PROSPECTS FOR ALKYL PYRIDINIUM ALUMINUM CHLORIDE MELTS

C.D. Desjardins, R.S. Salter, T.G. Cadger
New Brunswick Research & Productivity Council (RPC)
Fredericton, N.B. Canada E3B 5H1

and

E.J. Casey
Defence Research Establishment Ottawa (DREO)
Shirley Bay, Ottawa, Ontario

ABSTRACT

N-butyl pyridinium chloride: aluminum chloride (BPC:AC) melt mixtures have been synthesized under rigorously pure and dry conditions. The phase diagram and preliminary conductivity data are presented. Purified aluminum chloride, AlCl₃, has been found to be non-stoichiometric, that is, chloride deficient. In acidic melts (e.g. mole fraction of AlCl₃ > 0.5), the metals Li, Mg, In and Al are active; Pt, Mo, C and Zr are passive; and Cu, Ag and Ti are transitional. Less overall activity occurs in neutral (0.50 mole fraction AlCl₃) and basic (<0.5) melts. Preliminary electrochemical studies on Li, Mo and Cu in the 0.67 mole fraction melt at various temperatures permit some understanding of the different mechanisms operable. Suggestions for further fundamental investigations and prospects of these melts as battery electrolytes are discussed.

INTRODUCTION

The recent preparations of molten salts which are liquids at room temperature and below has led to speculation about their potential uses as electrolytes in electrochemical cells whether for batteries, electro-metallurgy or surface preparation. These melt systems (1), in particular, the alkyl pyridinium chloride-aluminum chloride
system developed by King et al (2) and Osteryoung et al (3) and the alkyl imidazolium-aluminum chloride system developed by Wilkes et al (4) have advantages over conventional electrolytes and/or molten salts in that, 1) they can exist as liquids to below -50°C, 2) they are non-aqueous media, 3) they exhibit better conductivity relative to aprotic electrolyte systems and 4) they do not necessarily require solute material. However, if their suitability for use with active metal anode materials is required, close attention must be paid to both purity and details of preparation.

Many electrochemical investigations at several laboratories have been completed on molten salts liquid at room temperature since first reported by Hurley and Weir (5) in 1951. For example, Suchentrunk (6) has shown that aluminum can be plated on nickel Electro-deposited aluminum has also been observed in pre-electrolysis cells for purifying melts (7); and anodic dissolution of aluminum is possible with 100% current efficiency (2). The results obtained with aluminum as well as other electrochemical investigations (8, 9) have shown the "potential" usefulness of melts as electrolytes in electrochemical cells. In a specific instance, an alkyl pyridinium-aluminum chloride melt showed suitability as a battery electrolyte (10, 11).

It has been the focus of this investigation to prepare pure, anhydrous n-butyl pyridinium chloride-aluminum chloride melts, to assess the relationship of composition and temperature and to examine the thermodynamics and kinetics of redox reactions which can occur on a variety of metals. These efforts will ultimately uncover new phenomena which could possibly be exploited in metallurgy, batteries or catalysis.

**EXPERIMENTAL METHODS**

General. - All phases of the preparation and purification of melts and melt materials were carried out, wherever possible, under the argon atmosphere of a Vacuum Atmosphere dry box equipped with a Model He-493 Dri Train (RPC). The dri box atmosphere was further purified by an additional recirculating chamber loaded with pre-treated molecular sieve and activated carbon. The atmosphere was periodically checked with a cracked light bulb which generally operated for at least 30 days under continuous use. Material
handling outside of the dry box for transfers and other procedures such as recrystallizations were carried out on a glass vacuum line with the appropriate accessories. The electrochemical measurements (DREO), in large part, were carried out under conditions similar to that above but less rigorous with respect to the removal of oxygen and/or moisture.

A Varian ESR spectrometer was used to determine the presence of free radicals. A Model 31YSi Conductivity Bridge and a micro-cell (K = 1.0) were used for conductivity studies. Cyclic voltammograms were obtained using a PAR 173 potentiostat/galvanostat and PAR 175 universal programmer. Open circuit potentials were measured with an electrometer (having an impedance of $\sim 10^{14}$ ohms). Other potentials, currents, etc., were measured with a Fluke digital multimeter (Model 8010A).

Preparation of AlCl$_3$. - AlCl$_3$ (Alfa Ventron) was sublimed by a modified method of Seegmiller et al (12). 20g AlCl$_3$ was placed in a sublimation apparatus (designed and constructed in-house) containing 1g NaCl and 4-5 1/4" pieces of aluminum. The apparatus was then removed from the dry box and heated to 220-230 °C under an HCl gas flow of approximately 1 ml/min. Translucent to white crystalline material was collected on the cool areas of the apparatus. After $\sim$5h, the apparatus was sealed, cooled and residual HCl gas was removed under vacuum. The crystals were removed from the apparatus in the dry box, crushed and stored in glass vials. The material was analyzed for Cl and Al and consistently gave a ratio of Al to Cl of 2.8 to 2.9 and less than 1% impurity (e.g., oxide material).

Preparation of BPC. - N-butyl pyridinium chloride (BPC) was synthesized by condensing, in a typical experiment, 324 ml of pyridine (Burdick and Jackson) and 418 ml of n-butyl chloride (Aldrich, distilled before use) as outlined by Osteryoung et al (3). The reagents were refluxed in a standard R.B. flask in the dark for $\sim$2d. The red oil product formed in the reaction crystallized on cooling. The crystals were filtered, recrystallized from acetonitrile, MeCN, and dried under vacuum. The crystals were further purified by recrystallization in a vacuum sealed filtering apparatus using specially purified and dried MeCN. The preparation and purification of dry MeCN has been reported elsewhere (13, 14). These procedures yielded highly crystalline,
pure BPC, the purity of which was verified by elemental analysis (Theoretical: C = 63.01, H = 8.16, N = 8.16, Cl = 20.66%; Found: C = 62.84, H = 8.33, N = 8.13; Cl = 20.88). The crystalline BPC prepared as above was ground, pumped under vacuum overnight and stored in glass vials.

Preparation of Melts. - AlCl₃:BPC melts (e.g., 2:1, 3:2, 1:1, 2:3, 1:2) were prepared by placing the appropriate molar quantities of each melt component in separate chambers of a melt apparatus (constructed in-house). The loaded apparatus was removed from the dri box and the lower portion (containing BPC) was immersed in liquid N₂. The valve separating the two melt components was then opened allowing small portions of AlCl₃ to contact BPC. The lower portion was then thermally cycled to room temperature at various intervals until all the AlCl₃ had been added. In some cases, the melts had to be cycled to 75-90°C for complete reaction to take place. Clear colourless liquids were obtained except for the acid rich melts (e.g., 2:1, AlCl₃:BPC) which always showed some discoloration.

The melts were characterized by proton nmr, laser Raman spectra and 27 Al nmr and no significant features were found using these methods beyond those reported by Wilkes et al. (15), Gray et al. (16), and Osteryoung et al. (17).

The 2:3 and 1:2 AlCl₃:BPC melts exist in two phases at R.T. Preliminary analytical data would suggest that the liquid phases are 1:1.2-1.3 AlCl₃:BPC melts.

RESULTS AND DISCUSSION

Melt Phenomena. - Analytical evidence has established that the AlCl₃ is chlorine-deficient, the Cl/Al ratio being typically 2.8-2.9. Both a powdery and crystalline material are observed as sublimation products. Attempts to relate these results to a possible second phase structure of AlCl₃ remain inconclusive. For example, x-ray diffraction and 27 Al NMR show only marginal differences, if any. The observation that a yellowish-amber tinge increased in the melt with increasing mole fraction of AlCl₃ may also be related to chlorine deficiency. Although it has been reported that the yellow discoloration can be eliminated using pre-electrolysis procedures (7), it should also be noted that the discoloration reappears in several weeks. Obviously, further study in this area is required.
The melting and freezing points were determined for each melt mixture to yield the phase diagram in Figure 1. The figure shows an A-B compound at 0.50 mole fraction (1:1 AlCl₃: BPC), as others have reported (2). However, not only supercooling to as much as 60°C below the mp, but also metastability of the super-cooled melt for protracted periods of time were observed. For example, the .67 AlCl₃ mole fraction melt (2:1 AlCl₃ : BPC) was used as an electrolyte for anodic oxidations and cathodic reductions while supercooled by 20°C for up to two weeks without freezing. The ability of these pure, chlorine deficient melts to supercool and remain so while being "seeded" by structural changes occurring at the electrode-electrolyte interface, needs theoretical attention. We suggest that, as in the molten polysulfide system which also shows supercooling phenomena (18), there may exist repetitive molecular structures which could promote meta-stable chains. Chain structures have been inferred from nmr studies of nitrogen heterocycles by Quereshi et al. (19) and more recently for these melts by Wilkes et al. (15). In the case of the melts, the chain structures have been postulated to be polymers of anion-cation complexes. The specific complexes are dependent on the AlCl₃ concentration. The free energy of formation of these chains need not be large to effect considerable meta-stability and it is possible that the non-stoichiometry in the AlCl₃ leads to chain-breaking.

Cyclic voltammetry shows generally that the melts are stable over a potential range of about 2.0V. This range has been observed on Al, Ag, Ti and Li in our case and on glassy carbon and W by other workers (7). For example, the cyclic voltammogram in a 1:1 AlCl₃ : BPC melt taken on Ti with a Al reference (see Figure 2) shows the major reduction wave at about -0.8V and the major oxidation at about +1.2V. The oxidation wave occurs between +0.8 and +1.2V with different metal surfaces. Figure 2 also demonstrates X, Y and Z oxidation processes by Ti, but no corresponding reduction activity. By contrast, as will be seen later, the X, Y, Z oxidation processes are not clear during anodic sweeps on Mo but can be separated on reduction. The major reduction at about -750mV versus an Al reference at R.T. on Li, Ti, and Ag produced a blue-colored transient product which reacts further and disappears. The blue product has an
absorption peak at 610 nm and was spin-active, as demonstrated by its 18-line ESR spectrum (see Figure 3). We have tentatively assigned the spin-active product to be the butyl pyridinium radical formed by reduction of the butyl pyridinium cation, BP⁺. The disappearance of the blue product is probably due to radical dimerization or formation of a dihydropyridine. Naarova et al. (20) have also observed blue colours during electrochemical reduction of a series of alkyl pyridinium ions. However, although they were unable to identify the main one-electron reduction products, they were able to detect and characterize a secondary dimeric radical product.

Preliminary conductivity measurements of the BPC:AlCl₃ melts gave values ranging from 3.3 x 10⁻³ (ohm.cm⁻¹)⁻¹ (AlCl₃-BPC 2:3 melt) to a high of 8.0 x 10⁻³ (ohm.cm⁻¹)⁻¹ for the 2:1 AlCl₃-BPC melt. These results are consistent with those of King et al. (2) where a specific conductivity of 8.9 x 10⁻³ (ohm.cm⁻¹)⁻¹ was obtained for the 2:1 AlCl₃-BPC melt. These values are comparable to those obtained for nonaqueous aprotic battery electrolyte systems.

Electromotive Series - Silver and copper metal electrodes show a potential difference of Ag positive to Cu by 30±2mV. Both show small anodic and cathodic over-potentials and are suitable as reference electrodes, although the Ag electrode is preferred. In preliminary work, Al was selected as the stable reference electrode since its activity in the melts is expected to be fixed. However, the Al potential against both Cu and Ag was found to drift slowly for several hours or days at room temperature. The drift may be due to slow dissolution of an oxide film on Al. Ti showed similar but more irreproducible open-circuit potential drift. Measurements of open-circuit voltages of several metals taken on a multi-electrode cell and on individual M/Ag cells yield a preliminary electromotive series (see Figure 4) for M/M⁺ in the 2:1 melt at 25°C. For example, the Li/Ag couple gave a potential close to the theoretical value given in redox tables, \[ \text{Li} + \text{AgCl} = \text{LiCl} + \text{Ag} \]; \( E = 2.70 \text{V} \).

Metal Dissolution and Displacement. - Of the group of metals studied in the acidic 2:1 AlCl₃-BPC melt, the alkali metals are easily corroded in the order Li>Na>K. For example, Na is destroyed in a few minutes, Li and Ca passivate, and K appears to passivate. A 0.5mm Li foil
reacts immediately on contact with the 2:1 melt (turns black). Mg tarnished after a few hours and appears to be protected by a loose reaction product. Al reacts slowly, showing tarnish after a few days. Other metals studied showed relatively no signs of corrosion. In fact, Mo appeared to be cleaned of darkening air-formed oxide by the melt; and Ti likewise at elevated temperatures, ~60°C. Generally, the reaction initiation period may be days. Pt and C showed no evidence of reaction.

By contrast with behavior in the 2:1 AlCl₃-BPC melt, Li is stable in the 1:1 melt, even at 60°C, over a period of three months. Li, however, does react with the liquid phase of the 2:3 AlCl₃-BPC melt to give the blue butyl pyridinium radical.

In a Al-Cu cell, a powder Cu deposition on the Al was observed. In a Ti-Cu cell, Cu deposition could be observed after stripping the protective oxide coating. Copper powder could be made by electrochemical reduction of Cu⁺² dissolved in a 2:1 AlCl₃-BPC melt.

As in aqueous systems all the metals examined showed anodic passivation at current densities or anodic potentials higher than some critical value. Electrochemical Studies.  

(a) Active metals: Li, Mg, In, Al.

The critical current density for anodic oxidation of pure Li foil at R.T. in a 2:1 AlCl₃-BPC melt was found to be 10 mA/cm² and much less, about 2 mA/cm² in a supercooled 1:1 melt (see Figure 5). Although LiCl is quite soluble to 0.1 mole fraction LiCl (~1M; a LiCl/BPC/AlCl₃ ratio of 1:1:2), it is probably the ratio of dissolution of the LiCl formed by anodic reaction which determines the critical current density. On the other hand, the corrosion reaction which proceeds in parallel with the anodic reaction probably aids the removal of reaction product, baring fresh Li surface for reaction. Independent measurements of the rates of these processes are needed.

The reversibility of the system, with respect to reduction of the reaction product LiCl to Li while still on the surface or nearby in solution, remains suspect although the reversibility of one or more species in solution is indicated. For example, in Figure 5, it has been observed that the potential remains within ~200mV of the open circuit potential for at least ten minutes if the current density during oxidation/reduction steps does not exceed 4 mA/cm². Obviously, the corrosion
reaction militates against the alkali metals (Li, Na, K) being a dependable, rechargeable anode in the 2:1 electrolyte. As in the Li/organic-electrolyte systems, a non-porous, adherent inhibiting corrosion-reaction product may be necessary.

The highly functional Mg alloy, Mg AZ61A (6% Al, 1% Zn, high purity) supports current densities of up to 5 mA/cm² at 25°C in the 2:1 AlCl₃-BPC melt but corrodes slowly. It may redeposit under special conditions.

(b) Passive metals: Pt, C, Mo.

Oxidation and reduction can be performed on passive metals in these melts. Osteryoung et al (21, 22) have recently reported work on soluble organic and inorganic redox systems, and Koch et al (7) on other organic systems.

In a cell containing freshly prepared 2:1 AlCl₃:BPC melt, Pt, C and Mo were positive 0.86, 0.82 and 0.31 initially against an Ag reference. Pt and C were steady while Mo was fluctuating and climbing. After aging the highest potential was observed for Mo at 1090 ±5mV.

Pt and Mo metals in a 2:1 AlCl₃-BPC melt were chosen for polarization and potential decay measurements. Anodic and cathodic charging currents on Mo are shown in Figure 6a. Critical current density was about 10 µA/cm² for both anodic oxidation and cathodic reduction at room temperature. During the anodic oxidation, potential arrests X, Y, Z were observed, at about 0.5, 1.1 and 1.2V. Cathodic reduction occurred at potentials strongly dependent upon current density; however, the charge stored in the anodic oxidation and retrievable in the cathodic reduction was appreciable, about 4mC. Some of this stored charge may be in surface Mo compounds, but most will be in the electrolyte: thus the overpotential at any current density decreases with agitation; during an open-circuit rest (Figure 6a) further stored charge becomes available; and the potential returns to about 1090mV following polarization to higher or lower values (Figure 6b).

The nature of the active redox system on Mo is not yet established. Similar behavior was found on Pt and on spec-pure (no metals) graphite. Candidate redox systems include Cl₂/Cl and OCl⁻/Cl⁻.

Attempts were made via ESR to detect any long-lived free radical formed as a result of anodic oxidation of the 2:1 AlCl₃-BPC melt on Mo and on C. Special care was taken
to eliminate the potentially spin active species Ag⁺ or Cu⁺⁺ from the anolyte which could originate from the reference electrodes. No active species were found.

(c) Transitional Metals: Cu, Fe.

The redox system Cu/Cu⁺⁺ does not display simple behavior. The anodic oxidation is much faster than cathodic reduction, even in a 2:1 AlCl₃-BPC melt saturated with Cu₂Cl₂. Both active and passivated copper were studied. At anodic potentials more positive than about 0.22V at room temperature the metal passivates (see Figure 7). The dependence of peak current iₚ, and of passivating current iₐ (at a potential 3.0V at which passivation was assured), was measured from -30° up to +80°C. The anode and reference were separated by a glass frit from reduction product(s) which might be formed at the Cu counter electrode, and the anode potential was swept at 1mV/sec from 0 to 3.00V and held there. After iₐ had stabilized and had been measured, the potential was swept at 5mV/s up to 3.50, then down to 2.50 and back to 3.00, and the average slope ΔV/Δi determined. Thus two measurements iₐ and ΔV/Δi, related to the resistance of the passivated electrode, were in hand. Then the temperature was re-set, up or down several degrees, and after stabilization of iₐ, the ΔV/Δi redetermined. Between -30° to +45°C this procedure gave a systematic measure of "resistance" as a function of temperature (see Figure 7). Repeated returns to 21°C gave values which indicated that no irreversible changes had occurred at higher or lower temperatures (although this observation does not prove that the films were not different at the different temperatures).

The activation energy for the peak rate iₚ is very low (20 KJ/mol) indicating mass transfer control in the electrolyte and perhaps diffusion of Cu⁺⁺ away from the anode. The value of 20 KJ/mol compares favourably with Osteryoung's (22) for diffusion controlled mass transfer of the Fe²⁺/Fe³⁺ couple in these melts. The mechanism changes below -20°C to a process with an activation energy of ~50 KJ/mol.

Above 46°C the activation energy for the anodic oxidation process for the passivated copper (held at 3.0V) is about 50 KJ/mol (slopes plus or minus 2.5 for resistance ΔV/Δi or rate iₐ). This suggests that a different, perhaps liquid crystal medium, controls transport processes at or in the surface film. Above 46°C the film apparently is much...
thinner because of dissolution. Some chemical-activation process with much higher activation energy (130 KJ/mol⁻¹), such as Cu⁺ = Cu²⁺ + e⁻, must be rate-determining.

The i/V sweeps in the range 3.0 - 0.5V at temperatures greater than about 40°C show a minimum in the i/V curve right at the formation potential of 3.00V. From this fact it could be argued that the resistance is really a back-emf due to concentration gradient of the conducting species in the film. Under these steady-state conditions the electrolyte should be saturated with the Cu²⁺. Solubility is low. By means of ESR Cu²⁺ was detected in the electrolyte, although there was no appearance of the characteristic blue color of Cu²⁺ in any of these experiments. The role of the Cu⁺/Cu²⁺ couple in the melt remains unknown.

Identification of electrolyte complexes and of anodic and cathodic reaction products. Attention to purity and analytical content is seen to be of primary importance, and is stressed.

The stability of supercooled melts is of fundamental interest, as well as is the effect of soluble metallic chlorides. The most fundamental question to be answered remains: Why are these mixtures liquid at R.T. and below?

Other melt systems such as the imidazolium based systems developed by Wilkes et al (15) may have the same prospects suggested for BPC based melts. The theoretical basis for the identification of alternate, more stable nitrogen heterocycles has been LUMO calculations. Our preliminary investigations indicate additional "potential" systems suitable for future study.

From a technological application viewpoint, the use of R.T. melts is limited by stability and electrical conductivity. Metallurgical uses such as the removal of scales or oxides from metals like Mo and Ti may be feasible. There is evidence for electrodeposition of Cu and Al.

PROSPECTS - FUNDAMENTAL AND APPLIED

Several opportunities for fundamental electrochemical work on metals in AlCl₃-BPC melts have been identified. They include: (a) redox processes on Pt and Mo; (b) anodic electrocrystallization on Cu and Ag; (c) dissolution of Li, Mg; (d) stripping of surface films from Al, Ti and Zr; (e) identification of electrolyte complexes and of anodic and cathodic reaction products. Attention to purity and analytical content is seen to be of primary importance, and is stressed.

Other melt systems such as the imidazolium based systems developed by Wilkes et al (15) may have the same prospects suggested for BPC based melts. The theoretical basis for the identification of alternate, more stable nitrogen heterocycles has been LUMO calculations. Our preliminary investigations indicate additional "potential" systems suitable for future study.

From a technological application viewpoint, the use of R.T. melts is limited by stability and electrical conductivity. Metallurgical uses such as the removal of scales or oxides from metals like Mo and Ti may be feasible. There is evidence for electrodeposition of Cu and Al.
Primary batteries based on Li, Ca or related alloys as anodes are possible. However, preliminary estimates indicate that the performance is not likely to exceed that of a good Zn-AgO reserve primary. As an alternative to organics now used in conventional lithium primaries, these melts may offer a useful alternative for special applications. Prospects for melts as media for electro-oxidizing oily organic wastes and recovering metals from them needs to be examined, as does the possibility of conducting more selective organic coupling reactions than are possible with the Friedel-Crafts reactions.

In the present work, we have concentrated on the acidic, low-freezing point melts. If low f.p. is not an important consideration, the neutral or basic melts become interesting. As would be expected, both the molecular structures and electrode processes vary with melt composition.

ACKNOWLEDGEMENT

RPC gratefully acknowledges the support of the Canadian Department of National Defence. Helpful discussions with personnel at CANMET, NRC, DREO and UNB are appreciated.

REFERENCES

(1) "Chemical and Electrochemical Studies in Room Temperature Aluminum-halide-containing Melts" by H.L. Chum and R.A. Osteryoung in IONIC LIQUIDS edited by D. Inman and D.G. Lovering, Plenum Press, New York, 1981, p. 407.

(2) R.A. Carpio, L.A. King, R.E. Lindstrom, J.C. Nardi and C.L. Hussey, J. Electrochem. Soc., 126, 1644 (1979).

(3) J. Robinson and R.A. Osteryoung, J. Amer. Chem. Soc., 101, 32 (1979).

(4) J.S. Wilkes et al, Inorg. Chem., 21, 1263 (1982).

(5) F.H. Hurley and T.P. Wier, J. Electrochem. Soc., 98, 203 (1951).
REFERENCES Cont'd

(6) R. Suchentrunk, "Corrosion Protection by Electrodeposited Al", in Materials Coating Techniques, NATO/AGARD-LS-106, p. 7-12 (1980).

(7) V.R. Koch, L.L. Miller, and R.A. Osteryoung, J. Amer. Chem. Soc., 98, 5277 (1976).

(8) C.L. Hussey, L.A. King and J.S. Wilkes, J. Electroanal. Chem., 102, 321 (1979).

(9) R.J. Gale and R.A. Osteryoung, Inorg. Chem., 18, 1603 (1979).

(10) A.A. Fannin, Jr. and L.A. King, F.J.S. R.L. Technical Report SRL-TR-76-19 (1976).

(11) J.C. Nardi, C.L. Hussey and L.A. King, U.S. Patent No. 4,122,245, Oct. 1978.

(12) D.W. Seegmiller, G.W. Rhodes, and L.A. King, Inorg. Nucl. Chem. Letters, 6, 885 (1970).

(13) M. Walter and L. Ramaley, Anal. Chem., 45, 165 (1973).

(14) G.A. Heath, G.T. Hefter, T.W. Boyle, C.D. Desjardins, and D.W.A. Sharp, J. Fluorine. Chem., 11, 399 (1978).

(15) J.S. Wilkes, J.L. Pflug, J.A. Levisky, C.L. Hussey, A.A. Fannin and L.A. King, F.J. Seiler Research Laboratory Technical Report, TR-82-0005, June 1982.

(16) J.L. Gray and G.E. Maciel, J. Amer. Chem. Soc., 103, 7147 (1981).

(17) R.J. Gall, B. Gilbert, and R.A. Osteryoung, Inorg. Chem., 18, 2723 (1979).

(18) G.J. Janz and D.J. Rogers, Extended Abstracts of the 162nd Electrochem. Soc. Meeting, Volume 82-2, p. 536 (abstract no. 333), Oct. 1982.

(19) M.S. Quereshi and I.M. Walker, Inorg. Chem., 14, 2187 (1975).
REFERENCES Cont'd

(20) J. Volke and M. Naarova, 
Coll. Czech. Chem. Commun., 38, 2670 (1973).

(21) G.T. Cheek and R.A. Osteryoung, 
J. Electrochem. Soc., 129, 2488 (1982).

(22) C. Nanjundiah, K. Shimizu and R.A. Osteryoung, 
J. Electrochem. Soc., 129, 2474 (1982).
FIGURE 1 - N-BUTYL PYRIDINIUM CHLORIDE - ALUMINUM CHLORIDE PHASE DIAGRAM

FIGURE 2 - Cyclic Voltammogram of Ti in a AlCl₃ - BPC melt.
FIGURE 3 - ESR Spectrum of blue reduction product. Envelope centered at 337.8G at 9.476 GHz.

FIGURE 4 - Open Circuit Voltages of several metals vs an Ag reference.
FIGURE 5 - Cyclability and Passivation of Li foil in a LiI melt.

FIGURE 6a - Oxidation and Reduction Behavior of a Mo electrode in a 2:1 AlCl₃-BPC melt.
FIGURE 6b - Decay of open circuit potentials of a Mo electrode after polarization.

FIGURE 7 - Effect of temperature on active peak current, \( i_A \), on passivation current, \( i_a \), and on passivating film resistance, \( \delta V/\delta i_a \) for a Cu electrode in a 2:1 melt.