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DIALKYLIMIDAZOLIUM CHLOROALUMINATE MOLTEN SALTS(U)
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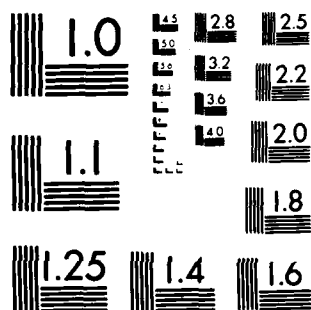
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DIALKYLIMIDAZOLIUM CHLOROALUMINATE MOLTEN SALTS

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ABSTRACT

Earlier work has shown that mixtures of 1-alkylpyridinium chlorides and aluminum chloride form electrolytes that are molten at room temperature. Molecular orbital calculations predicted that 1,3-dialkylimidazolium cations would be more stable cathodically than 1-alkylpyridinium cations. A series of 1-methyl-3-alkylimidazolium chlorides was synthesized and chloroaluminate melts were prepared from them. The imidazolium chlorides themselves have reduction potentials considerably cathodic of the corresponding pyridinium chlorides in DMF. The new melts have favorable physical properties and wider electrochemical windows than the earlier melts. The Lewis acidity of the melts may be varied over a very broad range.

INTRODUCTION

There has been considerable research in this laboratory in the area of low melting fused salt electrolytes, particularly for use in high density batteries (1). While mixtures of sodium chloride and aluminum chloride were successfully used as the electrolyte in a thermal battery, the minimum temperature for operation was about 175°C. In order to achieve lower operating temperature we investigated mixtures of 1-alkylpyridinium chlorides and aluminum chloride, some of which are molten at room temperature. Studies of the physical properties (2) of these melts and the electrochemistry of metal ions dissolved in them (3,4) indicated some promise as battery electrolytes. Osteryoung and coworkers have studied these types of melts extensively and have found them to be easily prepared (5) and have a very wide range of Lewis acidity (6).

One disadvantage of the alkylpyridinium chloroaluminate melts is that aluminum is oxidized in them when the melt is basic (chloride rich). Gale showed that in a melt composed of AlCl_3 and 1-butylpyridinium chloride the oxidation of aluminum is accompanied by the reduction of

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the 1-butylpyridinium cation (7). We have convincing EPR evidence that in the same melt 1,1'-dibutyl-4,4'-bipyridinium radical cation is formed (8) by reaction with aluminum or by cathodic reduction. The reactivity of these melts towards aluminum is unfortunate, since aluminum would be a useful anode in a battery using the room temperature melt as the electrolyte. We report here our effort to find a room temperature molten salt that would have the favorable physical properties of the melts described above, but would also have a wide enough electrochemical window that aluminum would be stable in them.

EXPERIMENTAL

The MNDO molecular orbital calculations were performed on either a Burroughs 6700 or Digital Equipment Corp. VAX computer using a program provided by Dr. M. J. S. Dewar.

Reduction half-wave potentials were obtained in DMF containing 0.1M tetrabutylammonium perchlorate at a rotating disc electrode (1500 RPM). Potentials were measured at 25°C versus a saturated calomel electrode isolated from the bulk solution via a Vycor tipped bridge tube. The solution was presaturated with and maintained under a blanket of dry nitrogen.

Cyclic voltammetry was performed using a Pt working electrode, a W counter electrode and a reference electrode consisting of an aluminum wire immersed in an AlCl_3 rich melt (usually 67 mol% AlCl_3) and separated from the cell with a glass frit or glass wool.

Liquidus temperatures were measured using a Perkin-Elmer model DSC-2 differential scanning calorimeter. Specific conductivities were measured using an ac impedance bridge.

All experiments involving moisture sensitive materials were performed in a Vacuum Atmospheres Corp. glove box containing a dry argon atmosphere. The 1-methylimidazole and 1,2-dimethylimidazole were obtained from the Aldrich Chemical Co. and were distilled before use. The 1-chloropropane and 1-chlorobutane were obtained from the Aldrich Chemical and were used without purification. The chloromethane and chloroethane were obtained from Linde Specialty Gasses. NMR spectra were run on a Varian T-60 spectrometer. IR spectra were run on a Beckman IR-20 spectrophotometer. Elemental analyses were performed by Gailbraith Laboratories. Melting points are uncorrected.

1,3-Dimethylimidazolium Chloride: 1-methylimidazole (62.3 g, 0.78 mol) was weighed in a 250 ml glass vessel and chloromethane (100 ml, 1.40 mol) condensed into it using a dry ice condenser. The container was sealed and heated overnight (16 hrs) at 65°C with magnetic stirring. The pressure in the vessel was reduced by cooling in a dry ice/acetone bath and the top was removed. The excess chloromethane was allowed to boil off through a drying tube. The white solid crude product was recrystallized from acetonitrile. Isolated yield was 66.6 g (67%). Melt-

ing point 124.5 - 128°C. Elemental analysis; calculated for $C_5H_9N_2Cl \cdot 0.3H_2O$: 43.23% C, 7.04% H, 20.17% N, 25.53% Cl, 3.17% O. Observed: 42.82% C, 7.32% H, 20.13% N, 26.01% Cl, 3.72% O.

1-Methyl-3-ethylimidazolium Chloride: 1-Methylimidazole (19.3 g, 0.235 mol) was weighed in a 250 ml glass pressure vessel and chloroethane (56.0 g, 0.867 mol) condensed into it using a dry ice condenser. The container was sealed and heated for two days at 75°C with magnetic stirring. The pressure in the vessel was reduced by cooling in a dry ice/acetone bath and the top was removed. The excess chloromethane was allowed to boil off through a drying tube. A slightly off white solid product was obtained that showed no starting material by NMR. Isolated yield was 34.38 g, (99.8%). The product was recrystallized by dissolving in a minimum amount of acetonitrile and dropping it into cold ethyl acetate. Melting point 82-87°C. Elemental analysis calculated for $C_6H_{11}N_2Cl \cdot 0.2H_2O$: 47.97% C, 7.65% H, 18.65% N, 23.60% Cl, 2.13% O. Observed: 48.18% C, 7.80% H, 18.66% N, 23.52% Cl, 1.84% O.

1-Methyl-2-propylimidazolium Chloride: 1-Methylimidazole (10.1 g, 0.123 mol) and 1-chloropropane (12.7 g, 0.161 mol) were mixed in a 250 ml glass pressure vessel. The mixture was heated at 85°C for 20 hours with magnetic stirring. The reaction flask was allowed to cool to room temperature and the excess chloropropane was removed at reduced pressure. The slightly yellow oily product was diluted with about 10 ml of acetonitrile and cooled in the freezer. Crystallization was induced with a seed crystal and took several days. The seed crystals were obtained with much difficulty. Yield was 18.7 g (94.3%). Melting point 58-66°C. Elemental analysis; calculated for $C_7H_{13}N_2Cl \cdot 0.3H_2O$: 50.63% C, 8.26% H, 16.87% N, 21.35% Cl, 2.89% O. Observed: 50.70% C, 8.45% H, 17.08% N, 21.55% Cl, 2.22% O.

1-Methyl-3-butyylimidazolium Chloride: 1-Methylimidazole (60 ml, 0.752 mol) and 1-chlorobutane (87 ml, 0.828 mol) were refluxed without additional solvent overnight with stirring. The reaction mixture was cooled to room temperature, the top liquid phase decanted and residual excess chlorobutane removed at reduced pressure. The slightly yellow oil was diluted in about 15 ml acetonitrile and crystallized in the freezer with the aid of a seed crystal. The original seed crystals were obtained with much difficulty. Melting point 65-69°C. Elemental analysis; calculated for $C_8H_{15}N_2Cl \cdot 0.1H_2O$: 54.45% C, 8.68% H, 15.87% N, 20.09% Cl, 0.91% O. Observed: 53.94% C, 8.90% H, 16.03% N, 20.52% Cl, 0.61% O.

1-Methyl-3-benzylimidazolium Chloride: 1-Methylimidazole (5.0 ml, 63.1 mmol) and benzyl chloride (8.0 ml, 69.4 mmol) were stirred together without solvent for 2 hours at room temperature. The reaction mixture set into a hard glass which could not be crystallized despite many attempts.

Chloroaluminate melts were prepared typically as in the following

example: Aluminum chloride (18.28 g, 0.1371 mol) was added in aliquots to 1-methyl-3-ethylimidazolium chloride (10.00 g, 0.0682 mol) with stirring under a dry argon atmosphere. The mixture was then stirred for several hours until dissolution of the aluminum chloride was complete. The material obtained was a clear water-white liquid.

RESULTS AND DISCUSSION

The probable reason for the low liquidus temperatures of the alkylpyridinium chloroaluminate melts is the size of the organic cation. As the size of the alkyl substituent increases, the liquidus temperature decreases. For example 1:1 mixture of the aluminum chloride and 1-methylpyridinium chloride melts at 145°C, while a similar mixture with 1-butylpyridinium chloride melts at 30°C. One might expect that any large organic cation could produce chloroaluminates that are also molten at or near room temperature. The most common source of positive charge in organic compounds is a quaternary nitrogen, as in the alkylpyridinium cations described above. For these reasons we focused our search on large (molecular weight >130) molecules containing quaternary nitrogen. The reason that aluminum is oxidized in the alkylpyridinium chloroaluminate melts and not in the alkali metal chloroaluminate melts is that the alkylpyridinium cation must be more easily reduced than sodium ion or Al(III). The best candidates should thus have reduction potentials significantly more negative than alkylpyridinium ions.

While one can tell by inspection of the structure of a molecule what its approximate size is and its charge, it is not possible to determine the reduction potential by simple inspection. The reduction potential may be estimated from the structure of the molecule alone using molecular orbital calculations. The newer semi-empirical techniques for performing molecular orbital calculations provide a rapid and relatively easy means for estimating the electron affinities of reasonably large organic molecules. In the MNDO method, developed by Dewar, the electron affinity of a closed shell cation is equal to the negative value of the energy of the lowest unoccupied molecular orbital (LUMO) (9). It is well established that the vacuum electron affinity may be correlated to the solution reduction potential as shown below (10).

$$EA = -LUMO \quad (1)$$

$$E(\text{red}) = EA + \Delta G(\text{solv}) + K \quad (2)$$

Where EA is the electron affinity, LUMO is the energy of the lowest unoccupied molecular orbital, E(red) is the solution reduction potential, $\Delta G(\text{solv})$ is the differential solvation energy, and K is related to the reference electrode. Calculations were performed on a variety of mostly heterocyclic cations chosen as possible cations for chloroaluminate melts. The criteria for the candidates was that the size be about the same as alkylpyridinium and that they be commercially available or readily synthesized. Since the molecules would all be of similar size, the equation (2) could be simplified to:

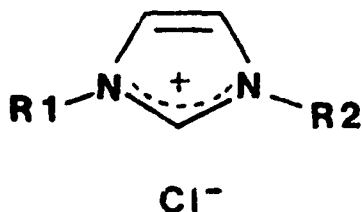
$$E(\text{red}) = EA + C \quad (3)$$

where the differential solvation energies are combined with the reference potential constant.

The linear relationship implied in equation (3) was tested with a few cations, as shown in Figure 1, where reduction half-wave potentials were used for the observed values. While the data are too few and scattered to make a convincing case for a straight line, it is heartening to note that the least-squares slope is very close to unity. The result in Figure 1 gave us confidence that the MNDO method was useful and reliable for screening candidates for their approximate reduction potentials.

The results of the calculations are tabulated in Table 1 and shown graphically in Figure 2. Tetraalkylammonium is predicted to be the most difficult of the cations to reduce. This is not surprising, since tetraalkylammonium salts are often used as the supporting electrolyte in electrochemical cells. Unfortunately the liquidus temperature for the chloroaluminate melt prepared from one of them (tetraethyl-) was relatively high, so no further consideration was given to that class of cations (11). One might expect that the addition of one or more electron donating substituents to the pyridine ring might lower (make more negative) the reduction potential of the well studied 1-alkylpyridinium system. Molecules with one, two or three methyl groups (ie. the picolines, lutidines and collidine) were actually estimated to have quite similar reduction potentials. In fact the 1-methylcollidinium cation was found to be reduced by aluminum when it was used as the cation in a chloroaluminate melt (12). All of the 6-membered heterocycles containing two nitrogens (the alkylpyridaziniums, -pyrimidiniums and -pyraziniums) have reduction potentials higher than alkylpyridinium, so they were removed from consideration. The 5-membered heterocycles containing two nitrogens were more promising. 1,2-Pyrazolium had a significantly lower predicted reduction potential and 1,3-dialkylimidazolium even lower yet. The salts based on imidazole are known compounds and may be prepared simply from commercially available starting materials, so they were chosen for further study.

A homologous series of 1,3-dialkylimidazolium chlorides were prepared (compounds I-V).



<u>R1</u>	<u>R2</u>	<u>COMPOUND</u>
methyl	methyl	II
methyl	ethyl	II
methyl	propyl	III
methyl	butyl	IV
methyl	benzyl	V



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The preparative procedures were similar to those described in the literature for the iodides (13-20), but were modified to accomodate gaseous reagents in the case of some of the chlorides. Briefly, the preparations involve heating 1-methylimidazole with the appropriate chloroalkane, sometimes under pressure. In most cases the products were hygroscopic white solids.

The chloroaluminate melts were prepared by simply mixing aluminum chloride with the imidazolium chloride. The two solids combined to produce a clear, slightly viscous liquid. All operations involving aluminum chloride or chloroaluminate melts were done in a glove box containing a dry argon atmosphere.

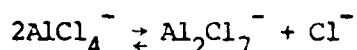
The liquidus temperature of the melts was an important physical property. The melting points of the dialkylimidazolium chlorides indicated that larger or more asymmetric cations resulted in lower melting points. This also proved to be true in chloroaluminates having dialkylimidazolium cations, as illustrated in Table 2. The melt having the 1-methyl-3-ethylimidazolium cation (from chloride II) was molten at room temperature over its entire composition range, and its liquidus temperatures were much lower than the closely related melt having the 1,3-dimethylimidazolium cation. Since the molecular weight difference was only 14 daltons, the effect was probably due mostly to the asymmetry of the methyl-ethyl cation rather than the size difference. While the liquidus temperature of the 1-methyl-3-ethylimidazolium melt is quite low, the melt would not be a useful electrolyte at very low temperatures due to the very high viscosity at the low temperatures.

The conductivities of various compositions of the 1-methyl-3-ethylimidazolium melt are tabulated in Table 3. They are not very high by molten salt standards, but this is probably largely due to the temperature at which they were measured. The values are approximately the same as for the 1-alkypyridinium chloroaluminate melts(2).

The new melts would be a major improvement over the 1-alkypyridinium melts only if they had a wider electrochemical window. The test for this would be if aluminum is stable in chloride rich compositions of the melts. If the materials met that test, then the organic cations must reduce cathodic of aluminum in the melt. Cyclic voltammetry is a convenient way of analyzing the anodic and cathodic limits of the melts. Figure 3 is a cyclic voltammogram of an acidic (2:1) melt having the dimethylimidazolium cation. At the anodic limit chloride oxidation was observed, as in all chloroaluminate melts. The wave at the cathodic limit is characteristic of metal deposition. In a basic melt (0.7:1)Al was unaffected when immersed for several hours at 110°C. The cyclic voltammogram (Figure 4) indicates that the melt decomposition is occurring at the cathodic limit, but that limit is at a high negative potential. The lack of aluminum deposition in the 0.7:1 melt is probably due to the very high chloride concentration at that composition.

In order to prove that aluminum was in fact reduced at the cathodic limit of a slightly acidic melt a deposition/stripping experiment was done, as shown in Figure 5. A constant cathodic current was passed until 0.200 coulombs had accumulated, then an anodic current was passed until a rapid rise in potential indicated that all of the plated material had been stripped. The 95% overall efficiency is much higher than expected for deposition of an organic species, which would probably be irreversible. In a separate similar experiment the surface of the electrode had metallic gray deposit after deposition, clear evidence that aluminum is reduced and not the organic cation. The experiment also demonstrated the usefulness of the new melt as an aluminum plating medium.

One attractive feature of the 1-alkylpyridinium chloroaluminate melts is the wide range of Lewis acidity accessible in them, as expressed by chloride concentration. The chloride concentration in the melts is controlled by the equilibrium:



For the alkylpyridinium chloroaluminate melts the value of the equilibrium constant is 3.83×10^{-13} . (16) The potentiometric titration curve for the 1-methyl-3-ethylimidazolium chloroaluminate melt (Figure 6) provided a value of 2.0×10^{-19} for the same equilibrium. This implies a range of acidity for the new melts at least as broad as the alkylpyridinium melts and much broader than the alkali halide chloroaluminate melts.

The use of the new melts in batteries requires that a suitable redox couple be available for the cathode half-reaction. Transition metal ions are commonly used for such purposes. Copper (II) chloride was dissolved in the 1-methyl-3-ethylimidazolium melt and reversible reduction was observed by cyclic voltammetry (Figure 7). Initial results indicate that the copper couple in the new melt is very similar to the same ion in the 1-alkylpyridinium melts (3).

In addition to dissolving inorganic compounds such as CuCl_2 , the new melts act as solvents for organic compounds. Benzene is miscible in the 1-methyl-3-ethylimidazolium melt to about equal volume. Some other aromatic compounds are also soluble and, as with the alkylpyridinium melts, some are spontaneously oxidized to the radical cation. For example, thianthrene dissolved in the 1,2-dimethylimidazolium melt immediately turns deep purple and exhibits an EPR spectrum characteristic of thianthrene radical cation.

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TABLE 1

Calculated Electron Affinities of Some Organic Cations

Cation	Electron Affinity (eV)	E_2^0 (red) (V)
1-methylpyridinium	5.84	-1.28
1-methyl-2-picolinium	5.74	
1-methyl-2,4-lutidinium	5.71	
1-methyl-2,4,6-collidinium	5.61	
1-methylpyridazinium	6.30	
1,2-dimethylpyrazolium	4.86	
1,3-dimethylimidazolium	4.86	-1.981
1-methyl-3-butylimidazolium	4.70	-2.001
tetramethylammonium	4.37	-2.7

TABLE 2

Liquidus Temperatures of Dialkylimidazolium
Chloroaluminate Melts

Cation	50 mol% AlCl_3	67 mol% AlCl_3
1,3-dimethylimidazolium	75° C	15° C
1-methyl-3-ethylimidazolium	8° C	-98° C

TABLE 3

Conductivities of Methylethylimidazolium
Chloroaluminate Melts

Composition (mol% AlCl_3)	Specific Conductivity (ohm-cm) ⁻¹	Temperature (°C)
44	0.0117	29.7
50	0.0227	30.9
67	0.0154	32.2

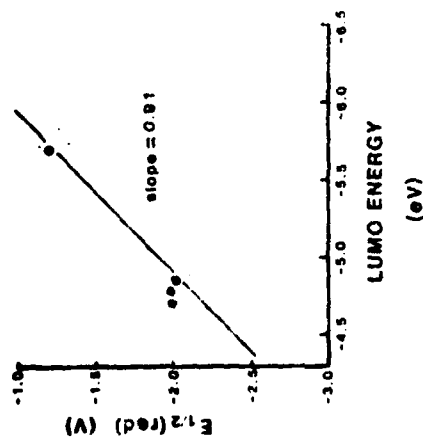


Fig. 1. Correlation of $E_{1/2}$ (red) and LUMO energy. $E_{1/2}$ values are from this work (●) or from the literature (x).

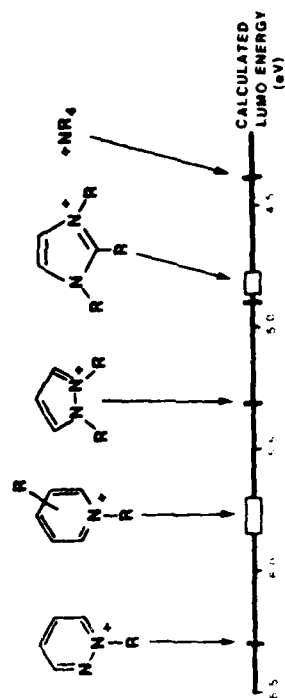


Fig. 2. Types of compounds selected for calculation of LUMO energies.

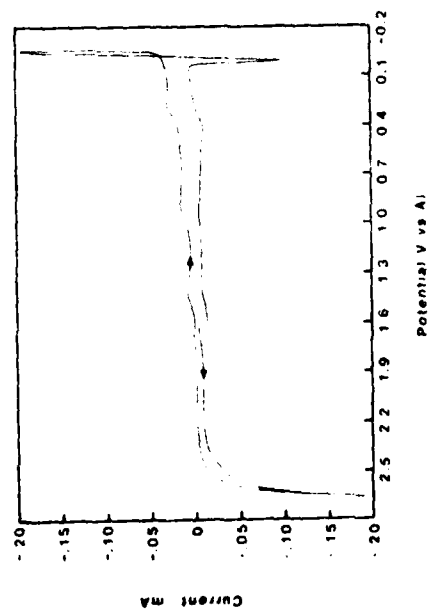


Fig. 3. Electrochemical window of 67 mol% AlCl_3 /dimethylimidazolium chloride melt.

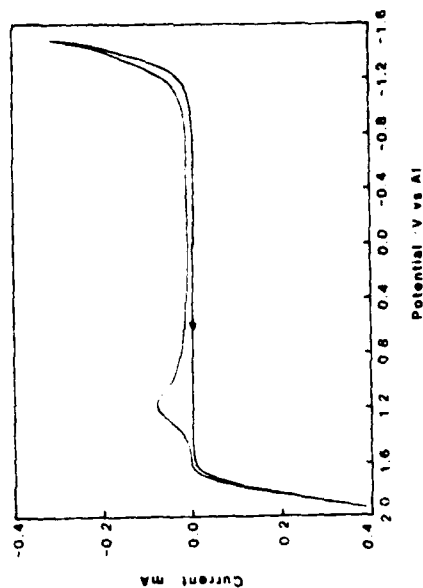


Fig. 4. Electrochemical window of 40 mol% AlCl_3 /methylethylimidazolium chloride melt.

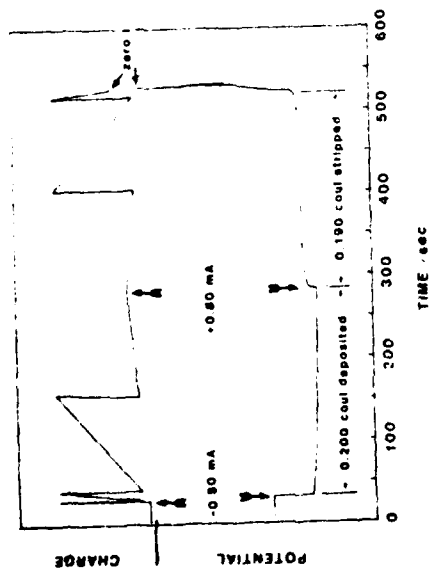


Fig. 5. Galvanostatic aluminum deposition/stripping on Pt in slightly acidic dimethylimidazolium melt.

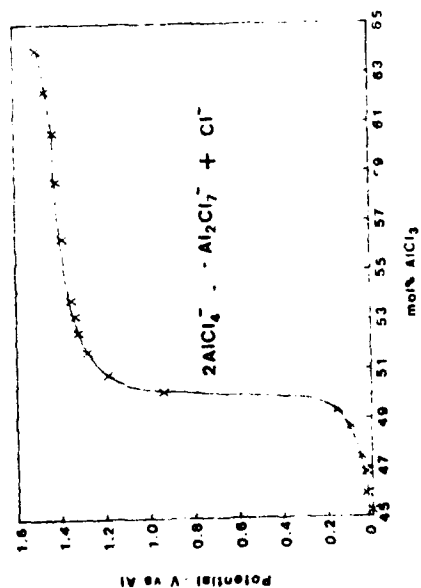


Fig. 6. Potentiometric titration of the melt. 1 methylethylimidazolium chloroaluminate melt.

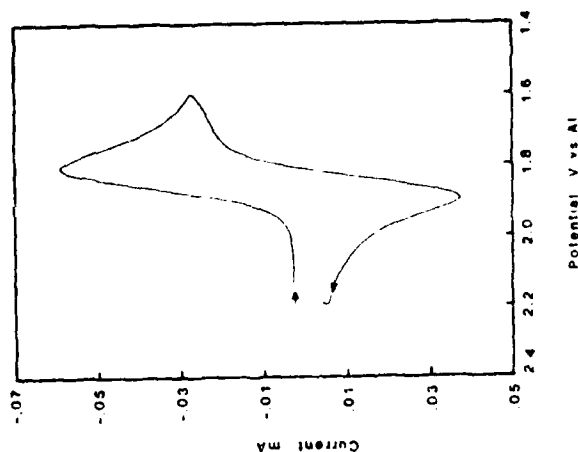


Fig. 7. Cyclic voltammetry of CuCl_2 in 67 mol% methylethylimidazolium chloroaluminate

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