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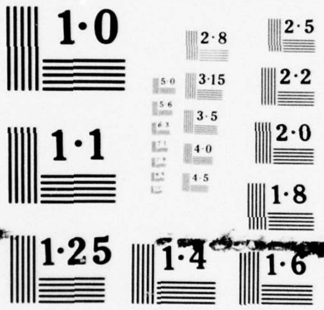
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Research and Development Technical Report

ECOM-74-0030-12

LITHIUM-INORGANIC ELECTROLYTE BATTERIES

J. R. Driscoll
G. L. Holleck
D. E. Toland
S. B. Brummer

EIC, Incorporated
Newton, MA 02158

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

This report is an annual summary which includes the past quarter's data. The major area of investigation during this time has been into the voltage delays and depression observed after storage at 71°C (160°F).

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20. Abstract (Cont.)

The voltage delay and depression are due to films which form on the Li surface. Emission spectrographic analysis has shown Cu and Fe are particulary enriched in this film.

The benefits in Li/$SOCl_2$ cell performance obtained by special precautions in cell preparation techniques were confirmed for storage times of ∿200 hours. These benefits are reflected in both capacity and rate capability improvements after storage. Such cells yielded ∿90% of their nominal capacity at ∿3.00V cell voltage (6 mA/cm^2). The precautions include storing the 1.5M $LiAlCl_4/SOCl_2$ electrolyte with Li metal (2 cm^2/ml) for greater than 150 hrs at 71°C. They also include storing the separators and cathodes in $SOCl_2$ with Li at 71°C, and preparing the cells in a very clean argon atmosphere. The improvements noted in these cells decline with storage times longer than 200 hrs, and by 400 hrs the cells show severe passivation.

Examination of a number of Li alloys has shown that Ca-coated Li anodes have major benefits. Li anodes were coated with Ca by exchange in a Ca^{++}-containing solution. Cells stored 800 hrs at 71°C have shown no voltage delay.

Without optimization, cells stored between 300 and 500 hrs have yielded between 80% and 95% of their nominal capacity at acceptable voltages and currents. A cell stored 494 hrs averaged 5.88 mA/cm^2 at an average cell voltage of 2.82V (2.0V cutoff). In the course of this work, some of the electrochemical characteristics of Ca in $SOCl_2$ solutions were investigated: Ca/$SOCl_2$ cells (Ca/1.5M $LiAlCl_4$, saturated $CaCl_2$, $SOCl_2$/carbon) have an open circuit voltage of 2.8-3.0V, and discharge at ∿2.4V at 5.0 mA/cm^2. The Ca anodes have proven resistant to passivation up to 350 hrs storage at 71°C.

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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 twelfth quarter work on this program and is also a summary of the work of the past year (September, 1975 to September, 1976). During this quarter and during the past year, 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). Cells were prepared in a very clean argon atmosphere with electrolyte and separators which had been previously stored with Li at 71°C. The second approach for alleviating the voltage delay and depression is the substitution of Li alloys for the pure Li anode. The electrochemical behavior of 12 Li alloys was explored. Five alloys have shown some improvement relative to Li. The Li/Ag(5 a/o), Li/Cd(5 a/o), and Li/Mg(1 a/o) have displayed slightly better recovery of rate capability during testing: the Li/Si(4 a/o) alloy has given better anode utilization than pure Li. The fifth alloying element, Ca, has shown considerable promise. Further details of these results are contained in earlier quarterly reports (7). The experimental data also suggest that surface modification of the Li anode is an effective approach to solving the voltage delay problem.

Earlier work on this program also concerned itself with the reaction stoichiometry of the cell discharge. This work, which included qualitative and quantitative analyses, indicated that the most reasonable discharge reaction at room temperature is

$$4Li + 2SOCl_2 \rightarrow SO_2 + S + 4LiCl \qquad (1)$$

Details of this work are contained in previous reports (8).

A question associated with the reaction stoichiometry is the SO_2 solubility. This is important because of the potential hazard of SO_2 gas pressure generated during discharge. Our experimental data show the solubility of SO_2 in 1.5M $LiAlCl_4/SOCl_2$ electrolyte is substantial, e.g., at 25°C the SO_2 is $\sim$2.6M, the mole fraction being 0.19. These data, in conjunction with a first-order theoretical analysis, suggest that high concentrations of SO_2 in the solution can be accommodated with only moderate pressure increases (6).

Section II of this report treats the question of cell purity and its relation to passivation. Section III deals with the use of alloys, particularly their performance as anodes in complete cells. Further work is summarized in Section IV.

II. ELECTROCHEMICAL EFFECTS OF IMPROVED SYSTEM PURITY

It has yet to be shown which are the major factors which influence the formation of the passivating film on the Li anode. One of these, however, must be the purity of the assembled cell. For instance, it has been demonstrated that 200 ppm of dissolved Fe causes severe Li anode passivation (9). In light of this, we have implemented cell preparation procedures designed to remove Li-reactive species in the cell components prior to cell assembly. These procedures have proven effective in alleviating the voltage delay. In conjunction with this, we have obtained some chemical characterization of the passivating film and the electrolytes. The possibility of reactive gases (e.g., SO_2, HCl) enhancing passivating film buildup has also been considered. The final cell assembly has been done outside of the normal glove box environment, which may contain SO_2 and HCl, in a glove bag under flowing argon in order to reduce this possibility. In the following sections, characterization and preparation procedures are detailed, and the effects of purification on storage of $Li/SOCl_2$ cells are presented.

A. Spectroscopic Characterizations

A survey of the passivating film and some electrolytes for their trace element constituents was obtained by emission spectroscopy. The detailed procedures and results are contained in our ninth quarterly report (10). Figure 1 presents in periodic table form the 50 elements to which the method is sensitive. The asterisks indicate the element was found in at least one of the samples. Fourteen elements were detected in the surface film; of these, only two, Cu and Fe, show major increases in concentration relative to the pure Li metal. Both of them are present in the Li metal at the 10-100 ppm level, yet in the surface film they appear to have concentrations as high as 1%. Spectroscopic examination of electrolyte salts showed no major metallic impurities. The maximum concentration for any of the metals was 10 ppm.

B. Electrolyte Purification and Characterization

Based on the information that significant quantities of Fe and Cu were present in the passivating film, we have been studying methods of removing them. We have started with a straightforward approach, storing the electrolyte with Li metal at 71°C. This is done before the electrolyte is used for cell preparation. We have also carried out both chemical and electrochemical characterization of this pretreated material.

Li*	Be											B			
Na*	Mg*											Al*	Si*	P	
K	Ca*		Ti	V	Cr*	Mn*	Fe*	Co*	Ni*	Cu*	Zn	Ga	Ge	As	
Rb	Sr		Zr	Nb	Mo		Ru	Rh	Pd	Ag*	Cd	In	Sn*	Sb	Te
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb*	Bi	

*Detected in at least one sample.

Fig. 1: Elements reported in spectrographic analysis.

1. Preparation

The electrolyte is prepared as has been described previously (6). In most cases, the $AlCl_3$ is added slowly to a cooled solution of $SOCl_2$ containing $\sim$5% excess LiCl. The solution temperature is maintained below -10°C during preparation. This limits any possible thermal decomposition of $SOCl_2$ due to the very exothermic dissolution of $AlCl_3$. Electrolyte prepared in this way maintains the original $SOCl_2$ color, a pale yellow. Electrolytes prepared without these precautions are typically a very deep brown.

The electrolyte is purified by pretreatment with Li at 71°C. This method suggested itself because, although Li is grossly stable in $SOCl_2$, it is somewhat reactive at elevated temperature. Hence, storage with excess Li at 71°C should remove any Li reactive impurities, without causing substantial solution decomposition. This storage procedure is carried out in a Pyrex container sealed with a Teflon O-ring. A coil of Li metal is placed in the electrolyte. A Pyrex glass weight was added to the Li to keep it submerged. The sealed container was placed in a 71°C oven.

2. Chemical Characterization

The chemical characterization of the electrolyte was begun in order to establish the changes engendered by storage with Li. It is clear that changes have occurred, as evidenced by the improved performance of cells utilizing this electrolyte, by the discoloration of the Li metal stored with the electrolyte, and by the change in the electrolyte color from essentially colorless to bright yellow. Whether the improved cell performance is due to the addition or the removal of substances from the electrolyte is still not clear. The color change of the electrolyte to bright yellow suggests something, as yet unidentified, is being added. To this point there was no direct evidence that the Li was removing impurities, except as suggested by the discolored Li surface. Previous spectroscopic analyses (10) had shown that Cu and Fe had relatively high concentrations in the passivating film. On this basis, these two are likely candidates for removal by the Li during storage with the electrolyte. We therefore chose to analyze the stored Li for Cu and Fe to determine if these increase on the Li during storage.

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

The analyses for Cu and Fe were by standard spectrophotometric methods. The Fe method, which we have used previously, uses o-phenanthroline as the sensitive reagent (11). The Cu method uses 2,2'-biquinoline as the sensitive reagent (12,13). Samples of fresh Li foil were also analyzed.

The analytical results are summarized in Table 1. The sample H62 was cut from the 24" piece used in our normal storage procedure. It was about 8% of the total sample. It shows about three times the Cu and twice the Fe found on fresh Li foil. These concentrations may not be the same over the complete length of the foil. The Li foil helix in the storage vessel was coiled such that some shading occurred. This caused irregular distribution of the surface darkening, which is probably indicative of the distribution of the materials removed from solution. Nonetheless, it is clear that the Li is removing Cu and Fe from the electrolyte, and probably other species which form reduced insoluble products (e.g., other metal ions).

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

The pretreatment of the electrolyte with Li at 71°C is removing some substances and adding at least one other. Which of these is the most beneficial is not yet clear. The removal of Cu and Fe should be helpful: It should reduce the rate of Li corrosion, by mitigating the depolarization caused by the plating of these relatively noble metals. Furthermore, these metals, once plated, can depolarize $SOCl_2$ reduction, perhaps preferentially to Li itself. The benefit of additives has not yet been proved, although some recently presented preliminary results indicate that an improvement can be realized with added SO_2 (14).

Further analytical studies on the pretreated electrolyte are clearly indicated. The identification of removed or added components will allow more certain determination of their potential benefit or harm.

Table 1

Cu and Fe Concentrations on Li Foil Stored with 1.5M $LiAlCl_4/SOCl_2$ at 71°C

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

a = error limits ± 5%

3. Electrochemical Characterization

The electrochemical characterization has been done via changes in the performance of complete Li/$SOCl_2$ cells after storage at 71°C. Voltage delay and depression data have been acquired on these cells. The cells which we have designated T-cells are described in detail in our ninth quarterly report. The T-cells are comprised of a flat anode and cathode separated by glass fiber paper and compressed into a tight package by Teflon discs (Figure 2). Our primary test procedure after storage is to apply a constant load of 480Ω. Then the cell voltage and the anode potential vs. a fresh Li reference are measured on a rapid time base. The 480Ω load was chosen because fresh cells have a current density of 6.5-7.0 mA/cm^2 with this load. For a practical D cell with a ∿400 cm^2 electrode area, this is equivalent to ∿3A rate. These cells were assembled with other safeguards with respect to purity: As indicated, they were assembled in a glove box under flowing argon. This reduces the probability of contamination from, for example, SO_2 and HCl and other gases generated by the decomposition of $SOCl_2$. A number of cells were assembled with glass fiber separators and cathodes which had previously been heated to 71°C in $SOCl_2$ in the presence of Li metal. This, again, is to remove $SOCl_2$-soluble, Li-reactive species.

The cell preparation procedures designed to remove Li-reactive species produced cells which, after 71°C storage, showed a remarkable improvement in discharge characteristics for storage times up to 209 hrs. At the moment, the limit of this improvement lies between 200 and 400 hrs storage at 71°C. Beyond 400 hrs storage, the performance, as evidenced both by the voltage delay and depression measurements, and by the complete discharge data, decays.

The voltage delay and depression characteristics of the normal Li/$SOCl_2$ cells become inferior after ∿100 hrs storage. After 136 hrs storage, the cell performance has degraded to unacceptable levels. This is illustrated in Figure 3. The voltage delay measurements on cells at 200 hrs and up to 400 hrs are comparable to this.

The Li/$SOCl_2$ cells prepared with purity precautions contrast sharply. Figure 4 presents the voltage vs. time response of 6 such cells. Two of them stored at 184 hrs and 4 at 208 hrs at 71°C. Only two of the cells show any voltage delay. The delays were about 2-4 sec. The performance of the clean cells degrade seriously for storage times of 400 hrs or greater, however, Figure 5 presents the voltage vs. time curves for 3 cells stored 400 hrs at 71°C. All 3 cells show voltage delays in excess of 72 sec, making them comparable to cells prepared without these precautions of cleanliness. The degradation of performance continues with increased storage time. Cells stored up to 740 hrs show unacceptable voltage delay and depression characteristics.

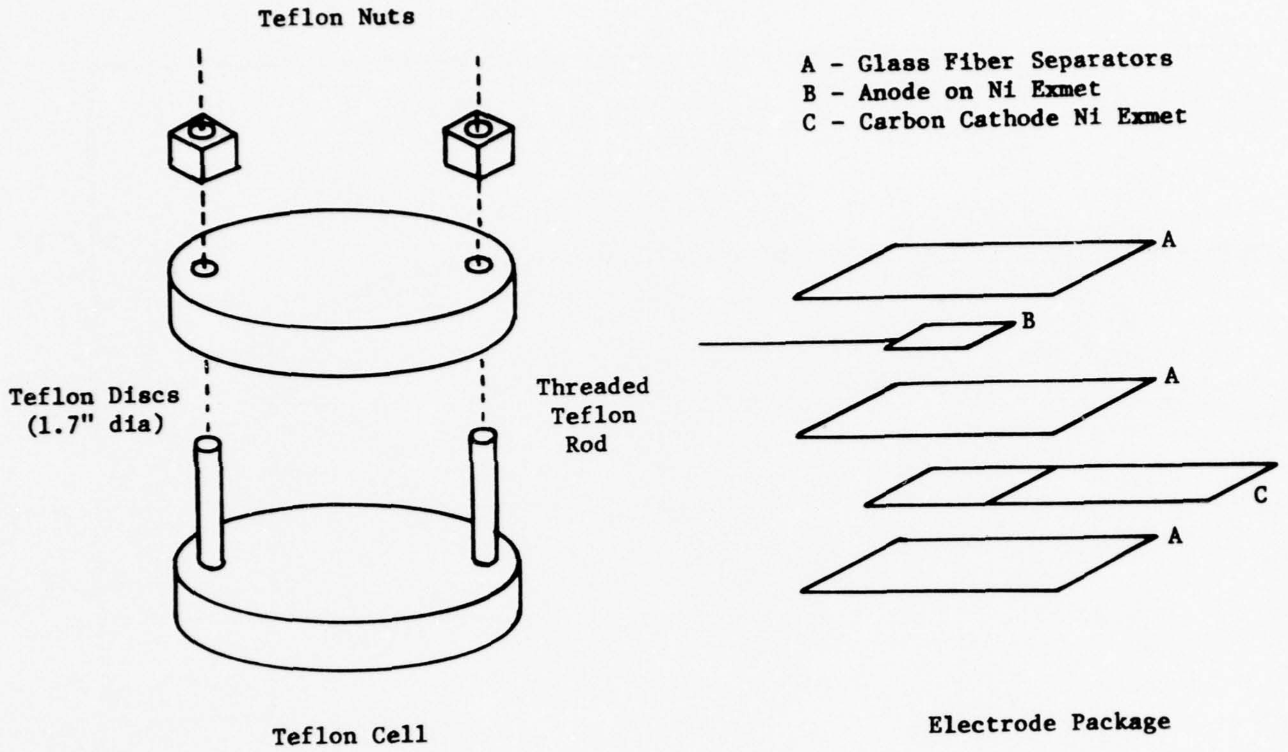

Fig. 2: Teflon (T-cell) cell and electrode package.

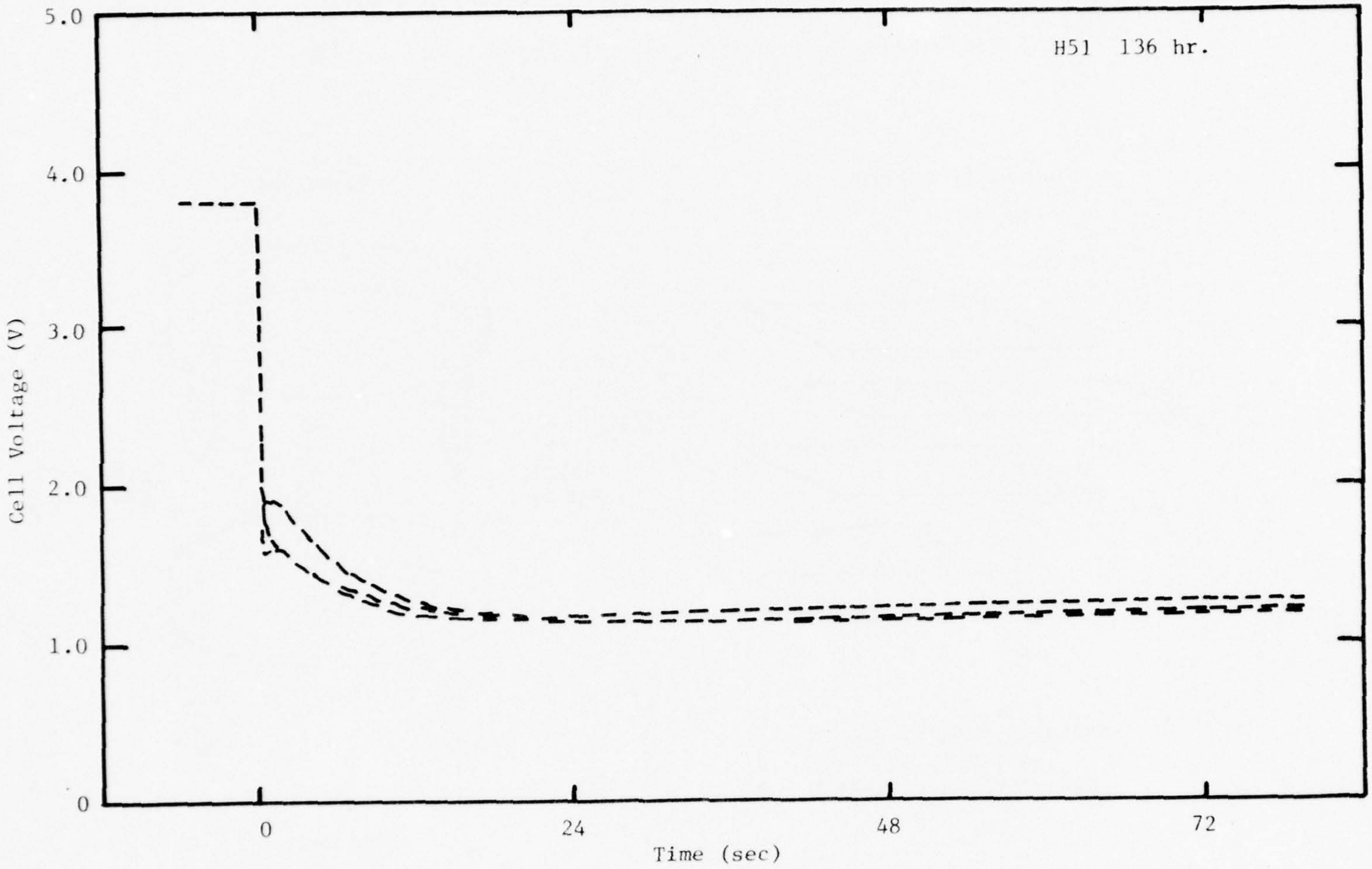

Fig. 3: Initial polarization of $Li/SOCl_2$ cells with 480Ω (∼1cm^2). H51 was stored 136 hr at 71°C with 1.5 M $LiAlCl_4/SOCl_2$.

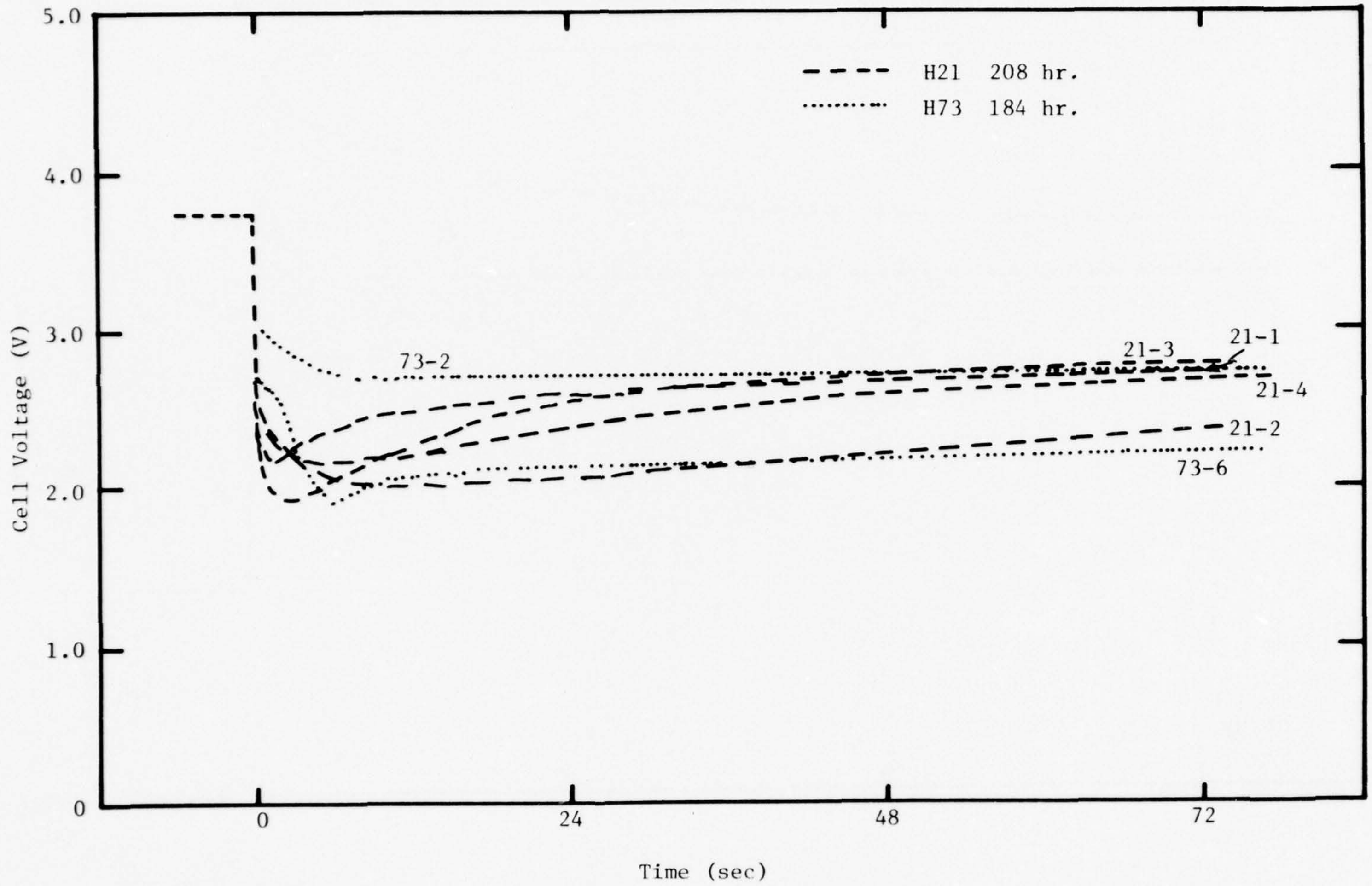

Fig. 4: Initial polarization of Li/$SOCl_2$ cells with 480Ω (**~1cm²**). H21 was stored 208 hr and H73 184 hr at 71°C. The 1.5M $LiAlCl_4$/$SOCl_2$ electrolyte was pretreated with Li metal.

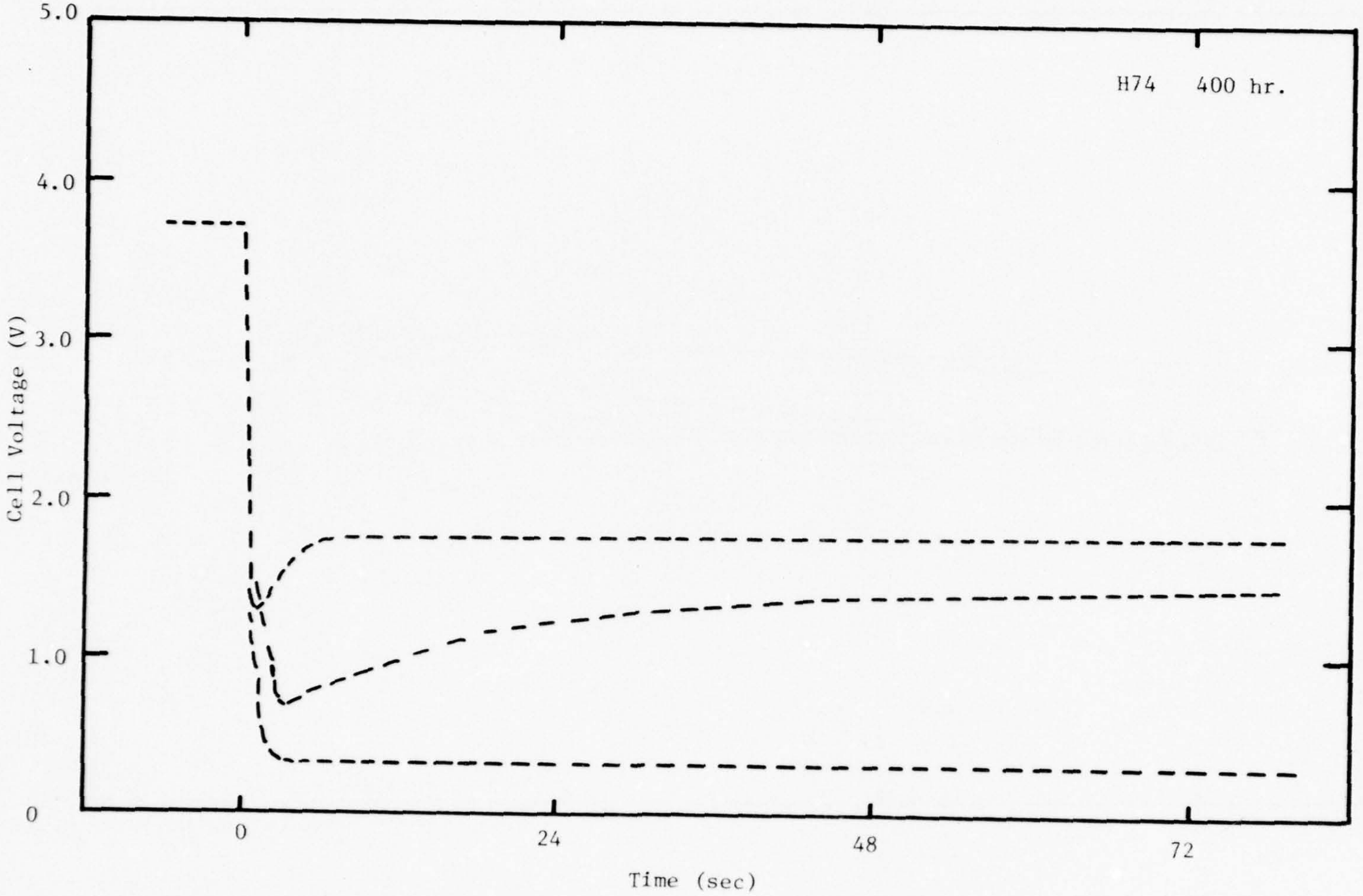

Fig. 5: Initial polarization of Li/$SOCl_2$ cells with 480Ω (~1cm^2). H74 was stored 400 hr. at 71°C. The 1.5M $LiAlCl_4$/$SOCl_2$ electrolyte was pretreated with Li metal.

The cause of the performance degradation between 200 hrs and 400 hrs storage time is unclear at the moment. It appears, however, it may be due to atmospheric contamination. Some critical tests have indicated that after approximately 300 hrs at 71°C, the H-cell allows measurable exchange with the atmosphere. Until this problem is resolved, the intrinsic passivation rate cannot be measured. Improved sealing techniques are currently being developed to resolve the problem.

Despite this problem it is apparent that pretreatment and assembly procedures designed to improve the purity of the final stored cell do improve its storage capability. These positive results suggest this area be explored more fully. Part of the work will be directed to analysis of the pretreated electrolyte, to determine the nature of the substances removed from solution and added to it. Naturally, any materials found to be significant, will be deliberately added to the solution to assess them. If appropriate, we will also look at other methods of preparing "pure" electrolytes.

III. LITHIUM ALLOY ANODES

The feasibility of modifying Li anode performance by alloying has been explored during the past year. The work has aimed at establishing the effects of Li alloy anodes on the performance of complete $SOCl_2$ cells after 71°C storage. Twelve alloys were tested. The twelve were: Li/Ag(5 a/o), Li/Al(5 a/o), Li/Au(2 a/o), Li/Bi(5 a/o), Li/Cd(5 a/o), Li/Cu(4 a/o), Li/Mg(1 a/o), Li/Mg(5 a/o), Li/Pb(3 a/o), Li/Si(4 a/o), Li/Sn(3 a/o) and Li/Zn(10 a/o). They were manufactured by the Foote Mineral Company. Based on the published phase data (15), they can be subdivided into three groups. The members of one group are mixtures of Li and a Li-alloying element compound. The majority of the alloys fall into this group. These are: Li/Al, Li/Au, Li/Bi, Li/Pb, Li/Si, Li/Sn and Li/Zn. The second group comprises four of the alloys, Li/Ag, Li/Cd, and both Li/Mg alloys. These are solid solutions or mixtures of solid solutions. The third group contains one member, Li/Cu. It is a mixture of the two metals. Cu and Li have little mutual solubility.

The primary evaluation procedure for the fresh alloys was through comparison with Li in complete cells. The bases of the comparison were the cell voltage and capacity during complete discharge. Ten of the twelve were generally comparable with pure Li. These were: Li/Ag, Li/Al, Li/Au, Li/Bi, Li/Cu, Li/Mg(1 a/o), Li/Pb, Li/Si, Li/Sn and Li/Zn. Cell voltages at 6-7 mA/cm^2 were with 0.2V of the pure Li cells. Anode utilization efficiencies were calculated from the cell capacity data. Except for the Li/Si alloy, the efficiencies ranged from 60-100% of the pure Li value. The utilization efficiency of Li/Si was high, exceeding 100% of the Li content, which suggests Si is also being oxidized. The Li/Cd and Li/Mg(5 a/o) alloys performed poorly. The Li/Mg(5 a/o) polarized very strongly at 6 mA/cm^2. Even at 0.6 mA/cm^2 the cell voltage was only 1.5V.

Assessment of the effects of Li alloy anodes on voltage delay after 71°C storage was made on complete cells identical to those used in testing the fresh alloys. The test procedure involved monitoring the cell voltage on a rapid time base during discharge at 6-7 mA/cm^2. Cells were also tested by complete discharge. These tests were primarily to assess capacity loss during storage. None of the alloys provided relief from severe voltage delay. The results did indicate that three alloys - Ag, Cd and 1 a/o Mg recover more rapidly to useable potentials during extended discharge. The complete discharge tests show little capacity loss during storage. The complete details of the experiments with both the fresh and stored alloy anode cells are contained in previous quarterly reports (7).

A. Lithium/Calcium Anodes

During the past year we have also initiated studies on the effects of Ca as an alloying element for Li anodes. These studies have become a major thrust of our work in the past quarter. Ca suggested itself as a potentially beneficial alloying metal because it discharges at a reasonable potential in $LiAlCl_4/SOCl_2$ electrolyte. Further, Ca metal was found to be more resistant than Li to passivation during storage at 71°C. Characterization of Ca-coated Li anodes after 71°C storage was made. Contrary to the alloys used previously, the Ca was deposited on the surface of pure Li metal foil by exchange with a solution of Ca^{++} in $SOCl_2$. Previously we have reported that cells with anodes prepared in this manner have much improved discharge characteristics after 500 hrs at 71°C. These measurements have been extended to 800 hrs storage with similar results. This work is discussed in more detail below. First, we review the $Ca/SOCl_2$ studies.

B. Characterization of $Ca/SOCl_2$ Cells

Our measurements have shown that Ca discharges effectively in $SOCl_2$ electrolyte. The tests were made with complete Ca/1.5M $LiAlCl_4$, $SOCl_2$/C cells in our T-cell configuration. The Ca (20 mil) was obtained from ROC/RIC. The foil as-received has a black surface. The surface was polished to the bright metal before use with fine sandpaper. An exploratory E-i scan indicated that the Ca can be oxidized at $\sim$20 mA/cm^2 at a polarization of +0.8V relative to open circuit. The voltage delay and depression testing, and the complete discharges were with the same procedures as for the $Li/SOCl_2$ cells. The open circuit potential of the $Ca/SOCl_2$ cells ranged between 2.8V and 3.0V. The discharge curves of 4 fresh cells are shown in Figure 6. Two cells were discharged through 480Ω and two through 1000Ω. The curves are qualitatively similar. After an initial increase, the cell voltage remains relatively constant for about 40% of the discharge, then declines to the 1.0V cutoff. The decline in the cell voltage of the cells tested at 480Ω is more rapid than the cells discharged at 1000Ω. The plateau for the cells discharged with 480Ω was $\sim$2.6V and for the 1000Ω load was $\sim$2.7V. The increased cell polarization in the latter 60% of discharge is probably due to the buildup of insoluble, anode-discharge products.

After discharge, we noted a white crystalline deposit on the anode. The anode had approximately the same shape as the original piece of Ca, although it is somewhat thicker. Further inspection revealed a dark center, which was Ca metal. The white crystalline material has not been analyzed, but it is probably either $CaCl_2$ or $Ca(AlCl_4)_2$. Both are rather insoluble in $SOCl_2$. The probable anode reaction is either

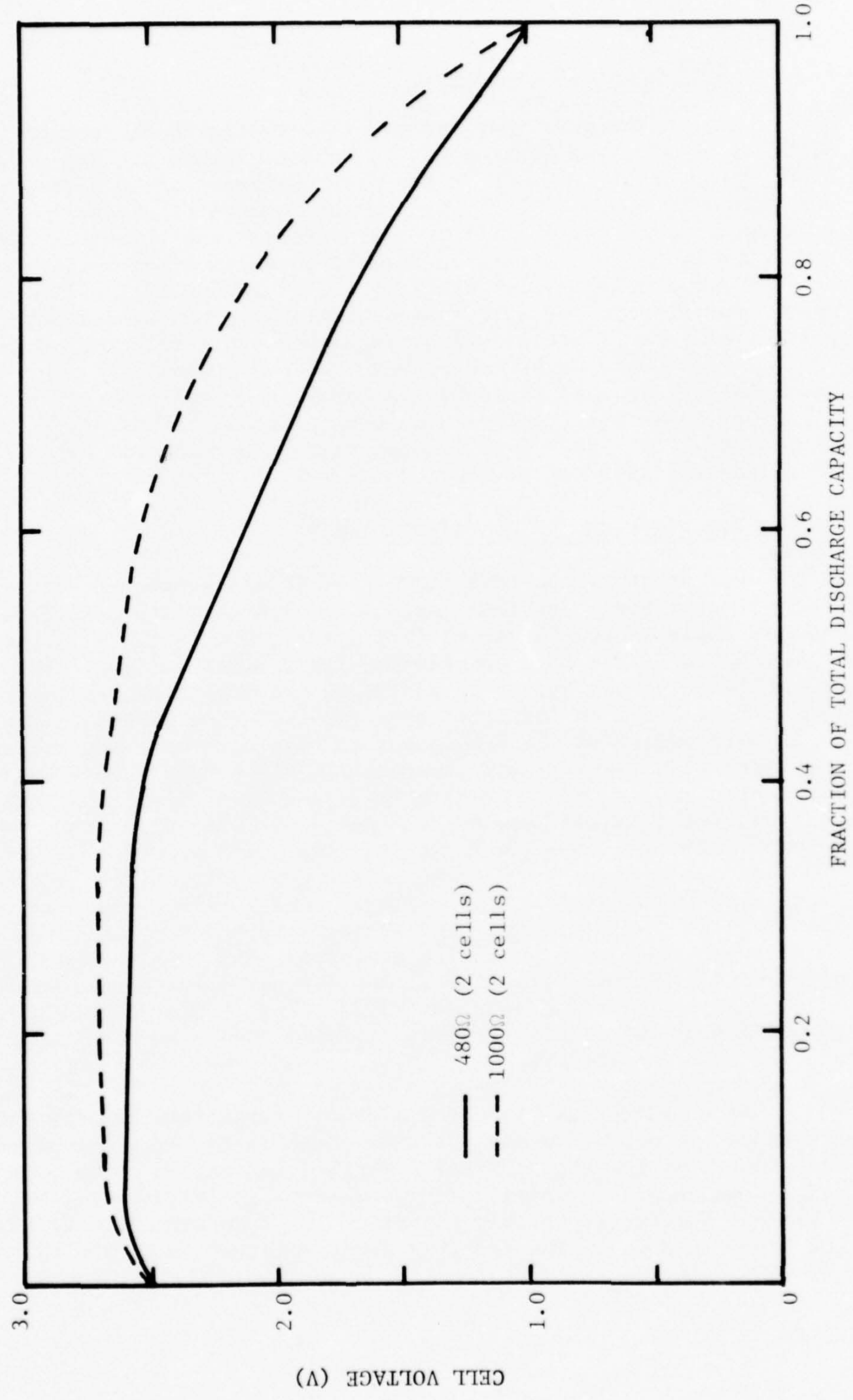

Fig. 6: Discharge voltage of fresh Ca anode, $SOCl_2$ cells discharged at 25°C with 1.5M $LiAlCl_4/SOCl_2$ electrolyte.

$$Ca + 2Cl^- \rightarrow CaCl_2 + 2e^- \quad (2)$$

or

$$Ca + 2AlCl_4^- \rightarrow Ca(AlCl_4)_2 + 2e^- \quad (3)$$

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

Storage of Ca/$SOCl_2$ cells at 71°C for up to 350 hrs does not seriously passivate the Ca anode. Figures 7 and 8 show the initial voltage-time curves for 8 Ca/$SOCl_2$ cells, 4 stored for 136 hrs and 4 for 351 hrs at 71°C. Only one of the cells, H50-4, has any significant polarization compared to fresh Ca anodes tested in the same manner, and this cell recovered within 180 sec to the same voltage as the other cells. The current and voltage data contained in Table 2 for the complete discharge of these cells, demonstrates that even after 351 hrs storage the voltage and current are comparable to fresh Ca. The capacity of the cell stored 135 hrs is comparable on a percentage basis with the fresh cells, while the 351 hr cell has lost some capacity. It has not been determined whether this is a real loss, due to Ca corrosion, or an apparent loss, due to anode polarization. Nevertheless, Ca metal appears suitable for testing as a protective film for Li electrodes.

C. Electrochemical Characterization of Li(Ca)/$SOCl_2$ Cells after 71°C Storage

The electrochemical activity and the relatively good resistance to passivation of Ca in the $LiAlCl_4/SOCl_2$ electrolyte system led to an exploration of the effects of Ca-coated Li anodes. We have prepared these anodes by exchange. The characterization of the anodes has been to test for voltage delay and for complete discharge behavior of cells prepared with these anodes after 71°C storage. In the exchange technique, the Ca film is produced by storing the cells in electrolyte saturated with $CaCl_2$. Methods are still being evolved, but the basic procedure is as follows: the assembled, liquid-free T-cells are vacuum impregnated with 1.5M $LiAlCl_4/SOCl_2$ electrolyte which is presaturated at 71°C with $CaCl_2$ and LiCl. The estimated maximum solubility of $CaCl_2$

Table 2

Discharge Characteristics of Ca/$SOCl_2$ Cells Tested at 25°C

Cell	Storage 71°C (hrs)	Load (Ω)	Discharge to 1.0V Cutoff		
			Avg. Voltage (V)	Avg. Current (mA/cm^2)	Capacity[a] (mAh)
Fresh					
1	-	480	2.01	4.18	58.4
2	-	480	2.02	4.21	44.9
3	-	1000	2.32	2.32	55.5
4	-	1000	2.26	2.26	47.1
Stored					
H50-4	135	480	2.04	4.25	56.0[b]
H59-4	350	480	2.06	4.29	28.6

[a] Nominal capacity 120 mAh.

[b] The nominal capacity of the H50-4 anode was 80 mAh and yielded 37.3 mAh. We have converted it proportionally to the 120 mAh basis for ease of comparison with the other electrodes.

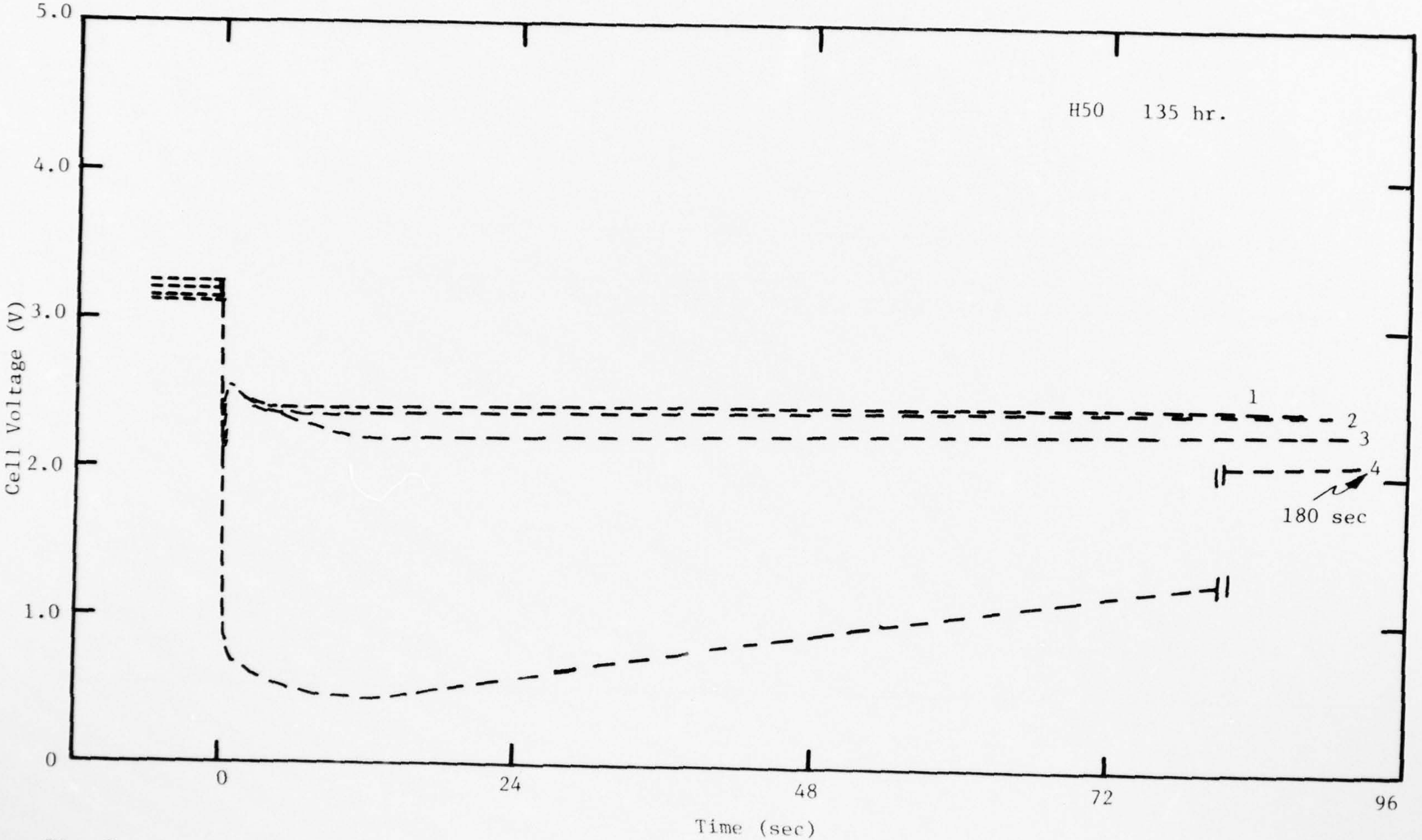

Fig. 7: Initial polarization of Ca/$SOCl_2$ cells with 480Ω (~1cm^2). H50 was stored 135 hr at 71°C. The 1.5M $LiAlCl_4$/$SOCl_2$ electrolyte was not pretreated with Li metal.

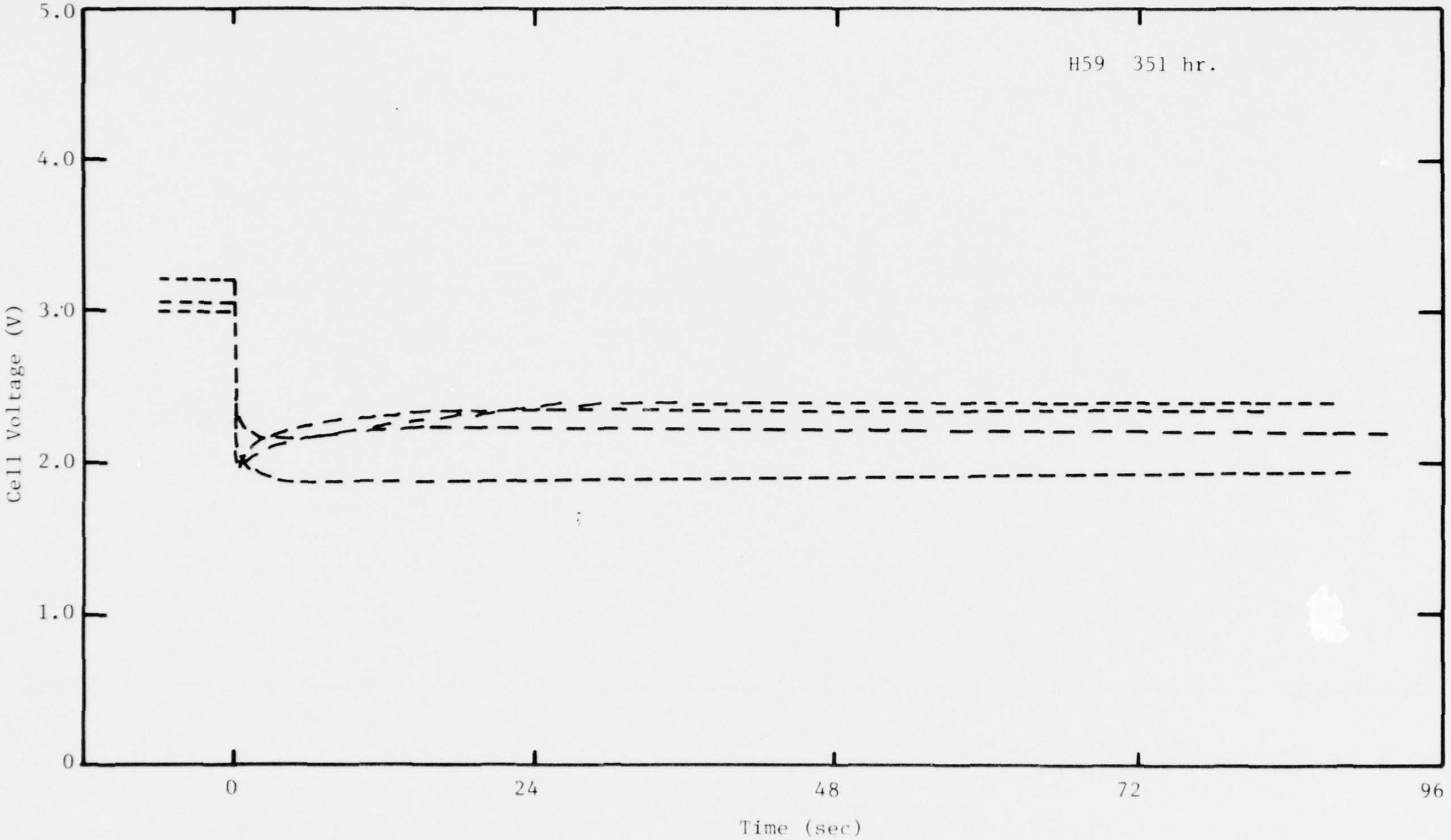

Fig. 8: Initial polarization of $Ca/SOCl_2$ cells with 480Ω (~1cm^2). The cells were stored 351 hr at 71°C. The 1.5M $LiAlCl_4/SOCl_2$ was not pretreated with Li metal.

is ∿5 mM. The active cells are also stored in this electrolyte. We have used electrolyte pretreated with Li and electrolyte not pretreated.

The initial testing of these cells for voltage delay and depression has demonstrated improvements over the standard Li/$SOCl_2$ cells, but there is some ambiguity in the measurements which will be discussed below. Cell H58, prepared with electrolyte not pretreated with Li, shows that after 284 hrs at 71°C the two Ca-treated cells are vastly superior to the pure Li metal cells (Figure 9). The Li(Ca) cells show no voltage delay, while the Li cells show severe voltage delay. The data for cells H69 (206 hrs) and H70 (494 hrs) are not as clear (Figures 10 and 11). These cells were prepared with electrolyte pretreated with Li. Although the Li(Ca) T-cells tend to show a little better response than the Li metal, they do not do so convincingly. The Li/$SOCl_2$ cell, H70-1, is atypical for Li cells stored this length of time at 71°C. The H70-2 cell is much more typical. The data for cells H78 and H79 prepared with Li-pretreated electrolyte, again show the improvement of the Li(Ca) cells over the Li metal (Figures 12 and 13). All 3 Li(Ca) in H78 cells have recovered above 2.0V within 48 sec, while the pure Li cells have not recovered to 1.5V within 80 sec.

The cells stored 798 hrs (H79) show excellent voltage delay characteristics. The difference between the H69 and H70 cells and H78 and H79 was that the H69 and H70 were originally impregnated with electrolyte not containing any Ca^{+2}, while the H78 and H79 were originally impregnated with Ca^{+2} containing electrolyte. Thus, the Ca deposited on the H69 and H70 anodes was limited by diffusion into the glass fiber separators. This cannot only modify the rate of Ca deposition, but may also affect the distribution of the Ca on the surface: Since the Ca^{+2} diffuses from the perimeter, it is probable that Ca will deposit preferentially at the edges of the Li anode. This, in turn, could allow the center of the anode to be passivated before effective amounts of Ca could reach it. Impregnating the H78 and H79 cells with Ca^{+2} containing electrolyte should reduce the problem, and the data seem to indicate this.

The most important significant improvements have been in the complete discharge behavior of these Li(Ca) cells. Despite the fact that the Ca-deposition procedures have not been optimized in any manner, we have obtained quite acceptable complete discharges. Figure 14 presents the cell voltage vs. capacity data for three cells discharged through 480Ω. The three cells show points of behavior in common. The initial cell voltage under load was between 2.75 and 2.80V. This dropped very quickly to between 2.3 and 2.6V. Continued discharge improved the cell voltage, so that it had reached between 2.9 and 3.0V at 10 mAh. Two of the cells discharged smoothly to completion at the 2.0V cutoff, with the majority of the capacity obtained at a plateau at about 3.0V. The third cell had poorer voltage regulation. After the maximum at about 2.9V

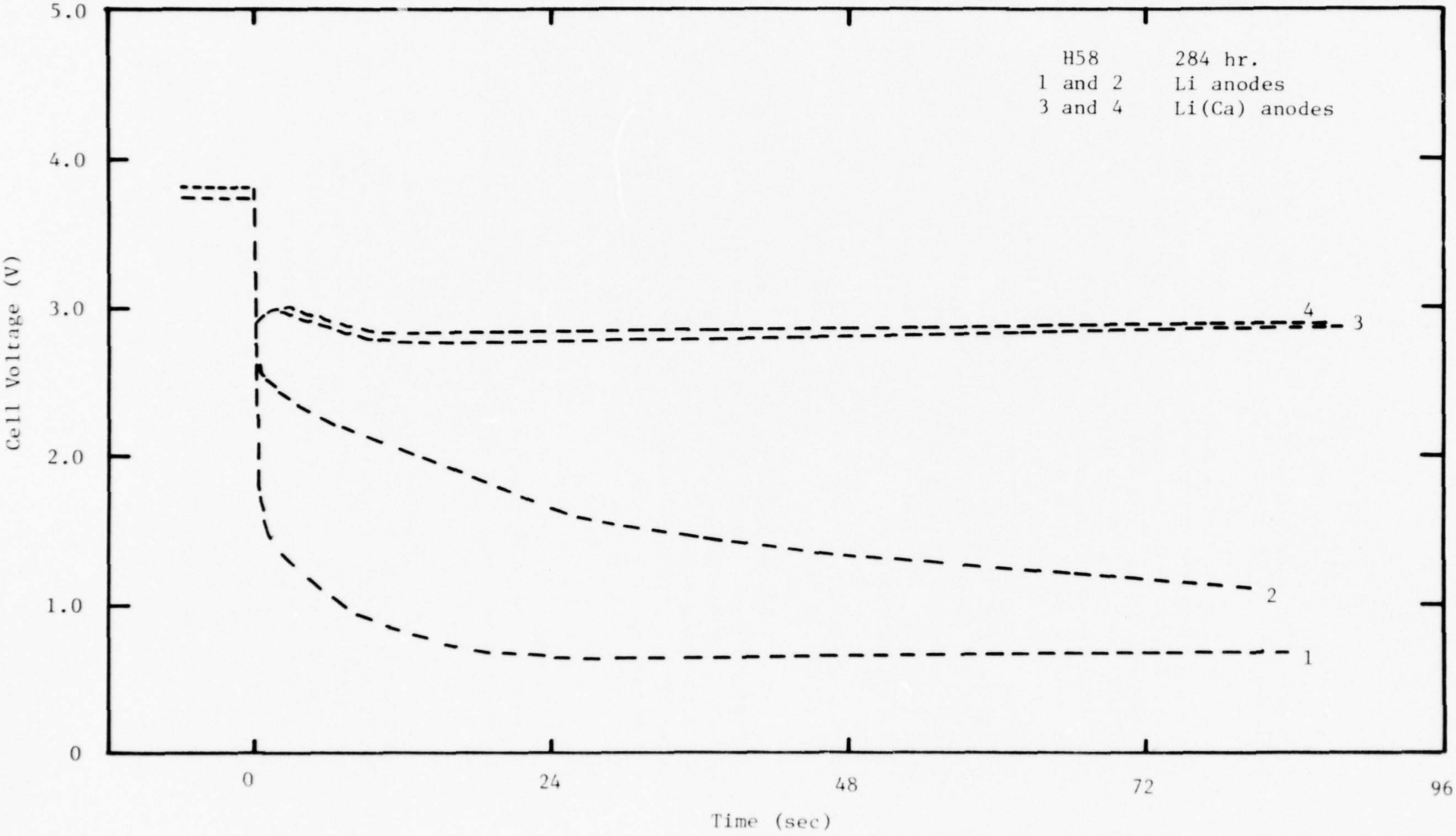

Fig. 9: Initial polarization of Li anode and Ca-coated Li anode, $SOCl_2$ cells with 480Ω (~1cm^2). The cells were stored 284 hr at 71°C.

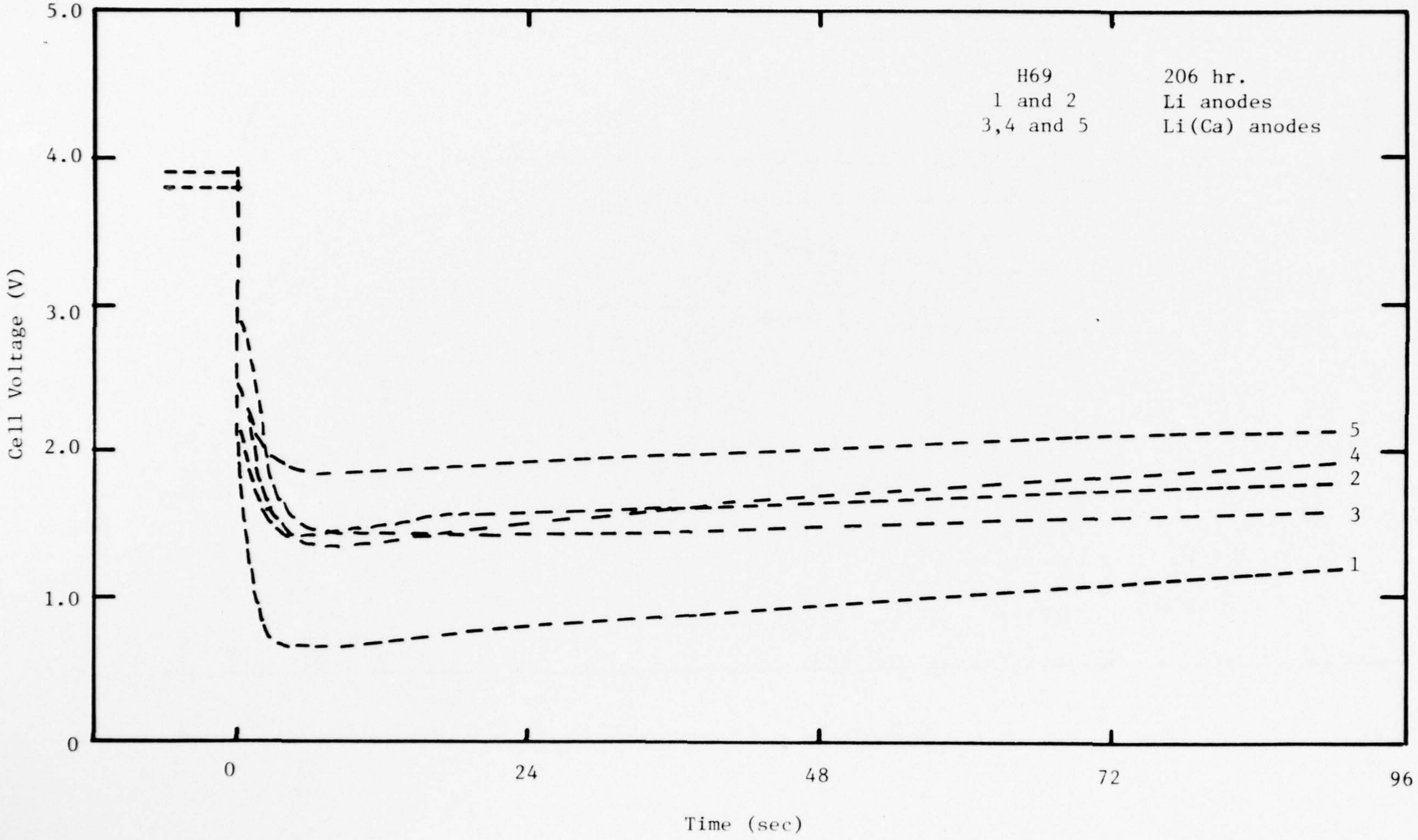

Fig. 10: Initial polarization of Li anode and Ca-coated Li anode, $SOCl_2$ cells with 480Ω (∿1cm²). The cells were stored at 71°C for 206 hr.

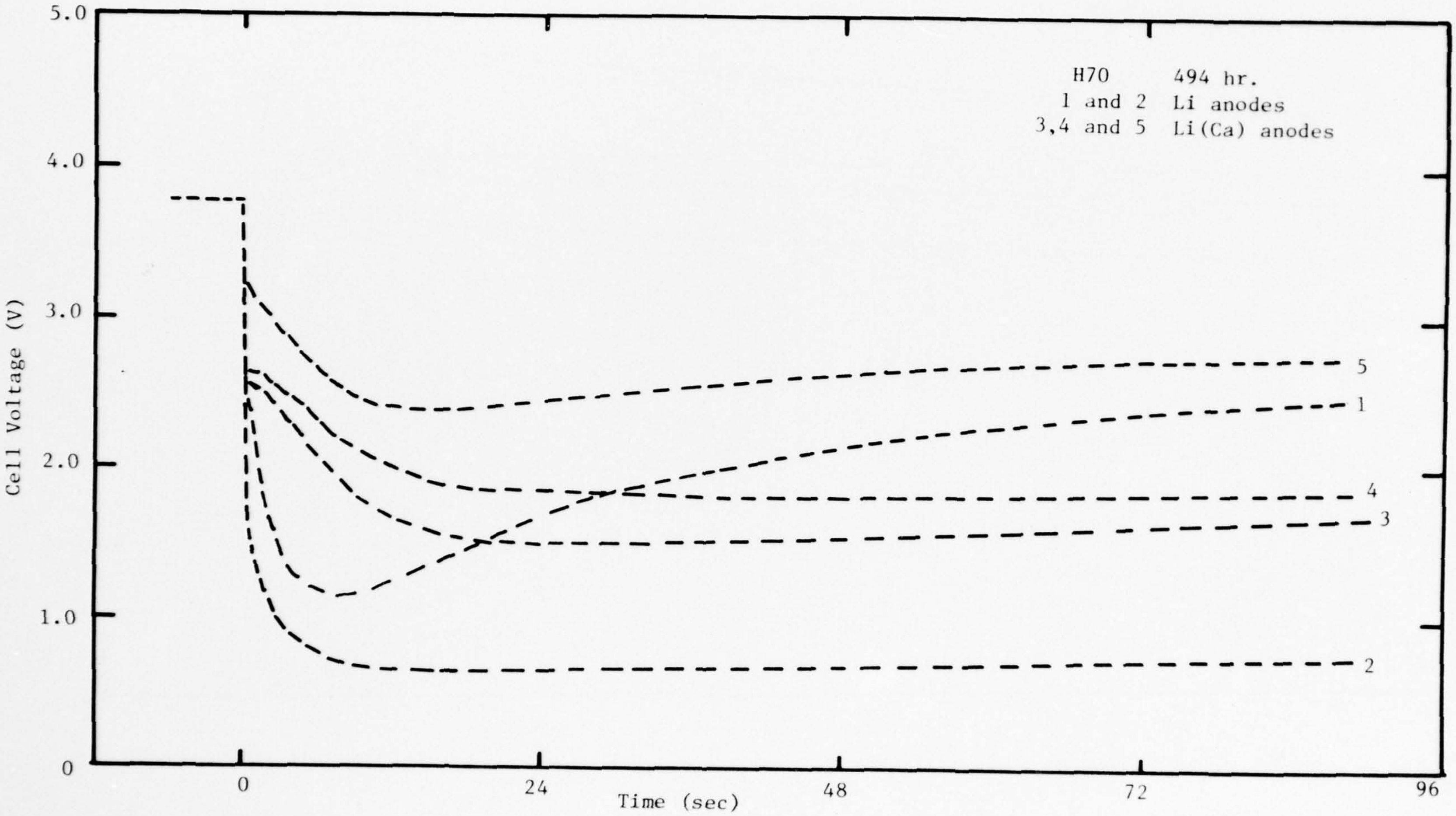

Fig. 11: Initial polarization of Li anode and Ca-coated Li anode, $SOCl_2$ cells with 480Ω (~1cm^2). The cells were stored at 71°C for 494 hr.

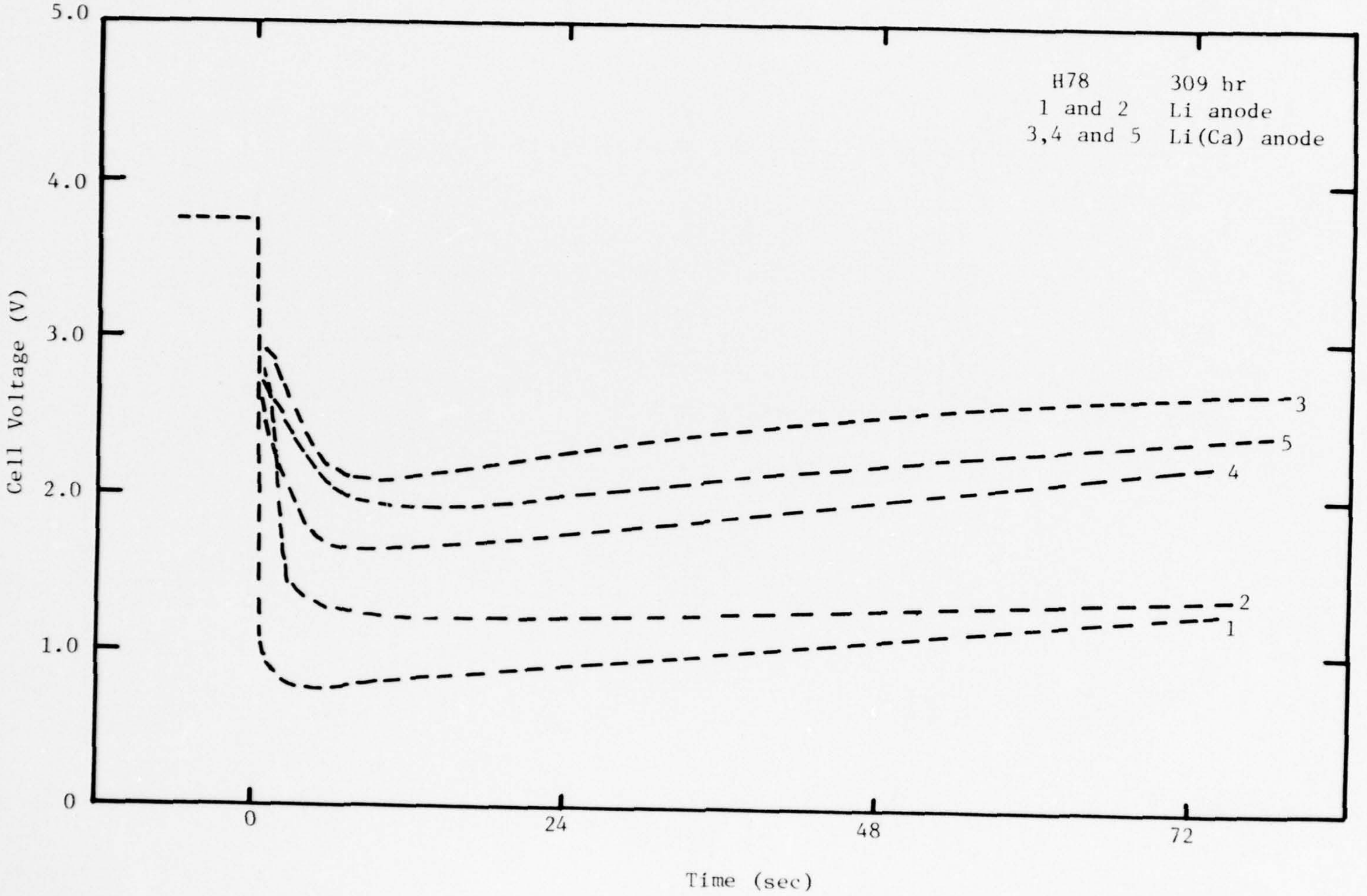

Fig. 12: Initial polarization of Li anode and Ca-coated Li anode, $SOCl_2$ cells with 480Ω (~1cm^2). They were stored at 71°C for 309 hr.

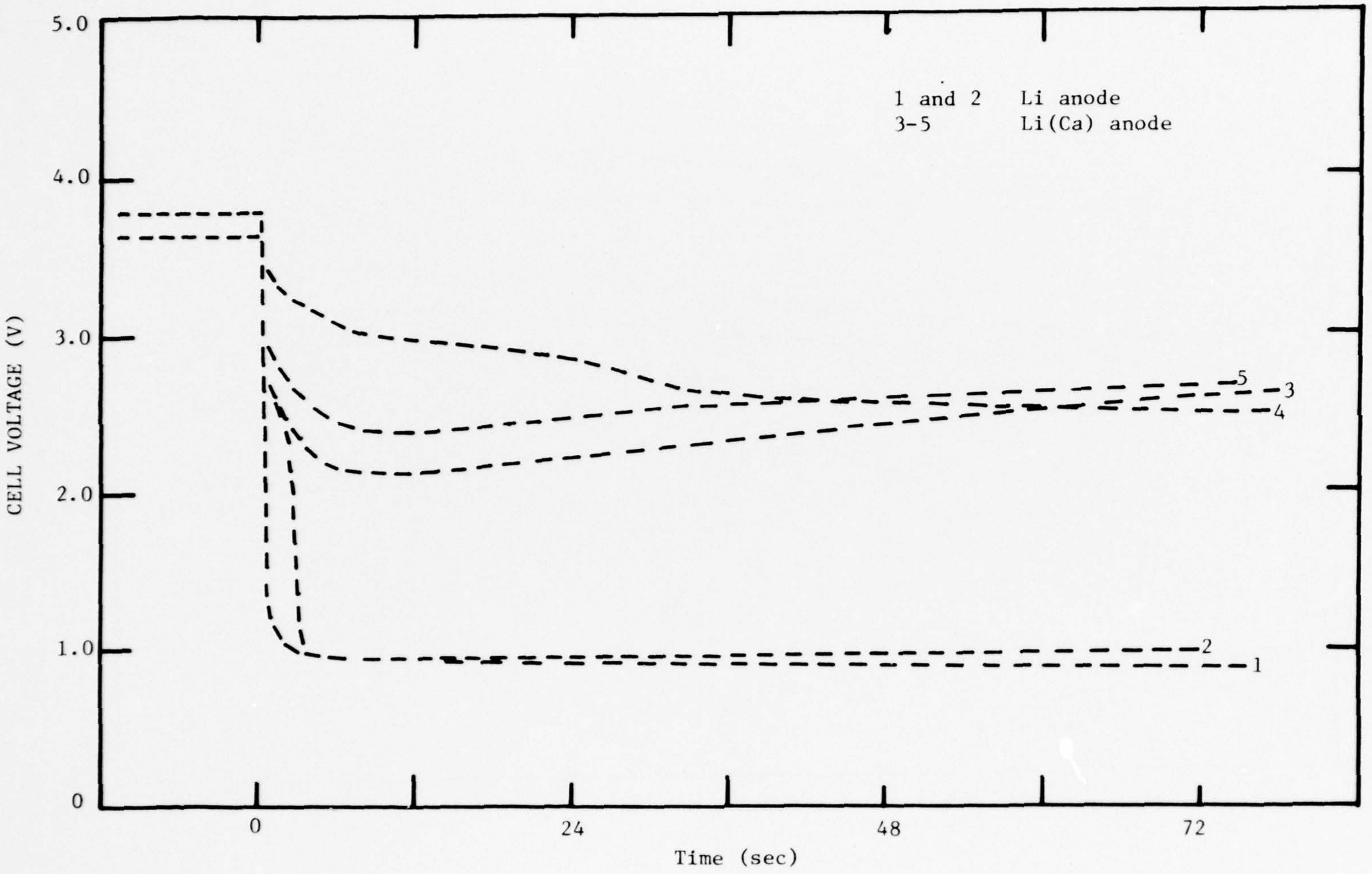

Fig. 13: Initial polarization of Li anode and Ca-coated Li anode, $SOCl_2$ cells with 480Ω (1 cm^2). They were stored at 71°C for 798 hr.

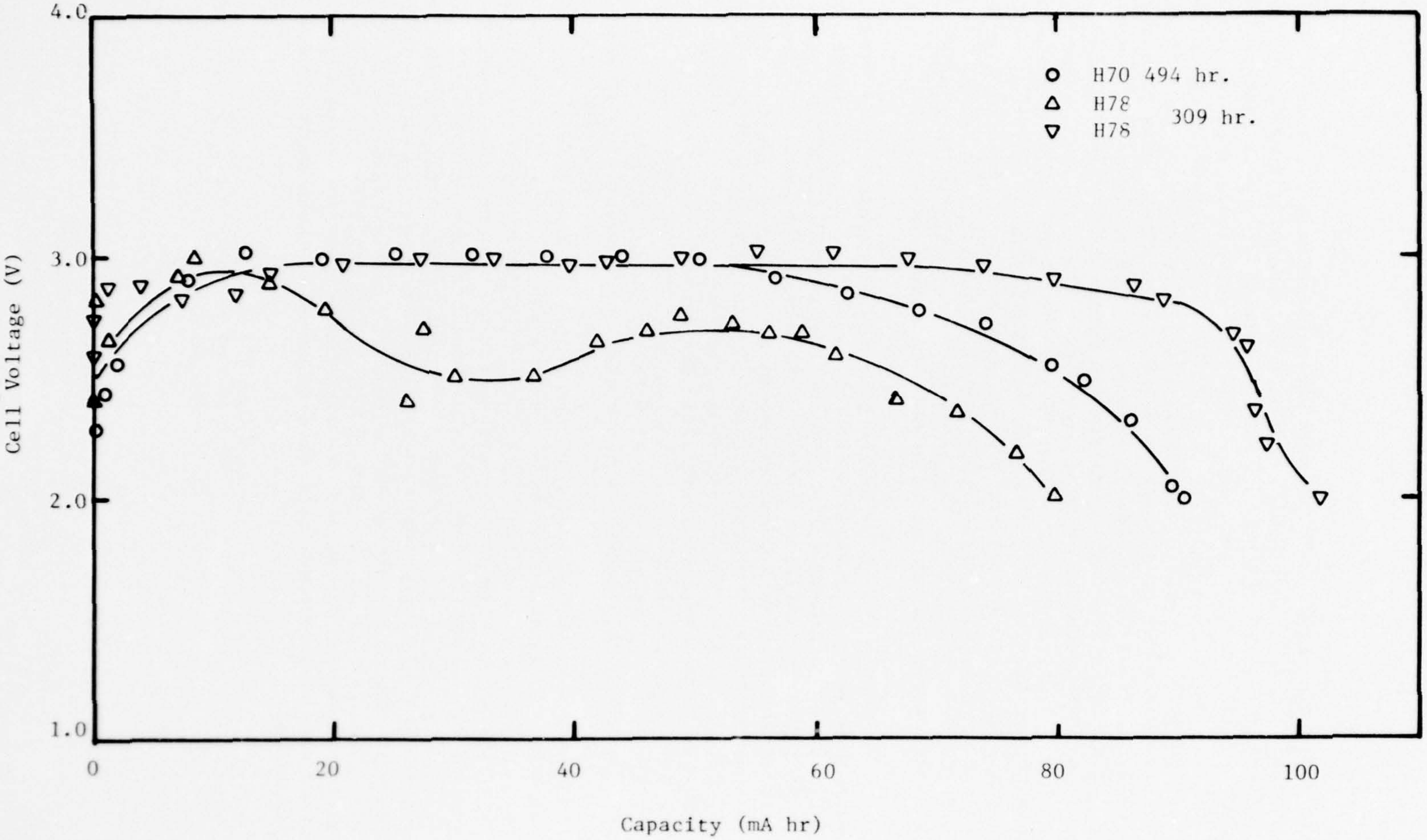

Fig. 14: Capacity of Ca-coated Li anode $SOCl_2$ cells discharged through 480Ω (~1cm^2). The cells were stored for the times indicated at 71°C.

it had a minimum at 2.5V and another maximum at 2.7V, before discharging smoothly to the 2.0V cutoff. Thus, even without optimization, we see that cells stored between 300 and 500 hrs at 71°C have yielded between 80% and 95% of their nominal capacity at acceptable voltages and currents. For example, cell H70-5 (494 hrs, 71°C) averaged 5.87 mA/cm^2 at an average cell voltage of 2.82V. Similarly, H78-4 discharged at an average current of 5.98 mA/cm^2 at an average of 2.87V. Even H78-5, with its poorer voltage regulation, yields an average of 5.06 mA/cm^2 with an average potential of 2.43V. The complete discharge of the H79 T-cells show similar improvements. Figure 15 presents the complete discharge record of H79-5. For comparison, similar data for a Li anode cell stored 664 hrs is presented also. Although the performance is still below acceptable limits, there is a vast improvement over the cell with the pure Li anode. The cell voltage averaged 2.32V during the discharge, averaged 4.83 mA/cm^2, and yielded about 60% of the theoretical capacity above the 2V cutoff. The cell potential of the Li anode cell never exceeded 1V.

Although the Li/Ca anodes prepared by exchange have shown remarkable improvements in performance, the effect is not consistent. Further tests have shown some cells with these improvements, while others have shown behavior similar to pure Li. We can, at the moment, identify two problem areas which may contribute to inconsistent results. The first is that during 71°C storage the H-cell's atmosphere begins to exchange significantly with the surrounding atmosphere somewhere around 350-400 hrs. While we have not identified this as a certain problem, it clearly has the potential to be a severe problem. By exchange, H_2O and O_2 can penetrate the cells and react with either the electrolyte and/or the anode. Improved experimental apparatus are currently being tested to eliminate this problem. The second potential problem area is more fundamental and concerns the state of the Li anode before and after Ca^{++} treatment. The state of the surface is essentially unknown. To date, our major characterization technique has been the voltage delay measurement. Thus, we have little information on how effectively the Ca is coating the Li surface and what the final surface state is. It is not unlikely that the state of the Li surface before treatment significantly effects the quality of the Ca exchange. The reactive nature of Li suggests that the state of the surface may differ from place to place. This problem will be explored in the coming quarter. The aim is to deposit coherent Ca plates. We anticipate that the inconsistencies in Li/Ca anode performance will be eliminated by these improvements in procedure.

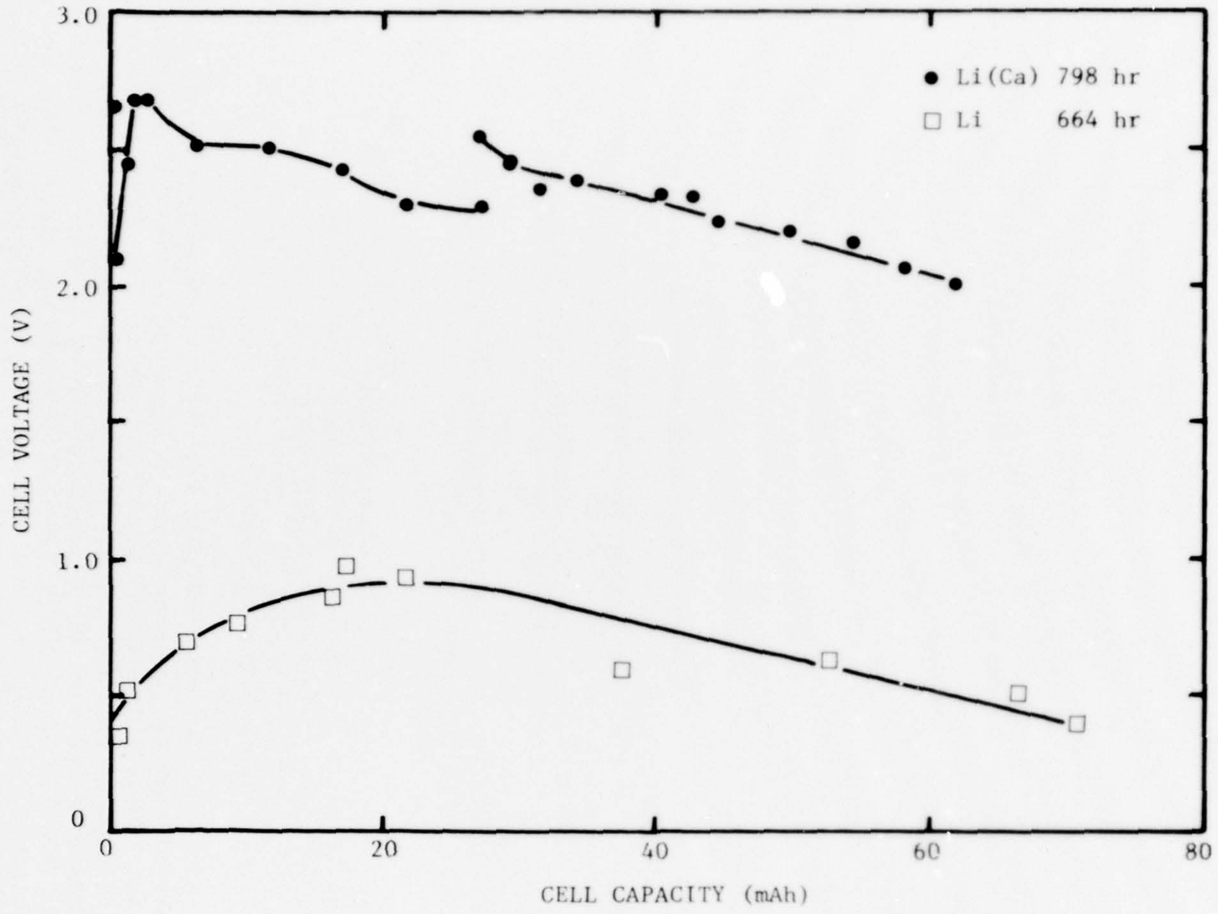

Fig. 15: Capacity of Li anode and Ca-coated Li anode, $SOCl_2$ cells discharged through 480Ω (∿1 cm^2) after storage at 71°C for the number of hours indicated.

IV. SUMMARY AND FUTURE WORK

During the past year our primary effort has centered on the problem of uncontrolled film growth on Li during storage at elevated temperatures. This results in severe voltage delay and depression in the Li/$SOCl_2$ cell. Our investigations of this problem have included measurements of electrolyte purity, studies of Li alloys, and measurements on cells stored at elevated temperatures with variations in electrode surface treatment and electrolyte composition. We have also measured the solubility of SO_2 in electrolyte in order to address the question of pressure buildup during cell discharge.

Efforts to establish the system purity have included a survey of elemental contamination by emission spectroscopy. Analysis of $LiAlCl_4$ salts and electrolyte have indicated no major metallic impurities. The passivating film from a Li anode stored at 71°C showed major enrichment in Cu and Fe, perhaps as much as 1%.

A substantial improvement in performance has been noted in cells assembled with careful attention to the purity. The cells were prepared with chemically pretreated components, and assembled in a specially controlled atmosphere: The electrolyte was stored a minimum of 140 hrs with Li metal at 71°C in sealed containers. The glass fiber separators and carbon cathodes were stored a minimum of 140 hrs in $SOCl_2$ with Li metal. Cells prepared by these techniques show much improved performance both in terms of reduced voltage delay and improved capacity in complete discharge. This improvement is noted for at least to 200 hrs storage at 71°C, but a marked decline is found between 200 and 300 hrs storage. Clearly, the pretreatments are introducing and/or removing substances, which strongly reduce the passivation in the early stages of the storage. The most probable explanation is that the Li pretreatment of the electrolyte is removing substances reducible by Li. These substances either form a passive film themselves or, more likely, depolarize the $SOCl_2$ reduction which enhances LiCl film formation.

Since we have observed that the electrolyte becomes bright yellow when stored with Li, it seems apparent that some unidentified material is being introduced into the solution. We have confirmed that substances are also removed from the electrolyte by Li, notably Cu and Fe. Since these elements had been found previously in relatively high concentration in the film of a heavily passivated electrode, quantiative analyses were obtained for them on the surface of Li stored with electrolyte. The analyses clearly prove that Cu and Fe are removed from the electrolyte by Li. This in itself may be beneficial for the cell, but it also suggests other potential Li-reactive species are being removed from solution by this pretreatment. Further characterization of the electrolyte after storage is indicated.

Twelve Li alloys were used as anodes in Li/$SOCl_2$ cells. Ten of these alloys had voltage characteristics similar to Li discharged under the same conditions. The discharge current was approximately 6.0 mA/cm^2. The ten alloys were: Li/Al(5 a/o), Li/Ag(5 a/o), Li/Au(2 a/o), Li/Bi(5 a/o), Li/Cu(4 a/o), Li/Mg(1 a/o), Li/Pb(3 a/o), Li/Si(4 a/o), Li/Sn(3 a/o) and Li/Zn(10 a/o).

The two alloys which displayed significantly different behavior were Cd(5 a/o) and Mg(5 a/o). The Cd alloys anode showed increasing polarization during the discharge. It was as much as 0.5V more positive than a pure Li anode. The Li/Mg alloy showed even more severe polarization during discharge at one-tenth the current density.

The Li utilization efficiencies of the alloys similar to Li ranged between 40% and 85% except for the Li/Si (4 a/o). The Li/Si had a Li utilization efficiency of greater than 100% when based only on Li oxidation. This is the first direct evidence of an alloying element oxidizing during discharge. Anode utilization based on Li plus Si (4 equivalents/mole) indicate 89-96%. This value is 10-15% greater than we have observed for pure Li.

The twelve Li alloys were tested after storage at 71°C. Storage times ranged from 70 to 207 hrs. The alloys were: Li/Ag(5 a/o), Li/Al (5 a/o), Li/Au(2 a/o), Li/Bi(5 a/o), Li/Cd(5 a/o), Li/Cu(4 a/o), Li/Mg (1 a/o), Li/Mg(5 a/o), Li/Pb(3 a/o), Li/Si(4 a/o), Li/Sn(3 a/o) and Li/Zn(10 a/o). None of the alloys completely alleviated the voltage delay. The Li/Ag alloy displayed some improvement. Three of the alloys, Li/Ag, Li/Cd, and Li/Mg(1 a/o), showed less passivation after testing. This indicates the possibility of anode surface modification for reduced voltage delay and depression. The Li/Mg(5 a/o) alloy has been eliminated from any future testing because of its inherently poor performance.

In further exploring the use of an alloying element with the Li to improve its storage capability, we have initiated work with Ca. Since the Ca was used in the form of a surface deposit, we have obtained some electrochemical characterization of pure Ca metal in $SOCl_2$. Ca discharges at 20 mA/cm^2 at +0.8V vs. a Ca reference in 1.5M $LiAlCl_4$, $SOCl_2$. In complete cells, Ca discharges with between 40% and 50% efficiency. With a 480Ω load, a typical discharge to a 1.0V cutoff yielded an average current of 4.18 mA/cm^2 with a mid-discharge voltage of 2.0V. Ca cells were also stored at 71°C for up to 350 hrs and these cells showed little or no passivation. Based on these results, Li-anode cells with Ca coatings (obtained by exchange with a Ca^{+2} solution in $SOCl_2$) were tested. These cells have shown excellent discharge characteristics with storage times up to 800 hrs at 71°C. The Ca coating techniques have not yet been optimized, and some inconsistencies have occurred. Nonetheless, the improvement vs. pure Li anodes is dramatic.

The main emphasis in the next quarter will be in further exploring the effects of improved system purity and in optimizing the effect of Ca.

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