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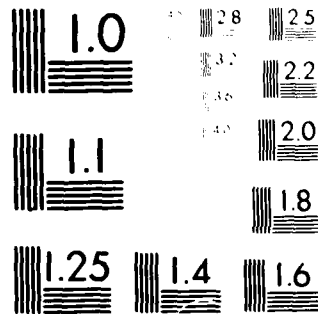
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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

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ELECTROCHEMICAL REDUCTION OF SULFURYL CHLORIDE IN SOLUTIONS
CONTAINING LITHIUM TETRACHLOROALUMINATE

Wishvender K. Behl
ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

September 1980

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The electrochemical reduction and oxidation of sulfuranyl chloride in 1 molar $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions were studied at glassy carbon electrodes using the technique of cyclic voltammetry. It was found that the reduction of chlorine, which is formed by the decomposition of sulfuranyl chloride, precedes and obscures the reduction of sulfuranyl chloride. Thus, in chlorine rich solu- tions, sulfuranyl chloride reduction peak in the cyclic voltammograms is com- pletely masked by the chlorine reduction peak. However, in solutions saturated with sulfur dioxide, the chlorine reduction peak is relatively smaller than the			

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sulfuryl chloride reduction peak. The reduction of both chlorine and sulfuryl chloride leads to the deposition of insoluble lithium chloride at the electrode surface and results in its passivation. The electrochemical oxidation of $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions leads to the formation of chlorine, first by the oxidation of AlCl_4^- ions followed by the oxidation of sulfuryl chloride.

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ELECTROCHEMICAL REDUCTION OF SULFURYL CHLORIDE IN SOLUTIONS CONTAINING LITHIUM TETRACHLOROALUMINATE

INTRODUCTION

During the past few years, a number of studies have been reported on the ambient temperature lithium-inorganic electrolyte battery systems. However, only a few of these studies have been devoted to the lithium-sulfuryl chloride system. The scarce literature includes studies of the discharge characteristics¹⁻⁴ and discharge reaction stoichiometry⁵ of lithium-sulfuryl chloride cells, conductivities,⁶ and voltammetric reduction of sulfuryl chloride⁷ in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions. The electrochemical reduction and oxidation of sulfuryl chloride in 1 molar $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions and in solutions containing excess of chlorine or sulfur dioxide were also investigated in this laboratory employing the technique of cyclic voltammetry. This report summarizes our results.

EXPERIMENTAL PROCEDURE

The preparation and purification of lithium tetrachloroaluminate have been described elsewhere.⁸ Sulfuryl chloride (Matheson, Coleman and Bell Co.) was refluxed over lithium metal and distilled as colorless liquid. However, on storage, the color slowly changed to light yellow. Solutions of lithium tetrachloroaluminate in sulfuryl chloride were light yellow in color.

A three electrode system was used for all measurements. The reference (1x5 cm) and counter (3.5x6 cm) electrodes were both made by pressing lithium ribbon (0.38 mm thick; Foote Mineral Co.) onto a nickel screen. The reference electrode was contained in a pyrex tube (10 mm diameter) with a coarse porosity fritted glass bottom. Both the reference and the counter electrodes were thoroughly washed with carbon tetrachloride before use. The working electrode consisted of a 3.18 mm diameter glassy carbon rod (Beckwith Carbon Co.) heat sealed in shrinkable Teflon tubing and the end ground flush with the seal so as to expose the cross section of the rod. The glassy carbon electrode, polished to a mirror finish using a 0.3 μm size powdered alumina, had an area of 0.079 cm^2 .

¹J. J. Auborn, R. D. Bezman, K. W. French, A. Heller, and S. I. Lieberman, Proc. 26th Power Sources Symposium, 26, 45 (1974).

²J. J. Auborn and N. Marincic, in "Power Sources 5," D. H. Collins, Editor, p. 683, Academic Press, London (1975).

³S. Gilman, Proc. 26th Power Sources Symposium, 26, 28 (1974).

⁴S. Gilman and W. Wade, Jr., "Abstract No. 33," The Electrochemical Society Extended Abstracts, Fall Meeting, Los Angeles, California, Oct. 14-19, 1979.

⁵S. Gilman, et al., *ibid*.

⁶L. Nanis, V. K. Kapur, and M. A. Gencer, "Lithium Sulfuryl Chloride Battery," Final Report, Contract DAAB07-75-C-1676(ECOM), University of Pennsylvania, April 1977.

⁷C. E. Blomgren, V. Z. Leger, M. L. Kronenberg, T. Kalnoki-Kis, and R. J. Brodd, Preprint, Paper presented at the 11th International Power Sources Symposium, Brighton, England, 1978.

⁸W. K. Behl, J. A. Christopulos, M. Ramirez, and S. Gilman, J. Electrochem. Soc., 120, 1619 (1973).

All experiments were performed inside a Dry-train, Dry-lab (Vacuum Atmospheres Corp.) in a pure, dried argon atmosphere. Other experimental details⁹⁻¹¹ were similar to those used for the voltammetric studies in phosphorous oxychloride and thionyl chloride solutions.

In order to obtain reproducible voltammograms, the passivating lithium chloride film on the working electrode was dissolved, after each scan, in an acidic $\text{AlCl}_3\text{-SO}_2\text{Cl}_2$ solution followed by washing with sulfuryl chloride and carbon tetrachloride. The electrode was then wiped clean and mechanically polished. The electrode could also be cleaned, in situ, by holding the electrode potential* at ~ 4.5 V for 1-2 minutes. However, this procedure was not employed since it led to the contamination of the solution by the oxidation products, namely, chlorine, aluminum chloride, etc. (see Discussion).

RESULTS

Typical cyclic voltammograms obtained in 1 molar $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solution, through which pure, dried argon was bubbled for 16 hours, at a scan rate of 0.1 V/s, are presented in Fig. 1. Voltammogram A was obtained by scanning the electrode from 4.0 to 0.25 V and voltammogram B by scanning the electrode from 4.0 to 5.0 V. Cyclic voltammogram A shows a large increase in cathodic current beginning at ~ 3.6 V with a shoulder (peak I) at ~ 3.05 V and peak (peak II) at ~ 2.85 V. A minor peak (peak III) is observed at ~ 2 V before a rapid increase in reduction current is observed at ~ 0.75 V. On reversing the direction of polarization at 0.25 V, only one small anodic peak (peak IV) is observed at ~ 1.0 V. The anodic peak IV is not observed if the direction of polarization is reversed at potentials positive to 0.75 V. Similar cyclic voltammograms were observed at scan rates of 0.01 to ~ 0.2 V/s. At higher scan rates, peaks I and II merged together and peak III was slightly more discernible. The peak currents increased with increasing scan rate and peak potentials shifted to less positive potentials.

Cyclic voltammogram B shows a small anodic peak (peak V) at ~ 4.6 V before a sharp increase in anodic current is observed at ~ 4.75 V. Cyclic voltammograms did not show any reduction peak during the reverse scan. Similar cyclic voltammograms were obtained at scan rates of 0.01 to 2 V/s.

In $\text{LiAlCl}_4\text{-SO}_2\text{-Cl}_2$ solutions containing excess of chlorine or sulfur dioxide, cyclic voltammograms for the anodic processes were similar to the voltammogram B presented in Fig. 1. However, voltammograms for the cathodic processes were distinctly different from voltammogram A. Thus, in saturated solutions of chlorine in 1 molar $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$, cyclic voltammograms (Fig. 2) showed only one major reduction peak at scan rates of 0.01 to 2 V/s. The peak potential for this reduction peak was closer to the peak potential for peak I in the cyclic voltammograms shown in Fig. 1. While peak II was not observed at all scan rates, the minor peak III became discernible only at scan rates greater than 1 V/s.

⁹W. K. Behl, J. Electroanal. Chem., 70, 213 (1976).

¹⁰W. K. Behl, Proc. 27th Power Sources Symposium, 27, 30 (1976).

¹¹W. K. Behl, J. Electroanal. Chem., 101, 367 (1979).

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

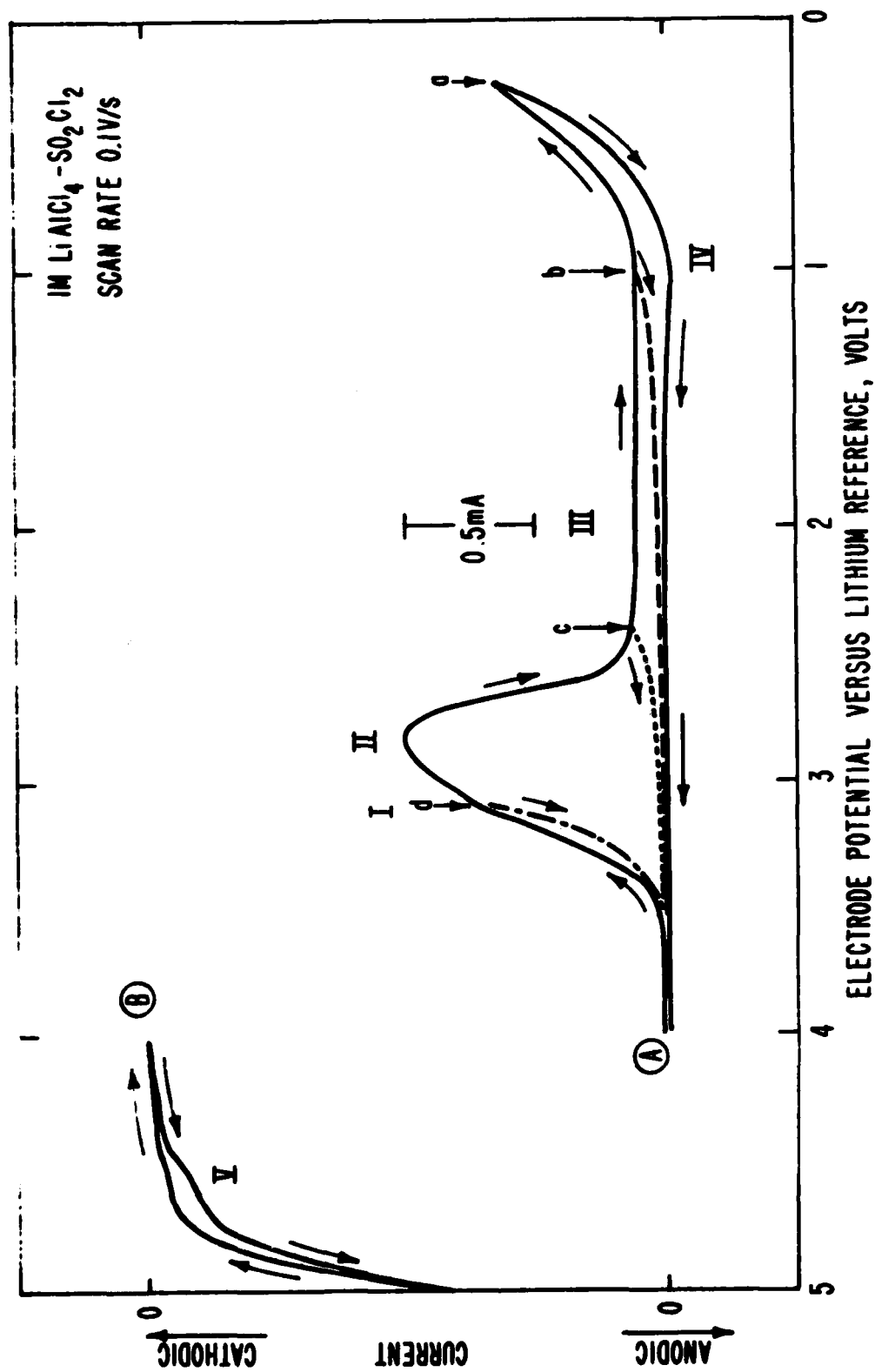
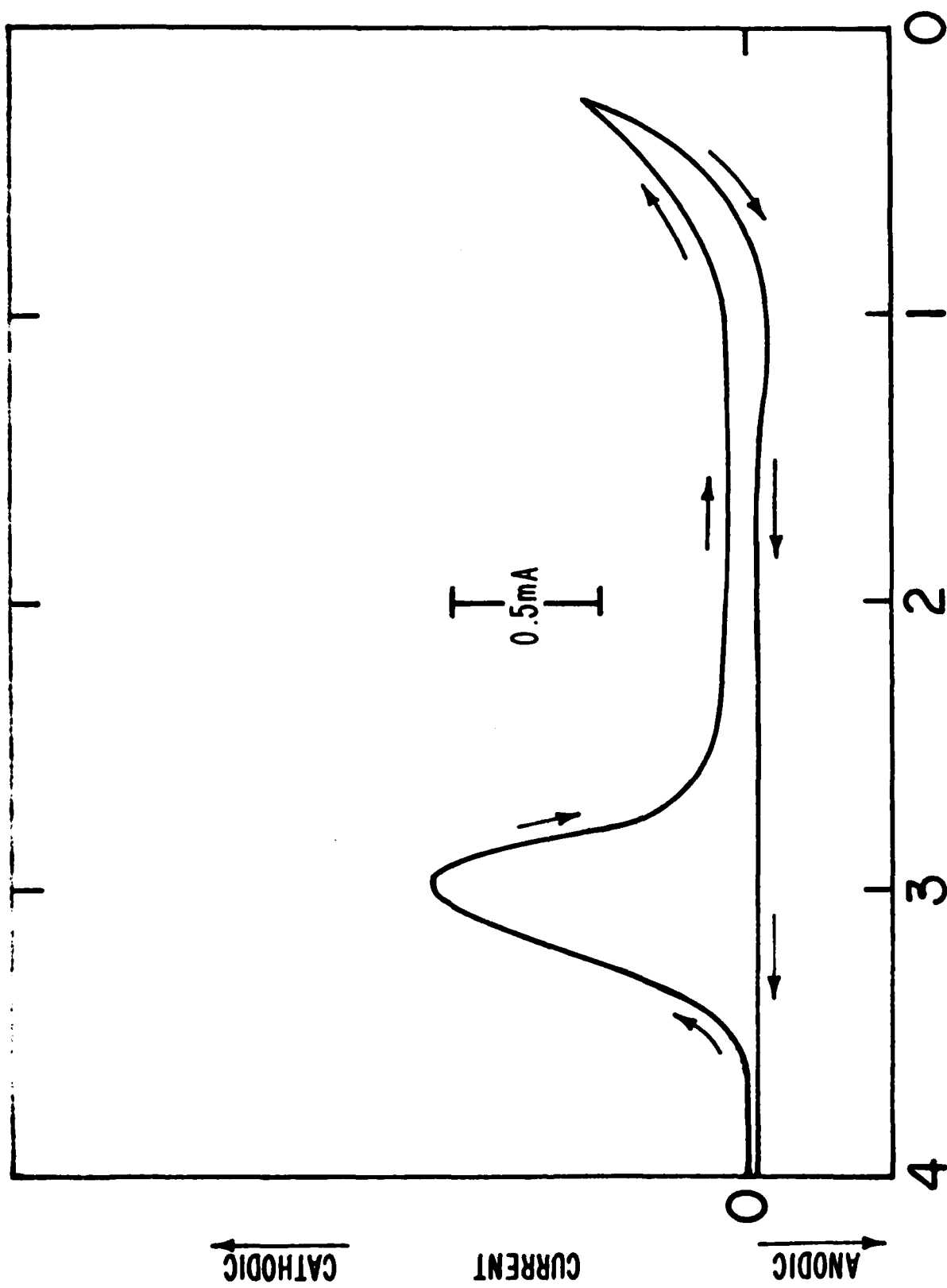


FIG.1 CYCLIC VOLTAMMOGRAMS IN ARGON PURGED SOLUTIONS.



ELECTRODE POTENTIAL VERSUS LITHIUM REFERENCE, VOLTS

FIG.2 CYCLIC VOLTAMMOGRAM IN CHLORINE SATURATED SOLUTIONS; SCAN RATE 0.1V/s.

Figure 3 shows the typical cyclic voltammograms obtained in 1 molar $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions, through which sulfur dioxide was bubbled for 16 hours, at a scan rate of 0.1 V/s. In these solutions, peak I appears as a small step at ~ 3.3 V and peak II is the major peak at ~ 2.75 V. Peak III appears as a wide peak beginning at ~ 2 V. Again no anodic peak corresponding to reduction peaks I, II, and III is observed on the reverse scan. Similar cyclic voltammograms were observed at scan rates of 0.01 to 2 V/s. Again the peak heights for peaks I, II, and III increased with increasing scan rate and peak potentials shifted to less positive potentials. Addition of chlorine to the sulfur dioxide saturated $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solution caused an increase in peak height for peak I (Fig. 4) and a corresponding decrease in peak height for peak II.

DISCUSSION

Sulfuryl chloride is known¹² to decompose to sulfur dioxide and chlorine according to the equation:



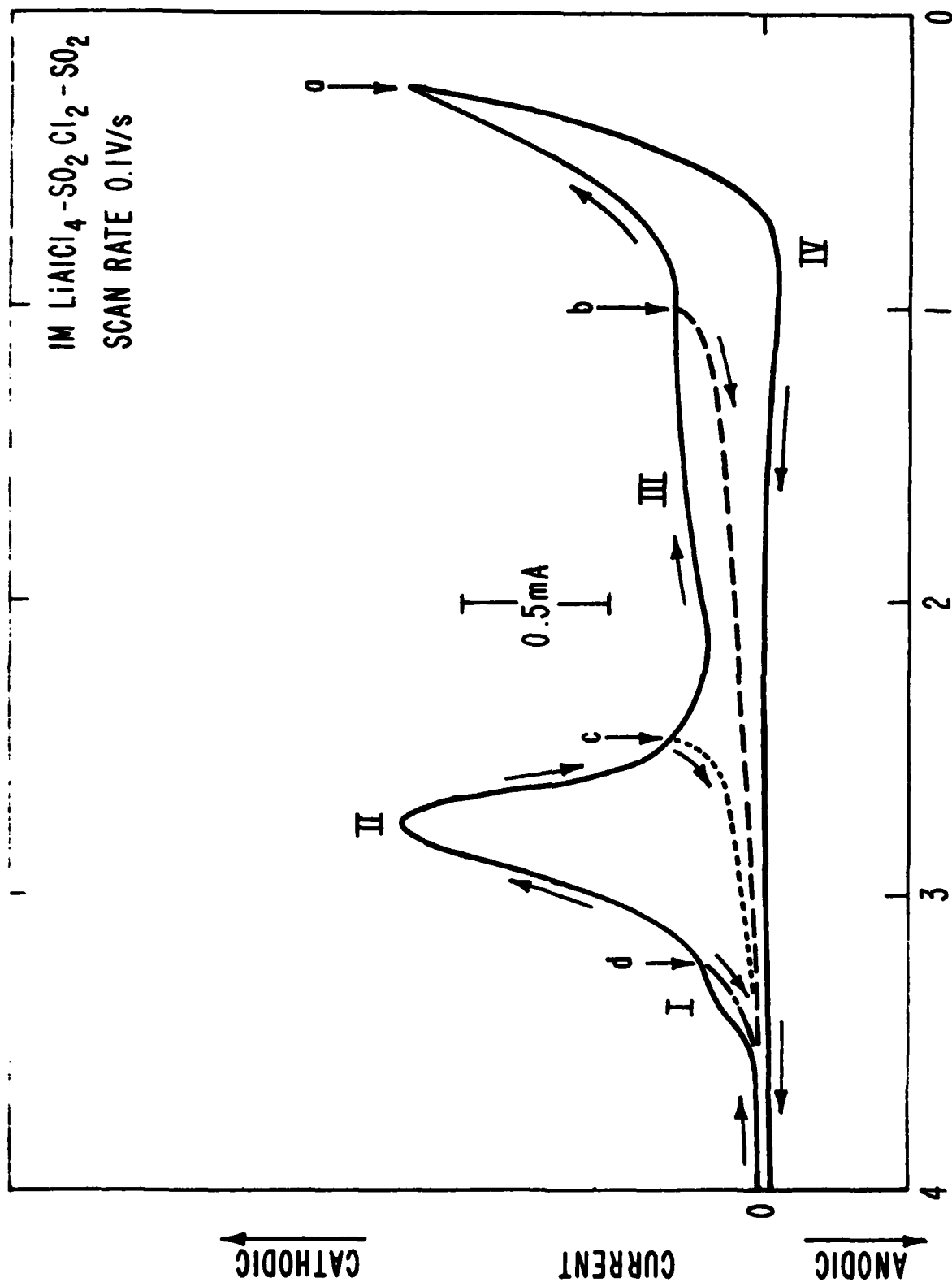
Both sulfur dioxide and chlorine are soluble¹³ in sulfuryl chloride and remain in solution. While solutions of sulfur dioxide in freshly distilled sulfuryl chloride are colorless, solutions of chlorine are light yellow in color. Solutions of lithium tetrachloroaluminate in freshly distilled sulfuryl chloride were always found to be light yellow in color. Both sulfuryl chloride and its solutions containing lithium tetrachloroaluminate became dark yellow in color on long storage. The yellow color in these solutions is attributed to chlorine which is formed by the decomposition of sulfuryl chloride according to Equation (1). It was not possible to completely remove the dissolved chlorine and the yellow color by purging the $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions with argon. However, it was possible to shift the equilibrium in Equation (1) to the left by bubbling sulfur dioxide to remove the dissolved chlorine. Thus, the $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions were almost colorless.

Electrochemical Reduction of Sulfuryl Chloride

Cyclic voltammograms (Fig. 1, Voltammogram A) obtained in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions show three reduction peaks before a rapid increase in cathodic current is observed at ~ 0.75 V due to the deposition of lithium metal at the electrode surface. On the reverse scan, only one anodic peak (peak IV) is observed at ~ 1.0 V. Since peak IV is not observed if the direction of polarization is reversed prior to lithium deposition, it may be ascribed to the dissolution of the deposited lithium metal. Similarly, the rapid increase in the cathodic current at ~ 0.75 V and the anodic peak IV at ~ 1.0 V in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-Cl}_2$ (Fig. 2) and $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ (Fig. 3) solutions may also be ascribed to the deposition and dissolution of lithium metal, respectively.

¹²J. W. Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Vol. 10, Longmans, Green and Co., London, 1930.

¹³J. W. Mellor, *ibid.*



ELECTRODE POTENTIAL VERSUS LITHIUM REFERENCE, VOLTS

FIG.3 CYCLIC VOLTAMMOGRAMS IN SULFUR DIOXIDE SATURATED SOLUTIONS.

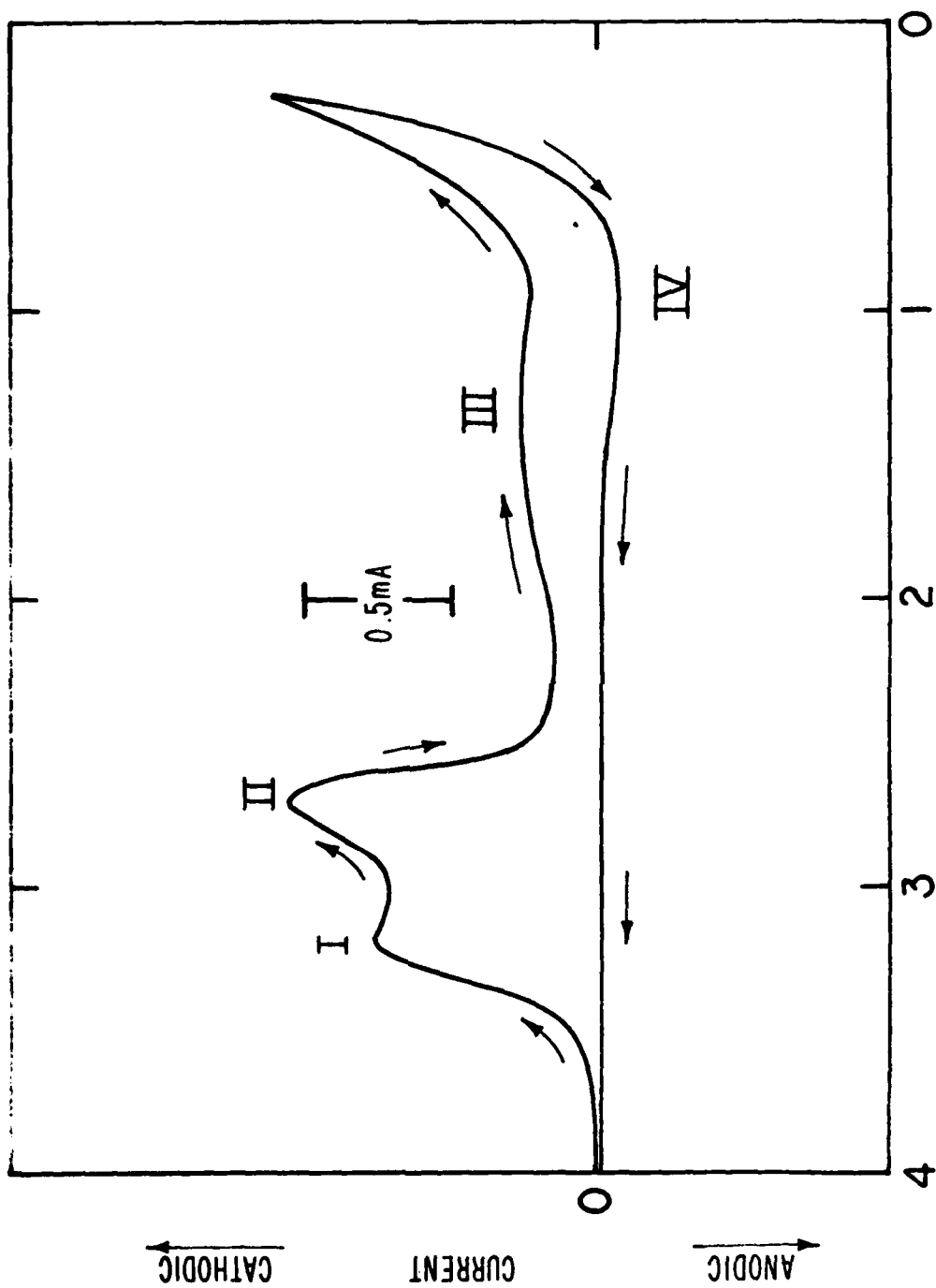
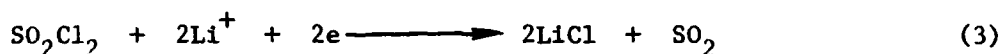


FIG.4 CYCLIC VOLTAMMOGRAM OBTAINED ON THE ADDITION OF CHLORINE TO SULFUR DIOXIDE SATURATED SOLUTIONS; SCAN RATE 0.1V/s.

In order to identify the other reduction peaks, let us first consider the cyclic voltammograms in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions (Fig. 3). The peak height for peak I in these voltammograms is strongly dependent on the concentration of dissolved chlorine as demonstrated by the addition of chlorine to $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions (Fig. 4). Further, if these solutions are allowed to stand for a few hours, or if argon is bubbled through the solutions to remove sulfur dioxide, the equilibrium in Equation (1) is shifted to the right resulting in an increase in the chlorine concentration and a corresponding increase in peak height for peak I. Thus, peak I may be ascribed to the reduction of chlorine:



The main reduction peak (peak II) in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions may be ascribed to the reduction of sulfuryl chloride. From a study of the discharge products in lithium-sulfuryl chloride cells, Gilman and Wade¹⁴ have identified lithium chloride as the only solid reaction product. Therefore, the reduction of sulfuryl chloride may be represented as:



The reduction of both chlorine (Equation (2)) and sulfuryl chloride (Equation (3)) leads to the deposition of insoluble lithium chloride at the electrode surface and causes its passivation. Since it would require a fixed amount of lithium chloride, at a fixed scan rate, to cover the electrode surface, the combined peak height for peaks I and II remains constant and independent of the chlorine concentration in the solution. Thus, the peak heights for peaks I and II are interdependent and an increase in the chlorine reduction peak (peak I), due to increased chlorine concentration, results in a corresponding decrease in the sulfuryl chloride reduction peak (peak II).

Similarly, peaks I and II in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions (Fig. 1) may be attributed to the reduction of chlorine and sulfuryl chloride, respectively. Since the chlorine reduction peak appears as the major reduction peak even in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions purged with argon for 16 hours, it seems likely that chlorine is supplied to the glassy carbon electrode not only by the migration of bulk chlorine but also by the decomposition of sulfuryl chloride at the electrode surface. Thus, at more catalytic surfaces such as platinum,¹⁵ the decomposition of sulfuryl chloride at the electrode surface is facilitated and the electrochemical reduction of sulfuryl chloride proceeds mainly through chlorine even in sulfur dioxide saturated $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions.

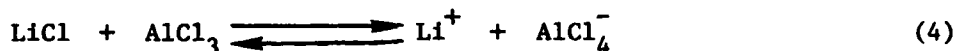
The minor reduction peak III (Fig. 1, 3, & 4) in the cyclic voltammograms may be assigned to the reduction of sulfur dioxide. While peak III is hardly discernible in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ and $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-Cl}_2$ solutions, it is easily distinguished in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions. Since the electrode is already passivated due to the deposition of lithium chloride, the reduction of

¹⁴S. Gilman, et al., op. cit., p. 1

¹⁵W. K. Behl, unpublished results.

sulfur dioxide does not occur significantly in these solutions and results in only a very small peak in the cyclic voltammograms.

In order to further differentiate between peaks I, II, and III in the cyclic voltammograms, a small amount of aluminum chloride was added to the $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions previously purged with argon. Since the excess of aluminum chloride increases the corrosion of lithium electrodes in the solution and eventually results in their complete disintegration, the cyclic voltammograms were recorded immediately after the addition of aluminum chloride (Fig. 5). The excess of aluminum chloride in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions partially dissolves the lithium chloride film on the electrode surface due to complex formation:



Thus, the electrode surface continues to be partially regenerated during the life of the voltage scan and results in distinct reduction peaks for the reduction of chlorine (peak I), sulfuryl chloride (peak II), and sulfur dioxide (peak III). The peak heights are also slightly higher than those obtained in neutral $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions. Further, due to the partial regeneration of the electrode surface, a small cathodic current is observed during the reverse scan of the cyclic voltammograms (Fig. 5) in contrast to almost no current in neutral $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions (Fig. 1).

In $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-Cl}_2$ solutions (Fig. 2), the reduction of chlorine completely obscures the reduction of sulfuryl chloride so that only one major reduction peak is observed in the cyclic voltammograms. Thus, in these solutions, the electrode surface is completely covered by lithium chloride produced as a result of chlorine reduction (Equation (2)) and is not available for the reduction of sulfuryl chloride and sulfur dioxide. Cyclic voltammograms similar to those presented in Fig. 2 are also obtained in aged $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions. The chlorine concentration in the aged solutions is rather large due to the decomposition of sulfuryl chloride and, thus, the chlorine reduction peak completely masks the sulfuryl chloride reduction peak. If the excess of chlorine in aged $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ or $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-Cl}_2$ solutions is removed by bubbling argon, cyclic voltammograms similar to those presented in Fig. 1 (voltammogram A) are obtained.

The total charge passed under peaks I and II of the cyclic voltammograms in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$, $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-Cl}_2$, and $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions was measured as a function of scan rate by integrating the area under the peaks. From the total charge passed, the thickness of the lithium chloride film on the glassy carbon electrode was then calculated taking the density of lithium chloride to be 2.068 g/cm^3 at 25°C . These results are plotted in Fig. 6. The total charge passed and the thickness of the lithium chloride film in all three solutions was found to decrease with increasing scan rate. However, at all scan rates, the film thickness in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions was found to be slightly higher than that obtained in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ or $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-Cl}_2$ solutions.

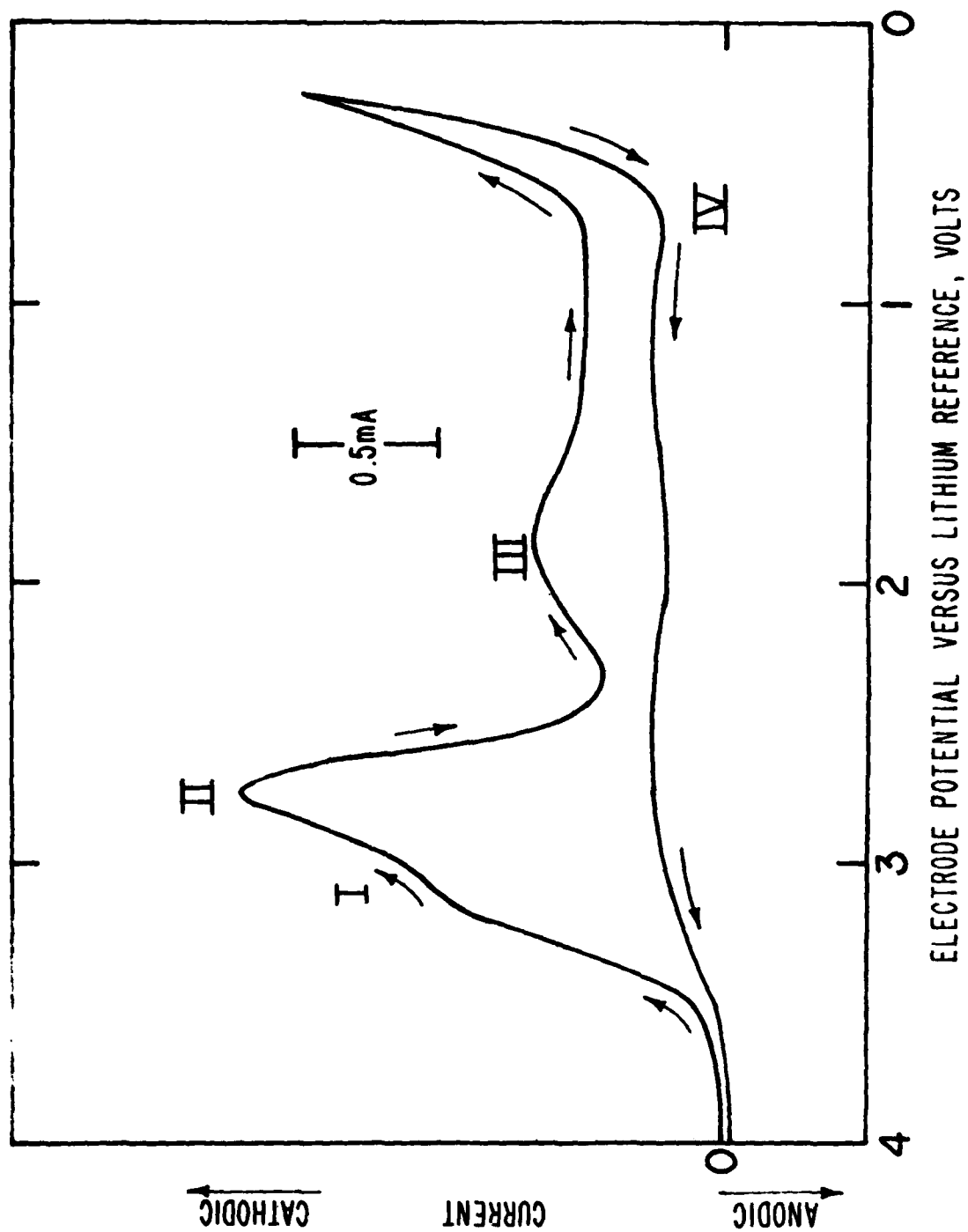


FIG.5 CYCLIC VOLTAMMOGRAM IN SOLUTIONS CONTAINING EXCESS ALUMINUM CHLORIDE; SCAN RATE 0.1V/s.

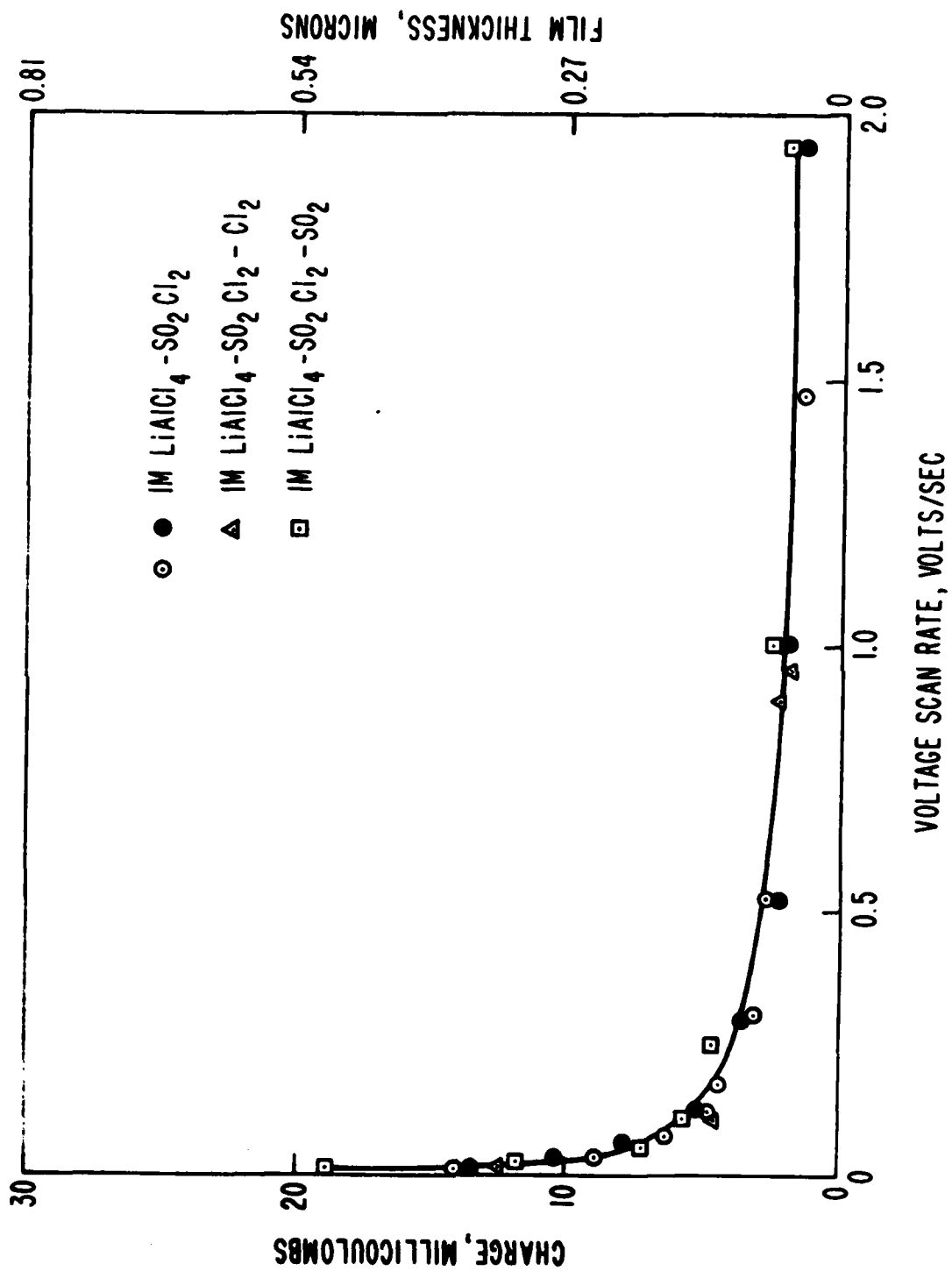
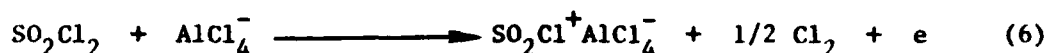


FIG.6 LITHIUM CHLORIDE FILM THICKNESS AS A FUNCTION OF SCAN RATE.

Electrochemical Oxidation of Sulfuryl Chloride

Cyclic voltammograms (voltammogram B, Fig. 1) for the oxidation of $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions at glassy carbon electrodes were similar to those obtained in $\text{LiAlCl}_4\text{-SOCl}_2$ solutions.^{16,17} Thus, analogous to $\text{LiAlCl}_4\text{-SOCl}_2$ solutions, anodic peak V at ~ 4.6 V and the sharp increase in anodic current at ~ 4.75 V in these voltammograms (Fig. 1) may be ascribed to the oxidation of AlCl_4^- ions and SO_2Cl_2 , respectively:



Thus, if the potential of the glassy carbon electrode is held at ~ 5 V for a few minutes before scanning it in the cathodic direction, the formation of chlorine at more positive potentials (Equations (5) and (6)) causes an increase in peak height for the chlorine reduction peak (peak I) in the cyclic voltammograms (Fig. 7 and Fig. 8). At the same time, aluminum chloride formed in Equation (5) partially dissolves the lithium chloride film on the electrode surface and causes an overall increase in combined peak heights for peaks I and II.

CONCLUSIONS

The results of the present study have shown that the reduction of chlorine in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions occurs at slightly more positive potentials than the reduction of sulfuryl chloride. The reduction of both chlorine and sulfuryl chloride leads to the deposition of insoluble lithium chloride at the electrode surface and may be represented by the following equations, respectively:



Since chlorine is always present in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions due to the decomposition of sulfuryl chloride, the deposition of insoluble lithium chloride by the reduction of chlorine passivates the electrode surface and obscures the reduction of sulfuryl chloride. It was shown that the decomposition of sulfuryl chloride can be suppressed by saturating the $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions with sulfur dioxide.

¹⁶W. K. Behl, Proc. 27th Power Sources Symposium, 27, 30 (1976).

¹⁷K. M. Abraham, R. M. Mank, and G. L. Holleck, "Investigation of the Safety of Li/SOCl_2 Batteries," Second Quarterly Report, Contract No. DAAB07-78-C-0564 (ERADCOM), EIC Corporation, July 1979.

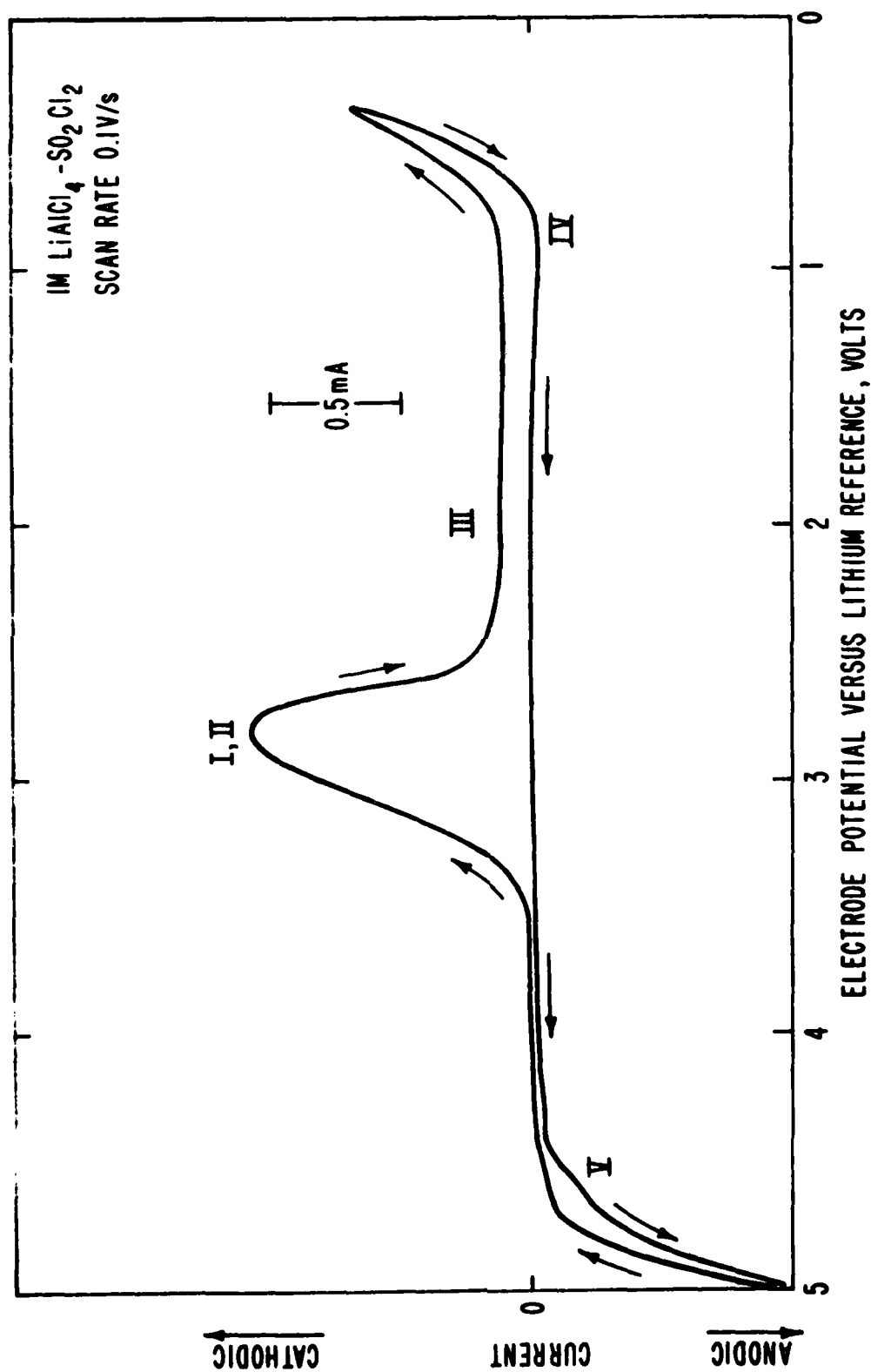


FIG.7 CYCLIC VOLTAMMOGRAM BETWEEN 5 AND 0.25 VOLTS IN ARGON PURGED SOLUTIONS

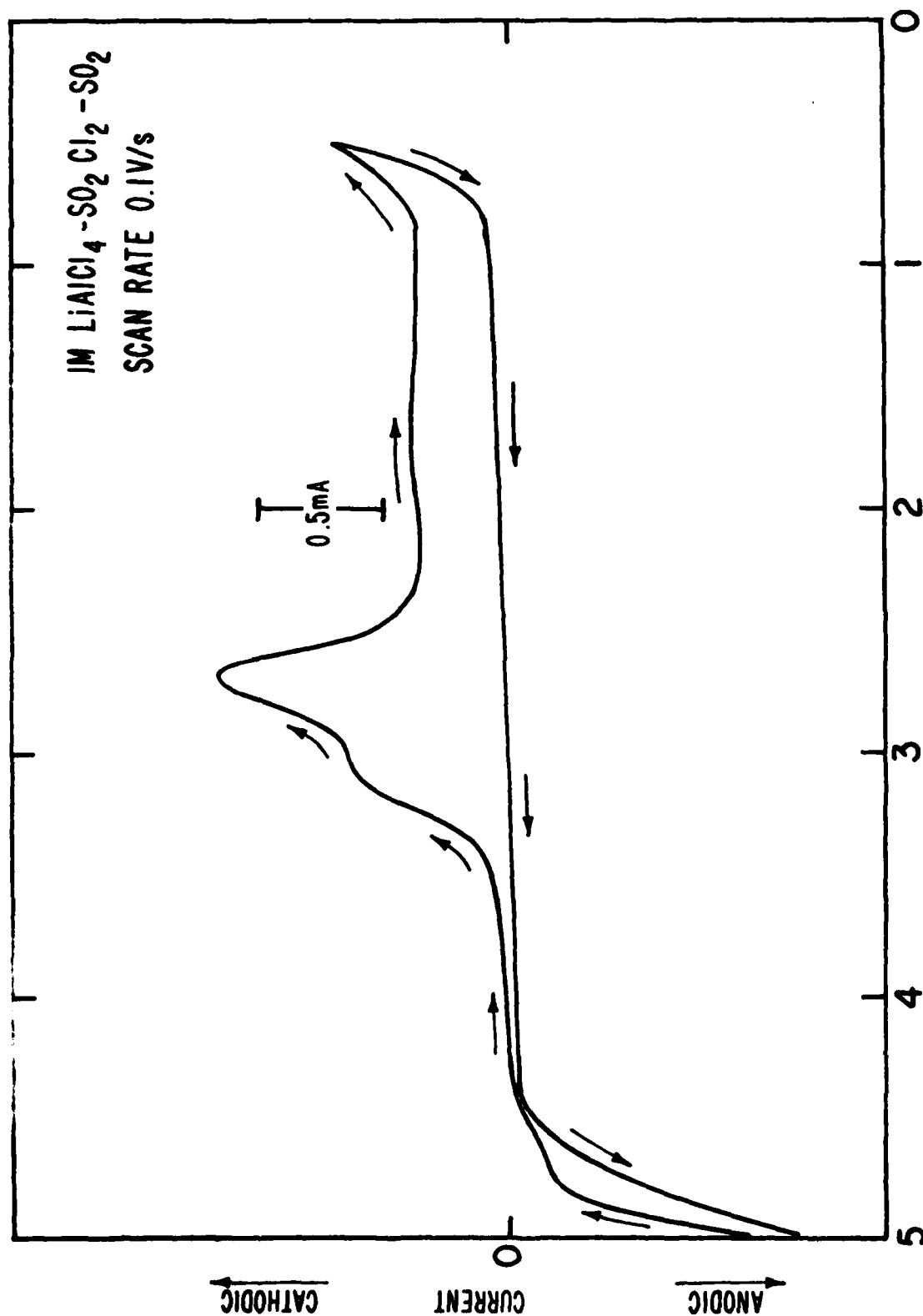


FIG.8 CYCLIC VOLTAMMOGRAM BETWEEN 5 AND 0.25 VOLTS IN SULFUR

DIOXIDE SATURATED SOLUTIONS

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