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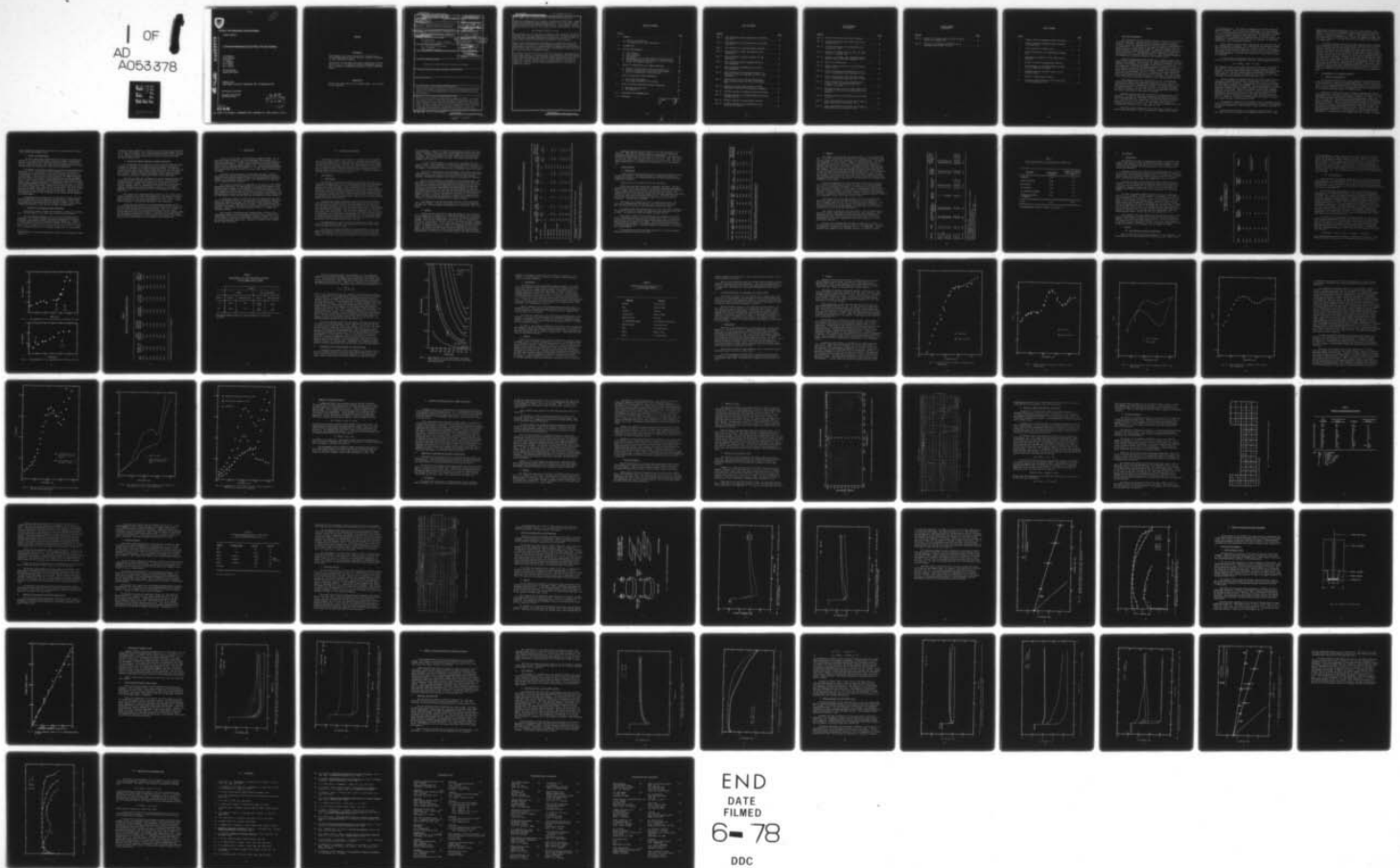
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### LITHIUM-INORGANIC ELECTROLYTE BATTERIES

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Final Report for Period 17 September 1973 - 30 September 1977

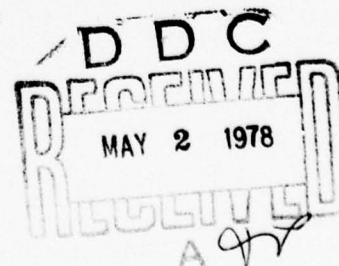
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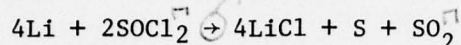
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71°C (160°F), with a particular view to finding practical solutions.

Analytical measurements were carried out on complete Li/SOCl<sub>2</sub> cells. Qualitative tests identified three discharge products, LiCl, S and SO<sub>2</sub>. Quantitative analyses were performed for these species. Of the several stoichiometries that can be written, the one most closely corresponding to the data is:



The analytical data for LiCl and S correspond to this reaction. The SO<sub>2</sub> is, however, twice the value predicted by this reaction. A reaction between S and SOCl<sub>2</sub> which generates SO<sub>2</sub> during the analysis may account for this. No other simple reaction stoichiometry corresponds to these analyses.

Near UV spectrophotometry was investigated as an analytical tool for the SOCl<sub>2</sub> system. The results of these experiments indicate that UV spectrophotometric techniques are a useful method for studying the Li/SOCl<sub>2</sub> system and, further, that it is possible to study the mechanism of SOCl<sub>2</sub> reduction in dilute solutions of organic solvents.

A protective film on the surface of the Li is essential to the operation of the Li/SOCl<sub>2</sub> battery. At the same time, film thickening, especially during high temperature storage, and associated voltage delays and voltage depressions, are a principal matter of concern. Three approaches were used to attack this problem: improved purity; alloying of the Li; and solution additions. Each of these has shown substantial effects to mitigate the passivation problem.

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## I. SUMMARY

### A. Reaction Stoichiometry

The stoichiometry of the Li/SOCl<sub>2</sub> discharge reaction was investigated by chemical analysis. Qualitative tests were used to identify reaction products. These were then quantitated by suitable analytical techniques. The resulting data was compared with the electrical data to establish product to charge ratios. In the course of this work the disposition of the discharge products was explored and a number of analytical methods useful for SOCl<sub>2</sub> electrolyte systems was developed. Measurements of SO<sub>2</sub> solubility in SOCl<sub>2</sub> were carried out. Attempts were made at establishing directly the coulomb number for the SOCl<sub>2</sub> reduction reaction. Near UV spectrophotometry was assessed as an analytical method for the Li/SOCl<sub>2</sub> system.

Analytical measurements were carried out on complete Li/SOCl<sub>2</sub> cells. The cells were assembled from Li metal foil, glass fiber separator and Teflon-bonded carbon cathodes. Both partially and completely discharged cells were analyzed. Some measurements were made at -40°C and +71°C, as well as at room temperature. Qualitative analyses indicated the presence of LiCl, S and SO<sub>2</sub> as reaction products of the cell discharge. Quantitative analyses for these species were performed and in the course of these, their distribution in the cell was determined. The LiCl is insoluble in the electrolyte and deposited essentially completely in the carbon cathode. The S and SO<sub>2</sub> were found almost completely in the electrolyte. They proved to be quite soluble in the 1.8M LiAlCl<sub>4</sub> electrolyte, S greater than 1M and SO<sub>2</sub> greater than 3M.

Flame photometry was used to quantitate the Li<sup>+</sup>. Potentiometric titration with AgNO<sub>3</sub> titrant was used to quantitate the Cl<sup>-</sup>. The S was quantitated by titration with NaCN and the SO<sub>2</sub> by gas chromatography. The analytical results may be summarized as follows: Li<sup>+</sup> and Cl<sup>-</sup> were found in equivalent amounts. In all cases, the ratio of LiCl/charge equivalent is equal to or greater than one. The state of discharge has no effect on this result between 25% to 100% depth of discharge.

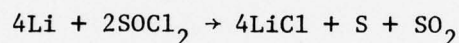
Analogous analyses were also carried out on cells operated at -40°C and +71°C. At -40°C, the results are essentially identical to the room temperature measurements. The Li<sup>+</sup>/Cl<sup>-</sup> ratio and the LiCl/charge ratio are  $1.03 \pm 0.01$  and  $0.98 \pm 0.01$  respectively. At 71°C, the Li<sup>+</sup>/Cl<sup>-</sup> ratio is still close to 1.0 at  $0.97 \pm 0.03$ . The LiCl/charge ratio, however, is slightly less than 1.0 at  $0.92 \pm 0.02$ . The LiCl loss is probably due to the increased salt solubility in the electrolyte at 71°C.

The sulfur analysis showed that 50% of the sulfur contained in the reduced SOCl<sub>2</sub> (assuming a 2 electron reduction) is present in the form of

S in discharged cells. This result is independent of current density and depth of discharge. One cell stored and discharged at 71°C was analyzed for S. Forty-five percent (45%) of the reduced  $\text{SOCl}_2$  was found as elemental S. Thus, it appears that high temperature results do not deviate significantly from results obtained at room temperature. An analysis of the components of one discharged cell showed that 90% of the S was found in the electrolyte. The rest was distributed over the components in approximate proportion to their electrolyte retention.

Sulfur dioxide concentrations in discharging cells were measured with gas chromatographic techniques. This technique has the advantage of being able to follow the  $\text{SO}_2$  concentration as a function of time. The  $\text{SO}_2$  concentration increased linearly with time during a constant current discharge. The average amount of  $\text{SO}_2$  per equivalent of charge for 7 cells was  $0.48 \pm 0.07$  moles/equivalent. The cells were tested over a current density range of 5-20 mA/cm<sup>2</sup>.

Of the several stoichiometries that can be written, the one proposed by Dey (4) most closely corresponds to the data. Dey's proposed reaction is



The qualitative data, and the analytical data for LiCl and S correspond to this reaction. The  $\text{SO}_2$  is, however, twice the value predicted by this reaction. A reaction between S and  $\text{SOCl}_2$  occurring during the analysis may account for this. No other simple reaction stoichiometry corresponds to these analyses. More complex stoichiometries can be written, and a clear resolution of the problem awaits further analytical data.

We have attempted to determine directly the coulomb number of  $\text{SOCl}_2$  reduction by monitoring the change in concentration of an inert tracer compound during cell discharge. This would be most valuable in resolving the stoichiometry question. The presumed value is  $2e^-$  per  $\text{SOCl}_2$  but this has never been experimentally established. Gas chromatography is a suitable analytical technique for this purpose, provided a tracer with necessary properties can be found. There are four basic criteria which a compound must meet in order to be useful as a tracer: it must be soluble in the  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolyte; it must have sufficient volatility for G. C. analysis; it must be chemically inert; and it must have high sensitivity for G. C. analysis. A series of volatile organic and inorganic compounds was screened but none of them proved suitable.

The analytical chemistry of the  $\text{Li}/\text{SOCl}_2$  system is complicated by the chemical reactivity of the reactants and products. Because of this complexity, it would be advantageous to have available as many analytical techniques as possible.

Thionyl chloride and many of its suspected reaction products, e.g.,  $\text{SO}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{SCl}_2$ , and S, absorb in the visible and near UV (5, 6). They



have moderate extinction coefficients ( $\epsilon \approx 10^3$ ) at  $\lambda_{\max} \approx 280$  nm. This suggests that VIS-UV spectrophotometry might provide a suitable analytical approach to the system. We began the survey by obtaining the spectra of several of the pure components (i.e.,  $\text{SOCl}_2$ , S,  $\text{SO}_2$ ,  $\text{S}_2\text{Cl}_2$ , and  $\text{LiCl}$ ). We then investigated the possibility that chloride ion complexes of  $\text{SOCl}_2$  might be present. Finally, we obtained spectra of the products of the reaction of Li with  $\text{SOCl}_2$ .

Since the extinction coefficient of  $\text{SOCl}_2$  is high enough to preclude direct measurement, hexanes and tetrahydrofuran (THF) were used as solvents. Lithium and  $\text{SOCl}_2$  react with each other in THF, but do not react in the hexanes. Standard spectra were obtained and, where comparison with literature data is possible, the correspondence was excellent. Thionyl chloride reduction with Li was carried out in THF. UV spectra were obtained directly on these solutions and it was possible to separate the contributions from all the known reaction products. Estimates of the S and  $\text{SO}_2$  produced were made from these data. The product to charge ratios were 0.23 S/e<sup>-</sup> and 0.36  $\text{SO}_2$ /e<sup>-</sup>. The value for S agrees closely with the values determined by the more complicated titration techniques. The value for  $\text{SO}_2$  is significantly lower than that established by the gas chromatographic techniques. The results of these experiments indicate that the UV spectrophotometric technique is a useful method for studying the Li/ $\text{SOCl}_2$  system and, further, that it is possible to study the mechanism of  $\text{SOCl}_2$  reduction in dilute solution using organic solvents.

## B. Investigation of Li Anode Passivation

### 1. Effects of Purification

The electrolyte purity is of crucial importance in the performance of Li/ $\text{SOCl}_2$  cells after storage at elevated temperatures. Marincic's data (7) clearly indicate the severe passivation problems caused by Fe in the electrolyte. We have investigated this question by analyses of the electrolyte and the electrolyte components, and by establishing the effects of purification of the electrolyte on the behavior of Li/ $\text{SOCl}_2$  cells.

Analysis of the electrolyte and electrolyte components was done by spectrophotometric, emission spectroscopic and infra-red techniques. Without purification, the electrolyte (1.8M  $\text{LiAlCl}_4$ ) contained  $\approx 2.3$   $\mu\text{g/ml}$  of Fe. The individual components contributed the following percentages:  $\text{SOCl}_2$ , 21%;  $\text{LiCl}$ , 5%;  $\text{AlCl}_3$ , 74%. Infra-red measurements revealed that distillation of  $\text{SOCl}_2$  at atmospheric pressure introduced substantial amounts of  $\text{SO}_2$  and small quantities of  $\text{SO}_2\text{Cl}_2$ . The IR studies also showed that without purification the electrolyte contains HCl and hydroxyaluminum compounds, and that the  $\text{SO}_2$  content is increased substantially over that of the pure solvent. The hydroxyaluminum compounds are reactive toward Li. Emission spectroscopic measurements show that there is a substantial increase in the Fe and Cu on the surface of a passivated Li anode compared with pure Li metal. Li/ $\text{SOCl}_2$

cells prepared with unpurified electrolyte shows voltage delays\* after as little as 100 hrs storage at 71°C.

## 2. Effects of Purification

The above results have established that Li-reactive impurities are present in the unpurified electrolyte, and that Li/SOCl<sub>2</sub> cells prepared with this electrolyte suffer relatively rapid passivation. They do not, however, correlate the two. This correlation was established by purifying the electrolyte and observing the effect on cell passivation.

The method of purification chosen was to store the electrolyte with Li metal at 71°C. Iron and Cu levels were monitored by analyzing the Li metal used for the purification. After one day storage, the Cu and Fe concentrations on the Li were more than three times the background in the Li solid itself. After six days, the Fe content of Li freshly introduced into the solution was reduced to the background levels in the unimmersed metal. After six days, the Cu content stabilized at about twice the background level. Infra-red analysis of the electrolyte stored with Li reveals that the hydroxyaluminum compounds are removed within two days. The removal of the HCl takes up to 10 days. Storage of the electrolyte with Li causes the color to change from a light tan to a bright yellow. The cause of this has not been clearly identified. We believe, however, it may be due to S generated by the slow reaction between Li and the SOCl<sub>2</sub>. Sulfur has not been identified directly, but an increase in SO<sub>2</sub> content has been observed by IR measurements.

Lithium/SOCl<sub>2</sub> cells prepared with Li-purified electrolyte show substantial improvement in their resistance to passivation. Voltage delays do not appear in these cells until after 300 hrs storage at 71°C. Thus, while electrolyte purification does not provide a complete solution to the voltage delay problem, it does provide an avenue for improvement.

## 3. Effects of Li Alloying on Anode Performance

Alloys with a high Li content were evaluated as anodes for the SOCl<sub>2</sub> cell. The performance of both fresh and stored alloys was measured.

The electrochemical behavior of 12 Li alloys was explored by two techniques: The current potential curves were measured and the various alloys were also tested as anodes in a battery configuration. Eleven of the alloys proved suitable as experimental anodes. These were: Li/Al (5 at. %), Li/Ag (5 at. %), Li/Au (2 at. %), Li/Bi (5 at. %), Li/Cd (5 at. %), Li/Cu (4 at. %), Li/Mg (1 at. %), Li/Pb (3 at. %), Li/Si (4 at. %), Li/Sn (3 at. %) and Li/Zn (10 at. %). One alloy, Li/Mg (5 at. %), did not show

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\*"Voltage delay" is arbitrarily defined as initial cell polarization on load below 2 V.

sufficient current capability. The majority of the alloys behave comparably to Li after 71°C storage. Four alloys have shown some improvement relative to Li. The Ag, Cd and Mg (1 at. %) have displayed slightly better recovery of rate capability during testing; the Si alloy has given better anode utilization than pure Li.

#### 4. Effects of Solution Additives on Anode Passivation

An investigation of the effects of various solution additives on the Li/SOCl<sub>2</sub> cell was made. The primary goal was to develop an additive to alleviate or eliminate the Li anode passivation problem. The additives tested were H<sub>2</sub>O, S<sub>2</sub>Cl<sub>2</sub>, AlCl<sub>3</sub>, SbCl<sub>5</sub>, Et<sub>4</sub>NCl, SO<sub>2</sub>, P<sub>2</sub>S<sub>5</sub>, PCl<sub>3</sub>, PCl<sub>5</sub> and Ca<sup>++</sup>. Of this group, we have found two that are beneficial to cell performance - PCl<sub>5</sub> and Ca<sup>++</sup>. Three of them were detrimental - AlCl<sub>3</sub>, SbCl<sub>5</sub> and Et<sub>4</sub>NCl. The remainder displayed no substantial effects on cell performance.

The AlCl<sub>3</sub> and SbCl<sub>5</sub> are detrimental to cell performance because they continually dissolve the LiCl film from the Li anode. This reduces the voltage delay due to passivation from LiCl film thickening but at the expense of anode corrosion. The Et<sub>4</sub>NCl causes corrosion of the Ni used in the cell assembly. This is apparently due to the fact that tetraalkyl ammonium chlorometallates are very soluble in SOCl<sub>2</sub> (8). The Et<sub>4</sub>NCl apparently causes the dissolution of the Ni cell components, to form the NiCl<sub>4</sub><sup>-</sup> ion.

PCl<sub>5</sub> reduces cell passivation during storage at 71°C. This is evidenced by improved cell voltage during discharge. The discharge voltage of cells stored 620 hrs with 1 wt % PCl<sub>5</sub> added to the electrolyte is ~1 volt higher than that of cells without the additive (2.8 V vs. 1.8 V). Further work is required to establish the mechanism of this improvement.

Calcium ion also reduces cell passivation during storage at 71°C. We have established that Ca metal is electrochemically active in SOCl<sub>2</sub>, and that it is more resistant to passivation than Li. Calcium ion is added to the electrolyte in the form of a sparingly soluble salt, e.g., CaCl<sub>2</sub>. Calcium then plates onto the surface of the Li anode. The Ca coating exhibits the resistance to passivation of pure Ca. Cells with Ca-coated Li anodes have an operating voltage of 2.7 V after 800 hrs of storage. This compares with 1.0 V for cells without the Ca<sup>++</sup> additive stored for 800 hrs.



## II. INTRODUCTION

This is the Final Report on ECOM Contract DAAB07-74-C-0030. It contains the results of work for the period September 1973-September 1977. This report summarizes our research and development effort on the Li/thionyl chloride battery system. In early studies, this system appeared promising both in terms of power and energy density (1, 2). Later work with complete sealed cells has confirmed this promise (3). D-cells have delivered 170 Whr/lb at the one-week rate and at the C/3 rate are still capable of delivering 100 Whr/lb.

The work on this program has centered along two lines: We have investigated the reaction stoichiometry of the cell discharge via chemical analysis of the reaction products; we have also investigated the problem of Li/SOCl<sub>2</sub> cell passivation during storage at 71°C (160°F), with a particular view to finding practical solutions.

The reaction stoichiometry is important to two aspects of cell design, optimization and safety. An understanding of the nature and behavior of the discharge products allows for an efficient cell design with respect to rate and/or capacity. Further, since Li/SOCl<sub>2</sub> is a very reactive chemical system, some consideration must be given to the safety aspects of cell operation. An understanding of the nature and behavior of the discharge products would input the cell design to allow safe and efficient accommodation of these products.

A protective film on the surface of the Li is essential to the operation of the Li/SOCl<sub>2</sub> battery. At the same time, film thickening, especially during high temperature storage, and associated voltage delays and voltage depressions, were a principal matter of concern. Three approaches were used to attack this problem: improved purity; alloying of the Li; and solution additions. Each of these has shown substantial effects to mitigate the passivation problem.

This report is organized in the following manner. Section I is a comprehensive summary of the experimental work and results. Section III is a description of the reaction stoichiometry analysis. Sections IV, V and VI are accounts of the work on the effects of improved purity, Li alloying and solution additives respectively. Section VII contains a brief summary, and the final conclusions.



### III. REACTION STOICHIOMETRY

An analysis of reaction stoichiometry is essential for the optimization of the Li/SOCl<sub>2</sub> primary battery system. A thorough understanding of the reactions involved in cell discharge will allow for optimal cell design for specified energy and power density. This understanding will also allow for cell design to accommodate the highly reactive Li/SOCl<sub>2</sub> chemical system from a safety viewpoint. Qualitative analyses were performed and three reaction products were identified: LiCl, S and SO<sub>2</sub>. Quantitative analysis for these three species was then carried out.

#### A. LiCl Analysis

##### 1. Experimental

For all the room temperature experiments discussed below, the cell configuration consisted of a Li foil anode mounted on Exmet Ni screen wrapped around the C cathode under test. The two electrodes were separated by a nonwoven glass fiber separator. The Li electrode (15 mil Li foil, Foote Mineral Co.) was pressed firmly around the C electrode and separator material, to provide a relatively parallel configuration and intimate contact between the separator and both electrodes. Carbon electrodes were manufactured by a manual pasting procedure and sintered under argon at 300°C for 15-20 minutes, as described in the First Quarterly Report. The electrode thicknesses varied between 40-45 mils (0.10-0.11 cm).

Each electrode package was placed between two Teflon hemicylinders, which provided an approximate 0.100" wide cell compartment when the entire unit was placed in a glass vial with an inside diameter of 0.650 inches. Each cell was fitted with a small Li foil reference electrode. This arrangement provided added uniformity of the test cell configuration and was used in all V-cell (vial cell) studies. The electrolyte amount was 3.5 cc in all tests using this configuration. Each vial cell, immediately upon the addition of electrolyte, was covered with a polyethylene cap. This was tight enough to impede substantial evaporation of the solvent, yet it allowed the passage of the nickel screen leads over the edge of the vial and direct electrical connection to the discharge and monitoring circuits.

The measurements at -40°C and 71°C were conducted in similar cells sealed in stainless steel tubes. The tubes were fitted with Conax connectors to provide the electrical leads.

The cells were dismantled immediately after discharge. The C electrodes were placed in separate vials each containing 12 cc of as-received SOCl<sub>2</sub>. The separator of one cell (A3) was placed in a separate vial containing 12 cc of SOCl<sub>2</sub> to determine the amount of Li<sup>+</sup> and Cl<sup>-</sup> precipitate

in the separator. Each of the samples was washed for a period of one week with five changes of  $\text{SOCl}_2$ , to remove soluble materials such as  $\text{S}_2\text{Cl}_2$  and  $\text{LiAlCl}_4$ . They were then placed in a vacuum chamber for 16 hours to remove all  $\text{SOCl}_2$ . After being weighed, they were leached with five successive changes of water over a period of one week. The aqueous leachates were analyzed for  $\text{Li}^+$  and  $\text{Cl}^-$ .

A carbon electrode similar to those used in discharged cells was used as control. After immersion in  $\text{LiAlCl}_4$ - $\text{SOCl}_2$  electrolyte for several minutes, it was removed and placed in a vial containing 12 cc of  $\text{SOCl}_2$ . From this stage, it was treated in the same way as discharged carbon electrodes.

The  $\text{Li}^+$  was determined on an Instrumentation Laboratories model 143A flame photometer. A 1.5 molar  $\text{K}^+$  internal standard is used for each sample. Precision and repeatability were better than 1% at the concentrations employed. Readings for unknowns were compared with standard  $\text{Li}^+$  solutions.

The  $\text{Cl}^-$  was determined by potentiometric titration with  $\text{AgNO}_3$ . The Ag sensing electrode and an Ag/AgCl reference electrode (fiber junction) were used in a stirred, doubled jacketed beaker thermostated at  $25^\circ \pm 0.1^\circ\text{C}$ . Silver nitrate solutions were standardized against primary standard NaCl solutions. Precision and repeatability were approximately 1%. From the data presented in Table 1, we note that the  $\text{SOCl}_2$  washing procedure was effective in removing  $\text{LiAlCl}_4$ , and that the evacuation procedure effectively removed the  $\text{SOCl}_2$ . Prior to  $\text{SOCl}_2$  washing, the amounts of  $\text{Cl}^-$  present as  $\text{LiAlCl}_4$  is about 3.3 m moles; another 10.7 m moles of  $\text{Cl}^-$  could come from  $\text{SOCl}_2$ . The  $\text{SOCl}_2$  washing and evacuation procedures removed 99.8% of this chloride, as shown by the results with the control electrode.

The separator was in intimate contact with the C and Li electrodes during cell discharge. However, the amount of  $\text{Cl}^-$  found in the separator was quite low. This indicates that precipitation is confined to the C electrode.

## 2. Results

Lithium chloride precipitates almost exclusively in the C electrode. Table 1 summarizes the results of the quantitative analysis for  $\text{Li}^+$  and  $\text{Cl}^-$  in room temperature discharged cells.  $\text{Li}^+$  and  $\text{Cl}^-$  were found in equivalent amounts. Only the first sample shows a  $\text{Li}^+$  excess over  $\text{Cl}^-$  exceeding the accuracy of the analysis of between 1 and 2%. The amount of LiCl is equivalent to the charge passed. In all cases, the ratio of LiCl/charge equivalent is equal or greater than one. The state of discharge has no effect on this result. As apparent from Table 1, cells were discharged from 25 to 100% depth. The carbon electrode loading too had no influence on the results. A comparison of the weight gain of the carbon electrode with the LiCl found shows, further, that LiCl is the only solid product in the carbon electrode.

Table 1

## Chemical Analysis Discharged Carbon Electrodes at Room Temperature

Test	Sample	Carbon (mg)	Charge Recorded* (coul)	Charge Density (coul/mg)	Approximate % Capacity	Weight Gain** (mg)	LiCl Analysis (mg)	Li <sup>+</sup> (m moles)	Cl <sup>-</sup> (m moles)	Charge Recorded (m equiv)	Moles LiCl per Equivalent of Recorded Charge
A1	electrode	123	1670 (approx)	12.2	100	844	819	20.4	19.1	17.3 (approx)	1.14 (approx)
A2	control electrode	147	-	-	-	-	-	-	0.032	-	-
A3	separator	-	-	-	-	-	-	-	0.07	-	-
A3	electrode	117	562	4.8	40	249	242	5.75	5.66	5.82	0.98
A4	electrode	115	562	4.9	40	280	276	6.60	6.43	5.82	1.12
A5	control electrode	60	-	-	-	-	-	-	0.005	-	-
A6	electrode	60	367	6.1	(?)	171	163	3.90	3.81	3.81	1.01
A7	electrode	116	367	3.2	25	198	201	4.73	4.76	3.81	1.25
A8	electrode	60	887	14.8	(?)	399	400	9.50	9.39	9.20	1.03
A9	electrode	116	887	7.6	60	397	406	9.56	9.58	9.20	1.04

\*Tests A4 and A7 may have been temporarily shorted during testing or disassembly

\*\*Weight gain for the carbon electrodes is the weight after SOCl<sub>2</sub> washing and evacuation minus the weight of the electrode before assembly into a cell.

Analogous analyses were also carried out on cells operated at  $-40^{\circ}\text{C}$  and  $+71^{\circ}\text{C}$ . These data are shown in Table 2. At  $-40^{\circ}\text{C}$ , the results are essentially identical to the room temperature measurements. The  $\text{Li}^+/\text{Cl}^-$  ratio and the  $\text{LiCl}/\text{charge}$  ratio are  $1.03 \pm 0.01$  and  $0.98 \pm 0.01$  respectively. At  $71^{\circ}\text{C}$ , the  $\text{Li}^+/\text{Cl}^-$  ratio is still close to 1.0 at  $0.97 \pm 0.03$ . The  $\text{LiCl}/\text{charge}$  ratio, however, is slightly less than 1.0 at  $0.92 \pm 0.02$ . The  $\text{LiCl}$  loss is probably due to the increased salt solubility in the electrolyte at  $71^{\circ}\text{C}$ .

## B. Sulfur Analysis

### 1. Experimental

Sulfur analysis was performed on cells of the same design as was used for the  $\text{LiCl}$  analysis. The method employed for quantitative analysis of elemental sulfur was that of Skoog and Bartlett (9) with appropriate sample preparation techniques.

Specifically, the procedure involves the following:

Sulfur was extracted from the cell components with  $\text{SOCl}_2$ . The discharged cell electrolyte was transferred to a beaker containing approximately 70 ml of  $\text{SOCl}_2$ . The  $\text{Li}$  anode and the  $\text{C}$  cathode were rinsed in this solution. 30 ml of additional  $\text{SOCl}_2$  were used to rinse the porous  $\text{C}$  cathode. The separator was left in the solution through the final  $\text{CS}_2$  extraction (see below). 0.2-0.3g of carbon black (Shawmigan Products Corp., 100% compressed) was stirred into this solution, to provide a large surface area for sulfur adsorption. The  $\text{SOCl}_2$  was evaporated.

The residue was treated with  $\sim 50$  ml of 3M  $\text{HCl}$  and filtered. The filtrate was discarded and the residue on the filter washed with 50 ml  $\text{H}_2\text{O}$ . The filter was dried at room temperature (usually overnight).

The dried solids were extracted with  $\text{CS}_2$ . The filter paper containing the solids was placed in a beaker and washed with four portions of  $\text{CS}_2$  ( $\sim 20$  ml each). The final  $\text{CS}_2$  volume was brought to exactly 100 ml.

Three 10 ml aliquots of the  $\text{CS}_2$  solution were evaporated to dryness in 125 ml Erlenmeyer flasks. The dried residue was wet with a few drops of  $\text{CS}_2$  and 50 ml of 20 vol %  $\text{H}_2\text{O}/\text{acetone}$  containing three drops of bromocresol purple indicator (1% aqueous) were added. The solution was heated to the boiling point and titrated to a permanent purple end point with  $\sim 0.05\text{M}$   $\text{NaCN}$  in 20 vol %  $\text{H}_2\text{O}/\text{isopropanol}$ . The  $\text{NaCN}$  solution was standardized by titration with standard  $\text{AgNO}_3$ .

The procedure was tested with known amounts of  $\text{S}$ , and good agreement between expected and measured  $\text{S}$  was found.



Table 2

Chemical Analysis Discharged Carbon Electrodes at -40 and +71°C

Temp.	Cell	Carbon (mg)	Charge Recorded (coul)	Charge Density (coul/mg)	Approximate % Capacity	Weight Gain * (mg)	LiCl Analysis (mg)	Li <sup>+</sup> (m moles)	Cl <sup>-</sup> (m moles)	Charge Recorded (m equiv)	Moles LiCl per Equivalent of Recorded Charge
71°C	33	335.3	2908	8.67	100	1495.2	1147.8	26.8	27.4	30.1	0.91
71°C	58	126.7	1696	13.38	100	707.9	695.2	16.2	16.6	17.6	0.93
71°C	59	121.6	1260	10.36	100	523.1	519.3	11.9	12.6	13.06	0.94
-40°C	90	122.1	567	4.64	100	242.1	243.7	5.8	5.7	5.9	0.97
-40°C	91	123.5	315	2.55	100	143.2	137.8	3.3	3.2	3.3	0.98

\*Weight gain for the carbon electrodes is the weight after SOCl<sub>2</sub> washing and evacuation minus the weight of the electrode before assembly into a cell.

## 2. Results

The results of the analysis are shown in Table 3. The data show that  $50\% \pm 2\%$  of the S contained in the reduced  $\text{SOCl}_2$  (assuming a 2-electron reduction) is present in the form of elemental S in discharged cells. This result was independent of current density. Depth of discharge probably also does not change the fraction of the reacted  $\text{SOCl}_2$  converted into elemental S. However, these data are not conclusive. Discharge to 50% of total capacity (see Table 3) was carried out in cells containing distilled, technical grade  $\text{SOCl}_2$  (Baker). All other data was obtained with reagent grade (MCB)  $\text{SOCl}_2$ . We used the distillation procedure described by Rigby (10). It is interesting to note that doubly distilled  $\text{SOCl}_2$  without electrolyte salts did not show any elemental S (less than  $0.02 \text{ m mol S per } 25 \text{ ml SOCl}_2$ ). However, electrolyte solutions prepared with this particular batch of distilled (Baker)  $\text{SOCl}_2$  generated sulfur by gradual interaction of the electrolyte salt, probably with an impurity in the  $\text{SOCl}_2$ .

Sulfur determinations for cells discharged to 50% of total capacity were corrected by subtracting the amount of sulfur ( $0.51 \text{ m mol}$ ) determined in  $3.5 \text{ ml}$  of electrolyte, the quantity of electrolyte used in these cells. This correction is probably too large, since it appeared that S production in the electrolyte was gradual, as indicated by the continuing intensification in color. It should be noted that while elemental S found in the electrolyte alone is a significant correction in the partially discharged samples of Table 3, it is equivalent to about 1% of the S found as  $\text{SOCl}_2$ .

One pressure cell stored and discharged at  $71^\circ\text{C}$  was analyzed for S. Forty-five percent (45%) of the reduced  $\text{SOCl}_2$  was found as elemental S. This is somewhat lower than the  $50\% \pm 2\%$  observed at room temperature. The data are insufficient to be sure whether this difference is significant. The results are in close enough agreement to suggest that there is no major difference in S yield at the two temperatures.

The S found is dissolved in the electrolyte. This is demonstrated by the data in Table 4 which shows S found in various cell components. After discharge, the cell components were separated and analyzed individually. Ninety percent (90%) of the S was found in the electrolyte. The rest is distributed over the other components in approximate proportion to their electrolyte retention.

Further tests confirmed the solubility of elemental S in  $\text{SOCl}_2$ . It was found that S solubility in  $\text{SOCl}_2$  is  $1.07\text{M}$  at room temperature. The rate of elemental S dissolution is relatively slow at room temperature. Sulfur dissolves very readily at  $70^\circ\text{C}$ , yielding solutions in excess of  $7 \text{ mol/l}$ .

Table 3

Sulfur Analysis of Li/SOCl<sub>2</sub> Cells

Cell No.	Temp.	Discharge Capacity (coul)	Fraction of Total <sup>a</sup> %	Current (mA/cm <sup>2</sup> )	Sulfur Found (m mol)	SOCl <sub>2</sub> Reduced <sup>b</sup> (m mol)	Fraction of Reduced SOCl <sub>2</sub> Found as S (%)
64-V-12	r.t.	930	100	7	2.36	4.84	48.8
68 V-13	r.t.	791	100	7	1.96	4.12	47.6
71-V-14	r.t.	844	100	7	2.19	4.38	50.0
V-118 <sup>c</sup>	r.t.	1493	100	7	4.17	7.75	53.8
98-V-1	r.t.	684	100	20	1.72	3.54	48.6
98-V-2	r.t.	684	100	20	1.85	3.54	52.5
98-V-3	r.t.	684	100	20	1.74	3.54	49.1
98-V-4	r.t.	684	100	20	1.75	3.54	49.4
99-V-5	r.t.	360	~50	20	(1.21) 0.70	1.86	(65.0) 37.6 <sup>d</sup>
99-V-6	r.t.	360	~50	20	(1.27) 0.76	1.86	(68.5) 40.9 <sup>d</sup>
99-V-7	r.t.	360	~50	20	(1.08) 0.57	1.86	(58.0) 30.6 <sup>d</sup>
99-V-8	r.t.	360	~50	20	(1.17) 0.67	1.86	(63.0) 36.0 <sup>d</sup>
85-P-6 <sup>e</sup>	71°C	1646	100	7	3.81	8.52	44.7

<sup>a</sup>100% discharge to 1.0 V.<sup>b</sup>It is assumed that SOCl<sub>2</sub> reduction involves 2 electrons.<sup>c</sup>Each component analyzed separately<sup>d</sup>Corrected for S in electrolyte, see text.<sup>e</sup>Cell stored 18 hrs at 71°C and discharged at 71°C.

Table 4

Sulfur Distribution in an Experimental Li/SOCl<sub>2</sub> Cell

<u>Cell Part</u>	<u>Sulfur Found</u> (m mol)	<u>Fraction of Reduced</u> <u>SOCl<sub>2</sub> Found as S*</u> (%)
Separator	0.25	3.3
Carbon electrode	0.09	1.2
Electrolyte	3.49	45.1
Li electrode	0.10	1.3
Li reference electrode	0.12	1.6
Reference electrode separator	0.11	1.3
Total	4.16	53.8

\*Assuming SOCl<sub>2</sub> reduction involves 2 electrons.



## C. SO<sub>2</sub> Analysis

### 1. Experimental

Measurements were made by withdrawing aliquots of electrolyte from Li/SOCl<sub>2</sub> cells before, during, and after galvanostatic discharge. These aliquots were analyzed for SO<sub>2</sub> and SOCl<sub>2</sub> by gas chromatography. The SO<sub>2</sub> content was then compared with charge passed in order to establish the reaction stoichiometry.

Analyses were made on a Varian 920 gas chromatograph with a 1/4" o.d. 25 foot stainless steel column packed with 15% Kel-F 210 wax on 70/80 mesh Kel-F 300 LD. The instrumental parameters were: He carrier gas, 55 ml/min; thermal conductivity detector at 140°C; injector at 150°C; and column at 80°C. The injected liquid sample size ranged from 0.5  $\mu$ l to 1.0  $\mu$ l.

Calibration curves were established for SO<sub>2</sub> and SOCl<sub>2</sub> with pure standards. The cell design used in these experiments was a modification of the vial cell described above in Section A. The cell was adapted to accommodate a magnetic stirring bar, and to allow free electrolyte flow between the electrodes without significantly increasing the electrolyte volume.

In order to determine possible generation of SO<sub>2</sub> by a mechanism other than cell discharge, the SO<sub>2</sub> content of an assembled cell's electrolyte was monitored over a period of 7 hours. The cell had an OCV of 3.6 volts. The SO<sub>2</sub> content increased at a rate of 0.043 mole/l.hr. The exact source of this increase was not determined. Reaction of SOCl<sub>2</sub> with the rubber septum may be responsible, as evidenced by the following: Firstly, no HCl was observed in the gas chromatographs and, secondly, after 24 hours the cap did show signs of attack. If atmospheric water vapor penetration were a significant source of the SO<sub>2</sub> increase, then HCl gas should also be a product. This rate of SO<sub>2</sub> increase does not significantly affect the results reported below. In any case, data were corrected for it.

The assembled cells, when removed from the glove box, stood at open circuit for approximately an hour during which time the electrolyte was sampled. Open circuit potentials were 3.6 volts. A selected current was then passed until the cell voltage dropped to 1.0 volt or the carbon vs. Li reference potential dropped to 1.0 volt. Electrolyte samples were taken during current flow. After discharge, further samples were taken.

### 2. Results

#### (a) SO<sub>2</sub> Generation during Cell Discharge

Table 5 gives cell and discharge parameters for the experiments. The electrolyte was 1.8M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> in all cells except LS-9, where it was

Table 5

Experimental Parameters of Cells  
Used for SO<sub>2</sub> Analysis

<u>Cell</u>	<u>Current</u> (mA)	<u>Current</u> Density (mA/cm <sup>2</sup> )	<u>Electrolyte</u> Volume (ml)	<u>Discharge</u> Time (hrs)	<u>Comments</u>
LS-1	70	7	3.5	4.2	-
LS-2	120	12	3.5	2.0	-
LS-4	100	20	3.5	0.97	LS-4 thru LS-9 are stirred cells
LS-5	50	10	4.0	3.3	-
LS-6	75	15	3.5	1.7	-
LS-8	25	5	4.0	3.6	-
LS-9	100	20	4.0	0.48	LS-9 1M LiSbCl <sub>6</sub>

1.0M LiSbCl<sub>6</sub>/SOCl<sub>2</sub>. Figures 1 and 2 show SO<sub>2</sub> concentrations vs. time for two of the experiments. Sulfur dioxide is clearly a product of cell discharge and its amount increases linearly with time. The G. C. analyses for SO<sub>2</sub> are shown in Table 6 together with calculated ratios of SO<sub>2</sub> to equivalent of charge. It is apparent that 0.5 moles of SO<sub>2</sub> are produced per equivalent of charge at 25°C. The average ratio for the seven measurements is  $0.48 \pm 0.07$  moles SO<sub>2</sub>/equivalent of charge. These results indicate no change in the ratio of SO<sub>2</sub> to charge for a range of current densities from 5 to 20 mA/cm<sup>2</sup>. Also, use of LiSbCl<sub>6</sub> instead of LiAlCl<sub>4</sub> did not significantly alter the ratio.

#### (b) SO<sub>2</sub> Solubility

The question of the potential hazard of SO<sub>2</sub> as a discharge product is an important one. Our investigation of the Li/SOCl<sub>2</sub> cell discharge stoichiometry established the SO<sub>2</sub> solubility to be ~3M in electrolyte at 25°C by gas chromatography. This solubility is much greater than previously reported in the literature (11) and suggests that SO<sub>2</sub> would not cause a significant pressure build-up in a discharged cell.

We also determined the solubility of SO<sub>2</sub> in 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> and pure SOCl<sub>2</sub> at 25°C (298K) and 0°C (273K). The solubility was determined gravimetrically. The SO<sub>2</sub> was Matheson anhydrous with minimum liquid purity of 99.98%. The cylinder was connected to three gas bubblers joined in series. The first bubbler contained glass wool, to remove any solid or non-volatile liquid particulates. The second bubbler contained a weighed aliquot of electrolyte (1.5M LiAlCl<sub>4</sub>) or SOCl<sub>2</sub>. The third and final bubbler contained concentrated H<sub>2</sub>SO<sub>4</sub> to act as a flow monitor and to isolate the system from atmospheric contamination. The sample bubbler was maintained at 25°C in air or at 0°C in an ice bath. The flow of SO<sub>2</sub> was set to minimize SOCl<sub>2</sub> loss from the solution by allowing little or no exit bubbling. Bubbling was continued until no more weight was gained. Four measurements were made on electrolyte, two at 25°C and two at 0°C, and two measurements were obtained with SOCl<sub>2</sub>, one at 25°C and one at 0°C.

The results of the measurements are shown in Table 7. They are presented as mole percentages, which was calculated directly from the weight data, and as molarity. The molarity values contain some uncertainty introduced by the values of the solution density. The densities have not been measured, but have been estimated from literature values for liquid SO<sub>2</sub>, SOCl<sub>2</sub> and electrolyte (12). The density was estimated on the assumption that each component contributed to the density its mole fraction of its pure state density.

$$\rho(\text{solution}) = \rho(\text{SO}_2) \cdot x(\text{SO}_2) + \rho(\text{solvent}) \cdot x(\text{solvent})$$

The calculated densities were all within  $\pm 0.03$  g/cm<sup>3</sup> of 1.60 g/cm<sup>3</sup>. This value was chosen to calculate all of the molarities presented in Table 7.

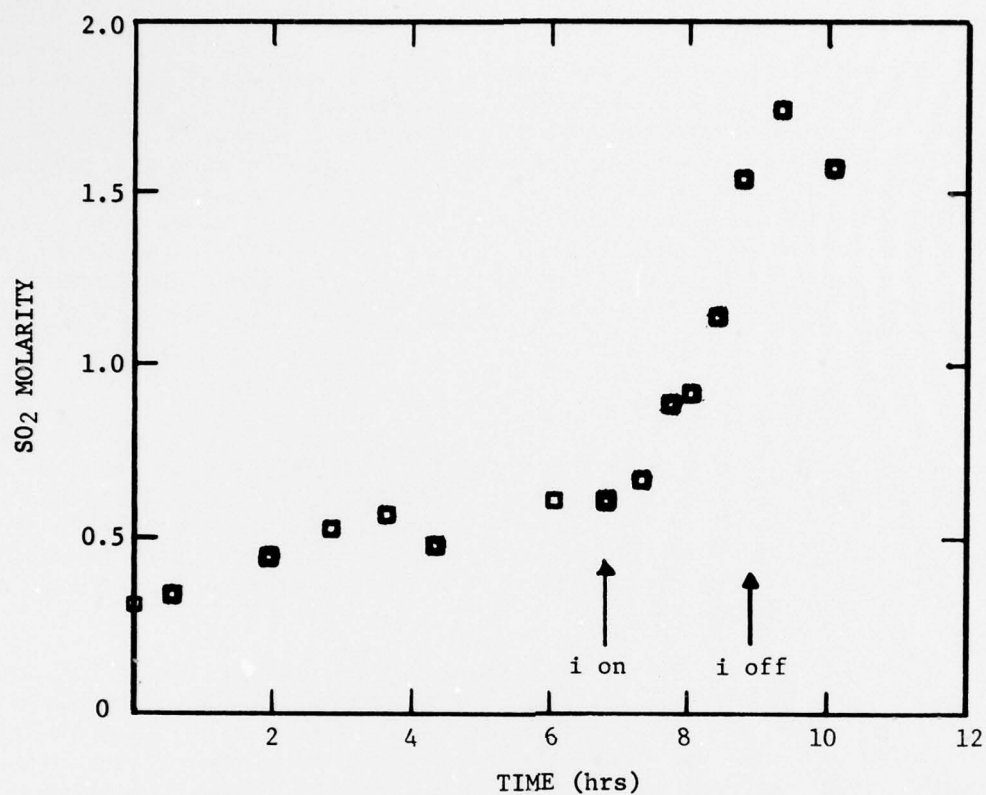


Fig. 1: Time dependence of SO<sub>2</sub> concentration in Li/SOCl<sub>2</sub> cell LS-2.

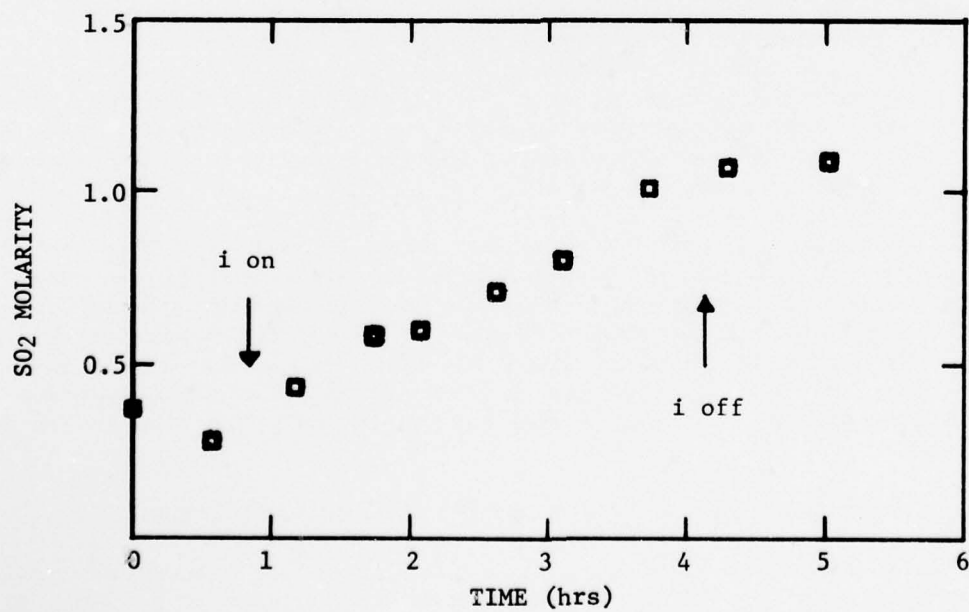


Fig. 2: Time dependence of SO<sub>2</sub> concentration in Li/SOCl<sub>2</sub> cell LS-5.



Table 6  
Results of SO<sub>2</sub> Gas Chromatographic Analysis

Cell	Initial SO <sub>2</sub> Molarity	Total Final SO <sub>2</sub> Molarity	Corrected Final SO <sub>2</sub> Molarity*	Increased SO <sub>2</sub> Molarity	Moles SO <sub>2</sub> x 10 <sup>3</sup>	Faradays x 10 <sup>3</sup>	Ratio Moles SO <sub>2</sub> / Faraday
LS-1	0.28	2.25	2.06	1.78	6.23	11.8	0.53
LS-2	0.61	1.57	1.48	0.87	3.28	8.95	0.37
LS-4	0.58	1.17	1.13	0.55	1.93	3.62	0.53
LS-5	0.33	1.09	0.95	0.62	2.49	6.16	0.40
LS-6	0.25	1.02	0.95	0.70	2.45	4.76	0.52
LS-8	0.38	0.90	0.75	0.37	1.48	3.36	0.44
LS-9	0.42	0.69	0.67	0.25	1.00	1.79	0.56

\*Corrected for the 0.043 mol/1.hr. of background.

Table 7

SO<sub>2</sub> Solubility in 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> and SOCl<sub>2</sub>  
at 25°C (298K) and 0°C (273K)

Temp °C	Solvent			
	SOCl <sub>2</sub>		1.5M LiAlCl <sub>4</sub> /SOCl <sub>2</sub>	
	Mole %	Molarity <sup>a</sup> (M)	Mole %	Molarity <sup>a</sup> (M)
0	46.5	8.0	>49.8	8.4
			51.2	8.7
25	16.0	2.3	19.2	2.7
			18.7	2.6

<sup>a</sup>Calculated molarity based on a solution density of 1.60 g/cm<sup>3</sup>,  
see text.

The data confirm the value of the solubility at 25°C established previously by gas chromatography. They also show very large solubilities at 0°C. There appears to be somewhat lower solubility in pure SOCl<sub>2</sub> relative to the electrolyte. More recent and extensive data are in substantial agreement with these data (33). Figure 3 is a comparison of the measured SO<sub>2</sub> solubilities with values calculated based on ideal solution behavior (13).

$$\ln x = \frac{\Delta H_v}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

Here  $x$  is the SO<sub>2</sub> mole fraction,  $\Delta H_v$  (cal/mol) is the SO<sub>2</sub> heat of vaporization at  $T_0$ (K),  $T$ (K) is the temperature of interest and  $R$  is the gas constant (1.98 cal/mol/K).  $T_0$  determines the SO<sub>2</sub> equilibrium pressure over the solution, and this pressure is the equilibrium vapor pressure of SO<sub>2</sub> over pure SO<sub>2</sub> liquid at  $T_0$ . The experimental data correlate reasonably well with the ideal solution model. This correlation, in conjunction with Dey's C-cell discharge data (14) and our reaction stoichiometry data, suggests that a sealed Li/SOCl<sub>2</sub> cell can accommodate the SO<sub>2</sub> produced with only moderate pressure increases (1-3 atm). Dey's C-cell yielded 4.1 Ahr from 20g of 1.0M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> at 25°C. The initial electrolyte composition is 0.150 mol SOCl<sub>2</sub> and 0.012 mol LiAlCl<sub>4</sub>. Our stoichiometry data give the final solution composition as 0.074 mol SOCl<sub>2</sub>, 0.012 mol LiAlCl<sub>4</sub>, 0.076 mol SO<sub>2</sub> and 0.038 mol S. The mole fraction of SO<sub>2</sub> is ~0.5 which, based on ideal solution behavior, would be in equilibrium with SO<sub>2</sub> vapor at 1.2 atm (18 psi). The measured pressure increase in this cell was 10 psi (14).

We used the measured pressure values rather than those corrected for the volume of the pressure gauge. This is justified if we assume the gas to consist solely of SO<sub>2</sub> and vapors (e.g., SOCl<sub>2</sub>). In this case, the actual pressure will not change due to the volume increase from 3 to 8 cc (i.e., the case during Dey's pressure measurements). The cell pressure would be maintained by evaporation of additional SO<sub>2</sub> without significantly affecting the SO<sub>2</sub> concentration in solution (e.g., 5 cc of SO<sub>2</sub> at 0.68 atm (10 psi) corresponds to  $1.4 \cdot 10^{-4}$  moles vs. a total of  $8 \cdot 10^{-2}$  moles in solution). While the calculated and measured pressure values differ by a factor of almost 2, we feel the agreement is still sufficiently good that the ideal solution model can be used as a first approximation in estimating pressure build-up in other cell configurations. Additional SO<sub>2</sub> solubility measurements at elevated temperatures and pressures would refine the model further.

#### D. Measurement of the Coulomb Number for SOCl<sub>2</sub> Reduction

It appears that no simply written stoichiometry can reconcile all of the data for SOCl<sub>2</sub> reduction, and that a more complex system must be specified. To help resolve the reaction stoichiometry, we have attempted to measure directly the number of electrons involved per molecule of SOCl<sub>2</sub>

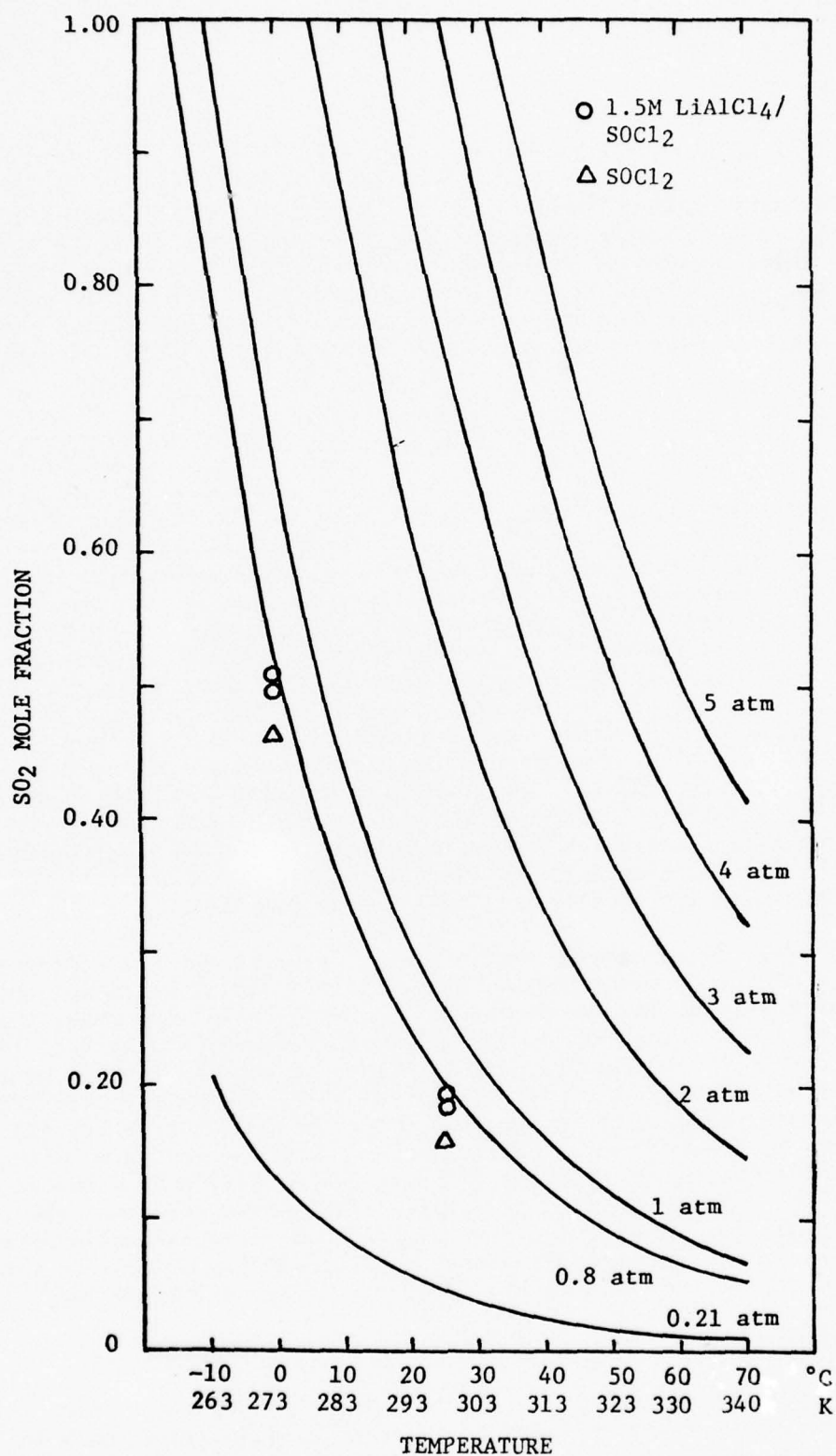


Fig. 3:  $\text{SO}_2$  solubility in  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$  and  $\text{SOCl}_2$ . Solid line (—) calculated solubility from ideal solution equations.



reduced. This number, particularly with reference to whether it is an integer or a fractional value, should give evidence to the primary products of the  $\text{SOCl}_2$  reduction.

### 1. Experimental

The decrease in  $\text{SOCl}_2$  concentration during discharge of a  $\text{Li}/\text{SOCl}_2$  cell can be measured by monitoring its concentration versus an inert substance which will not change during discharge. Gas chromatography is a suitable analytical technique for this purpose, provided a tracer with necessary properties can be found. There are four basic criteria which a compound must meet in order to be useful as a tracer: it must be soluble in the  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolyte; it must have sufficient volatility for G. C. analysis; it must be chemically inert; and it must have high sensitivity for G. C. analysis. This last criterion is necessary because the discharge system must be perturbed as little as possible by the added material, thus requiring a low concentration of tracer.

Table 8 contains a list of the compounds which have been tested as candidate tracers. With the exception of benzene,  $\text{POCl}_3$  and the  $\text{S}_2\text{Cl}_2$ , all of the compounds were fractionally distilled prior to use. Benzene,  $\text{POCl}_3$  and  $\text{S}_2\text{Cl}_2$  were used as received.

The tests were conducted by first obtaining gas chromatographs of the compounds. From these gas chromatographs, we established the purity of the tracers, the position of the G. C. peak relative to the components normally found in a discharged cell, and the relative sensitivity of the G. C. method for the particular compound.

In order to test compound compatibility with  $\text{SOCl}_2$ , and to substantiate the results of the initial testing, solutions ranging from 1 to 5 volume % of test compound in  $\text{SOCl}_2$  were prepared and injected into the gas chromatograph. The final testing was done in complete  $\text{Li}/\text{SOCl}_2$  cells. These cells were vial cells, as described previously.

### 2. Results

None of the compounds tested to date are suitable for various reasons. A summary of the test results is presented in Table 8. Tetrahydrofuran (THF) was eliminated in the first round of testing because the G. C. peak was very broad and tailed severely. Adjustment of the G. C. conditions (specifically column, injector and detector temperatures) within the limits allowed to maintain a good analytical peak for  $\text{SOCl}_2$  did not improve the THF analysis sufficiently to allow its use. Benzene, carbon tetrachloride, acetonitrile, and  $\text{POCl}_3$  were unsuitable because the peaks were essentially coincident with the  $\text{SOCl}_2$  peak. Sulfur monochloride and methyl formate did not provide sufficient instrument response to be useful. In the full cell tests, the 1,2 dimethyloxyethane precipitated sufficient electrolyte salts to lower the

Table 8

Compounds Tested as Possible Tracers  
in the Li/SOCl<sub>2</sub> System

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<u>Compound</u>	<u>Results</u>
Benzene	peak on SOCl <sub>2</sub>
CCl <sub>4</sub>	peak on SOCl <sub>2</sub>
Acetone	reaction
Acetonitrile	peak on SOCl <sub>2</sub>
Methyl Acetate	reaction
1,2 Dimethyloxyethane	low solution conductivity
Methyl Formate	low sensitivity
THF	G.C. peak trails
POCl <sub>3</sub>	peak on SOCl <sub>2</sub>
S <sub>2</sub> Cl <sub>2</sub>	low sensitivity

---

solution conductivity below useful limits, while acetone and methyl acetate reacted during the discharge.

While the above additives were not suitable, they do indicate possible compound types which might prove applicable. The carbon tetrachloride G. C. peak was a good analytical peak and the  $\text{CCl}_4$  appeared unreactive with  $\text{SOCl}_2$ . It appears that chlorinated or fluorinated hydrocarbons are worth further testing.

#### E. UV Spectrophotometric Investigation of Li/ $\text{SOCl}_2$ System

The analytical chemistry of the Li/ $\text{SOCl}_2$  cell is complicated by the reactivity of the components. The reactants and many of the potential products are air, water, and temperature sensitive. Because of this complexity, and the above-described discharge-reaction, it would be advantageous to have available as many analytical techniques as possible.

Thionyl chloride, and many of its suspected reaction products, e.g.,  $\text{SO}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{SCl}_2$ , and S, absorb in the visible and near UV (5, 6). They have moderate extinction coefficients ( $\epsilon \approx 10^3$ ) at  $\lambda_{\text{max}} \approx 280$  nm. This suggests that VIS-UV spectrophotometry might provide a suitable analytical approach to the system. We began the survey by obtaining the spectra of several of the pure components (i.e.,  $\text{SOCl}_2$ , S,  $\text{SO}_2$ ,  $\text{S}_2\text{Cl}_2$ , and LiCl). We then investigated the possibility that chloride ion complexes of  $\text{SOCl}_2$  might be present. Finally, we obtain spectra of the products of the reaction of Li with  $\text{SOCl}_2$ .

##### 1. Experimental

Thionyl chloride (Eastman 246) was used as-received. Lithium (Foote Mineral Co.) was 0.015" thick foil. Hexanes (Fisher H-292) was purified before use. It was shaken with 1:1  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  three times and washed thoroughly with doubly distilled  $\text{H}_2\text{O}$ . It was then distilled on a spinning band column (Perkin-Elmer 251). The middle fraction was retained and dried by slow passage over freshly activated 4A molecular sieves. The sieves were activated by heating under flowing argon for four hours at  $260^\circ\text{C}$ . Tetrahydrofuran (Burdick & Jackson UV grade) was dried by slow passage over freshly activated 4A molecular sieve. Sulfur monochloride (Eastman P-716) was used as-received. Lithium chloride (Fisher L-121) was dried by heating under flowing argon for four hours at  $300^\circ\text{C}$ .

Spectra were recorded at room temperature with a Coleman 124D spectrophotometer using 0.1 cm or 1 cm quartz cells.

All of the preparative work was done in an argon-filled glove box. The majority of the samples were prepared by dilution of small aliquots of the materials under study. Typically 5-50  $\mu\text{l}$  samples were diluted to 10 to 25 ml.

## 2. Spectra

Spectra of the two solvents showed no impurities and both showed their literature cutoff values. The spectra of  $\text{SOCl}_2$  and  $\text{S}_2\text{Cl}_2$  in hexanes (Figs. 4 and 5) are comparable to those published by Koch (5). The spectrum of  $\text{SOCl}_2$  in THF was comparable to that of  $\text{SOCl}_2$  in hexanes except that the  $\epsilon$  values on the plateau were slightly greater.

The spectra of  $\text{SO}_2$  were obtained by shaking a slight excess of  $\text{H}_2\text{O}$  with 6.85 mM  $\text{SOCl}_2$  dissolved in hexanes or THF (Fig. 6). There is a significant difference between the two solvents. The maximum in  $\epsilon$  is shifted to shorter wave lengths in the THF. It is at 290 nm in hexanes and at 274 nm in THF. Further the  $\epsilon$  values are greater in THF than in hexanes. These effects are due to the solvent polarity differences (15, 16). The spectrum of S in THF was obtained.

Complex chlorides of  $\text{SOCl}_2$  have been observed in the presence of tetra alkyl ammonium cations (17, 18). In order to test for this possibility with LiCl, LiCl-saturated  $\text{SOCl}_2$  was measured in both hexanes and THF. The resulting spectra were essentially identical with those of pure  $\text{SOCl}_2$  in these solvents. It appears then that these complexes do not form as readily in the presence of  $\text{Li}^+$ . Thus, they should not cause complications in the interpretation of the spectra. A spectrum of LiCl in THF was also obtained (Fig. 7).

The reaction of Li and  $\text{SOCl}_2$  was studied in THF. The reaction of 6.85 mM  $\text{SOCl}_2$  with metallic Li is essentially complete within 24 hours. In the hexanes there was no reaction apparent after 84 hours at room temperature. The spectrum of that solution was essentially identical with that of  $\text{SOCl}_2$ . This suggests that hexanes could act effectively as a quenching diluent. This observation suggests that very effective time-composition studies could be made on discharging cells. Aliquots of electrolyte could be removed at time intervals during discharge and quenched in hexanes. UV analysis of these samples would reveal product concentrations. Since only small volumes ( $\sim 5$   $\mu\text{l}$ ) of electrolyte are necessary. The sample removal would be an insignificant perturbation of the discharging system.

In contrast to the hexanes, Li and  $\text{SOCl}_2$  react readily with each other in THF. Experiments were designed not only to obtain spectra of the reaction mixture, but also to isolate some of the non-volatile reaction products. The experimental procedure was as follows. Strips of Li foil were submerged in 6.85 mM  $\text{SOCl}_2$ /THF in a sealed glass container. UV spectra were measured at one hour, 24 hours and 66 hours. The experiment was terminated after 66 hours and an aliquot was reduced to dryness on a rotary evaporator. The dried material appeared to be a mixture of white and yellow solids. The solids were redissolved in THF and their UV spectrum measured. A second aliquot was brought to dryness, then dissolved



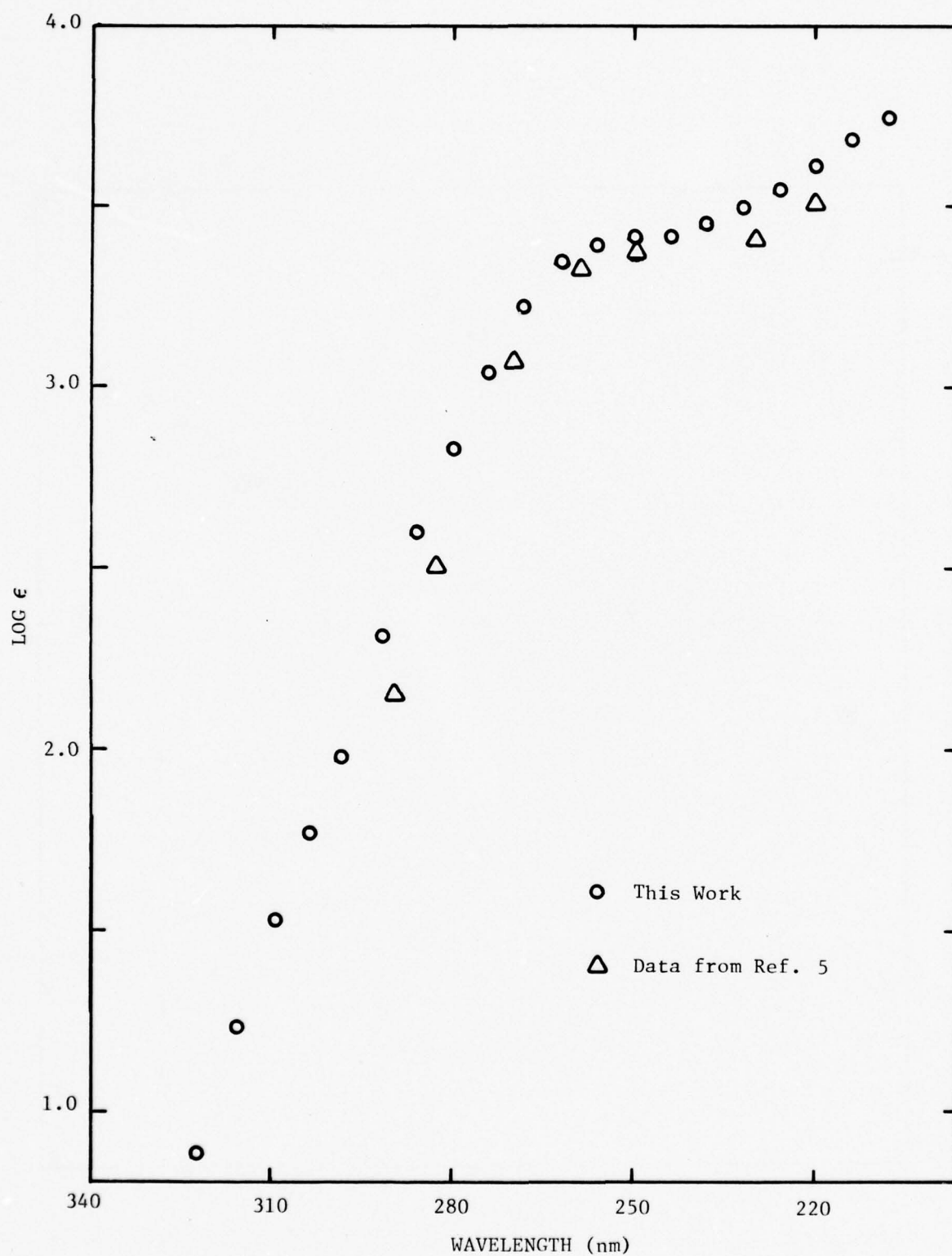


Fig. 4: Near UV spectra at  $\text{SOCl}_2$  in hexanes at room temperature.

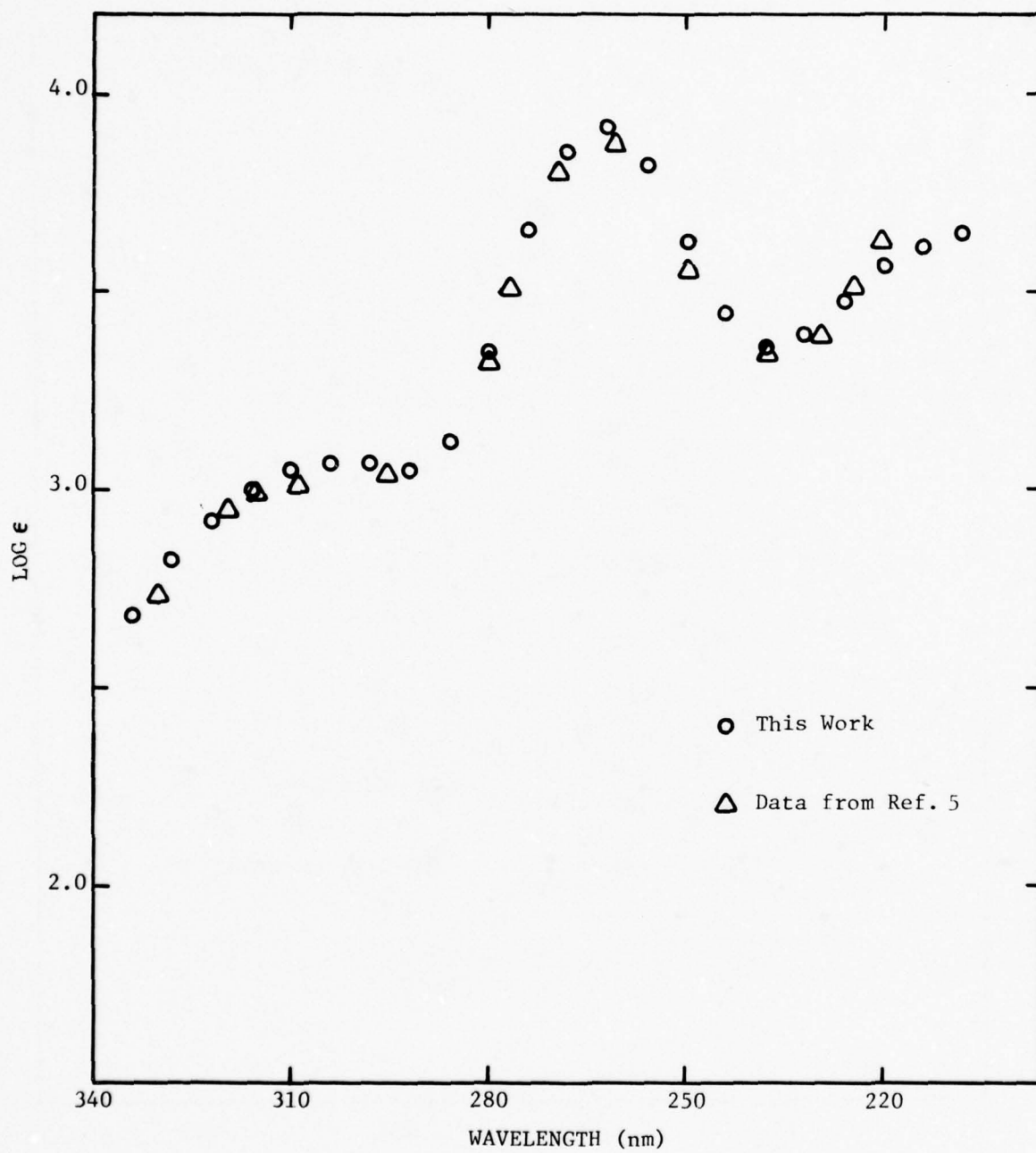


Fig. 5. Near UV spectrum of  $S_2Cl_2$  in hexanes at room temperature.

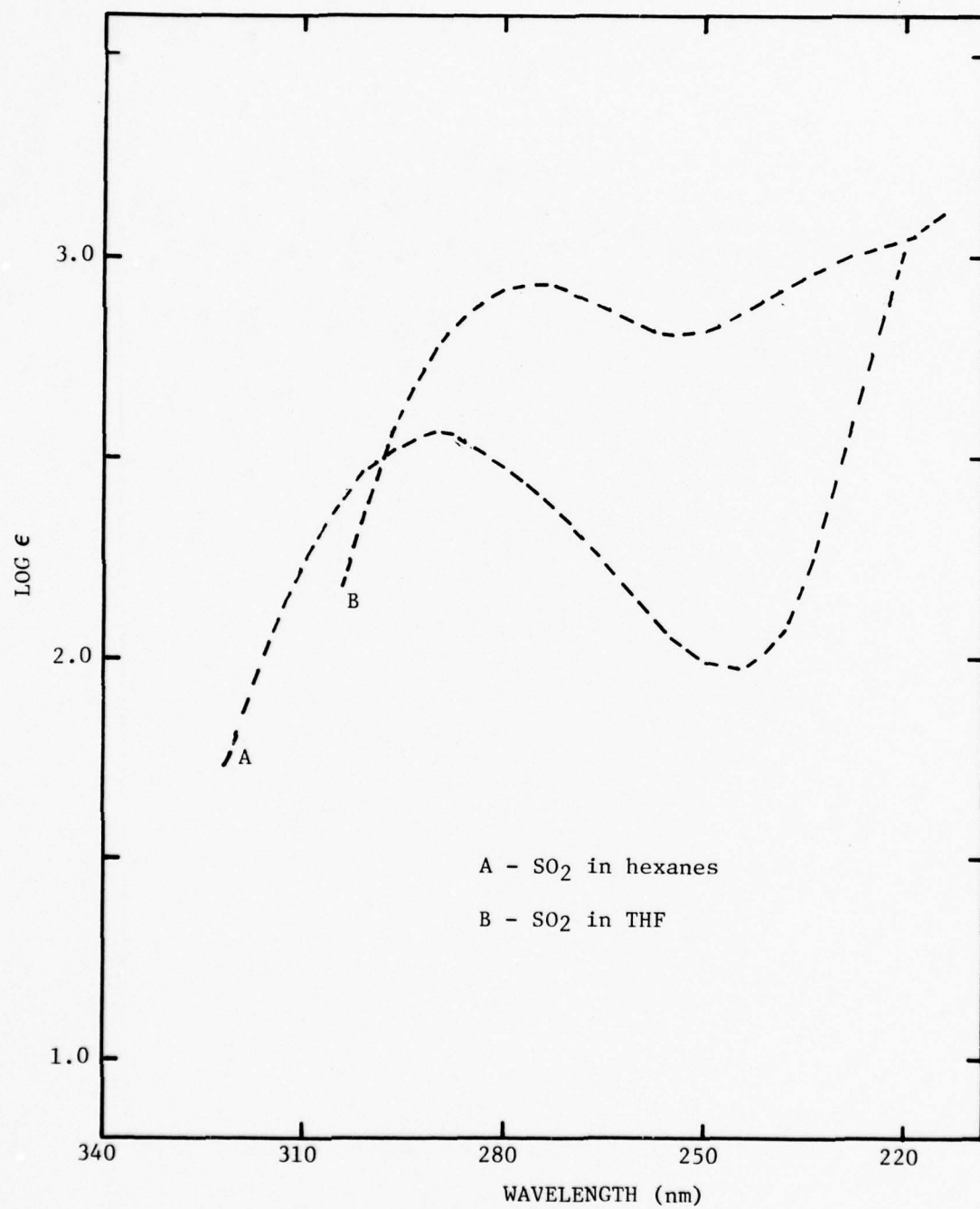


Fig. 6: Near UV spectra of  $\text{SO}_2$  in hexanes and THF at room temperature.

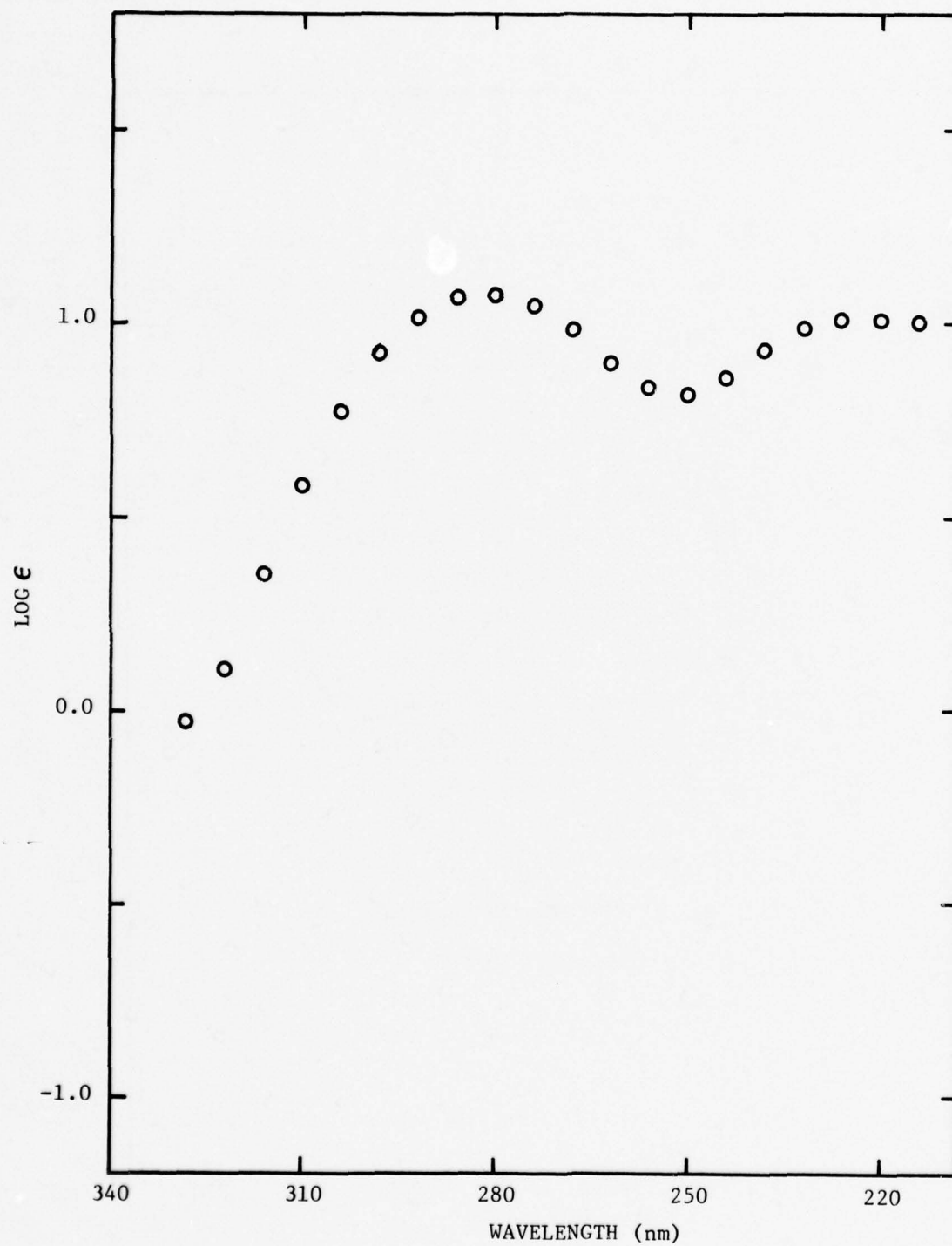


Fig. 7: Near UV spectrum of anhydrous LiCl in THF at room temperature.



in 0.05N HCl and analyzed for  $\text{Li}^+$  by atomic absorption. A third aliquot was brought to dryness and the residue subjected to qualitative tests for elemental S.

The spectra of the aliquots taken at 1, 24 and 66 hours suggest the reaction is relatively rapid (Fig. 8). The spectrum of the one hour sample is changed considerably from that of  $\text{SOCl}_2$ . A maximum has developed at 276 nm and a minimum at 256 nm. The spectra of the 24 hour and 66 hour samples are essentially identical, indicating the reaction is completed between one and 24 hours. Figure 9 shows the spectrum of the solid reaction products redissolved in THF. The spectrum of pure S in THF is included for comparison. While the spectra are not identical, they are similar. The shapes are similar between 292 nm and 256 nm. The major dissimilarities occur above 310 nm and below 256 nm. Above 310 nm, the reaction solids have a higher absorbance than the pure sulfur. Below 256 nm, there is no minimum in the spectrum of the reaction solids. This is observed in the spectrum of pure S. Qualitative tests on the solid residue indicate that sulfur is present in the mixed yellow-white solid. A small sample was dried at  $100^\circ\text{C}$  for two hours. A melting point was taken and the yellow material melted between  $112$ – $117^\circ\text{C}$  to a red liquid. The melting point of sulfur is  $\sim 112^\circ\text{C}$ . The red liquid burns with a blue flame, giving the characteristic choking smoke. Thus, sulfur is present in the residue, along with at least one other component. LiCl will contribute little to the absorbance. The  $\text{Li}^+$  analysis determined the concentration to be 0.0161M. Assuming this is all LiCl, the maximum absorbance would be 0.018 at 280 nm and would be a relatively minor adjustment of the measured absorbance curve. If we assume that the absorbance in the region from 298 nm to 256 nm is due to sulfur, the sulfur concentration would be 3.18 mM. This is 46.4% of the original  $\text{SOCl}_2$  concentration. This is very close to the ratio 0.25 S/ $\text{e}^-$ , the value we determined previously by chemical analysis.

In order to establish something of the nature of the volatile components of the Li/ $\text{SOCl}_2$  reaction, the spectrum of the solid residue was subtracted from the spectrum of the total mixture. The result is shown in Figure 10. The maximum in the resultant curve is at 274 nm, which is the same as  $\text{SO}_2$ . The curve beyond 250 nm is not identical to the authentic  $\text{SO}_2$  curve, however. Excluding this difference, the calculated  $\text{SO}_2$  would be 0.36  $\text{SO}_2/\text{e}^-$ .

The above results suggest that UV spectrophotometry is a useful analytical method for analysis of the Li/ $\text{SOCl}_2$  system. Many of the involved substances absorb in the UV range. Hexanes, a non-polar solvent, solubilizes  $\text{SOCl}_2$  and its potential Li-reduction products, except for salts such as LiCl, and quenches further reaction. This makes it useful for analysis of electrolyte aliquots from complete cells. THF, a polar solvent, is a suitable medium for reacting Li and  $\text{SOCl}_2$  under controlled conditions and, with careful experimental design, could allow separation of volatile and non-volatile products for further analysis. Thus, further developmental work on the use of UV spectrophotometry for analysis of reaction paths would be valuable.

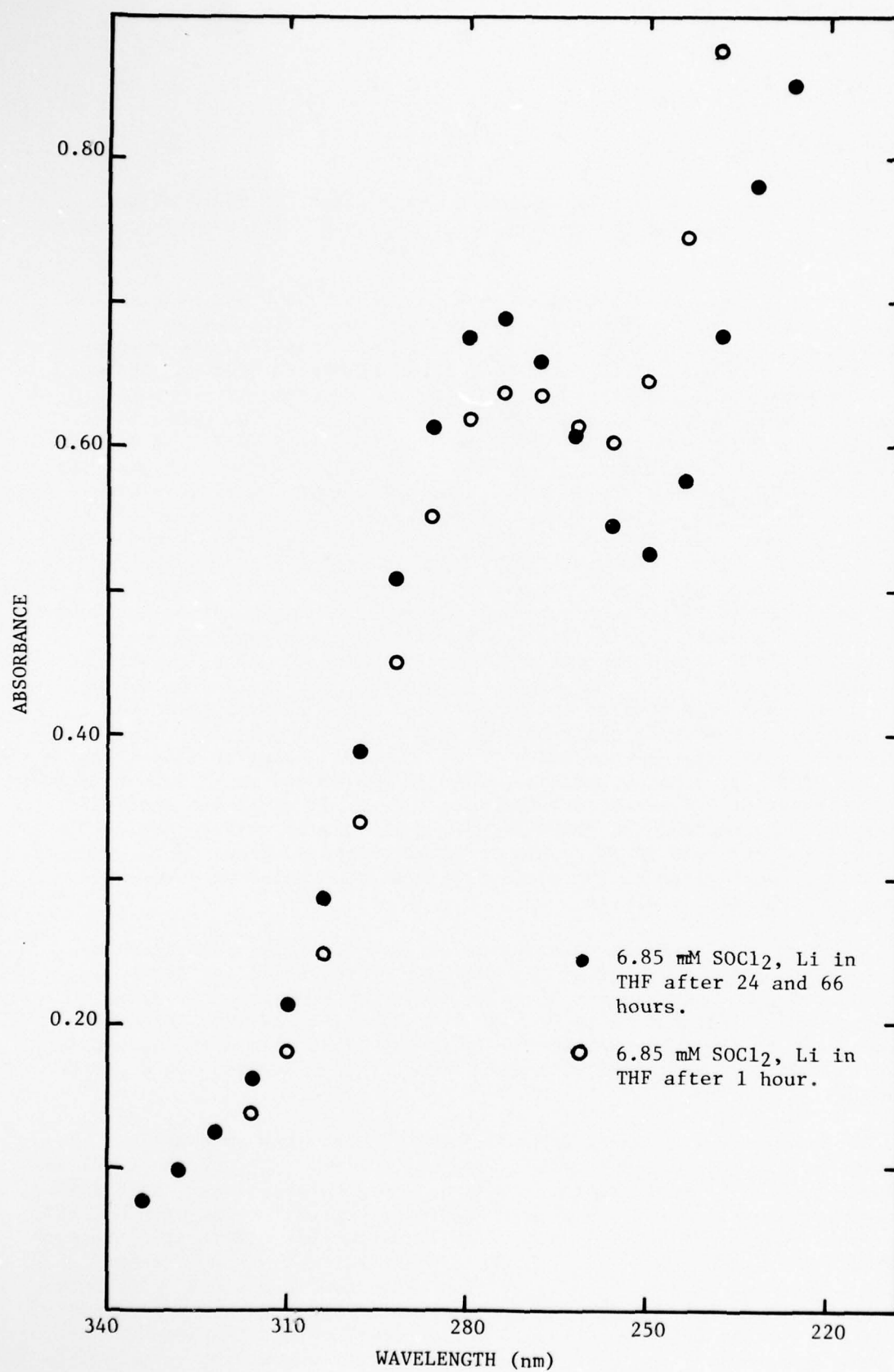


Fig. 8: Near UV spectra at the reaction products of Li and SOCl<sub>2</sub> in THF at room temperature.

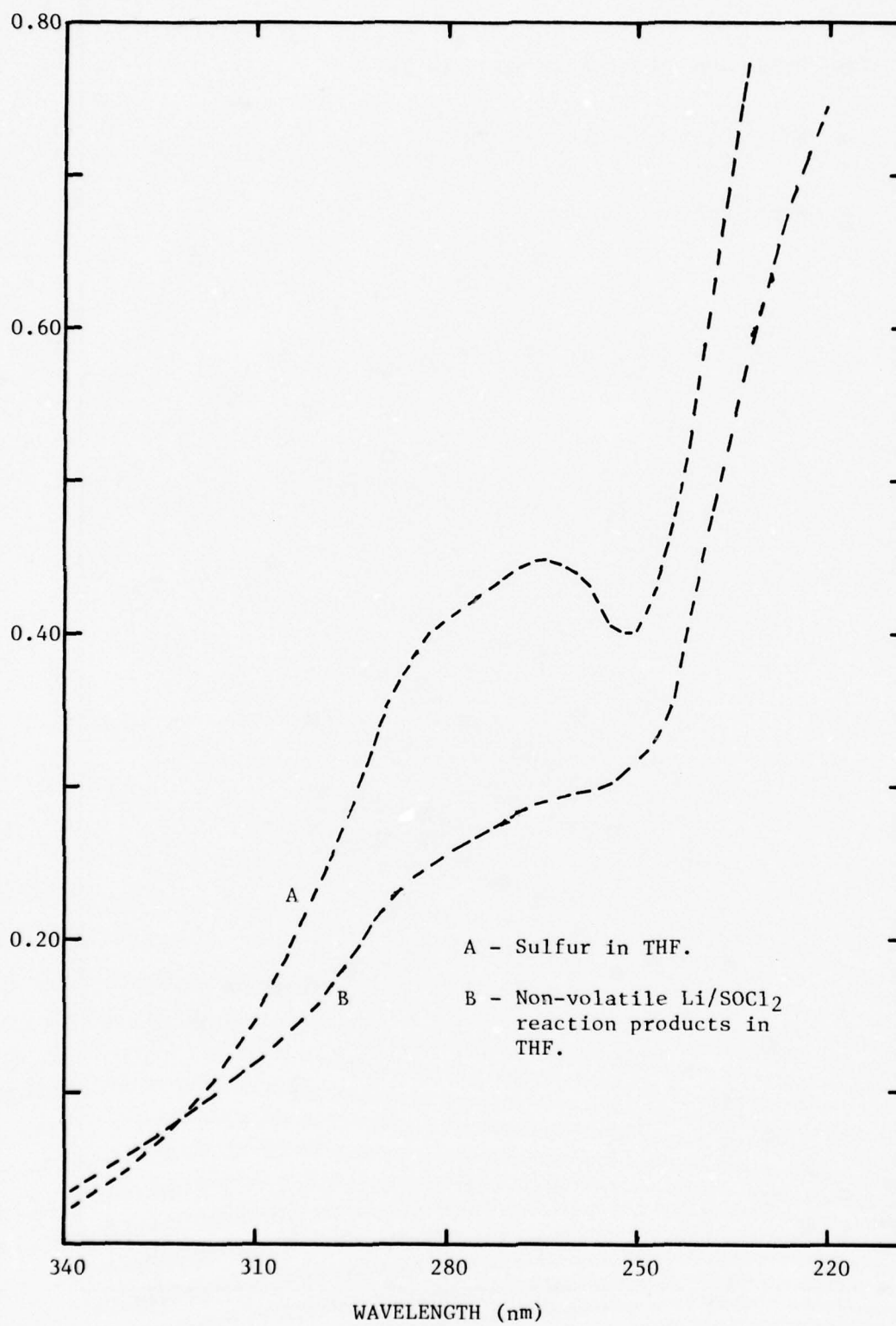


Fig. 9: Near UV spectra of S in THF and non-volatile SOCl<sub>2</sub> reaction products in THF at room temperature.

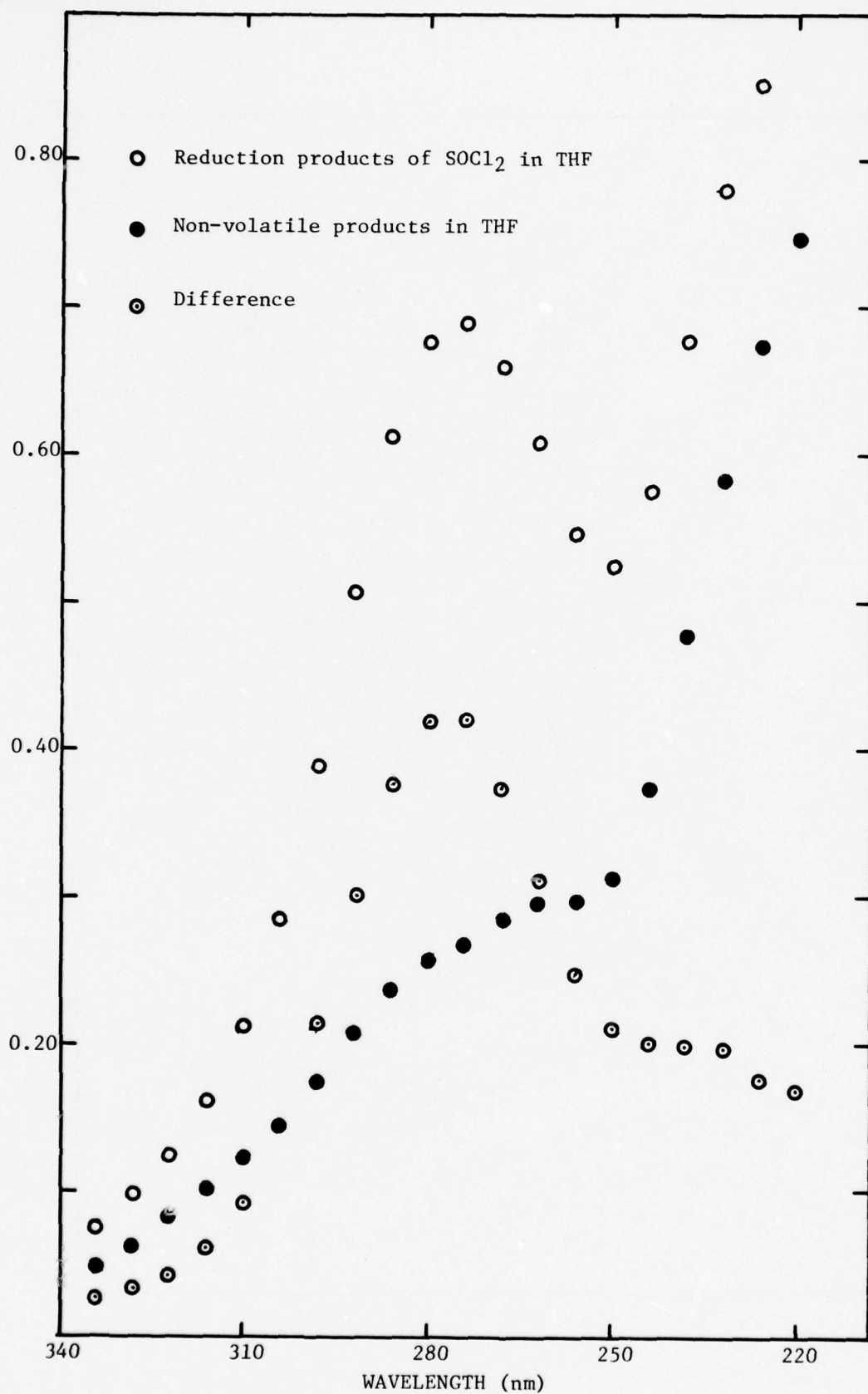
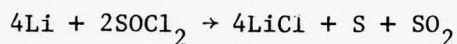


Fig. 10: Comparison of total product mixture of  $\text{SOCl}_2$  reduction in THF with the non-volatile component.

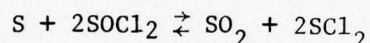


F. Summary of Analytical Results

To summarize briefly, the analytical results show the following: LiCl is the only insoluble product of the discharge reaction and its ratio to charge passed is 1 mole LiCl/equivalent at room temperature and at  $-40^{\circ}\text{C}$ , and to a lower level of significance at  $71^{\circ}\text{C}$ . Sulfur is produced during the discharge. It is soluble in the electrolyte and is produced in the ratio of 0.25 mole S/equivalent. Sulfur dioxide is also generated and is very soluble in the electrolyte. Its production ratio is 0.5 mole  $\text{SO}_2$ /equivalent. Of the relatively large number of reaction stoichiometries that can be written, the data most closely fit that proposed by Dey (4):



The nature of the products agrees and the amounts of LiCl and S agree. The measured amount of  $\text{SO}_2$  exceeds that predicted by a factor of two. No other simple reaction stoichiometry accounting for this product distribution can be written. The anomalous  $\text{SO}_2$  result may be due to the reaction of S and  $\text{SOCl}_2$  in the gas chromatograph injector. It has recently been suggested that at temperatures greater than  $127^{\circ}\text{C}$  the reaction



is shifted to the right (33). This could account for the excess  $\text{SO}_2$  found since the injector temperature was  $150^{\circ}\text{C}$  for these analyses. Further analytical work is necessary to resolve this question.

The measurements of  $\text{SO}_2$  solubility suggest pressure build up will not be a serious safety hazard. The  $\text{SO}_2$  is very soluble in  $\text{SOCl}_2$  and they may in fact be infinitely miscible. Beyond that the pressure of  $\text{SO}_2$  cannot exceed its own vapor pressure, which at room temperature is about 3 atm.

#### IV. EFFECTS OF PURIFICATION ON Li ANODE PASSIVATION

Electrolyte purity is an important factor influencing anode passivation in Li/SOCl<sub>2</sub> cells during storage at 71°C. The importance was suggested by experiments reported by Marincic (7). He found that 200 ppm of dissolved Fe caused rapid and severe Li anode passivation. In order to define the effect more closely, we investigated system purity and the effect of purity on stored cells.

These investigations are discussed in this section. The section is divided into three parts. The first part presents analytical data for the Li/SOCl<sub>2</sub> system before purification. Various chemical and physical analytical techniques were applied. Iron levels in the electrolyte and the electrolyte components were determined by colorimetric methods. Infra-red measurements were used to investigate other substances in the electrolyte, such as H<sub>2</sub>O, HCl and SO<sub>2</sub>. Emission spectroscopy was used to investigate the chemical composition of the film on the Li anode. In the second section, data for similar analyses of the electrolyte after purification are discussed. The electrolyte was purified by storage with Li metal. Analyses were performed to determine the efficiency of Cu and Fe removal, and infra-red spectrometry was used to determine the residual levels of H<sub>2</sub>O, HCl and other species. Finally, in the third section, the impact of electrolyte purification on the discharge characteristics of cells after storage at 71°C is discussed. A comparison is made between cells prepared with purified electrolyte and as-prepared electrolyte. The cells prepared with purified electrolyte show a substantial improvement in discharge voltage and capacity.

##### A. Analysis of System Before Electrolyte Purification

The nature of the electrolyte prior to purification was studied. An analysis for Fe in the electrolyte and the electrolyte components was done by colorimetry. Infra-red spectrometry was used to define the levels of HCl and other products of the reaction between H<sub>2</sub>O and the electrolyte.

The electrolyte was prepared from reagent grade LiCl and AlCl<sub>3</sub> (Fluka, puriss.) Dried LiCl in 5% excess of the stoichiometry amount was added to SOCl<sub>2</sub>. The mixture was cooled to ~0°C. AlCl<sub>3</sub> in the stoichiometric amount was added in small portions with stirring. The solution temperature was kept between 0°C and 10°C. The solution was filtered to remove suspended particulates and the excess LiCl. The solution color was light tan.

##### 1. Fe Analysis

The analytical procedure was a standard method using 1,10-phenanthroline reagent (19). The aqueous solutions from the samples prepared

as described below were transferred to 50 ml volumetric flasks; the liquid volumes were approximately 25 ml. Two ml of 10%  $\text{NH}_2\text{OH}\cdot\text{HCl}$  were added, and the pH adjusted to between 3 and 4 with 1M NaOAc. Then, 4 ml of 0.25% 1,10-phenanthroline were added, and the color allowed to develop for at least 15 min.

Iron standards were prepared from  $\text{FeSO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot 6\text{H}_2\text{O}$  dissolved in dilute HCl.

The absorbance of these solutions was measured at 508 nm using 10 mm path length quartz cells on a Coleman 124D spectrophotometer. The absorbance spectra of a standard and the electrolyte sample without added Fe were recorded between 400 and 600 nm.

The  $\text{AlCl}_3$  samples were prepared by dissolving weighed quantities in doubly distilled water. The initial addition of water to the solid samples is done carefully because of the vigorous, exothermic reaction. The spectrophotometric determination was carried out directly on these solutions with no further pretreatment.

The electrolyte samples were prepared as follows. Three 10 ml aliquots of the electrolyte were allowed to evaporate at room temperature. The residual solids were reacted with double distilled  $\text{H}_2\text{O}$ . The addition of the water was again done carefully because of the vigorous, exothermic reaction. These solutions contained some insoluble, suspended material. This is probably elemental S resulting from the hydrolysis of  $\text{SCl}_2$  or  $\text{S}_2\text{Cl}_2$  contaminants in the  $\text{SOCl}_2$ . No positive identification of this material was made. In order to assess the effects of the insoluble matter on the Fe analysis (e.g., by adsorption), known quantities of Fe were added to two of the samples after the dissolution step. The solutions were heated gently and the insoluble matter changed appearance from flocculent to a more granular condition. The measurements were made directly on these solutions and the insoluble material was removed by filtration just before the spectrophotometric measurement.

Samples of LiCl were prepared by dissolution in doubly-distilled water and acidifying slightly with a few drops of HCl. The  $\text{SOCl}_2$  samples were prepared by evaporating the  $\text{SOCl}_2$ , wetting the residue with concentrated  $\text{HNO}_3$ , drying, and taking up the residue with dilute (0.1N) HCl.

## 2. Results

The analytical results are as follows: The MCB LiCl had an Fe content of  $1.7 \pm 1.1 \mu\text{g/gm}$  for six samples. The amounts of Fe found are near the method's limits of detection. This is the reason for the high limits of error. This quantity of Fe is below the limits of purity listed for the product by the manufacturer (0.0004% Fe). The Fe contribution to the 1.8M  $\text{LiAlCl}_4$  electrolyte by LiCl will be  $0.13 \pm 0.08 \mu\text{g Fe/ml}$ .

The results of the Fe determination for the  $\text{SOCl}_2$  were as follows: Three 10 ml samples of both undistilled  $\text{SOCl}_2$  (MCB) and  $\text{SOCl}_2$  once-distilled from Li were analyzed. There was no difference between the two. Both had  $0.3 \pm 0.1 \mu\text{g Fe/ml}$ . The large limits of error arise again because the results were near the detection limits of the method. The contribution of Fe to the 1.8M  $\text{LiAlCl}_4$  electrolyte from  $\text{SOCl}_2$  is  $0.5 \pm 0.2 \mu\text{g Fe/ml}$ . The  $\text{AlCl}_3$  contains  $6.9 \pm 0.9 \mu\text{g Fe/g}$ , which contributes  $1.7 \pm 0.2 \mu\text{g/ml}$  to the electrolyte. The electrolyte contained  $3.8 \pm 0.3 \mu\text{g Fe/ml}$ . The Fe from the individual components sums to a total of  $2.3 \pm 0.3 \mu\text{g Fe/ml}$  1.8M  $\text{LiAlCl}_4$  (i.e.,  $1.7 \pm 0.2 \mu\text{g/ml}$  from  $\text{AlCl}_3$ ,  $0.13 \pm 0.08 \mu\text{g/ml}$  from  $\text{LiCl}$ , and  $0.5 \pm 0.2 \mu\text{g/ml}$  from the  $\text{SOCl}_2$ ). The difference of  $\sim 1 \mu\text{g/ml}$  between the directly determined value and the value calculated from the individual components may be due to inhomogeneous distribution of the Fe impurity in the  $\text{AlCl}_3$ .

Marincic and Lombardi (7) have shown that Fe at an initial solution level of  $\sim 30 \mu\text{g}$  per  $\text{cm}^2$  of Li anode area causes severe voltage delay and anode inactivation problems. In our test cells, the initial solution values range from 1.5 to  $2.0 \mu\text{g Fe/cm}^2$  of Li surface. While these levels are 15 to 20 times lower than those used by Marincic and Lombardi, they could still be sufficient to lead to significant effects.

Assuming as a first approximation that the deposit is Fe, then, based on the density, atomic weight and Avogadro's number, we can estimate the area ratio of the Fe to the Li anode. This is at best a rough approximation since it is not clear that Fe metal is the deposited species, and we are using the geometric area of the Li anode, but it gives a sufficiently clear comparison of the relative film thicknesses: Using an Fe atom area of  $5.18 \times 10^{-16} \text{ cm}^2$ , the estimated area ratios are  $166 \text{ cm}^2 \text{ Fe/cm}^2 \text{ Li}$  for  $30 \mu\text{g/cm}^2$  and  $8 \text{ cm}^2 \text{ Fe/cm}^2 \text{ Li}$  for  $1.5 \mu\text{g/cm}^2$ . The implied film thickness is significant in both cases. Further, this discussion considers only Fe contamination. It is possible that other dissolved metallic impurities must be taken into account also.

### 3. Infra-red Analysis

The infra-red analysis of the  $\text{SOCl}_2$ -based electrolyte system concentrated mainly on the purity of the system, but other related aspects were also investigated. These included attempted identification of possible discharge and decomposition products, and the effect of  $\text{H}_2\text{O}$  on the system.

Spectra were recorded on a Beckman Acculab 5 dual beam spectrophotometer. The instrument covers the range from  $4000 \text{ cm}^{-1}$  to  $375 \text{ cm}^{-1}$ . Several commercial cells were tested. All of the spectra reported here were obtained with Beckman TAC cells. These have  $\text{AgCl}$  windows and can be sealed permanently. Two path lengths were used, 0.025 mm and 0.10 mm. The IR cells were filled and sealed in an argon-filled glove box.



#### 4. Spectra of $\text{SOCl}_2$

The spectrum of undistilled Eastman 246  $\text{SOCl}_2$  is shown in Figure 11. The major feature is a strong absorption at  $1225\text{ cm}^{-1}$ , with a weaker band at  $2420\text{ cm}^{-1}$ . There are still weaker bands at  $920\text{ cm}^{-1}$  and  $765\text{ cm}^{-1}$ . This spectrum agrees substantially with published spectra for  $\text{SOCl}_2$  (20, 21). The Aldrich Library spectrum (20) shows only the  $1225\text{ cm}^{-1}$  band. Since that spectrum is of the pure liquid, and the  $1225\text{ cm}^{-1}$  is on scale, a capillary cell was most probably used. This would reduce the weaker bands below the limits of detection. The data of Martz and Lagemann (21) are more complete. The main band at  $1225\text{ cm}^{-1}$  is assigned to the S-O stretching. The band at  $2420\text{ cm}^{-1}$  is the first overtone. The weaker bands below  $1000\text{ cm}^{-1}$  are summation bands of the lower energy S-Cl stretch, molecular deformation and torsion.

The spectrum of distilled  $\text{SOCl}_2$  shows two additional bands, at  $1340$  and  $1410\text{ cm}^{-1}$ . Eastman 246  $\text{SOCl}_2$  was distilled at atmospheric pressure under argon from Li chips. The middle fraction, boiling between  $75.5\text{--}77^\circ\text{C}$  (uncorr.), was used. The  $1340\text{ cm}^{-1}$  band is most probably due to  $\text{SO}_2$  (21, 22). This band was reported by Martz and Lagemann and, as reported below, the band appears to be a reaction product of  $\text{H}_2\text{O}$  and  $\text{SOCl}_2$ . We have obtained the spectrum of  $\text{SO}_2\text{Cl}_2$ , which agrees substantially with published spectra.  $\text{SO}_2\text{Cl}_2$  has two prominent bands at  $1410\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$ , assigned to the asymmetric and symmetric S-O stretching (21). The  $1200\text{ cm}^{-1}$  band would be obscured by the  $1225\text{ cm}^{-1}$  band of  $\text{SOCl}_2$ . These results indicate that distillation of  $\text{SOCl}_2$  under the conditions specified above introduces some decomposition products.

#### 5. Spectra of 1.5M $\text{LiAlCl}_4$ , $\text{SOCl}_2$

The spectrum of freshly prepared 1.5M  $\text{LiAlCl}_4$ ,  $\text{SOCl}_2$  is shown in Figure 12. The electrolyte was prepared from undistilled Eastman 246  $\text{SOCl}_2$  and  $\text{LiAlCl}_4$  prepared and purified in the melt. Spectra of electrolyte prepared by dissolving  $\text{LiCl}$  in a solution of  $\text{AlCl}_3/\text{SOCl}_2$  have the same features.

Comparison of this spectrum with that of  $\text{SOCl}_2$  reveals three major changes. There is a broad band centered at  $3350\text{ cm}^{-1}$ ; there is a shoulder on the lower wave number side of the  $\text{SOCl}_2$  overtone band centered at about  $2350\text{ cm}^{-1}$ ; there is a new band at  $1330\text{ cm}^{-1}$ . There is also a slight indication of  $\text{HCl}$  at  $2780\text{ cm}^{-1}$ . The  $1330\text{ cm}^{-1}$  band is due to  $\text{SO}_2$  contained in the salts. The  $\text{SO}_2$  concentration is about 0.07M. The band at  $3350\text{ cm}^{-1}$  is probably due to H-O stretching on aluminum hydroxy compounds (23, 24).

These species are relatively stable in  $\text{SOCl}_2$ . In tests with electrolyte to which water was added, the intensity of this band remained unaltered after seven days at room temperature. It is quite clear that added  $\text{H}_2\text{O}$  reacts

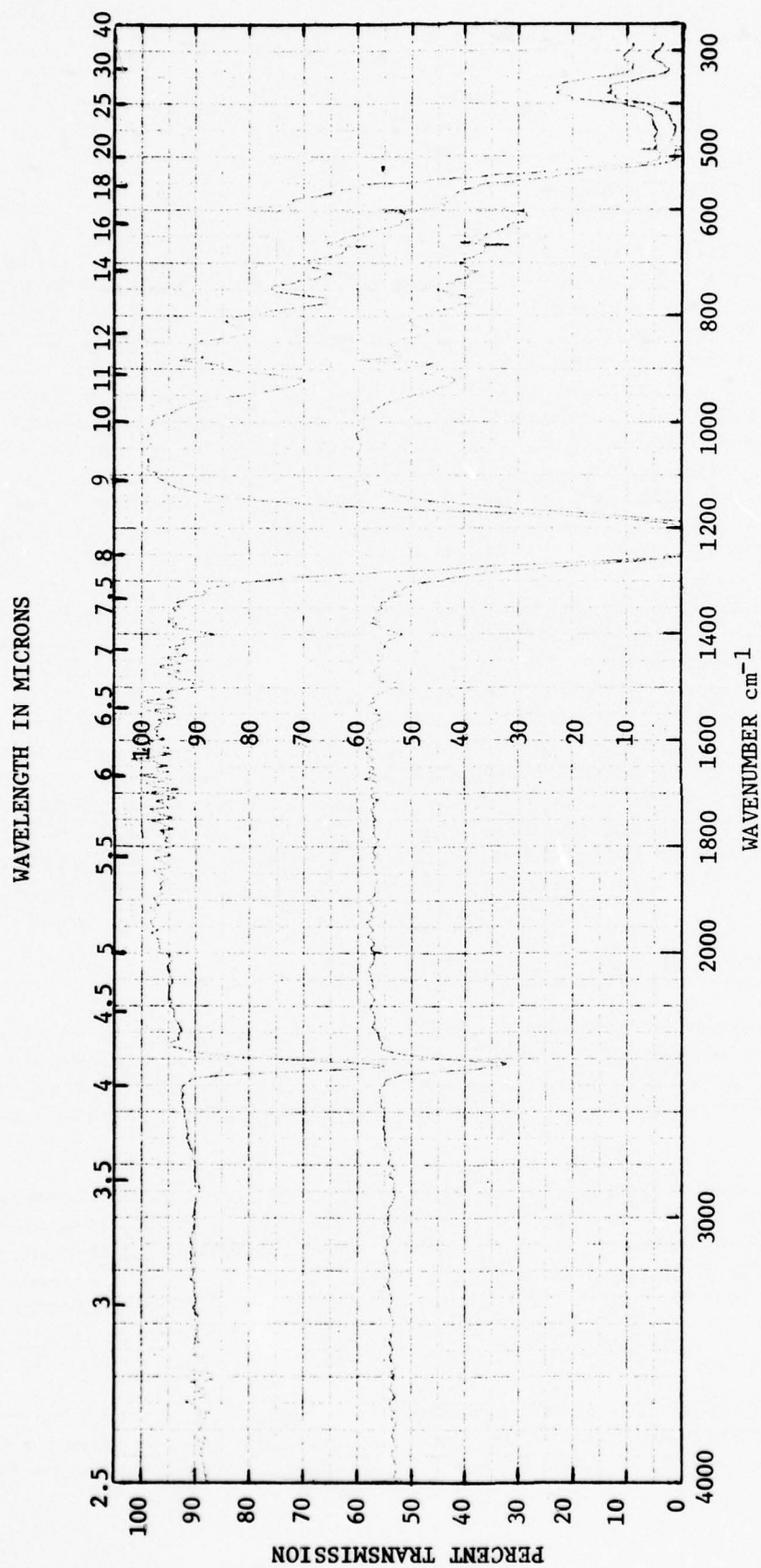


Fig. 11: Infrared spectrum of Eastman 246 undistilled  $\text{SOCl}_2$ . Pathlength 0.10 mm, AgCl windows.

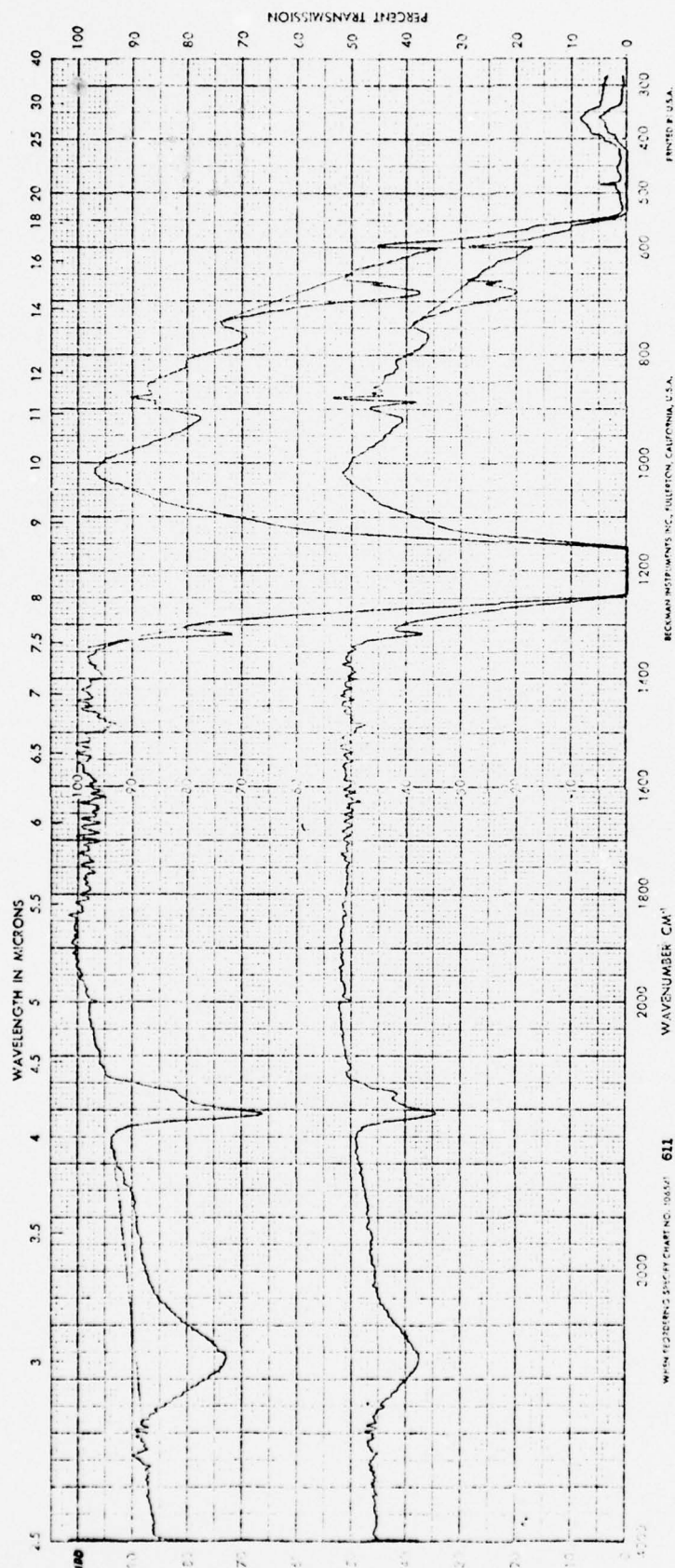


Fig. 12: Infrared spectrum of 1.5M  $\text{LiAlCl}_4/\text{SOCl}_2$  before pretreatment with Li.

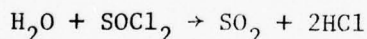
preferentially with the  $\text{AlCl}_4^-$  rather than with  $\text{SOCl}_2$  because a precipitate formed which did not redissolve even after seven days.

#### 6. Spectra of $\text{SOCl}_2$ with Added S, HCl and $\text{H}_2\text{O}$

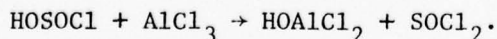
Solutions of S, HCl and  $\text{H}_2\text{O}$  in  $\text{SOCl}_2$  were studied in order to establish the nature of the spectra and to determine if the IR is suitable to quantify the species generated during cell discharge. A 1M S solution was prepared using undistilled  $\text{SOCl}_2$ . The solution was bright yellow. The IR spectrum was identical to  $\text{SOCl}_2$ . At room temperature S and  $\text{SOCl}_2$  apparently form a stable system.

A solution of HCl-saturated  $\text{SOCl}_2$  was prepared with anhydrous HCl gas and undistilled  $\text{SOCl}_2$ . We have estimated the solubility of HCl to be about 0.5M. There was some experimental difficulty in obtaining the spectra. The temperature of the cells increased sufficiently to cause the cells to split. The spectrum showed only one additional band at  $2780\text{ cm}^{-1}$ , which is most probably the HCl stretching frequency (25).

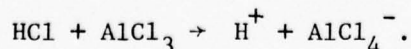
The effect of  $\text{H}_2\text{O}$  on the IR spectra of  $\text{SOCl}_2$  has been reported by French *et al.* (23). They report that the addition of  $\text{H}_2\text{O}$  produces a band at  $2800\text{ cm}^{-1}$ , which is ascribed to hydrogen band H-O stretching in  $\text{HOSOCl}$ . They worked with relatively long path length cells 0.5-10 cm and water concentrations less than 100 ppm. Our measurements have begun with larger water concentrations (300-3000 ppm) and shorter path length cells (0.1 mm). The addition of water does cause a peak to appear at  $2780\text{ cm}^{-1}$  and it also causes a peak at  $1340\text{ cm}^{-1}$ . The absorbance of both increases with increasing water addition. The increase is linear for the  $2780\text{ cm}^{-1}$  band and apparently linear for the  $1340\text{ cm}^{-1}$  band. We believe the bands are due to HCl ( $2780\text{ cm}^{-1}$ ) and  $\text{SO}_2$  ( $1340\text{ cm}^{-1}$ ) resulting from the reaction



The  $2780\text{ cm}^{-1}$  band resulting from the addition of water is identical to the band we observe for HCl-saturated  $\text{SOCl}_2$ . The presence of  $\text{SO}_2$  after  $\text{H}_2\text{O}$  addition suggests that the  $\text{HOSOCl}$  species postulated by French *et al.* cannot be present in high concentrations, if it exists at all. When they added  $\text{AlCl}_3$  to the solution of  $\text{H}_2\text{O}$  in  $\text{SOCl}_2$ , the  $2780\text{ cm}^{-1}$  band began to disappear, which they attributed to the reaction



We feel that the disappearance of the  $2780\text{ cm}^{-1}$  band is due to the reaction of HCl with  $\text{AlCl}_3$  according to





This reaction seems probable, due to the high stability of  $\text{AlCl}_4^-$  in  $\text{SOCl}_2$ . For example,  $\text{AlCl}_3$  will dissolve  $\text{LiCl}$  and  $\text{SOCl}_2$ . Lithium chloride has a heat of formation of 97 kcal/mol but  $\text{HCl}$  has a heat of formation of only 22 kcal/mol. Thus it seems unlikely that  $\text{HCl}$  would be stable in the presence of  $\text{AlCl}_3$ .

## 7. Li Surface Analysis

The impact of unpurified electrolyte on the surface of Li anodes was assessed by emission spectroscopy. Samples of fresh Li and the surface of a passivated electrode were tested. Also included in the analysis were samples of  $\text{LiAlCl}_4$ . One obtained from the U.S. Army Electronics Command, Fort Monmouth, NJ, and the other was the solid recovered by evaporation from our electrolyte.

The analytical method was as follows: A 3.4 meter Ebert Spectrograph was used with a DC arc source. The sample and counter electrodes were graphite. The emission spectra were recorded in photographic plates and evaluated with a microphotometer.

The results for 50 elements, including Li and Al, are reported. Figure 13 presents, in periodic table form, the elements reported. Those marked with an asterisk were detected in at least one sample. The majority of the elements detectable are metals. Table 9 lists the elements and the levels of these elements found in the four samples. Lithium results are not included, nor are Al results for the ECOM  $\text{LiAlCl}_4$  or the electrolyte salts, while they are included for the metal samples.

Neither of the  $\text{LiAlCl}_4$  samples has any major impurities. The level of Na in the ECOM sample and Cu in the electrolyte sample are somewhat high. The Na, as well as the Mg and Si, in the ECOM sample may be spurious as, on inquiry we learn that, the sample was prepared for analysis by grinding in a porcelain mortar and pestle.

Six elements were detected in the electrolyte salt sample. Four of these (Pb, Ag, Fe, Mn) were indicated at the  $\sim 1$  ppm level, Ca in the 1-10 ppm range, and Cu in the 10-100 ppm range. Six elements were also detected in the ECOM  $\text{LiAlCl}_4$ , excluding the Na, Mg, and Si as explained above. Three of these (Ag, Fe and Mn) were found at the 1 ppm level and three (Ca, Ni and Cu) at the 1-10 ppm level. We believe that the values quoted for both samples must be taken as very approximate and only an indication of the presence of an element and its general concentration level. For example, our own analysis for Fe indicates 2-4 ppm versus the less than 1 ppm indicated spectroscopically.

Ten elements were detected in the pure Li metal sample. Four of these (Mg, Si, Ag, Sn) were present at the 1 ppm level. Four (Na, Ca, Mn, Fe) were present at the 10-100 ppm level. Two elements, Al and Cu, appeared as relatively major contaminants.

[illegible]

\*Detected in at least one sample.

Fig. 13: Elements reported in spectrographic analysis.

Table 9  
Results of Spectroscopic Analysis

	<u>ECOM</u> <u>LiAlCl<sub>4</sub></u>	<u>1.8M Electrolyte</u> <u>Salts</u>	<u>Li Metal</u>	<u>Passivated Anode</u> <u>Surface</u>
Na	FT-T	ND	FT	L
Mg	VFT	ND	VVFT	FT
Al	-	-	T-L	M
Si	VVFT	ND	VVFT	T-L
Ca	VFT	VFT	FT	T
Cr	ND	ND	ND	VFT
Mn	VVFT	VVFT	FT	FT
Fe	VVFT	VVFT	FT	T-L
Co	ND	ND	ND	VFT
Ni	VFT	ND	ND	T
Cu	VFT	FT	FT-T	L
Ag	VVFT	VVFT	VVFT	VFT
Sn	ND	ND	VVFT	VVFT-VFT
Pb	ND	VVFT	ND	VVFT

Key: ND - not detected  
 VVFT - <0.0001%  
 VFT - 0.0001% - 0.001%  
 FT - 0.001% - 0.01%  
 T - 0.01% - 0.1%  
 L - 0.1% - 1.0%  
 M - 1% - 10%  
 H - >10%

Fourteen elements were detected in the surface film sample. Five elements (Cr, Co, Ag, Sn, Pb) were minor contaminants at the 1-10 ppm level. The Ag and Sn were present at these levels in the Li metal itself. The Cr, Co and Pb were probably plated out of the solution, the Pb arising from the electrolyte. The source of Cr and Co are unknown, but probably from very low levels in the electrolyte. Na and Si show high concentrations on the surface, where neither element is a major impurity of the Li or electrolyte. The high concentrations of two elements are probably spurious, arising from the glass knife used to scrape the film from the electrode. The high concentration of Al in the film probably arises from two major sources, the Li metal itself and from electrolyte salt entrained in the surface film which could not be removed during the washing process. Mn is found in the film at the same level (10-100 ppm) it is found on the Li metal. Five elements (Mg, Ca, Fe, Ni, Cu) appear to be concentrated in the film.

Since no Ni was detected in either the electrolyte or in the Li, its relatively high concentration in the film appears anomalous. The Ni may be from the leads used in the cell. Dey (26) has shown that Ni is stable in  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolyte. It is probable, however, that the Ni has a surface oxide film. The reaction of  $\text{SOCl}_2$  with metal oxides to produce the metal chlorides is well characterized (27). Some or all of the nickel chloride could dissolve in the electrolyte and eventually plate on the Li surface.

Copper and Fe show remarkably large concentration in the surface film. Both of these are present in the Li metal at the 10-100 ppm level.

The emission spectrographic survey has shown the following: There are no major contaminations from the 48 elements reported in either the ECOM  $\text{LiAlCl}_4$  or in the electrolyte prepared from  $\text{LiCl}$  (MCB),  $\text{AlCl}_3$  (Fluka) and undistilled  $\text{SOCl}_2$  (MCB). In the Li metal (Foote), the only two contaminants of any significance are Al and Cu. The Li surface film contains two major impurities, Cu and Fe. Al could possibly be a major contaminant also (e.g., by plating), but this fact is obscured by the high Al concentration in the Li metal and by the possibility of  $\text{LiAlCl}_4$  entrainment in the film.

The analytical data suggest that purification procedures aimed at reducing the metallic impurity levels in the cells should be concerned with Cu, Fe and Ni. The levels of Ni can presumably be reduced by reducing the amount of Ni exposed to the electrolyte.

#### B. Analysis of System After Electrolyte Purification

The correlation between electrolyte purity and improved Li anode resistance to passivation was established. The effect of the purification procedure was confirmed by analysis and by the discharge behavior of complete  $\text{Li}/\text{SOCl}_2$  cells.



The electrolyte is purified by pretreatment with Li at 71°C. This method suggested itself because, although Li is grossly stable in  $\text{SOCl}_2$ , it is somewhat reactive at elevated temperature. Hence, storage with excess Li at 71°C should remove any Li-reactive impurities, without causing substantial solution decomposition. This storage procedure was carried out in a Pyrex container sealed with a Teflon O-ring. A coil of Li metal were placed in the electrolyte. A Pyrex glass weight was added to the Li to keep it submerged. The sealed container was placed in a 71°C oven.

### 1. Chemical Analyses

The chemical characterization of the electrolyte was begun in order to establish the changes engendered by storage with Li. It is clear that changes have occurred, as evidenced by the improved performance of cells utilizing this electrolyte, by the discoloration of the Li metal stored with the electrolyte, and by the change in the electrolyte color from essentially colorless to bright yellow. The color change of the electrolyte to bright yellow suggests something, as yet unidentified, but probably S is produced in the solution. The S would arise from the slow reaction between  $\text{SOCl}_2$  and Li.

The spectroscopic analyses had shown that Cu and Fe had relatively high concentrations in the passivating film. On this basis, these two are likely candidates for removal by the Li during storage with the electrolyte. We therefore chose to analyze the stored Li for Cu and Fe to determine if these increase on the Li during storage.

The analyses were obtained on Li by two different procedures. The first was on Li foil recovered from our normal pretreatment method. The second set of Li samples were designed to elucidate the time dependence of the Cu and Fe removal. They were obtained by changing the Li in the solution at intervals during the storage. The Li foils ( $\sim 100 \text{ cm}^2$ ) were placed on glass frames, both to keep the Li submerged and also provide a reproducible surface exposure.

The analyses for Cu and Fe were by standard spectrophotometric methods. The method for Fe, as described above, uses o-phenanthroline as the sensitive reagent (19). The Cu method uses 2,2'-biquinoline as the sensitive reagent (28, 29). Samples of fresh Li foil were also analyzed.

The analytical results are summarized in Table 10. The sample H62 was cut from the 24" piece used in our normal storage procedure. It was about 8% of the total sample. It shows about three times the Cu and twice the Fe found on fresh Li foil. These concentrations may not be the same over the complete length of the foil. The Li foil helix in the storage vessel was coiled such that some shading occurred. This caused irregular distribution of the surface darkening, which is probably indicative of the distribution of the materials removed from solution. Nonetheless, it is

Table 10  
Cu and Fe Concentrations on Li Foil Stored  
with 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> at 71°C

<u>Sample</u>	<u>Storage (days)</u>	<u>ppm Cu<sup>a</sup></u>	<u>ppm Fe<sup>a</sup></u>
H62	13	126	41
H63-1	1st	134	66
H63-2	2nd-4th	104	42
H63-3	5th&6th	76	28
H63-4	7th-13th	79	28
Li metal	-	35	23

} Same  
Solution

a = error limits  $\pm$  5%

clear that the Li is removing Cu and Fe from the electrolyte, and probably other species which form reduced insoluble products (e.g., other metal ions).

The H63 samples, which were stored in the same electrolyte consecutively for the number of days indicated, again show increases in Cu and Fe content, at least for the first two samples. After four days the Fe content of the Li is back at background, indicating the removal of Fe from the electrolyte had ceased. The Cu content does not return to the base line value of the fresh Li, although it is approximately the same for the H63-3 and H63-4 samples. These measurements clearly show the time dependence of the Cu and Fe removed from the system by the Li. The reason for the failure of the Cu to return to base line concentrations has not been determined. There are two immediately apparent possible causes. Either the distribution of Cu in the Li metal itself is non-uniform, which seems unlikely, or the removal rate of Cu deposition is slower than that of Fe.

The pretreatment of the electrolyte with Li at  $71^{\circ}\text{C}$  is removing some substances and adding at least one other. Which of these is the most beneficial is not yet clear. The removal of Cu and Fe should be helpful: It should reduce the rate of Li corrosion, by mitigating the depolarization caused by the plating of these relatively noble metals. Furthermore, these metals, once plated, can depolarize  $\text{SOCl}_2$  reduction, perhaps preferentially to Li itself.

## 2. Infra-red Analysis

The 1.5M  $\text{LiAlCl}_4/\text{SOCl}_2$  electrolyte after preparation and before storage (Fig. 12) with Li shows IR bands at  $\sim 3320\text{ cm}^{-1}$ , indicative of O-H stretching (probably from hydroxyaluminum compounds), at  $1313\text{ cm}^{-1}$  (indicative of  $\text{SO}_2$ ), and an unidentified peak at  $685\text{ cm}^{-1}$ . After 44 hrs of storage at  $71^{\circ}\text{C}$  with Li (Fig. 14), the bands at  $3320\text{ cm}^{-1}$  and  $685\text{ cm}^{-1}$  disappear from the spectra. Bands appear at  $2750\text{ cm}^{-1}$  and  $1060\text{ cm}^{-1}$ . The  $2750\text{ cm}^{-1}$  band is indicative of HCl. The band at  $1060\text{ cm}^{-1}$  is still unidentified but is probably due to some S-O containing compound. A large number of such compounds have absorbances in this region (30, 31). The  $\text{SO}_2$  band also increases. After 205 hrs of storage, the  $3320\text{ cm}^{-1}$  and  $685\text{ cm}^{-1}$  bands are still absent. The HCl band at  $2750\text{ cm}^{-1}$  has diminished by a factor of 3 and the band at  $1060\text{ cm}^{-1}$  has remained unchanged. After 330 hrs of storage, the HCl band is reduced further and again the  $1060\text{ cm}^{-1}$  band remained unchanged.

These data indicate that the hydroxyaluminum compounds react readily with Li to produce HCl. This HCl subsequently reacts, but more slowly, with the Li. The exact reaction mechanism is unclear, but must involve the hydroxy compound, Li and  $\text{SOCl}_2$ . The  $\text{SOCl}_2$  must be involved because a direct reaction between only the Li and the hydroxy compounds would most likely produce  $\text{H}_2$  and not HCl. Thus it must be a Li-mediated reaction between the  $\text{SOCl}_2$  and the hydroxy compounds.  $\text{SOCl}_2$  and these compounds do not react directly at any appreciable rate since the  $3320\text{ cm}^{-1}$  band has been observed to be stable for at least three weeks at room temperature.

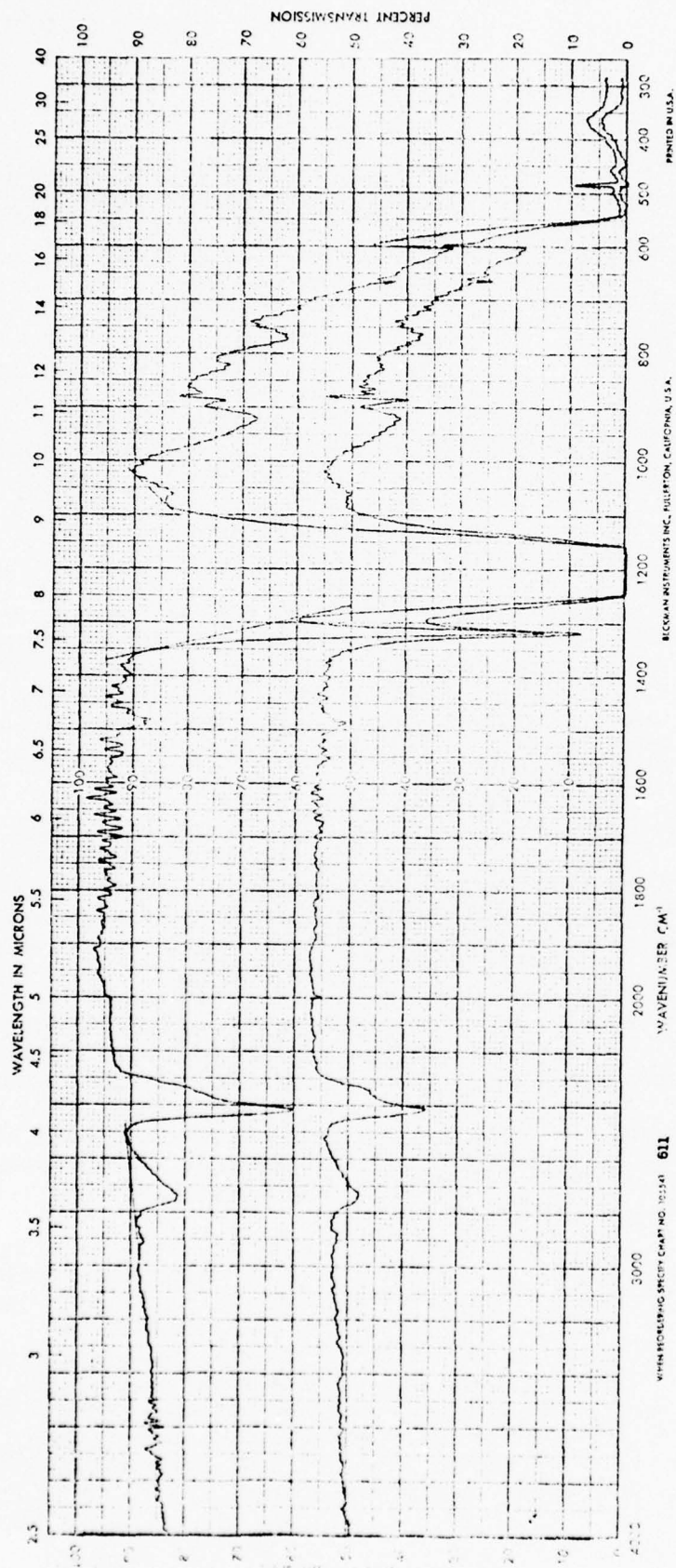


Fig. 14: Infrared spectrum of 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> after 44 hrs at 71°C with Li.



The disappearance of the  $685\text{ cm}^{-1}$  band along with the  $3320\text{ cm}^{-1}$  suggests they may be related. It is possible that this band may be due to Al-O stretching. This needs further confirmation.

### C. Effect of Purification on Cell Discharge

The positive effect of purified electrolyte on the ability of stored cells to resist passivation was established. Complete Li/SOCl<sub>2</sub> cells were assembled, stored and tested. Both the early time voltage characteristics and the complete discharge characteristics were measured.

The design of the test cells is shown in Figure 15. These cells were developed for high temperature storage testing. They are used here to develop base line information. The electrode package is a 5 layer structure. The anode and cathode are separated by a layer of glass fiber paper. A piece of glass fiber paper is used to separate the anode and cathode from the Teflon discs. The anodes were prepared by pressing a  $1\text{ cm} \times 1\text{ cm}$  15 mil Li foil piece onto each side of a Ni Exmet screen (3 Ni 5 - 4/0). A Ni lead wire was previously welded to the screen. The anodes were approximately 0.03" thick. The cathodes were bonded carbon, and were prepared as described previously, except that Shawinigan 50% compressed carbon black was substituted for the Ashland XC-6310-4 originally used. The assembled cells were vacuum impregnated with electrolyte and stored in O-ring sealed Pyrex containers.

Our primary test procedure after storage is to apply a constant load of  $480\Omega$ . Then the cell voltage and the anode potential vs. a fresh Li reference are measured on a rapid time base. The  $480\Omega$  load was chosen because fresh cells have a current density of  $6.5\text{--}7.0\text{ mA/cm}^2$  with this load. For a practical D cell with an  $\sim 400\text{ cm}^2$  electrode area, this is equivalent to  $\sim 3\text{A}$  rate. For some cells the complete discharge performance was also measured.

#### 1. Results

The cell preparation procedures designed to remove Li-reactive species produced cells which, after  $71^\circ\text{C}$  storage, showed a remarkable improvement in discharge characteristics. At the moment, the limit of this improvement lies at about 400 hrs of storage at  $71^\circ\text{C}$ . Beyond 400 hours storage, the performance, as evidenced both by the voltage delay and depression measurements, and by the complete discharge data, decays.

The voltage delay and depression characteristics of the normal Li/SOCl<sub>2</sub> cells become inferior after  $\sim 100$  hrs storage. After 87 hrs storage, the cell performance has degraded to unacceptable levels. This is illustrated in Figure 16. The voltage delay measurements on cells at 200 hrs and up to 400 hrs are comparable to this.

The Li/SOCl<sub>2</sub> cells prepared with purified electrolyte contrast sharply. Figure 17 presents the voltage vs. time response of such cells stored 208 hrs at  $71^\circ\text{C}$ . Only one of the cell shows any voltage delay. Here "voltage delay"

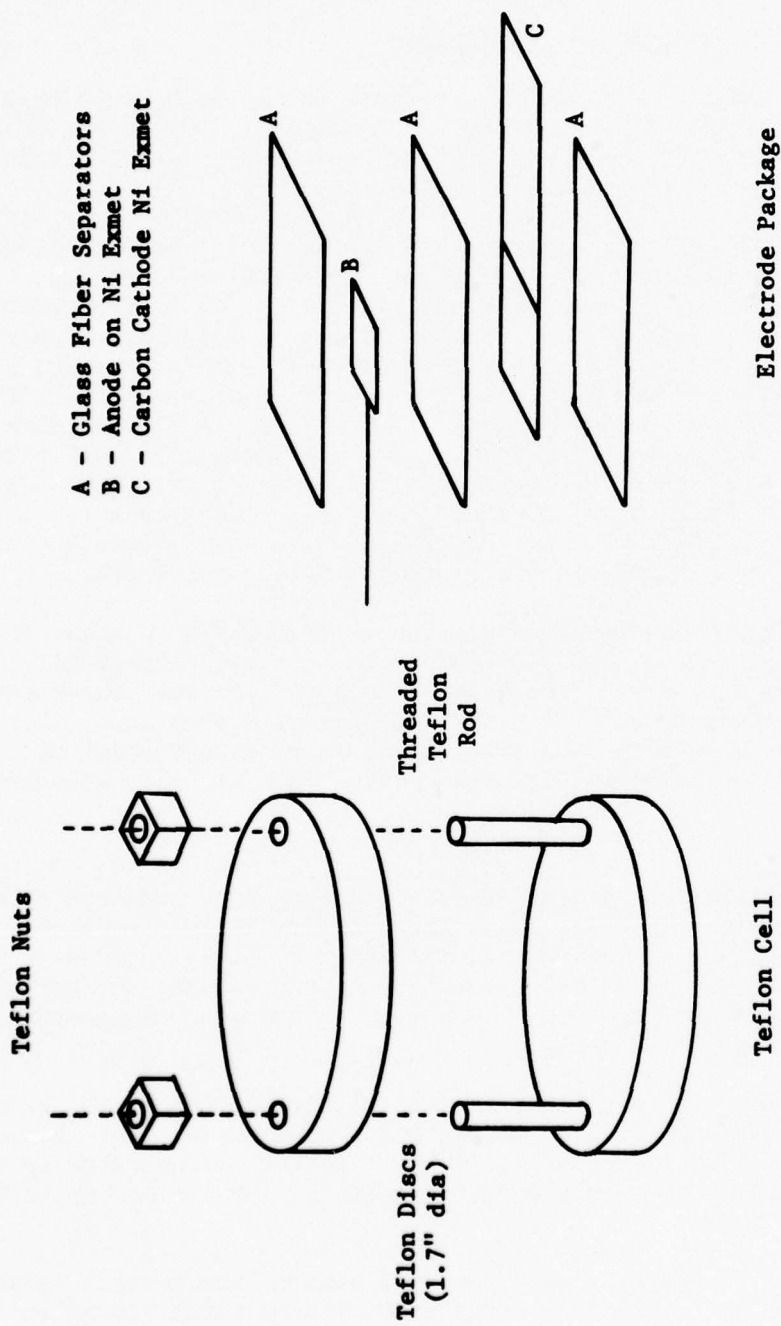


Fig. 15: Teflon (T-cell) cell and electrode package.

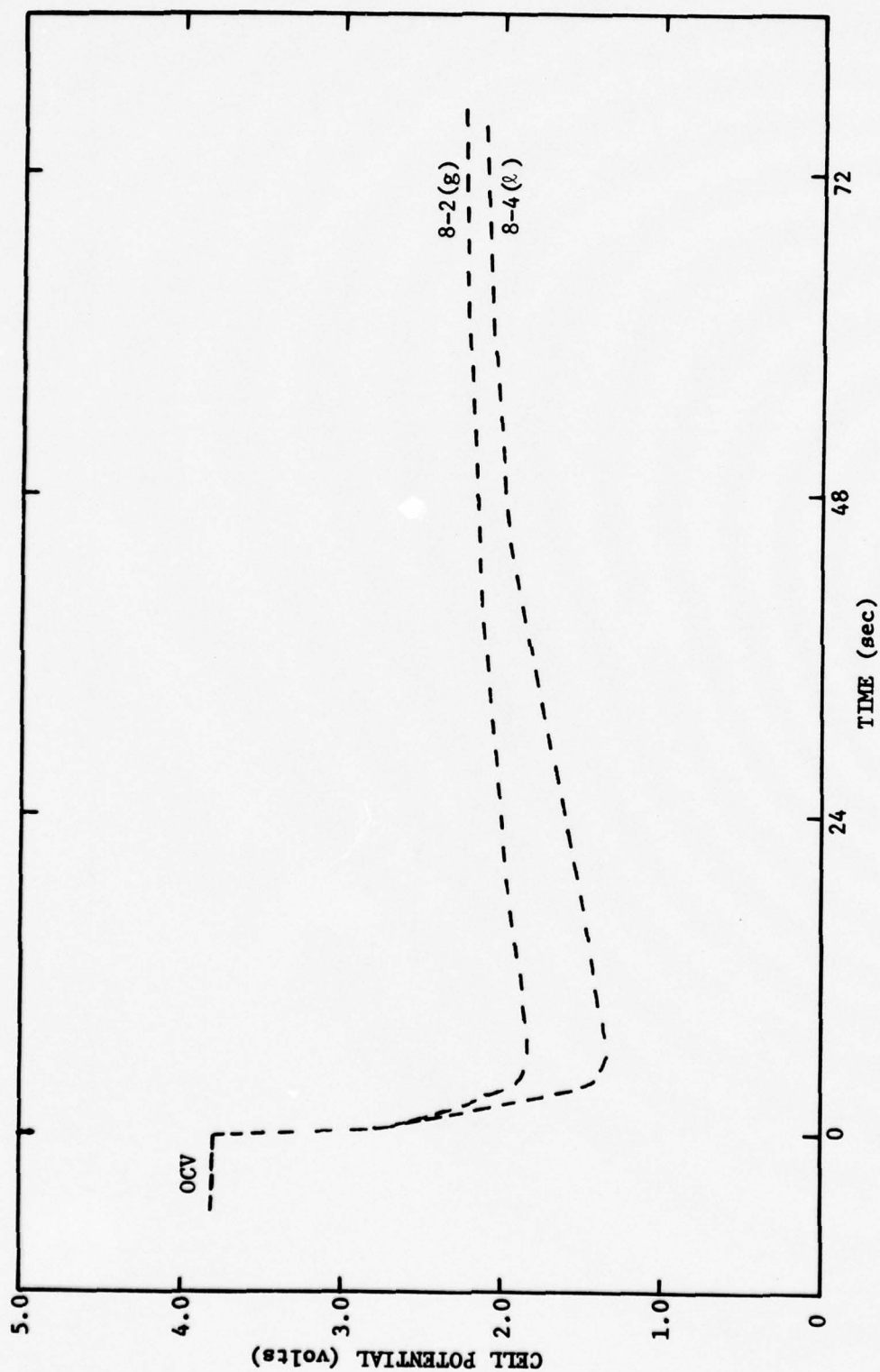


Fig. 16: Initial polarization of Li anode,  $\text{SOCl}_2$  cells with  $480\Omega$  load. Cell H8 stored 87 hrs at  $71^\circ\text{C}$  with  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$ .

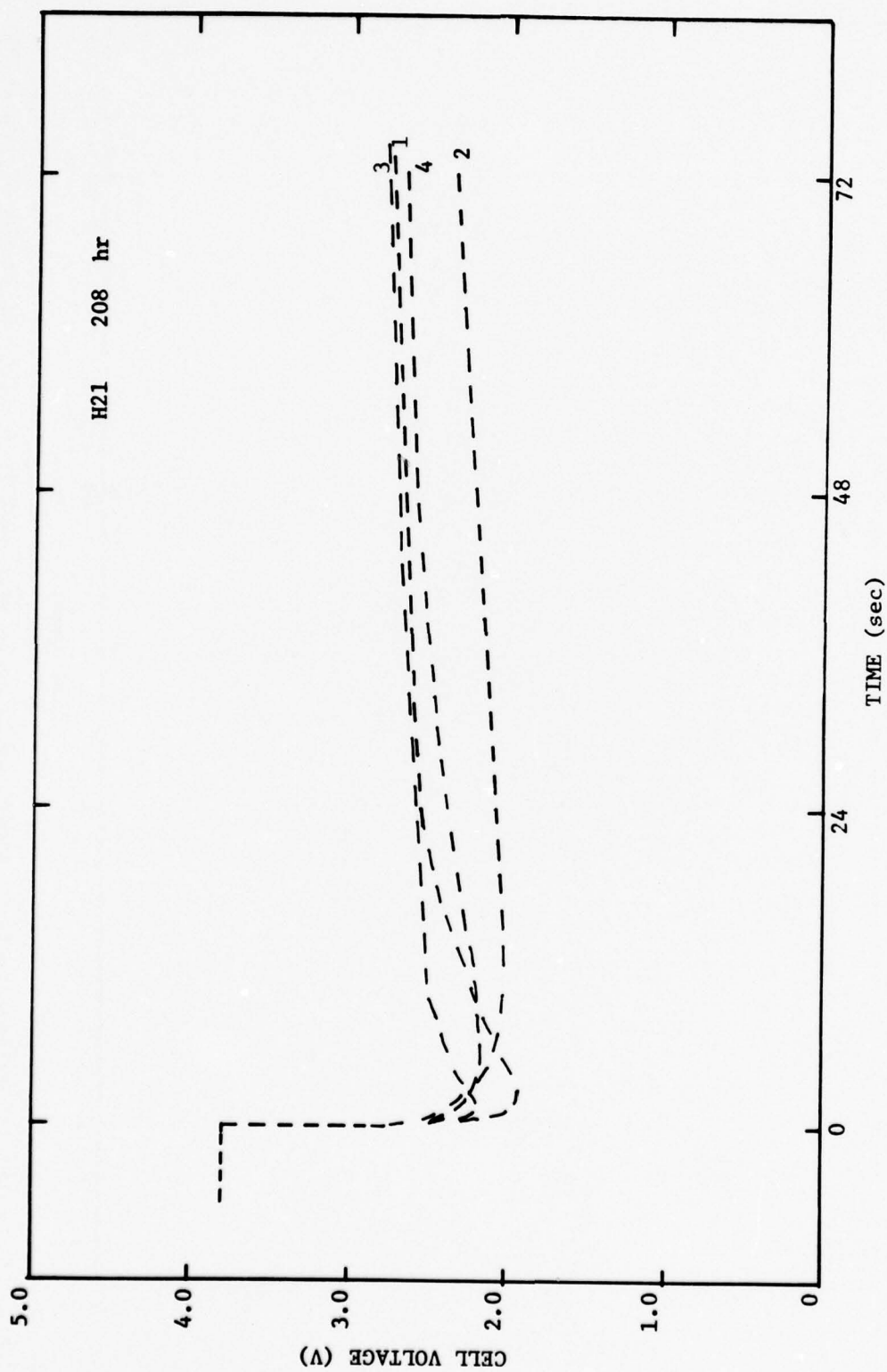


Fig. 17: Initial polarization of Li anode/SOCl<sub>2</sub> cells with 480Ω (0.1 cm<sup>2</sup>). H21 was stored 208 hr at 71°C with LiCl saturated 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub>.



is arbitrarily defined as the length of time the cell voltage remains below two volts when discharged. The delay was about 2-4 sec. The performance of the clean cells degrade seriously for storage times of 400 hrs or greater. The improvement in cell performance with the use of purified vs. as-prepared electrolytes is further illustrated by a comparison of the cell voltages 60 sec after the initiation of discharge. These data are shown in Figure 18. The cell voltage at 60 sec appears to decrease linearly with storage time in both cases. With the as-prepared electrolyte the slope is much steeper. On the average, the voltage delays with the as-prepared electrolyte begin to exceed 60 sec after ~110 hrs of storage, while with the purified electrolyte they began to exceed 60 sec after ~480 hrs.

The difference between the cells assembled with as-prepared electrolyte and purified electrolyte is also illustrated by their behavior during complete discharge. Figure 19 shows the complete discharge of three cells, two prepared with purified electrolyte and one with as-prepared electrolyte. The difference is striking. The nominal capacity of these cells is about 120 mAh. Both of the cells prepared with purified electrolyte gave their full capacity. The other cell barely gave half of its full capacity at much reduced voltages.

These data clearly establish a direct relation between electrolyte purity and cell performance after 71°C storage. The electrolyte is purified by storage with Li. This reduces the amounts of dissolved Li-reactive species. Iron, Cu, HCl and hydroxyaluminum compounds were the specific species monitored. These were reduced or eliminated by the purification process. Li/SOCl<sub>2</sub> cells prepared with this electrolyte have a much greater resistance to passivation during storage. Further analytical work and improvement of purification procedures may prove beneficial.

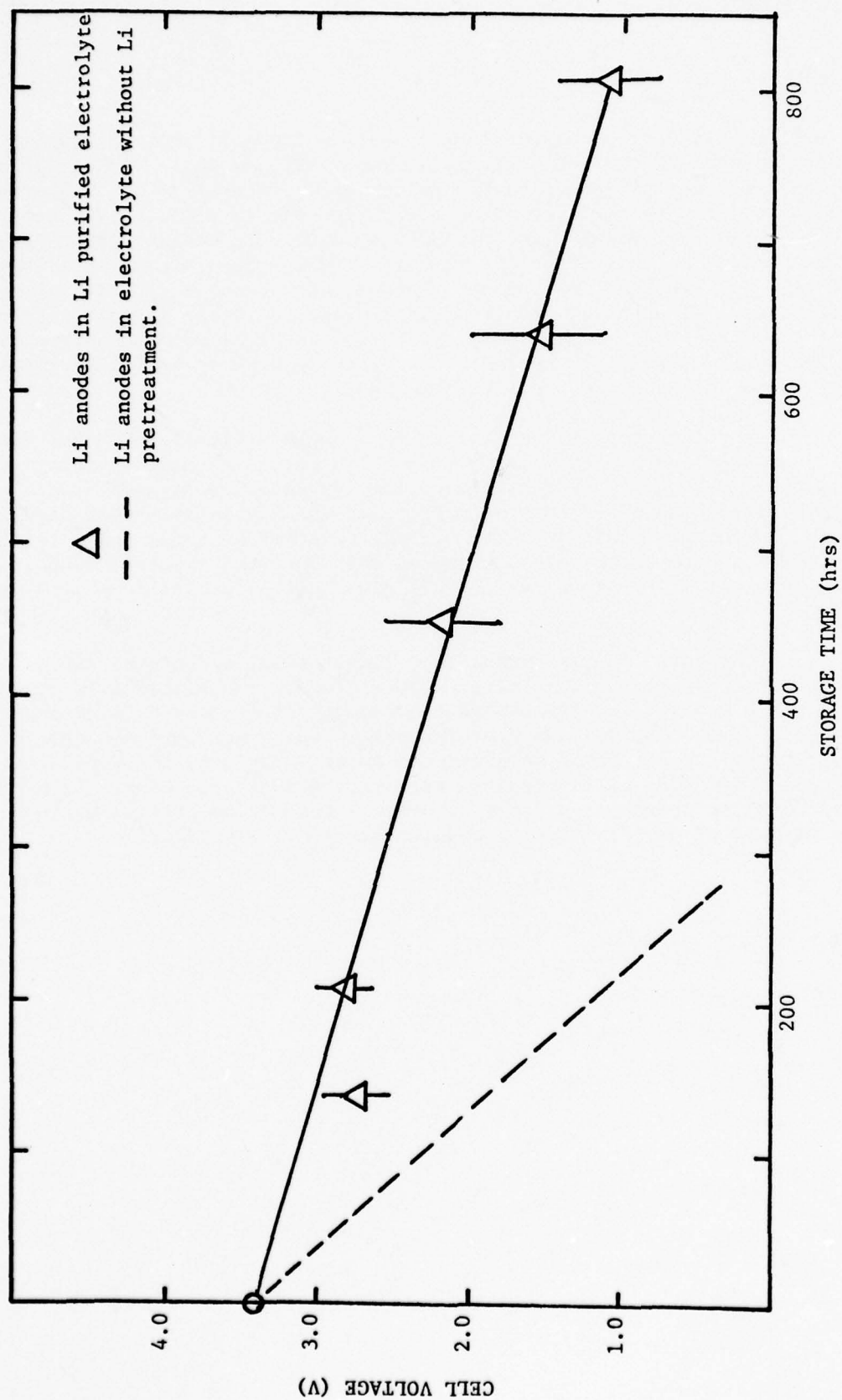


Fig. 18: Average cell voltage at 60 sec after the application of a constant load. The load will draw  $\sim 7.0 \text{ mA/cm}^2$  from a fresh cell.

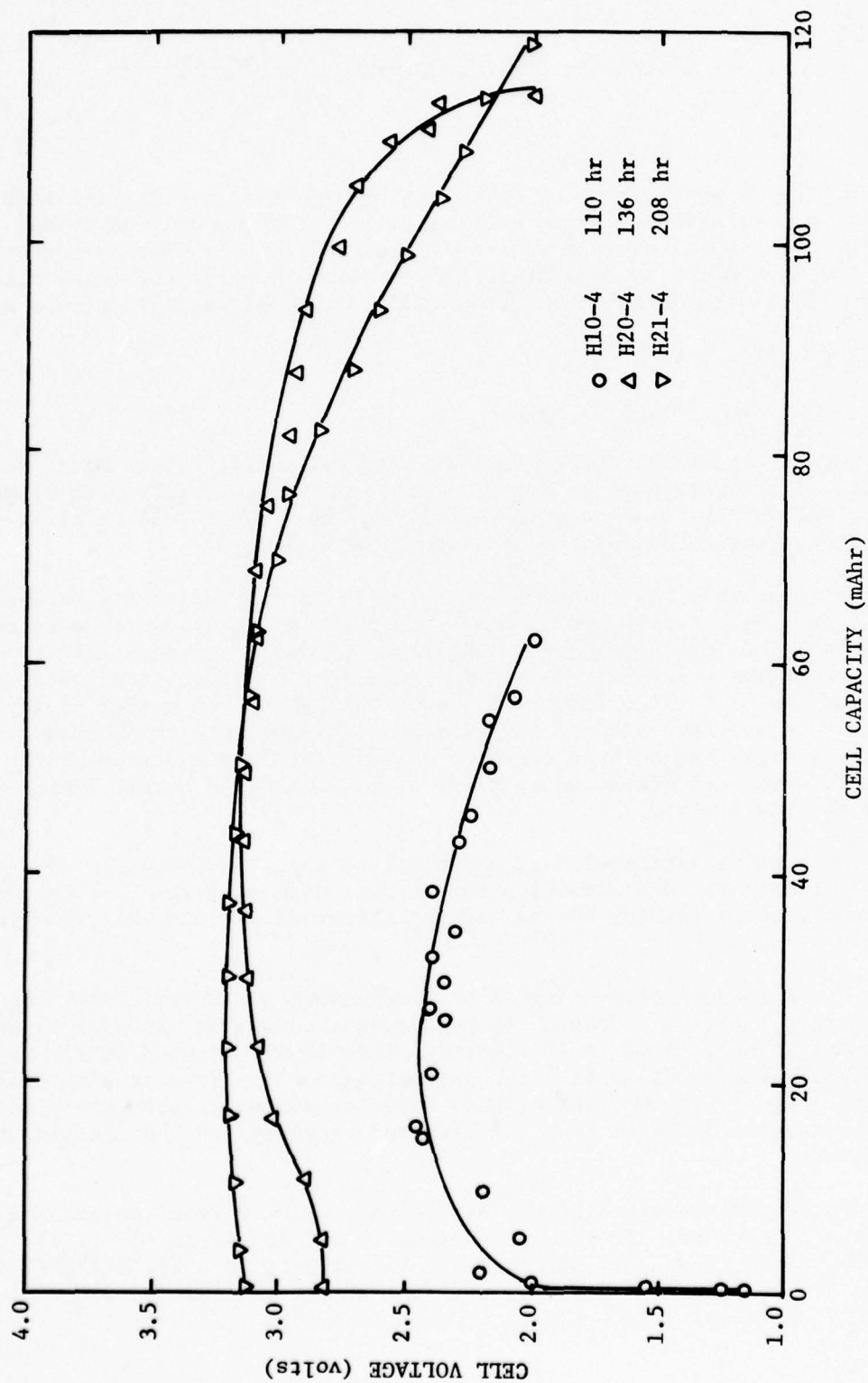


Fig. 19: Potential of Li/SOCl<sub>2</sub> cells discharged through 480Ω (≈1 cm<sup>2</sup>) at 25°C after storage at 71°C. H10 used type A electrolyte and H20 and 21 used type E.

## V. EFFECT OF ALLOYING ON ANODE PERFORMANCE

Another aspect of the Li/SOCl<sub>2</sub> cell design that was investigated with a view toward alleviating anode passivation was the composition of the anode. Alloys with a high Li content were evaluated as anodes. Current-potential curves and discharges in complete cells were obtained for the fresh alloys. Discharge data were obtained on alloy anodes in complete cells stored at 71°C.

### A. Fresh Alloy Performance

#### 1. Current-Potential Data

Current-potential curves for 12 Li alloys as well as Li metal were obtained. These data gave an initial survey of the materials with respect to their suitability as anodes in Li/SOCl<sub>2</sub> cells. The Li and Li alloy foils were potentiostatically oxidized in 1.8M LiAlCl<sub>4</sub>/SOCl<sub>2</sub>.

The test cell was comprised of a Teflon working electrode holder. The working electrodes were Li metal discs 0.375" in diameter, which were punched out of the 15 mil Li foil. Figure 20 shows the design of this holder. Electrical connection was made by a Ni wire lead spot welded to a Ni metal disc set behind the Li working electrode disc. The end of the holder containing the electrode was immersed in 1.8M LiAlCl<sub>4</sub> contained in a small beaker. The counter electrode was a large piece of Li foil set on the bottom of the beaker and the reference electrode was a piece of Li metal in a Luggin capillary containing the electrolyte.

The current potential data was obtained potentiostatically using a PAR 373 potentiostat and recording the current with a strip chart recorder. The open circuit potential of the working electrode was typically within  $\pm 7$  mV of zero.

This method of evaluating alloy performance is suitable only for a preliminary estimation. Details of performance cannot be assessed because the current in most cases is  $iR$  limited. This is illustrated in Figure 21 by the data for pure Li metal. The current increases linearly with applied potential. The resistance, calculated from the slope, matches the electrolyte resistance calculated from the electrode spacing and the electrolyte conductivity.

The measurements indicated that of the twelve alloys tested, ten were comparable to pure Li. These were: Li/Al (5 at. %), Li/Ag (5 at. %), Li/Au (2 at. %), Li/Bi (5 at. %), Li/Cu (4 at. %), Li/Mg (1 at. %), Li/Pb (3 at. %), Li/Si (4 at. %), Li/Sn (3 at. %) and Li/Zn (10 at. %). Two alloys were substantially inferior: Li/Cd (5 at. %) and Li/Mg (5 at. %).



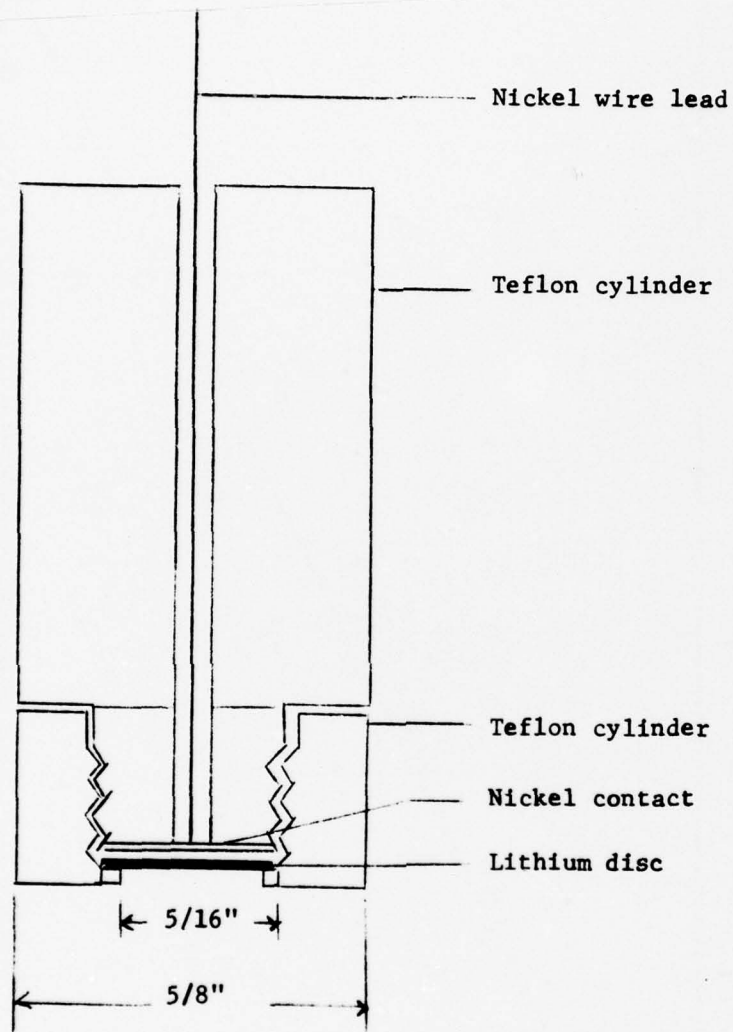


Fig. 20: Holder for lithium discs.

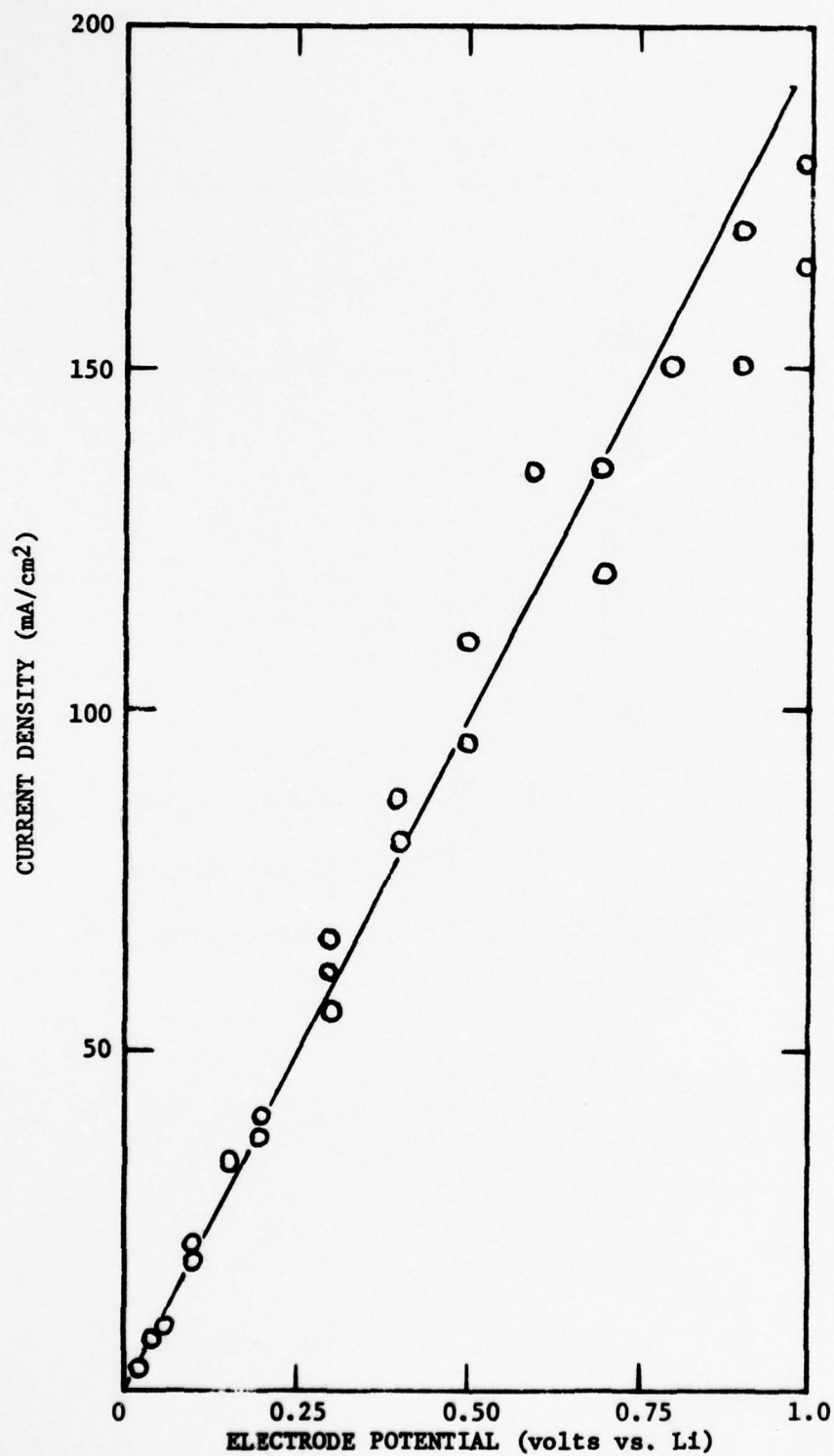


Fig. 21: Current potential curve of Li in 1.8M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> at 25°C.

## 2. Discharge of Complete Cells

Complete Li/SOCl<sub>2</sub> cells were assembled with Li alloy anodes. The cell design was the same as described above (Section IV, C). The cells were discharged fresh at  $\sim 7$  mA/cm<sup>2</sup>. The ten alloys which were similar to Li in the potentiostatic tests discharged at voltages comparable to Li, i.e., between 3.2 and 3.4 V. As was expected, the Li/Cd (5 at. %) and Li/Mg (5 at. %) alloys showed much inferior behavior. Excluding the Li/Si alloy for the moment, the nine other alloys had anode utilizations of 47% to 81% of the Li present. The utilization of pure Li in identical cells was  $\sim 80\%$ . The utilization of the Li/Si alloy was exceptional at 107%. This was the average of three cells. This performance suggests that the Si is being oxidized as well as the Li, although measurements with pure Si indicate it does not oxidize at appreciable rates at these potentials. This is, nevertheless, an interesting result and deserves further attention. More specific details of this work can be found in our 7th, 8th and 9th Quarterly Reports.

Based on these results storage tests were made with cells containing alloy anodes.

### B. Alloy Anode Performance After Storage

The Li alloys were tested for their resistance to passivation by storage at 71°C in complete cells. After storage the cells were tested by applying a load which draws  $\sim 7$  mA/cm<sup>2</sup> from a fresh cell, and monitoring the cell voltage. The test results indicate that none of the alloys tested are resistant to passivation. The data show that all of them behave similarly to Li stored under similar conditions.

Despite the similarity to Li, three of the alloys showed an ability to recover more rapidly than Li or the other alloys. The test scheme that led to this observation was the following. The cells were tested initially under constant load. They were then tested potentiostatically, to evaluate anode performance, and finally again tested under constant load. Figure 22 illustrates the typical response of Li and most of the alloys. Three of the alloys, however, show great improvement on the second constant load test. These were Li/Ag, Li/Cd and Li/Mg (1%). This is illustrated in Figure 23. These data suggest it is possible to modify the anode surface to reduce the strength or adherence of the passivating film. More details can be found in our 9th and 10th Quarterly Reports.

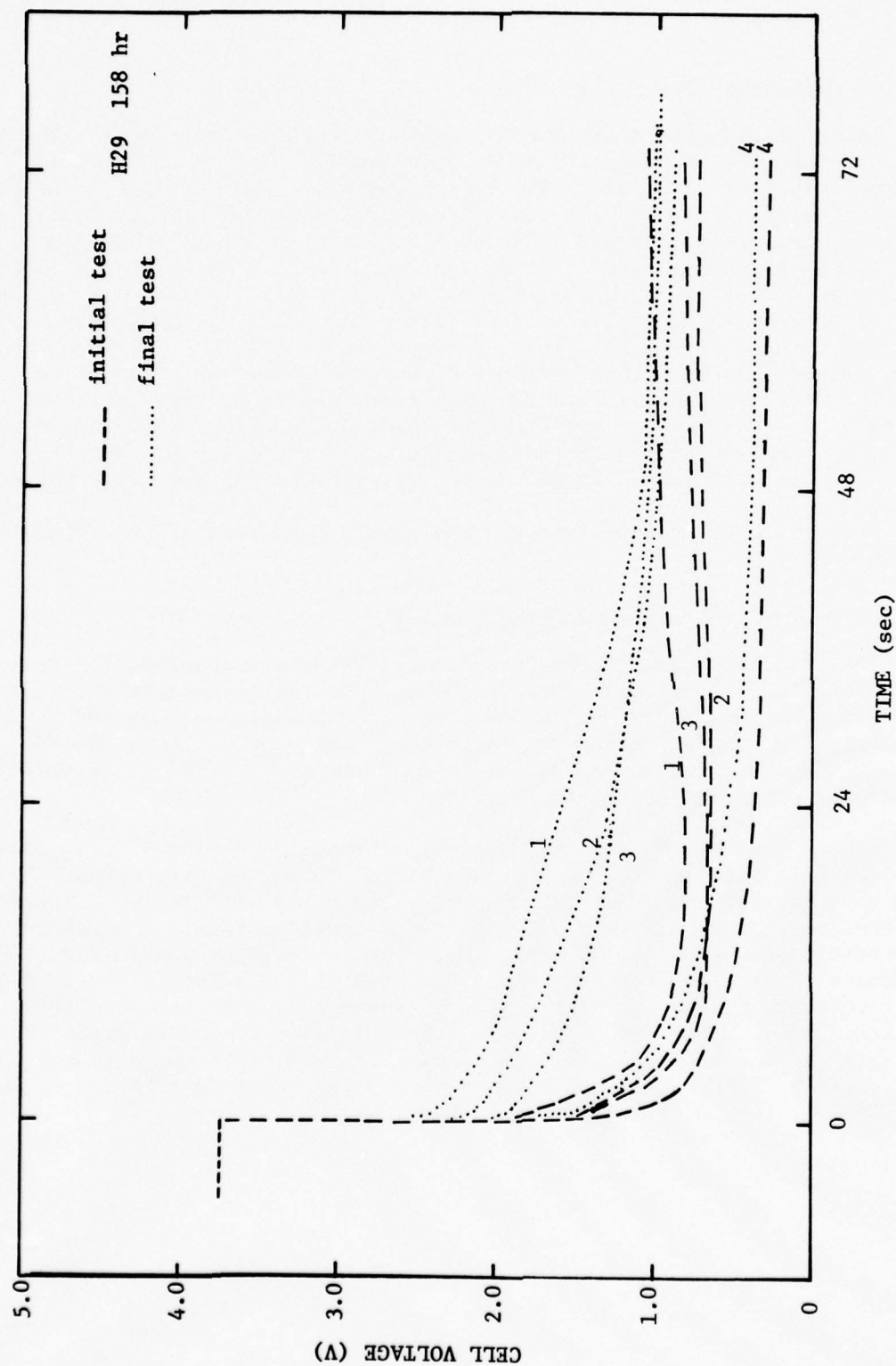


Fig. 22: Initial (---) and final test (.....) polarization of Li/Si(4 at.%) anode/SOCl<sub>2</sub> cells with 480Ω (≈1 cm<sup>2</sup>). H29 was stored 158 hr at 71°C with LiCl saturated 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub>.



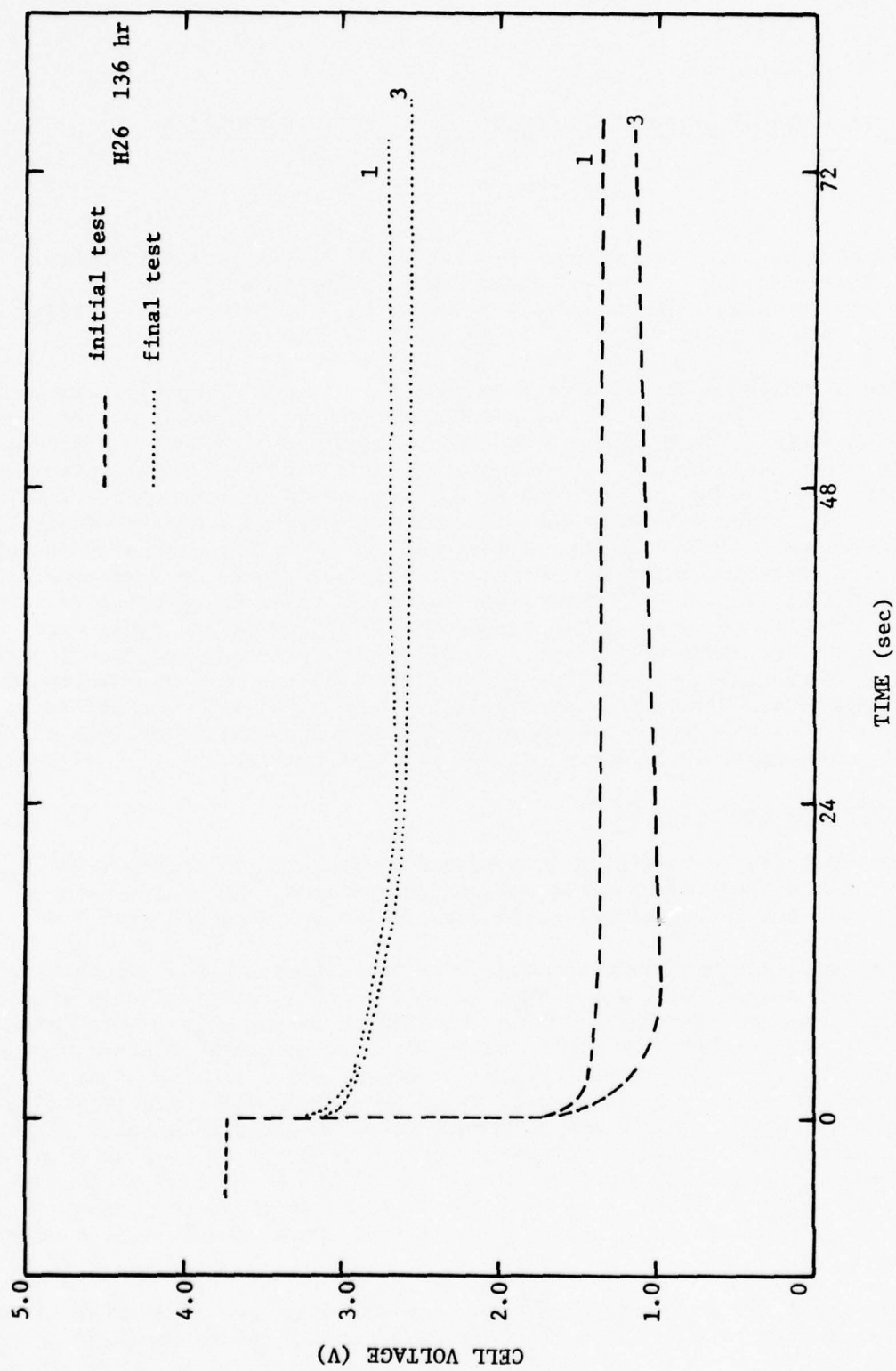


Fig. 23: Initial (----) and final test (.....) polarization of Li/Mg(1 at.%) anode/SOCl<sub>2</sub> cells with 480Ω (~1 cm<sup>2</sup>). H26 was stored 136 hr at 71°C with LiCl saturated 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub>.

## VI. EFFECT OF SOLUTION ADDITIVES ON ANODE PASSIVATION

We have explored the effect of solution additives on the Li/SOCl<sub>2</sub> system. The primary goal was to develop an additive to alleviate the voltage delay problem. The additives tested were H<sub>2</sub>O, S<sub>2</sub>Cl<sub>2</sub>, AlCl<sub>3</sub>, PCl<sub>3</sub>, PCl<sub>5</sub>, P<sub>2</sub>S<sub>5</sub>, SO<sub>2</sub>, Et<sub>4</sub>NCl, SbCl<sub>5</sub>, S, I<sub>2</sub> and Ca<sup>++</sup>.

These additives were chosen to assess the effects of specific chemical groups. One group consisted of potential or known contaminants and reaction products. These included H<sub>2</sub>O, S, S<sub>2</sub>Cl<sub>2</sub> and SO<sub>2</sub>. The Lewis acids, AlCl<sub>3</sub> and SbCl<sub>5</sub>, were used to investigate the possibility of maintaining a thin protective film on the Li anode by continuous dissolution of the LiCl formed on the surface. A Lewis base, Et<sub>4</sub>NCl, was used to test the feasibility of forming a dense, thin film on the Li anode which could potentially inhibit further film formation and which could be easily penetrated on discharge. Two other substances, I<sub>2</sub> and Ca<sup>++</sup>, were also tested as potential protective film formers. Finally, three phosphorous compounds, PCl<sub>3</sub>, PCl<sub>5</sub> and P<sub>2</sub>S<sub>5</sub>, were tested. These compounds are known to stabilize sulfur chlorides, particularly SCl<sub>2</sub>, against thermal decomposition (34). Their use was more speculative in the sense that they might add some stability to the system if thermal decomposition of sulfur chlorides, to Cl<sub>2</sub>, or SOCl<sub>2</sub>, to sulfur chlorides, was a mechanism enhancing the thickening of the passivating film.

### A. Additives Excluding Ca<sup>++</sup>

The additives were tested in complete Li/SOCl<sub>2</sub> cells. They were dissolved in the electrolyte in various concentrations. The cells were stored at 71°C and tested either galvanostatically or under constant load.

The test results divide the additives into three groups. One group, including H<sub>2</sub>O, S<sub>2</sub>Cl<sub>2</sub>, PCl<sub>3</sub>, P<sub>2</sub>S<sub>5</sub>, SO<sub>2</sub>, S and I<sub>2</sub>, seems to have little effect on cell performance. Another group is detrimental to the cell. These are AlCl<sub>3</sub>, SbCl<sub>5</sub> and Et<sub>4</sub>NCl. The AlCl<sub>3</sub> and SbCl<sub>5</sub> are detrimental because they are strong acids in the SOCl<sub>2</sub> solvent system. They dissolve the LiCl film from the anode, which reduces passivation. This, however, greatly accelerates Li anode corrosion which reduces the cell capacity at unacceptable rates. The Et<sub>4</sub>NCl causes Ni dissolution. Chlorometallate anions are very soluble in SOCl<sub>2</sub> with the tetra-alkyl ammonium cation (8). This solubility allows the Ni cell components to dissolve as NiCl<sub>4</sub><sup>-</sup>. This causes rapid corrosion of the Ni cell components, e.g., the Ni current collectors used for the anodes and cathodes.

The third group contained only one compound PCl<sub>5</sub> was beneficial to cell performance. A typical test for the PCl<sub>5</sub> additive was the following:

The electrolyte was 1.5M  $\text{LiAlCl}_4/\text{SOCl}_2$  containing 1 weight %  $\text{PCl}_5$  (Eastman, pract. P-470). Cells were tested after 282 hours and 622 hours. The initial polarization curves for the cells are shown in Figure 24. The cells stored 282 hours had an average cell voltage of 2.95 V at the 60 sec point and the cells stored 622 hours had an average cell voltage of 2.80 V. These correspond to current densities of 87.1% and 82.6% of that of fresh cells.

$\text{PCl}_5$  used as an additive clearly improves the performance of  $\text{Li}/\text{SOCl}_2$  cells stored at  $71^\circ\text{C}$ . The mechanism by which it acts is at present unknown and deserves further attention.

B.  $\text{Ca}^{++}$  Additive

$\text{Ca}^{++}$  additive in a  $\text{Li}/\text{SOCl}_2$  has a very beneficial effect with regard to preventing anode passivation. We believe that  $\text{Ca}^{++}$  has this beneficial effect because it deposits on the surface of the Li, forming a film of Ca metal or a Li/Ca alloy which retains the resistance to passivation that we have observed with pure Ca metal in the  $\text{SOCl}_2$  system. In the following section we will first discuss the  $\text{Ca}/\text{SOCl}_2$  system and then the Ca-coated  $\text{Li}/\text{SOCl}_2$  system.

1. Characterization of the  $\text{Ca}/\text{SOCl}_2$  System

Our measurements have shown that Ca discharges effectively in  $\text{SOCl}_2$  electrolyte. The tests were made with complete  $\text{Ca}/1.5\text{M LiAlCl}_4, \text{SOCl}_2$  cells. The Ca (20 mil) was obtained from ROC/RIC. The surface was polished to the bright metal before use with fine sandpaper. An exploratory E-i scan indicated that the Ca can be oxidized at  $\sim 20 \text{ mA/cm}^2$  at a polarization of +0.8 V relative to open circuit. The open circuit potential of the  $\text{Ca}/\text{SOCl}_2$  cells ranged between 2.8 V and 3.0 V. The discharge curves of four fresh cells are shown in Figure 25. Two cells were discharged through  $480\Omega$  and two through  $1000\Omega$ . The curves are qualitatively similar. After an initial increase, the cell voltage remains relatively constant for about 40% of the discharge, then declines to the 1.0 V cutoff. The decline in the cell voltage of the cells tested at  $480\Omega$  is more rapid than the cells discharged at  $1000\Omega$ . The plateau for the cells discharged with  $480\Omega$  was  $\sim 2.6 \text{ V}$  and for the  $1000\Omega$  load was  $\sim 2.7 \text{ V}$ . The increased cell polarization in the latter 60% of discharge is probably due to the buildup of insoluble, anode-discharge products.

After discharge, we noted a white crystalline deposit on the anode. The anode had approximately the same shape as the original piece of Ca, although it is somewhat thicker. Further inspection revealed a dark center, which was Ca metal. The white crystalline material has not been analyzed, but it is probably either  $\text{CaCl}_2$  or  $\text{Ca}(\text{AlCl}_4)_2$ . Both are rather insoluble in  $\text{SOCl}_2$ . The probable anode reaction is either

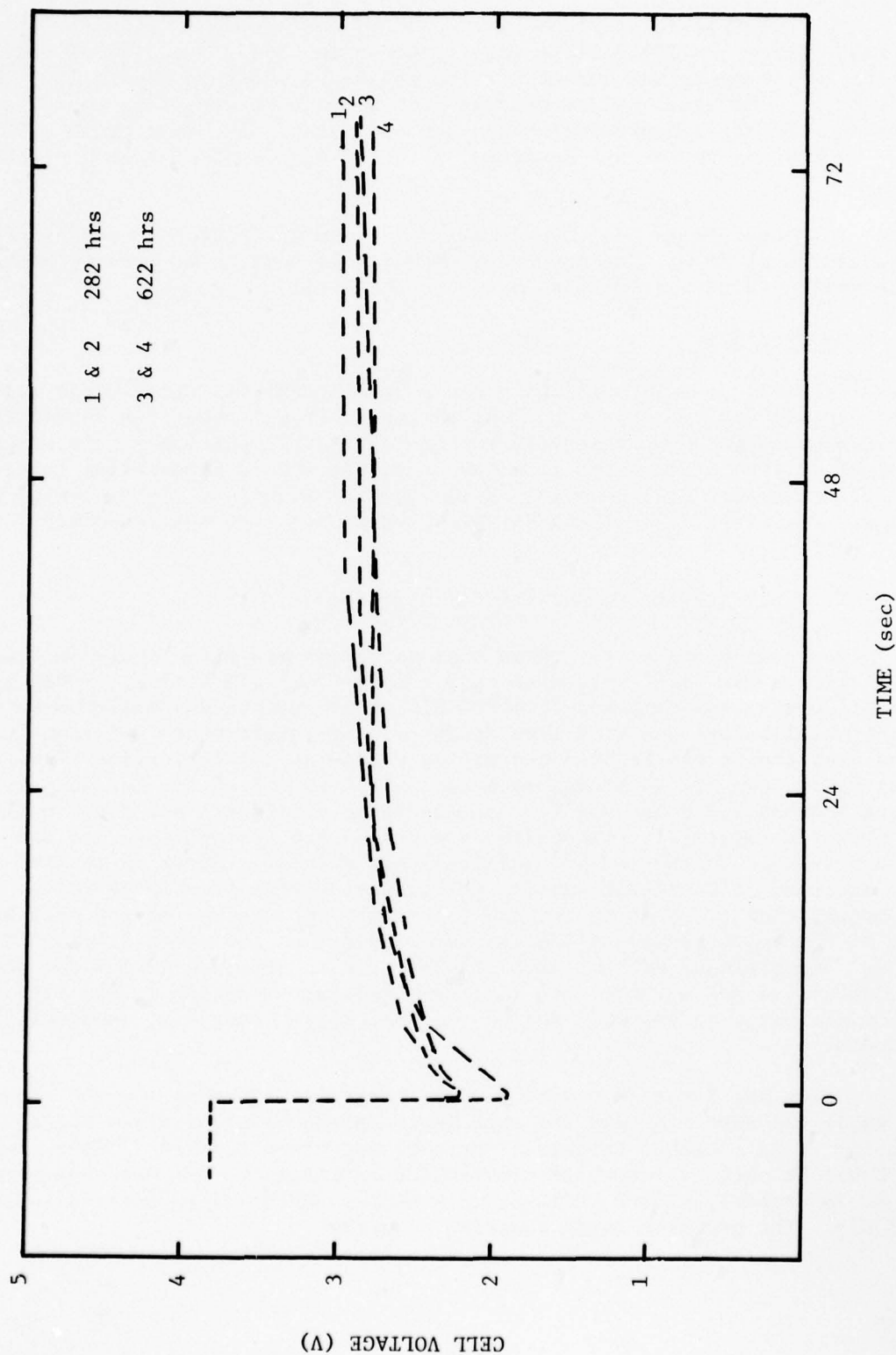


Fig. 24: Initial polarization curves of Li/SOCl<sub>2</sub> cells stored at 71°C in 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> with 1 weight % PCl<sub>5</sub> added.



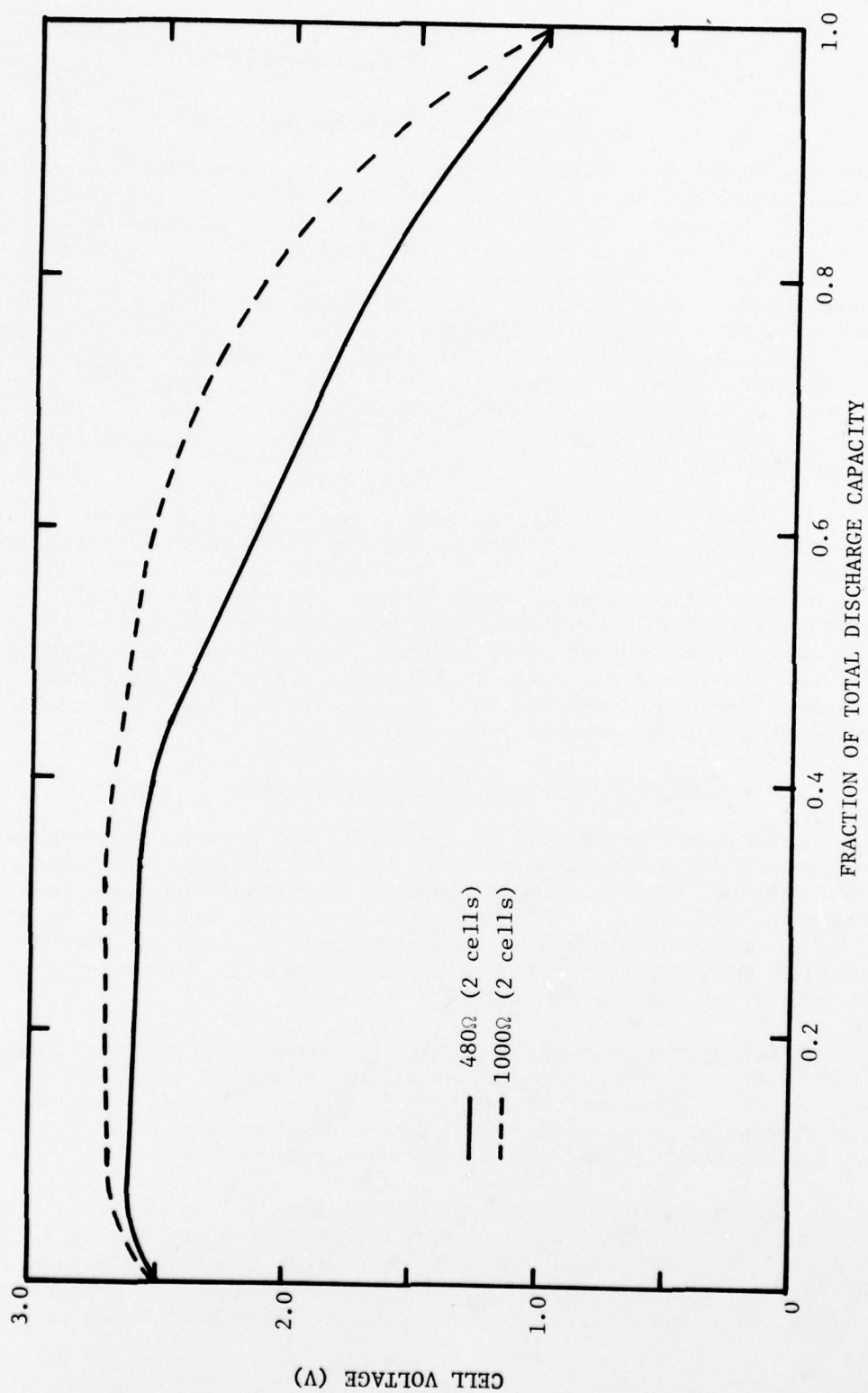
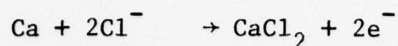
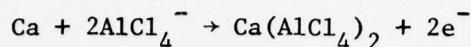


Fig. 25: Discharge voltage of fresh Ca anode,  $\text{SOCl}_2$  cells discharged at  $25^\circ\text{C}$  with  $1.5\text{M LiAlCl}_4/\text{SOCl}_2$  electrolyte.



or



The accumulation of either at the Ca surface would then increase the anode polarization during the progress of discharge. Despite this, it is clear that Ca discharges at acceptable potential and with reasonable capacity. The capacity was less than 50% of the nominal capacity, based on the mass of Ca and a 2-electron oxidation. When a free-standing Ca electrode was discharged at approximately 1 mA/cm<sup>2</sup>, the capacity was 65% of nominal. We believe the relatively inefficient use of the Ca is due to two sources: Firstly, the discharge product buildup discussed above and, secondly, an experimental difficulty. Because of the relatively hard and brittle nature of the Ca, there is some problem in ensuring good electrical contact with the Ni Exmet screen current collector. This can be eliminated by annealing the Ca in vacuo at ~600°C.

Storage of Ca/SOCl<sub>2</sub> cells at 71°C for up to 350 hours does not seriously passivate the Ca anode. Figure 26 shows the initial voltage-time curves of Ca/SOCl<sub>2</sub> cells stored for 351 hours at 71°C. These curves are comparable to those of fresh cells. The capacity of cells stored 135 hours is comparable with the fresh cells. The capacity of cells stored 351 hours is reduced to 56% of a fresh cell, but the mid-discharge voltage is the same as a fresh cell, 2.02 V, at the same current density. It has not been determined whether this is a real loss, due to Ca corrosion, or an apparent loss, due to anode polarization.

## 2. Characterization of Li/Ca Anode Cells

The characterization of the anodes has been to test for voltage delay and for complete discharge behavior of cells prepared with these anodes after 71°C storage. The Ca film is produced by storing the cells in electrolyte saturated with CaCl<sub>2</sub>. The basic procedure is as follows: the assembled, liquid-free T-cells are vacuum impregnated with 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> electrolyte which is presaturated at 71°C with CaCl<sub>2</sub> and LiCl. The estimated maximum solubility of CaCl<sub>2</sub> is ~5 mM.

Attempts were made to prepare Ca-coated anodes from a solution of Ca(SbCl<sub>6</sub>)<sub>2</sub>. This compound is soluble up to at least 1M, but the concentration of free Ca<sup>2+</sup> is apparently small, ~30 mM (32) and the deposit formed is not adherent. Chemical analysis and electrochemical measurements suggest that the deposit is not pure Ca but also contains Sb.

The initial polarization curves shown in Figures 27 and 28 illustrate the superiority of the Li/Ca anodes compared to pure Li anodes. Even the Li/Ca anode cells stored 798 hours at 71°C show no voltage delay. The superiority is further illustrated in Figure 29. This is a comparison of the cell voltage 60 sec after the initiation of discharge as a function of storage

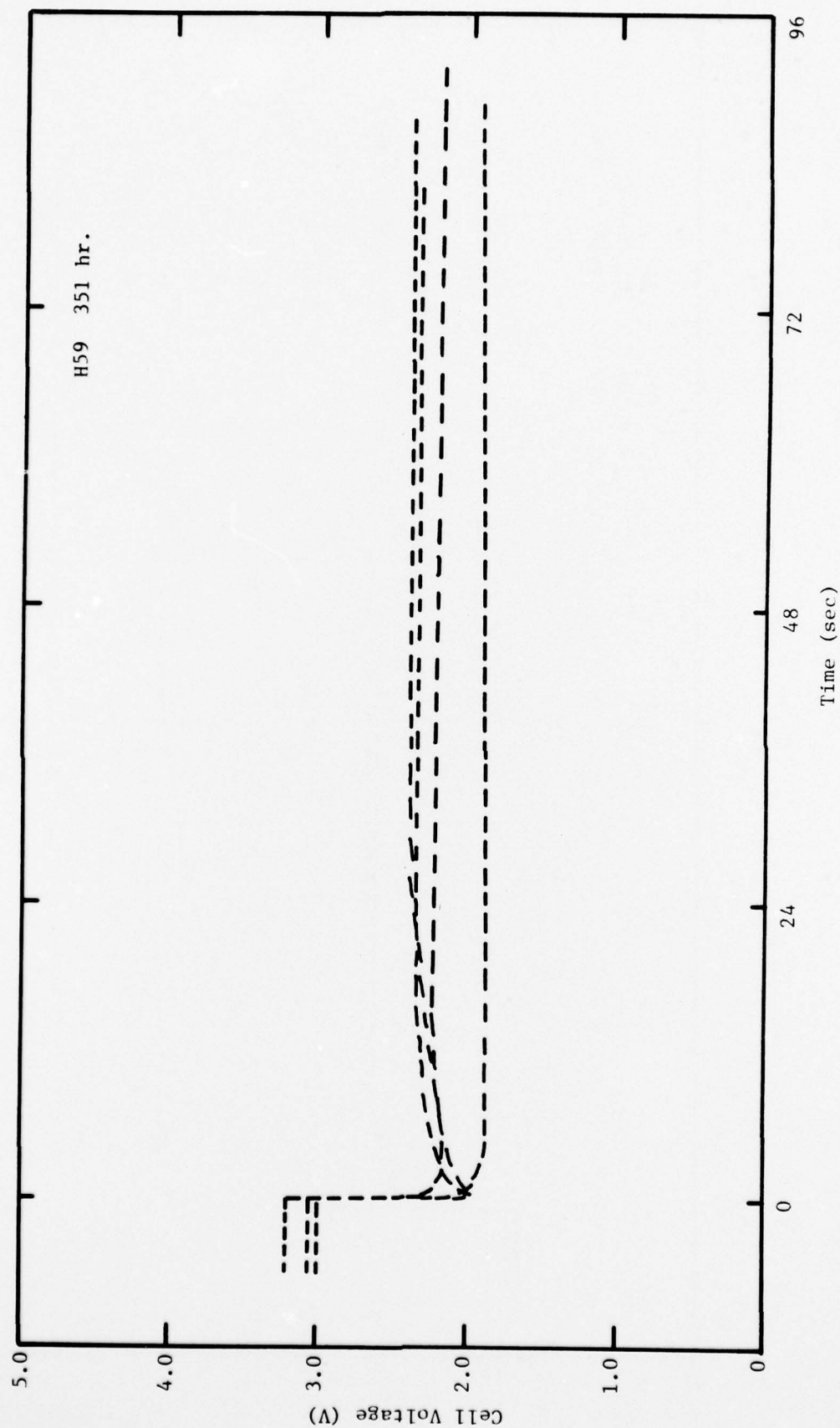


Fig. 26: Initial polarization of Ca/SOCl<sub>2</sub> cells with 480Ω (√1cm<sup>2</sup>). The cells were stored 351 hr at 71°C. The 1.5M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> was not pretreated with Li metal.

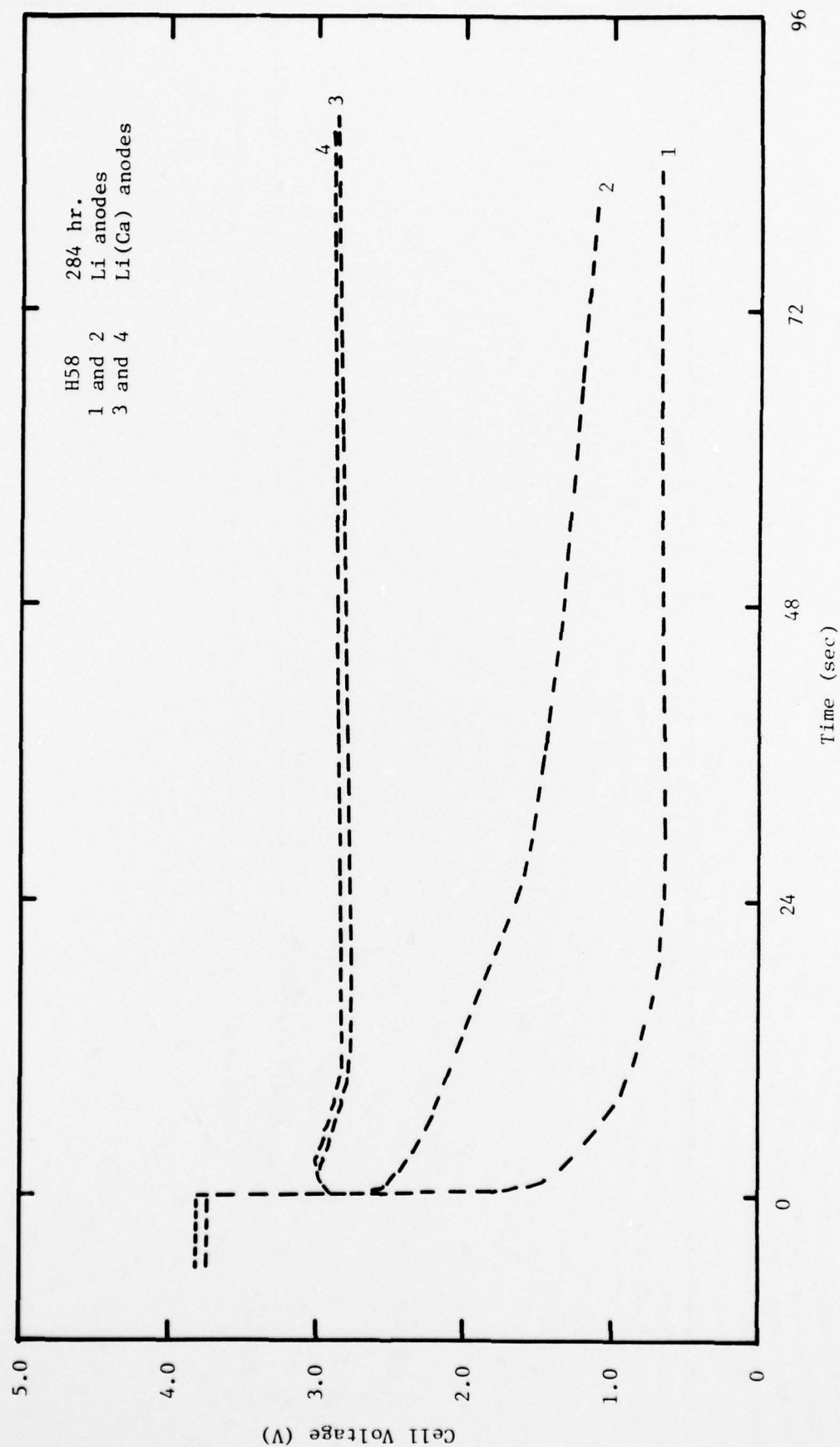


Fig. 27: Initial polarization of Li anode and Ca-coated Li anode,  $\text{SOCl}_2$  cells with  $480\Omega$  ( $1\text{cm}^2$ ).



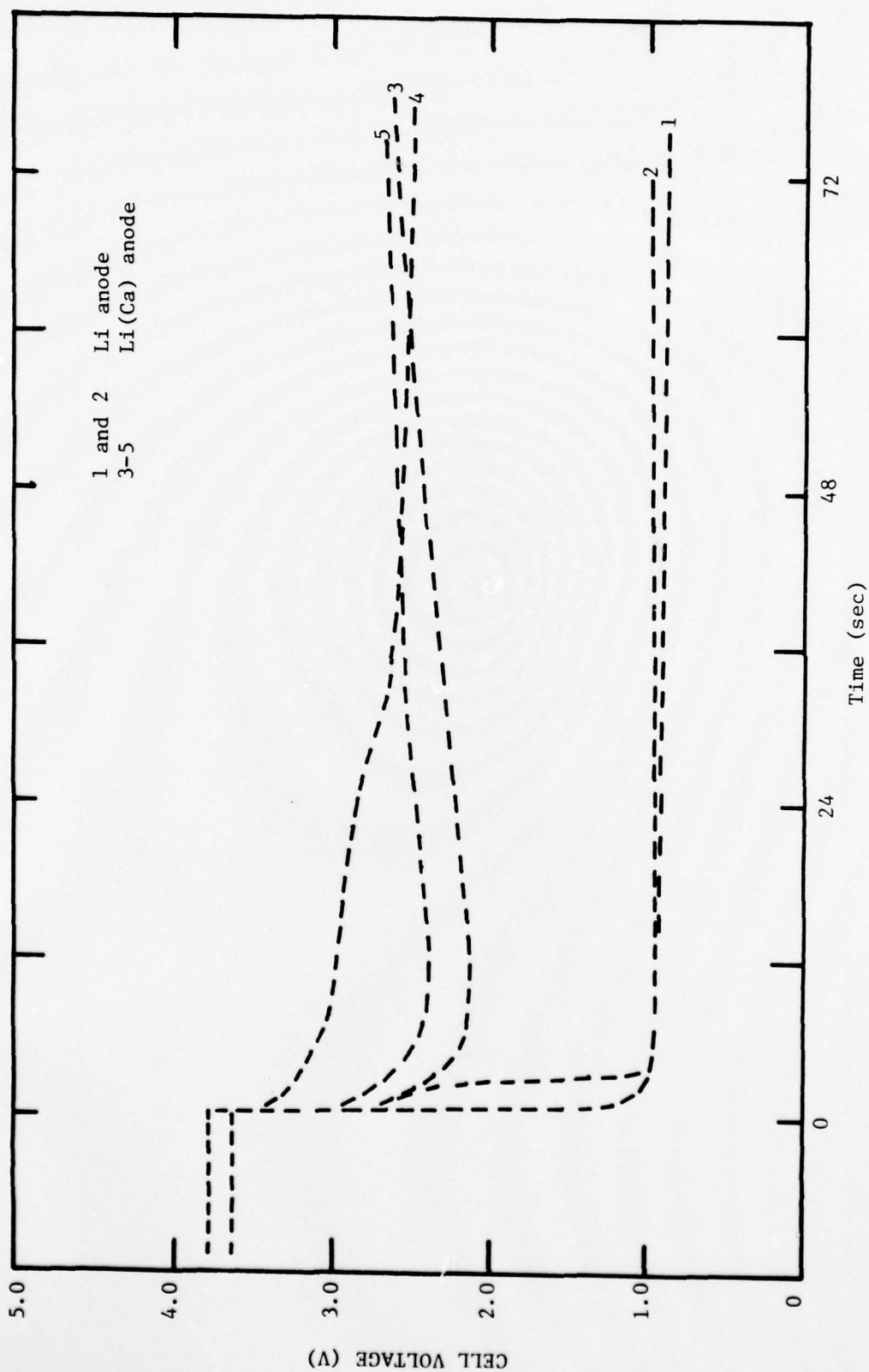


Fig. 28: Initial polarization of Li anode and Ca-coated Li anode,  $\text{SOCl}_2$  cells with  $480\Omega$  ( $1 \text{ cm}^2$ ). They were stored at  $71^\circ\text{C}$  for 798 hr.

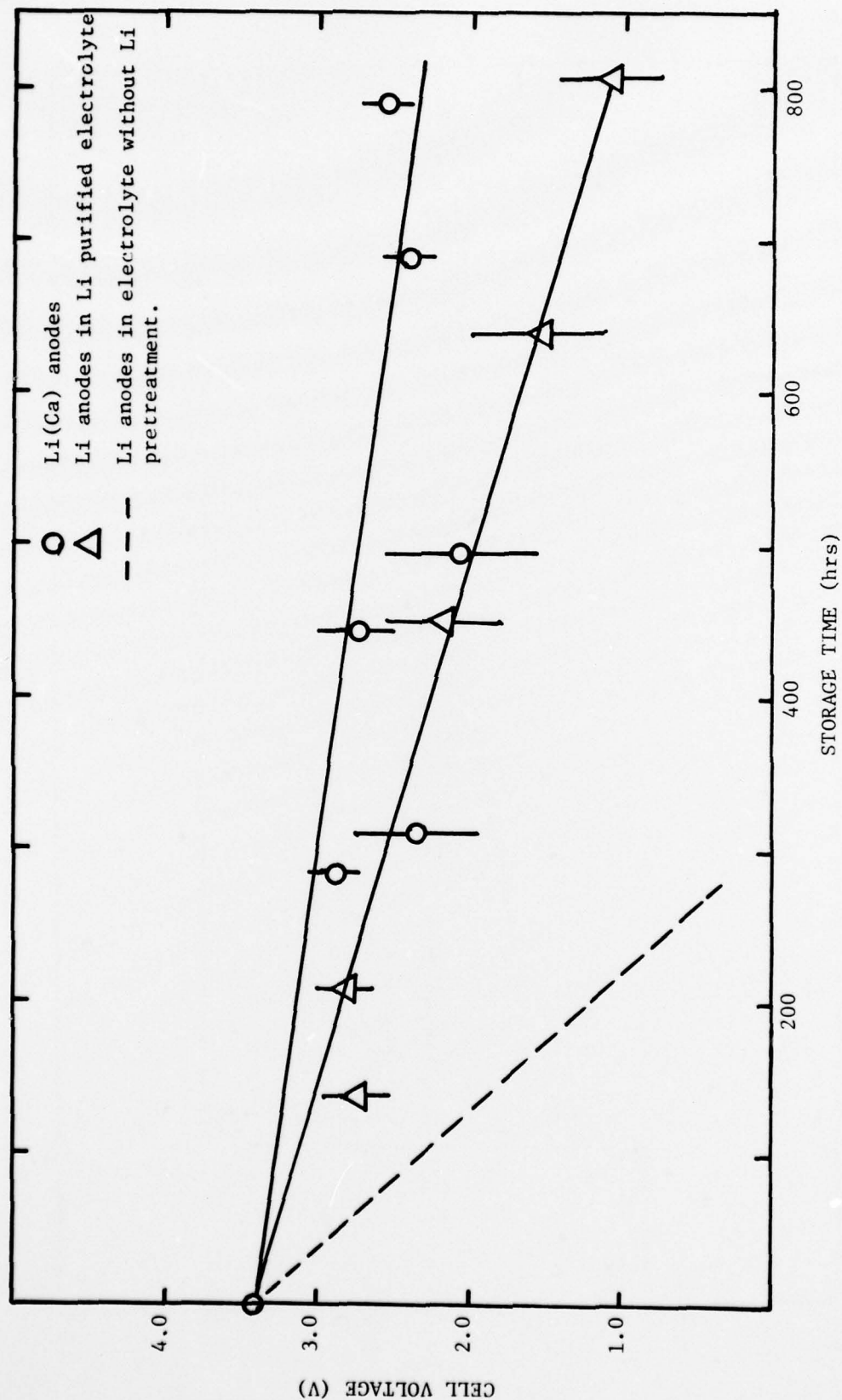


Fig. 29: Average cell voltage at 60 sec after the application of a constant load.  
The load will draw  $\sim 7.0 \text{ mA/cm}^2$  from a fresh cell.

time for Li/Ca anode cells vs. pure Li anode cells. The better of the pure Li anode cells have voltage delays as long as 60 sec after 480 hours, while the Li/Ca anode cells do not, even after 800 hours.

The more significant improvements have been in the complete discharge behavior of these Li(Ca) cells. Despite the fact that the Ca-deposition procedures have not been optimized, we have obtained quite acceptable complete discharges. Figure 30 presents the cell voltage vs. capacity data for three cells discharged through 480 $\Omega$ . The three cells show points of behavior in common. The initial cell voltage under load was between 2.75 and 2.80 V. This dropped very quickly to between 2.3 and 2.6 V. Continued discharge improved the cell voltage, so that it had reached between 2.9 and 3.0 V at 10 mAhr. Two of the cells discharged smoothly to completion at the 2.0 V cutoff, with the majority of the capacity obtained at a plateau at about 3.0 V. The third cell had poorer voltage regulation. After the maximum at about 2.9 V it had a minimum at 2.5 V and another maximum at 2.7 V, before discharging smoothly to the 2.0 V cutoff. Thus, without optimization, we see that cells stored between 300 and 500 hours at 71°C have yielded between 80% and 95% of their nominal capacity at acceptable voltages and currents.

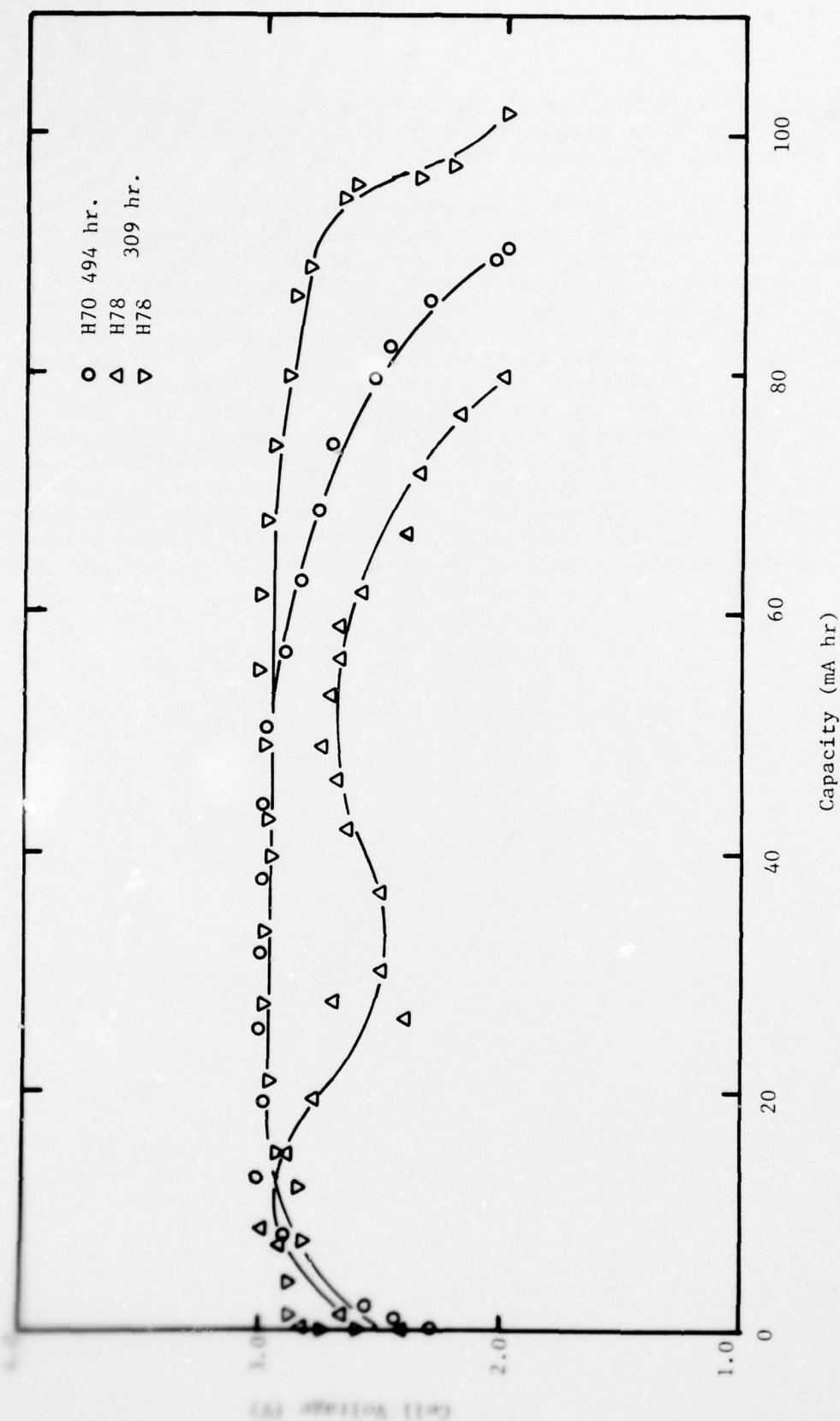
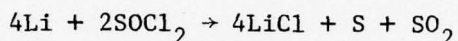


Fig. 30: Capacity of Ca-coated Li anode  $\text{SOCl}_2$  cells discharged through  $480\Omega$  ( $\sqrt{1\text{cm}^2}$ ). The cells were stored for the times indicated at  $71^\circ\text{C}$ .

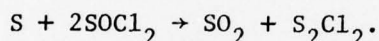


## VII. CONCLUSIONS AND RECOMMENDATIONS

The Li/SOCl<sub>2</sub> cell discharges with the formation of LiCl, S and SO<sub>2</sub>. LiCl is found essentially completely in the cathode. S and SO<sub>2</sub> dissolve in the electrolyte. The nature of the products is described by the equation



Quantitative analysis reveals the amounts of LiCl and S predicted by this equation, but the SO<sub>2</sub> found is twice that predicted. There is no immediate resolution of this discrepancy. Other stoichiometries can be written, but none of them fit all of the known data. A possible source of the excess SO<sub>2</sub> beyond that predicted by the above equation may be due to the reaction of S with unreacted SOCl<sub>2</sub> in the injector of the gas chromatograph according to



Further data are required to resolve this issue.

In the course of this work UV and IR spectrometry were found to be valuable analytical techniques. Further development of both for analysis of the SOCl<sub>2</sub> system is indicated.

In the search for methods of alleviating Li anode passivation during storage at 71°C, two approaches yielded positive results, electrolyte purification and solution additives. The electrolyte as-prepared was found to contain Fe, Cu, HCl and hydroxyaluminum compounds. These were removed by pretreating the electrolyte with Li at 71°C. Li/SOCl<sub>2</sub> cells prepared with this electrolyte have much better resistance to passivation than cells using as-prepared electrolyte. Two solution additives were found to improve Li/SOCl<sub>2</sub> cell performance after 71°C storage. These were PCl<sub>5</sub> and Ca<sup>++</sup>. PCl<sub>5</sub> at 1 wt % in the electrolyte provided substantial improvement in the storage characteristics of Li/SOCl<sub>2</sub> cells. The mechanisms of this improvement is unknown and worthy of further study. Ca<sup>++</sup> when introduced via a sparingly soluble salt, e.g., CaCl<sub>2</sub> improves the Li/SOCl<sub>2</sub> cell's ability to resist passivation during storage. It appears to operate by depositing Ca onto the anode surface either as Ca or a Li/Ca alloy. Separate measurements have shown Ca to be more resistant to passivation than Li and thus this layer acts to keep the anode surface active. Further effort should be applied in optimizing these effects.

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