition and oxide concentration.
Figure II. Titration of initial melt using AlCl₃. AlCl₃ is added and either the Cl⁻ oxidation (●), or the aluminum deposition (■), is monitored. In the basic melt compositions, Cl⁻ oxidation is monitored. In acidic melt compositions, the aluminum deposition is monitored. The break point is a neutral melt. Lines are the linear least squared fit to the data points.

Figure III. Electrochemical window present in oxide buffered melts. 250 μm diameter tungsten electrode with Al(0) / Al(III) in a 1.5:1.0 melt reference electrode.
Figure IV. Observed current obtained using normal pulse voltammograms and a 250 μm diameter tungsten electrode vs. $\text{Al}_2\text{Cl}_7^-$ concentration in a series of melts with a 75 mM concentration of oxide. $\text{Al}_2\text{Cl}_7^-$ concentration has been corrected to remove X axis offset. Negative currents correspond to the oxidation of chloride while positive currents correspond to the deposition of aluminum. Negative $\text{Al}_2\text{Cl}_7^-$ concentrations correspond to $\text{Cl}^-$ concentration. Lines are the linear least square fit to that portion of the data.

Figure V. $^{17}\text{O}$ NMR spectrum of melt containing 75 mM oxide at 85 °C. This sample contained $\text{Al}_2\text{Cl}_7^-$ using the corrected stock solution compositions. The portion of the sample which was characterized using normal pulse voltammetry had a current of 10.85 μA for aluminum deposition.
Figure VI. $^{17}$O NMR spectrum of melt containing 75 mM oxide at 85 °C. This sample contained 64 mM Al$_2$Cl$_7^{2-}$ using the corrected stock solution compositions. The portion of the sample which was characterized using normal pulse voltammetry had a current of 5.79 μA for aluminum deposition.

Figure VII. $^{17}$O NMR spectrum of melt containing 75 mM oxide at 85 °C. This sample contained 14 mM Al$_2$Cl$_7^{2-}$ using the corrected stock solution compositions. The portion of the sample which was characterized using normal pulse voltammetry had a current of 0 μA.

Figure VIII. $^{17}$O NMR spectrum of melt containing 75 mM oxide at 85 °C. This sample contained 24 mM Cl$^{-}$ using the corrected stock solution compositions. The portion of the sample which was characterized using normal pulse voltammetry had a current of 16.38 μA for chloride oxidation.