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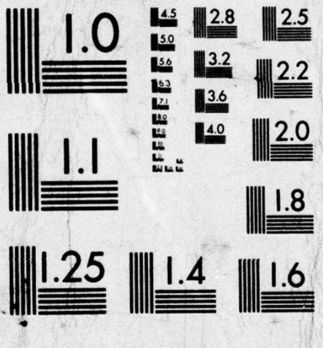

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Research and Development Technical Report

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LITHIUM-INORGANIC ELECTROLYTE BATTERIES

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The major area of investigation during this report period has been the voltage delay and depression in $Li/SOCl_2$ cells after storage at 71°C. These are due to films on the Li anode surface which arise from reaction with the electrolyte. The effects of test-cell design and variation in storage procedures have been assessed. Calcium deposited onto the anode →

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20. Abstract (Cont.)

decreases the voltage delay. The efficiency of Ca deposition onto Li metal was investigated. An infrared spectrophotometric survey of the $LiAlCl_4/SOCl_2$ electrolyte system was initiated.

Our $Li/SOCl_2$ test cell design was reviewed. The cells were modified in three areas. Quartz substituted for Teflon as the cell-body material. A larger anode was used ($4\ cm^2$ vs. $1\ cm^2$) and the Ni Exmet current collector was removed. These changes provided substantial improvement. No voltage delay was observed in 6 cells stored 256 hours. There was still voltage depression.

The question of atmospheric exchange with the storage cells was explored. Argon-filled Al containers were used to store the cells. There was evidence of improvement in the $Li/SOCl_2$ cells with regard to voltage delay up to 300 hours of storage.

A new method of preparing the electrolyte salt was tested. It is synthesized and purified in the metal at 180°C. The purification was done by electrolysis. Storage tests indicate it is approximately equivalent to electrolyte prestored with Li.

Infrared spectrophotometry was used to survey the $LiAlCl_4/SOCl_2$ electrolyte system. Eastman 246 $SOCl_2$ contains <200 ppm HCl and SO_2. After distillation, more SO_2, and SO_2Cl_2, are detected. Water reacts with $SOCl_2$ to produce SO_2 and HCl in direct proportion to the amount added. Solutions of the electrolyte contain HCl, SO_2 and hydroxy aluminum compounds. Storage of the electrolyte with Li removes HCl and hydroxy compounds but introduces low levels of other products. Water reacts with the electrolyte solution to produce SO_2 and HCl, and also hydroxy aluminum components.

END

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I. INTRODUCTION

In recent years there has been considerable research and development on ambient-temperature, high energy density Li cells. A particularly promising system is based on thionyl chloride, $SOCl_2$ (1,2). Here, $SOCl_2$ serves both as solvent and depolarizer for the cell. D cells have delivered 100 Whr/lb and 40 W/lb at the 2.5 hr rate and, as usual, have delivered higher energy densities at lower discharge rates (3).

The purpose of the present program is to study the feasibility of an all-inorganic electrolyte Li primary battery operable and storable over the temperature range of -40°F to +160°F. The desired energy density is 150 watt-hours per pound of total battery weight and the desired power density is 50 watts per pound.

This report contains the results of the thirteenth quarter work on this program. During this quarter the emphasis of the program has been on an investigation of the problem of cell passivation during storage at 71°C (160°F). Our studies (4), and others (3,5), show that the cause of the Li passivation is the formation of a nonconductive film on the Li anode during storage, especially at elevated temperatures. Our research efforts have been directed at studying film formation, and modifying the film to improve cell performance. As a result of our investigation at least two promising leads have been developed for the alleviation of the passivation problem.

A remarkable improvement was obtained with cell preparation techniques designed to eliminate Li-reactive impurities (6). $Li/SOCl_2$ cells were prepared in a very clean argon atmosphere with electrolyte, separators and in some cases cathodes which had been previously stored with Li at 71°C in $SOCl_2$. The improvement with regard to voltage delay was substantial in comparison to cells prepared without these procedures. Cells stored up to 200 hours had no voltage delay and only slight voltage depression. Beyond 250 hours storage, however, these cells begin to suffer voltage delays. During this quarter we have continued to explore the mechanism which cause this degradation in performance. Electrolyte prepared and purified by a new method has been tested. A new test cell design has been used and new storage procedures have been implemented.

The second promising method of eliminating voltage delay has utilized Ca as an alloying element at the Li anode surface (7). Calcium is added to the system by saturating the electrolyte with $CaCl_2$. The cells are stored with this electrolyte. Under these conditions, Ca most likely deposits onto the Li surface by exchange, since the Ca open circuit potential vs. Li^+/Li in this solution is +0.8V. During the present quarter we have explored methods of producing a more defined surface state by deposition from Ca^{+2} solutions.

In order to explore the $SOCl_2$ electrolyte system more completely with regard to purity and reaction products, a survey by infrared spectrophotometry was initiated. The effects of water and Li prestorage have been studied.

II. ELECTROCHEMICAL EFFECTS OF SYSTEM PURITY

In seeking to alleviate the voltage delay in Li/$SOCl_2$ cells after storage at 71°C, we have established procedures designed to reduce or remove the effects of Li reactive species before cell assembly. The effect of such species has been clearly demonstrated by Marincic and Lombardi (8). Their work showed that 200 ppm of Fe in the $SOCl_2$ electrolyte will severely passivate the Li anode within 24 hours, even at room temperature. Clearly, Fe need not be the only species of concern. In order to increase the system purity, cells have been assembled in a very clean argon atmosphere, electrolyte has been prestored with Li at 71°C, and separators and, in some cases cathodes, have been prestored with Li in $SOCl_2$ at 71°C. The effect of these has been to substantially improve cell performance (i.e., eliminate voltage delay) up to 200 hours. Beyond about 250 hours, however, cell performance degrades sharply.

Some data developed during the last quarter suggested that the degradation at ∿250 hours may not be intrinsic to the cell but rather relate to artifacts of the test procedure. For example, tests indicated that the containers used to hold the actual Li/$SOCl_2$ cells during storage have measurable exchange with the atmosphere at about 300 hours. These results have prompted a revision in the cell design and storage procedures. These are discussed below. A new method of preparing and purifying the electrolyte salt has also been tested.

A. Cell Design and Storage Revisions

Concern over exchange between the atmosphere and the storage cell during long term storage tests has prompted a change in the storage procedures. At the same time, Li/$SOCl_2$ cell design was reviewed. Based on this, modifications were made to enhance chemical inertness and stability during long term tests.

The original Li/$SOCl_2$ design, the so-called T-cell, is described in detail in the ninth quarterly report. Briefly it comprises two Teflon discs which sandwich the electrode package. The electrode package consisted of a flat Li anode and carbon black cathode with a glass fiber separator. Two additional glass fiber separators are used at the external faces of the anode and cathode to prevent contact with the Teflon and to act as electrolyte reservoirs. The Teflon discs were compressed onto the electrode package by threaded Teflon rods and nuts. The anodes were 1 cm^2 (one side), formed by pressing 15 mil Li foil onto both sides of a Ni Exmet grid to which a Ni lead wire was welded.

The revised cell design incorporates three major changes: Quartz plates (0.125" thick) are substituted for the Teflon discs; the area of the anode has been increased from 1 cm^2 to 4 cm^2 (one side) and the Ni Exmet grid and lead wires have been eliminated. The 15 mil Li foil anode is cut with a tab to provide the electrical connection.

The quartz plates are more attractive as cell materials because of the reduced probability of contamination. It was thought that the more porous Teflon material may possibly contain leachable substances which are residual from its manufacture or cleaning. As a test of this possibility, several of the Teflon discs used for the T-cells were stored with electrolyte at 71°C. The solution darkened to a brown color within 3 hours of reaching temperature. Gas chromatographic analysis showed no new major components, but the SO_2 content did increase by at least a factor of 2. These are initial results and more extensive analysis is currently underway. Whether the darkening is indicative of the presence of substances harmful or beneficial to Li anode storage properties is unknown. Nonetheless, they represent a random factor in the tests which is best eliminated at present and left for future evaluation.

The possible effects of the increased anode size, and elimination of the Ni grid are discussed below.

The groups of the individual $Li/SOCl_2$ cells are normally placed in Teflon O-ring-sealed glass containers for storage. These glass containers are fabricated from commercial O-ring joints (Ace Glass Co.) and clamped shut with Al rings. In order to substantially reduce any exchange between the interior of these cells and the atmosphere, they are now placed in sealed containers fabricated from Al. These containers were formed from Al tubing. One end was sealed by welding onto a plate. The container is sealed for storage with an O-ring seal, using another plate. The cover plate has a pressure gauge for monitoring the system integrity. When sealed, empty cells are heated at 71°C, the indicated pressures are 2-2.5 psig. This corresponds to the value anticipated based on the ideal gas law ($\sim$2.3 psig). The variation is probably due to imprecision in the gauges (0-30 psig) at their low pressure end. These containers have shown no pressure loss after 3 weeks at 71°C.

B. Double Sealed vs. Single Sealed H-Cells

The importance of possible atmospheric exchange in the degradation of cell performance has been assessed by comparison of the voltage delay between T-cells stored in the normal H-cell and T-cells stored in the H-cells inside the Al containers. Two of the double sealed assemblies were prepared. One contained 4 T-cells, the other 6 T-cells. They were prepared under the highest purity conditions. Once the T-cells were prepared and placed in the H-cell, and the H-cell sealed and placed in the Al container, the Al cell was flushed with dry argon and sealed. The sealed combination was then placed in the 71°C oven for storage. This combination cell is designated an HAL cell.

The two HAL cells were stored 288 hours (HAL 1) and 360 hours (HAL 2). The individual T-cells were tested for voltage delay at room temperature. The tests were, as before, constant load with the cell voltage and Li anode potential vs. a Li reference electrode monitored on a rapid time base.

The results are shown in Figures 1 and 2. The resistive load chosen draws ∿6 mA/cm^2 from a fresh cell, which corresponds to the ∿3A rate from a practical D-cell with a 400 cm^2 electrode area. All nine of the T-cells tested had severe voltage delays. One of the T-cells in HAL 1 had shorted. The behavior of the T-cells was consistent within the individual HAL cell. The observed behavior is similar to that of T-cells stored similar times in only the H-cells. This suggests that for the T-cells, at least, atmosphere contamination is not the major source of the voltage delay problem at the 250-350 hour mark.

C. Quartz Plate vs. Teflon Disc Cells

Initial testing of the quartz plate $Li/SOCl_2$ test cells has shown them to be superior to the Teflon disc cells (T-cells) with regard to voltage delay characteristics after 71°C storage. The quartz plate cells were assembled and described above. They were stored at 71°C in the HAL cell configuration. Three HAL cells (HAL 3, 4 and 5) were assembled, each containing 6 $Li/SOCl_2$ quartz-plate cells. HAL 3 was designed to assess the differences between the quartz plate cell and the T-cell. HAL 4 was designed to assess the effect of briefly anodizing the Li anode before storage. A 2 sec current pulse of $1A/cm^2$ (4A) was used. The third HAL cell (HAL) contained quartz plate cells with electrolyte prepared from $LiAlCl_4$ synthesized and purified by a new method (9).

For this purpose, the $LiAlCl_4$ was synthesized as the melt and purified by electrolysis: 1.5 mol of LiCl (Fisher L-121) and 1.5 mol $AlCl_3$ (Fluka, puriss) were melted together in a Pyrex container. The temperature was maintained at 180 ± 5°C. The product was dark brown. The melt was purified by anodizing a piece of pure Al (Ventron m5N ingot) against an Al wire cathode. The anodization was continued for 2 weeks at 4.4 mA/cm^2 (40 mA). There was gassing at both electrodes when they were initially inserted into the melt. When the current was applied, gassing was observed only at the cathode. The gassing is due to hydrogen ion reduction. The gassing ceased after 3-3.5 hours. At the end of the electrolysis, the melt was water-white. The cooled melt was powdered with a mortar and pestle. The 1.5M $LiAlCl_4/SOCl_2$ electrolyte was prepared by dissolving the salt in $SOCl_2$ kept at -10 to -20°C. An empirical test of purity suggests that this electrolyte is a significant

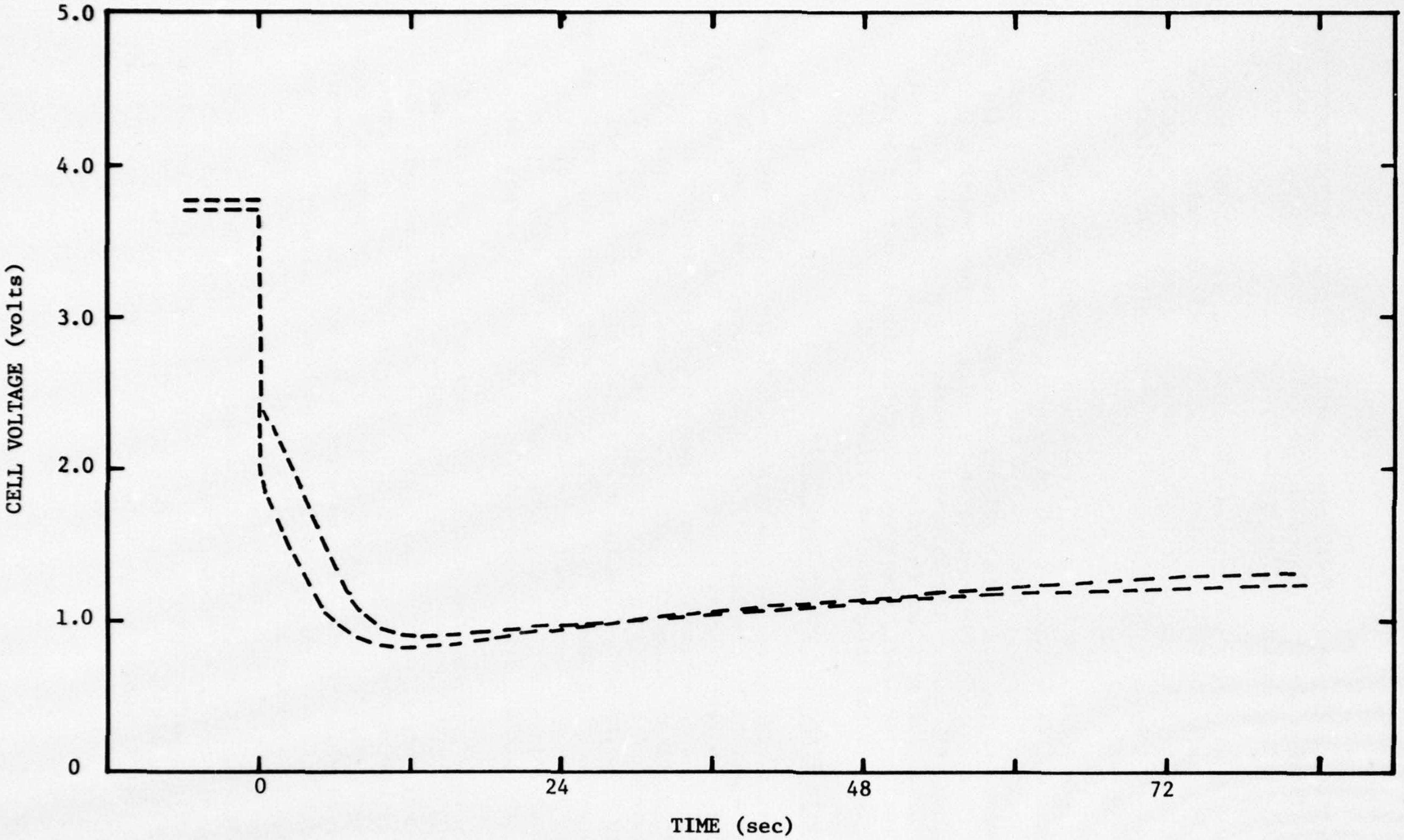

Fig. 1: Initial polarization of $Li/SOCl_2$ cells with 480Ω (∿1 cm^2). These were stored 288 hr at 71°C in the HAL cell configuration.

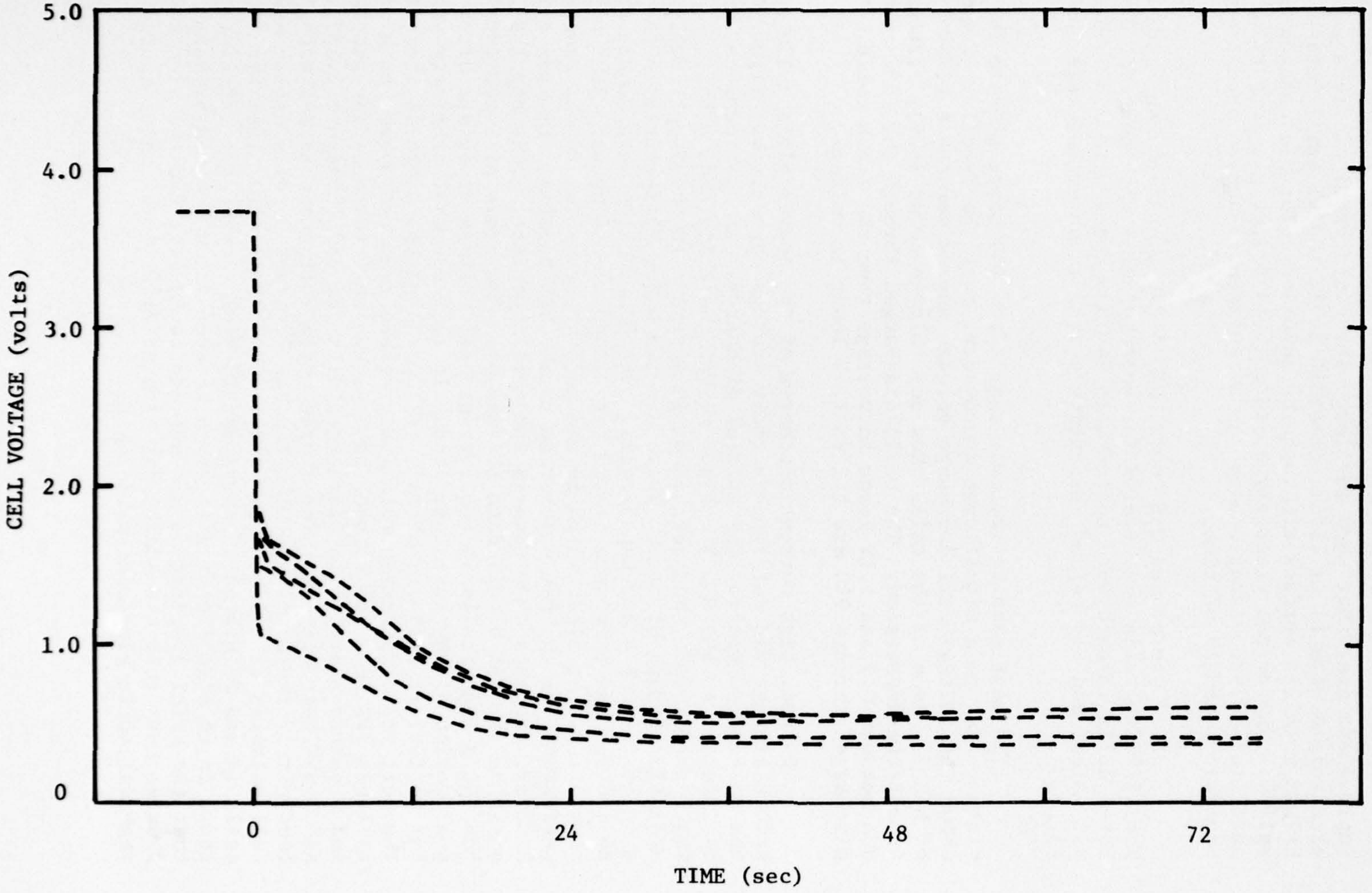

Fig. 2: Initial polarization of Li/SOCl$_2$ cells with 480Ω (∿1 cm^2). These were stored 360 hr in the HAL configuration.

improvement over that used earlier. The test comprised storage of the electrolyte with Li at 71°C. After 10 days, the Li still retained its bright metallic surface although the solution color had changed to bright yellow. The normal electrolyte stored this way, e.g., as part of its purification procedure, causes the Li surface to darken when stored an equivalent length of time.

HAL 3 was stored 256 hours, HAL 4 278 hours and HAL 5 281 hours. The $Li/SOCl_2$ cells were tested for voltage delay with constant load. Three cells in each were tested with 94Ω and three with 153Ω. These draw 9.0 mA/cm^2 and 5.6 mA/cm^2 respectively from fresh cells, as shown in Figure 3.

The test results indicate that after 250 hours storage the quartz plate cells are a significant improvement over the T-cells. Figure 4 shows the initial cell discharge voltage curves for the 6 $Li/SOCl_2$ cells of HAL 3. None of the cells show any voltage delay (<2V), although there is voltage depression. The cells discharged through the 153Ω resistor are between 0.7 and 1.1V lower in voltage than the fresh cells. The cells discharged through 94Ω are 1.2 to 1.4V lower in voltage.

Pulsed, high current discharge of the quartz plate cells of HAL 4 before storage did not improve their storage capability. Figure 5 shows the voltage curves for the initial discharge. The performance, in fact, is inferior to the HAL 3 cells. All of the cells show a voltage delay. Their performance, however, is still superior to the T-cell design stored a similar length of time. There are two major differences in the preparation of the HAL 4 and HAL 3 cells. The HAL 4 cells were anodized prior to storage and they were stored for 22 additional hours. At the present time, it is not clear which is the major contributor to the poorer performance of the HAL 4 relative to the HAL 3 cells. Limited evidence, however, suggests that time is the more important. This conclusion is based on the HAL 5 cell data (Figure 6). The basis of comparison with the HAL 3 and 4 cells is the average cell voltage at 60 sec after the application of the resistive load. It is a somewhat arbitrary choice, but we feel it reflects overall cell performance, since in these tests, the cell voltages remain relatively stable from the 30 sec mark out to at least 120 sec. At 60 sec, the average cell voltages for the HAL 3, 4 and 5 quartz plate cells discharged with the 153Ω load are 2.53V, 1.87V and 2.04V respectively. The average cell voltages obtained with the 94Ω load mirror these values, with the HAL 3, 4 and 5 cells having average cell voltages of 2.13V, 1.51V and 1.60V. It is clear that the two HAL cells (4 and 5) stored 22 hours and 25 hours longer are inferior. Further, there is no significant difference between the HAL 4 and 5, which suggests that the brief anodization has not adversely affected the electrodes. Thus we feel that the additional time at 71°C is the major source of the degradation in electrode performance.

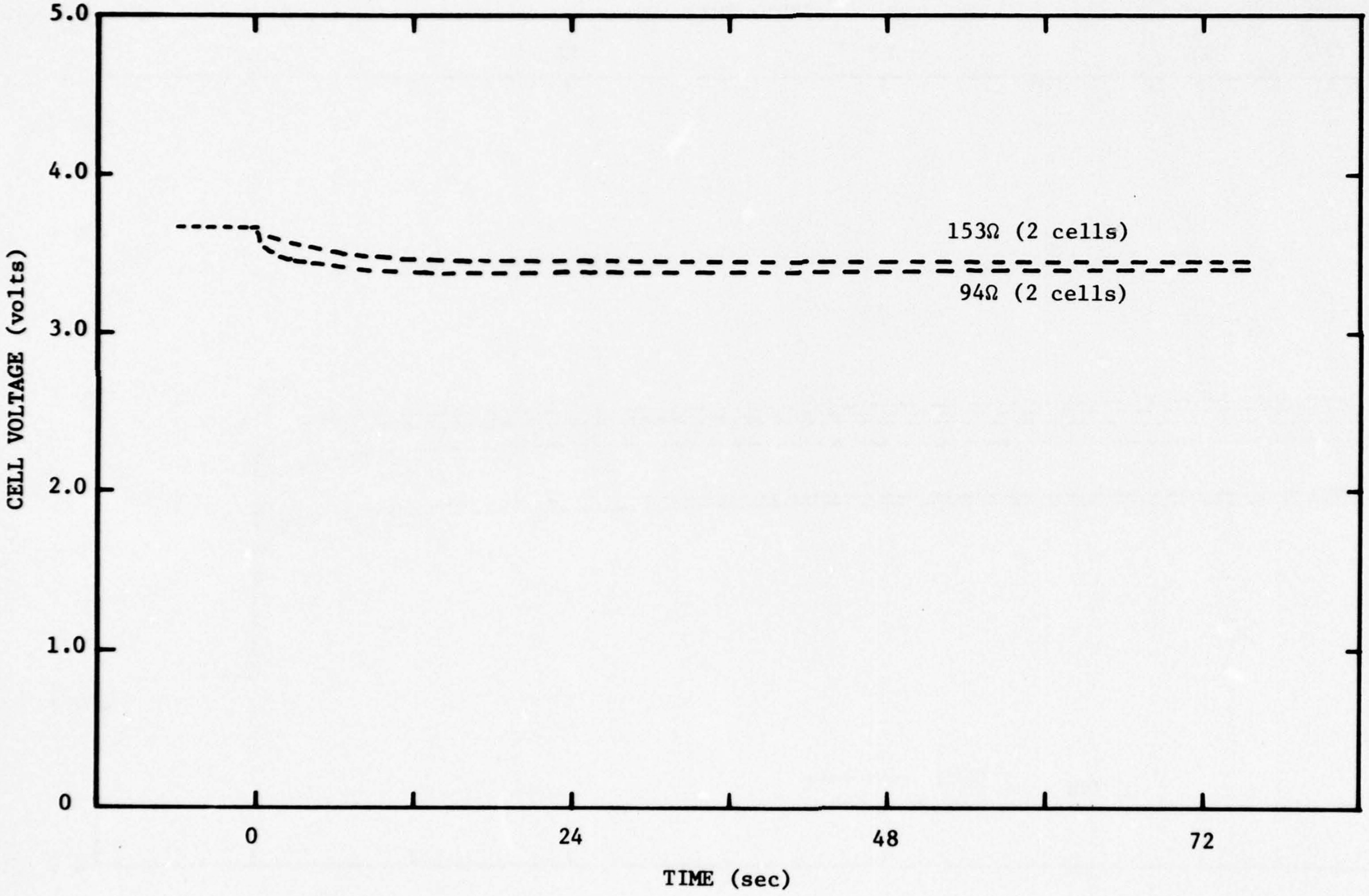

Fig. 3: Initial polarization of fresh Li/$SOCl_2$ cells (4 cm^2 anodes). Quartz plates were substituted for the Teflon discs.

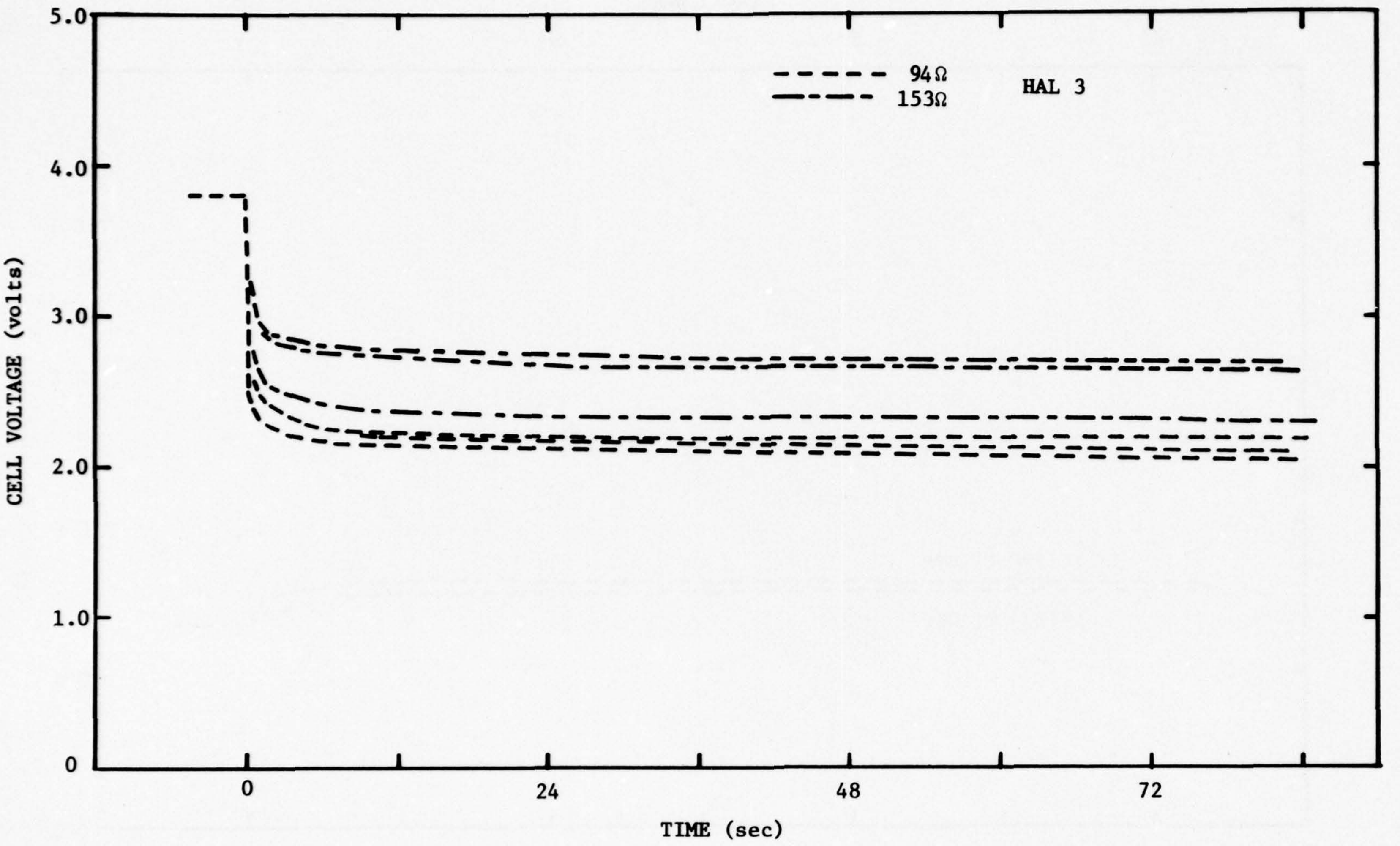

Fig. 4: Initial polarization of Li/$SOCl_2$ cells stored 256 hr at 71°C in the HAL configuration. The anodes were 4 cm^2.

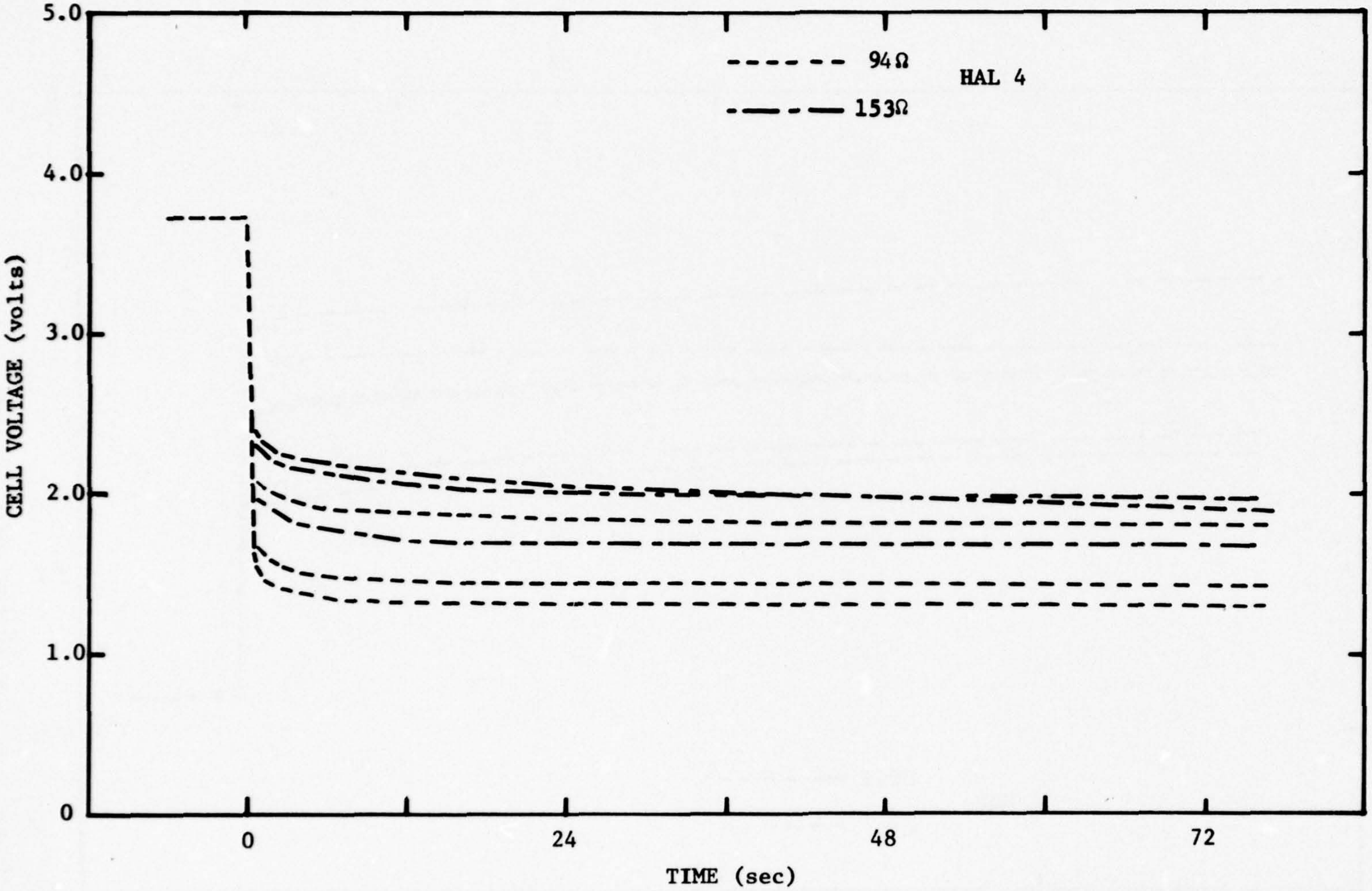

Fig. 5: Initial polarization of Li/$SOCl_2$ cells stored 278 hr at 71°C in the HAL configuration. The anodes were 4 cm^2. The cells were discharged at 1 A/cm^2 for 2 sec prior to storage.

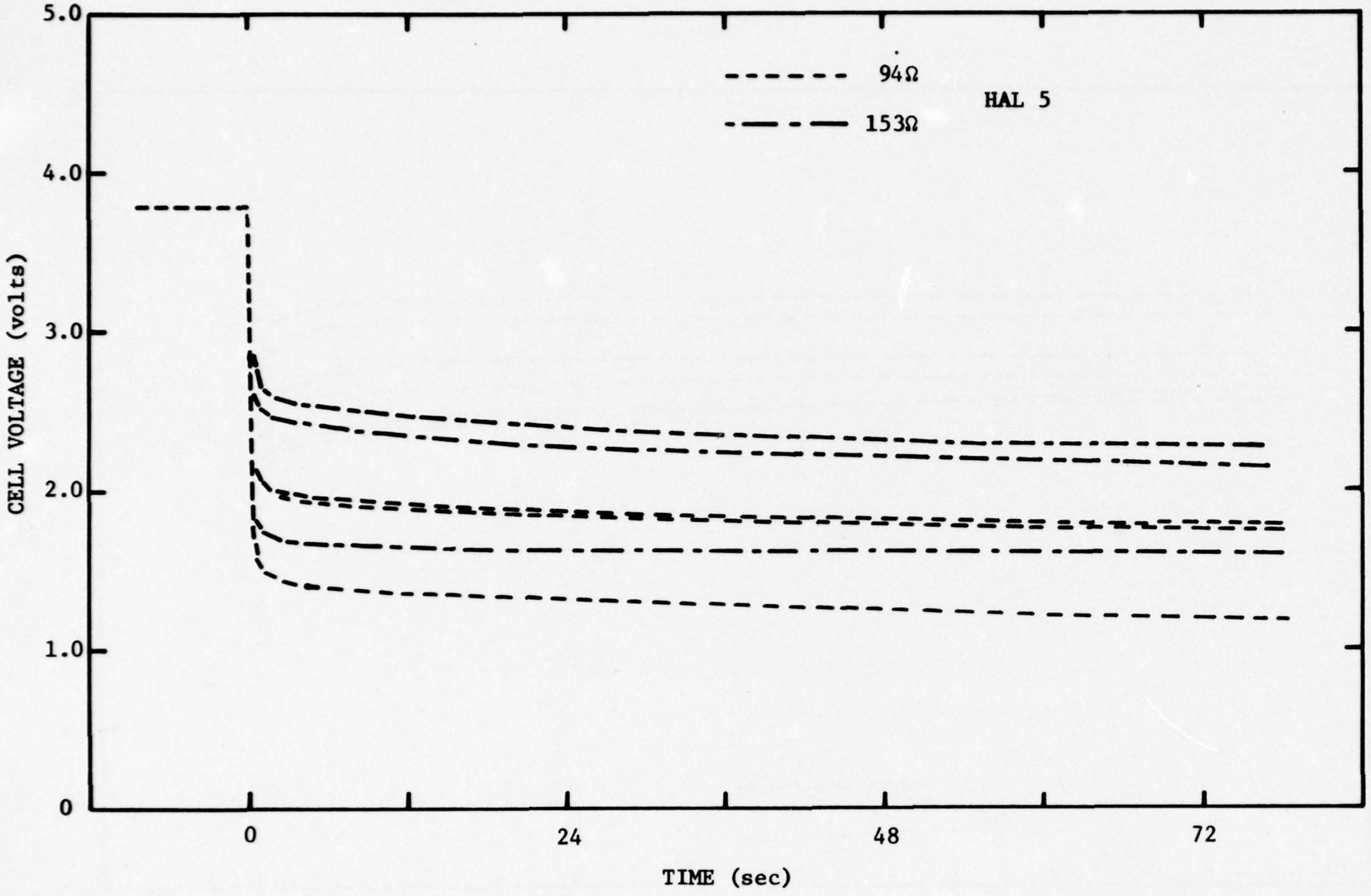

Fig. 6: Initial polarization of $Li/SOCl_2$ cells stored 281 hr at 71°C in the HAL configuration. The anodes were 4 cm^2. The electrolyte salt was prepared and purified as a melt.

There is one caveat to the argument. The HAL 5 cells were prepared with a different electrolyte. This was electrolyte prepared from $LiAlCl_4$ synthesized and purified in the melt. We feel, however, that this electrolyte is not significantly different from the normal electrolyte prestored with Li, since storage tests with Li at 71°C for 10 days have shown no discoloration or corrosion of the Li. This is the same behavior we observe with prestored electrolyte.

The quartz plate cells are better in overall performance than the T-cells. The reason or reasons for the improvement must lie in one or more of the three areas of major difference between the two types of cell. We explained above the anticipated advantages with the substitution of quartz for Teflon. Basically it is a concern that the Teflon may be a source of contaminants.

The use of larger anodes, the second difference, can have two possible advantages. A greater probability of finding areas of faulty film epitaxy. This will be important if after storage the discharge is very localized, as we have observed (10). Another advantage of larger anodes is that they should be much freer from possible edge effects. The third area of change, elimination of the Ni Exmet current collector, may also have two advantages. If the electrolyte penetrates between the grid and the Li, it is possible that an insulating film will build up, causing poor electrical contact between the Ni grid and the Li. It may also be that $SOCl_2$ reduction on the exposed Ni will help depolarize the corrosion of the anode, although it is by no means clear how this would result in a voltage delay.

In summary, atmospheric exchange is not a significant problem in the H-cell storage container up to $\sim$300 hours. Quartz plate $Li/SOCl_2$ test cells perform better than Teflon disc cells (T-cells) after storage at 71°C. This is an important finding, although the specific cause or causes of the improvement have not yet been established. Brief anodization of the Li in the complete cell before storage does not improve its storage capability. A new electrolyte salt preparation and purification procedure have been used. The results suggest it is at least as good as the normal electrolyte.

Further work will concentrate on identifying the source or sources for the improvement on the quartz cells. Experiments will isolate each of the three major areas to determine its contribution to the improvement in performance. In order to establish the effect of the substitution of quartz for Teflon, electrode packages identical to the T-cell design will be assembled and used with the quartz plate design. These will have 1 cm^2 anode area and have Ni Exmet current collectors. In order to investigate the effect of the Ni Exmet, electrode packages of 1 cm^2 without Ni Exmet and 4 cm^2 with Ni Exmet will be tested. The performance of these will be compared to data already available for 1 cm^2 anodes with Exmet and 4 cm^2 anodes without Exmet. In order to assess the effect of anode area on cell performance, a series of cells with increasing anode area will be tested. Two cell designs will be used, multiplate prismatic and spiral wound. These may have anode areas in excess of 120 cm^2.

Once the sources of the improvement are determined, cells will be designed around these to maximize the benefits. We also feel that there is a need for a more time-efficient test procedure for storage cells. We will attempt to establish such a procedure. The fundamental concept is to reduce the amount of storage time by testing a cell under conditions more adverse than would normally be used. For example, cells could be cooled to -30°C for testing and current densities in excess of 7 mA/cm^2 could be used. The ultimate validity of this type of testing must be established, but if it is successful it would substantially increase the data yield.

III. INFRARED SPECTROMETRY

An investigation of $SOCl_2$-based electrolyte systems by infrared spectrophotometry has been initiated. The ultimate aim is to provide a more complete understanding of the chemistry. Particularly important areas to be explored are the electrolyte purity, discharge reaction products and solution decomposition products. We report here on the results of a survey of $SOCl_2$ and 1.5M $LiAlCl_4/SOCl_2$ electrolyte. Part of this initial work is to assess the areas where infrared spectrophotometry will be most valuable.

A. Experimental

All spectra were recorded on a Beckman Acculab 5 dual beam spectrophotometer. The instrument covers the range from 4000 cm^{-1} to 375 cm^{-1}. Several commercial cells were tested. All of the spectra reported here were obtained with Beckman TAC cells. These have 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.

B. Results

- $SOCl_2$

The spectrum of undistilled Eastman 246 $SOCl_2$ is shown in Figure 7. The major feature is a strong absorption at 1225 cm^{-1}, with a weaker band at 2420 cm^{-1}. There are still weaker bands at 920 cm^{-1} and 765 cm^{-1}. This spectrum agrees substantially with published spectra for $SOCl_2$ (11,12). The Aldrich Library spectrum (11) shows only the 1225 cm^{-1} band. Since that spectrum is of the pure liquid, and the 1225 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 (12) are more complete. The main band at 1225 cm^{-1} is assigned to the S-O stretching. The band at 2420 cm^{-1} is the first overtone. The weaker bands below 1000 cm^{-1} are summation bands of the lower energy S-Cl stretch, molecular deformation and torsion.

The spectrum of distilled $SOCl_2$ shows two additional bands, at 1340 and 1410 cm^{-1}. Eastman 246 $SOCl_2$ was distilled at atmospheric pressure under argon from Li chips. The middle fraction, boiling between 75.5-77°C (uncorr.), was used. The 1340 cm^{-1} band is most probably due to SO_2 (12,13). This band was reported by Martz and Lagemann and, as reported below, the band appears with a reaction product of H_2O and $SOCl_2$. We have obtained the spectra of SO_2Cl_2, which agrees substantially with published spectra. SO_2Cl_2 has two prominent bands at 1410 cm^{-1} and

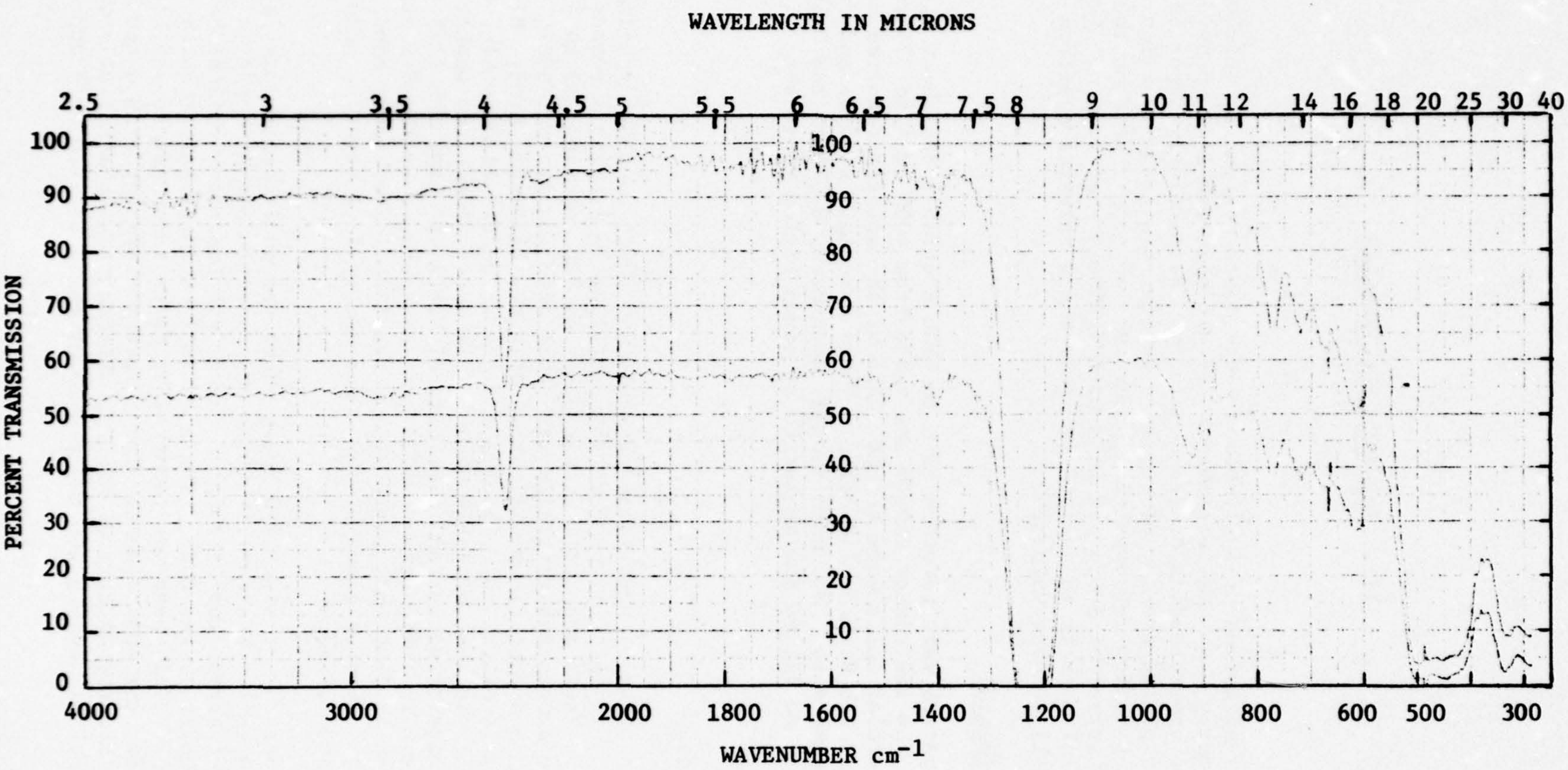

Fig. 7: Infrared spectrum of Eastman 246 undistilled $SOCl_2$. Pathlength 0.10 mm, AgCl windows.

1200 cm^{-1}, assigned to the asymmetric and symmetric S-O stretching (12). The 1200 cm^{-1} band would be obscured by the 1225 cm^{-1} band of $SOCl_2$. These results indicate that distillation of $SOCl_2$ under the conditions specified above introduces some decomposition products.

- $SOCl_2$ with added S, HCl and H_2O

Solutions of S, HCl and H_2O in $SOCl_2$ were studied in order to establish the nature of 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 $SOCl_2$. The S dissolved slowly at room temperature, requiring three days to dissolve completely. The solution was bright yellow. The IR spectrum was identical to $SOCl_2$. The presence of S causes no detectable decomposition of $SOCl_2$.

A solution of HCl-saturated $SOCl_2$ was prepared with anhydrous HCl gas and undistilled $SOCl_2$. 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 cm^{-1}, which is most probably the HCl stretching frequency (14).

The effect of H_2O on the IR spectra of $SOCl_2$ has been reported by French et al. (15). They report that the addition of H_2O produces a band at 2800 cm^{-1}, which is ascribed to hydrogen band H-O stretching in 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 cm^{-1} and it also causes a peak at 1340 cm^{-1}. The absorbance of both increases with increasing water addition. The increase is linear for the 2780 cm^{-1} band and apparently linear for the 1340 cm^{-1} band (Figure 8). We believe the bands are due to HCl (2780 cm^{-1}) and SO_2 (1340 cm^{-1}) resulting from the reaction

$$H_2O + SOCl_2 \rightarrow 2HCl + SO_2.$$

The 2780 cm^{-1} band resulting from the addition of water is identical to the band we observe for HCl-saturated $SOCl_2$. The presence of SO_2 after H_2O addition suggests that the HOSOCl species postulated by French et al. cannot be present in high concentrations, if it exists at all. When they added $AlCl_3$ to the solution of H_2O in $SOCl_2$, the 2780 cm^{-1} band began to disappear, which they attributed to the reaction

$$HOSOCl + AlCl_3 \rightarrow HOAlCl_2 + SOCl_2.$$

We feel that the disappearance of the 2780 cm^{-1} band is due to the reaction of HCl with $AlCl_3$ according to

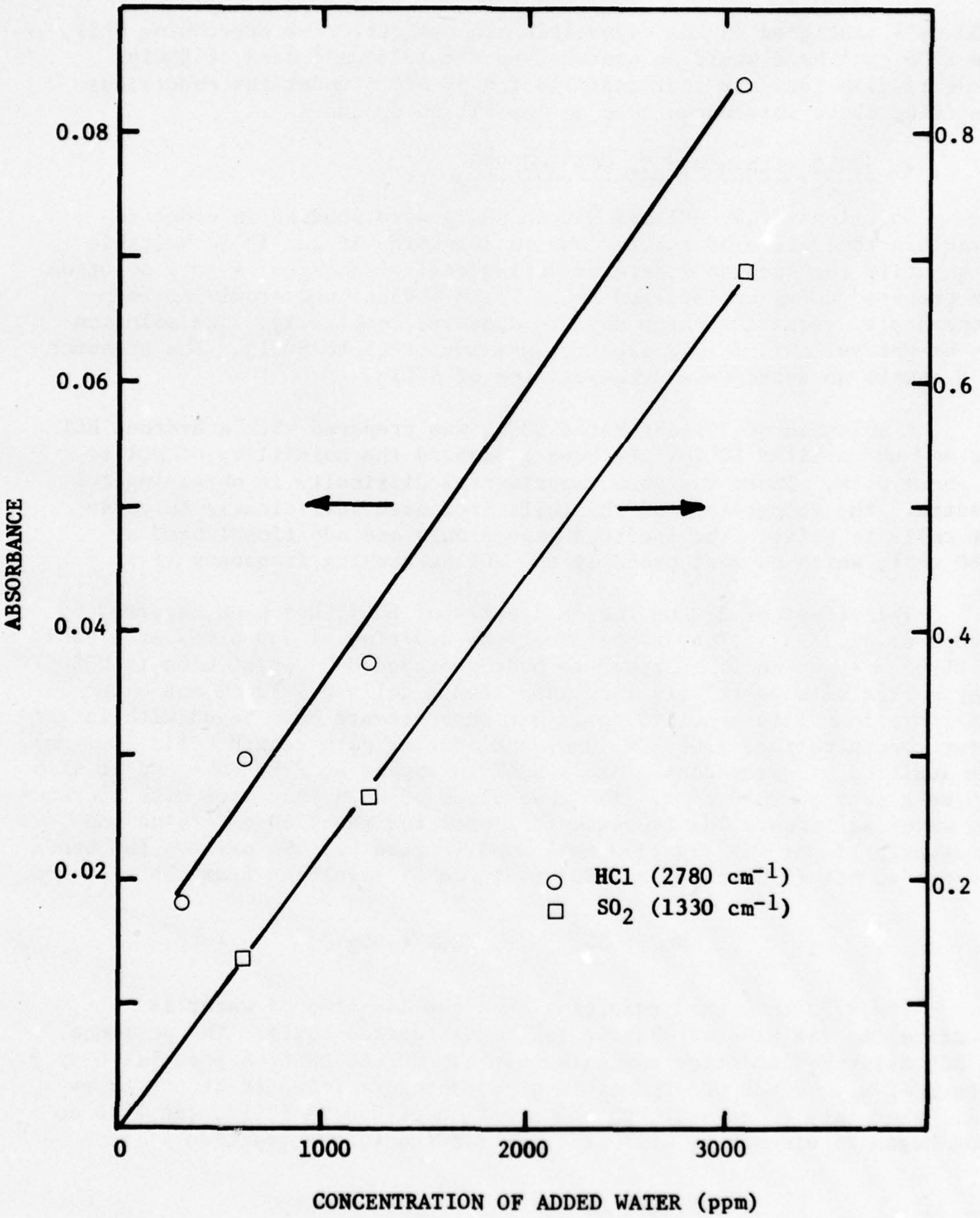

Fig. 8: Absorbance of the SO_2 and HCl infrared bands as a function of added water in $SOCl_2$ at 25°C. AgCl window cells, 0.10 mm pathlength were used.

$$HCl + AlCl_3 \rightarrow H^+ + AlCl_4^-.$$

This reaction seems probable, due to the high stability of $AlCl_4^-$ in $SOCl_2$. For example, $AlCl_3$ will dissolve LiCl in $SOCl_2$. Lithium chloride has a heat of formation of 97 kcal/mol but HCl has a heat of formation of only 22 kcal/mol. Thus it seems unlikely that HCl would be stable in the presence of $AlCl_3$. Further measurements are underway to resolve this question.

- 1.5M $LiAlCl_4$, $SOCl_2$

The spectrum of freshly prepared 1.5M $LiAlCl_4$, $SOCl_2$ is shown in Figure 9. The electrolyte was prepared from undistilled Eastman 246 $SOCl_2$ and $LiAlCl_4$ prepared and purified in the melt, as described above. Spectra of electrolyte prepared by dissolving LiCl in a solution of $AlCl_3/SOCl_2$ have the same features.

Comparison of this spectrum with that of $SOCl_2$ reveals three major changes. There is a broad band of centered at 3350 cm^{-1}; there is a shoulder on the lower wave number side of the $SOCl_2$ overtone band centered at about 2350 cm^{-1}; there is a new band at 1330 cm^{-1}. There is also a slight indication of HCl at 2780 cm^{-1}. The 1330 cm^{-1} band is due to SO_2 which, along with the HCl, probably results from the reaction with H_2O contained in the salt. The SO_2 concentration is about 0.07M, as estimated from Figure 8. The band at 3350 cm^{-1} is probably due to H-O stretching on aluminum hydroxy compounds (15,16).

These species are relatively stable in $SOCl_2$. In tests with electrolyte to which water was added, the intensity of this band remained unaltered after 7 days at room temperature. It is quite clear that added H_2O reacts preferentially with the $AlCl_4^-$ rather than with $SOCl_2$ because a precipitate formed which did not redissolve even after 7 days.

Storage of the electrolyte at 71°C with Li causes the 3350 cm^{-1} band to disappear. This indicates that these hydroxy compounds will react with Li. The HCl band at 2780 cm^{-1} is also removed, but the SO_2 band at 1330 cm^{-1} increases. Quantitative measurements are presently underway. The stored electrolyte shows a weak band at 1070 cm^{-1}, not evident in $SOCl_2$ or unstored electrolyte. This band has not yet been identified. It is not SCl_2 whose spectrum is featureless above 600 cm^{-1}. The S-Cl stretching bands overlap with the S-Cl bands of $SOCl_2$. No other changes in spectrum are evident.

Figure 10 shows the spectrum of electrolyte stored with Teflon. This electrolyte had previously been stored with Li to remove the hydroxy and HCl components. Several features have been introduced by the Teflon. The HCl band at 2780 cm^{-1}, a shoulder on the SO_2 peak at 1330 cm^{-1}, an absorbance at 1110 cm^{-1} and a shoulder at 1075 cm^{-1}. These have not yet

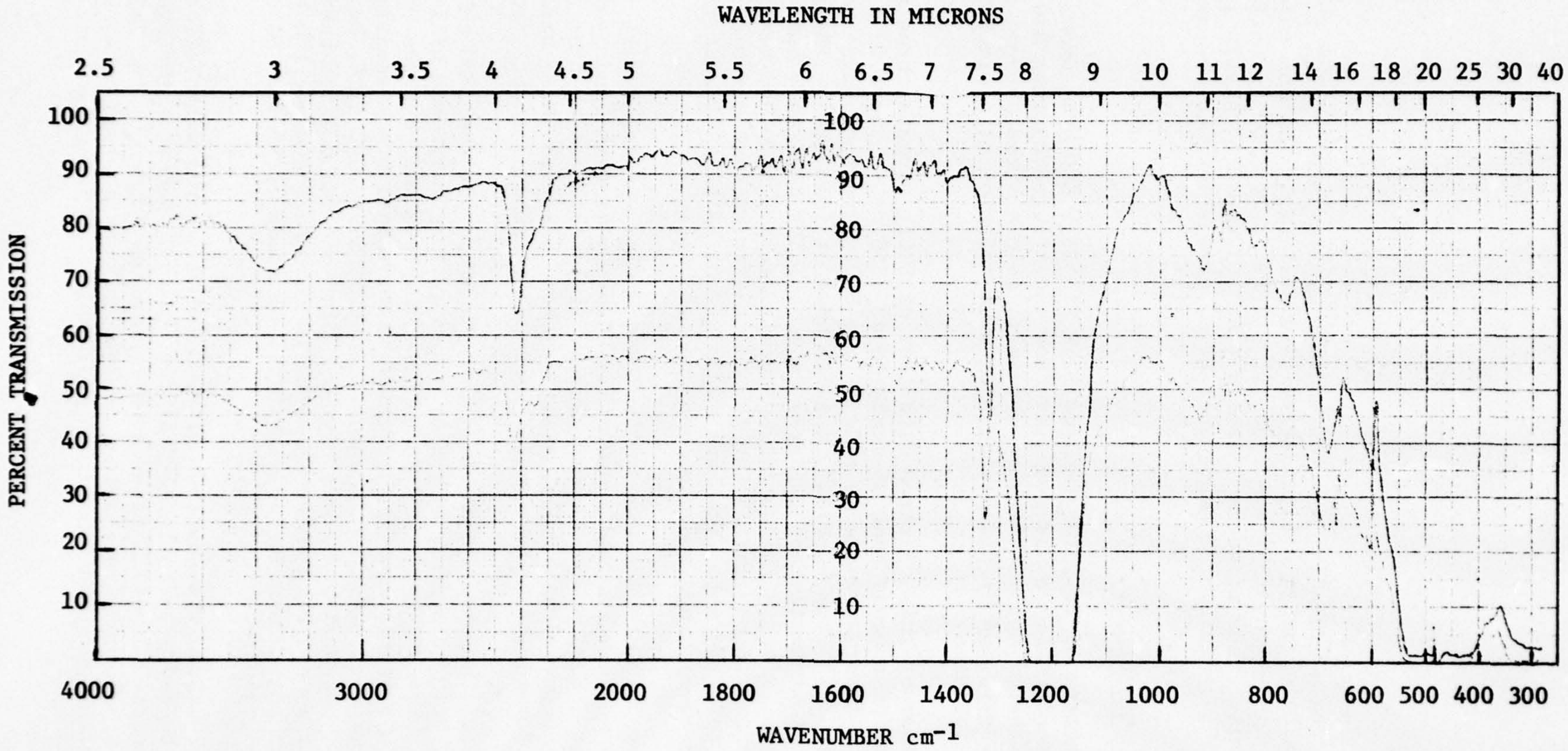

Fig. 9: Infrared spectrum of freshly prepared 1.5M $LiAlCl_4/SOCl_2$ electrolyte before storage with Li. Pathlength 0.10 mm, AgCl windows.

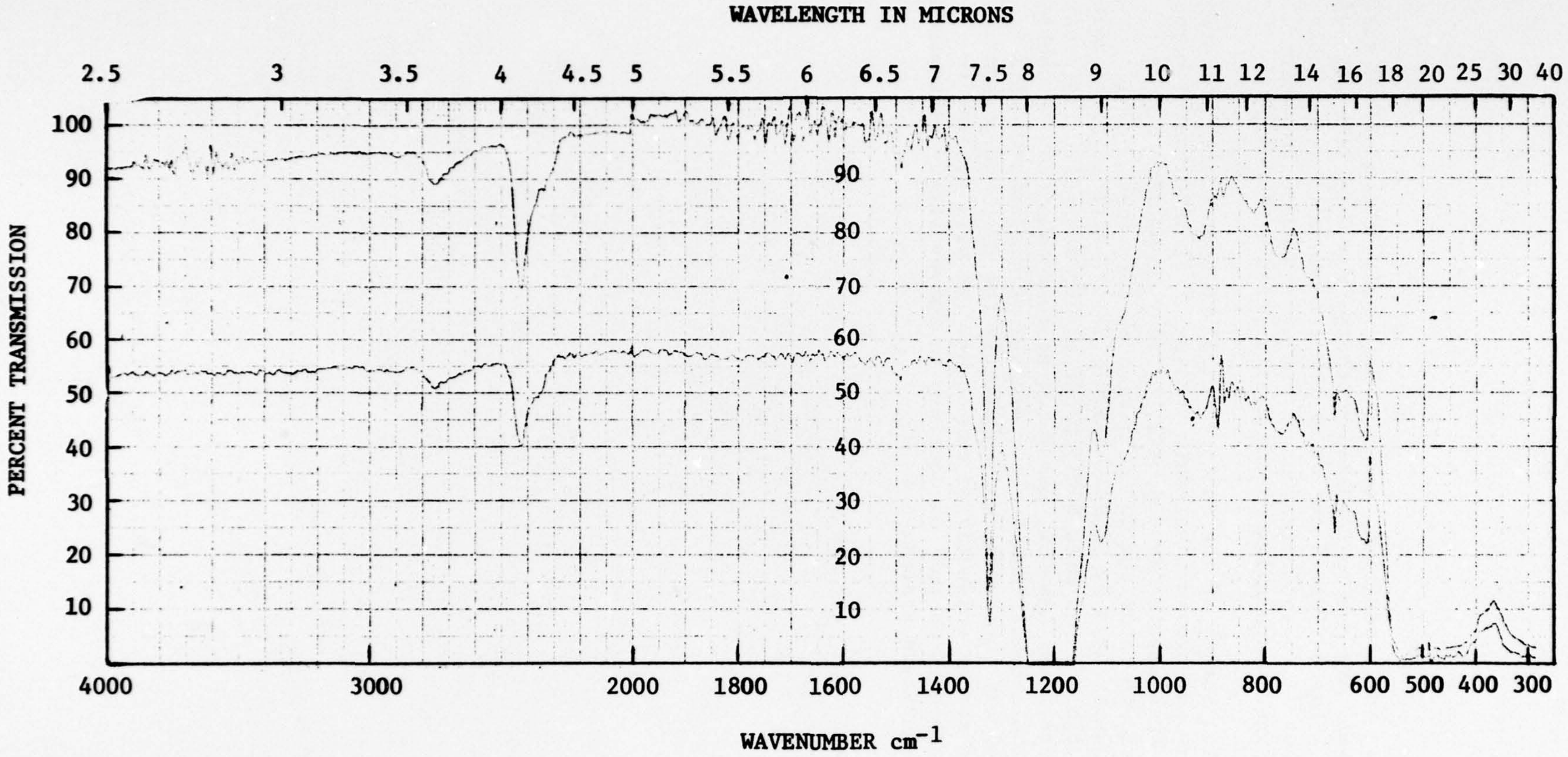

Fig. 10: Infrared spectrum of 1.5M $LiAlCl_4/SOCl_2$ electrolyte after storage at 71°C with Teflon discs used in T-cells. Pathlength 0.10 mm, AgCl windows.

been identified. Their position, however, is in the region of S-O stretching and most likely are due to reaction products from materials leached from the Teflon. Exact identification of these components is probably not necessary, but it is an indication of the improvements in purity that can be obtained by changing to the quartz plate cell design.

The initial survey of the $SOCl_2$ electrolyte system with infrared spectrophotometry has provided valuable insights. It is a useful method for analysis of such species as SO_2, HCl, hydroxy compounds, SO_2Cl_2. It is not an adequate technique for SCl_2 because SCl_2 does not have absorbance band unobscured by $SOCl_2$. Neither is it suitable for S solutions. The reaction of H_2O with $SOCl_2$ produces SO_2 and HCl. The reaction of H_2O with electrolyte, however, generates hydroxy compounds, probably of aluminum, which are reactive to Li. Storage of electrolyte with Li removes these hydroxy compounds, and apparently the HCl, but generates a new and at the moment unidentified component. We will attempt to identify this component as well as continue to survey likely contaminants of the $SOCl_2$ electrolyte system.

IV. CALCIUM DEPOSITION FROM SOLUTIONS IN $SOCl_2$

Calcium has proven to be an effective alloying element for Li anodes for the reduction in the severity of the voltage delay after storage at 71°C (7). Cells stored 800 hours have shown no voltage delay. The Ca was introduced by saturating the electrolyte with $CaCl_2$. Although $CaCl_2$ shows very limited solubility, it provides sufficient Ca^{2+} to diffuse to the Li anode and to deposit by exchange. This method of preparing cells has shown promise, as indicated above, but also has been subject to inconsistencies. During this quarter we have approached this problem by investigating methods of depositing Ca coatings before cell assembly.

In order to deposit Ca onto Li, a more soluble Ca salt would be beneficial. $Ca(SbCl_6)_2$ is soluble in $SOCl_2$ up to at least 1M. The solution is prepared by addition of a 5% excess of anhydrous $CaCl_2$ to a solution 2M $SbCl_5$ in $SOCl_2$. The dissolution reaction is very exothermic. Conductivity measurements show this Ca(II) solution to be about as conductive as 1.5M $LiAlCl_4$, but we believe that the solution contains little free Ca^{2+}. Chemical and electrochemical evidence suggests that the Ca(II) is present as a complex, perhaps as $Ca(SbCl_6)^+$: For example, previous tests show that $Ca(AlCl_4)_2$ has very limited solubility in $SOCl_2$ and a solution of $AlCl_3$ will not dissolve $CaCl_2$. However, the addition of a 1.5M $LiAlCl_4/SOCl_2$ solution to 1M $Ca(SbCl_6)_2/SOCl_2$ produces no precipitate even at a 1:1 volume ratio. This indicates that the Ca(II) must be stabilized by the $SbCl_6^-$.

Further evidence is afforded by attempts to electroplate Ca onto Ni and Li substrates. In these tests, the 2.25 cm^2 working electrodes were immersed in 1M $Ca(SbCl_6)_2/SOCl_2$ with a Ca counter electrode. The tests were run galvanostatically. If the free Ca^{2+} concentration were 1M, a transition time of $\sim 10^5$ sec should be observed at a cathodic current density of 1 mA/cm^2. In the case of Ni, a fresh electrode shows an open circuit potential of +3.6V vs. Li^+/Li. This potential is determined by the $SOCl_2$-reduction reaction. For current densities less than ~ 0.7 mA/cm^2, the potential remains above +3.0V vs. Li. With current densities greater than ~ 0.8 mA/cm^2, a potential of -0.2 to -0.3V vs. Li is rapidly established. After ~ 1 $coul/cm^2$ of charge has been passed, the Ni electrode potential becomes more negative, exceeding -5.0V vs. Li (Figure 11). At this time, the electrode is covered with a black film which is air sensitive. When the electrode is removed to the air, the film rapidly becomes white, then transparent. Qualitative analysis has shown the presence of both Ca and Sb.

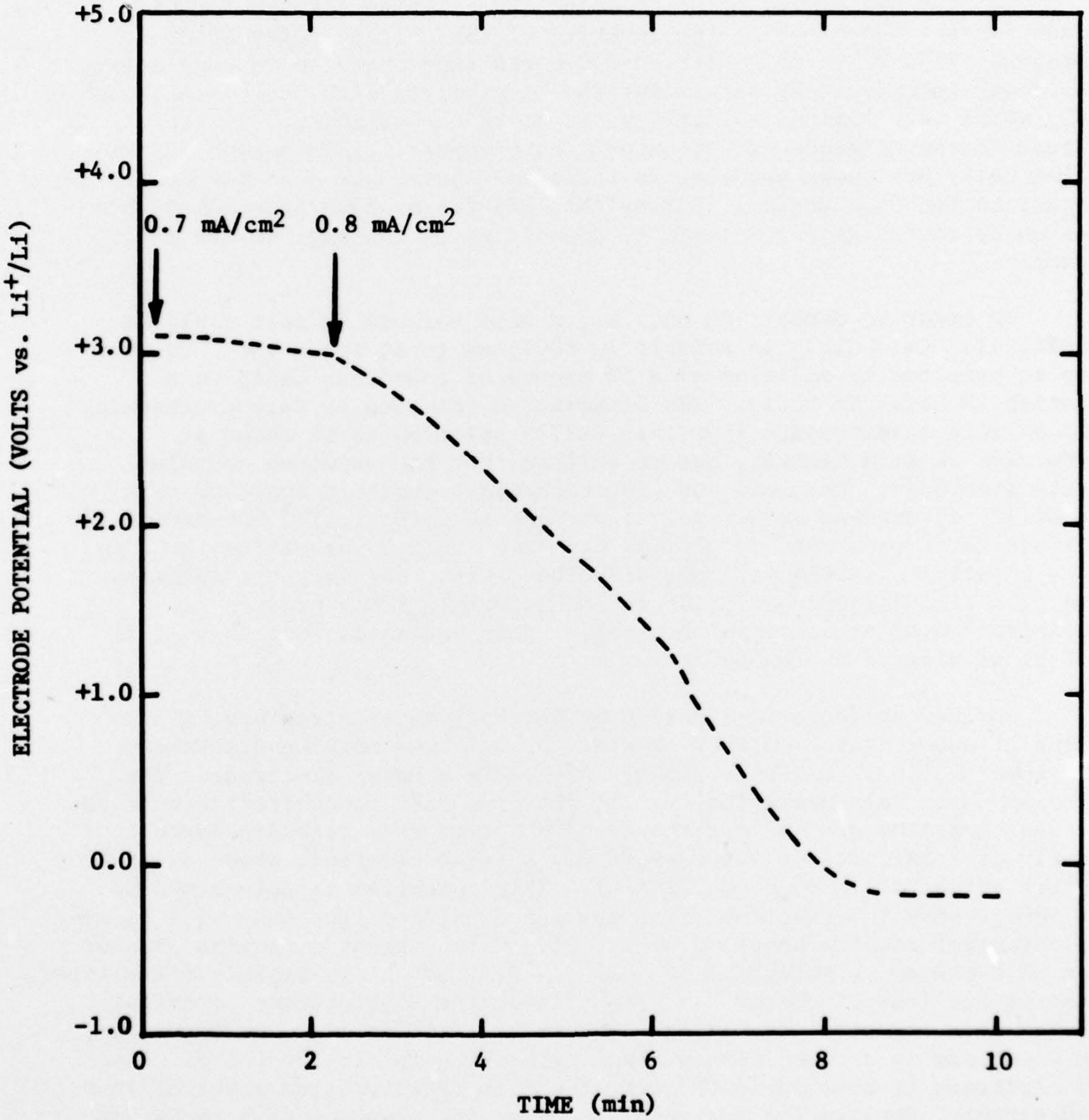

Fig. 11: Polarization of a 2.25 cm^2 Ni electrode in 1M $Ca(SbCl_6)_2/SOCl_2$ at 25°C at the specified current densities.

The possible presence of a LiCl film from the concurrent reduction of $SOCl_2$ should not seriously interfere with the plating process in these tests. For example, we have found that Li may be plated onto Ni at current densities greater than 10 mA/cm^2 at potentials a few tens of millivolts cathodic of the Li open circuit potential.

With Li working electrodes, the fresh Li had an open circuit potential of ± 20 mV vs. Li^+/Li. At cathodic current densities of 0.5 to 1.2 mA/cm^2, a Li electrode rapidly polarized to -0.2 to -0.3V vs. Li. After about 10 coul/cm^2 of charge had been passed, the electrode polarized sharply to greater than -5.0V vs. Li (Figure 12). This electrode was also coated with a black film. Analysis of this film is currently in progress.

These data for the Ni and Li electrodes suggest that the free Ca^{2+} concentration in the 1M $Ca(SbCl_6)_2/SOCl_2$ solution is not 1M, but rather that the majority of the Ca^{2+} is in the form of a complex. The data further suggest that it is a very strong complex, since pure Ca is not plated from solution at potentials ∿1 volt negative of the Ca open circuit potential (∿ +0.8V vs. Li). Rather a mixture of Ca and Sb are found on the electrode. Analyses are currently underway to determine the Ca to Sb ratio. If the ratio is stoichiometric, it would suggest that a single species is being reduced and perhaps the data will yield an estimate of the nature of that species. For example, if the mole ratio of Ca to Sb were 1:1, the solution species might then be $Ca(SbCl_6)^+$. All of the above results suggest a very interesting chemistry for the $Ca(SbCl_6)_2/SOCl_2$ system. It may be appropriate to investigate this chemistry further using the methods of complex chemistry. For example, ligand-exchange titrations or precipitation reactions may prove useful. Whether it is possible to electrodeposit only Ca onto Li from 1M $Ca(SbCl_6)_2/SOCl_2$ is unknown at present. Further testing at cathodic current densities less than 0.5 mA/cm^2 will be carried out.

We have established that Ca does deposit by exchange onto Li from $Ca(SbCl_6)_2$ solution. In these experiments, pieces of Li foil (6 cm^2, two sides) were immersed in 0.1M, 0.3M and 1.0M $Ca(SbCl_6)_2/SOCl_2$ for varying lengths of time. The Li pieces were removed, thoroughly rinsed with $SOCl_2$, and analyzed for their Ca content by atomic absorption. The analytical results are presented in Table 1. The Ca depletion in the solutions was small. For example, the sample stored for 88 hours in 0.1M $Ca(SbCl_6)_2$ removed only 6% of the Ca present. These deposits contain only trace amounts of Sb, possibly from entrainment of electrolyte.

These data show the accumulation of Ca to be relatively slow and relatively insensitive to $Ca(SbCl_6)_2$ concentration. Both of these suggest that the deposition is not controlled by solution processes. Of possible solution processes, diffusion is the most likely to be limiting.

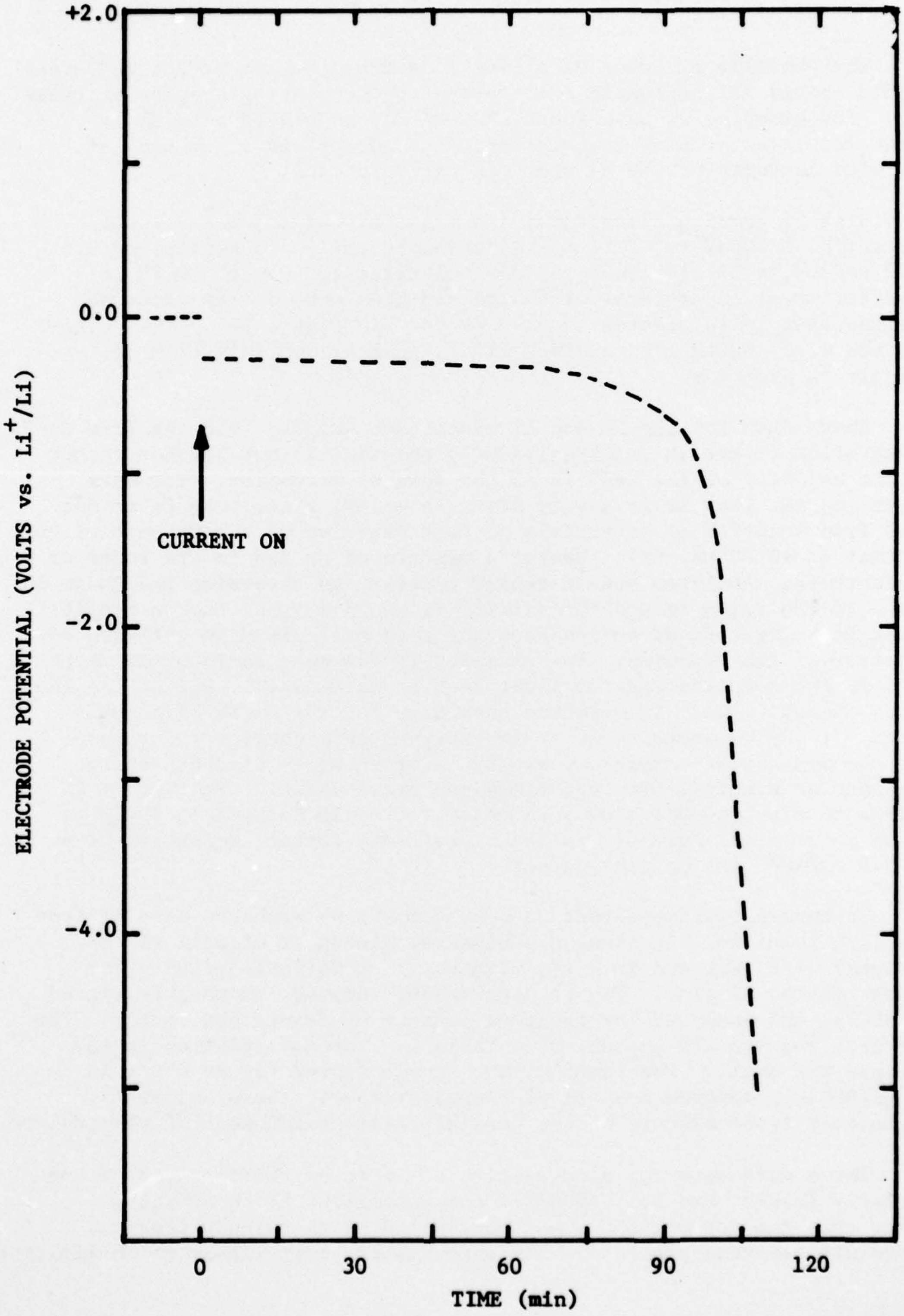

Fig. 12: Polarization of a 2.25 cm^2 Li electrode in 1M $Ca(SbCl_6)_2$ at 25°C with 0.9 mA/cm^2.

Table 1

Ca Deposition on Li Metal from $Ca(SbCl_6)_2/SOCl_2$ at 25°C coul/cm^2

Time (hr) / Conc	1	3	19	88(A)	88(B)
0.1M	0.052	0.088	0.398	0.969	1.81
0.3M	0.065	0.163	0.458	2.25	1.99
1.0M	0.093	-	0.404	-	-

Yet calculations show that diffusion would permit deposition rate orders of magnitude greater than those observed. For example, assuming $D = 5 \times 10^{-6}$ cm^2/s, then with $t = 1$ hr, $C = 10^{-4}$ mol/cm^3, the charge deposited would be 4.6 $coul/cm^2$ vs. the 0.052 $coul/cm^2$ measured. This view is further substantiated by the relative insensitivity of the deposition rate to solution concentration of $Ca(SbCl_6)_2$.

Since we can deposit Ca onto Li by chemical exchange, our next step will be to prepare Li(Ca) anodes by this technique for storage testing. Chemical analyses of the $Ca(SbCl_6)_2$ solutions will be carried out to ascertain impurity levels. We feel this is necessary to determine if purification of these solutions is necessary to remove species known to be detrimental (e.g., Fe and Cu).

V. SUMMARY AND FUTURE WORK

During the past quarter, work has continued on the voltage delay problem suffered by Li/$SOCl_2$ cells during storage at 71°C. We have reviewed our test cell design and storage procedures. Test cells assembled with quartz plates have shown improved performance compared with our Teflon test cells. The quartz plate cells have larger anode areas and do not have Ni Exmet anode current collectors. The specific source of the improvement has not been identified. The substitution of the quartz for Teflon certainly removes a source of contamination. IR spectrophotometry had been used to ascertain that Teflon introduces HCl and at least one other component into 1.5M $LiAlCl_4/SOCl_2$ electrolyte during storage at 71°C. The larger anode can provide a larger number of defect sites on the surface which are capable of being activated during discharge and/or reduce edge effects. The removal of the Ni Exmet precludes the possibility of poor electrical contact during testing.

Atmospheric exchange between our storage cells and air does not appear to be a problem up to $\sim$300 hours storage.

A new salt preparation method was used. The salt is prepared as the melt at 180°C and purified by electrolysis. Electrolyte prepared with this $LiAlCl_4$ gave cell performance closely equivalent to that of our normal electrolyte, which is prestored with Li.

In an effort to further elucidate the chemistry of the $LiAlCl_4/SOCl_2$ system, a study by infrared spectrophotometry was initiated. This study has several aims: We wish to survey the system to identify and quantify possible impurities. We further wish to study the discharge reaction products, especially possible minor products. Undistilled Eastman 246 $SOCl_2$ has shown no extraneous absorption bands. This limits the HCl and SO_2 concentrations to less than ≤ 200 ppm. Distillation introduces SO_2 and SO_2Cl_2 into the solvent. Preparation of the electrolyte introduces small amounts of SO_2 and HCl, probably from reaction with H_2O contained in the salt. The salt also introduces hydroxy aluminum compounds, which are relatively stable in $SOCl_2$. Storage with Li at 71°C removes the hydroxy aluminum compounds and the HCl. The storage also introduces an as yet unidentified component.

Water reacts with $SOCl_2$ to produce HCl and SO_2 in proportion to the water added. Water reacts with electrolyte to produce some HCl and SO_2 but primarily hydroxy aluminum compounds.

HCl and SO_2Cl_2 have identifiable absorbances in the IR, which $SOCl_2$ solutions of S and SCl_2 do not.

Calcium plating studies from $Ca(SbCl_6)_2/SOCl_2$ solution have indicated that chemical exchange between a Li sufrace and the solution will deposit Ca. These studies suggest that the free Ca^{2+} is stabilized, for example, as the $Ca(SbCl_6)^+$ species.

During the next quarter, we will continue to explore the problem of voltage delay. The improvement in performance observed in the quartz plate cells will be fully explored in order to establish the precise cause or causes. Lithium (Ca) anodes will be prepared by exchange from $Ca(SbCl_6)_2$ solution and will be tested in complete cells after storage at 71°C. The infrared spectrophotometric survey of the $SOCl_2$ system will be continued.

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