AD-A148 490 A NEW CLASS OF ROOM TEMPERATURE MOLTEN SALTS FOR BATTERY APPLICATIONS(U) FRANK J SEILER RESEARCH LAB UNITED STATES AIR FORCE ACADEMY C.. 1/1

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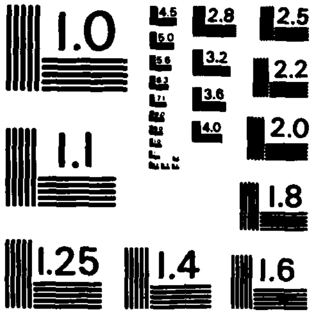

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Salts which are molten at and below room temperature could be used as the electrolyte in a battery which might have the high energy density typical of molten salt thermal batteries, but have none of the problems associated with the elevated operating temperatures of thermal batteries. This presentation describes some physical, chemical, and electrochemical properties of a room temperature molten salt formed by combining aluminum chloride with 1-methyl-3-ethylimidazolium chloride.

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from lithium ordering in the van der Waals gap, they do not lead to classical reorganisation of the base structure. Moreover, this initial diphased ordering, consequence of the enthalpic interactions between the intercalated species and the slabs, is destroyed during the first few cycles (formation), and the lattice changes in order to lower the power dissipation. This explanation of the formation is obviously wrong if an electronic transition occurs with a rearrangement of the lattice. In addition, it is clearly shown that the improvements depend on the solvent, the nature, and the quality of which must be thoroughly controlled. This fondamental conclusion explains the LdM
interest on studying Li_xMPX_3
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conclusion: from LdM point
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characterized by a limited amount of electrolyte in a porous geometry. Technological progresses have to be done in order to optimize the positive and negative efficiencies. Some LdM tests using now classical materials (TiS_2, MoS_3) suggests that some difficulties could be solved in the near future, if determined efforts go on.

Nevertheless, specific application should be taken into account in order to test the lithium systems limits with respect to the others. Such a point of view would allow us to define the future research fields. The present unpublished results until now should be added to K. M. Abraham's review paper in order to reach a better understanding of the point of view of the LdM, about its compounds.

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Advanced Rechargeable Batteries Session

A NEW CLASS OF ROOM TEMPERATURE MOLTEN SALTS FOR BATTERY APPLICATIONS

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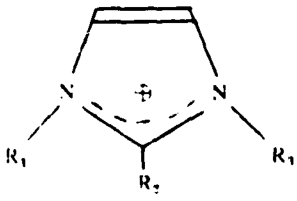
Introduction

One of the particularly useful applications of molten salts is as the electrolyte for high energy density batteries. Unfortunately, elevated temperatures are usually required to maintain the salt in the liquid state and in general, the higher the operating temperature, the greater the problems associated with the battery system. As a result, much work has been directed towards developing thermal batteries with lower operating temperatures.

Along these lines, the goal of our research is to develop low-melting salts suitable for use as battery electrolytes. Our approach to this goal has three steps: first, synthesize the materials which comprise the molten salt; second, determine the physical and electrochemical properties of the molten salt; and third, construct electrochemical cells which demonstrate the feasibility of using the molten salt as an electrolyte. Our research into these new molten salts is the subject of this paper.

Results and D'scussion

Mixtures of inorganic salts such as those historically used in thermal batteries require high temperatures to maintain the mixture in the liquid state, even around eutectic points. However, when certain organic salts were mixed with an inorganic salt, the melting points were lower. Indeed, mixtures of some 1-alkylpyridinium chlorides and aluminum chloride were molten at room temperatures (1). Further, the electrochemistry of that melt was somewhat promising, with one major exception: the alkylpyridinium cation was too easily reduced. To combat this problem, we used a semiempirical molecular orbital calculation to screen a variety of large organic cations, searching for those that would not be readily reduced in a melt. The search revealed the alkylimidazolium salts to be attractive candidates for producing chloroaluminate melts (2). Further, these salts could easily be synthesized from commercially available starting materials (3). The alkylimidazolium chlorides studied are shown below:



R_1	R_2	R_3
CH_3	H	CH_3
CH_3	CH_3	C_2H_5
CH_3	H	C_2H_5
CH_3	H	$n\text{-}C_3H_7$
CH_3	H	$n\text{-}C_4H_9$
$n\text{-}C_4H_9$	H	$n\text{-}C_4H_9$

1-methyl-3-ethylimidazolium chloride (MeEtImCl) was selected as the baseline for detailed study, as it was particularly easy to prepare, and was found to form chloroaluminate melts with very desirable properties. The preparation of the chloroaluminate melts involved simply mixing the $R_1R_2R_3$imidazolium chloride with aluminum chloride

$$R_1R_2R_3ImCl + AlCl_3 \rightarrow R_1R_2R_3Im^+ + Cl^- + AlCl_4^- + Al_2Cl_7^-$$

Combining the two white solid salts yields a clear, slightly viscous liquid that contains only ionic species. All of the negatively charged species shown on the right side of the equation are present in the chloroaluminate melt, but their relative proportions depend on the ratio of $AlCl_3$ and $R_1R_2R_3ImCl$ used in the preparation. As we shall see below, the physical and electrochemical properties of the melt are highly dependent on the relative proportions of ingredients.

In characterizing a melt, the first step is to determine its physical properties. Thus for $AlCl_3$ + MeEtImCl (the base line melt), melting points were measured for many different compositions ranging from 30 to 67 mol percent $AlCl_3$. Similar compositions were used in measuring densities, viscosities, and conductivities of the baseline melt over the temperature range of approximately 10°–*JA*100*°C.

Figure 1 is a liquid-solid phase diagram for MeEtImCl + $AlCl_3$ as a function of $AlCl_3$ content. Note that at room temperature (*ca.* 25°C), the melt is liquid from about 30 to 67 $AlCl_3$. Also note that in two regions, the liquid state is maintained down to −72°C and −98°C. This is where only glass transitions occurred, and true freezing could not be induced.

Figure 2 shows the density of the MeEtImCl + $AlCl_3$ melt as a function of temperature. The densities range from about 1.1 to 1.4 gm/ml, increasing monotonically with increasing $AlCl_3$ content and linearly with decreasing temperature.

Figure 3 shows the absolute viscosity as a function of temperature for melts comprised of $AlCl_3$ and MeEtImCl in varying ratios. The absolute viscosities of all the melts are rather large, ranging from 70 to 700 centipoise. Furthermore, the viscosity, while a strong function of composition in the basic (organic rich) region, is almost insensitive to composition in the acidic ($AlCl_3$ rich) region.

Figure 4 shows the dependence of specific conductivity of $AlCl_3$ + MeEtImCl melts on composition and on temperature. The data show the specific conductivity is somewhat lower than is typical of molten salts; however, most molten salts are at significantly higher temperatures, so when allowance is made for the lower temperatures of the alkylimidazolium chloroaluminate melts, the specific conductivity is in the range expected. Indeed, the specific conductivity monotonically increases as the temperature increases. Also, the data indicate that as the $AlCl_3$ mol fraction is changed, the specific conductivity is a maximum at eqimolar melts, falling off more rapidly in the basic (organic rich) region.

In addition to the measurements on the baseline melt, we measured likewise the physical properties of 33, 50, and 66 m/o $AlCl_3$ melts with most of the remaining alkylimidazolium chlorides shown

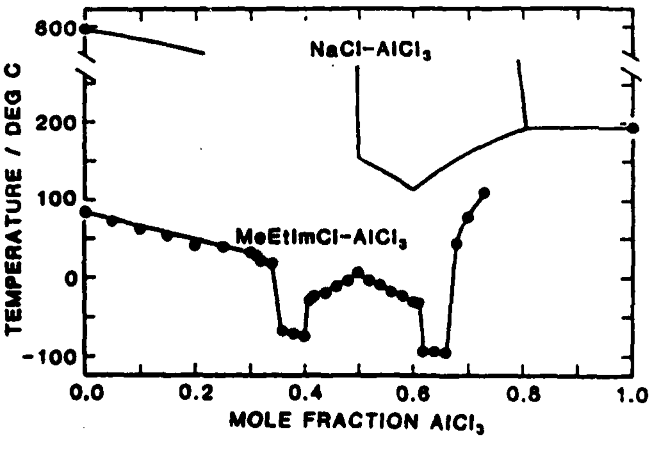


Fig. 1. Liquid-solid phase diagram for MeEtImCl-AlCl$_3$ and NaCl-AlCl$_3$.

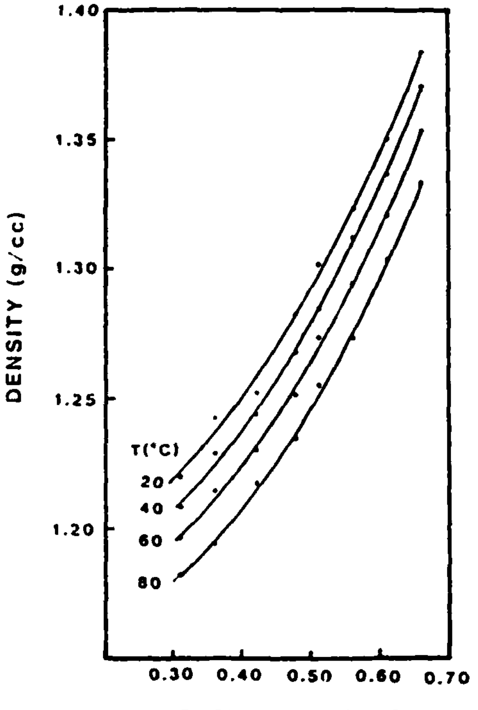


Fig. 2. Dependence of density on MeEtImCl-AlCl$_3$ melt composition.

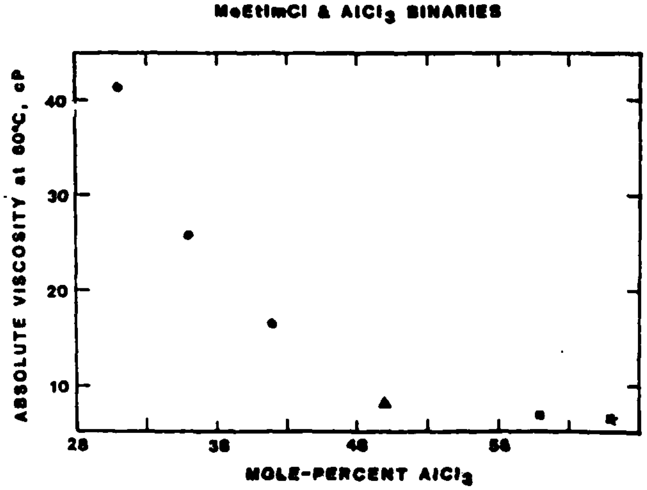


Fig. 3. Dependence of absolute viscosity on dialkylimidazolium chloride AlCl$_3$ melt composition and temperature.

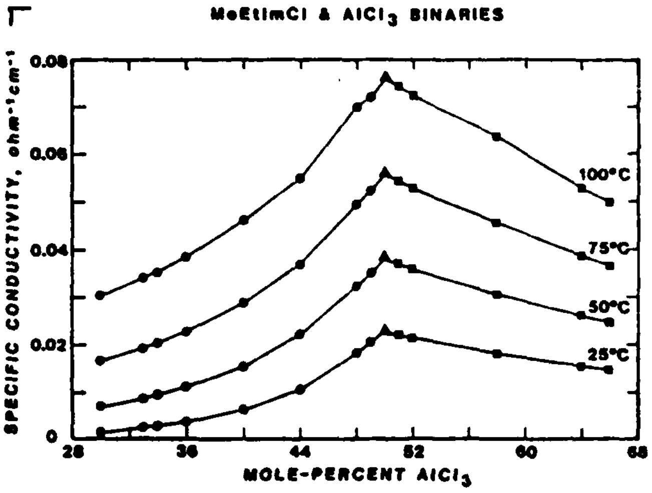


Fig. 4. Dependence of specific conductivity on MeEtImCl-AlCl$_3$ melt composition and temperature.

before. The melting points, densities, viscosities, and conductivities of these other melts were found to follow the trends shown above for the baseline melts.

While the physical properties discussed above are invaluable to the understanding of the nature of the melts, even more important is an understanding of the electrochemical behavior of the melts. The initial work in the electrochemical study used cyclic voltammetry to examine the electrochemical window. The electrochemical window is that region of potential in which no significant electrode reaction occurs (arbitrarily defined as when the current is less than 5 mA), and, thus, is the usable potential span of the melt. The cyclovoltammetric study of the $R_1R_2R_3$ImCl + AlCl$_3$ melts showed large electrochemical windows, ranging from 2.40 to 2.65V in the acidic (AlCl$_3$ rich) melts and from 2.57 to 2.82 in the basic (organic rich) melts, using a glassy carbon electrode. (In all the electrochemical experiments with the melts, the reference electrode was an aluminum wire in a 60 m/o AlCl$_3$ baseline melt.) To see the effects of different electrodes, twenty one electrodes were examined for stability in the baseline (MeEtImCl + AlCl$_3$) melt; the three electrodes having the greatest stability and their electrochemical windows (in volts) in basic and acidic melt were (*i*) glassy carbon, 2.57 and 2.43; (*ii*) tungsten, 1.70 and 2.48; and (*iii*) Ta/20%Ru, 2.95 and 2.40.

The next step was to study the electrochemical behavior of various cations added to the baseline melt. The chloride salts of twenty five cations were surveyed in the MeEtImCl + AlCl$_3$ melts using cyclicvoltammetry. For the purpose of developing batteries, the cations which exhibit reversible oxidation-reduction behavior closest to the anodic limit of the melts are the more desirable and merit further study. The relative positions of the cations in this respect can be conveniently displayed by $E_{p/2}$, the sum of the potential of the cathodic and the anodic peak divided by 2. In the acidic baseline melt (which has an anodic limit of 2.35V), the three cations having the largest $E_{p/2}$ were Fe^{3+}, 2.22V; Mo^{3+}, 2.07V; and Cu^{2+}, 1.98V.

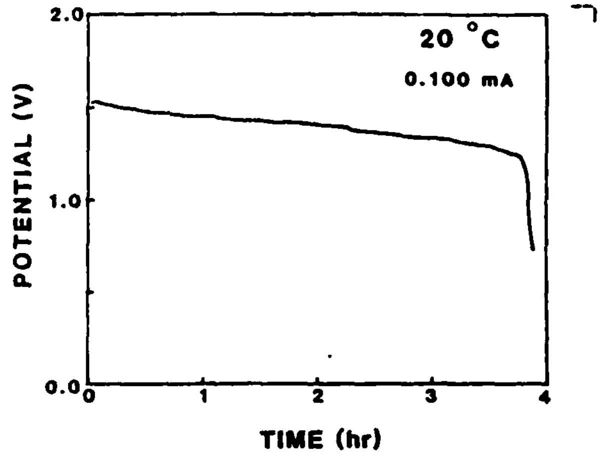


Fig. 5. Discharge curge of an Al//FeCl$_3$ cell.

Similarly in the basic baseline melt (anodic limit = 1.00V), the three largest $E_{1/2}$ values were W^{6+}, 0.62V; Mo^{3+}, 0.31V; and Fe^{3+}, 0.30V. These results have been used to select cations for more detailed studies.

The goal of this research, as mentioned earlier, is to develop low melting salts suitable for use as battery electrolytes. Thus, the feasibility of battery cells using the newly developed electrolytes must be demonstrated.

To design a cell properly, more electrochemical experiments must be performed on potential cathodes and anodes in the melts. Nevertheless, we constructed a prototype battery cell using an aluminum anode and an iron(III) chloride cathode. The anode was simply a disk of aluminum; the cathode was FeCl$_3$ in electrical contact with a tungsten collector. The melt (60 m/o MeEtImCl, 40 m/o AlCl$_3$) combined with an equal volume of benzene served as both the anolyte and the catholyte. (Benzene is soluble in the melt, but causes the FeCl$_3$ to become insoluble in the melt.) The anode and cathode compartments were separated by a fine-porosity glass frit. This cell design is clearly not optimal, either chemically or mechanically. Fig. 5 shows a discharge curve at constant current for the crude cell. The discharge is quite flat, dropping sharply when the Fe(III) is depleted. This is the first true molten salt battery that operates as low as 20°C.

This cell, although not optimized, does constitute a proof-of-concept, and is an important milestone in our effort to develop an ambient-temperature rechargeable molten salt battery. In the future, our efforts will include a systematic study to develop a prototype cell which will demonstrate the feasibility of using the chloroaluminate melts as battery electrolytes.

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