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P. R. MALLORY AND COMPANY, INCORPORATED
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SEALED PRIMARY
LITHIUM - INORGANIC ELECTROLYTE CELL

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Although the hermetic Li/$SOCl_2$ D cells developed by P. R. Mallory & Co. Inc met and exceeded all the objectives in regard to the energy density and the power density, the cells presented an explosion hazard on abuse and a voltage delay problem after high temperature storage and we investigated both these problem areas and made significant progress in both.

Recently, we have been examining the Li anode film which causes the voltage-

delay problem using SEM. We gathered data on the morphology and the rate of film growth as a function of various electrolyte variables such as $LiAlCl_4$ concentration, additives such as S_2Cl_2, and SO_2. Based on the available data we proposed a tentative model to describe the Li film growth process. We found earlier that film growth rate could be reduced by reducing the $LiAlCl_4$ concentration in the electrolyte. We also found that the LiCl film morphology can be changed dramatically by the addition of SO_2. During the last quarter we evaluated the effect of the above electrolyte variables on the voltage-delay characteristics of the $Li/SOCl_2$ D cells. We found that the $LiAlCl_4$ concentration affects both the voltage-delay and the intrinsic energy density of the $Li/SOCl_2$ D cells. The 1.0 and 0.5 (M) $LiAlCl_4$-$SOCl_2$ was the best from both the voltage-delay and the energy density stand points. We found that 10% (6 wt %) S_2Cl_2 did not affect the voltage-delay significantly.

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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). The cells contain an Li anode, a carbon cathode and an $LiAlCl_4$-$SOCl_2$ electrolyte. $SOCl_2$ acts both as a solvent and as a depolarizer. We carried out a systematic investigation of the system over the 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 (1) of the system for the realization of maximum possible energy density in a commercially viable structure (hermetic D cell), and (b) the identification and definition of problems (2-12) associated with the system and the development of approaches to solve these problems.

The original objective of this program (3-12) was to develop a D cell which is storable and operable in the temperature range of -40 to 160°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 $Li/SOCl_2$ D cells developed by us (3-7). However, we found that the system suffered from two inherent deficiencies:

(a) Explosion hazard, particularly on shorting and forced as well as on resistive load overdischarge.

(b) Voltage delay, particularly after storage at high temperatures and test at low temperature.

We investigated the explosion hazard problem in a phenomenological manner (4-7). First we established the conditions under which the hermetic $Li/SOCl_2$ D cells explode. Then we attempted to develop ways and means to prevent the explosion. We found that the lowering of the 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 on the system. All known batteries including Li/SO_2 render themselves harmless from thermal runaway after all the energy has been drained by prolonged resistive load over discharge. However, this is not the case with the thionyl chloride system. A completely discharged battery, while sitting on the shelf at 25°C, may explode quite unexpectedly. This is of particular concern since it is impossible to prevent resistive load over discharge and/or storage of partially and/or completely discharged battery in any normal use. We believe, that this problem needs to be solved before the field use of the system, particularly in a D cell size, can be recommended.

In order to address this problem we need to know the chemistry, particularly the thermochemistry of the system in a discharged and partially discharged state. We procured a Differential Thermal Analyzer (DTA) for carrying out DTA analysis of the chemical compounds and their mixtures that may be present in a partially discharged Li/$SOCl_2$ cell. The purpose of the DTA approach is to identify the exothermic reactants that might either initiate or propagate any explosive reactions in the system. Once these are identified, one may then attempt either to eliminate the reactants, if possible, or render them inactive by means of suitable inhibitors. The details of the DTA experiments and some initial results are reported in the 10th quarterly report (12). We plan to resume this important work during the next quarter.

We studied the voltage delay problem in sufficient detail to define its undrlying cause (2, 4-12). We established that the voltage-delay of the Li/$SOCl_2$ cells was due to 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. We also established that the film is primarily composed of LiCl crystals. The main objective for this part of the investigation was to establish the extent to which 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 initial results are reported in the 8th, 9th and 10th quarterly reports (10-12). It was possible to reduce the film growth substantially by reducing the $LiAlCl_4$ concentration in the electrolyte. We presented the SEM photographs of the Li anode film formed at the various temperatures in the various inorganic electrolytes in the previous reports (10-12) in order to demonstrate the morphology of the film. We showed that the addition of SO_2 definitely altered the morphology of the film. We found that the LiCl film displayed a high level of epitaxy in the presence of SO_2.

We completed the collection of the SEM data during the last quarter and developed a qualitative model to describe the Li film growth phenomenon to the systems studied. The model and the results are described in this report.

We also evaluated the effects of the salt concentration and of additive such as S_2Cl_2 and SO_2 on the voltage-delay of the $Li/SOCl_2$ D cells. The results are discussed here.

II. A Qualitative Model for the Li Film Growth

We continued the Li film growth measurements in the following electrolytes for storage durations extending to 280 days for some of the electrolytes.

1. 0.5 (M) $LiAlCl_4$-$SOCl_2$
2. 0.25 (M) $LiAlCl_4$-$SOCl_2$
3. 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 1 gm $AlCl_3$/100 ml of electrolyte
4. 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 0.01 gm H_2O/100 ml of electrolyte
5. 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 0.1 gm H_2O/100 ml of electrolyte
6. 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 10 gm S_2Cl_2/100 ml of electrolyte (6 wt %)
7. 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 17.3 gm SO_2/100 ml of electrolyte(11 wt % SO_2)

The growth rate curves are shown in Figures 1 through 7.

The following observations were made in regard to the film growth.

1. Two general types of film growth were observed: one consisted of a cluster type of growth over a bed of small crystals, the clusters became taller and thicker with storage and finally a third layer of smaller crystals grown on top of all this. This is shown schematically in Fig. 8 (a) which represents the type of growth experienced in all the electrolytes studied particularly at lower temperatures except in the 11 wt % SO_2 electrolyte. In the case of the SO_2 containing electrolyte, large well defined cubic crystals grew in a regular manner over a bed of small crystals, the large crystals became larger and larger on storage and covered the whole surface as shown schematically in Fig. 8 (b).

2. The rate of film growth was reduced significantly by decreasing the $LiAlCl_4$ concentration from 0.5 (M) to 0.25 (M).

3. High temperature storage some time resulted in the formation of large interlocking crystals and the growth rates tended to level off, whereas at lower temperatures (25°C) the crystals were smaller and the film growth continued without leveling off.

A qualitative model of Li film growth which conforms to the above general observation is described below.

The Li metal used in all the studies mentioned was processed by the manufacturer in dry air (RH $\simeq$ 2%) instead of in dry argon. This was done because of the extremely low reactivity (13) of Li metal with dry O_2, CO_2 and N_2. Moisture enhances the rate of the above reaction leading to the tarnishing of the Li foil. Therefore, it is reasonable to assume that the apparent stability of Li in dry air is due to the kinetic inhibition of the following thermodynamically favorable reactions caused by the presence of Li_2O, LiOH, Li_2CO_3 and Li_3N films on the Li surface:

$$6\,Li + N_2 \rightarrow 2\,Li_3N \qquad [1]$$

$$\Delta H = -94.4 \text{ k.cal}$$

$$4\,Li + O_2 \rightarrow 2\,Li_2O \qquad [2]$$

$$\Delta H = -284.8 \text{ k.cal}$$

$$2\,Li + H_2O + CO_2 \rightarrow Li_2CO_3 + H_2 \qquad [3]$$

$$\Delta H = -138.7 \text{ k.cal}$$

$$2\,Li + 2\,H_2O \rightarrow 2\,LiOH + H_2 \qquad [4]$$

$$\Delta H = -117.4 \text{ k.cal}$$

The effectiveness of the above protective coatings may be judged according to Pilling-Bedworth (14) ratio (R),

$$R = \frac{V_s}{n V_{Li}} , \qquad [5]$$

V_s = molar volume of the Li compound,

n = no. of gram atoms of Li in one mole of the compound,

V_{Li} = gram atomic volume of Li

which has to be one or more to provide corrosion protection. The R values of some of the Li compounds are shown in Table 1. It appears that both LiOH and Li_2CO_3 film are expected to be protective in nature. However, LiOH forms monohydrate and could continue (12) to react further with Li metal and other film forming materials such as Li_3N to continue the film build-up process without giving any protection. Li_2O and Li_3N forms a porous film since the R values are less than one. Only Li_2CO_3 can provide good protection by virtue of its high R value. Therefore, it is reasonable to assume that before the Li metal is brought in contact with the inorganic electrolyte, the metal surface is already coated with

(i) A thin protective relatively dense film of Li_2CO_3, and

(ii) A porous film of Li_2O and Li_3N.

On contact with the $SOCl_2$ the Li_2CO_3 film may chemically react to form the protective LiCl film as:

$$Li_2CO_3 + SOCl_2 \rightarrow 2\,LiCl + CO_2 + SO_2 \qquad [6]$$

The rate of the LiCl film forming reactions in the regions covered with Li_2CO_3 is expected to be low because of the slow diffusion of the reacting species through the Li_2CO_3 and LiCl protective films. The bed of small LiCl crystals which form initially, as depicted in Figs. 5 (a) and (b) may have formed in these regions.

In view of the fact that Li was found to be non-reactive (13) towards dry O_2 and CO_2 even at temperatures as high as 250°C, it is reasonable to assume that the major portion of the surface remains covered with the protective film of Li_2CO_3 and a minor portion of the Li surface is covered with the porous Li_2O and Li_3N films. The growth of tall stacks of LiCl crystals as shown in Fig. 8 may have occurred in the latter region which is covered by the porous Li_2O and Li_3N films, since the rate of reaction with $SOCl_2$ is expected to be greater through the porous film. The general observations in regard to the growth of clusters of large crystals or single large crystals (Figs. 8 (a) and (b)) over a bed of uniformly grown smaller crystals is explained in this manner. According to this model, the thin films which are present on the Li surface prior to its contact with the electrolyte, controls the initial phase of the LiCl growth in the inorganic electrolyte.

The subsequent growth of the LiCl film is controlled by the electrolyte variables. In view of the fact that the SEM pictures of the LiCl films (which are as thick as 384 microns) were taken without applying any conducting coating such as vapor deposited Al or Au, as is customary for photographing the insulating oxides for preventing charging up of the surface, it is reasonable to assume that the LiCl crystals grown in the inorganic electrolytes containing $LiAlCl_4$-$SOCl_2$ must have sufficient defects (caused by the impurities present in the crystals) to make these electronically conducting. One may view the growth of LiCl film as a result of a local cell reaction which is shorted through the LiCl film as schematically shown in Fig. 9. The anodic reaction involving the dissolution of Li occurs near the pores of the film and the cathodic reaction involving the formation of LiCl occurs on the LiCl film itself, thus causing the LiCl crystals and the film to grow. The steps that could control this film growth are as follows:

1. Li^+ transport through the pores.
2. Electronic conduction of the LiCl film, and
3. Li^+ ion conduction of a LiCl film.

The fact that the film growth rate is dependent on the $LiAlCl_4$ concentration in the electrolyte, indicates that step 1 is the controlling step for the film growth.

Thus, the rate of film growth, $\frac{d\theta}{dt}$ may be related to the surface concentration of the pores and the length of the pores.

(a) Film growth controlled by the surface concentration of pores.

The surface concentration of the pores can be expressed as the area of the surface not covered by the film, $(A-\theta)$ where A is the total available area which can be covered with LiCl cubic crystal, and θ is the dimension for cubic crystal related to the film thickness. The idealized process is shown schematically in Fig. 10 (a).

The rate of film growth can be expressed as

$$\frac{d\theta}{dt} = k\,(A-\theta) \qquad [7]$$

where k is a rate constant. Integration of [7] yields

$$\theta = A\,(1 - e^{-kt}) \qquad [8]$$

when $t = 0,\ \theta = 0$

and when $t \to \infty,\ \theta = A$.

this represents an asymptotic type of film growth. According to this type of growth, θ increases rapidly at first and then slowly levels off. The LiCl film growth in the $LiAlCl_4$-$SOCl_2$ electrolytes with SO_2 and at high temperatures (72°C) give rise to this type of growth (Figs. 1, 3, 5, 7). The large crystals which gradually grow and cover pores thus stopping further film buildup.

(b) Film growth controlled by the length of the pores.

This type of process is shown schematically in Fig. 10 (b). As the film grows thicker, the length of the pores increases, thus impeding the transport of Li^+. Therefore, the rate of growth is inversely proportional to the film thickness.

$$\frac{d\theta}{dt} = \frac{k}{\theta} \qquad [9]$$

Integration of [9] yields

$$\theta^2 = 2\,kt \qquad [10]$$

This is the well known parabolic law of film growth. According to this, the growth of the film continuous with time without even stopping. The Li film growth in all the electrolytes, particularly at low temperature (25°C) except in SO_2 containing electrolyte conforms to this type of behavior (Figs. 1-7).

Thus, the tentative model of film growth proposed above qualitatively conforms to all the experimental observations. The data available to date are insufficient to do any quantitative analysis.

III. Performance Characteristics of Fresh $Li/SOCl_2$ D Cells with 1.8 (M), 0.5 (M), 0.25 (M) and 0.1 (M) $LiAlCl_4$-$SOCl_2$ Electrolytes

We found earlier, that the concentration of $LiAlCl_4$ in $SOCl_2$ had a significant effect on the Li anode film growth. We planned to evaluate the effect of the $LiAlCl_4$ concentration on the voltage-delay characteristics of the $Li/SOCl_2$ D cell. But, before that, we decided to determine the effect of the $LiAlCl_4$ concentration on the rate capability and the energy density of the fresh $Li/SOCl_2$ cells. Accordingly, we made D size cells using 1.8 (M), 0.5 (M), 0.25 (M) and 0.1 (M) $LiAlCl_4$-$SOCl_2$ electrolytes and discharged these at 25°C at constant current ranging from 0.01 to 3.0 A depending upon the $LiAlCl_4$ concentration. The performance characteristics of the cells are discussed below.

A. Experimental

Hermetic D cells were made in Ni cans with G/M seals and welded tops using the methods described in the second quarterly report (4). The electrode dimensions of both the Li anode and the carbon cathode were 20" x 1.75". The electrolytes were made according to the procedure described earlier (3). The cells were discharged at constant currents at ambient (25°C) temperature within one week of electrolyte filling.

B. Results and Discussion

The discharge curves of the $Li/SOCl_2$ D cells with 1.8 (M) electrolyte on constant current loads of 0.1, 0.3, 1.0 and 3.0 A at 25°C are shown in Fig. 11. The capacities delivered at the above currents were 13.8, 12.0, 13.5 and 10.5 A.Hrs respectively. The short second plateau on the 0.1 A discharge is rather peculiar. This has never been shown before at 25°C. Also, the poor voltage regulation at 3 A is noteworthy. However, the delivered capacities remained virtually unchanged up to 1.0A, considering the cell to cell variation. This is typical of the high rate D cell designs. D cells having similar construction and with 1 (M) electrolyte were tested earlier (7). They delivered 12.7, 13.2, 12.0, 12.2 and 9.7 A.Hr at drains of 0.25, 0.75, 1.0, 2.0 and 3.0 A respectively. Again, considering the usual cell to cell variation, the capacities were unchanged up to 1.0 A. Thus, the performance characteristics of the high rate D cells remained unaffected by decreasing the salt concentration from 1.8 to 1.0 (M).

The discharge curves of the $Li/SOCl_2$ D cells with 0.5 (M) electrolyte on constant current drains of 0.03, 0.1, 0.3, 1.0 and 3.0 A at 25°C are shown in Fig. 12. Note that the voltage regulation is excellent at low rates, as usual, but it deteriorates at high rates. The capacities delivered at the above currents were 14.5, 13.8, 13.4, 8.5 and 4.5 A.Hrs respectively. Note that the capacities remained quite high up to a drain of 0.3 A; it began to drop drastically above 1.0A. This reflects the effect of the salt concentration on the rate capability of the cells. The conductivity of the 0.5 (M) electrolyte (0.7 x 10^{-2} $ohm^{-1}cm^{-1}$) is almost half that of the 1.0 (M) electrolyte (1.5 x 10^{-2} $ohm^{-1}cm^{-1}$). This results in poorer ionic transport in the cathode thus causing a lowering of the rate capability, as expected.

The discharge curves of the D cell with the 0.25 (M) electrolyte are shown in Fig. 13. The cells delivered 16.3, 14.9, 12.1 and 6.8 A.Hr at 0.01, 0.03, 0.1 and 0.3 A drains respectively. Note that the cell capacity began to drop sharply at even a slow current as 0.3 A, showing even further reduction in the rate capability of the cells with the lower salt concentration in the electrolyte.

With the 0.1 (M) electrolyte, the rate capability of the D cells decreased further as evidenced by the discharge curves shown in Fig. 14. The cells delivered 13.1, 13.7, 8.9 and 3.5 A.Hr at 0.01, 0.03, 0.1 and 0.3 A respectively. Here, the capacity degradation began at 0.1 A.

The capacity-rate curves of the Li/$SOCl_2$ D cells with 1.8, 1.0, 0.5, 0.25 and 0.1 (M) $LiAlCl_4$-$SOCl_2$ electrolytes are shown in Fig. 15. The lowering of the $LiAlCl_4$ concentration beyond 1 (M) leads to a lowering of the rate capability of the cells but an increase in the intrinsic capacity (capacity at low rate) of the cells. The latter has been found (15) to be true in C size cells, and was presumed to be due to the increased precipitation of $LiAlCl_4$ in the cathode with the higher initial $LiAlCl_4$ concentration in $SOCl_2$ which is depleted on discharge.

Thus, the lowering of the $LiAlCl_4$ concentration appears to be beneficial with respect to the cell capacity at low rates, but detrimental with respect to the rate capability in so far as the fresh performance at room temperature is concerned.

The performance characteristics of all the above cells are summarized in Table 2.

IV. Effect of Electrolyte Variables on the Voltage-Delay of $Li/SOCl_2$ Hermetic D Cell

From SEM studies (10-12) we found that electrolyte variables affected the morphology and the growth rates of Li anode film. The purpose of this investigation was to determine the effect the above changes might have on the voltage-delay of the $Li/SOCl_2$ D cells. We found that a lowering of the $LiAlCl_4$ concentration in the electrolyte resulted in a lowering of the rate of film growth. Although we carried out the SEM studies using only two $LiAlCl_4$ concentrations viz. 0.5 and 0.25 (M) we felt that it is necessary to examine the voltage-delay characteristics of the cells with a wider range of salt concentrations since the cause and effect relationship between the Li film and the voltage-delay may be quite complicated. For example, according to our model, based on our earlier findings (2), the initial voltage depression on load occurs as a result of the concentration polarization across the pores of the LiCl film on the Li anode. A lowering of the $LiAlCl_4$ concentration leads to a thinner LiCl film and a lower pore length thus decreasing the concentration polarization. But, at the same time, the lowering of the $LiAlCl_4$ concentration also leads to a decreasing of the electrolytic conductivity of the electrolyte, thus leading to an increase in the anode polarization. Therefore, it is necessary to determine the optimum $LiAlCl_4$ concentration where the above opposing effects are minimized for a minimum initial anode polarization. This can be accomplished by experiments with actual cells.

We found that S_2Cl_2 (electrolyte additive) did not change either the morphology or the film growth rates in any significant way. We included it in this investigation also in order to determine whether S_2Cl_2 might affect the voltage-delay of the D cells. We included the SO_2 additive in this study, in view of its dramatic effects on the LiCl film morphology. The experimental details and the results are presented below.

A. Experimental

$Li/SOCl_2$ D cells were made with the following electrolyte variables, using the methods and in the procedure described in the previous section.

1. 1.8 (M) $LiAlCl_4$-$SOCl_2$
2. 1.0 (M) $LiAlCl_4$-$SOCl_2$
3. 0.5 (M) $LiAlCl_4$-$SOCl_2$
4. 0.25 (M) $LiAlCl_4$-$SOCl_2$
5. 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 10% S_2Cl_2 (6 wt %)
6. 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 17% SO_2 (11 wt %)

All the cells were fitted with low pressure vents.

The cells were stored at 72°C and were taken out every month and were cooled to -30°C for at least two hours and the voltage-delays were measured at constant currents of 3.0, 1.0 and 0.25 A. As soon as the cell voltage reached 2.0 volt, the tests were discontinued and the cells were re-stored at 72°C. The cell voltages were recorded on a strip chart recorder to determine the initial voltage depression and the subsequent recovery. The cells which exhibited no voltage depression below 2.0 volt on load were considered to have no voltage-delay. The cells which exhibited an initial voltage depression on load to a voltage below 2.0 volt, were considered to have a voltage delay measured as the time required for the voltage to reach 2.0 volt. The cells which did not recover to a 2.0 volt level within an hour of test, were considered to have infinite voltage-delay and to be inoperative. The results of all the voltage-delay tests are shown in Table 3.

B. Results and Discussion

Nine cells with 1.8 (M) $LiAlCl_4$-$SOCl_2$ electrolyte were tested at -30°C after the first month at 72°C, three cells at each current. The voltage delays of the three cells were 23, 33 and 31 seconds at 3.0 A test. However, after a second month at 72°C, none of the three cells recovered above 2.0 volt in 3.0 A test and were considered to be inoperative. On the 1.0 A test, although none of the three cells showed any voltage delay after the first month at 72°C, two of the three cells became inoperative after the second month. On the 0.25 A test none of the three cells showed any voltage-delay even after the second month at 72°C. The tests will be continued with longer periods of storage.

Ten cells with 1.0 (M) $LiAlCl_4$-$SOCl_2$ electrolyte, were tested after the first month at 72°C. After the second month, three cells were rejected because of cell venting during storage. Two of these cells were tested at 3.0 A and the other at 1.0 A after the first month. It is possible that the partial discharge during the voltage-delay measurement may have generated enough SO_2 according to cell reaction [11] to have caused the internal cell pressure to exceed 100 psi (the vent rating) at 72°C.

$$2\,SOCl_2 + 4\,Li \rightarrow 4\,LiCl + S + SO_2 \qquad [11]$$

After the first month, one of the three cells tested at 3.0 A was found to be inoperable. The other two showed voltage-delays of 162 and 204 seconds. One of these became inoperative after the second month and the other had its vent opened during storage. Three of the four cells tested at 1.0 A showed no delay after the first month, the fourth one had a voltage-delay of 27 seconds.

After the second month, one cell vented and the other three showed no voltage-delay. None of the three cells tested at 0.25 A showed any voltage-delay even after the second month of storage.

Only six cells with the 0.5 (M) $LiAlCl_4$-$SOCl_2$ electrolyte were tested after the first month at 72°C, two cells at each of the three currents. The cells showed voltage-delays of 290 and 177 seconds at 3.0 A after the first month and 172 and 665 seconds after the second month. Whereas none of the cells showed any voltage-delay at 1.0 and 0.25 A even after the second month of storage. Although, the statistical significance of the data is difficilt to ascertain because of the limited number of cells tested, the fact that none of the cells showed any delay at 1 A and that none of the cells became inoperative at 3.0 A even after two months of storage at 72°C, may indicate some improvement in the voltage-delay with the 0.5 (M) and 1.0 (M) electrolytes over the 1.8 (M) electrolyte.

Nine cells with the 0.25 (M) $LiAlCl_4$-$SOCl_2$ electrolyte were ready for test after the first month at 72°C. Eight of them were tested after the first month, two at 3.0A, three at 1.0 and 0.25 A each. The ninth one was tested at 3.0 A after the second month. At 3.0 A, the two cells showed voltage-delays of 124 and 352 seconds after the first month. The former of these two was tested with an external resistive load of 1 Ω (corresponding to current of approx. 3.0A, when the cell voltage is 3.0 volt) after the second month, and it showed no voltage-delay. The latter showed a voltage-delay of 464 seconds after the second month. The cell which was tested at 3.0 A after the second month for the first time, showed a voltage-delay of 300 seconds. The three cells tested at 1.0 A, after the first month showed voltage-delays of 110, 525 and 120 seconds respectively. The third cell was tested with an external resistive load of 3 ohms after the second month and showed a voltage-delay of 1150 seconds. The other two were tested at 1.0 A as usual after the second month of storage and showed voltage-delays of 290 and 261 seconds, respectively. Although none of the cells showed any voltage-delay at 0.25 A after the first month, two of the three cells tested at 0.25 A after the second month showed a voltage-delay of 55 and 350 seconds, respectively. The third cell was tested with a resistive load of 300 ohm after the second month of storage and showed no voltage-delay. The voltage-delays of these cells, in general, were found to be somewhat greater than that of the cells with 1.0 and 0.5 (M) electrolytes. This may be due to the lower electrical conductivity of the 0.25 (M) electrolyte. It is interesting to note that none of the cells with the 0.25 (M) electrolyte became totally inoperative even after the second month at 72°C as it did with the 1.8 (M) electrolyte.

Based on the above data, it may be tentatively concluded that from voltage-delay consideration the 1.0 and 0.5 (M) electrolytes are the best in terms of the $LiAlCl_4$ concentration. We showed earlier (1,15) that the above two electrolytes are also best from an energy density standpoint.

Nine cells with a 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 10% S_2Cl_2 electrolyte were tested after the first month at 72°C, three cells at each of the three currents. After the first month, although the cells tested at 1.0 and 0.25 A did not show any voltage-delays, the three cells tested at 3.0 A showed consistent voltage-delays of 138, 156 and 136 seconds respectively. One of the three cells became inoperative after the second month at the 3.0 A and the other two showed voltage-delays of 900 and 600 seconds, respectively. One of the three cells tested at 1.0 A became inoperative, one showed a voltage-delay of 330 seconds and the third one did not show any delay at all. None of the three cells showed any voltage-delay at 0.25 A after the second month. It is concluded, that the overall voltage-delay characteristics of these cells are similar to those with the 1.0 (M) electrolytes. Addition of 10% (6 wt.%) S_2Cl_2 to the above electrolytes did not cause any significant change in the voltage-delay characteristics of the cells. In this respect, the cause and effect relationship between the Li anode film and the voltage-delay is supported by these data.

Only three of the ten cells with 1.0 (M) $LiAlCl_4$-$SOCl_2$+17%(11 wt%) SO_2 electrolytes survived the first month of storage at 72°C, the rest vented during the 72°C storage due to the excessive pressure caused by the SO_2. Three cells were tested at the three currents and showed no voltage delay. However, these cells vented during the second month of storage at 72°C. We plan to repeat this experiment with cells having high pressure vents.

V. Conclusion and Future Work

The $LiAlCl_4$ concentration in $SOCl_2$ was found to have a significant effect on both the intrinsic energy density and the voltage-delay characteristics of the $Li/SOCl_2$ D cells. We found 1.0 and 0.5 (M) $LiAlCl_4$-$SOCl_2$ to be the best from both the energy density and the voltage-delay point of view.

Addition of 10% (6 wt %) S_2Cl_2 did not have any significant effect on the voltage-delay characteristics of $Li/SOCl_2$ D cells.

During the next quarter, we plan to make another batch of $Li/SOCl_2$ D cells with 1 (M) $LiAlCl_4$-$SOCl_2$+17% (11 wt %) SO_2 electrolytes and with a high pressure vent in order to evaluate the effect of SO_2 on the voltage-delay characteristics of the cells. We also plan to resume our work on the safety aspect of the $Li/SOCl_2$ system.

VI. References

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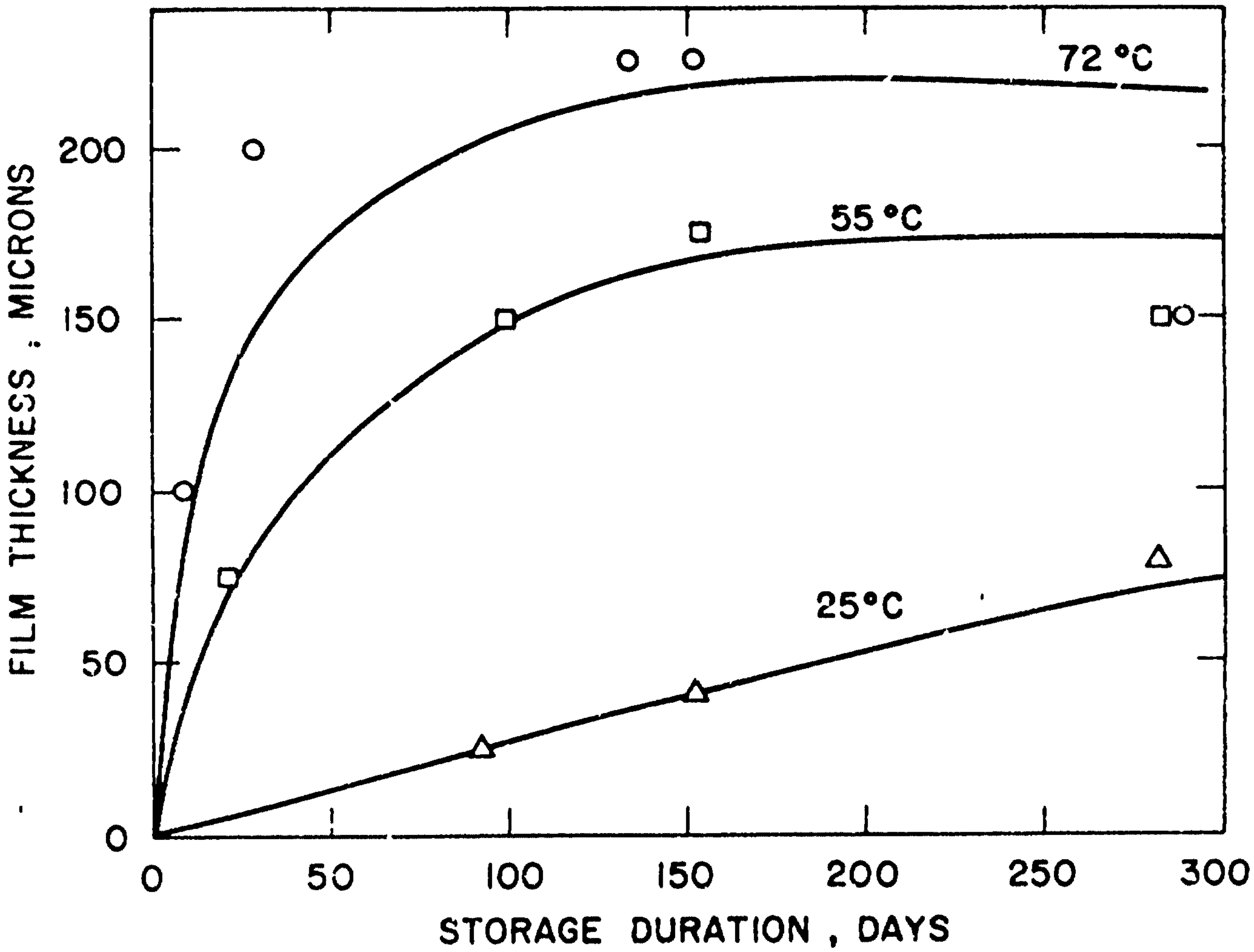

Figure 1. Li Film Growth on Storage in 0.5 (M) LiAlCl$_4$-SOCl$_2$ at 72°, 55° and 25°C

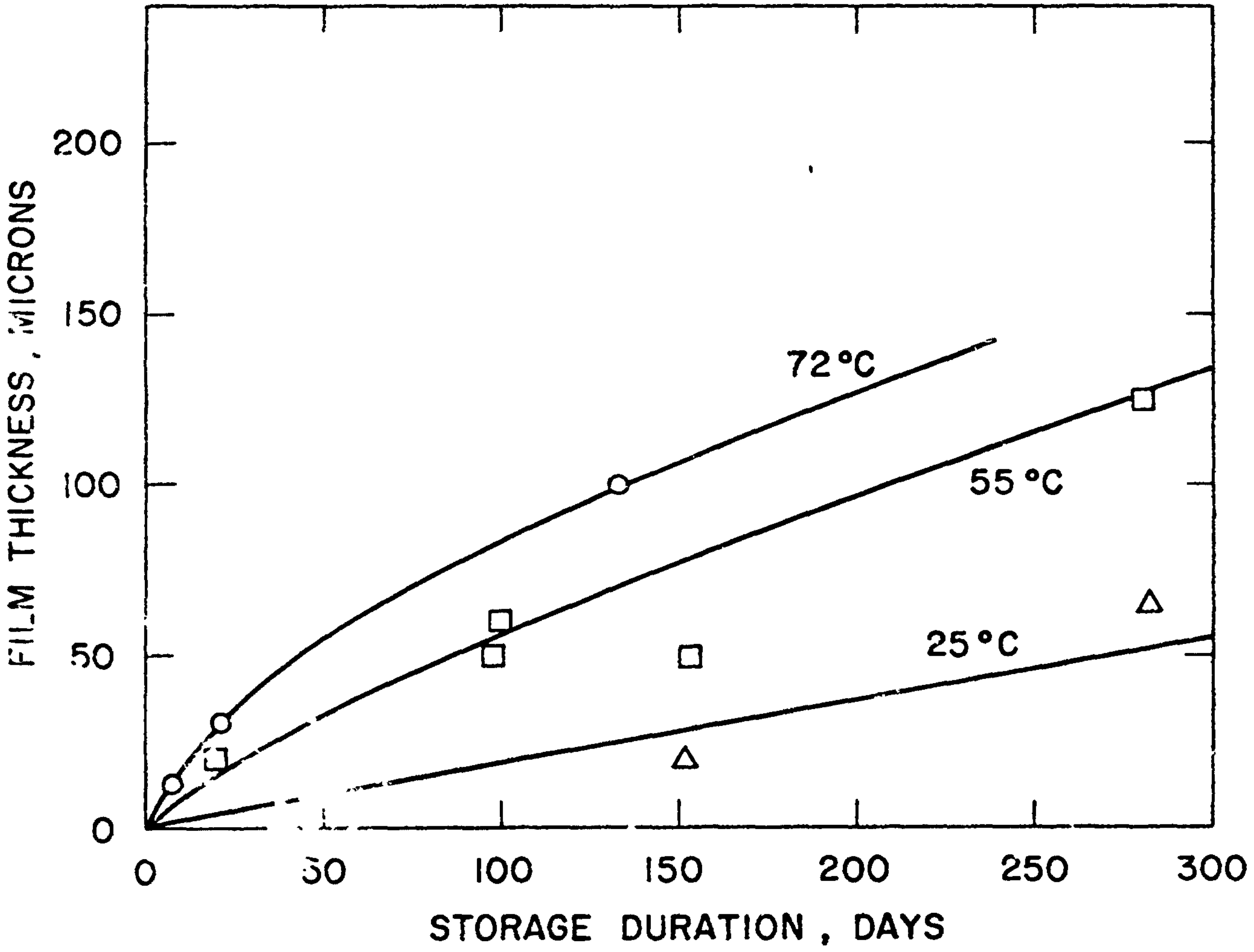

Figure 2. Li Film Growth on Storage in 0.25 (M) $LiAlCl_4$-$SOCl_2$ at 72°, 55° and 25°C

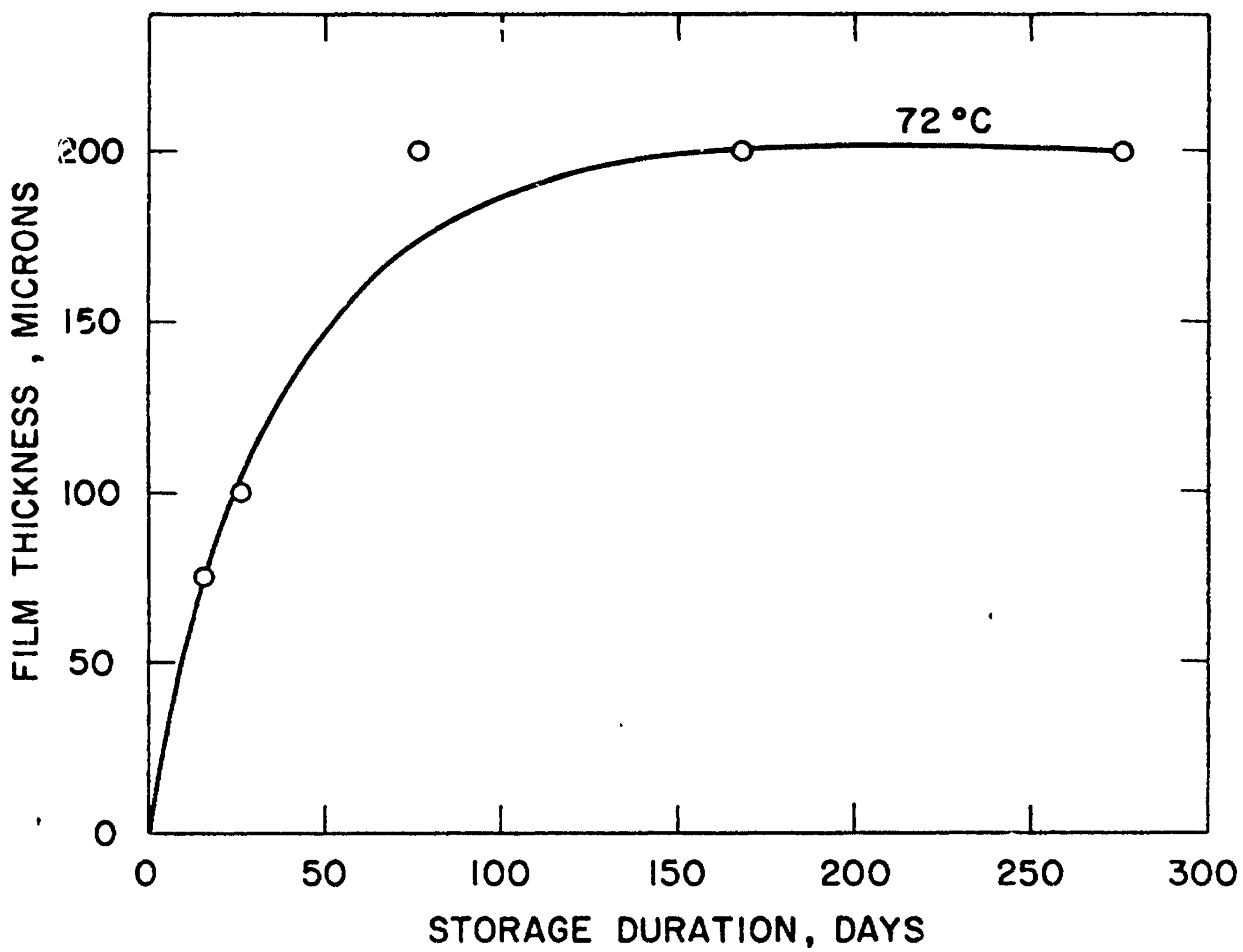

Figure 3. Li Film Growth on Storage in 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 1% $AlCl_3$ at 72°C

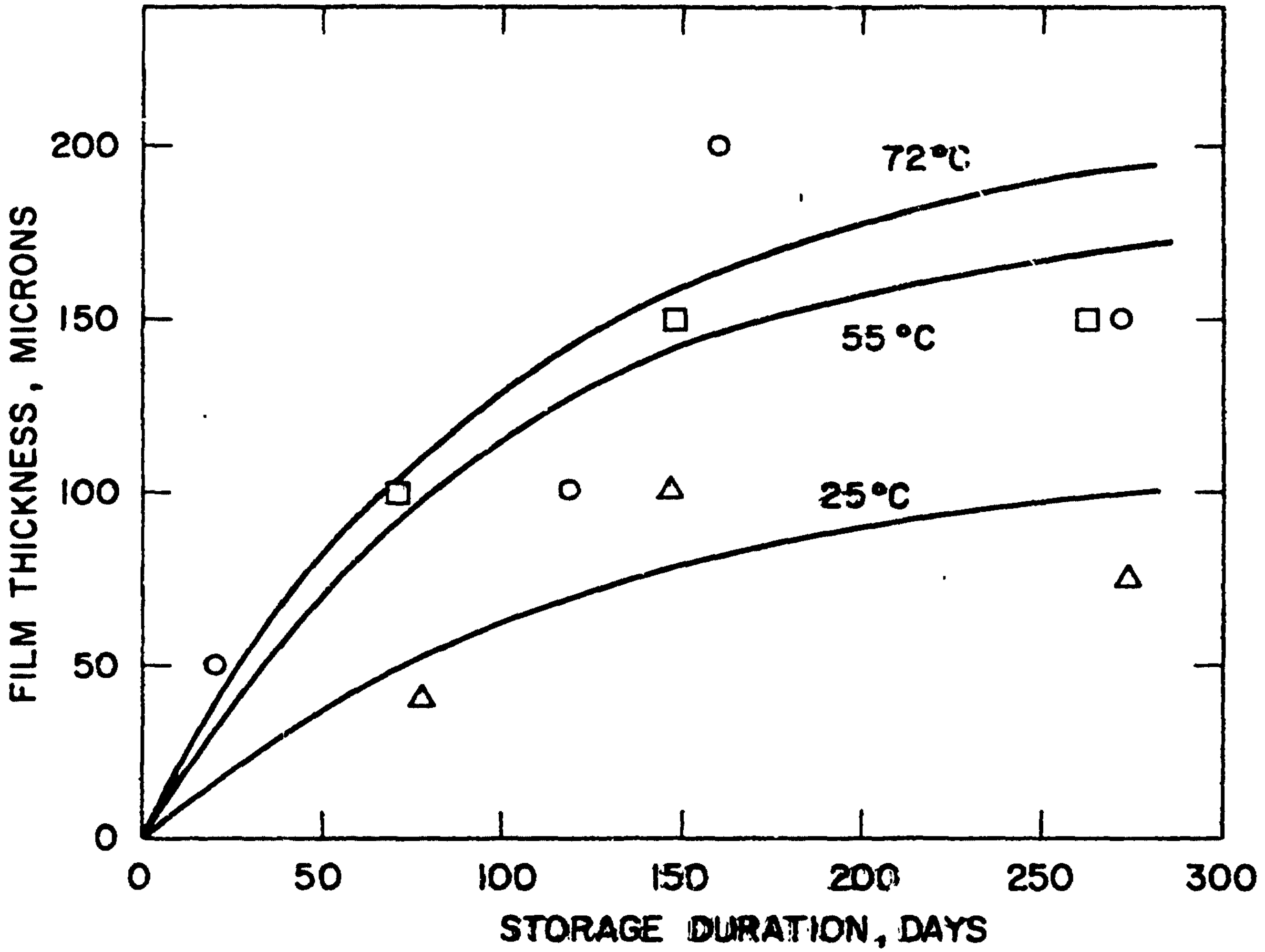

Figure 4. Li Film Growth on Storage in 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 0.01% H_2O at 72°, 55° and 25°C

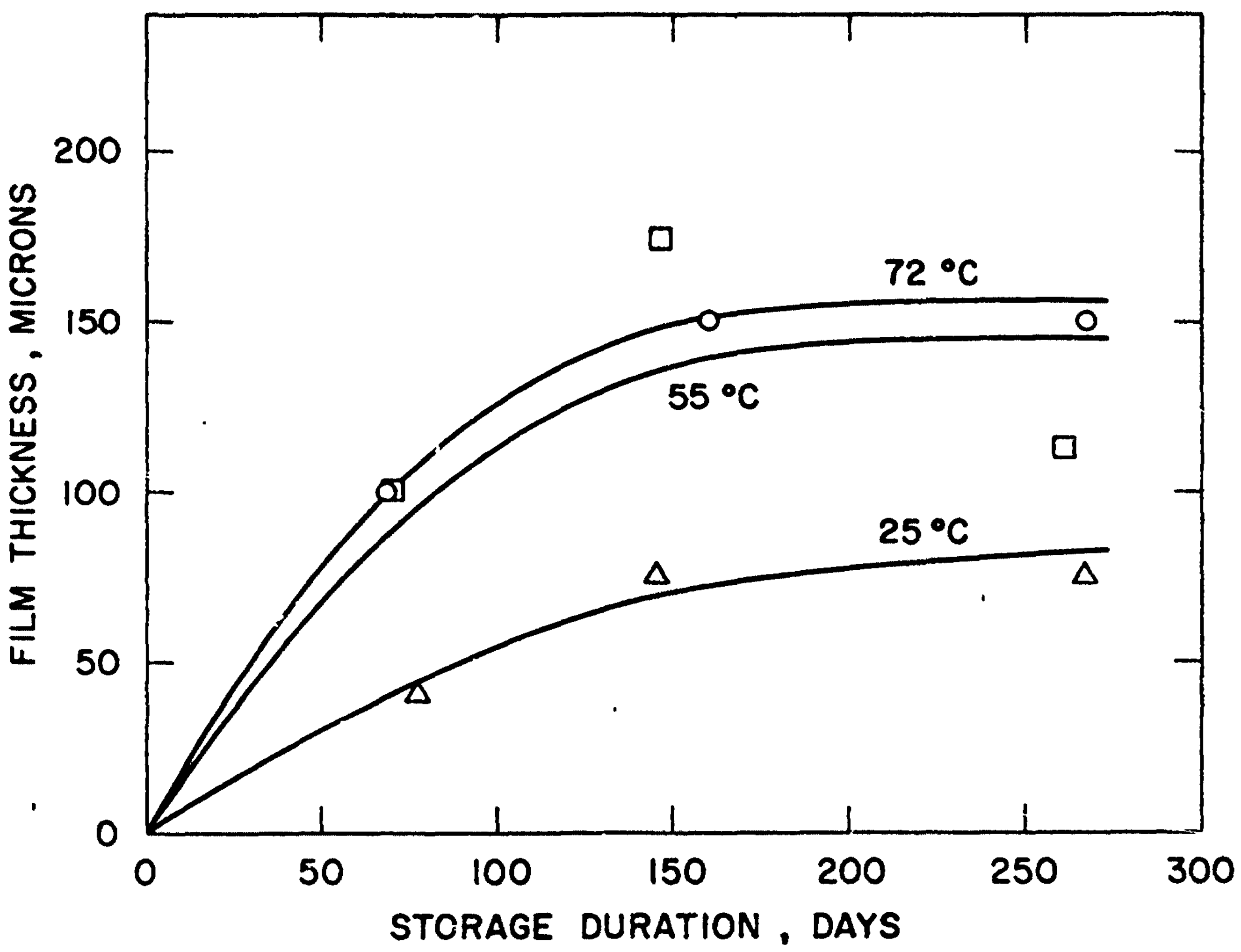

Figure 5. Li Film Growth on Storage in 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 0.1% H_2O at 72°, 55° and 25°C

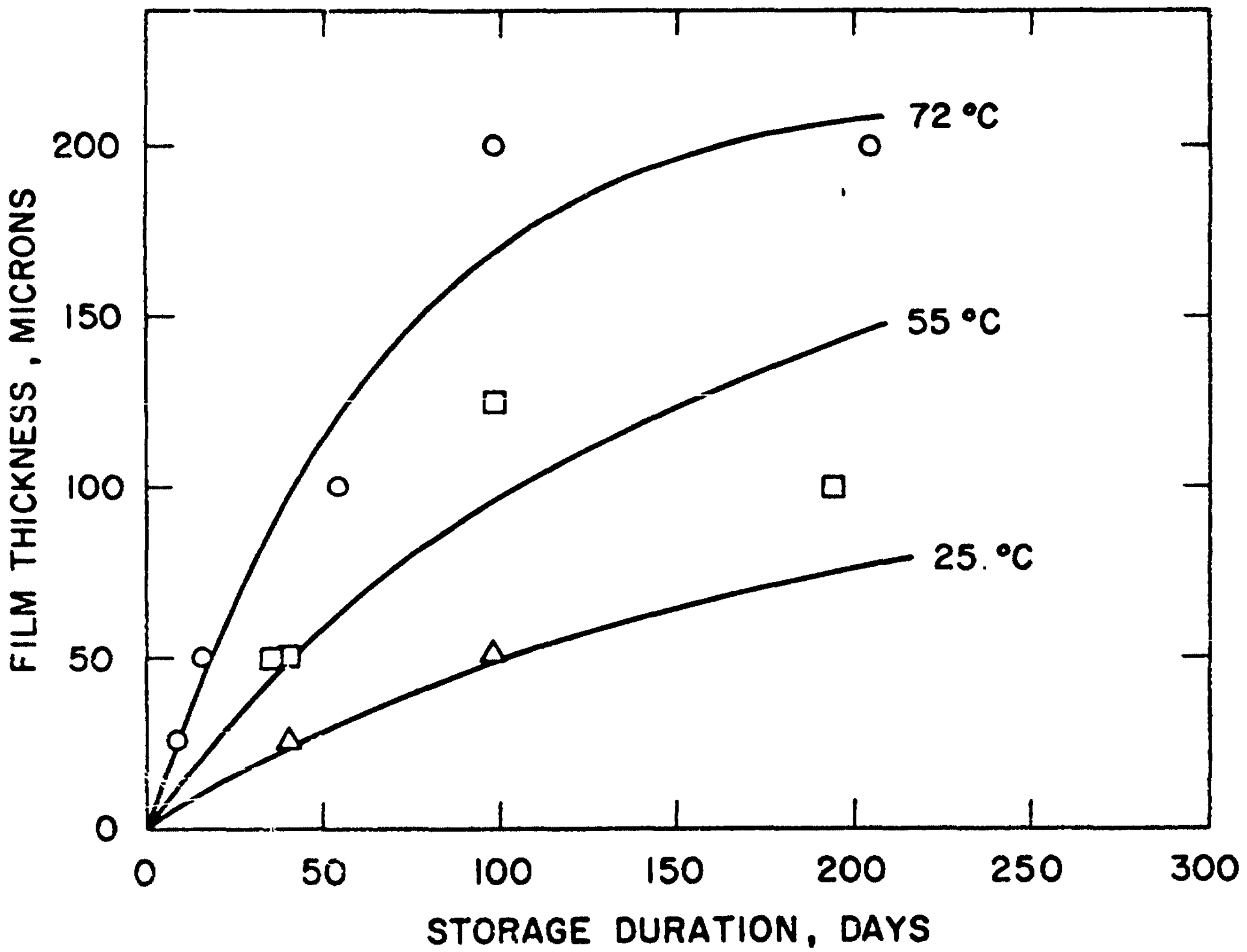

Figure 6. Li Film Growth on Storage in 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 10% (6 wt %) S_2Cl_2 at 72°, 55° and 25°C

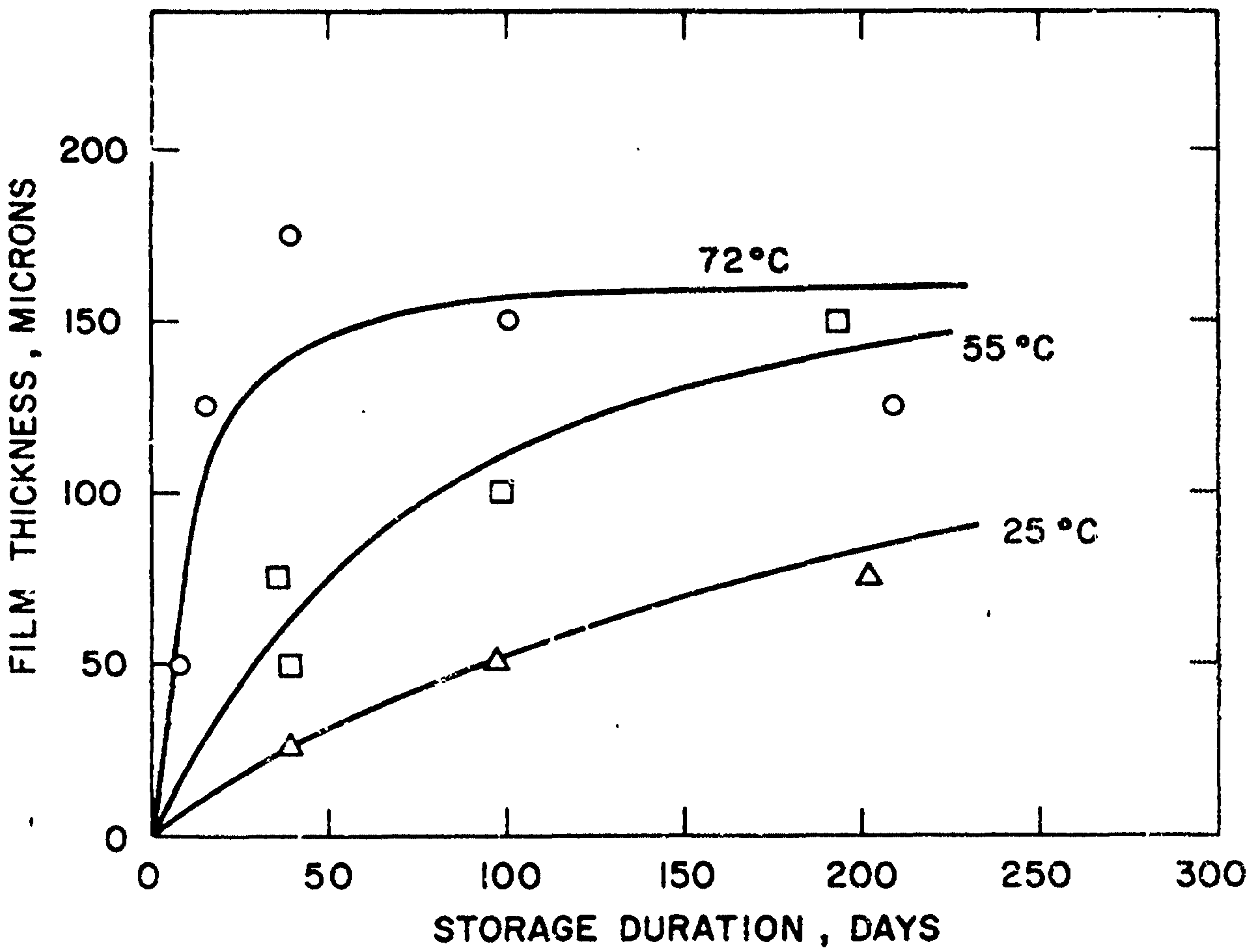

Figure 7. Li Film Growth on Storage in 1.0 (M) $LiAlCl_4$-$SOCl_2$ + 17.3%(11 wt %) SO_2 at 72°, 55° and 25°C

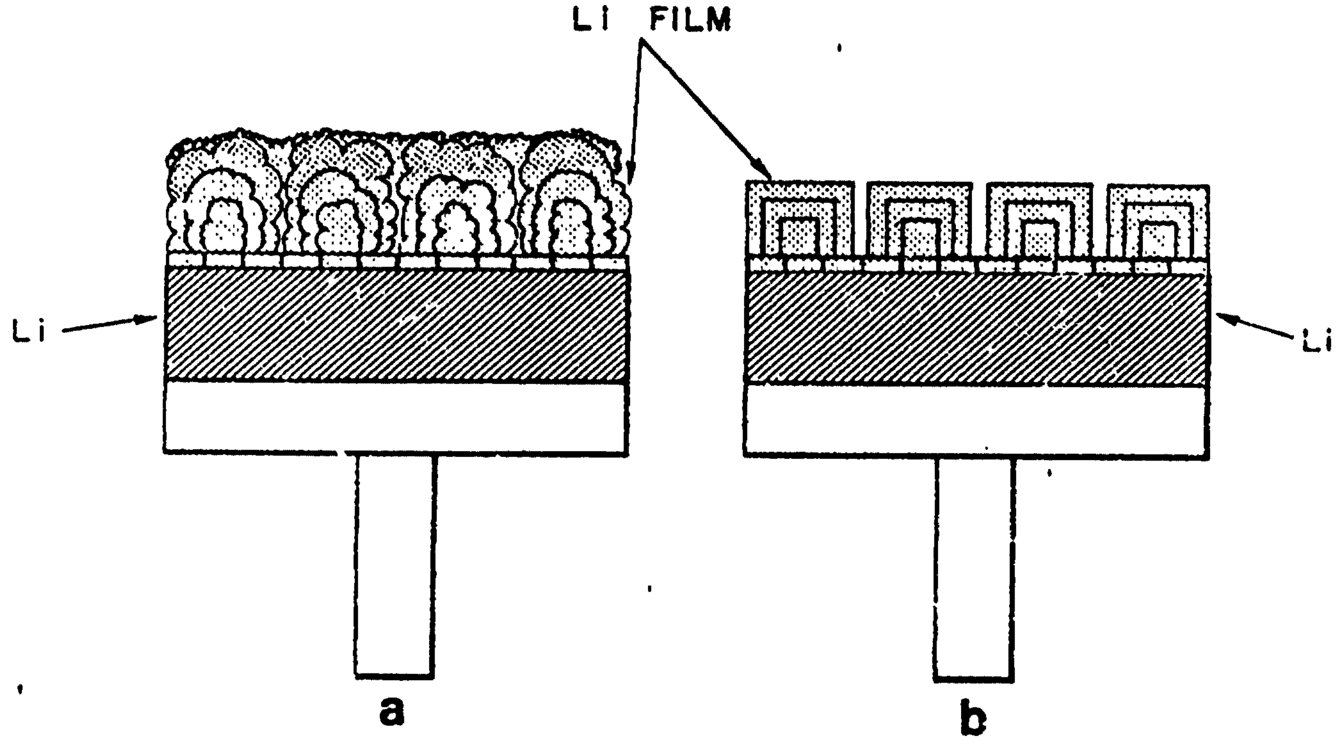

Figure 8. Schematic Representation of Two Types of Film Growth:
(a) Formation of Tall Clusters Over a Bed of Small Crystals.
(b) Formation of Large Crystals Over the Bed of Small Crystals.

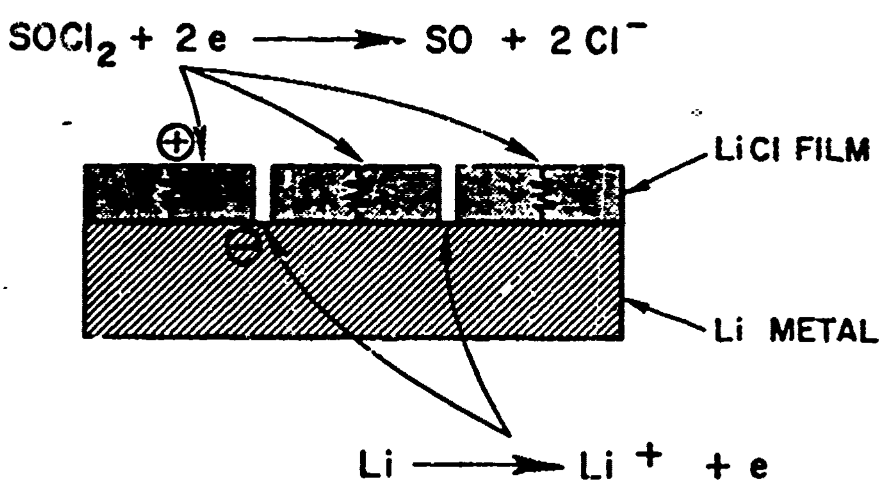

Figure 9. Schematic Representation of Film Growth by Local Action Through the Pores of the Electronically Conducting Film

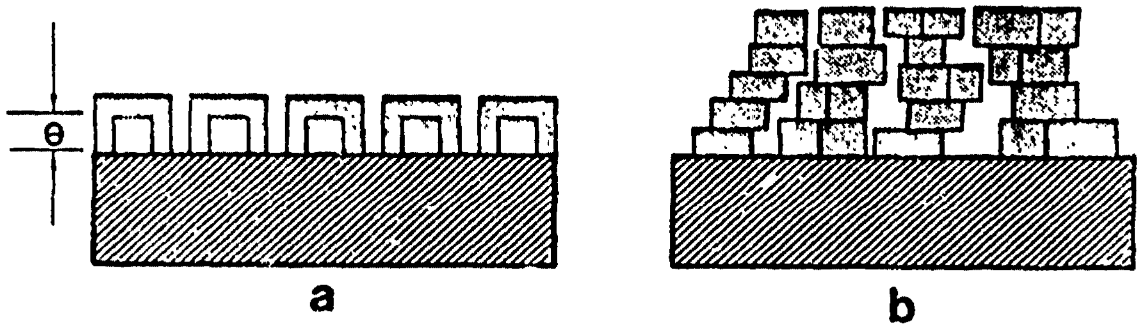

Figure 10. Idealised Representation of Film Growth
(a) Orderly Growth of Large Cubic LiCl Crystals
(b) Growth of Tall Clusters of Cubic LiCl Crystals

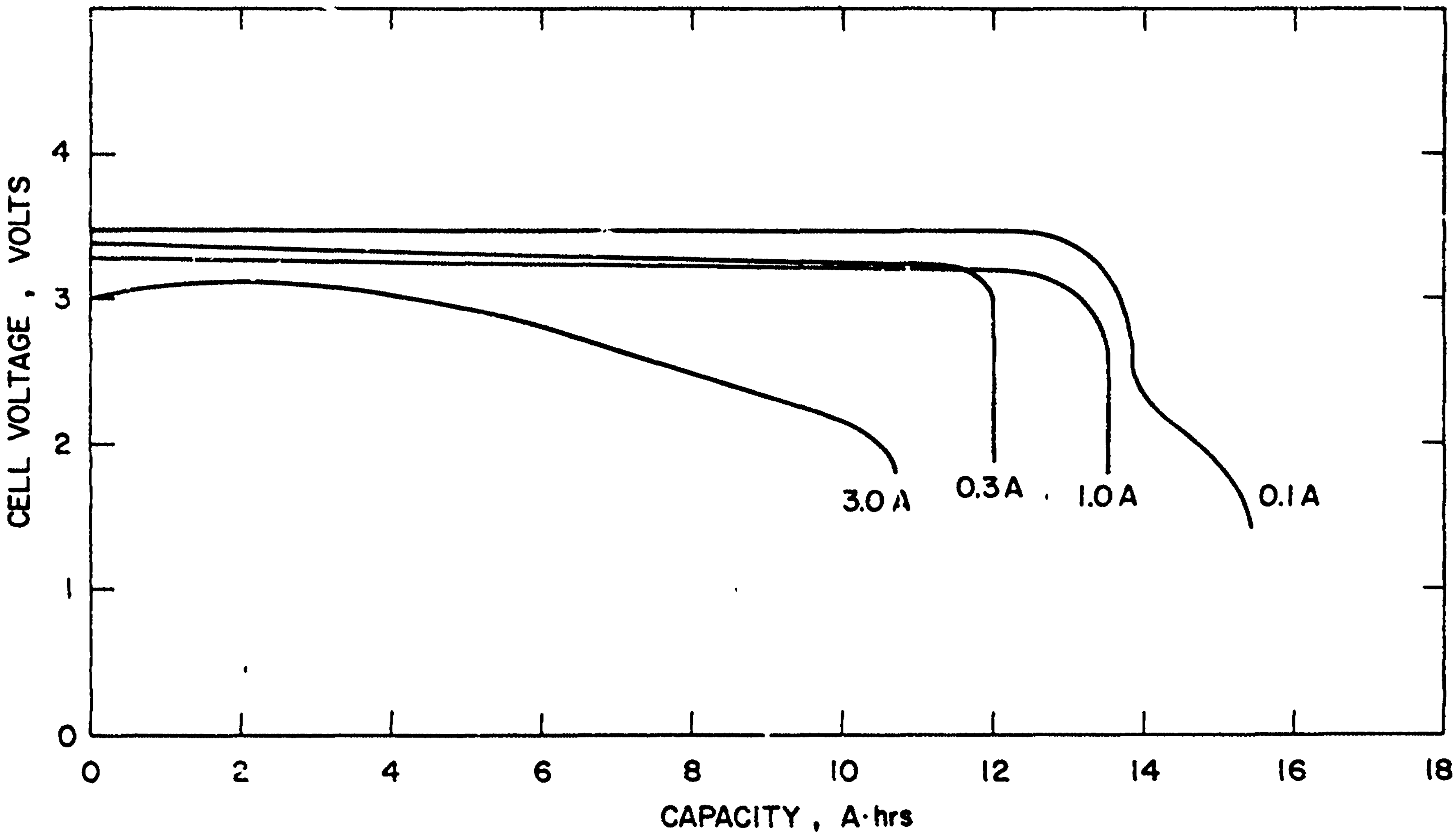

Figure 11. Discharge Curves of $Li/SOCl_2$ D Cells with 1.8 (M) $LiAlCl_4$-$SOCl_2$ Electrolyte at 25°C

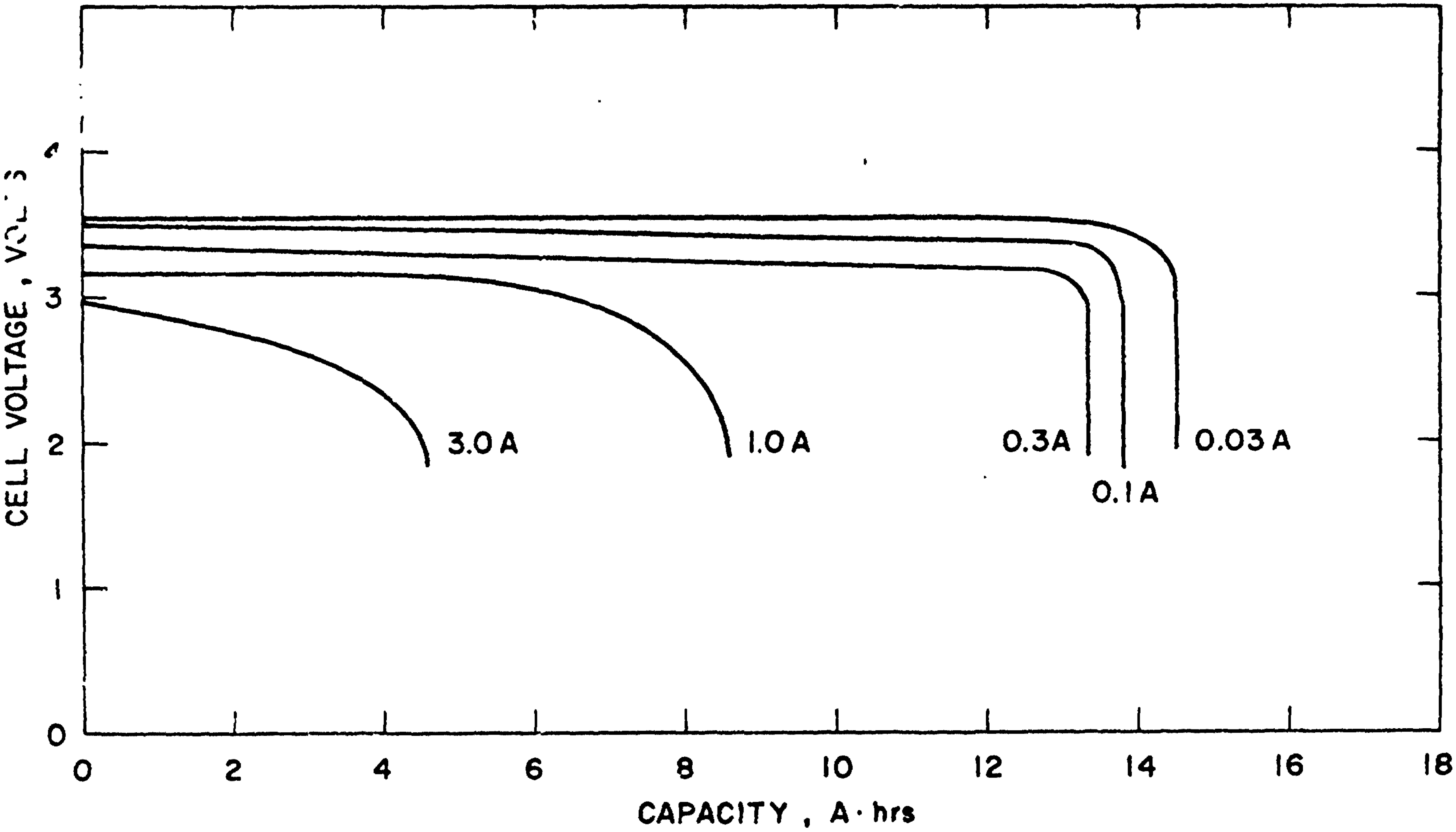

Figure 12. Discharge Curves of Li/$SOCl_2$ D Cells with 0.5 (M) $LiAlCl_4$-$SOCl_2$ Electrolyte at 25°C

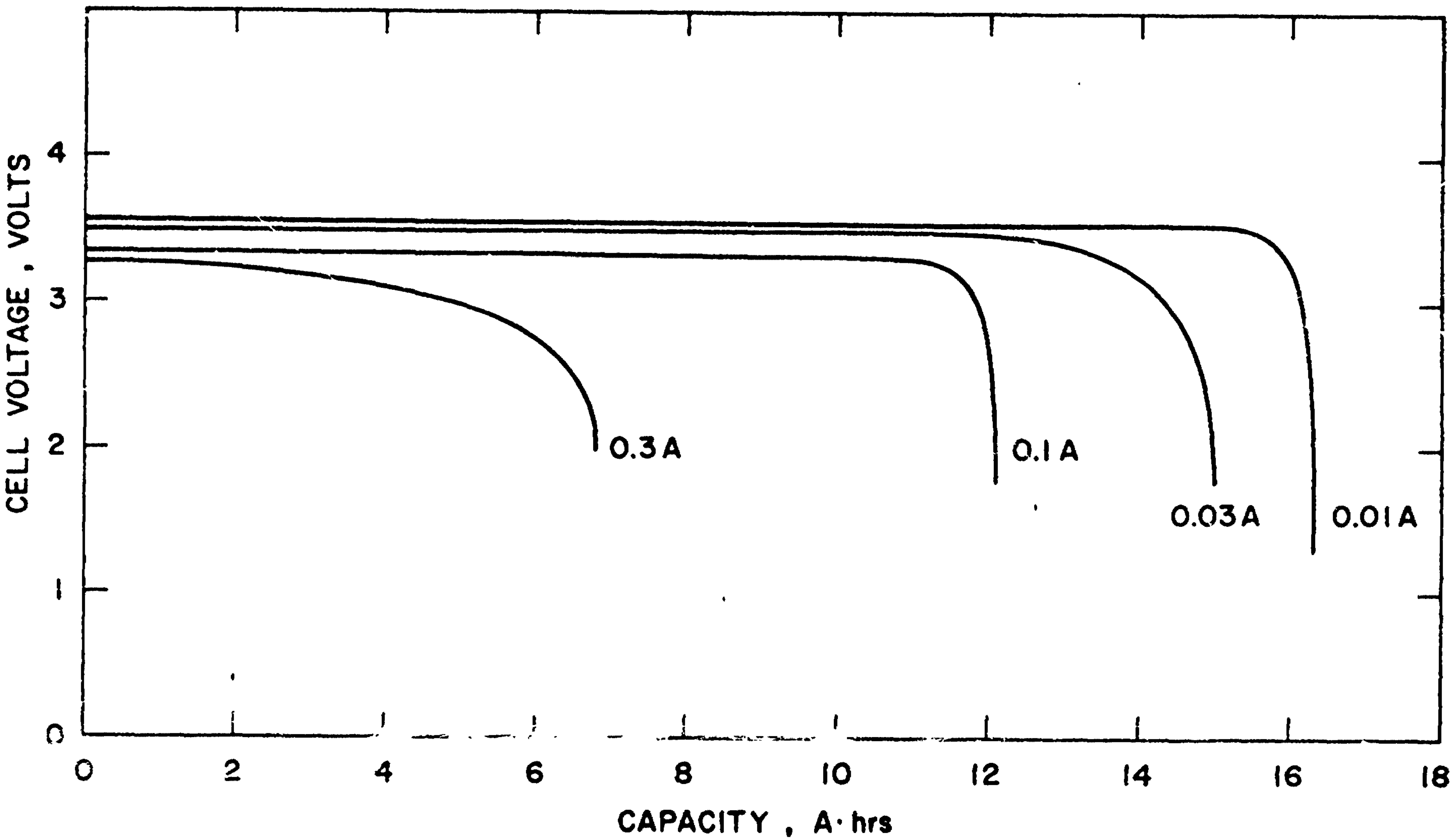

Figure 13. Discharge Curves of Li/$SOCl_2$ D Cells with 0.25 (M) $LiAlCl_4$-$SOCl_2$ Electrolyte at 25°C

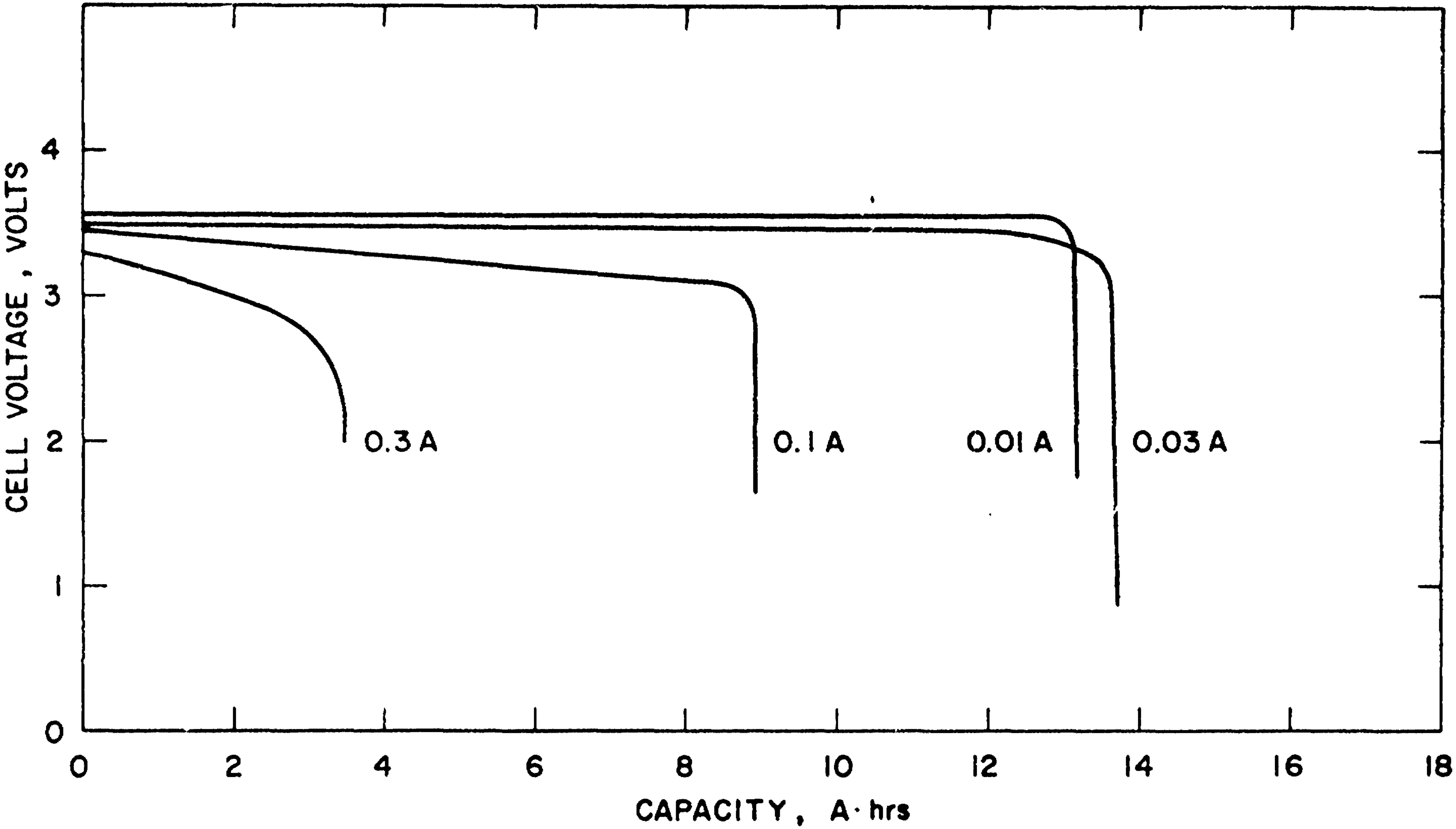

Figure 14. Discharge Curves of Li/$SOCl_2$ D Cells with 0.1 (M) $LiAlCl_4$-$SOCl_2$ Electrolyte at 25°C

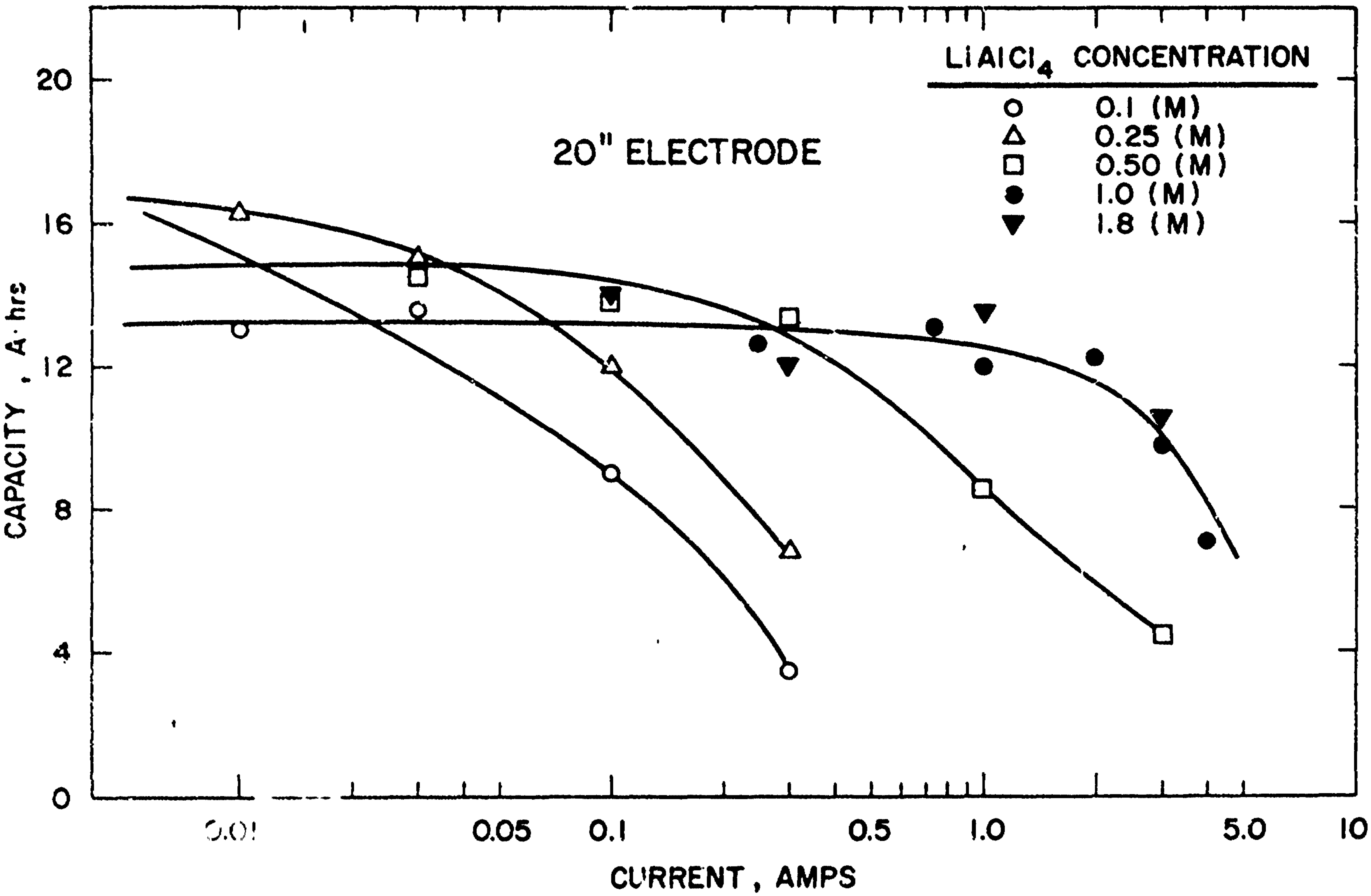

Figure 15. Capacity Rate Curves of Li/SOCl$_2$ D Cells with 1.8, 1.0, 0.5, 0.25 and 0.1 (M) LiAlCl$_4$-SOCl$_2$ Electrolyte

Table 1.

Pilling-Bedworth (14) Ratio of Some Li Compounds

Li Compounds	$R = \frac{\text{molar vol. of compound}}{\text{no. of gm. atom of Li x gm. atomic vol. of Li}}$
Li_2O	0.57
Li_3N	0.64
LiOH	1.26
Li_2CO_3	1.34
LiCl	1.58

Table 2. Performance Characteristics of the Li/$SOCl_2$ D Cells with 1.8, 0.5, 0.25 and 0.1 (M) $LiAlCl_4$-$SOCl_2$ Electrolytes

Cell No.	$LiAlCl_4$ Concentration (M)	Test Current (A)	Cell Capacity to Volt (A.Hr)	Average Cell Voltage	Total Energy (W.Hr)	Energy Density	
						W.Hr/lb	W.Hr/in^3
51	1.8	3.0	10.5	2.8	29.4	127	9.3
47	1.8	1.0	13.5	3.2	43.2	187	13.7
49	1.8	0.3	12.0	3.3	39.6	171	12.6
50	1.8	0.1	13.8	3.4	46.9	202	14.9
37	0.5	3.0	4.5	2.7	12.2	52	3.9
40	0.5	1.0	8.5	3.0	25.5	110	8.1
38	0.5	0.3	13.4	3.2	42.9	185	13.6
39	0.5	0.1	13.8	3.4	46.9	202	14.9
41	0.5	0.03	14.5	3.5	50.8	219	16.1
34	0.25	0.3	6.8	3.0	20.4	88	6.5
35	0.25	0.1	12.1	3.3	39.9	172	12.7
36	0.25	0.03	14.9	3.4	50.7	219	16.1
33	0.25	0.01	16.3	3.5	57.1	246	18.1
42	0.1	0.3	3.5	3.0	10.5	45	3.3
43	0.1	0.1	8.9	3.2	28.5	123	9.0
46	0.1	0.03	13.7	3.4	46.6	201	14.8
45	0.1	0.01	13.1	3.5	45.9	198	14.6

Table 3. Voltage-Delay Characteristics of Li/$SOCl_2$ D Cells with the Various Electrolytes; Storage at 72°C, Test at -30°C

Electrolyte	Test Current (A)	Voltage-Delay (Seconds) on Storage of 1 Month	 2 Months
1.8 (M) $LiAlCl_4$-$SOCl_2$	3.0	23	∝
	3.0	33	∝
	3.0	31	∝
	1.0	No-delay	∝
	1.0	No-delay	∝
	1.0	No-delay	300
	0.25	No-delay	No-delay
	0.25	No-delay	No-delay
	0.25	No-delay	No-delay
1.0 (M) $LiAlCl_4$-$SOCl_2$	3.0	162	∝
	3.0	204	-
	3.0	∝	-
	1.0	No-delay	No-delay
	1.0	No-delay	-
	1.0	No-delay	No-delay
	1.0	27	No-delay
	0.25	No-delay	No-delay
	0.25	No-delay	No-delay
	0.25	No-delay	No-delay

Table 3. Voltage-Delay Characteristics of Li/$SOCl_2$ D Cells with the Various Electrolytes; Storage at 72°C, Test at -30°C (cont.)

		Voltage-Delay (Seconds) on Storage of	
Electrolyte	Test Current (A)	1 Month	2 Months
0.5 (M) $LiAlCl_4$-$SOCl_2$	3.0	290	172
	3.0	177	665
	1.0	No-delay	No-delay
	1.0	No-delay	No-delay
	0.25	No-delay	No-delay
	0.25	No-delay	No-delay
0.25 (M) $LiAlCl_4$-$SOCl_2$	3.0	124	(1 Ω) No-delay
	3.0	352	464
	3.0	No test	300
	1.0	110	290
	1.0	525	261
	1.0	120	(3 Ω) 1150
	0.25	No-delay	55
	0.25	No-delay	350
	0.25	No-delay	(300 Ω) No-delay

Table 3. Voltage-Delay Characteristics of Li/$SOCl_2$ D Cells with the Various Electrolytes; Storage at 72°C, Test at -30°C (cont.)

Electrolyte	Test Current (A)	Voltage-Delay (Seconds) on Storage of	
		1 Month	2 Months
1 (M) $LiAlCl_4$-$SOCl_2$ + 10% S_2Cl_2	3.0	138	900
	3.0	156	$\propto$
	3.0	138	660
	1.0	No-delay	$\propto$
	1.0	No-delay	330
	1.0	No-delay	No-delay
	0.25	No-delay	No-delay
	0.25	No-delay	No-delay
	0.25	No-delay	No-delay
1 (M) $LiAlCl_4$-$SOCl_2$ + 17% SO_2	3.0	No-delay	-
	1.0	No-delay	-
	0.25	No-delay	-