

The Role of Additives In the Electroreduction of Sodium Ions in Ionic Liquids

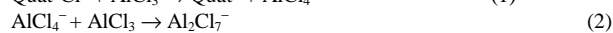
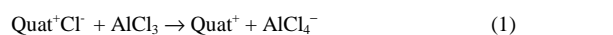
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The investigation of new electrolytes and materials for use in batteries is driven by the need for high-energy density, durable, low cost batteries. In order to meet these goals, an ionic liquid must provide a conductive environment in which the reduction and oxidation reactions at the anode and cathode can occur with high efficiency over a wide potential window.

Considerable work has been done in the investigation of sodium and lithium for use as the anode in batteries^{1,2,3}. Lithium-based anodes have been particularly successful, leading to the widespread implementation of lithium and lithium-ion batteries. Sodium is an appealing material for use in batteries due to its relative abundance, low cost, and absence of dendrites, especially if the metallic anode were compared to an intercalation one. The low atomic weight of sodium could also lead to a system with a high-energy density. The Zebra Cell, which utilizes sodium as an anode material, has demonstrated encouraging results⁴. However, the Zebra Cell operates at a high temperature that causes the sodium anode to be molten. A room temperature sodium battery analogous to the Zebra Cell is of interest.

Quaternary ammonium chloroaluminates (AlCl_4^-) have been investigated in place of NaAlCl_4 used in the Zebra Cell. Equations 1 and 2 show the acid-base reactions with quaternary ammonium salts (Quats) and AlCl_3 . The Lewis acid, AlCl_3 , forms AlCl_4^- (Lewis neutral) and Al_2Cl_7^- (Lewis acid) when mixed with the quaternary ammonium chloride, as shown in Equation 1 and 2. Neutralization of the Al_2Cl_7^- occurs by reacting Al_2Cl_7^- with a Lewis base (e.g. Cl^- from NaCl or Quat^+Cl^-) to produce neutral AlCl_4^- ions⁵ (Equation 3).



The make-up of the melts is shown in terms of the mole fraction of AlCl_3 , N . For example, neutral melts containing equal moles of AlCl_3 and Quat ($N = 0.5$) contain only the AlCl_4^- ions. Acidic melts contain an excess of AlCl_3 , $N > 0.5$, and form AlCl_4^- and Al_2Cl_7^- anions. Melts containing an excess of Quat, $N < 0.5$, are basic and contain AlCl_4^- and Cl^- anions.

Sodium chloride has been used to neutralize acidic melts and provide a source of sodium ions for electrodeposition of sodium metal. Excess sodium chloride is added to buffer the melt. The neutral melt has a wide potential window allowing sodium plating and stripping to occur.

The anodic half cell reaction is monitored on a Pt or a W (tungsten) electrode.



However, in order to electrodeposit sodium, an additive is required, such as, HCl or SOCl_2 ^{3,6}. The role of the additive is not fully understood. The aim of this work is to investigate the role of the additive in the electrodeposition of sodium.

In a neutral melt, sodium ions can precipitate as NaAlCl_4 or NaCl . Since the solubility of NaCl in the melt is very low⁷, NaAlCl_4 is the primary source of Na^+ for deposition of the larger anion due to its higher solubility. Without the addition of a trace of acid, no sodium deposition is observed. In this paper we suggest the added acid interacts with the Na^+ -anion complex freeing the Na^+ for electroreduction. Without the acid additive, no sodium ions are available for deposition due to ion pairing.

In our work, benzyldimethylethylammonium chloride was made and utilized for the investigation.

Figure 1 shows the conductivity vs. weight % of SOCl_2 . The SOCl_2 was added to the neutral melt. In the figure, we observe 6% conductivity increase by adding 1 % of the additive. We believe that the additive interact with NaAlCl_4 to release some available Na^+ for the electroplating. Figure 2 describes the interactions between the NaAlCl_4 and the additives. From our work, we have found that there is no available free sodium ion for the electroplating without an additive. Additional conductivity and cyclic voltammetry measurements are supporting the strong ionic interaction (coulombic interaction) between two species.

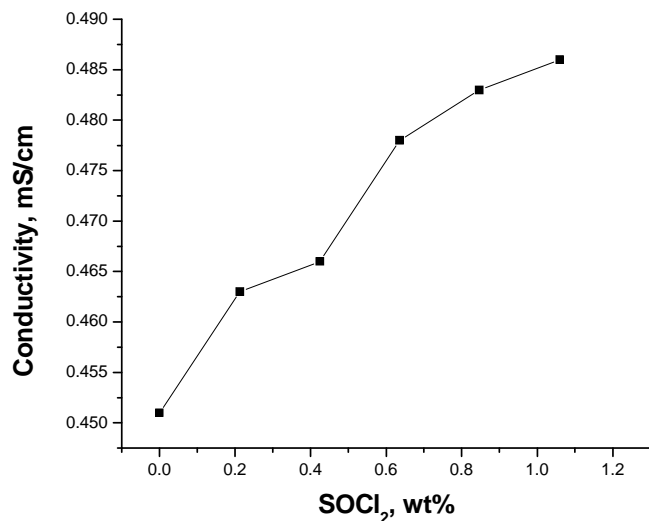
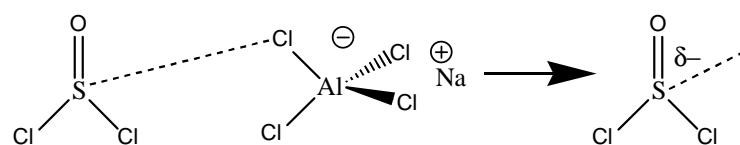


Figure 1. Conductivity at 30°C versus weight % SOCl_2 for an initial mixture of 50% AlCl_3 , 40.9% BDMEACl , and 9.1% NaCl .

(A)



(B)

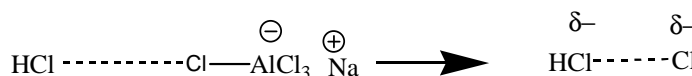


Figure 2. Interaction between additives and NaAlCl_4 ion.

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