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in Sulfuryl Chloride Solutions**

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ABSTRACT

The electrochemical reduction and oxidation of sulfuryl chloride in 1M $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ 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 sulfuryl chloride, precedes and obscures the reduction of sulfuryl chloride. Thus, in chlorine-rich solutions, sulfuryl chloride reduction peak in the cyclic voltammograms is completely masked by the chlorine reduction peak. However, in solutions saturated with sulfur dioxide, the chlorine reduction peak is relatively smaller than the 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.

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 characteristics (1-4) and discharge reaction stoichiometry (4) of lithium-sulfuryl chloride cells, conductivities (5), and voltammetric reduction of sulfuryl chloride (6) in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions. The electrochemical reduction and oxidation of sulfuryl chloride in 1M $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions and in solutions containing excess of chlorine or sulfur dioxide were also investigated in this laboratory employing the technique of cyclic voltammetry. This paper summarizes our results.

Experimental

The preparation and purification of lithium tetrachloroaluminate have been described elsewhere (7). Sulfuryl chloride (Matheson, Coleman and Bell Company) 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 (1×5 cm) and counter (3.5×6 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 the counterelectrodes were thoroughly washed with carbon tetrachloride before use. The working electrode consisted of a 3.18 mm diam glassy carbon rod (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 glassy carbon electrode was then polished to a mirror finish using a $0.3 \mu\text{m}$ size powdered alumina and had an area of 0.079 cm^2 .

All experiments were performed inside a Dry-train, Dry-lab (Vacuum Atmosphere Corporation) in a pure dried argon atmosphere. Other experimental details (8-10) were similar to those used for the voltammetric studies in phosphorous oxychloride and thionyl chloride solutions.

* Electrochemical Society Active Member.

Key words: electrolyte, battery, voltammetry.

In order to obtain reproducible voltammograms, the passivating lithium chloride film on the working electrode was dissolved, after each scan, in 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 potential¹ at $\sim 4.5\text{V}$ for 1-2 min. 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 $1\text{M LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solution, through which pure dried argon was bubbled for 16 hr, at a scan rate of 0.1 V/sec , are presented in Fig. 1. Voltammogram A was obtained by scanning the electrode from 4.0 to 0.25V and voltammogram B by scanning the electrode from 4.0 to 5.0V . Cyclic voltammogram A shows a large increase in cathodic current beginning at $\sim 3.6\text{V}$ with a shoulder (peak I) at $\sim 3.05\text{V}$ and peak (peak II) at $\sim 2.85\text{V}$. A minor peak (peak III) is observed at $\sim 2\text{V}$ before a rapid increase in reduction current is observed at $\sim 0.75\text{V}$. On reversing the direction of polarization at 0.25V , only one small anodic peak (peak IV) is observed at $\sim 1.0\text{V}$. The anodic peak IV is not observed if the direction of polarization is reversed at potentials positive to 0.75V . Similar cyclic voltammograms were observed at scan rates of 0.01 to $\sim 0.2\text{ V/sec}$. 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 $\sim 4.6\text{V}$ before a sharp increase in anodic current is observed at $\sim 4.75\text{V}$. Cyclic voltammograms did not show any reduction peak during the reverse scan. Similar cyclic voltammograms were obtained at scan rates of $0.01\text{-}2\text{ V/sec}$.

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 $1\text{M LiAlCl}_4\text{-SO}_2\text{Cl}_2$, cyclic voltammograms (Fig. 2) showed only one major reduction peak at scan rates of $0.01\text{-}2\text{ V/sec}$. 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

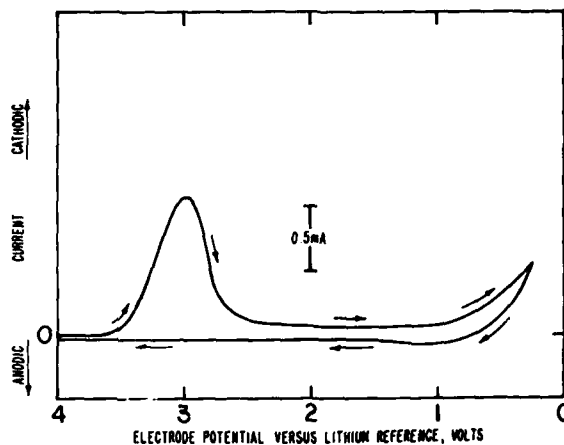


Fig. 2. Typical cyclic voltammograms at glassy carbon electrodes in saturated solutions of chlorine in $1\text{M LiAlCl}_4\text{-SO}_2\text{Cl}_2$ at a scan rate of 0.1 V/sec .

observed at all scan rates, the minor peak III became discernible only at scan rates greater than 1 V/sec .

Typical cyclic voltammograms obtained in $1\text{M LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions, through which sulfur dioxide was bubbled for 16 hr, at a scan rate of 0.1 V/sec are shown in Fig. 3. In these solutions, peak I appears as a small step at $\sim 3.3\text{V}$ and peak II is the major peak at $\sim 2.75\text{V}$. Peak III appears as a wide peak beginning at $\sim 2\text{V}$. 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 $0.01\text{-}2\text{ V/sec}$. 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 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 known (11) to decompose to sulfur dioxide and chlorine according to the equation



Both sulfur dioxide and chlorine are soluble (11) in sulfuryl chloride and remain in solution. While solu-

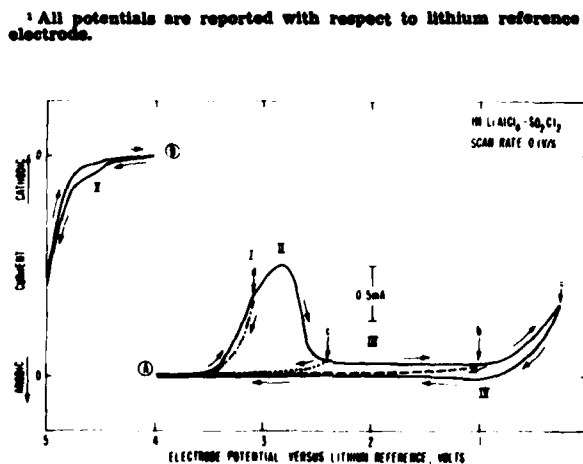


Fig. 1. Typical cyclic voltammograms at glassy carbon electrodes in argon purged $1\text{M LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions at a scan rate of 0.1 V/sec . Roman numerals refer to the different peaks and letters a-d indicate the potential of scan reversal of different sweeps.

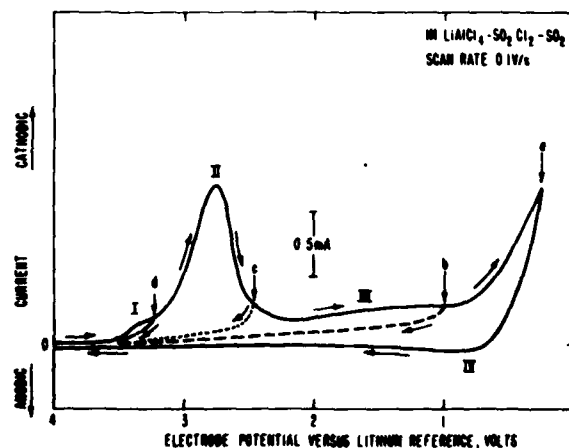


Fig. 3. Typical cyclic voltammograms at glassy carbon electrodes in saturated solutions of sulfur dioxide in $1\text{M LiAlCl}_4\text{-SO}_2\text{Cl}_2$ at a scan rate of 0.1 V/sec . Roman numerals refer to the different peaks and letters a-d indicate the potential of scan reversal of the different sweeps.

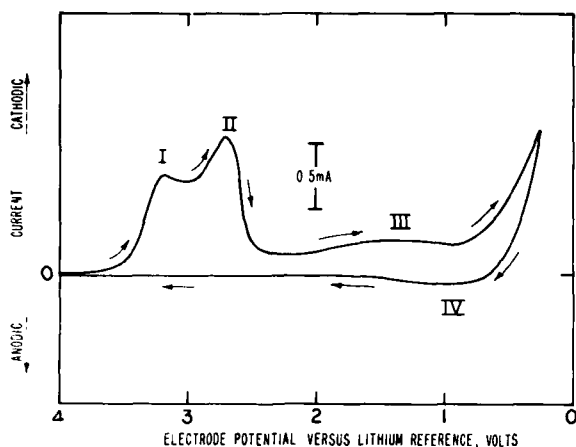


Fig. 4. Typical cyclic voltammograms at glassy carbon electrodes at a scan rate of 0.1 V/sec in 1M $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions to which a small amount of chlorine is added.

tions of sulfur dioxide in freshly distilled sulfonyl chloride are colorless, solutions of chlorine are light yellow in color. Solutions of lithium tetrachloroaluminate in freshly distilled sulfonyl chloride were always found to be light yellow in color. Both sulfonyl 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 sulfonyl chloride according to Eq. [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, especially in the presence of lithium electrodes. It was, however, possible to shift the equilibrium in Eq. [1] to the left by bubbling sulfur dioxide and remove the dissolved chlorine. Thus, the $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2\text{-SO}_2$ solutions were almost colorless.

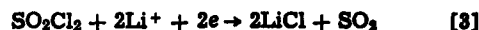
Electrochemical reduction of sulfonyl chloride.—Cyclic voltammograms (Fig. 1, voltammogram A) obtained in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions show three reduction peaks before a rapid increase in cathodic current is observed at $\sim 0.75\text{V}$ due to the deposition of lithium metal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

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). 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 Eq. [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 regarded as due 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 regarded as due to the reduction of sulfonyl chloride. From a study of the dis-

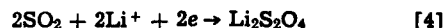
charge products in lithium-sulfonyl chloride cells, Gilman and Wade (4) have identified lithium chloride as the only solid reaction product. The reduction of sulfonyl chloride may, therefore, be represented as



The reduction of both chlorine (Eq. [2]) and sulfonyl chloride (Eq. [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 chlorine reduction peak (peak I) due to increased chlorine concentration results in a corresponding decrease in sulfonyl chloride reduction peak (peak II).

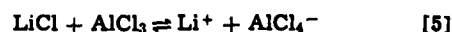
Similarly, peaks I and II in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions (Fig. 1) may be attributed to the reduction of chlorine and sulfonyl chloride, respectively. Since the chlorine reduction peak appears as the major reduction peak even in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions purged with argon for 16 hr, 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 sulfonyl chloride at the electrode surface. Thus, at more catalytic surfaces such as platinum (12), the decomposition of sulfonyl chloride at the electrode surface is facilitated and the electrochemical reduction of sulfonyl 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 through 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 distinguishable 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 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 counterelectrode by dissolving the protective lithium chloride film and eventually results in its complete disintegration, the cyclic voltammograms were recorded immediately after the addition of aluminum chloride and are shown in Fig. 5. The excess of aluminum chloride in $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions also partially dissolves the lithium chloride film on the glassy carbon 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), sulfonyl 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 sulfonyl chloride so that only one major reduction

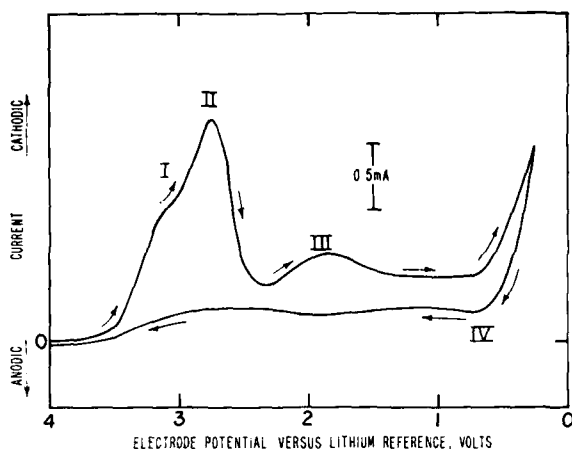


Fig. 5. Typical cyclic voltammograms at glassy carbon electrodes at a scan rate of 0.1 V/sec in 1M $\text{LiAlCl}_4\text{-SO}_2\text{Cl}_2$ solutions containing slight excess of aluminum chloride.

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 (Eq. [2]) and is not available for the reduction of suluryl 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 suluryl chloride and thus the chlorine reduction peak completely masks the suluryl 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/cm³ at 25°C. These results are plotted in Fig. 6. The total charge passed and hence the thickness of the lithium chloride film in all three solutions was found to decrease with increasing scan rate. However, at all scan

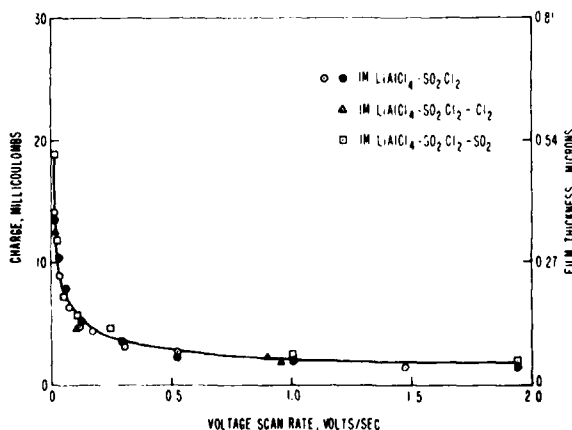
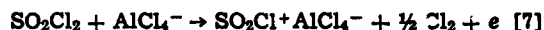
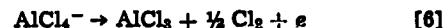


Fig. 6. Total charge passed under peaks I and II of the cyclic voltammograms and the thickness of lithium chloride film as a function of scan rate.

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.

Electrochemical oxidation of suluryl 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 (9, 13). Thus, analogous to $\text{LiAlCl}_4\text{-SOCl}_2$ solutions, anodic peak V at ~4.6V and the sharp increase in anodic current at ~4.75V in these voltammograms (Fig. 1) may be regarded as due to the oxidation of AlCl_4^- ions and SO_2Cl_2 , respectively



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

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