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ELECTROCHEMICAL REDUCTION OF THIONYL CHLORIDE
IN SOLUTIONS CONTAINING LITHIUM TETRACHLOROALUMINATE

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CONTENTS

	<u>Page</u>
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	2
EXPERIMENTAL RESULTS	2
DISCUSSION OF RESULTS	3
CONCLUSIONS	8

FIGURE

1. Cyclic Voltammograms at Glassy Carbon Electrodes
in Thionyl Chloride Solutions..... 5

TABLES

1. Peak Current Data for the Reduction of Thionyl
Chloride in 0.5, 1.0, and 1.5M Solutions 4
2. Peak (E_p) and Half-Peak ($E_{p/2}$) Potential Data for
the Reduction of Thionyl Chloride in 0.5, 1.0,
and 1.5M Solutions 6

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**ELECTROCHEMICAL REDUCTION OF THIONYL CHLORIDE
IN SOLUTIONS CONTAINING LITHIUM TETRACHLOROALUMINATE**

INTRODUCTION

Solutions of lithium tetrachloroaluminate (LiAlCl_4) in thionyl chloride 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 electrochemical reduction of thionyl chloride in 0.5, 1.0, and 1.5 molar LiAlCl_4 - SOCl_2 solutions was examined at glassy carbon microelectrodes using the technique of cyclic voltammetry.

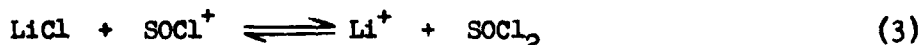
Thionyl chloride, like other oxychloride solvents, ionizes^{3,4} as:



Covalent metal chlorides, such as aluminum chloride, are highly soluble⁵ in thionyl chloride and behave as Lewis acids because of their tendency to form complex ions,



Lithium chloride, on the other hand, is only slightly soluble⁶ in thionyl chloride but readily dissolves to neutralize acidic AlCl_3 - SOCl_2 solutions, i.e.,



Solutions of lithium tetrachloroaluminate are, however, not strictly neutral from the standpoint of chloroacidity but, analogous to LiClO_4 and LiBCl_4 solutions^{7,8} in phosphorous oxychloride, would behave as weak chloroacid through its Li^+ ions and as weak chlorobase through its AlCl_4^- ions.

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- ¹W.K. Behl, J.A. Christopoulos, M. Ramirez and S. Gilman, J. Electrochem. Soc., 120, 1619 (1974).
 - ²J.J. Auburn, K.W. French, S.I. Lieberman, V.K. Shah and A. Heller, J. Electrochem. Soc., 120, 1613 (1974).
 - ³V. Gutmann, Coordination Chemistry in Non-Aqueous Solutions, New York: Springer-Verlag, 1968.
 - ⁴V. Gutmann, Halogen Chemistry, Vol. II. London-New York: Academic Press, 1965.
 - ⁵V. Gutmann, *ibid.*
 - ⁶V. Gutmann, *ibid.*
 - ⁷J. Devynck, Ann. Chim., 7, 321 (1972),
 - ⁸W.K. Behl, J. Electroanal. Chem., 70, 213 (1976).

EXPERIMENTAL PROCEDURE

The preparation and purification of thionyl chloride and lithium tetrachloroaluminate have been described in detail elsewhere.⁹ 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 chloride 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 Mineral Company) pressed onto a nickel screen was used as the reference electrode; this 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 accomplished¹⁰ 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.

EXPERIMENTAL RESULTS

A typical cyclic voltammogram obtained in a 1.5M LiAlCl_4 - SOCl_2 solution by scanning the electrode from 3.5 to 0.6 V at a scan rate of

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

⁹W.K. Behl, et al., op. cit., p. 1

¹⁰J.A. Christopoulos and S. Gilman. Record of the 10th Intersociety Energy Conversion Engineering Conference, p. 437. August 1975.

0.1 V/s is shown in Figure 1. The voltammogram shows a large reduction peak (peak I) beginning at 3.1 V followed by two almost indiscernible reduction peaks (peak II and III) at ~ 1.67 V and 1.32 V, respectively, before a rapid increase in cathodic current is observed at 1.0 V due to the deposition of lithium metal. On reversing the direction of polarization at 0.6 V, two small anodic peaks (peak IV and V) are observed at ~ 1.0 V and ~ 2.6 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.

The reduction peaks I - III may be regarded due to the electrochemical reduction of thionyl chloride. It is seen from the cyclic voltammograms present in Figure 1 that while a corresponding anodic peak (peak V) is observed for reduction peaks II and III, 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 Procedure 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.

In 0.5 and 1.0 molar LiAlCl_4 - SOCl_2 solutions, the cyclic voltammograms were identical to those obtained in the 1.5 molar solution. Thus, at a fixed scan rate, the peak heights for the different peaks (Figure 1) were of the same order of magnitude in each of the three concentrations studied. At all concentrations, the peak height for reduction peak I increased with increasing scan rate. The peak height data as a function of scan rate in 0.5, 1.0, and 1.5 molar solutions are summarized in Table 1.

At all concentrations, the peak and half-peak potentials (E_p and $E_{p/2}$) shifted towards more cathodic potentials with increasing scan rate. The peak and half-peak potential data as a function of scan rate are presented in Table 2.

DISCUSSION OF RESULTS

The electrochemical reduction of thionyl chloride was first studied by Spandau et al.¹¹ It was reported by these workers that the cathodic

¹¹H. Spandau, A. Beyer and F. Preugschat, Z. Anorg. Allgem. Chem., 306, 13 (1960).

Table 1. Peak Current Data for the Reduction of Thionyl Chloride in 0.5, 1.0, and 1.5M Solutions

Scan Rate (volts/sec.)	1.5M LiAlCl ₄ -SOCl ₂		1.0M LiAlCl ₄ -SOCl ₂		0.5M LiAlCl ₄ -SOCl ₂	
	i _p , mA	i _p /V ^{1/2}	i _p , mA	i _p /V ^{1/2}	i _p , mA	i _p /V ^{1/2}
0.003	0.066	1.20	0.070	1.27	-	-
0.0035	-	-	-	-	0.072	1.29
0.005	0.072	1.17	0.091	1.25	-	-
0.006	-	-	-	-	0.096	1.26
0.008	0.099	1.11	0.110	1.23	-	-
0.009	-	-	-	-	0.120	1.30
0.011	-	-	0.122	1.16	-	-
0.012	-	-	-	-	0.121	1.12
0.017	0.145	1.12	0.153	1.18	0.147	1.13
0.045	0.265	1.25	0.250	1.18	0.248	1.17
0.074	0.305	1.12	0.340	1.25	0.311	1.14
0.108	0.365	1.11	0.41	1.25	0.382	1.16
0.167	0.40	0.98	0.52	1.27	-	-
0.20	-	-	-	-	0.47	1.07
0.333	0.64	1.11	-	-	-	-
0.40	-	-	0.775	1.23	0.67	1.06
0.50	0.90	1.27	-	-	-	-
0.67	-	-	0.960	1.17	0.85	1.04
1.0	1.23	1.23	1.275	1.28	1.01	1.01
2.0	1.60	1.13	1.50	1.06	-	-
4.0	2.5	1.25	2.40	1.20	-	-
10	3.8	1.20	4.05	1.28	-	-
20	5.0	1.12	4.90	1.10	-	-
Mean i _p /V ^{1/2} }	-	1.16	-	1.21	-	1.15

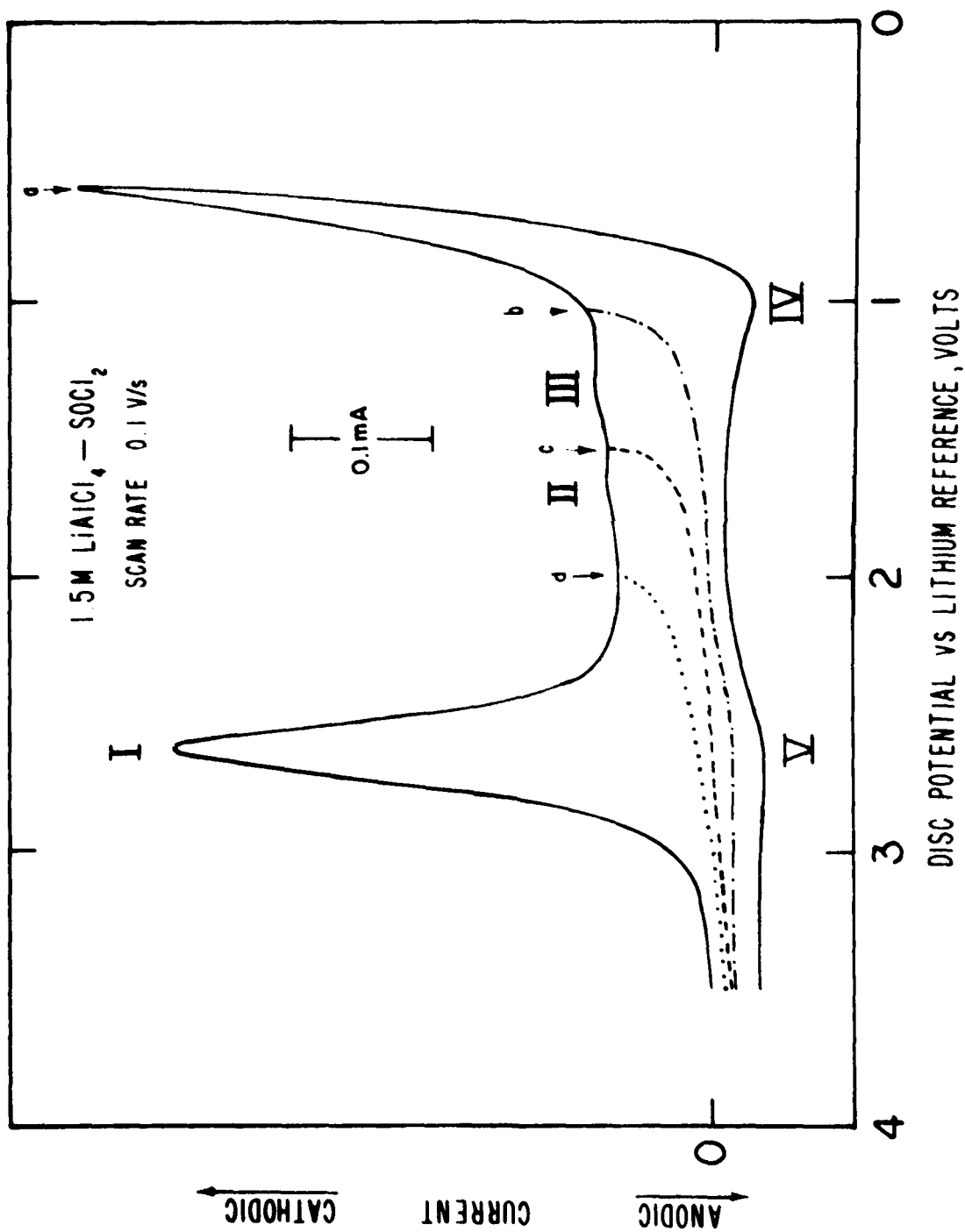


Figure 1. Cyclic Voltammograms at Glassy Carbon Electrodes in Thionyl Chloride Solutions

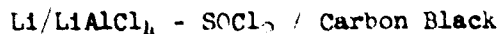
Table 2. Peak (E_p) and Half-Peak ($E_{p/2}$) Potential* Data for the Reduction of Thionyl Chloride in 0.5, 1.0, and 1.5M Solutions

Scan Rate (volts/sec.)	1.5M LiAlCl ₄ -SOCl ₂			1.0M LiAlCl ₄ -SOCl ₂			0.5M LiAlCl ₄ -SOCl ₂		
	E_p	$E_{p/2}$	$E_p - E_{p/2}$	E_p	$E_{p/2}$	$E_p - E_{p/2}$	E_p	$E_{p/2}$	$E_p - E_{p/2}$
0.003	2.83	2.93	-0.10	2.81	2.92	-0.11	-	-	-
0.0035	-	-	-	-	-	-	2.81	2.93	-0.12
0.005	2.80	2.91	-0.11	2.80	2.91	-0.11	-	-	-
0.006	-	-	-	-	-	-	2.80	2.92	-0.12
0.008	2.79	2.90	-0.11	2.77	2.89	-0.12	-	-	-
0.009	-	-	-	-	-	-	2.78	2.91	-0.13
0.011	-	-	-	2.75	2.88	-0.13	-	-	-
0.012	-	-	-	-	-	-	2.78	2.91	-0.13
0.017	2.77	2.88	-0.11	2.73	2.86	-0.13	2.76	2.90	-0.14
0.045	2.73	2.86	-0.13	2.70	2.84	-0.14	2.72	2.87	-0.15
0.074	2.68	2.82	-0.14	2.67	2.83	-0.16	2.68	2.84	-0.16
0.108	2.65	2.80	-0.15	2.65	2.82	-0.17	2.66	2.84	-0.18
0.167	2.63	2.79	-0.16	2.60	2.78	-0.18	-	-	-
0.20	-	-	-	-	-	-	2.60	2.79	-0.19
0.333	2.60	2.77	-0.17	-	-	-	-	-	-
0.40	-	-	-	2.59	2.79	-0.20	2.59	2.76	-0.17
0.50	2.56	2.75	-0.19	-	-	-	-	-	-
0.67	-	-	-	2.54	2.75	-0.21	2.49	2.73	-0.24
1.0	2.47	2.69	-0.22	2.50	2.74	-0.24	2.43	2.70	-0.27
2.0	2.42	2.67	-0.25	2.45	2.71	-0.26	-	-	-
4.0	2.32	2.65	-0.33	2.32	2.65	-0.33	-	-	-
10	2.20	2.60	-0.40	2.10	2.50	-0.40	-	-	-
20	2.05	2.53	-0.48	1.92	2.40	-0.48	-	-	-

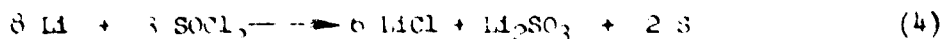
* Volts Versus Lithium Reference

products, obtained by the electrolysis of 0.14 molar $(C_2H_5)_3N HCl - SOCl_2$ solution, were temperature dependent. However, at temperatures above $0^\circ C$, 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 $(C_2H_5)_3N HCl - SOCl_2$ solutions.

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



Auborn, et al.¹² concluded that the cathodic reduction products consisted of lithium chloride, lithium sulfite, and sulfur and proposed the following cell reaction

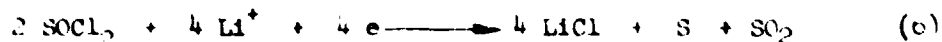


On the other hand, Driscoll, et al.¹³ reported that the reaction products in the discharged lithium-thionyl chloride cells mainly consist of lithium chloride, sulfur, and sulfur dioxide and proposed the following cell reaction



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 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.¹⁴

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 Driscoll, et al.¹⁵ The electrochemical reduction of thionyl chloride may, therefore, be represented by the equation



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 (Table 2) 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 expected¹⁶

¹²

J. J. Auborn, et al., op. cit., p. 1.

¹³J. R. Driscoll, G.L. Holleck and D.E. Toland, Proc. 27th Power Sources Symposium, 27, 28 (1976).

¹⁴A.N. Dey and C.R. Schlaikjer, Proc. 26th Power Sources Symposium, 26, 47 (1974).

¹⁵J.R. Driscoll, et al., op. cit.

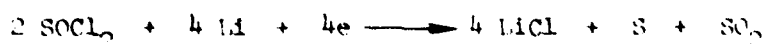
¹⁶G. Mamantov, D.L. Manning and J.M. Dale, J. Electroanal. Chem., 9, 253 (1965).

for the reversible process leading to the deposition of an insoluble substance. The peak heights for reduction peak I increase with increasing scan rate and i_p (peak height) versus $V^{1/2}$ (square root of voltage scan rate) plots result in straight lines passing through the origin. Thus, the $i_p V^{1/2}$ values presented in Table 1 are constant within experimental error over the wide range of scan rates from 3 mV/s to 20 V/s. It is also evident from the data presented in Table 1 that the peak heights for the reduction of thionyl chloride (peak I) are independent of electrolyte concentration. The mean $i_p V^{1/2}$ values in 1.5, 1.0, and 0.5 molar $\text{LiAlCl}_4\text{-SOCl}_2$ solutions were, respectively, found to be 1.16, 1.21, and 1.15 $\text{mA}(\text{volts})^{-1/2}$. From the data presented in Tables 1 and 2, it should be possible to determine the kinetic parameters of the charge transfer process for the reduction of thionyl chloride. However, since the deposition of lithium chloride on the glassy carbon microelectrodes introduces iR effects which are similar^{17,18} to kinetic effects, it would be erroneous to determine the kinetic parameters without adequate iR compensation.¹⁵

The other reduction peaks (peaks II and III) in Figure 1 may either be due to the subsequent reduction of sulfur and/or sulfur dioxide or may be simply due to some inherent impurities in the solutions. Since an anodic peak (peak V), corresponding to the reduction peaks II and III, is observed in the cyclic voltammograms, it is evident that the reduction product obtained at potentials negative to peaks II and III can be reoxidized at more positive potentials.

CONCLUSIONS

The results of the present study have shown that the electrochemical reduction of thionyl chloride in $\text{LiAlCl}_4\text{-SOCl}_2$ solutions occurs irreversibly and may be represented by the reaction:



Both sulfur and sulfur dioxide are soluble in the solutions while lithium chloride is only sparingly soluble and precipitates on the electrode surface and causes its passivation. It was also shown that the passivating film can be either removed by washing the electrode in acidic $\text{AlCl}_3\text{-SOCl}_2$ solution or by electrogenerating chlorine, in situ, at the electrode surface.

¹⁷P. Delahay, New Instrumental Methods in Electrochemistry, New York: Interscience, 1954.

¹⁸R. S. Nicholson, *Anal. Chem.*, **37**, 667 (1965).

¹⁹F. E. Wells, *Anal. Chem.*, **43**, 57 (1971).