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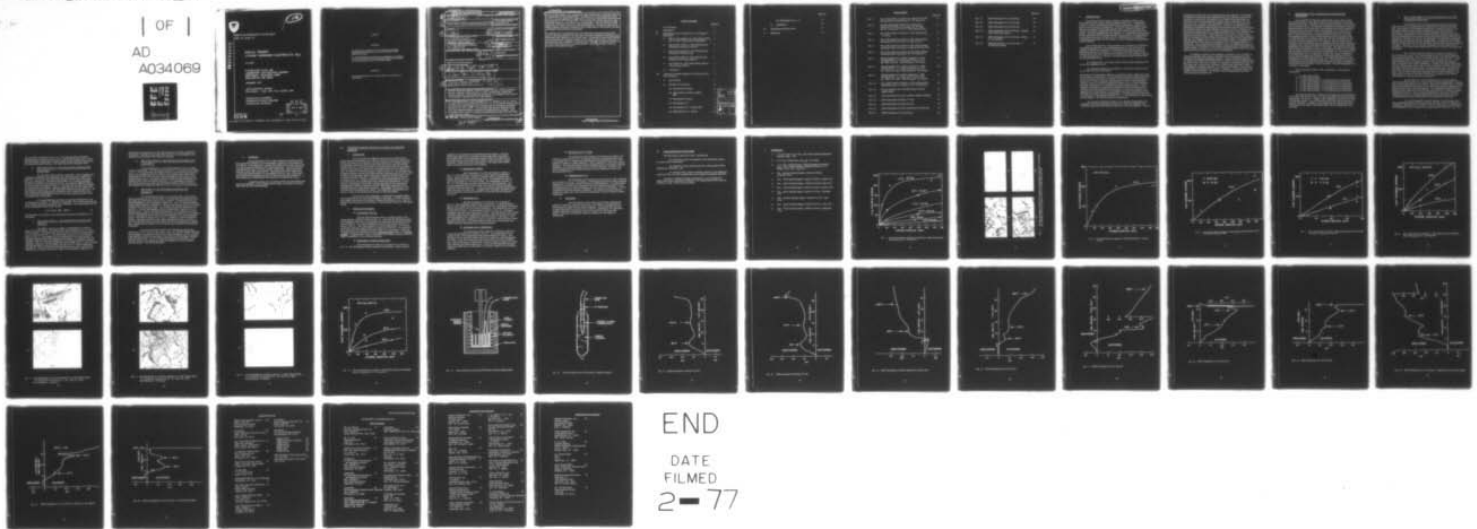
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Research and Development Technical Report  
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**SEALED PRIMARY  
LITHIUM - INORGANIC ELECTROLYTE CELL**

A.N. DEY

P.R. MALLORY & CO., INC.  
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NORTHWEST INDUSTRIAL PARK  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Li/SOCl <sub>2</sub> hermetic D cell developed by P. R. Mallory & Co. Inc. met or exceeded all the initial objectives such as E. D. of 150 WHr/lb at thirty hours rate and a peak power density of 50 watts/lb and the storage and operating temperature of -40 to 160°C. The two major deficiencies exhibited by the cells were explosion hazard on abuse and voltage delay on storage. Both the problems were studied in detail and considerable progress has been made in both the above areas.		

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During the last quarter, we continued the SEM studies of the Li that was found to be responsible for the voltage delay. We obtained LiCl film growth rate curves for the Li samples stored in the electrolytes containing various salt concentrations and additives at 72°, 55° and 25°C. We found that the growth rates were substantially reduced by reducing the salt concentration. Also the addition of SO<sub>2</sub> caused the LiCl film to grow in a more orderly fashion. We plan to examine the effect of these electrolyte variables on the voltage delay of the practical hermetic Li/SOCl<sub>2</sub> D cells during the next quarter.

We have set up a DTA apparatus for doing differential thermal analysis of the various chemicals present in a fresh and/or partially discharged Li/SOCl<sub>2</sub> D cell. Preliminary data obtained so far indicate that it is possible to distinguish between pressure bursts and a thermal runaway by this method. We believe, this type of measurement will be valuable in identifying the chemical combinations present in the cells which may lead to a thermal runaway. Once this is done, it may be possible to find ways to stop it.

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## I. INTRODUCTION

The Lithium-Thionyl chloride inorganic electrolyte system is one of the highest energy density systems known to date (1-4). It comprises a Li anode, a carbon cathode and a  $\text{LiAlCl}_4\text{-SOCl}_2$  electrolyte.  $\text{SOCl}_2$  acts both as a solvent and as a depolarizer. We carried out a systematic investigation of the system over the last several years in an effort to define the intrinsic performance capabilities as well as the intrinsic limitations of the system. Our basic approach has been twofold: (a) optimization of the system for the realization of the maximum possible energy density in a commercially viable structure (hermetic D cell), and (b) identification and definition of the problems associated with the system, and the development of approaches to their solution.

The original objective of this program was to develop a D cell which is storable and operable in the temperature ranges of  $-40$  to  $160^\circ\text{F}$  and is capable of delivering in excess of 150 WHr/lb at the thirty hour rate and peak power density of 50 watts/lb. We showed at the early stages of our program that all the above objectives are easily met by the hermetic Li/ $\text{SOCl}_2$  D cells developed by us. However, we found that the system suffered from two inherent deficiencies:

(a) Voltage-delay, particularly after storage at high temperature and test at low temperature, and

(b) Chemical instability, particularly on shorting and forced as well as on resistive load overdischarge.

We studied the voltage-delay problem in sufficient detail to define the underlying causes of the problem. We found that the build-up of a passivating LiCl film as a result of the reaction between Li and the  $\text{LiAlCl}_4\text{-SOCl}_2$  electrolyte caused the Li anode to polarize instantaneously on load. The subsequent recovery occurs as a result of mechanical rupture of the LiCl film caused by the anodic dissolution of Li underneath the film through pin holes. We developed a technique for examining the morphology and the thickness of the LiCl film using Scanning Electron Microscope. We used this method to investigate the Li film build-up in the inorganic electrolyte containing various additives and various  $\text{LiAlCl}_4$  concentrations. We reported some of this work in the 8th and the 9th quarterly reports (10, 11). We continued this work during the last quarter. The latest results are reported here.

The chemical instability resulted in an explosion hazard that we investigated in a phenomenological manner (4-8). First we established the conditions under which the hermetic Li/ $\text{SOCl}_2$  D cells may explode. Then we



attempted to develop ways and means to prevent the explosion. For example, we found that a lowering of rate capability may not necessarily prevent cell explosion as long as the cell could get hot enough by other extraneous circumstances such as high temperature storage, heavy insulation of the cell wall and so on. We found that low pressure venting is an effective way for preventing cell explosion on external short. However, this approach was ineffective in preventing explosion from forced and/or resistive over discharge. The fact that some of the cells explode on resistive load over discharge is particularly unsettling since it is neither predictable nor easily comprehensible based on the present state of knowledge about the system. All the known batteries including  $\text{Li}/\text{SO}_2$ , render themselves harmless from thermal runaway after all the energy has been drained by prolonged resistive load overdischarge. However, this appears not to be the case with this system. A completely discharged battery, while sitting on the shelf at  $25^\circ\text{C}$ , may explode quite unexpectedly. This is particularly problematic since it is impossible to prevent resistive load overdischarge and/or storage of partially and/or completely discharged battery in normal use. We believe that this problem needs to be solved before the field use of the system can be recommended.

In seeking a solution to this problem, we believe it will be useful to study the chemistry of the system, particularly the thermochemistry of the discharged and partially discharged system. We have assembled apparatus for carrying out Differential Thermal Analyses (DTA) of the chemical compounds and their mixtures that may be present in a partially discharged  $\text{Li}/\text{SOCl}_2$  cell. The object was to identify any exothermic combinations that might initiate or propagate an explosive reaction. Once these are identified, one may then attempt either to eliminate the reactants, if possible, or one may render them inactive by various means. The details of the DTA experiments and some initial results are reported here.

## II. SEM STUDIES OF THE LI ANODE FILM IN THE INORGANIC ELECTROLYTE

We established (2) that the voltage-delay of the Li/SOCl<sub>2</sub> cells was caused by the Li anode film formed due to the reaction of Li with the inorganic electrolyte. Therefore, we focussed our attention on the study of the Li anode film itself. We mounted Li specimens on stainless steel SEM specimen holders and stored them in the inorganic electrolytes containing various additives and various salt concentrations at 72°, 55° and 25°C for various periods of time. Then we examined the Li anode film using SEM in order to determine the morphology and the thickness of the film. We established earlier that both the morphology and the thickness of the Li anode film affects the voltage-delay (2). We also established (2) that the film is primarily composed of LiCl crystals. Our main objective for this part of the investigation was to establish whether or not the electrolyte variables such as salt concentrations and additives could affect either the morphology or the thickness of the Li anode film. The experimental details and the results reported in the 8th and 9th quarterly reports (10, 11) showed that the answer to the above question is definitely yes. We displayed the SEM photographs of the Li anode film formed at the various temperatures in the various inorganic electrolytes in the previous reports in order to demonstrate the morphology of the film. We showed that addition of SO<sub>2</sub> definitely altered the morphology of the film. We continued the storage of Li specimens in the inorganic electrolytes with SO<sub>2</sub> for longer durations. We now have SEM data after 99 days of storage. The SEM photographs will be shown in this report.

We continued the storage of the Li specimens in the following electrolytes:

1. 0.5 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub>
2. 0.25 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub>
3. 1.0 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> + 1 gm AlCl<sub>3</sub>/100 ml of electrolyte
4. 1.0 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> + 10 gm AlCl<sub>3</sub>/100 ml of electrolyte
5. 1.0 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> + 0.01 gm H<sub>2</sub>O/100 ml of electrolyte
6. 1.0 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> + 0.1 gm H<sub>2</sub>O/100 ml of electrolyte
7. 1.0 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> + 10 gm S<sub>2</sub>Cl<sub>2</sub>/100 ml of electrolyte
8. 1.0 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> + 17.3 gm SO<sub>2</sub>/100 ml of electrolyte.

We obtained SEM data in regard to the morphology and the thickness of the anode film after as long as 170 days of storage in some of the above electrolytes. We found no change in the morphology of the film as a result of the longer storage. Only the thickness of the film and the size of the crystals increased. Therefore, in this report we will examine the rate of film growth in the various electrolytes rather than the morphology of the LiCl film.



A. Rate of Film Growth in 0.5 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> and 0.25 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> Electrolytes

The thickness of the Li anode film was measured by making a cross section of the Li specimen and by looking at the cross section with SEM. The smearing of the boundary between the Li metal and the LiCl film is a major problem in the accurate determination of the film thickness. Furthermore, film thickness was not uniform throughout the specimen. For these reasons the absolute values of the average film thickness reported here are not as dependable as the general trends of the film thickness with time and temperature. Although we have not yet established a quantitative relationship between the film thickness and the voltage-delay, the general trend is clear; both the voltage-delay and the film thickness increase with time and temperature of storage. Therefore, for a given film morphology, the film growth rate is indicative of the voltage-delay characteristics of the Li anode in any particular electrolyte.

The Li anode film growth rates were obtained by plotting the film thickness as a function of time of storage in the various electrolytes at the various temperatures. The Li film growth curves in 0.5 (M) and 0.25 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> electrolytes at 72°, 55° and 25°C are shown in Fig. 1. The film thickness grows with storage duration, and the growth rates increase with an increase in the storage temperature. We also find that the film growth rates are significantly higher in the 0.5 (M) electrolyte compared to that in the 0.25 (M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> electrolyte at all three temperatures. We made this observation in the 8th quarterly report (10) based on storage durations of 28 days. The extended storage data available now for storage durations of 155 days confirm our earlier conclusion that the Li film growth can be reduced significantly by reducing the salt concentration.

Another feature of the film growth curves which are apparent from the extended storage data is that the film thickness approaches an asymptotic value of approximately 200 microns. These are very thick films. It should also be noted that the leveling off occurs faster with the higher temperature of storage and the higher salt concentration. It is particularly important to note that the steady growth of the film continues for as long as 155 days at storage temperatures of 55°C. This continuing growth of the "protective" film may indicate its porous and imperfect nature which allows the chemical and/or electrochemical reactions responsible for the film growth to continue.

It is also noteworthy, that the increase in the thickness of the film corresponds closely with the increase in the size of the LiCl crystals, in a direction parallel to the Li surface. This is visible in Fig. 2 which shows the photographs of the Li surface at a magnification of 1000 after 8, 28, 133

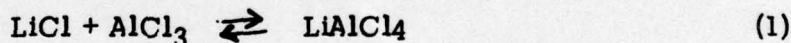


and 152 days of storage at 72°C in a 0.5 (M)  $\text{LiAlCl}_4 \cdot \text{SOCl}_2$  electrolyte corresponding to the points shown in Fig. 1 for the film growth curve. Note that the average crystal sizes increase rapidly at first and then level off with the increased storage duration, very much like the film thickness itself.

B. Rate of Film Growth in 1 (M)  $\text{LiAlCl}_4 \cdot \text{SOCl}_2$  Electrolyte With  $\text{AlCl}_3$  Additive

We used two levels of  $\text{AlCl}_3$ , 1% and 10%. The Li samples were completely consumed in the electrolyte with 10%  $\text{AlCl}_3$  after 75 days at 72° and 55°C. We did not have sufficient data point in that solution to obtain the rate of film growth. The rate of film growth in the 1%  $\text{AlCl}_3$  electrolyte solutions is similar to that observed earlier. We obtained sufficient data at 72°C and these are presented in Fig. 3. Note that the LiCl film grows rapidly at first and then more slowly. Both the morphology and the film growth rates are similar to those in the 0.5 (M) electrolyte without any  $\text{AlCl}_3$  additive. The film thickness again approaches an asymptotic value of about 200 microns. This constitutes a major portion of the Li since the original thickness of the Li substrate was 381 microns.

It is noteworthy that 10%  $\text{AlCl}_3$  is extremely deleterious to the Li compared to 1%  $\text{AlCl}_3$ . In 10%  $\text{AlCl}_3$ , presumably, the Li reacts continuously and at a more rapid rate until all the Li is consumed. We may postulate that the  $\text{AlCl}_3$  complexes with the solid LiCl film



and dissolves it as  $\text{LiAlCl}_4$ , thus diminishing the protection afforded by the film itself.

C. Rate of Film Growth in 1 (M)  $\text{LiAlCl}_4 \cdot \text{SOCl}_2$  Electrolyte With Added  $\text{H}_2\text{O}$

We added 0.01 and 0.1%  $\text{H}_2\text{O}$  in the electrolyte to study its effect on the film growth. The growth rates were measured at 72°, 55° and 25°C as before. The growth rate curves for both 0.01 and 0.1%  $\text{H}_2\text{O}$  solution at 72°C are shown in Fig. 4. The growth rate curves at 55°C and 25°C are shown in Fig. 5. There appears to be no difference in the Li film growth in the above solutions at all the temperatures of storage. We showed in the 9th quarterly report (11) that the morphology of the film was identical in both the solutions. However, the film growth rate curves shown in Fig. 4 and 5 indicates that film continues to grow even after 100 days at 72°C without completely leveling off. We do not know the significance of this as yet, since the film thickness is just about 200 microns. This is the thickness at which the Li

film of previous samples in 0.5 (M) electrolytes and 1%  $\text{AlCl}_3$  electrolytes leveled off. The rate of film growth with 0.01 and 0.1%  $\text{H}_2\text{O}$  appears to be somewhat less than that in the other two solutions.

D. Rate of Film Growth in 1 (M)  $\text{LiAlCl}_4\text{-SOCl}_2$  Electrolyte With  $\text{S}_2\text{Cl}_2$  Additive

We used 10%  $\text{S}_2\text{Cl}_2$  in 1 (M)  $\text{LiAlCl}_4\text{-SOCl}_2$  to study its effect on the Li film growth. The film growth curves at 72°, 55° and 25°C are shown in Fig. 6. The growth rates are similar to those in the electrolytes with  $\text{H}_2\text{O}$ . Again, the available data do not indicate any cessation of the film growth, particularly at 72°C where the film with a thickness of 200 microns is still growing after 98 days. We showed earlier (11) that the film morphology was similar to that in the electrolytes with  $\text{H}_2\text{O}$ . It is reasonable to conclude that 10%  $\text{S}_2\text{Cl}_2$  does not cause any appreciable change in either the rate of film growth or the morphology relative to 0.01 or 0.1%  $\text{H}_2\text{O}$  in the electrolyte.

E. Film Growth in 1 (M)  $\text{LiAlCl}_4\text{-SOCl}_2$  Electrolyte With  $\text{SO}_2$  Additive

We investigated the effect of 17.3%  $\text{SO}_2$  in the 1 (M)  $\text{LiAlCl}_4\text{-SOCl}_2$  electrolyte on the Li film growth. We found that the morphology of the LiCl film was significantly altered in this solution. We showed some of the SEM photographs in the 9th quarterly report (11). The LiCl crystals appeared to grow with a preferred orientation. We found this characteristic on Li samples stored at 72°C for 8 and 15 days. We now have data for the storage at 55°C and 25°C. The SEM photographs of the Li surface after 35 days at 55°C are shown in Fig. 7. Again, the ordered growth of the LiCl crystals are visible. The SEM photographs of LiCl films after 99 days of storage at 55°C are shown in Fig. 8. The epitaxial growth of LiCl crystals persists. The SEM photograph of the Li film after 97 days at 25°C, Fig. 9, displays the same orientational feature. The data available to date clearly establish that the 17.3%  $\text{SO}_2$  in the 1 (M)  $\text{LiAlCl}_4\text{-SOCl}_2$  electrolyte cause the LiCl film morphology to change from a random type of growth to a more orderly type of growth with a preferred orientation.

The LiCl film growth curves in the electrolytes with the  $\text{SO}_2$  additive at 72°, 55° and 25°C are shown in Fig. 10. The film growth characteristics appear to be similar to that in the 0.5 (M) electrolyte. At 72°, the film grows rapidly at first and then tends to level off at a film thickness somewhat less than 200 microns. We do not know whether this is significant. With the  $\text{SO}_2$  additive, the changes in morphology appears to be more dramatic than the change in the film growth rates.



F. Conclusion

The determination of the Li film thickness by the SEM method was successful although it may be desirable to improve on the accuracy of the method. It was possible to estimate the growth rates of LiCl film on the Li in the inorganic electrolytes with various additives. The salt concentration affected the rate of LiCl film growth significantly. Lower rates were obtained at lower salt concentration. The presence of AlCl<sub>3</sub> enhanced the Li film build-up particularly at a concentration of 10%. SO<sub>2</sub>, on the other hand affected the morphology of the LiCl film rather than the growth rate. A more ordered LiCl crystal growth was observed in the presence of SO<sub>2</sub>.

A detailed analysis will be performed when all the planned data have been collected. Also, attempts will be made to correlate the voltage delay with the LiCl film parameters.

### III. DIFFERENTIAL THERMAL ANALYSIS OF Li/SOCl<sub>2</sub> CELL REACTION PRODUCTS

#### A. Experimental

We have assembled apparatus for carrying out DTA analysis of the cell reaction products in an effort to identify the chemical constituents which could lead to the exothermic reaction necessary for a thermal runaway. A temperature programmer (Fisher Model 360) was used to heat the samples linearly with time. A special furnace was designed and built for this purpose because of the corrosive nature of the chemicals (SOCl<sub>2</sub>) that we planned to test. A schematic view of the furnace is shown in Fig. 11. We also designed a sample container in which the corrosive liquid chemicals such as SOCl<sub>2</sub> could be kept in a hermetically sealed state while keeping the thermocouple wires in contact with the chemicals. A schematic view of the sample containers is shown in Fig. 12. A blank container filled with alumina powder was used as a reference for the measurement of the differential temperatures. A two channel potentiometric strip chart recorder was used for the simultaneous measurement of sample temperature and the differential temperature of the chemicals present in the sample container. The samples were heated at the 10°C/mt rate to temperatures of 300°C. The differential temperatures were shown in terms of the thermocouple readings in the thermograms.

After setting up the apparatus, we checked the reproducibility of our measurements by running the samples in duplicate. Initially we started with single chemicals such as SOCl<sub>2</sub>, cathode mix (carbon), S, Li. Next we obtained the thermograms of the mixture. The preliminary results are discussed below.

#### B. Results and Discussion

##### (a) Thermograms of SOCl<sub>2</sub>

The first DTA thermogram with 0.2 ml SOCl<sub>2</sub> alone in the sealed sample container is shown in Fig. 13. Note that the thermogram peaks are endothermic most likely corresponding to boiling and the thermal decomposition of SOCl<sub>2</sub>. The second thermogram with the same amount of SOCl<sub>2</sub> is shown in Fig. 14. The results appear to be quite reproducible. In one case, the sample container exploded after the completion of the run. The explosion point coincided with a sharp endothermic peak in the thermogram. This type of explosion can be described as a typical pressure bursts instead of a thermal-runaway. It appears that it might be possible to distinguish between these two types of explosions by the DTA measurements.

##### (b) Thermograms of Carbon Cathode Mix

DTA thermogram of 0.0281 gm of cathode mix is shown in Fig. 15. The thermogram consists primarily of endotherms. These represent



dehydration and desorption of adsorbed materials present in the high surface area cathode mix consisting of Shawinigan Black and Teflon. The gradual drifts in the thermograms usually reflect the difference between the thermal conduction of the reference material and the sample chemicals. These are of little consequence. The sharp peaks reflect physico-chemical transitions of the samples.

(c) Thermograms of Sulfur

DTA thermograms of 0.0467 gm of sulfur is shown in Fig. 16. The exothermic transitions are quite untypical of elemental sulfur. These most likely indicate a chemical reaction between the S and the chromel-aluminal thermocouple wires. We repeated the DTA run with a large sample (0.1429 gm) of sulfur. The thermogram is shown in Fig. 17. The exotherms are quite accentuated in this thermogram. The visual examination of the thermocouple wires after the DTA run revealed extensive chemical attack by S. In fact the chromel-aluminal thermocouples broke off at the end of the run. It appears that the sample containers need to be modified for running DTA analysis of chemically reactive materials such as S.

(d) Thermogram of Li

The DTA thermogram of 0.0327 gm of Li is shown in Fig. 18. The thermogram consists only of exotherms. A sharp exothermic jump at 195°C which is near the melting point of Li is particularly interesting. This is associated with a mild form of explosion. We repeated the run using 0.0352 gm of Li again. The thermogram is shown in Fig. 19. The sharp exothermic jump was again observed at 200°C. The examination of the sample containers after the run revealed that the glass container reacted with Li and was disintegrated due to exothermic reaction between Li and glass. With the knowledge that in Li/SOCl<sub>2</sub> D cells, Li remains in contact with the glass separator at all times, this observation indicates one of the possible exothermic reactions contributing to the thermal runaway.

(e) Thermogram of S + Cathode Mix

The thermogram of the mixture of 0.0653 gm of sulfur and 0.0165 gm of cathode mix is shown in Fig. 20. The endotherms are very similar to that in the thermogram of the carbon cathode mix alone. Note that there are no exothermic peaks which were observed in the thermograms of S alone. This may indicate the lack of reactivity of S with the cathode mix. Also the presence of cathode mix may have helped to prevent the sulfur from attacking the thermocouple wires. It may be concluded that the above mixture by itself does not contribute to the thermal runaway of the Li/SOCl<sub>2</sub> batteries.



(f) Thermograms of Li + SOCl<sub>2</sub>

The thermogram of the mixture of 0.0256 gm of Li and 0.1 ml of SOCl<sub>2</sub> is shown in Fig. 21. It consists of two short exotherms followed by a very sharp one at a temperature slightly above the melting point of Li. This exotherm resulted in a minor explosion. This is expected in view of the thermodynamics. The rapid exothermic reaction between molten Li and SOCl<sub>2</sub> certainly contributes to the thermal runaway of the Li/SOCl<sub>2</sub> batteries. However, this does not explain why the thermal runaways occur at temperatures lower than the melting point of Li.

(g) Thermogram of Li + S

The thermogram of the mixture of 0.0135 gm of Li and 0.0680 gm of S is shown in Fig. 22. Here again, the thermogram shows two small exotherms followed by a very large one which leads to a small explosion. It is particularly interesting to note that the temperature (178°C) at which this exotherm occurs is substantially lower than the temperatures (195-210°C) at which the Li + SOCl<sub>2</sub> combinations showed exothermic explosion. The results do indicate that the presence of sulfur may indeed lower the temperature at which a thermal runaway could start.

C. Conclusion

The DTA analysis of the chemicals and their combinations present in Li/SOCl<sub>2</sub> cells has been shown to be useful in distinguishing between pressure bursts and the thermal runaways. The limited data obtained to date demonstrate the efficacy of the method in establishing the potentially unstable chemical combinations that may be present in Li/SOCl<sub>2</sub> cells. Hence, it provides a systematic means of studying the cell explosion phenomenon.

#### IV. CONCLUSION AND FUTURE WORK

The SEM studies carried out so far, indicate that

(a) Reduction of salt concentration in the electrolyte results in a lower rate of film growth.

(b) Addition of  $\text{AlCl}_3$  enhances the rate of film growth without altering the morphology, and

(c) Addition of  $\text{SO}_2$  causes a dramatic change in the morphology of the  $\text{LiCl}$  film, the  $\text{LiCl}$  crystals grow with a preferred orientation (epitaxy).

We plan to complete the SEM measurements, and to evaluate the effect of the above electrolyte variables on the voltage-delay of the hermetic  $\text{Li/SOCl}_2$  D cells, during the next quarter.



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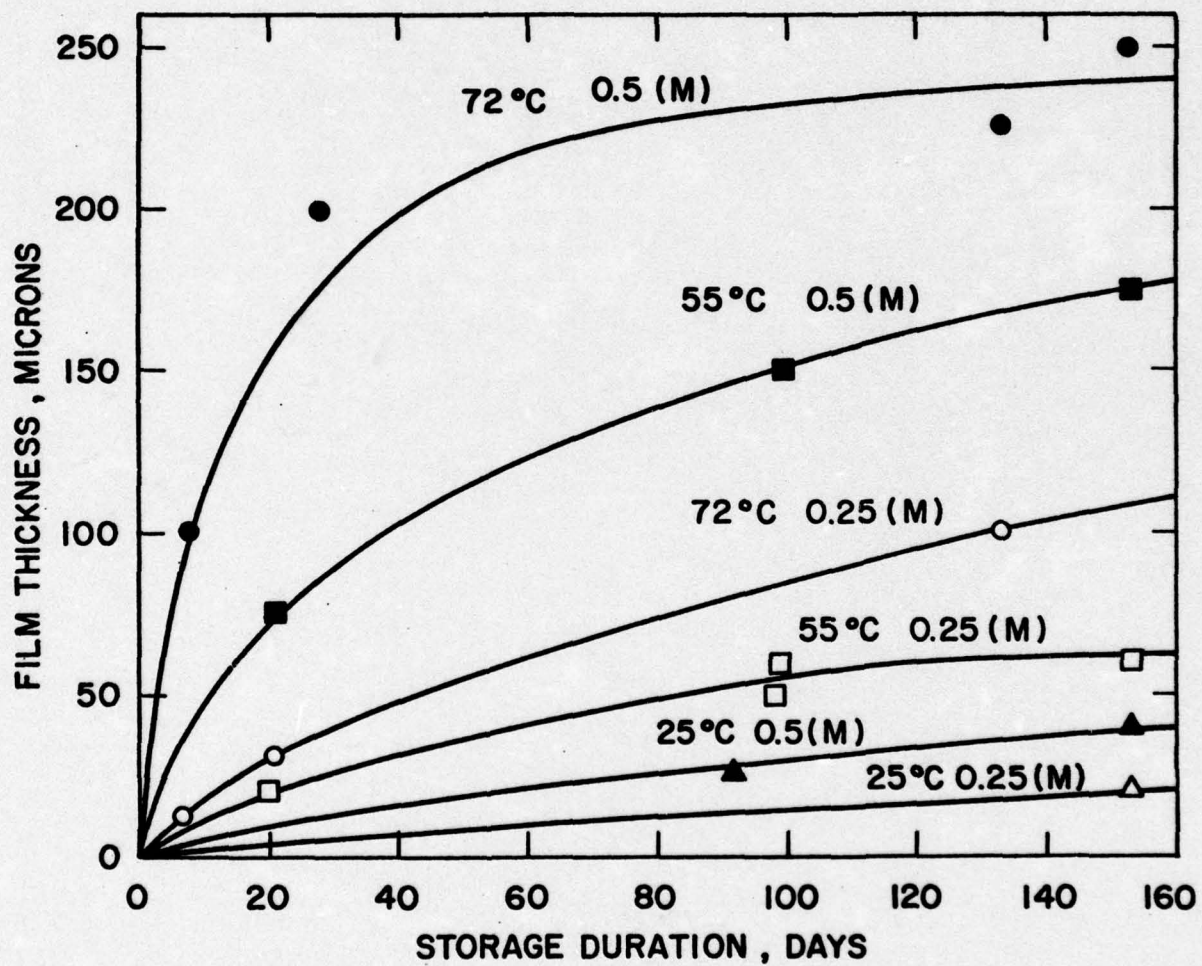
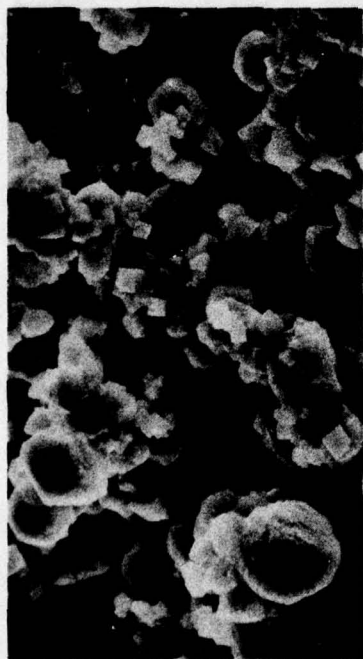
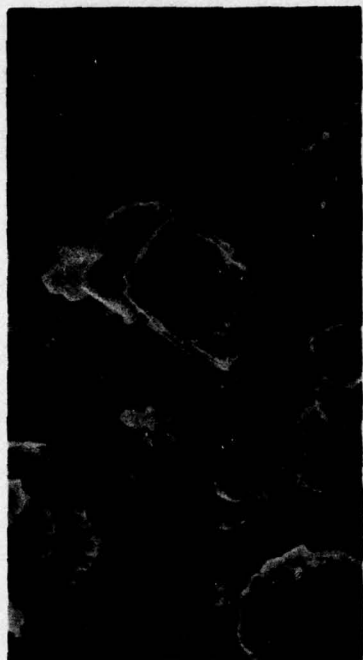


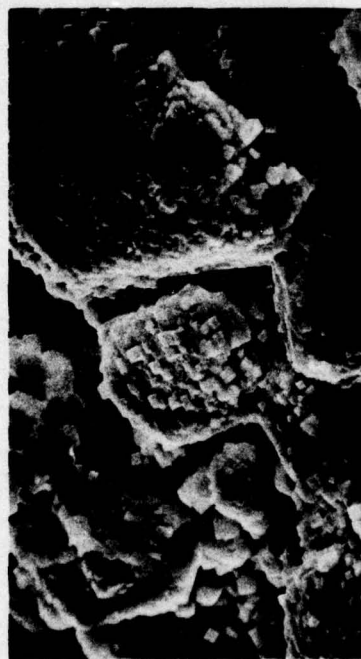
Fig. 1. The Li film growth on storage in 0.5(M) and 0.25(M)  $\text{LiAlCl}_4\text{-SOCl}_2$  electrolytes at 72°, 55° and 25°C.



(a)



(b)



(c)



(d)

Fig. 2. The SEM photograph (X1000) of Li surface after storage of (a) 8 days, (b) 28 days, (c) 152 days, and (d) 152 days at 72°C in 0.5(M)  $\text{LiAlCl}_4\text{-SOCl}_2$



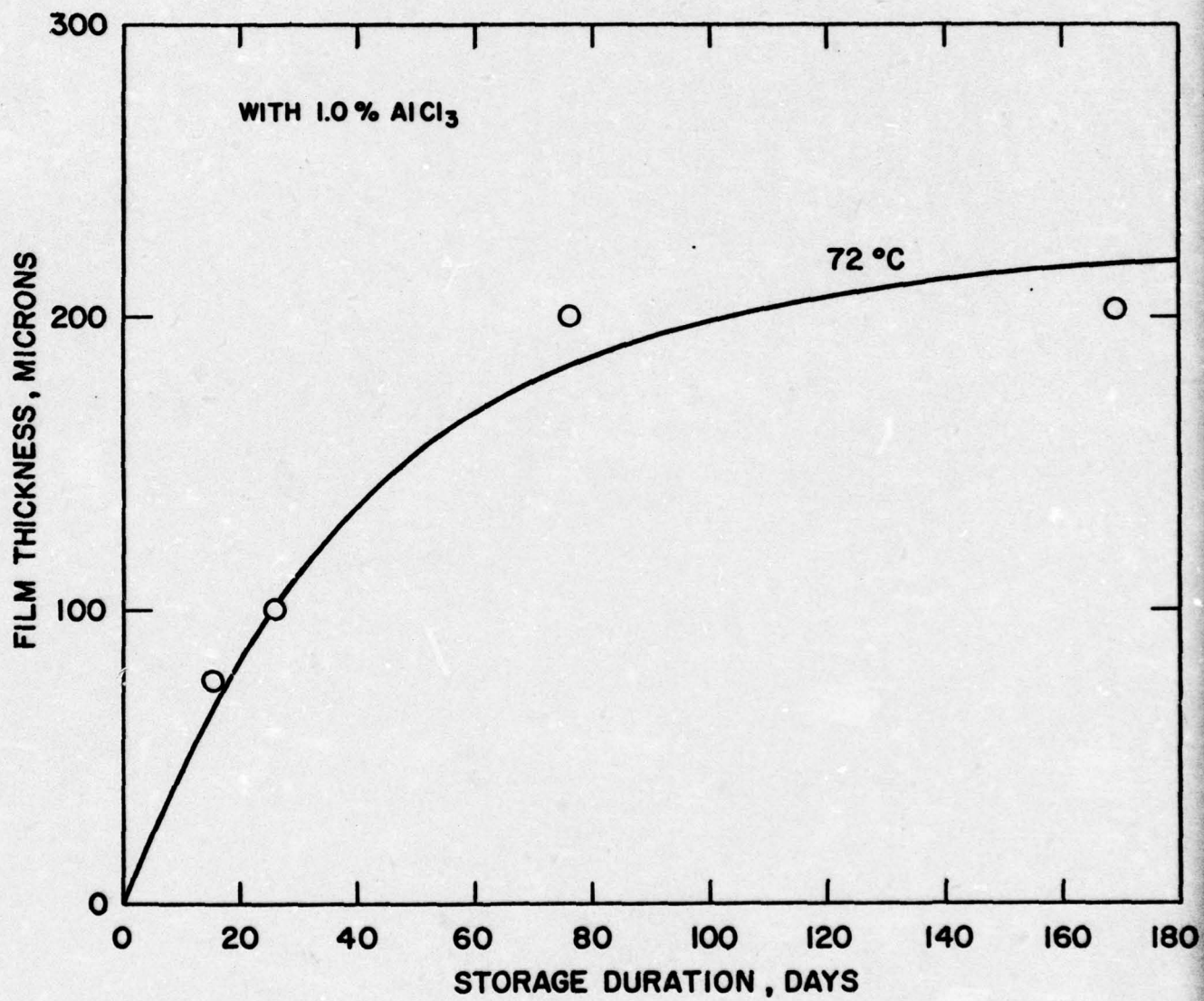


Fig. 3. The Li film growth on storage in 1(M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> + 1% AlCl<sub>3</sub> at 72°C

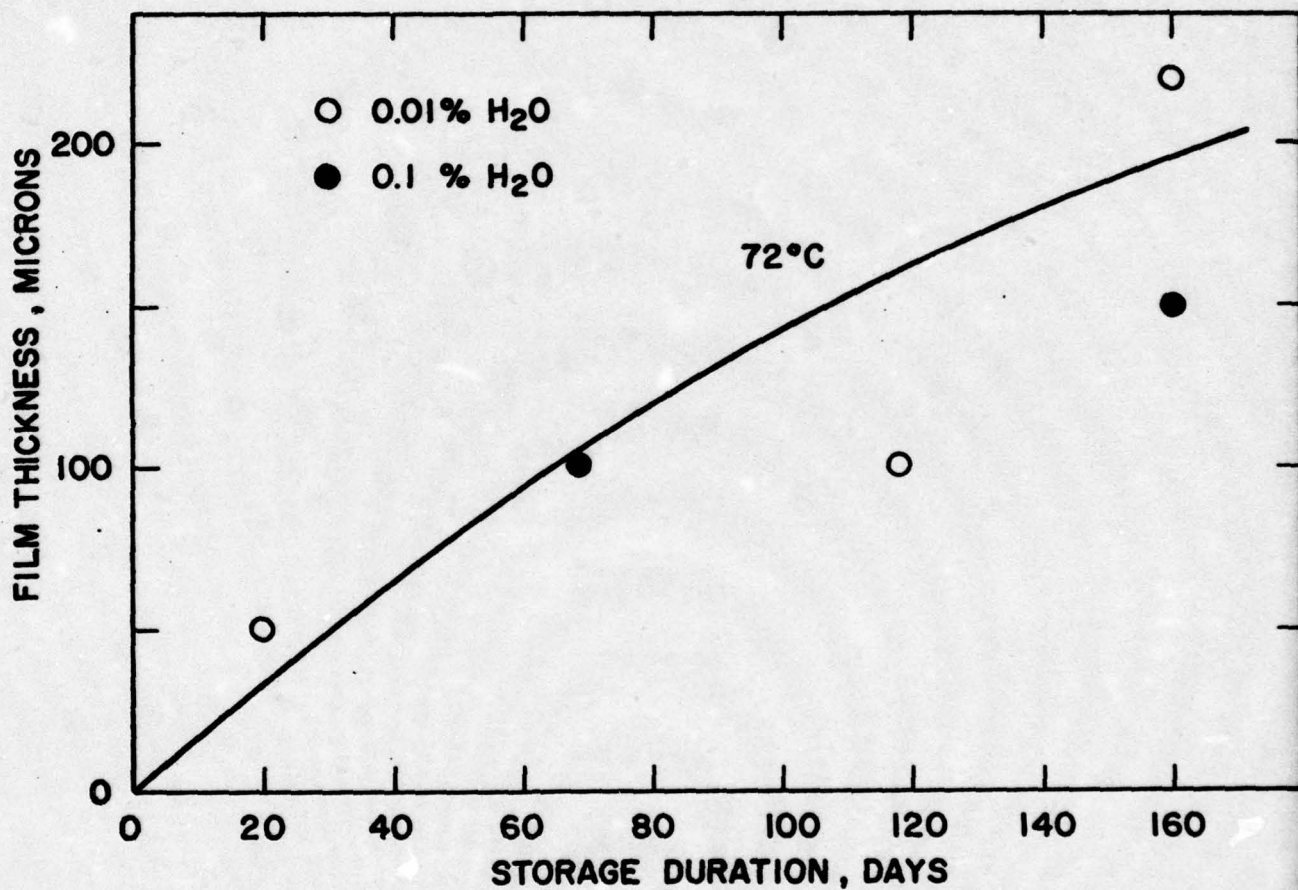


Fig. 4. The Li film growth on storage in 1(M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> electrolyte with 0.01% and 0.1% H<sub>2</sub>O at 72°C



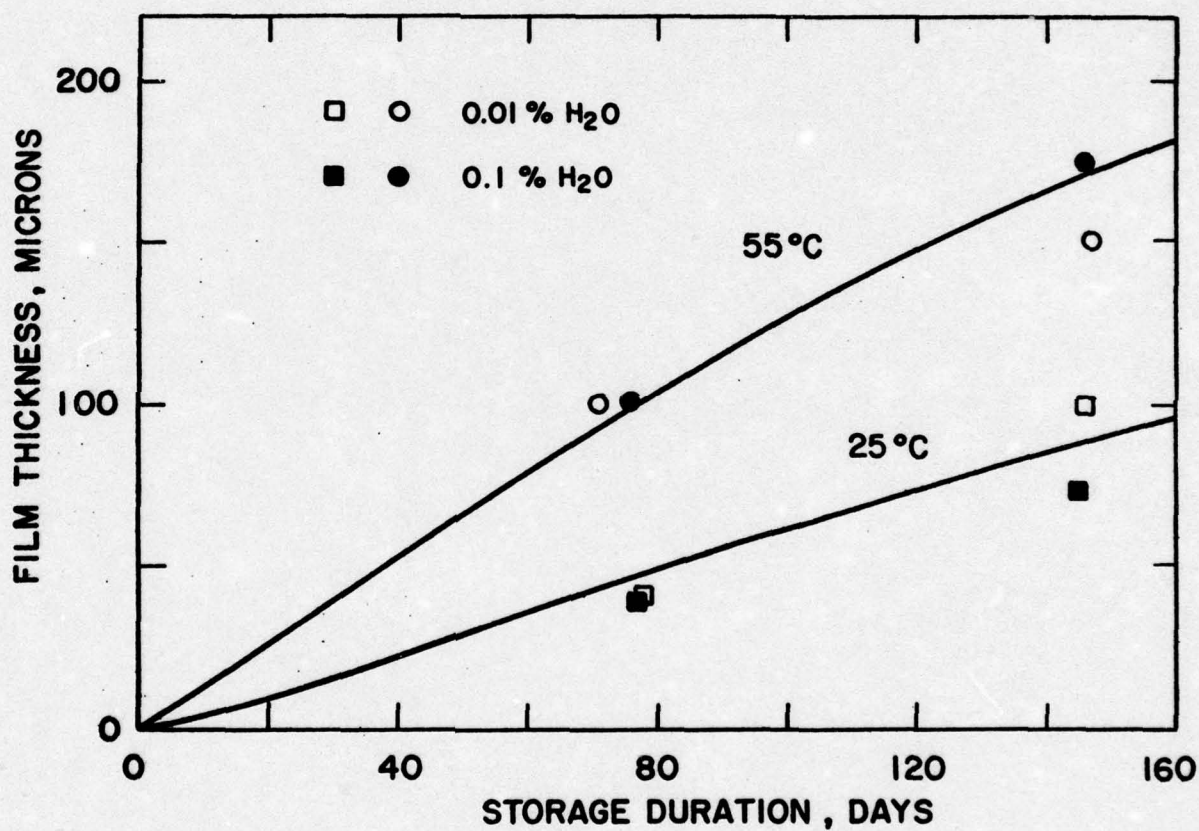


Fig. 5. The Li film growth on storage in 1(M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> electrolyte with 0.01% and 0.1% H<sub>2</sub>O at 55° and 25°C

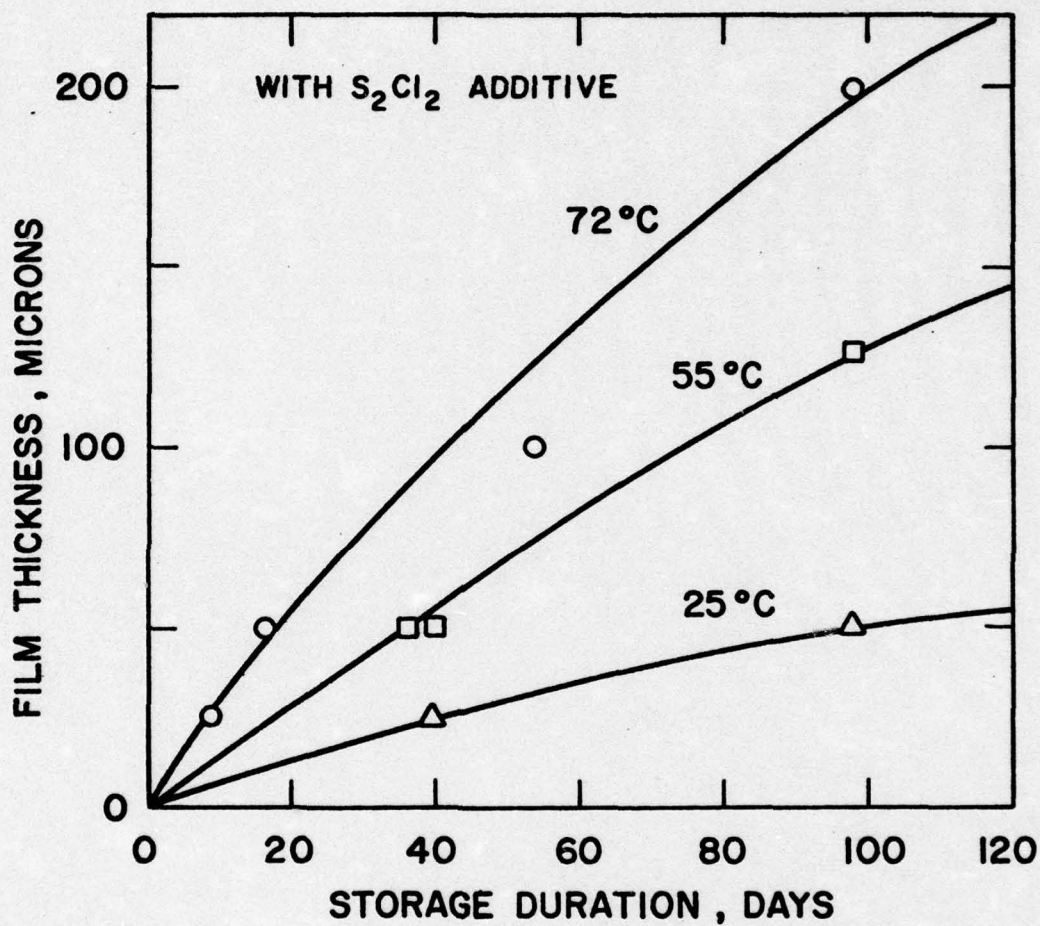
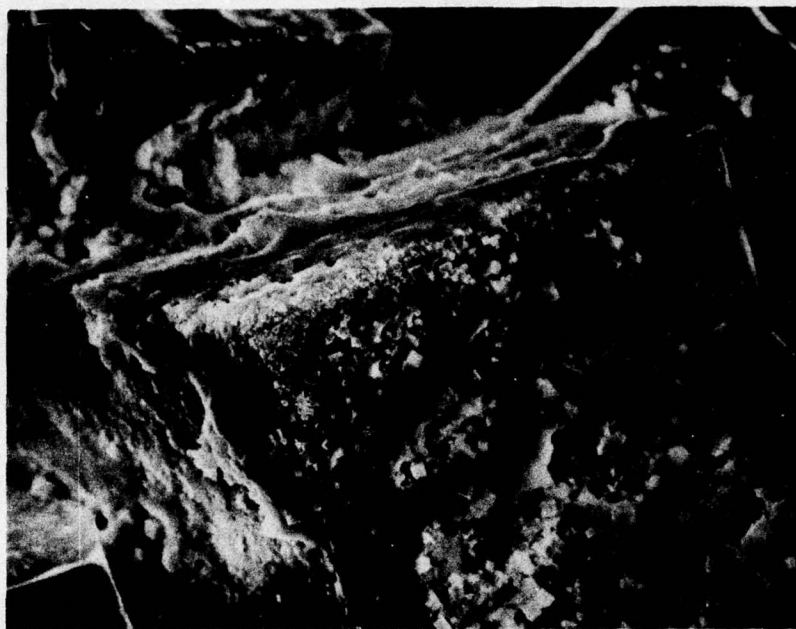


Fig. 6. The Li film growth on storage in 1(M)  $\text{LiAlCl}_4\text{-SOCl}_2$  electrolyte with 10%  $\text{S}_2\text{Cl}_2$  at 72°, 55° and 25°C.



(a)

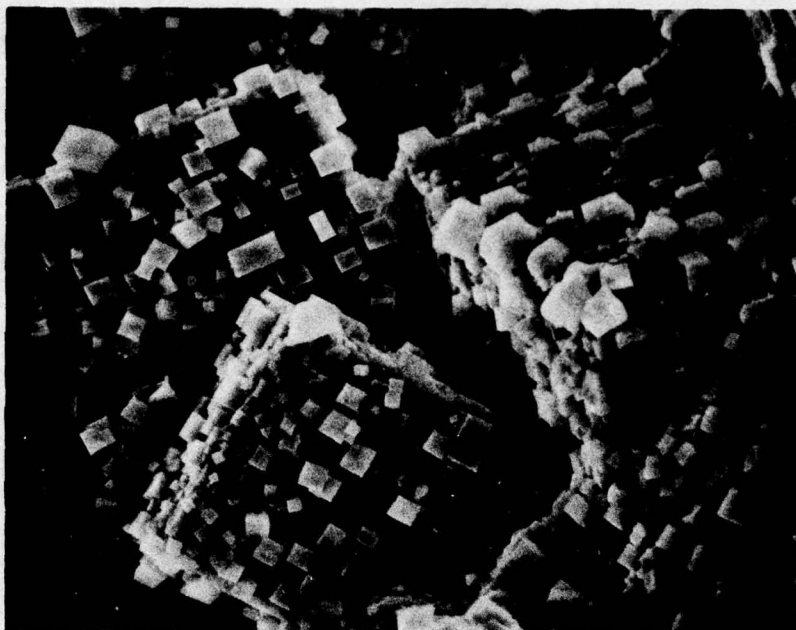


(b)

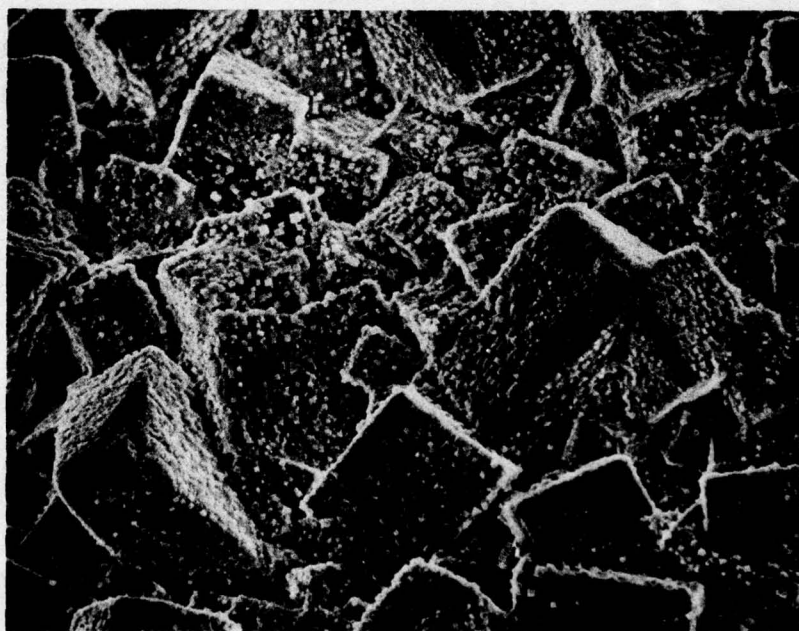


Fig. 7. SEM photographs of Li surface exposed to 1.0(M)  $\text{LiAlCl}_4\text{-SOCl}_2$  + 17.3%  $\text{SO}_2$  for 35 days at 55°C. (a) 1000X (b) 200X  
Film Thickness: 75 microns

(a)



(b)



**Fig. 8.** SEM photographs of Li surface exposed to 1.0(M)  $\text{LiAlCl}_4\text{-SOCl}_2$  + 17.3%  $\text{SO}_2$  for 99 days at 55°C. (a) 1000X (b) 200X  
Film Thickness: 100 microns



(a)



(b)

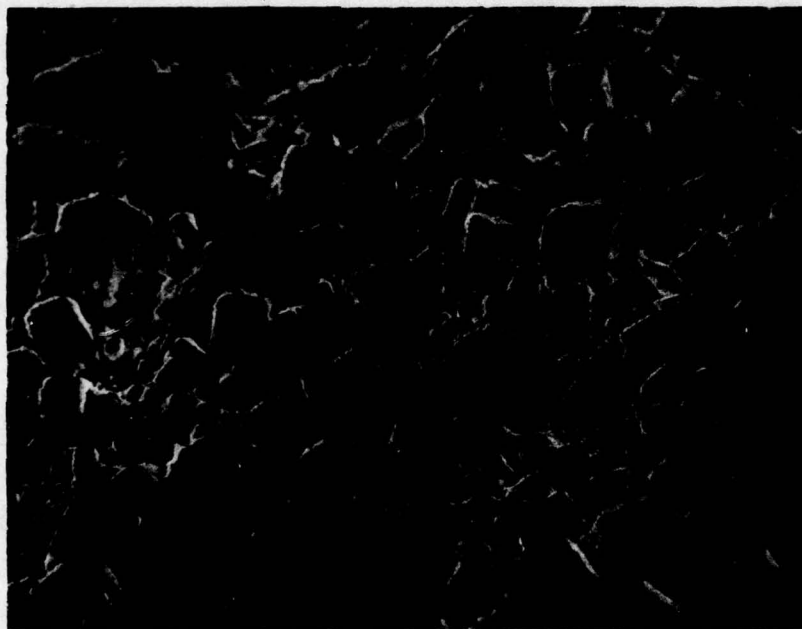


Fig. 9. SEM photograph of Li surface exposed to 1.0(M)  $\text{LiAlCl}_4\text{-SOCl}_2$  + 17.3%  $\text{SO}_2$  for 97 days at 25°C. (a) 1000X (b) 200X. Film Thickness: 50 microns

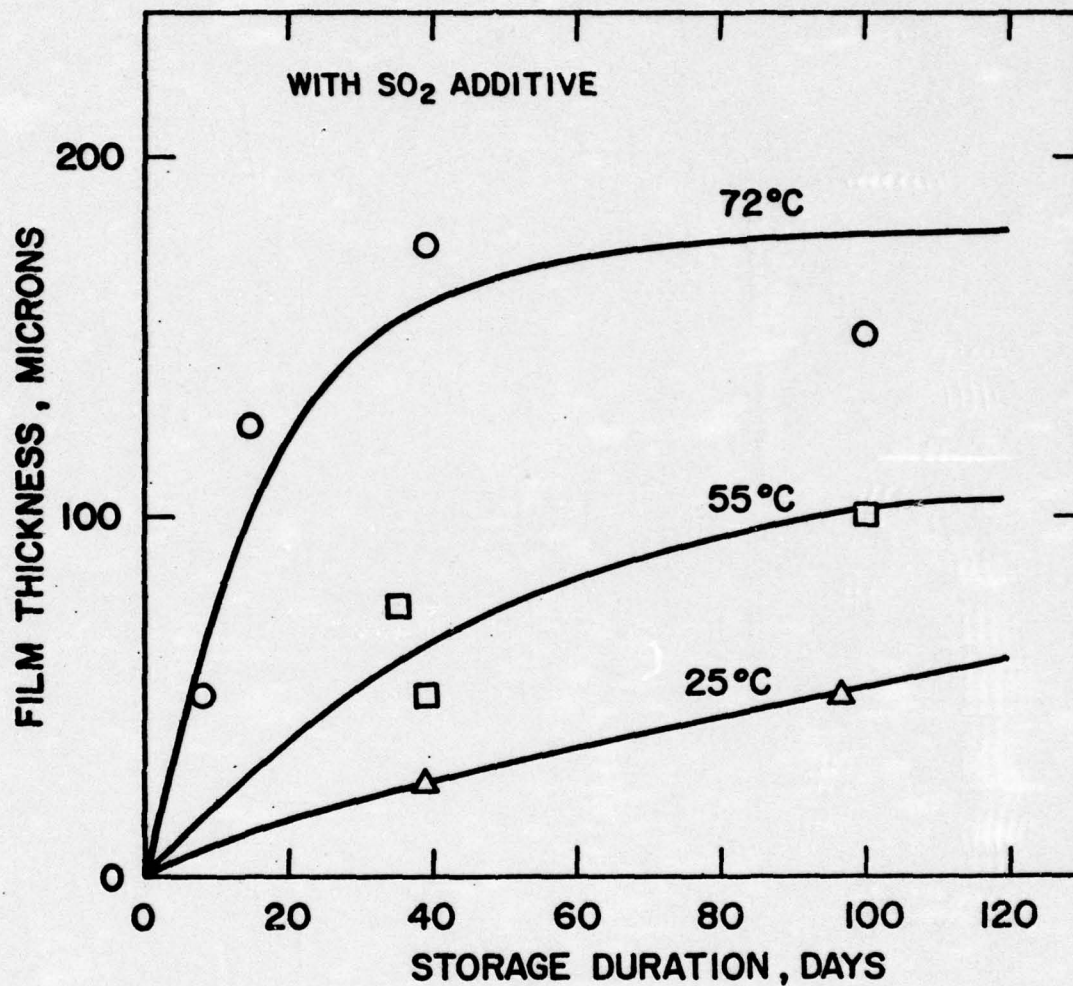


Fig. 10. The Li film growth on storage in 1(M) LiAlCl<sub>4</sub>-SOCl<sub>2</sub> electrolytes with 17.3% SO<sub>2</sub> at 72°, 55° and 25°C.



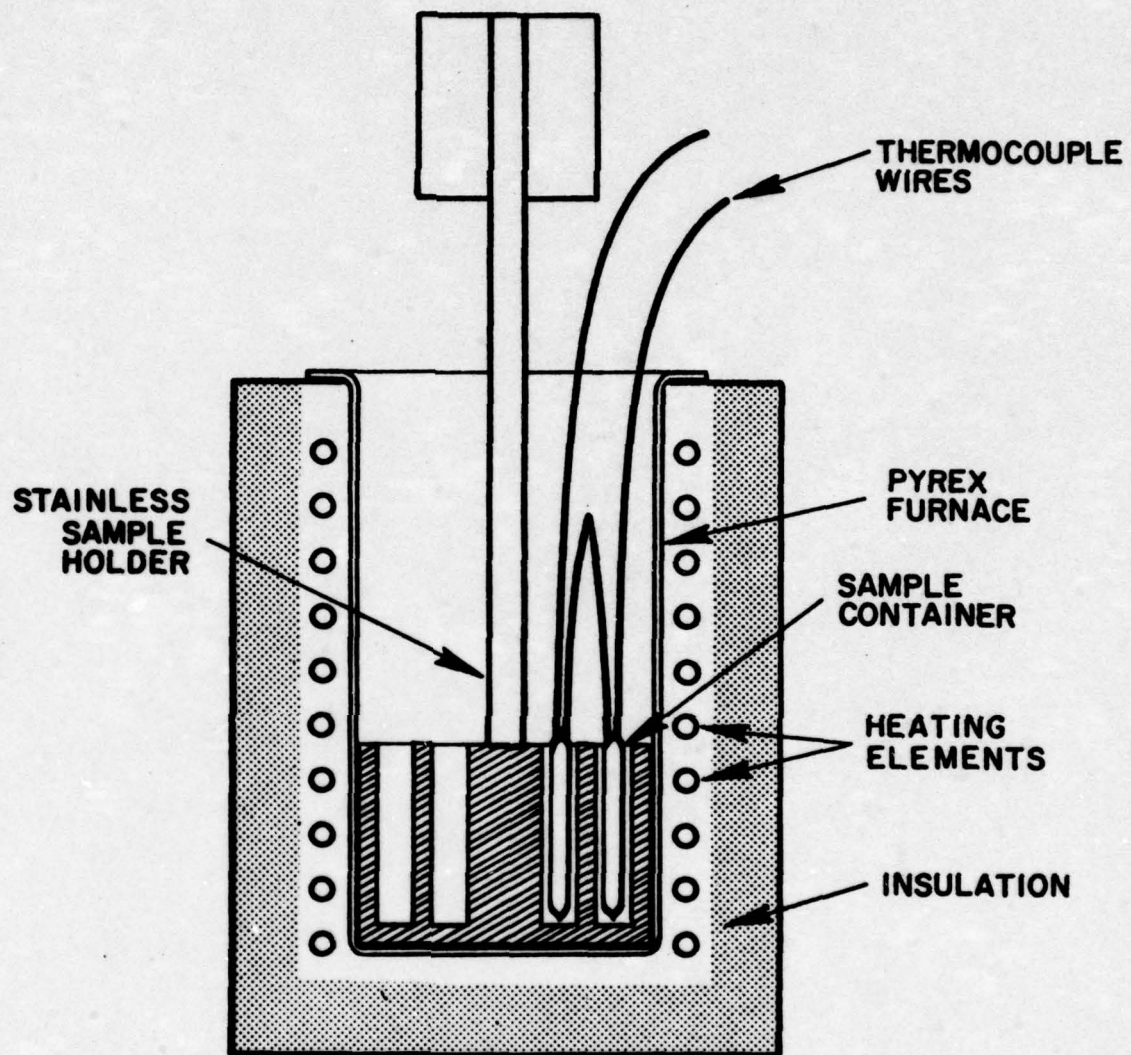


Fig. 11. Cross sectional view of the DTA furnace with the sample holder

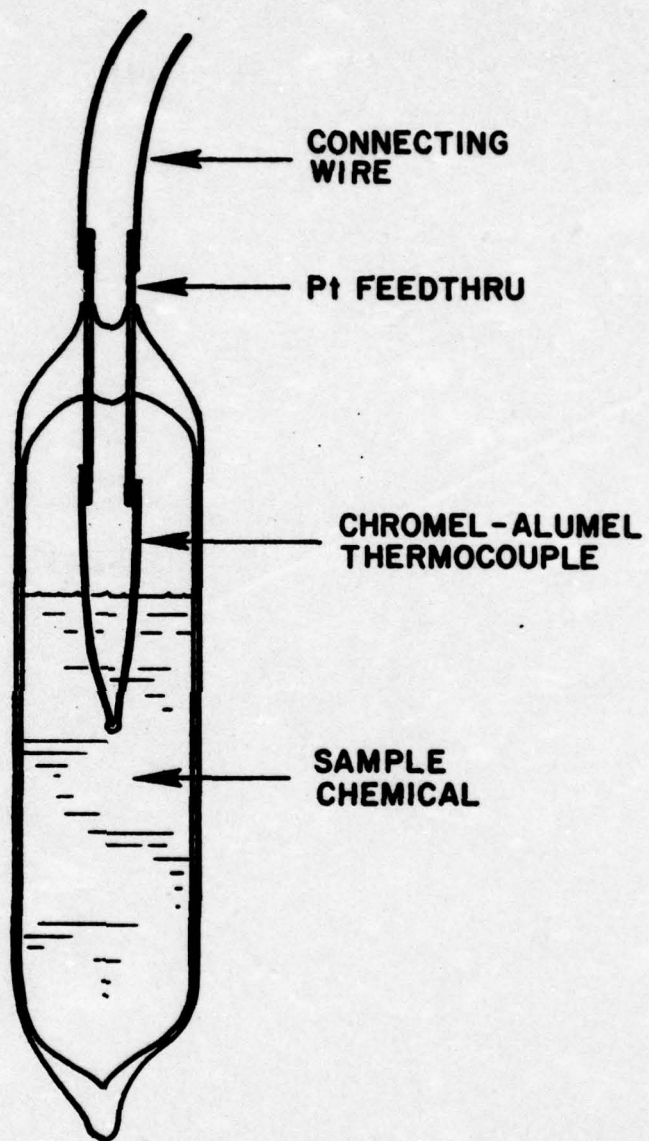


Fig. 12. Cross sectional view of the hermetic sample container.



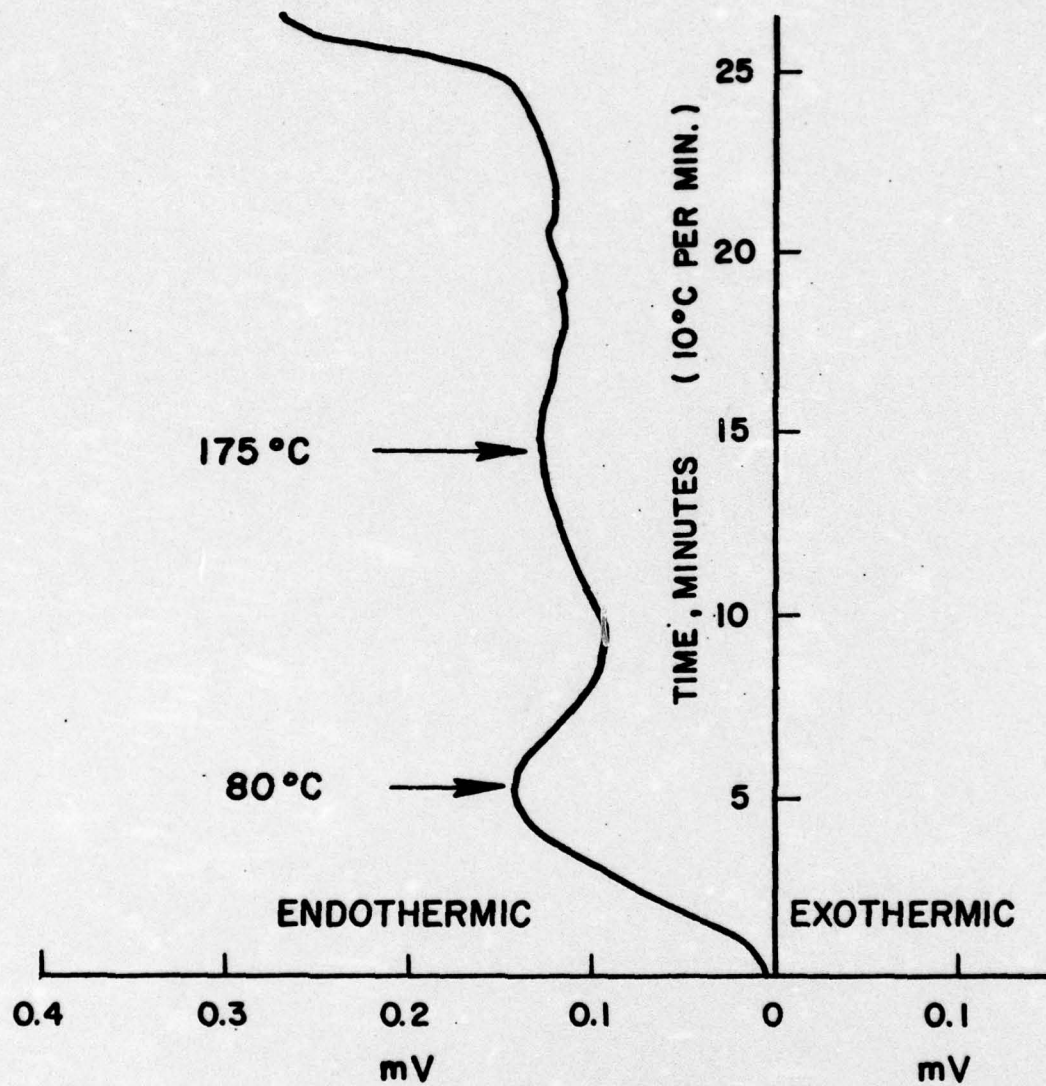


Fig. 13. (DTA) thermogram of  $\text{SOCl}_2$  (0.2 ml).

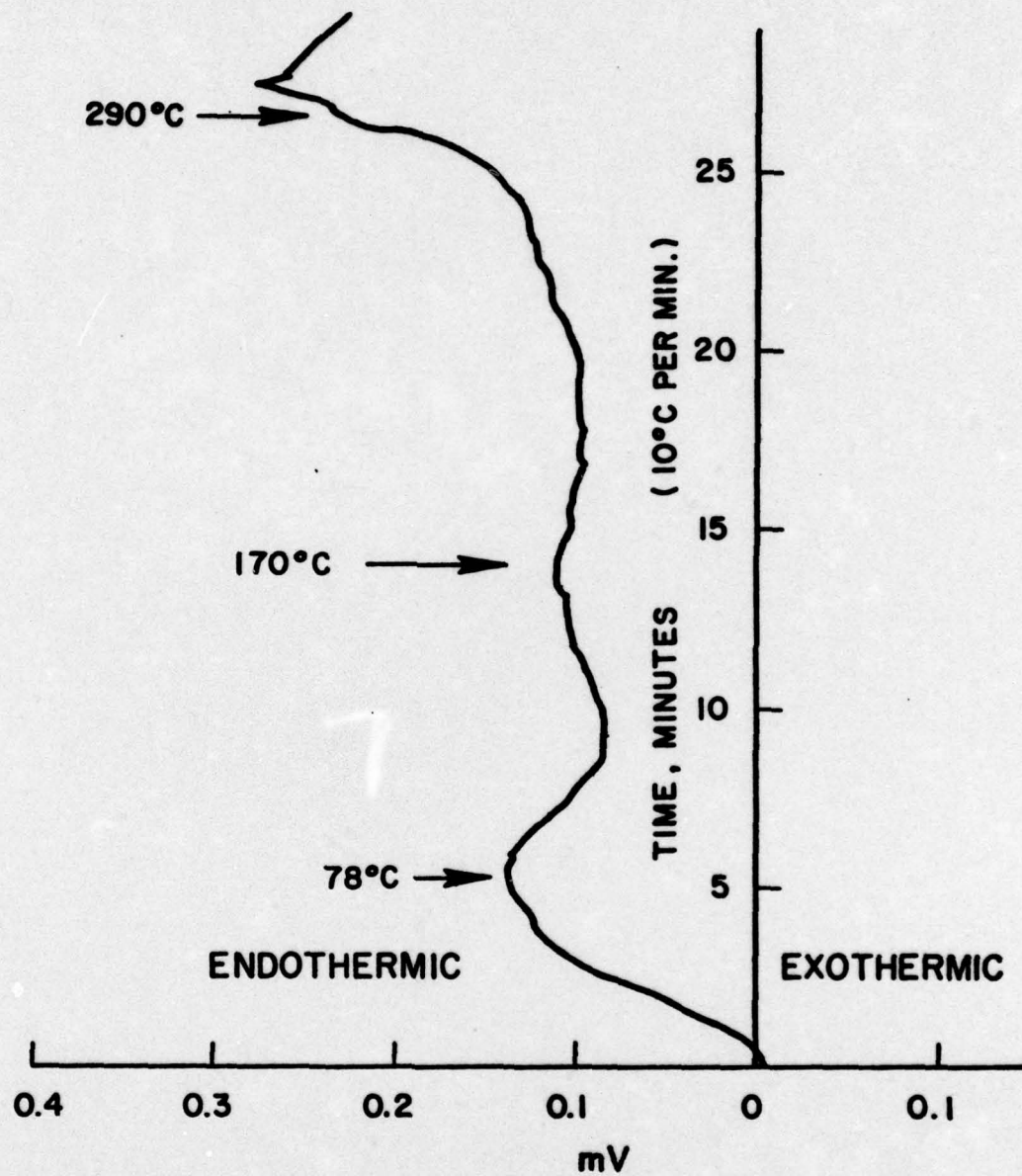


Fig. 14. (DTA) thermogram of  $\text{SOCl}_2$  (0.2 ml)



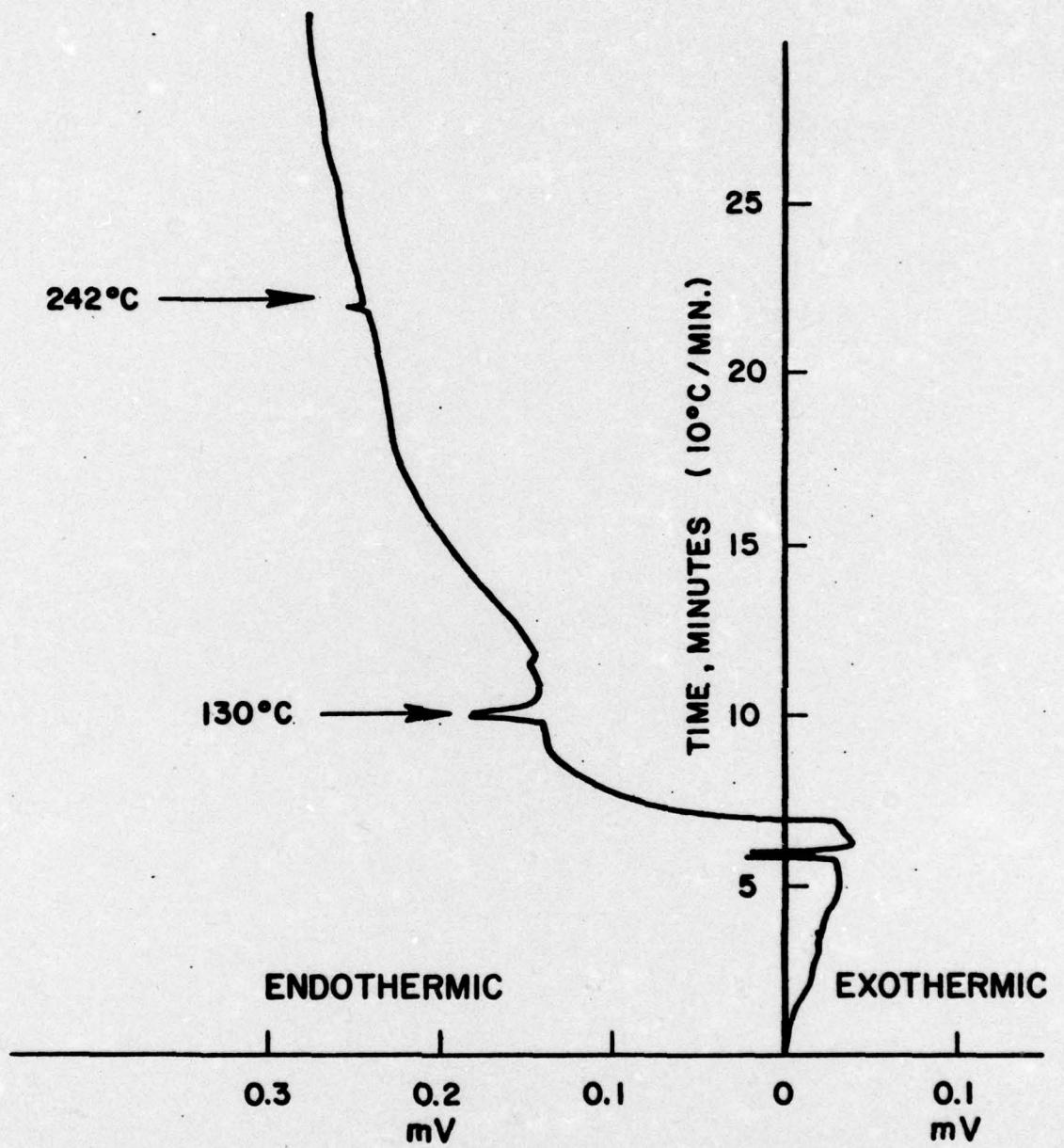


Fig. 15. (DTA) thermogram of carbon cathode mix (0.0281 gm)

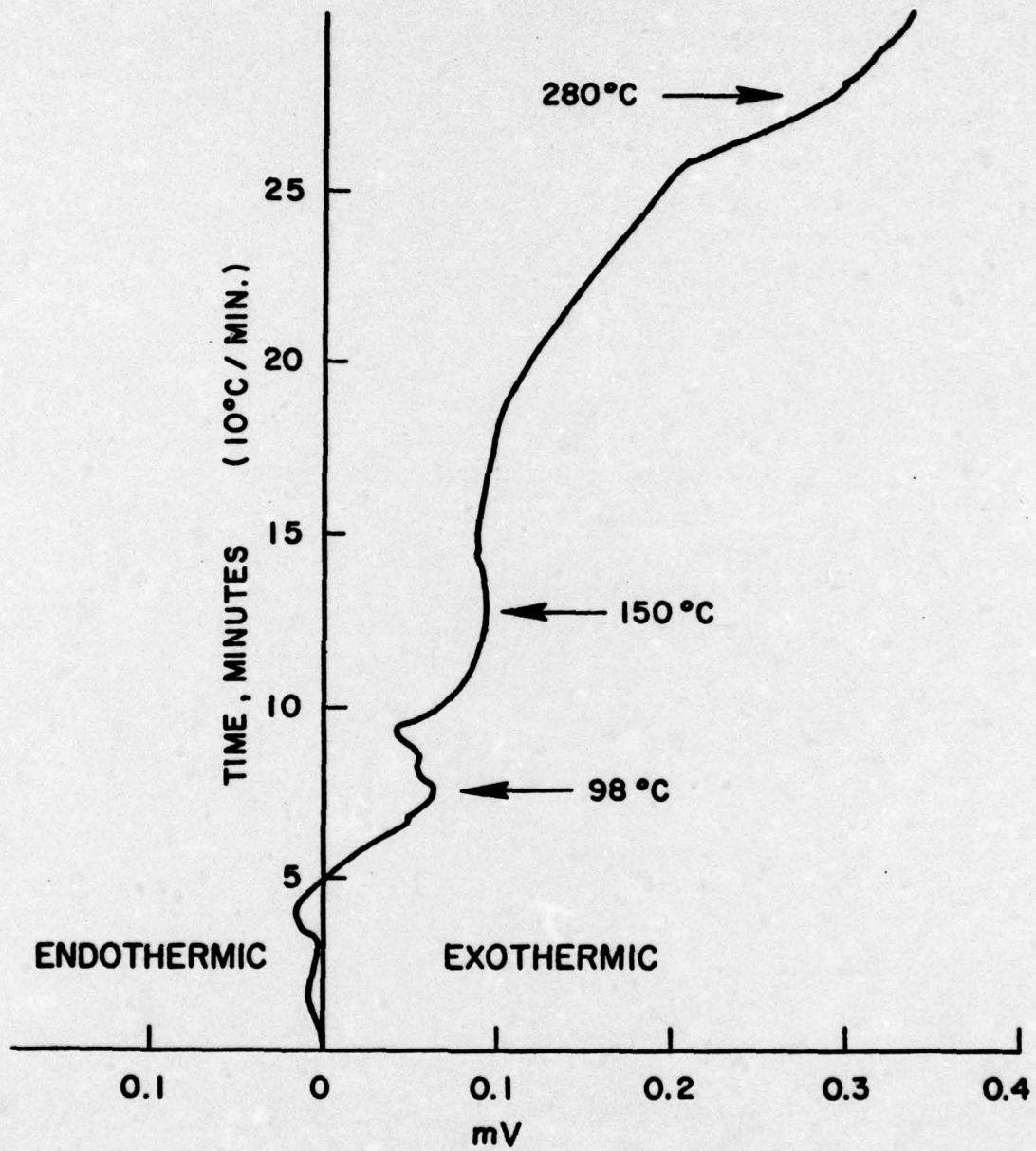


Fig. 16. (DTA) thermogram of S (0.0467 gm)



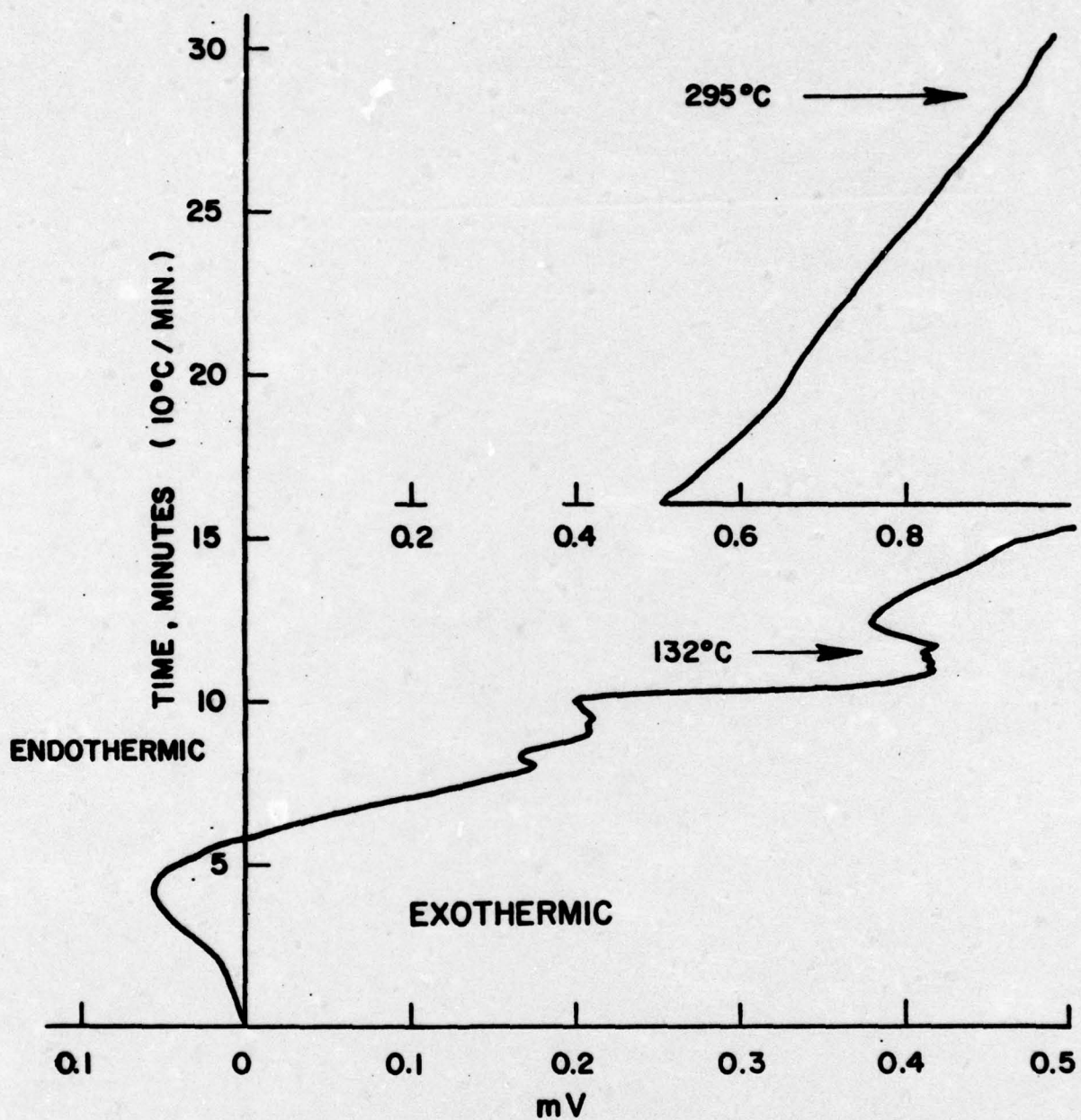


Fig. 17. (DTA) thermogram of S (0.1429 gm)

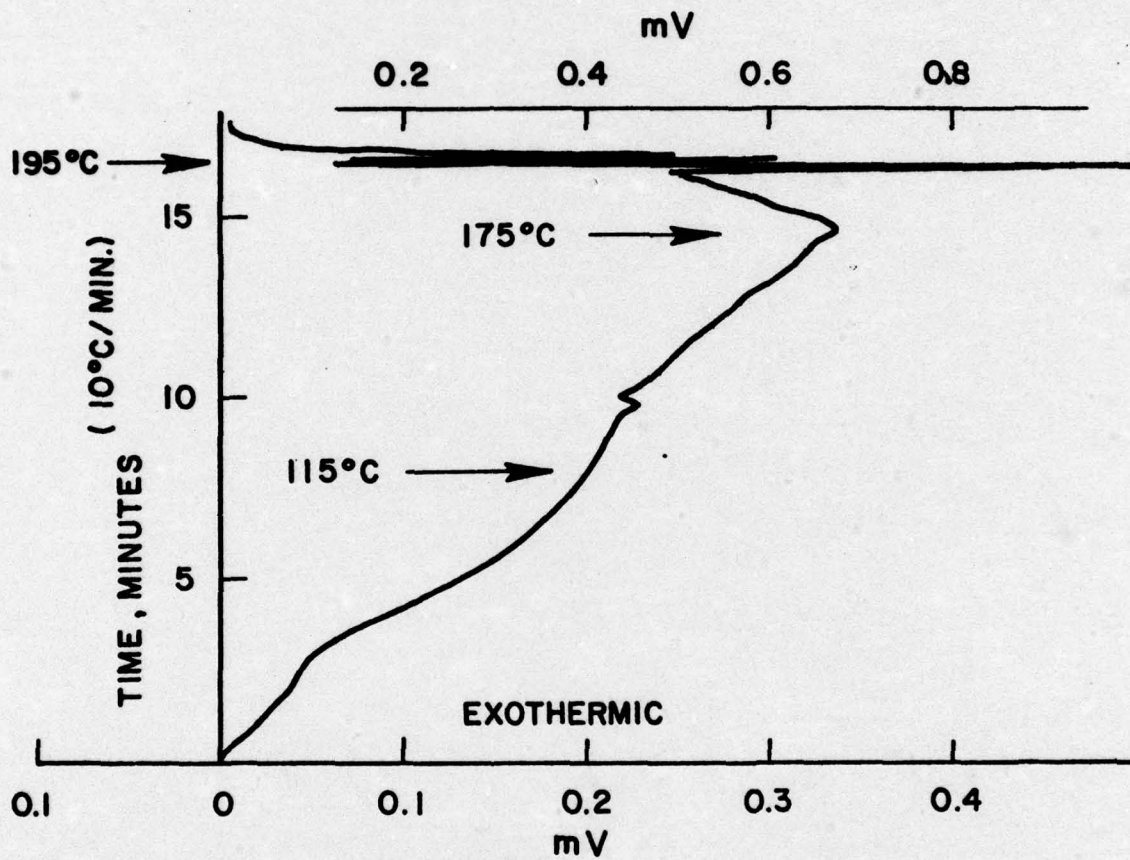


Fig. 18. (DTA) thermogram of Li (0.0327 gm)



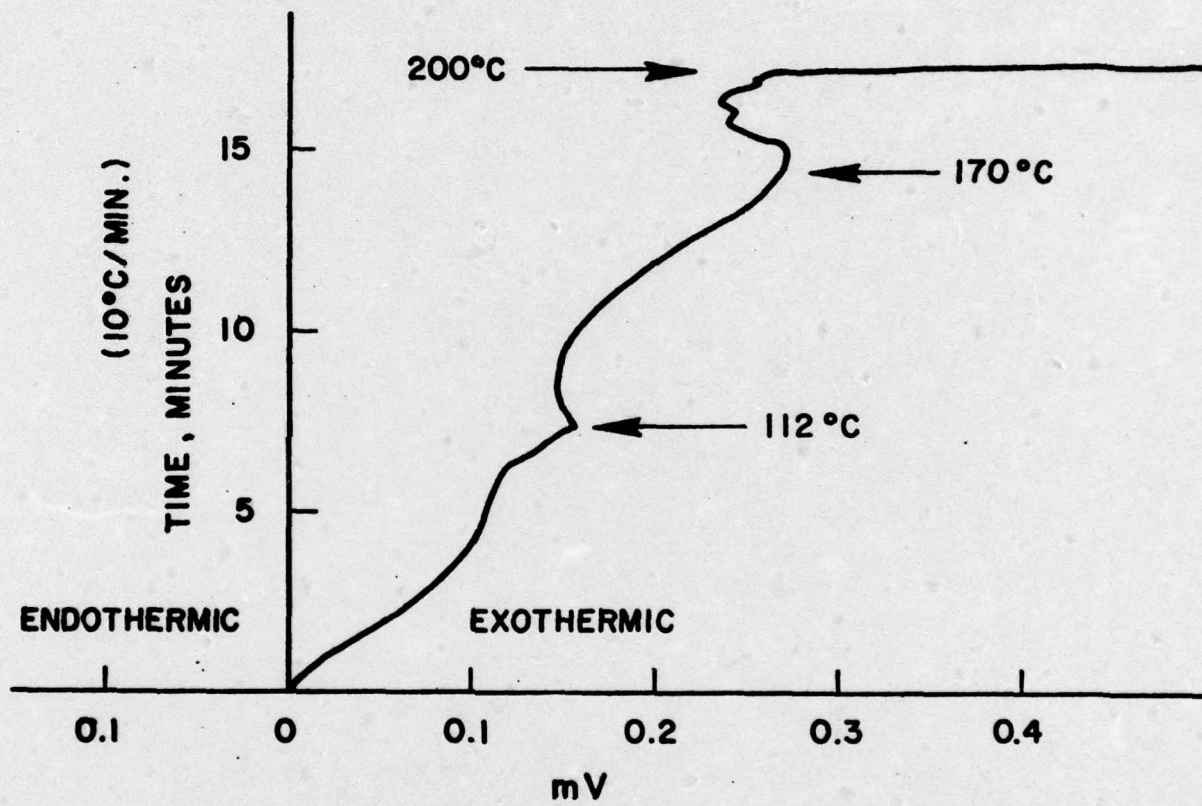


Fig. 19. (DTA) thermogram of Li (0.0352 gm)

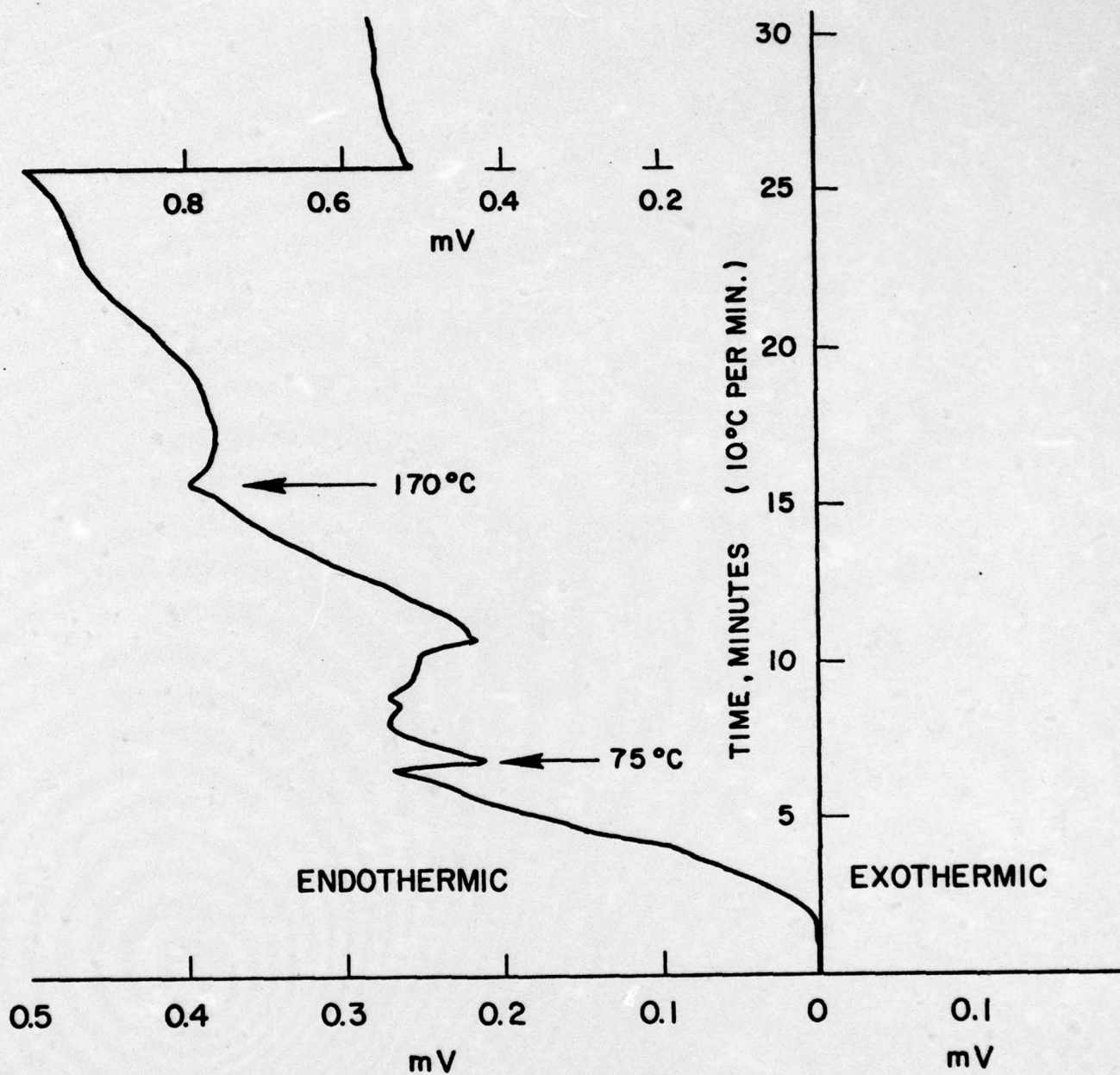


Fig. 20. (DTA) thermogram of S (0.0653 gm) + cathode mix (0.0165 gm) mixture



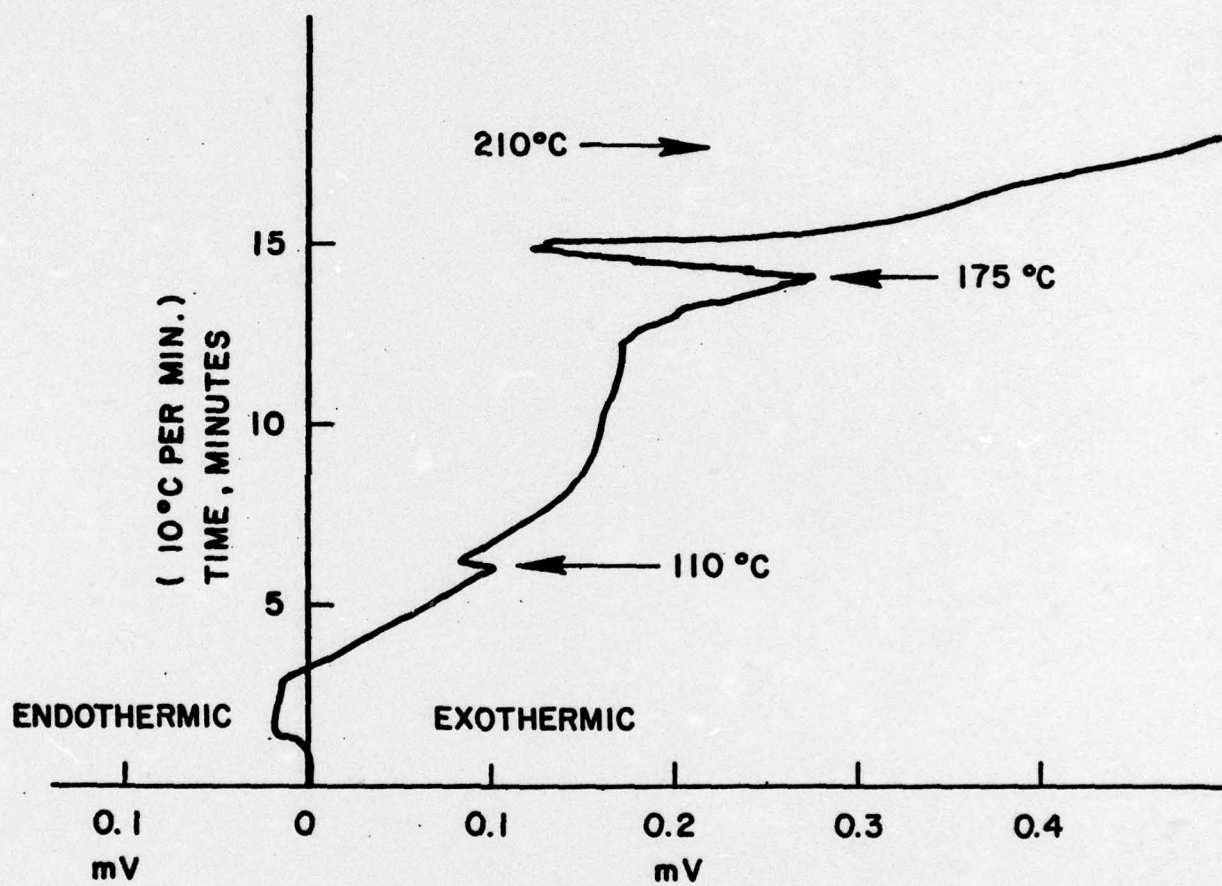


Fig. 21. (DTA) thermogram of Li (0.0256 gm) + SOCl<sub>2</sub> (0.1 ml) mixture.

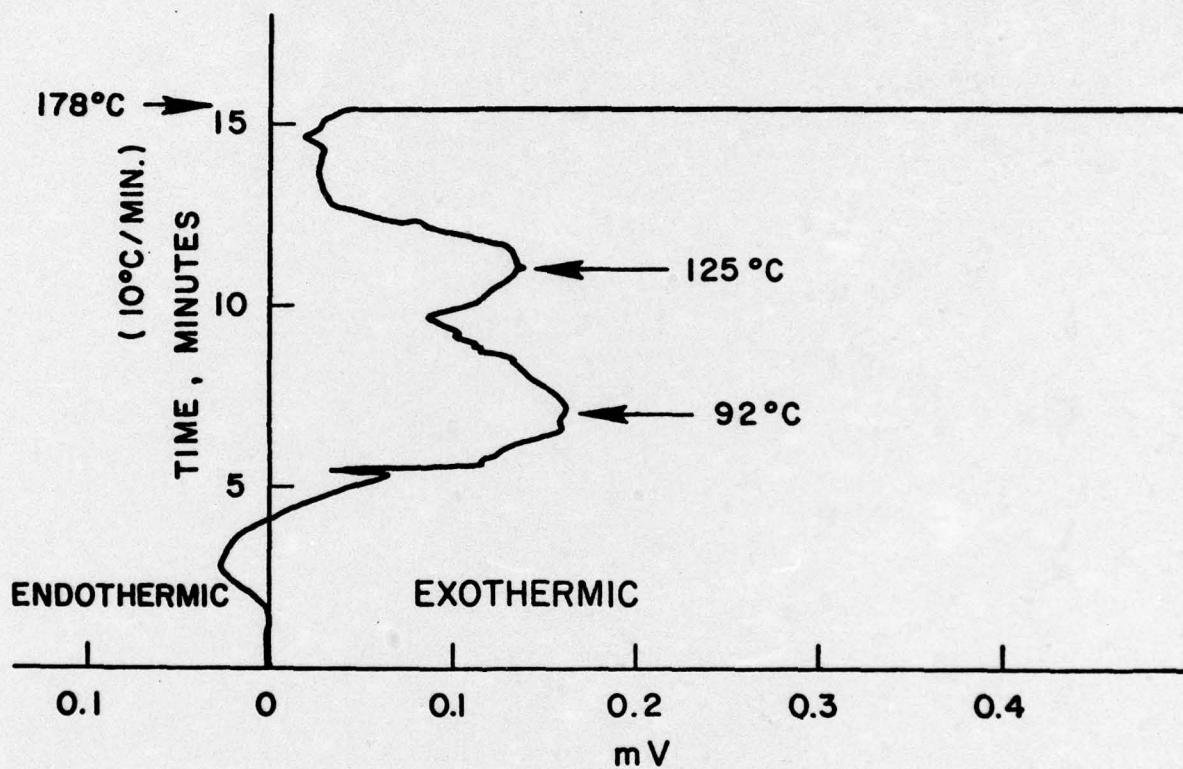


Fig. 22. (DTA) thermogram of Li (0.0135 gm) + S (0.0680 gm) mixture.



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