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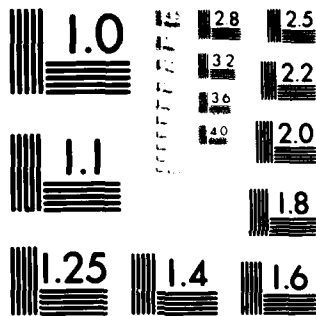
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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

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**ELECTROCHEMICAL BEHAVIOR OF COPPER IN THIONYL CHLORIDE
SOLUTIONS**

**Wishvender K. Behl
ELECTRONICS TECHNOLOGY & DEVICES LABORATORY**

December 1980

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The electrochemical and chemical behavior of copper and copper chlorides was studied in 1.5 molar $\text{LiAlCl}_4\text{-SOCl}_2$ solutions using cyclic voltammetric, controlled potential electrolysis and x-ray techniques. It was shown that copper metal reacts with thionyl chloride even at ambient temperatures resulting in the formation of cuprous chloride and cupric sulfide. In $\text{LiAlCl}_4\text{-SOCl}_2$ solutions, cuprous chloride is further oxidized, chemically as well as electrochemically, to cupric chloride. Cupric chloride was found to be electroactive in these solutions and undergoes reduction in the solid state			

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to cuprous chloride and copper, respectively. It was also found that due to the presence of copper chloride films at the copper metal electrode in these solutions, the electrochemical reduction of thionyl chloride at copper electrodes occurs at more negative potentials than observed at carbon electrodes.

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ELECTROCHEMICAL BEHAVIOR OF COPPER IN THIONYL CHLORIDE SOLUTIONS

INTRODUCTION

Copper metal has been recently used as a cathode additive¹ to enhance the performance of lithium-thionyl chloride batteries. Thionyl chloride is known^{2,3} to react rapidly with a number of metals at high temperatures and more slowly at ambient temperatures but the chemical literature is devoid of any information on the reaction of copper metal with thionyl chloride. Further, to-date, no studies have been reported on the electrochemical behavior of copper metal in thionyl chloride solutions. Therefore, we have investigated the chemical, as well as electrochemical, behavior of copper metal in 1.5 molar LiAlCl_4 - SOCl_2 solutions using the cyclic voltammetric technique and x-ray analysis. This report summarizes our results.

EXPERIMENTAL PROCEDURES

The preparation and purification of thionyl chloride (SOCl_2) and lithium tetrachloroaluminate (LiAlCl_4) have been described in detail elsewhere.⁴ A three electrode system was used for all cyclic voltammetric experiments. The reference (1 x 5 cm) and counter (3.5 x 6 cm) electrodes were both made by pressing lithium ribbon (0.38 mm thick; Foote Mineral Company) onto a nickel screen. The reference electrode was contained in a Pyrex tube (10 mm diam) with a coarse porosity fritted glass bottom. Both the reference and counter-electrodes were thoroughly washed with carbon tetrachloride followed by washing with thionyl chloride before use. The working electrode was fabricated by machining a piece of pure copper rod (m5N+ purity, Alfa Division, Ventron Corporation) to 4.064 mm diameter and threading it to another copper rod of unknown purity. The electrode was then heat sealed in a shrinkable teflon tubing and the end ground flush with the seal so as to expose the cross section of the pure copper rod.

The copper electrodes were mechanically polished on crocus cloth and soft paper before recording each voltammogram. The cross section area of the copper electrode was 0.13 cm². For controlled potential electrolysis experiments, a strip of pure copper metal foil (m5N purity; Alfa Division, Ventron Corporation, 1 x 5 cm; 0.127 mm thick) was used as the working electrode.

All experiments were performed inside a dry-train, dry-lab (Vacuum Atmospheres Corporation) in a pure, dried, argon atmosphere. Other experimental details were similar to those described previously.⁵⁻⁷

¹L. R. Giattino, US Patent 4,167,608, September 11, 1979.

²J. W. Mellor, A Comprehensive Treatise of Inorganic and Theoretical Chemistry, Vol. 10, Longmans, Green, and Co., London, 1930.

³M. Davis, H. Szkuta, and A. J. Krubsack, Mechanisms of Reactions of Sulfur Compounds, pp. 4-57, Vol. 5, Intra-Science Research Foundation, Santa Monica, California, 1970.

⁴W. K. Behl, J. A. Christopoulos, M. Ramirez, and S. Gilman, J. Electrochem. Soc., **120**, 1619 (1973).

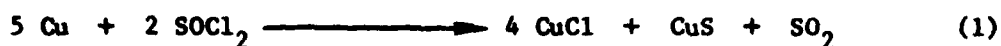
⁵W. K. Behl, J. Electroanal. Chem., **70**, 213 (1973).

⁶W. K. Behl, "Cyclic Voltammetric Studies in Lithium Tetrachloroaluminate-Thionyl Chloride Solutions," Proc. 27th Power Sources Symposium, p. 30 (1976).

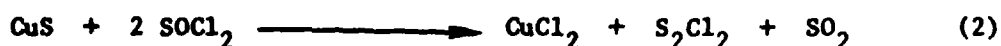
⁷W. K. Behl, J. Electroanal. Chem., **101**, 367 (1979).

RESULTS AND DISCUSSION

Thionyl chloride was found to react with copper metal even at room temperature resulting first in the formation of a black film followed by its complete disintegration in a few days. X-ray analysis of the product indicated it to be mainly cuprous chloride (CuCl). However, the product was only partially soluble in hydrochloric acid and left behind a small residue after a number of washings with hydrochloric acid. The hydrochloric acid solution was analyzed and gave positive tests⁸ for cuprous chloride. The black residue was analyzed⁹ and found to be cupric sulfide (CuS). The reaction of copper with thionyl chloride at ambient temperatures may, therefore, be represented by the equation:

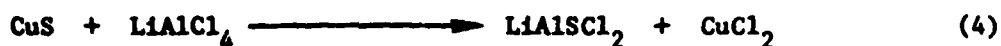
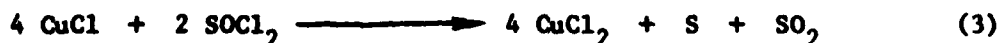


Cupric sulfide is known^{10,11} to react with thionyl chloride at 150°C according to the equation:



However, it appears that this reaction (Equation (2)) does not occur significantly at ambient temperatures.

In $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions, a black film is formed on the copper metal first, but it rapidly transforms into a yellow film. After a few hours, the copper metal foil covered with the yellow film was removed, washed with thionyl chloride, and vacuum dried. The yellow film was identified by x-ray analysis to be cupric chloride (CuCl_2). Therefore, it appears that in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions, both cuprous chloride and cupric sulfide are at least partially converted to cupric chloride. The reactions may be represented by equations:



A reaction similar to Equation (4) has been shown to occur¹² between lithium sulfide and lithium tetrachloroaluminate in thionyl chloride solutions. Lithium thiocloroaluminate (LiAlSCl_2) is soluble in thionyl chloride and has been proposed¹³ as a new electrolyte for lithium-thionyl chloride batteries.

⁸R. K. McAlpine and B. A. Soule, Prescott and Johnson's Qualitative Chemical Analysis, D. Van Nostrand Co., Inc., New York, 1933.

⁹J. W. Mellor, A Comprehensive Treatise of Inorganic and Theoretical Chemistry, Vol. 3, Longmans, Green, and Co., London, 1930.

¹⁰J. W. Mellor, *ibid.*

¹¹H. B. North and C. B. Conover, *J. Amer. Chem. Soc.*, **37**, 2486 (1915).

¹²K. M. Abraham, R. M. Mank, and G. L. Holleck, "Investigations of the Safety of Li/SOCl_2 Batteries," Final Report, Contract DAAB07-78-C-0564 (ERADCOM), EIC Corporation, February 1980.

¹³K. M. Abraham, et al., *ibid.*

The reactions of cuprous chloride and cupric sulfide in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions were independently confirmed by treating reagent grade samples with 1.5 molar solutions. While the cuprous chloride sample was completely converted to brown cupric chloride in a few hours, the reaction of cupric sulfide was much slower and only a part of the black cupric sulfide sample was converted to brown cupric chloride. The specific role of lithium tetrachloroaluminate in these reactions, however, needs to be further investigated.

The copper metal electrode momentarily exhibited an open circuit potential* of ~ 2.9 V when first introduced in 1.5 molar $\text{LiAlCl}_4 - \text{SOCl}_2$ solution, but the potential quickly increased to ~ 3.36 V. This increase in open circuit potential can be explained by the chemical transformation of the original mainly cuprous chloride film to cupric chloride film as discussed above. Thus, the copper electrode assumed the $\text{Cu(I)}-\text{Cu(0)}$ couple potential when first introduced in $\text{LiAlCl}_4 - \text{SOCl}_2$ solution but as some of the cuprous chloride film was chemically converted to cupric chloride, the electrode assumed a mixed potential involving the two processes.

A typical cyclic voltammogram at the copper electrode obtained by scanning it in the anodic direction from 3.3 V to 5.8 V at a scan rate of 0.09 V/s is shown in Figure 1. The cyclic voltammogram shows an increasing anodic current as the potential becomes more positive and exhibits an anodic peak at ~ 3.63 V. After the anodic peak, the electrode is passivated due to the formation of a yellow film on the electrode surface. Thus, due to the passivation of the electrode, the cyclic voltammogram does not show the anodic peaks for the oxidation of $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions which are observed^{14,15} at glassy carbon electrodes at potentials above 4.0 V. The electrode remains passivated during the reverse scan till the onset of a reduction process at ~ 3.55 V.

Cyclic voltammograms similar to those presented in Figure 1 were obtained at scan rates of 0.01 to 1.0 V/s and the anodic peak height increased with increasing scan rate.

Controlled potential electrolysis of a strip of copper foil at 4.0 V for 16 hours resulted in the formation of a thick yellow film. After the electrolysis, the copper foil covered with the yellow film was removed, repeatedly washed with thionyl chloride and vacuum dried. The yellow film was then identified as cupric chloride (CuCl_2) by x-ray analysis.

Thus, the anodic peak at ~ 3.63 V in the cyclic voltammogram presented in Figure 1 may be assigned to the oxidation of cuprous chloride to cupric chloride.



¹⁴W. K. Behl, Proc. 27th Power Sources Symposium, op. cit., p. 1

¹⁵K. M. Abraham, et al., op. cit., p. 2.

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

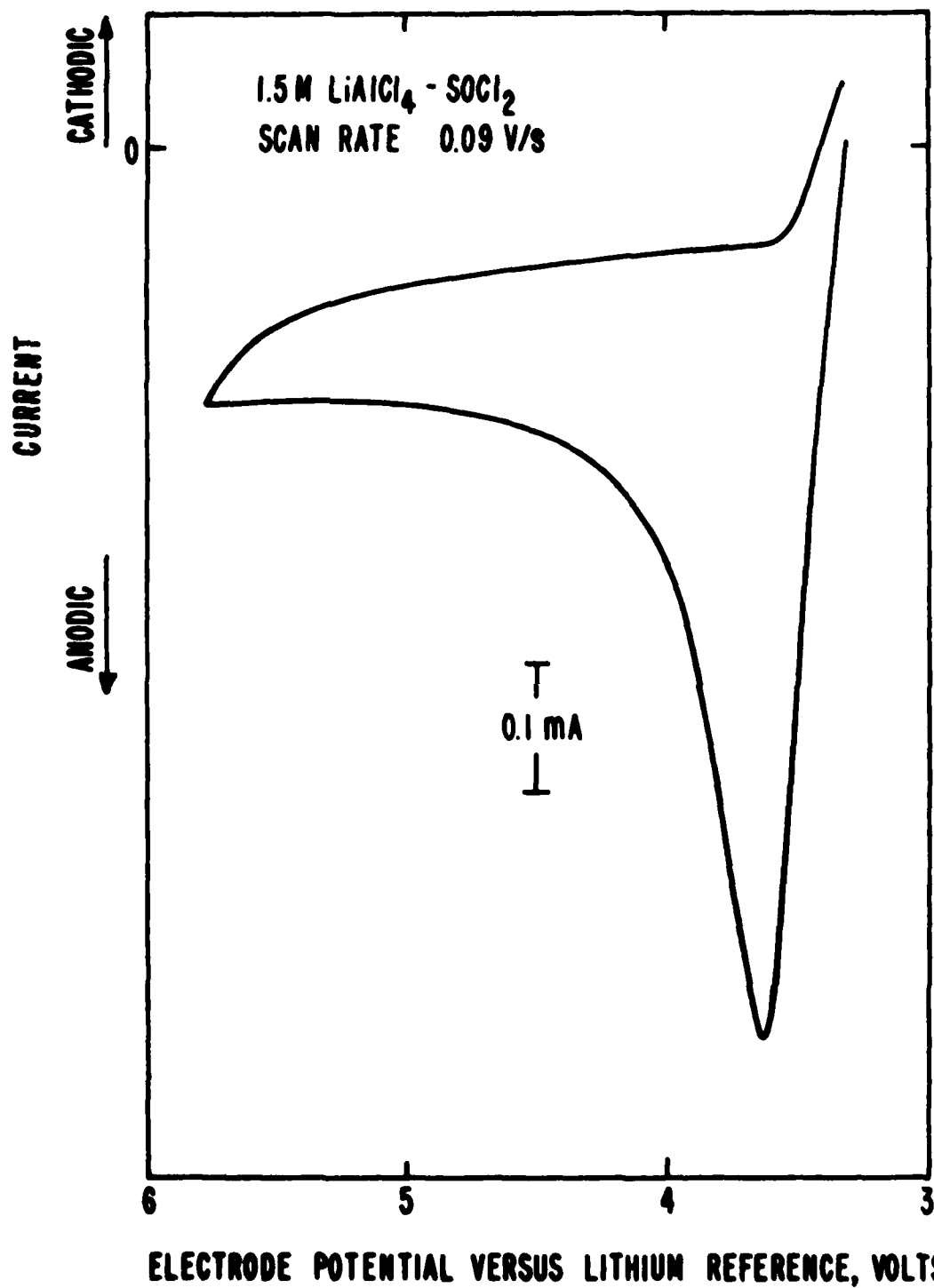


Figure 1. Typical Cyclic Voltammogram at Copper Electrode Between 3.3 and 5.8 Volts

The anodic peak height in these voltammograms was found to depend to a large extent on the time for which the electrode was held at open circuit before recording the cyclic voltammograms. Thus, as the time interval was increased, a larger part of the cuprous chloride film converted chemically to cupric chloride (Equation (2)) so that only a smaller anodic peak, due to the electrochemical oxidation of cuprous chloride to cupric chloride, was observed.

In the next series of experiments, the copper metal electrode was held at 4.0 V for a few minutes before recording the cyclic voltammograms in the cathodic direction. A large anodic current was initially observed at 4.0 V due to the formation of cupric chloride but it quickly decreased to a small steady state anodic current. A typical cyclic voltammogram obtained by scanning the copper electrode from 4.0 V to 2.0 V at a scan rate of 0.05 V/s is shown in Figure 2. The cyclic voltammogram shows two reduction peaks at ~ 2.7 V and ~ 2.1 V and corresponding anodic peaks are observed at ~ 3.7 V and ~ 2.9 V, respectively, during the reverse scan. If the copper electrode is scanned to 2.5 V, only the reduction peak at ~ 2.7 V and the corresponding oxidation peak at ~ 3.7 V are observed in the cyclic voltammograms. Similar cyclic voltammograms were obtained at scan rates of 0.01 V/s to 0.1 V/s. At higher scan rates, the reduction peak at ~ 2.1 V was indistinguishable and only one large anodic peak was observed during the reverse scan.

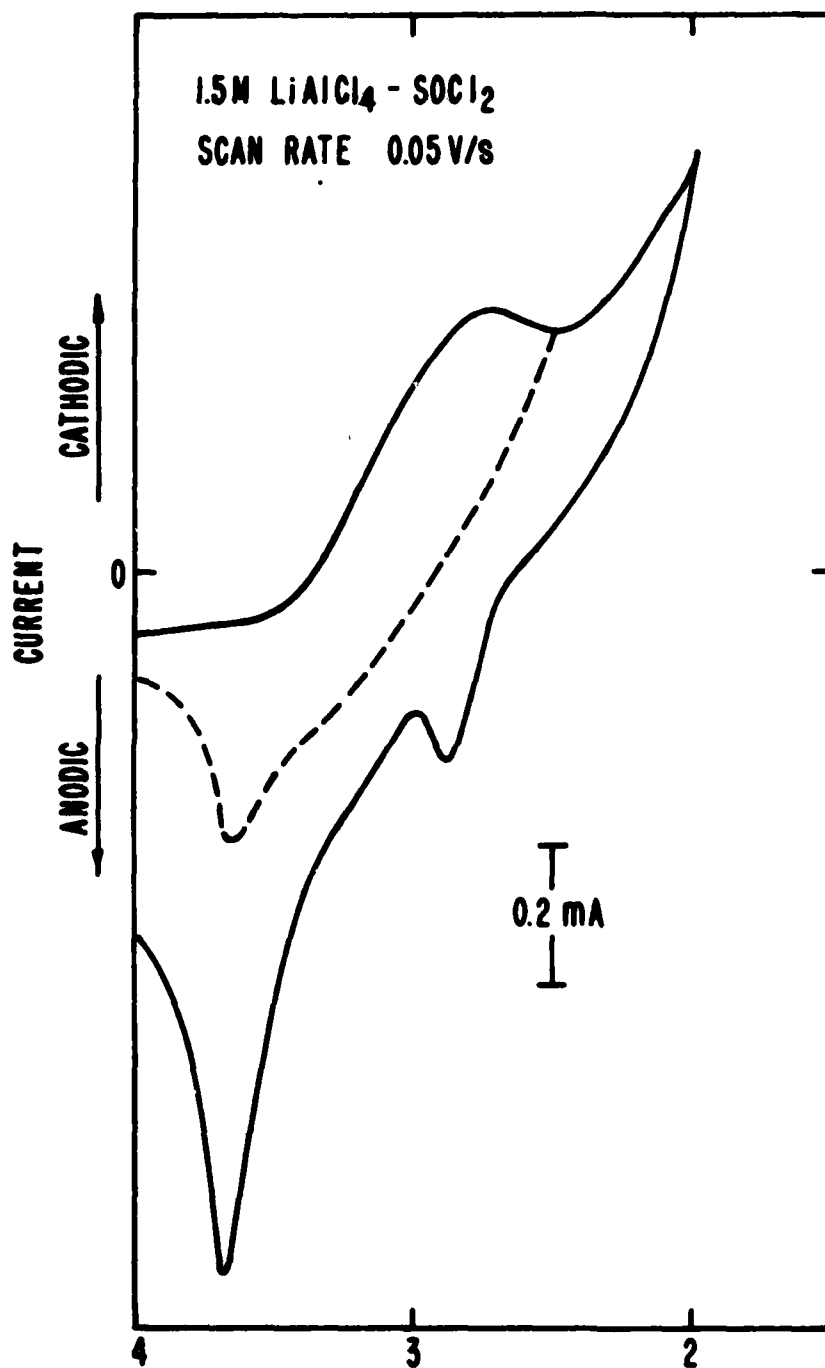
Controlled potential electrolysis of a strip of pure metal foil at 2.75 V for ~ 16 hours resulted in a thick light blue film on the metal surface. The copper metal foil was removed, washed with thionyl chloride, and vacuum dried. The light blue film was identified as cuprous chloride (CuCl) by x-ray analysis. Thus, the reduction peak in the cyclic voltammograms at ~ 2.7 V (Figure 2) may be ascribed due to the reduction of cupric chloride to cuprous chloride according to the equation:



and the corresponding anodic at ~ 3.7 V to the oxidation of cuprous chloride to cupric chloride according to Equation (5) as discussed above.

During the course of these experiments, it was noticed that a thin layer of metallic copper deposited on the lithium counterelectrode. Since cupric chloride was found to have negligible solubility in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions, it appears likely that during the reduction of cupric chloride to cuprous chloride, part of cupric chloride complexes with chloride ions and goes into solution as CuCl_4^{--} ions. A similar explanation was offered by Rao¹⁶ to account for the increased solubility of cuprous chloride during discharge in LiAlCl_4 -propylene carbonate solutions. Copper metal is then plated on the lithium counterelectrode by the reaction of lithium metal with CuCl_4^{--} ions in solutions.

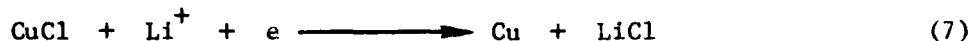
¹⁶M. L. B. Rao, J. Electrochem. Soc. 114, 13 (1967).



ELECTRODE POTENTIAL VERSUS LITHIUM REFERENCE, VOLTS

Figure 2. Typical Cyclic Voltammogram at Copper Electrode Between 4.0 and 2.0 Volts

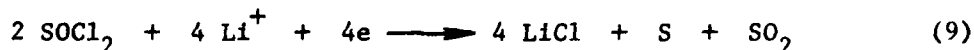
Controlled potential electrolysis of copper metal foil electrodes at a potential of 1.5 V resulted only in a lithium chloride film free of any cuprous chloride. The reduction peak at ~ 2.1 V in the cyclic voltammograms may, therefore, be ascribed to the reduction of cuprous chloride to copper metal;



and the corresponding anodic peak at ~ 2.9 V to the oxidation of copper metal to cuprous chloride according to the equation:



Cyclic voltammograms were also recorded by scanning the copper electrodes to more negative potentials and a typical cyclic voltammogram between 4.0 V and -0.35 V at a scan rate of 0.05 V/s is presented in Figure 3. In addition to the cathodic peaks for the reduction of cupric chloride and cuprous chloride at ~ 2.7 V and ~ 2.1 V, respectively, these voltammograms also exhibit other reduction peaks at more negative potentials. Thus, as soon as some cuprous chloride is reduced to copper metal, the cathodic current rapidly increases at ~ 2.0 V due to the simultaneous reduction of thionyl chloride at bare copper metal surface and a large reduction peak is observed at ~ 1.6 V in the cyclic voltammograms. Thus, the reduction of thionyl chloride at the copper surface occurs at more negative potentials than observed at carbon electrodes.¹⁷⁻²⁰ At more positive potentials, the copper electrode surface is covered with copper chloride films which block the reduction of thionyl chloride. As soon as the copper chloride films are reduced, the copper metal surface becomes available for the reduction of thionyl chloride. The reduction of thionyl chloride may be represented by the generally accepted equation:



Due to high background currents at copper electrodes in the potential region of 1 to 2 Volts, other minor reduction peaks observed at carbon electrodes in this potential region are not discernible in the cyclic voltammograms. At more negative potentials (~ -0.25 V), a large increase in cathodic current is observed due to the deposition of lithium metal. On the reverse scan, an anodic peak for the dissolution of deposited lithium metal is observed at ~ 0.15 V and at more positive potentials, a minor oxidation peak is observed at ~ 1.9 V followed by the anodic peaks for the oxidation of copper to cuprous chloride at ~ 2.95 V and cuprous chloride to cupric chloride at ~ 3.7 V, respectively.

¹⁷W. K. Behl, J. Electroanal. Chem., 70, op. cit., p. 1.

¹⁸K. M. Abraham, et al., op. cit., p. 2.

¹⁹G. E. Blomgren, V. Z. Leger, M. L. Kronenberg, T. Kalnoki-Kis, and R. J. Brodd, "Projected Mechanism for Thionyl Chloride and Sulfuryl Chloride Cathode Reactions," Proc. 11th International Power Sources Symposium, p. 583, Brighton, England (1978).

²⁰YU. M. Povarov, T. D. Nikolaeva, and V. S. Bagotskii, Soviet Electrochemistry, 14, 732 (1978).

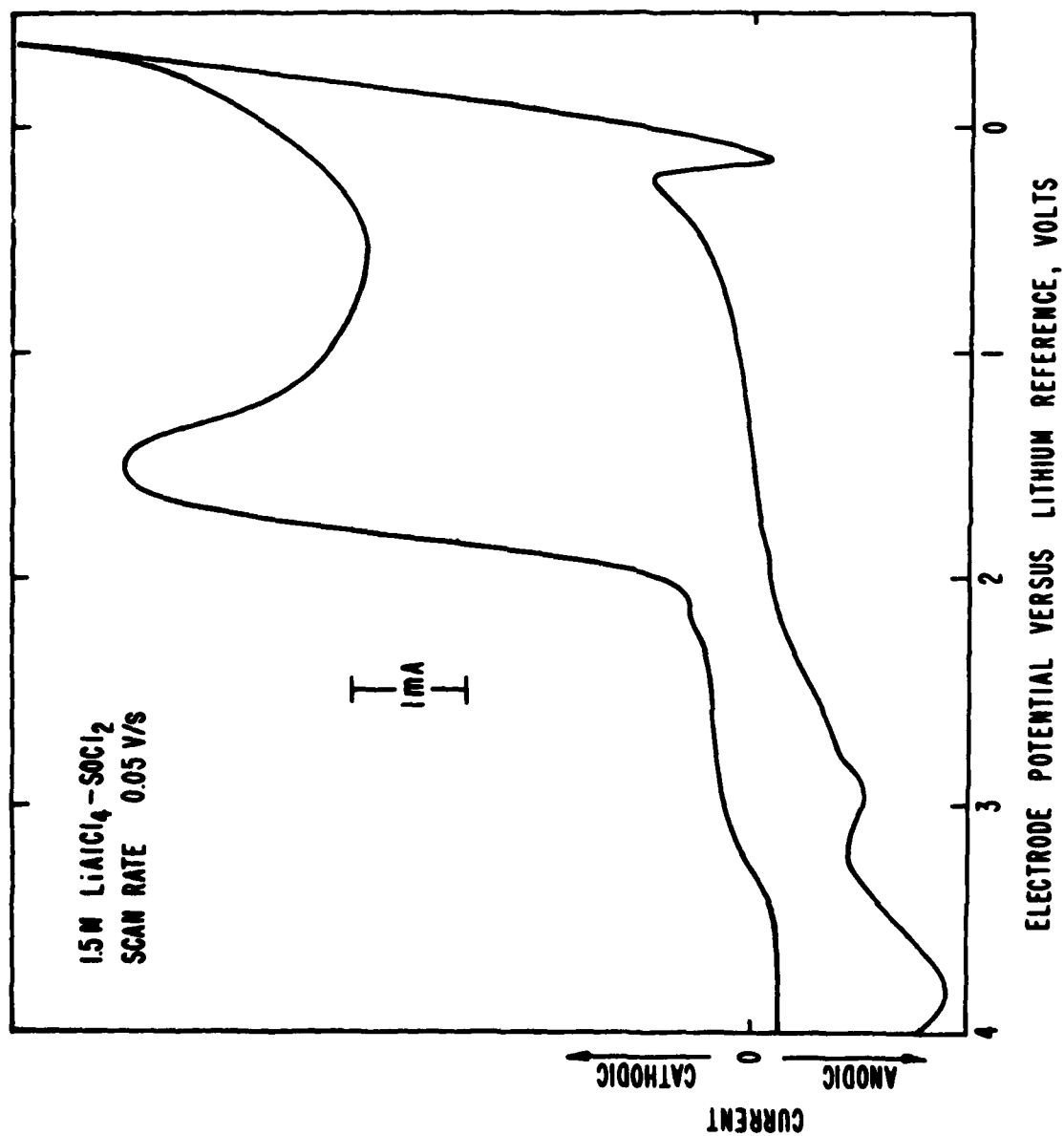


Figure 3. Typical Cyclic Voltammogram at Copper Electrode Between 4.0 and -0.35 Volts

Cyclic voltammograms similar to those presented in Figure 3 are observed at scan rates of 0.01 to 0.1 V/s. At higher scan rates, the cuprous chloride reduction peak merges with the thionyl chloride reduction peak.

CONCLUSIONS

The results of the present study have shown that copper metal reacts with thionyl chloride in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions to form cuprous chloride which in turn is converted to cupric chloride. Cupric chloride was found to be electroactive in these solutions and undergoes electrochemical reduction in the solid state to cuprous chloride at ~ 3.55 Volts versus the lithium reference. Since the reduction of cupric chloride occurs at about similar potentials as the reduction of thionyl chloride at Shawinigan black carbon electrodes, cupric chloride appears to be a useful cathode additive for lithium-thionyl chloride batteries. Preliminary results²¹ with Shawinigan black carbon cathodes containing about 21.7 weight percent of cupric chloride indicate that these electrodes show less polarization at high current densities than the Shawinigan black carbon cathodes without the cupric chloride additive.

ACKNOWLEDGMENT

The author wishes to thank D. Eckart of this laboratory for x-ray analyses.

²¹W. K. Behl, US Patent Application 171,515, July 23, 1980.

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