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LITHIUM BATTERIES SESSION .

CYCLIC VOLTAMMETRIC STUDIES IN LITHIUM TETRACHLOROALUMINATE-THIONYL CHLORIDE SOLUTIONS

(10) Wishvender K. Behl
Power Sources Technical Area
US Army Electronics Technology
and Devices Laboratory (ECOM)
Fort Monmouth, New Jersey 07703

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Introduction

Solutions of lithium tetrachloroaluminate ($LiAlCl_4$) in thionyl chloride ($SOCl_2$) have been recently employed as electrolytes for high energy density lithium battery systems.[1,2] In these battery applications, thionyl chloride serves the dual role of an electrolyte carrier as well as an active cathodic depolarizer because of its ability to undergo electrochemical reduction. In the present studies the voltammetric behavior of thionyl chloride in 1.5 molar $LiAlCl_4$-$SOCl_2$ solutions was examined at glassy carbon microelectrodes using the technique of cyclic voltammetry.

Thionyl chloride, like other oxychloride solvents, ionizes as:[3,4]

$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^- \qquad (1)$$

Covalent metal chlorides, such as aluminum chloride, are highly soluble[4] in thionyl chloride and behave as Lewis acids because of their tendency to form complex ions,

$$AlCl_3 + SOCl_2 \rightleftharpoons SOCl^+ + AlCl_4^- \qquad (2)$$

Lithium chloride, on the other hand, is only slightly soluble[4] in thionyl chloride but readily dissolves to neutralize acidic $AlCl_3$-$SOCl_2$ solutions, i.e.,

$$LiCl + SOCl^+ \rightleftharpoons Li^+ + SOCl_2 \qquad (3)$$

Solutions of lithium tetrachloroaluminate are, however, not strictly neutral from the standpoint of chloroacidity but, analogous to $LiClO_4$ and $LiBCl_4$ solutions[5,6] in phosphorous oxychloride, would behave as weak chloroacid through its Li^+ ions and as weak chlorobase through its $AlCl_4^-$ ions.

Experimental

The preparation and purification of thionyl chloride and lithium tetrachloroaluminate have been described in detail elsewhere.[1] Briefly stated, thionyl chloride was refluxed over lithium and distilled. Lithium tetrachloroaluminate was prepared by melting an equimolar mixture of anhydrous lithium chloride (Fisher Scientific) and aluminum chloride (Fluka, AG) in a flowing atmosphere of hydrogen chloride gas. The treatment with hydrogen chloride gas was followed by bubbling chlorine gas for 2-3 hours. The excess of hydrogen chloride gas and chlorine gas was removed by bubbling argon and the molten mixture solidified by gradual cooling. Lithium tetrachloroaluminate, so obtained, was stored in a dry argon atmosphere.

A three electrode system was used for all cyclic voltammetric experiments. A 0.38 mm thick lithium ribbon (Foote

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Mineral Company) pressed onto a nickel screen was used as the reference electrode. The reference electrode was contained in a 10 mm diameter pyrex tube with a fritted glass bottom. A cylindrical platinum screen (3.18 x 3.18 cm; 52 mesh) electrode was used as the counter electrode. The indicator electrode consisted of a 3.18 mm diameter glassy carbon electrode (Beckwith Carbon Company) heat sealed in a shrinkable Teflon tubing and the end ground flush with the seal so as to expose the cross section of the rod. The indicator electrodes were polished to a mirror finish using 0.3 μ m size powdered alumina.

The cyclic voltammetric scans were performed with a Tacussel Model PIT 20-2A potentiostat coupled with a Tacussel GSTP-2A function generator. The current flowing through the cell was measured across a precision resistor in the counter electrode circuit. The i-E curves were recorded on a Moseley XY Recorder (Model 7000A). All experiments were performed inside a Dry-Train, Dry-Lab (Vacuum Atmosphere Corporation) in a pure dried argon atmosphere.

To obtain reproducible voltammograms, it was necessary to clean the indicator electrode after each scan. This was accomplished[7] by dipping the electrode in an acidic 1.5M $AlCl_3$-$SOCl_2$ solution followed by washing with thionyl chloride and carbon tetrachloride. The electrode was then wiped clean with a Kimwipe tissue paper. The electrode could also be regenerated, in situ, by electrogenerating chlorine at the indicator electrode at a potential of 4.5* volts for 2-3 minutes. The dissolved chlorine in the solution was removed by bubbling argon gas before taking the next voltammogram.

RESULTS AND DISCUSSION

Electrochemical Reduction of Thionyl Chloride in $LiAlCl_4$-$SOCl_2$ Solutions

A typical cyclic voltammogram obtained in a 1.5M $LiAlCl_4$-$SOCl_2$ solution by scanning the electrode from +4 to 0 V at a scan rate of 0.1 V/s is shown in Figure 1. The voltammogram shows a large reduction peak (peak I) beginning at ~ 3 V followed by an almost indiscernible reduction peak (peak II) at ~ 1.6 V before a rapid increase in cathodic current is observed at ~ 0.5 V due to the deposition of lithium metal. On reversing the direction of polarization at 0 V, two small anodic peaks (peak III and IV) are observed at ~0.5 V and 2.3 V, respectively. The anodic peak III is not observed if the direction of polarization is reversed at potentials positive to the lithium deposition potential. Thus, the anodic peak III may be ascribed to the dissolution of the deposited lithium metal.

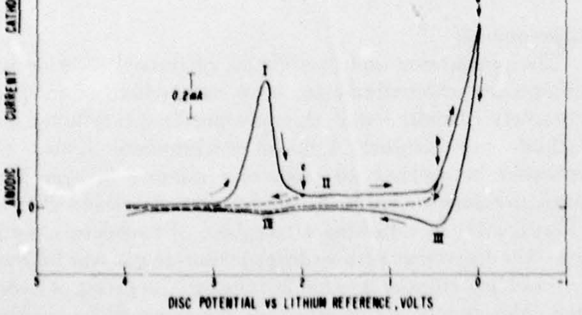

Figure 1. Cyclic voltammograms obtained at glassy carbon microelectrodes for the reduction of thionyl chloride in 1.5 molar $LiAlCl_4$-$SOCl_2$ solutions.

The reduction peaks I and II may be regarded due to the electrochemical reduction of thionyl chloride. It is seen from the cyclic voltammograms presented in Figure 1 that while a corresponding anodic peak (peak IV) is observed for reduction peak II, no corresponding anodic peak is observed for reduction peak I.

At the end of reduction peak I, the glassy carbon microelectrode was found to be passivated due to the deposition of a thin film of an insoluble substance. Thus, any successive voltammograms obtained on the same electrode resulted in a large decrease in the peak heights for reduction peak I. To obtain reproducible voltammograms, it was necessary to remove the passivating film after each scan as described in the Experimental Section.

In order to determine the nature of the passivating film formed on the microelectrode, a platinum foil was substituted as the indicator electrode and its potential held at ~ 2.5 V for about ten hours. The platinum foil was then removed and washed with thionyl chloride and carbon tetrachloride and subjected to an Electron Microprobe Analysis. From this analysis it was concluded that the passivating film consists solely of lithium chloride.

The electrochemical reduction of thionyl chloride was first studied by Spandau et al.[8] It was reported by these workers that the cathodic products, obtained by the electrolysis of 0.14 molar $(C_2H_5)_3$ $NHCl$-$SOCl_2$ solution, were temperature dependent. However, at temperatures above 0° C, the cathodic products predominantly consisted of SO_2, Cl_2, and S_2Cl_2. In $LiAlCl_4$-$SOCl_2$ solutions, the cathodic reduction products are somewhat different than those obtained in $(C_2H_5)_3$ $NHCl$-$SOCl_2$ solutions.

Thus, from a study of the discharged lithium-thionyl chloride cells of the type

$$Li / LiAlCl_4 - SOCl_2 / \text{Carbon Black}$$

Auborn et al.[2] concluded that the cathodic reduction products consisted of lithium chloride, lithium sulfite, and sulfur and proposed the following cell reaction

$$8\,Li + 3\,SOCl_2 \longrightarrow 6\,LiCl + Li_2SO_3 + 2\,S \qquad (4)$$

On the other hand, Holleck et al.[9] reported that the reaction products in the discharged lithium-thionyl chloride cells mainly consist of lithium chloride, sulfur, and sulfur dioxide and proposed the following cell reaction

$$4\,Li + 2\,SOCl_2 \longrightarrow 4\,LiCl + S + SO_2 \qquad (5)$$

Both sulfur and sulfur dioxide were found to be soluble in $LiAlCl_4$-$SOCl_2$ solutions, whereas lithium chloride, being insoluble, precipitated exclusively in the carbon electrodes. These workers further reported that for each equivalent of

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*All potentials are reported with respect to the lithium reference electrode.

charge passed, one equivalent of LiCl is produced in the discharged carbon cathodes. This observation is consistent only with the cell reaction represented by Equation (5). A cell reaction identical to Equation (5) was also proposed by Dey and Schlaikjer.[10]

Since the passivating film on the microelectrodes in the present studies was also found to consist of lithium chloride only, it is reasonable to assume that the cathodic reduction products are identical to those found by Holleck et al.[9] The electrochemical reduction of thionyl chloride may, therefore, be represented by the equation

$$2\,SOCl_2 + 4\,Li^+ + 4\,e \longrightarrow 4\,LiCl + S + SO_2 \qquad (6)$$

Since no anodic peak is observed corresponding to the reduction peak I, it is apparent that the reduction of $SOCl_2$ in $LiAlCl_4$-$SOCl_2$ solutions does not occur reversibly. Thus, the peak and half-peak potentials for reduction peak I are not independent of scan rate but instead shift to less positive potentials with increasing scan rate. The difference between the peak and half-peak potentials is also much greater than that expected[11] for the reversible process leading to the deposition of an insoluble substance. However, since the deposition of lithium chloride on the glassy carbon microelectrodes during the voltammograms introduces iR effects which are similar[12,13] to kinetic effects, it is not possible to determine the kinetic parameters of the charge transfer process from the recorded voltammograms.

The other reduction peak (peak II) in Figure 1 may be ascribed to the reduction of sulfur or sulfur dioxide. Both sulfur and sulfur dioxide are formed as products of thionyl chloride reduction as shown in Equation (6). Since the cyclic voltammograms exhibit an anodic peak (peak IV) corresponding to reduction peak II, it is evident that the reduction product of sulfur or sulfur dioxide can be reoxidized at more positive potentials.

Electrochemical Oxidation of Thionyl Chloride in $LiAlCl_4$-$SOCl_2$ Solutions

Typical cyclic voltammograms for the oxidation of thionyl chloride in $LiAlCl_4$-$SOCl_2$ solutions are presented in Figure 2. These voltammograms were obtained by scanning the electrode from +3.0 to +5.0V and from +3.0 to +4.5V, respectively. Both voltammograms show a sharp increase in the anodic current at ~4.1 V and exhibit a reduction peak beginning at ~3.6 V on the reverse scan. If the potential of scan reversal is greater than 4.5 V, a small break is observed in the anodic current at ~4.6 V. The height of the reduction peak depends largely on the potential of scan reversal, i.e., the peak height increases as the potential of scan reversal is made more positive. The reduction peak in these voltammograms is not observed if the direction of polarization is reversed prior to the onset of the anodic current.

The reduction peak V in this voltammogram (Figure 2) was identified as due to the reduction of chlorine by studying the chlorine solution in $LiAlCl_4$-$SOCl_2$. A typical cyclic voltammogram, obtained at glassy carbon microelectrode in a dilute solution of chlorine in 1.5M $LiAlCl_4$-$SOCl_2$, is presented in Figure 3. Except for the additional reduction peak (peak V) at ~3.25 V, the cyclic voltammogram in Figure 3 is similar to the cyclic voltammogram obtained in chlorine free 1.5M $LiAlCl_4$-$SOCl_2$ solution (Figure 1). The reduction peak V is, therefore, due to reduction of chlorine which may be represented by the equation[5,6]

$$Cl_2 + 2Li^+ + 2e \longrightarrow 2LiCl \qquad (7)$$

The reduction peak V in Figure 3 increases with increasing chlorine concentration and in concentrated solutions overlaps with the thionyl chloride reduction peak (peak I).

Since the reduction peak in the voltammograms presented in Figure 2 occurs at the same potential as the chlorine reduction peak in Figure 3, the sharp increase in the anodic

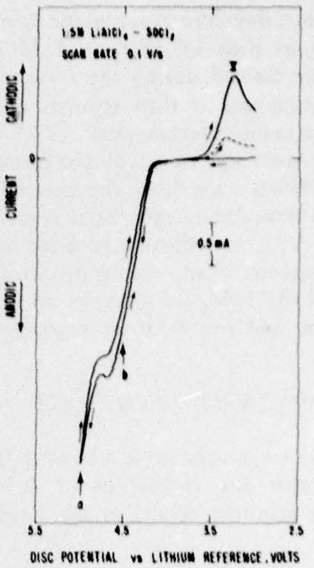

Figure 2. Cyclic voltammograms obtained at glassy carbon microelectrodes for the oxidation of thionyl chloride in 1.5 molar $LiAl_4$-$SOCl_2$ solutions.

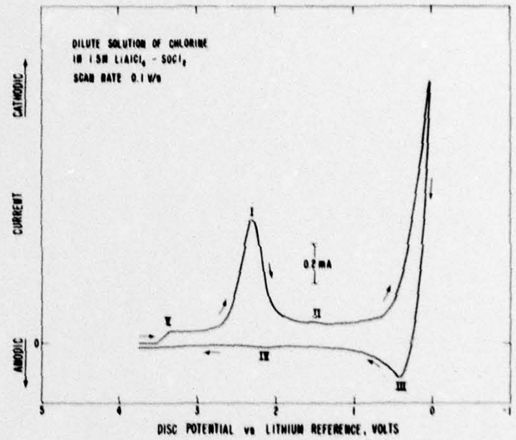

Figure 3. Cyclic voltammograms obtained at glassy carbon microelectrodes in a dilute solution of chlorine in 1.5 molar $LiAlCl_4$-$SOCl_2$.

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current at ~4.1 V must, therefore, result in the formation of chlorine. Because of its high solubility in $LiAlCl_4$-$SOCl_2$ solutions, the chlorine formed during the forward scan is retained in the solution and is then reduced during the reverse scan giving rise to the reduction peak ~3.25 V at scan rates >0.01 V/s. At lower scan rates, chlorine formed at the indicator electrode diffuses away from the electrode and is not available for reduction during the reverse scan. Thus, at scan rates of <0.01 V/s, no reduction peak is observed in the cyclic voltammograms. Thus, the electro-oxidation of thionyl chloride in $LiAlCl_4$-$SOCl_2$ solutions results in the formation of chlorine and the electrode reaction may be represented as

$$2\,SOCl_2 + 2\,AlCl_4 \longrightarrow 2\,SOCl^+\ AlCl_4^- + Cl_2 + 2\,e \qquad (8)$$

The above conclusions are in agreement with Spandau et al.[8] who also reported that the electrolysis of 0.14 molar $(C_2H_5)_3NHCl$-$SOCl_2$ solutions results in the formation of chlorine at the anode.

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