



A Novel Electrolyte for the Sodium/Iron Chloride Battery

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Introduction and Background

As now configured, the Na/FeCl₂ battery, which operates at 250° C, utilizes molten AlCl₃-NaCl as the electrolyte, liquid sodium as the anode, FeCl₂ as the cathode, and a conductive ceramic, solid β"-alumina, as the separator^(1,2,3).

The high operating temperature and the use of β"-alumina as the solid electrolyte are the two shortcomings of this battery. The β"-alumina presents substantial resistance to sodium ion transfer and also has high manufacturing cost and uncertain physical integrity⁽⁴⁾. Improvement to this battery can be achieved by using a low melting temperature molten salt, that is, T_{mp} < 98° C, the melting point of Na. With this improvement, the beta"-alumina is no longer necessary and the sodium has intimate contact with the electrolyte, reducing the resistance to charge transfer.

In this study, a low melting temperature organic chloroaluminate salt was mixed with AlCl₃-NaCl to form a low melting temperature mixture. Basic or neutral melts are required to keep the solubility of FeCl₂ low⁽³⁾. Based on the difficulty of preparing exactly neutral melt, the basic melt has been investigated. The organic chloroaluminate salt utilized was a mixture of AlCl₃ and 1-methyl-3-ethylimidazolium chloride (MEICl), resulting in AlCl₃-MEICl. The AlCl₃-MEICl melts are liquid well below room temperature for a wide range of N, the mole fraction of AlCl₃⁽⁵⁾. The high electrochemical stability of this melt also allows the deposition of materials over a wide range of potentials. Gallium, cadmium and lithium have been plated out from the AlCl₃-MEICl melts^(6,7). This paper is the first report of the deposition of sodium from this melt.

The electrolyte for this investigation is a combination of AlCl₃-NaCl and AlCl₃-MEICl salts, resulting in the ternary AlCl₃-MEICl-NaCl system. There are several requirements for the AlCl₃-MEICl-NaCl mixture. First, it must be liquid below 98° C. Second, both electrode materials must be stable in the melt. Third, it must have an electrochemical 'window' which allows sodium reduction at the cathodic end and iron oxidation at the anodic end. This report focuses on the sodium anode to the exclusion of the FeCl₂ cathode.

Results and Discussion

All melt preparations were carried out in a N₂-atmosphere dry box. The preparation of MEICl, AlCl₃-MEICl, and AlCl₃-NaCl was conducted following previously published procedures^(8,9).

NaCl is soluble in acidic AlCl₃-MEICl melts.

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However, dissolving NaCl into acidic AlCl₃-MEICl melts can only provide acidic or neutral AlCl₃-MEICl-NaCl melts⁽¹⁰⁾. A method for making basic melts was found in this laboratory. This technique involves mixing basic AlCl₃-MEICl (pale yellow) and AlCl₃-NaCl (white). An AlCl₃-NaCl melt whose melting point is around 160° C was added as a powder into an AlCl₃-MEICl melt and heated until no solid remained. The basic AlCl₃-MEICl-NaCl melt was a milky-white colloidal suspension of two liquids, which becomes milkier with increasing NaCl content. Before mixing, the upper phase was MEICl-rich (pale yellow) and the lower phase was NaCl-rich (white). Upon stirring, these two phases give a basic colloidal mixture. The melt was stirred before each experiment to form the colloidal mixture. During the electrochemical experiments, the melt was not stirred. The formation of the two-phase basic melts may be due to the strong binding force between AlCl₃ and NaCl.

One piece of sodium metal was placed into the melt. A shiny surface was recognized as the condition of sodium metal stability; blackening indicated an undesirable chemical reaction. An electrolyte with composition of 47:45:8 (mole percent) AlCl₃:MEICl:NaCl was found to meet the temperature and stability requirements and was used for this investigation.

Cyclic voltammetry experiments with a basic AlCl₃-MEICl-NaCl (50° C) mixture at glassy carbon (GC) and Pt electrodes for this composition did not show the sodium plating or stripping peaks. However, with a mercury electrode, prepared by attaching a mercury drop to a gold disk (surface area is ~0.15 cm²), the cathodic deposition current and anodic stripping current of Na can be seen at E_{peak} = -1.53 and -1.21 V in Figure 1. This couple appeared only when the melt contained NaCl. The peak at -0.5 V was probably due to the reduction of protons; it decreased on subsequent scans to an insignificant value after 5 cycles. The reference electrode was a high purity Al wire (Alfa) in a 2:1 AlCl₃:MEICl melt. The anodic stripping efficiency of the sodium was 71%. A plot of peak current vs. square root of scan rate for the reduction of Na⁺ was linear which shows diffusion controlled behavior at sweep rates from 10 mV/sec to 200 mV/sec (see Figure 2). Additional cyclic voltammetry studies are currently being performed to understand the characteristics of these two phases by placing the working electrode in each phase. The mercury electrode was primarily used to examine the sodium deposition and stripping potentials. Its use in a battery is hopefully not required because of weight and environmental considerations.

Two tests were performed to confirm sodium reduction. Following the cathodic deposition of Na at -1.53 V, a fraction of the mercury electrode was removed from the molten salt cell and

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tested for the presence of metallic Na. When the Hg was placed in water, bubbles were observed due to the oxidation of Na to Na^+ and the reduction of water. The measured pH was ~ 13 , apparently due to formation of NaOH. A Varian Techtron Model 1200 Atomic Absorption Spectrophotometer (AA) was used to quantitatively measure the sodium in a 20 ml sample of water in which a measured fraction of the Hg electrode had been immersed. Two-thirds of the sodium anticipated from the plating coulombs was found. Some residual sodium in the amalgam is a possible source of error. A sample of the Hg electrode taken in the absence of plating current gave an insignificant AA response. Control experiments showed that if NaCl was absent from the melt, no cathodic peak was observed at -1.53 V and no anodic stripping peak was observed at -1.21 V. If NaCl was added to the melt but the potential of the Hg was held positive of -1.53 V, no reaction between the Hg and the water and no change in the color of the pH paper occurred.

These results indicate that the 47:45:8 (mole fraction) AlCl_3 -MEICl-NaCl may be suitable for the Na/FeCl₂ battery, reducing the operation temperature, eliminating the need for a beta"-alumina separator and allowing a solid sodium anode.

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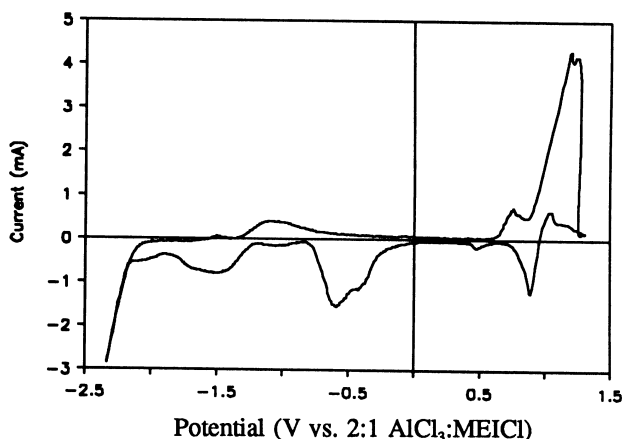


Figure 1. Cyclic voltammogram at Hg electrode for 47:45:8 AlCl_3 :MEICl:NaCl melt ($v=100$ Mv/sec). The melt temperature was 50°C .

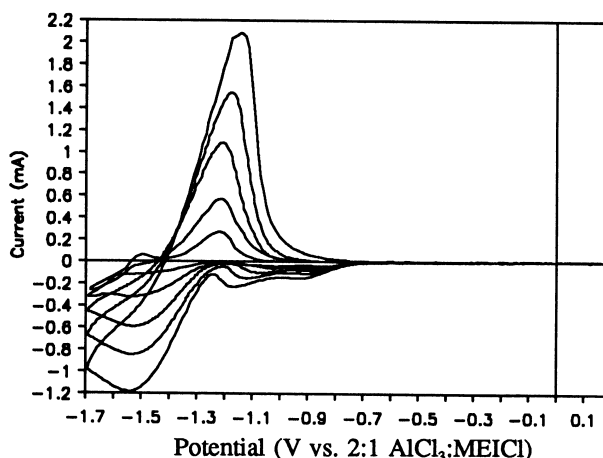


Figure 2. Cyclic voltammogram at Hg electrode for 47:45:8 AlCl_3 :MEICl:NaCl melt with different scan rates: (a) 200 mV/sec (b) 100 mV/sec (c) 50 mV/sec (d) 20 mV/sec (e) 10 mV/sec. The melt temperature was 50°C .

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