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LITHIUM-INORGANIC ELECTROLYTE BATTERIES

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LITHIUM-INORGANIC ELECTROLYTE BATTERIES

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JUNE 1976

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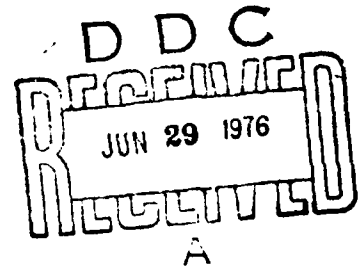
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A SOCl ₂ -based, Li primary battery operable over the temperature range -40° to +160°F is being evaluated. The desired energy density is 150 watt-hours per pound of total battery weight and the desired power density is 50 watts per pound.		

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20. Abstract (Cont.)

The major area of investigation during this report period has been into the voltage delays and depression observed after storage at 71°C (160°F). These are due to formation of films on the Li electrode because of its reaction with the solution. The effects on these films of storage time, electrolyte modification, and alloying of the Li have been explored.

According to previously reported data, SO₂ is a product of SOCl₂ reduction. SO₂ solubility in 1.5M LiAlCl₄/SOCl₂ electrolyte and in SOCl₂ was measured at 25°C and 0°C. The SO₂ mole fraction in the electrolyte at 25°C was 0.19 and at 0°C was 0.50. In pure SOCl₂, it was slightly less. Calculations based on this data and on ideal solution behavior indicate that pressure increase in discharged cells should be moderate, in agreement with observations.

Three additional alloys were tested as anodes in complete Li/SOCl₂ cells. These were: Li/Bi(5 at.%), Li/Mg(1 at.%) and Li/Si(4 at.%). They have discharge behavior similar to Li metal. The Li/Si alloy shows a utilization of 89-96% based on dissolution of both Li and Si (4 eq./mol).

The effect of storage time, cell preparation procedure, and alloying on the behavior of Li/SOCl₂ cells at 71°C was investigated. Storage tests with LiCl-saturated electrolyte show accelerated passivation. This procedure was used in all subsequent storage tests. A significant improvement was achieved when cells were prepared with purified electrolyte and in a specially pure atmosphere: Three of these cells showed no voltage delay after 208 hr at 71°C. One, discharged through a constant load to a 2.0V cutoff, had an average current density of 5.99 mA/cm² (equivalent to a fresh cell) and a mid-discharge voltage of 3.11V. Li/SOCl₂ cells prepared without these procedures have poorer performance.

None of the eleven alloys improved the passivation for storage times between 70 and 207 hr. These eleven alloys were: Li/Ag(5 at.%), Li/Al(5 at.%), Li/Au(2 at.%), Li/Bi(5 at.%), Li/Cd(5 at.%), Li/Cu(4 at.%), Li/Mg(1 at.%), Li/Mg(5 at.%), Li/Pb(3 at.%), Li/Si(4 at.%) and Li/Zn(10 at.%). The Li/Ag alloy did show some improvement. This alloy, as well as Li/Cd and Li/Mg(1 at.%), showed significant diminution of voltage depression during the evaluation process. This indicates that surface modification of some alloys takes place during anodization after storage.

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1. INTRODUCTION

In recent years there has been considerable research and development on ambient temperature, high energy density lithium 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 slower discharge rates (3).

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

The program work has centered along two lines: We have investigated the reaction stoichiometry of the cell discharge via chemical analysis of the reaction products, and we have also investigated the problem of Li/ SOCl_2 cell passivation during storage at 71°C (160°F), with a view to finding practical solutions to this problem.

Qualitative analyses indicated the presence of LiCl , S and SO_2 as reaction products of the cell discharge. We performed quantitative analyses for these species and, in the course of these, determined their distribution in the cell. The LiCl is insoluble in the electrolyte and deposited essentially completely within the carbon cathode. The S and SO_2 were found almost completely in the electrolyte. They proved to be quite soluble in the 1.8M LiAlCl_4 electrolyte, S greater than 1M and SO_2 greater than 3M. The quantitative analytical data showed the following ratios of product to charge; 1 mole $\text{LiCl}/\text{eq.}$, 0.25 mole S/ eq. , and 0.5 mole $\text{SO}_2/\text{eq.}$ No simple reaction stoichiometry corresponds to these analyses. More complex stoichiometries can be written, and a clear resolution of the problem awaits further analytical data. Attempts at establishing the coulomb number for SOCl_2 reduction proved unsuccessful, since a suitable inert tracer compound could not be found. Additional data and details are contained in our earlier quarterly reports, fourth through the seventh (4).

Storage of Li/ SOCl_2 cells at elevated temperature and subsequent discharge at room temperature results in large voltage delays and voltage depression. This continues to be a major problem in the utilization of the Li/ SOCl_2 cell. Our studies (5), and others (3,6), show that the cause of the 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.

Emphasis in the study of the passive films has been on establishing a well-characterized system. This provides base line performance for assessing possible improvements. Cell characterization has been both chemical and electrochemical. Cell components, both before and after storage, have been analyzed chemically and spectroscopically for metallic impurities. For the electrochemical characterization, potentiostatic, galvanostatic and constant load techniques have been employed with complete Li/SOCl₂ cells and with cells containing only Li electrodes. Concurrently, alleviation of the voltage delay was sought by modifying the cells: Both the electrolyte and the anode were modified by additives or alloying.

The chemical and spectroscopic analyses of cell components were obtained to explore the problem of electrolyte purity. Measurements by Marincic and Lombardi (7) indicated Fe at 200 ppm caused severe cell passivation during storage at 71°C. We have determined the levels of Fe electrolyte and the individual electrolyte components by colorimetry. Our electrolyte (1.8M LiAlCl₄) contained 3.8 µg Fe/ml. The LiCl, AlCl₃ and SOCl₂ contributed 0.13 µg Fe/ml, 1.7 µg Fe/ml and 0.5 µg Fe/ml, respectively. The details of the analysis are contained in previous reports (8,9). We obtained an emission spectrographic survey of elemental contamination which was sensitive to 50 elements. It revealed that Fe and Cu are present at significant levels in the surface film of a passivated anode (9). These levels could be as high as 1%. The analysis of electrolyte salts showed no major contamination in either our salts or in a sample provided by the Army Electronics Command (ECOM). These overall results suggest that purification of the cell components be directed specifically at Cu and Fe.

Electrochemical characterization of passivated Li anodes has developed some interesting results. Galvanostatic tests indicate that the Li electrode polarization is due to at least two sources: The initial electrode polarization results from the resistive film developed during elevated temperature storage; subsequently, additional concentration polarization is observed due to the local increase of Li⁺ concentration generated by the very nonuniform discharge. Potentiostatic testing of heavily passivated electrodes shows low current densities (~0.3 mA/cm²), essentially independent of potential above +0.5V vs. Li up to at least +3.0V vs. Li. We have also shown that electrolyte saturated with LiCl at 71°C causes more rapid development of the passivating film. Further details of these experiments are contained in earlier quarterly reports (4).

Modifications were made to the electrolyte in order to investigate possibilities of relieving the voltage delay problem. The modifications tested included the use of additives (SO₂, SbCl₅, EtN₄Cl, S, I₂), substituting 1.0M LiSbCl₆ for the 1.8M LiAlCl₄, or substitution of Li/Sn

alloy (3 at.% Sn) for Li. These modifications did not significantly alter the voltage delay or voltage depression after storage at 71°C (4).

In conjunction with this work, the electrochemical behavior of nine Li alloys were explored by two techniques: The current potential curves were measured and the various alloys were also tested as anodes in a battery configuration. Eight of the alloys proved suitable as experimental anodes. These were: Li/Al(5 at.%), Li/Ag(5 at.%), Li/Au(2 at.%), Li/Cd(5 at.%), Li/Cu(4 at.%), Li/Pb(3 at.%), Li/Sn(3 at.%) and Li/Zn(10 at.%). One alloy, Li/Mg(5 at.%), did not show sufficient current capability. Further details of these experiments are contained in earlier quarterly reports (8,9).

During the present quarter, study of the passivating film problem has continued. The major thrust of the experimental work has been to establish the effect on the cell voltage delay or depression of various preparation procedures.

The increased passivation caused by solutions pre-saturated with LiCl was confirmed. Cells prepared with electrolyte and separators pre-stored with Li at 71°C, and prepared in a very clean atmosphere, have shown remarkable improvements with much reduced voltage delays and depressions.

The effort to characterize the effect of alloying the anode has continued. Three more alloys have been tested as anodes in a battery configuration. These are: Li/Bi(5 at.%), Li/Mg(1 at.%), and Li/Si(4 at.%). Eleven alloys have been tested by storage at 71°C.

During the present quarter, we have also extended the measurements of the solubility of SO₂ in electrolyte. This is important because of the potential pressure build-up hazard during discharge. The measurements indicate the solubility is large enough to present no substantial problems.

II. SO₂ SOLUBILITY

The question of the potential hazard of SO₂ as a discharge product is an important one. During our investigation of the Li/SOCl₂ cell discharge stoichiometry, we established the SO₂ solubility to be ~3M in electrolyte at 25°C by gas chromatography (10). This solubility is much greater than previously reported in the literature (11) and suggests that SO₂ would not cause a significant pressure build-up in a discharged cell.

We have expanded the solubility information by determining the solubility of SO₂ in 1.5M LiAlCl₄/SOCl₂ and in SOCl₂ at 25°C (298K) and 0°C (273K). The SO₂ solubility was determined gravimetrically. The SO₂ was Matheson anhydrous with minimum liquid purity of 99.98%. The cylinder was connected to three gas bubblers joined in series. The first bubbler contained glass wool to remove any solid or non-volatile liquid particulates. The second bubbler contained a weighed aliquot of electrolyte (1.5M LiAlCl₄) or SOCl₂. The third and final bubbler contained concentrated H₂SO₄ to act as a flow monitor and to isolate the system from atmospheric contamination. The sample bubbler was maintained at 25°C in air or at 0°C in an ice bath. The flow of SO₂ was set to minimize SOCl₂ loss from the solution by allowing little or no exit bubbling. Bubbling was continued until no more weight was gained. Four measurements were made on electrolyte, two at 25°C and two at 0°C, and two measurements were obtained with SOCl₂, one at 25°C and one at 0°C.

The results of the measurements are shown in Table 1. They are presented as mole percentages, which is calculated directly from the weight data, and as molarity. The molarity values contain some uncertainty introduced by the values of the solution density. The densities have not been measured, but have been estimated from literature values for liquid SO₂, SOCl₂ and electrolyte (12). The density was estimated on the assumption that each component contributed to the density its mole fraction of its pure state density.

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

The calculated densities were all within $\pm 0.03 \text{ g/cm}^3$ of 1.60 g/cm^3 . This value was chosen to calculate all of the molarities presented in Table 1.

The data confirm the value of the solubility at 25°C established previously by gas chromatography. They also show very large solubilities at 0°C. There appears to be somewhat lower solubility in pure SOCl₂ relative to the electrolyte. Figure 1 is a comparison of the measured SO₂ solubilities with values calculated based on ideal solution behavior (13).

TABLE 1

SO₂ Solubility in 1.5M LiAlCl₄/SOCl₂ and SOCl₂
at 25°C (298K) and 0°C (273K)

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

^aCalculated molarity based on a solution density of 1.60 g/cm³,
 see text.

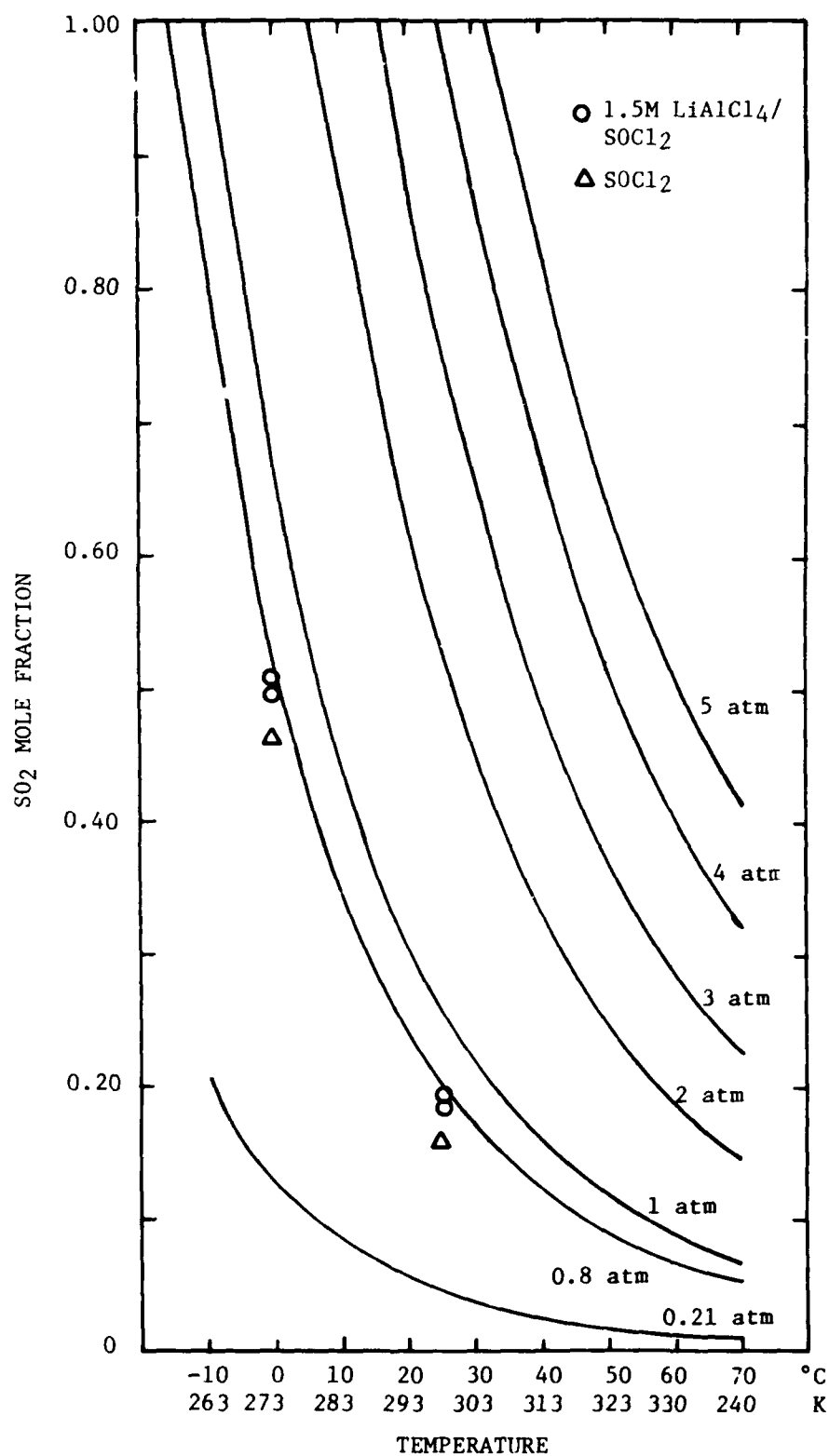


Fig. 1: SO_2 solubility in 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$ and SOCl_2 . Solid line (—) calculated solubility from ideal solution equations.

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

Where x is the SO_2 mole fraction, ΔH_v (cal/mol) is the SO_2 heat of vaporization at T_0 (K), T (K) is the temperature of interest and R is the gas constant (1.98 cal/mol/K). T_0 determines the SO_2 equilibrium pressure over the solution, and this pressure is the equilibrium vapor pressure of SO_2 over pure SO_2 liquid at T_0 . The experimental data correlate reasonably well with the ideal solution model. This correlation in conjunction with Dey's C-cell discharge data (14) and our reaction stoichiometry data (10) suggests that a sealed Li/ SOCl_2 cell can accommodate the SO_2 produced with only moderate pressure increases (1-3 atm). Dey's C-cell yielded 4.1 Ahr from 20g of 1.0M LiAlCl₄/ SOCl_2 at 25°C. The initial electrolyte composition is 0.150 mol SOCl_2 and 0.012 mol LiAlCl₄. Our stoichiometry data give the final solution composition as 0.074 mol SOCl_2 , 0.012 mol LiAlCl₄, 0.076 mol SO_2 and 0.038 mol S. The mole fraction of SO_2 is ~0.5, which based on ideal solution behavior would be in equilibrium with SO_2 vapor at 1.2 atm (18 psi). The measured pressure increase in this cell was 10 psi (14).

We use the measured pressure values rather than those corrected for the volume of the pressure gauge. This is justified if we assume the gas to consist solely of SO_2 and vapors (e.g., SOCl_2). In this case, the actual pressure will not change due to the volume increase from 3 to 8 cc (i.e., the case during Dey's pressure measurements). The cell pressure would be maintained by evaporation of additional SO_2 without significantly affecting the SO_2 concentration in solution (e.g., 5 cc of SO_2 at 0.68 atm (10 psi) corresponds to $1.4 \cdot 10^{-4}$ moles vs. a total of $8 \cdot 10^{-2}$ moles in solution). While the calculated and measured pressure values differ by a factor of almost 2, we feel the agreement is still sufficiently good that the ideal solution model can be used as a first approximation in estimating pressure build-up in other cell configurations. Additional SO_2 solubility measurements at elevated temperatures and pressures would refine the model further.

III. ELECTROCHEMICAL CHARACTERISTICS OF Li/SOCl₂ CELLS AFTER STORAGE AT 71°C

We have continued the characterization of voltage delays and/or depressions of Li/SOCl₂ cells after storage at 71°C. The characteristics of cells with Li alloy anodes are discussed in Section IV. In the previous quarterly report, evidence was presented indicating that LiCl-saturated electrolyte enhances voltage delays and depressions (9). Investigation of this effect was continued. In this regard, an estimate of LiCl solubility in the electrolyte at 71°C was made. During this quarter, we have also assembled and tested Li/SOCl₂ cells which show remarkable improvements in voltage delay and depression. These cells were prepared with chemically pre-treated electrolyte and separators, and assembled in a clean atmosphere.

The voltage delay and depression data have been acquired on complete Li/SOCl₂ 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. Our primary test procedure after storage is composed of three parts: the initial test is a constant load of 480Ω wherein 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/cm² with this load. For a practical cell with a ~400cm² electrode area, this is equivalent to ~3A rate (3). The second test phase is a galvanostatic test at current densities between 0.10 mA/cm² and 5.0 mA/cm². Here again the cell voltage and Li anode potential are measured. The third and final test phase repeats the first, and any changes in voltage delay and depression as the result of the testing anodization are assessed.

A. Effect of LiCl-Saturated Electrolyte

In previous work (9), it was observed that the severity of the voltage delay and depression was strongly dependent on whether the T-cells were stored on the vapor or liquid phase. This effect was explained in the basis of LiCl solubility in the electrolyte: as LiCl forms at the anode surface it will also dissolve into the solution, and will continue to do so until the cell electrolyte is saturated. T-cells in the vapor phase will clearly reach this solubility limit before cells stored in the liquid phase. In the former case, the available electrolyte is limited to the three glass fiber separators and the carbon cathode. For the cell in the liquid phase, as long as the storage time is less than the time necessary for the excess electrolyte to reach saturation with LiCl, voltage delay remains minimal.

We have reaffirmed these results with further tests. Two H-cells were prepared, each containing 4 T-cells. Two of the T-cells were in the liquid and two in the vapor in each H-cell. In one H-cell (H-10) solid LiCl was added to the electrolyte. In the other H-cell (H-11) no LiCl was added. The cells were stored 110 hrs at 71°C and tested. Figure 2 shows the results of the initial constant load test of the eight T-cells. The difference between the two H-cells is dramatic. None of the T-cells from H-11 show any voltage delay, while all of those from H-10 do. Three of the four H-11 cells have little voltage depression. The fourth cell does have a voltage depression, with a cell voltage of 2.7V at 60 sec after application of the load. The four H-10 T-cells all have severe voltage depressions. Cell voltages range from only 1V up to 2V 60 sec after application of the load. More evidence of the passivation of the H-10 T-cells is shown by the anode polarization curves obtained galvanostatically. Figure 3 shows the anode potential vs a Li reference as a function of current density for the eight T-cells. Three of the four T-cells of H-11 have polarizations of less than +0.20V at 4 mA/cm² and the fourth shows only +0.30V at 4 mA/cm². The polarization is much greater for the H-10 T-cells. The anode polarization is greater than +0.20V at current density less than 2 mA/cm² for all four cells.

The H-10 data further suggest a "transition" current density above which the polarization increases catastrophically with increased current density. This behavior is similar to that observed in our previous potentiostatic measurements of highly passivated Li anodes. These indicated a limiting current of ~0.3 mA/cm², independent of polarization between +0.5V and +3.0V vs Li (8). Fresh and slightly passivated anodes did not display this behavior over the current density range measured. Such anodes show a gradual increase in polarization with increased current density. While there is probably no fundamental significance to this "transition" current density, it perhaps may be interpreted as the maximum current density at which the cell will discharge efficiently.

The large polarization above the transition current density is probably due to concentration polarization. The active surface of the filmed Li anode is much smaller than the geometric area causing very large real current densities. These in turn cause large local concentrations of Li⁺, which either can not diffuse away at a sufficient rate or can exceed the solubility limits of LiAlCl₄, which precipitates. This causes further blockage of the active surface.

Based on the results of cells H-8, H-10 and H-11, we are using LiCl saturated electrolyte in all further testing. This will more closely duplicate the conditions of a practical cell, and simultaneously provide an accelerated test program. The small electrolyte volume and large Li surface area normally encountered in a practical cell will certainly encourage rapid saturation of the electrolyte.

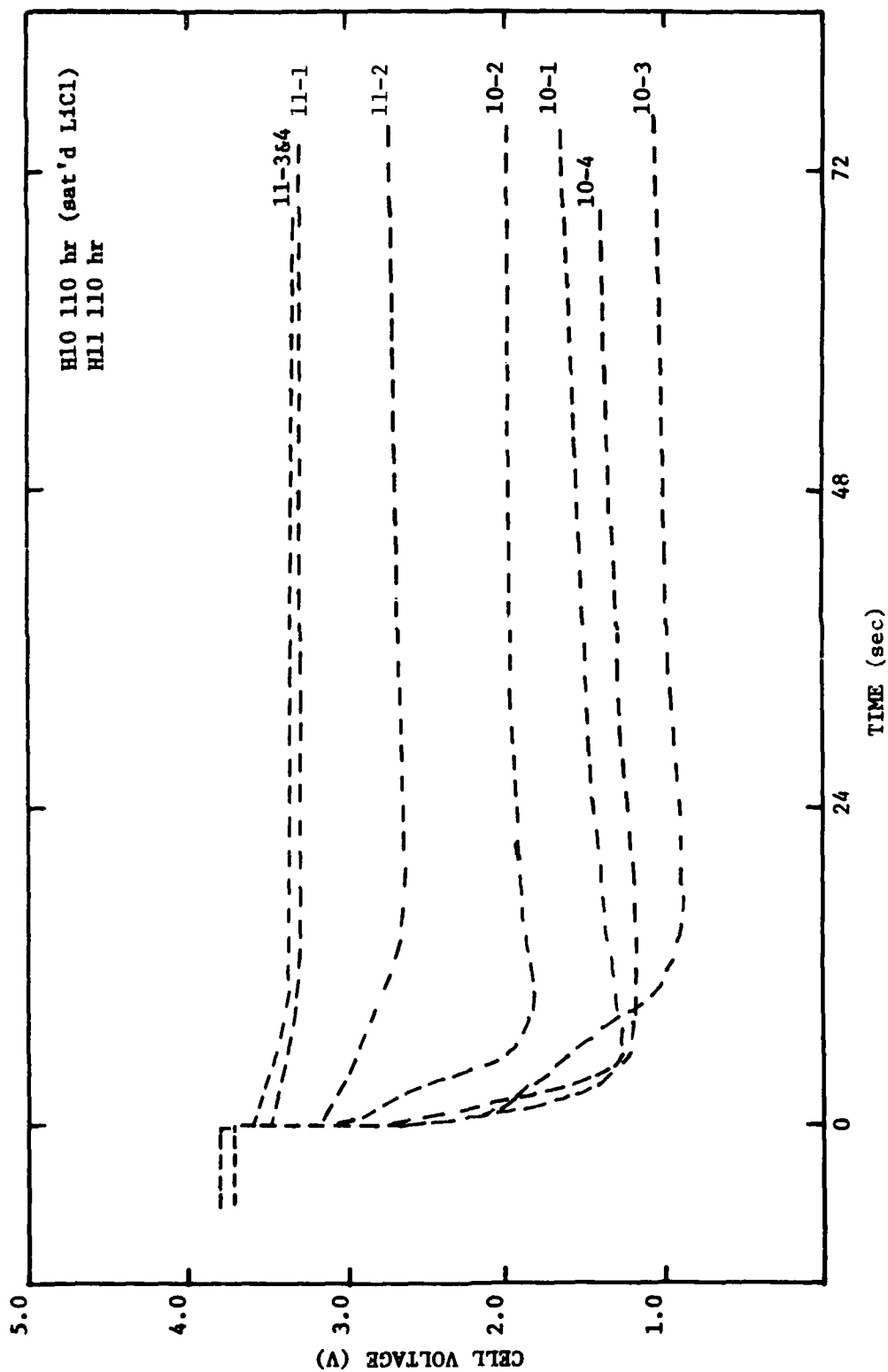


Fig. 2: Initial polarization of Li anode, SOCl_2 cells with 480 Ω load ($\sim 1 \text{ cm}^2$). Cells H10 and H11 stored 110 hr at 71°C with 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$, H10 electrolyte was saturated with LiCl .

LiCl Solubility in Electrolyte

In conjunction with the above work we have made an estimate of the solubility of LiCl in 1.5M LiAlCl₄/SOCl₂ at 71°C. The solubility was determined by adding increments of LiCl to a weighed aliquot of 1.5M LiAlCl₄/SOCl₂. After each LiCl addition, the solution was stored at 71°C in a sealed cell. The LiCl solubility is between 0.092M and 0.156M, which is much higher than at room temperature. After the last addition of LiCl, the solution was held at 71°C for 7 days to insure equilibrium. Two observations made during the experiment suggest this high solubility may not be purely a physical dissolution but also a chemical reaction: Firstly, the initial increments of LiCl which did dissolve did so relatively slowly, taking up to 5 days. Secondly, the dissolved LiCl did not precipitate when the cell was cooled to 25°C and allowed to stand for up to 8 hrs at this temperature.

B. Li/SOCl₂ Storage Cell Tests

During this quarter we have measured the voltage delay and discharge characteristics of Li/SOCl₂ cells prepared under three different sets of conditions: one series of cells contained our type A electrolyte. This comprises distilled MCB SOCl₂ (TX535) to which LiCl (MCB) and AlCl₃ (Fluka) are then added. The addition of AlCl₃ is controlled to maintain the temperature below 30°C during preparation. Another series of cells contained our type D electrolyte. This comprises distilled Eastman SOCl₂ (246) to which LiCl (MCB) and AlCl₃ (Fluka) are added. This solution was kept at or below -20°C during preparation. The color of this solution was the same as that of distilled SOCl₂, pale yellow. The type A was a slightly darker brown. A third series of cells was prepared with chemically pre-treated components and in an argon purged glove bag instead of the glove box. The glove bag was used to ensure a completely clean atmosphere. Here, the type A electrolyte was treated for 140 hr at 71°C with Li metal foil (4 cm²/ml). The solution became yellow during storage and the Li metal surface developed a brown coat. This electrolyte is designated type E. The separators used in these cells were treated in SOCl₂ containing Li metal foil for 140 hr at 71°C before use.

Table 2 lists the cells tested, and the experimental conditions. The T-cells were all stored in the vapor phase over LiCl saturated electrolyte. Table 2 also contains a summary of the test results. The voltage delay and depression data were obtained as described previously with a 480Ω load. The discharge data were obtained for a 480Ω load discharge.

We see that up to 90 hours neither the type A or D electrolyte cells show any voltage delay. The 60 sec cell voltage does, however, show voltage depression for all three H-cells (11 T-cells). The voltage delay tests for the individual cells are shown in Figures 2, 4, and 5. These data also indicate reasonably good the cell-to-cell reproducibility.

TABLE 2

Test Conditions and Voltage Delay Results for
Li Anode/SOCl₂ T-Cells Stored at 71°C

<u>Cell</u>	<u>Electrolyte^a</u>	<u>Hrs Storage at 71°C</u>	<u>Voltage Delay (sec)^b</u>				<u>Cell Voltage at 60 sec</u>
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	
H10	A	110	x	70	x	x	1.51 ± 0.29
H25	A	88	o	o	o	-	2.63 ± 0.14
H17	D	89	o	o	o	o	2.74 ± 0.04
H18	D	91	o	o	o	o	2.74 ± 0.18
H26	D	136	x	x	-	-	1.80 ± 0.00
H20	E	136	8.4	o	-	29	2.59 ± 0.12
H21	E	208	o	o	3.6	o	2.61 ± 0.16

Discharge Data for Li/SOCl₂ Cells

<u>Cell</u>	<u>OCV</u>	<u>Average Current (mA/cm²)</u>	<u>MDV^c V</u>	<u>Capacity Coul</u>	<u>Efficiency^d %</u>
H10-4	3.74	4.86	2.35	224	35
H20-4	3.64	6.11	3.11	410	65
H21-4	3.61	5.99	3.11	428	68

a - A-15M LiAlCl₄, dist. MCB SOCl₂, prepared at less than 30°C.

D-1.5M LiAlCl₄, dist Eastman SOCl₂, prepared at -20°C.

E-Type A heated with Li metal for 140 hr at 71°C.

All electrolytes saturated with LiCl.

b - Test with 480Ω load, x - voltage delay greater than 72 sec

o - no voltage delay

c - Mid-discharge voltage.

d - Efficiency based on original Li content and at a 2.00V cell cutoff voltage.

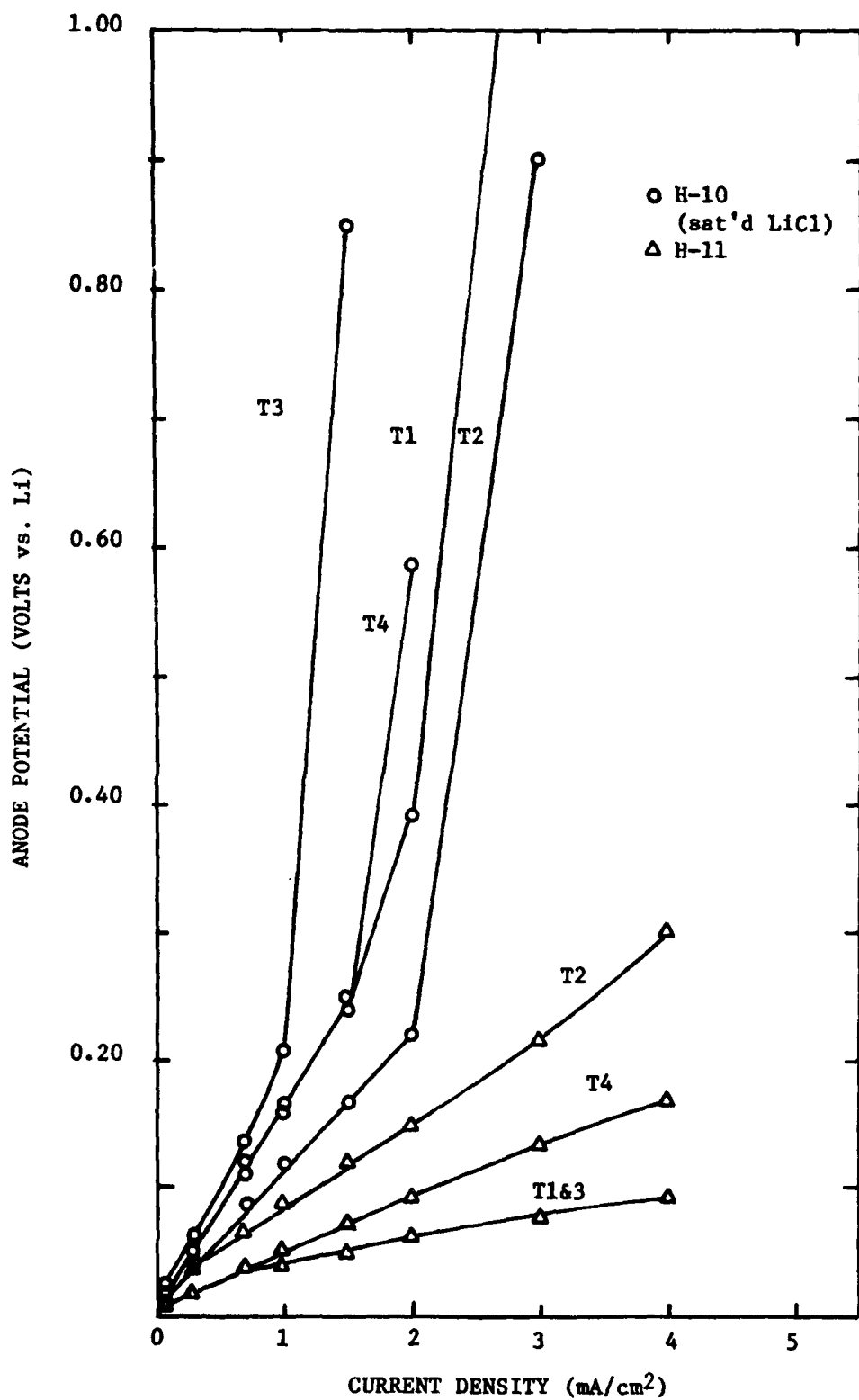


Fig. 3: Anode polarization of Li/SOCl₂ cells. H10 and H11 stored 110 hr at 71°C with 1.5M LiAlCl₄/SOCl₂. H10 electrolyte was saturated with LiCl.

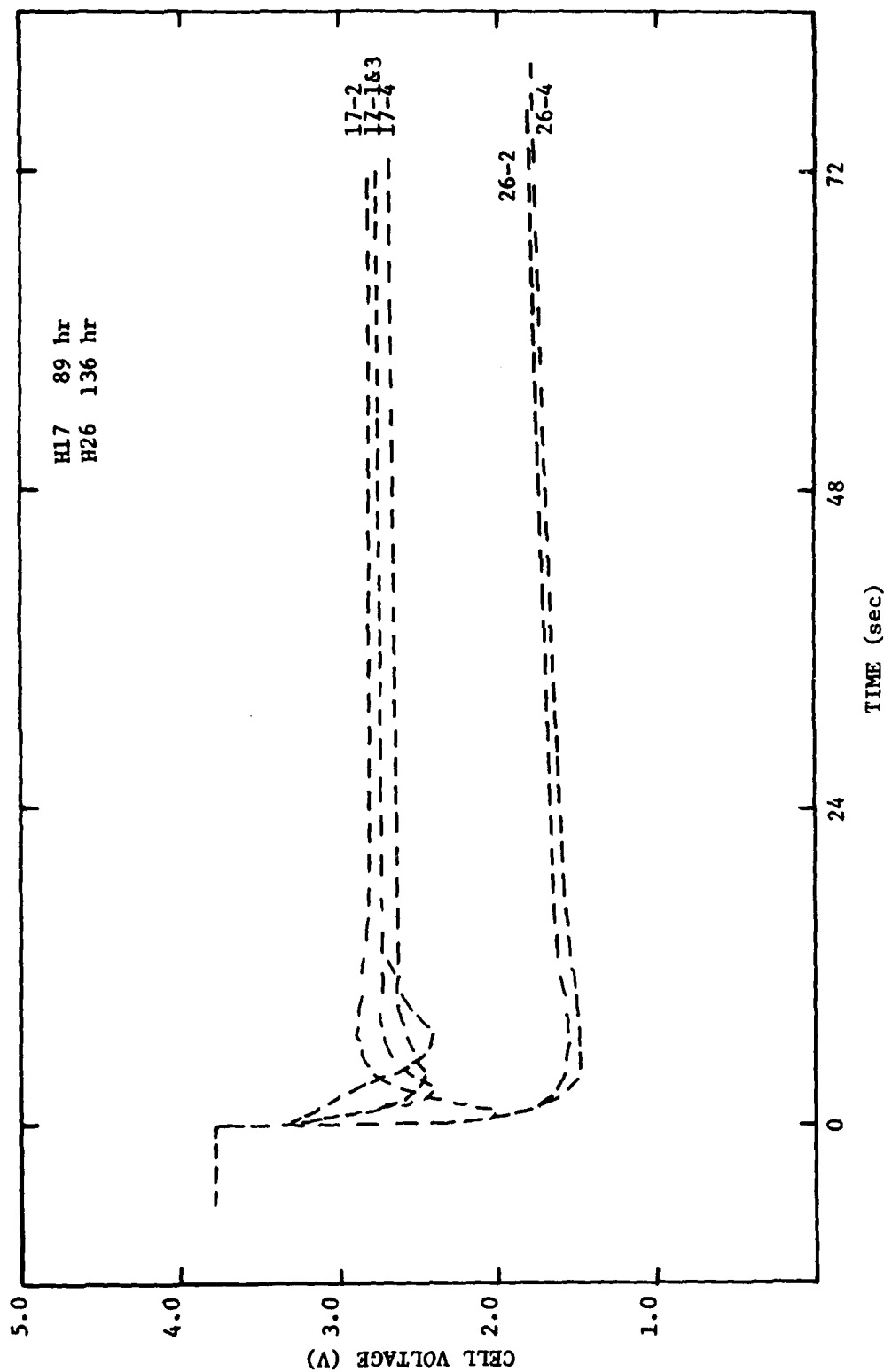


Fig. 4: Initial polarization of Li anode/SOCl₂ cells with 480C (0.1 cm²). H17 was stored 89 hr and H26 stored 136 hr in LiCl saturated 1.5M LiAlCl₄/SOCl₂.

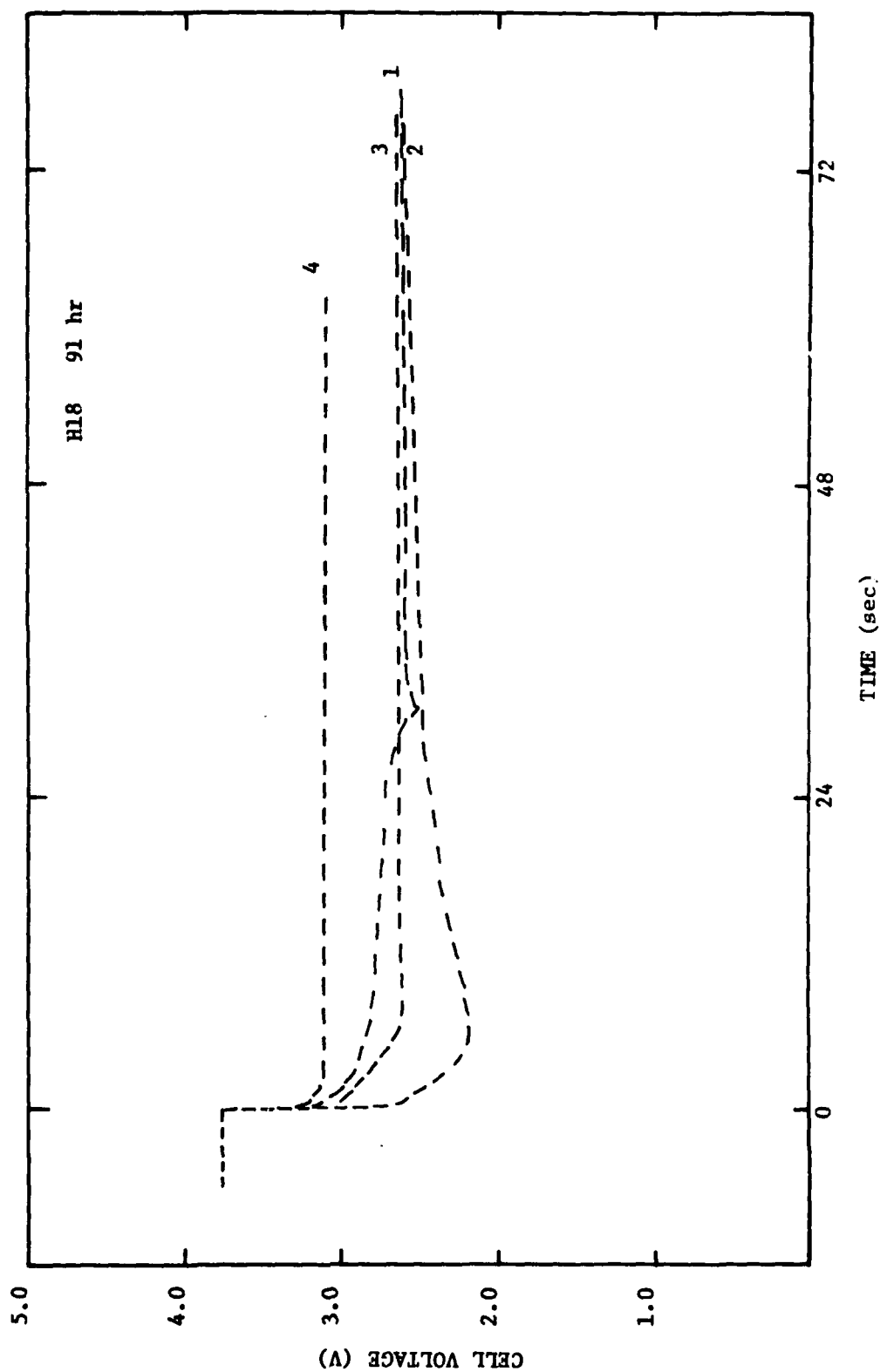


Fig. 5: Initial polarization of Li anode/SOCl₂ cells with 480Ω (0.1 cm²). H18 was stored 91 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

At 110 hr and greater the type A and D electrolyte cells show voltage delay and, after 60 sec discharge, the voltage depression is severe. Figures 5 and 6 show the individual T-cell test curves. These test data indicate that there is no significant difference between the type A and type D electrolytes in modifying the voltage delay characteristics.

A remarkable improvement in the voltage delay and depression is seen in the chemically pretreated cells prepared in the glove bag. These were cells H-20 stored 136 hr at 71°C and H-21 stored 208 hr at 71°C. After 136 hr storage, one T-cell from H-20 has no voltage delay and the other two are less than 30 sec. This is a clear improvement compared with the H-26 T-cells. There is also a clear improvement in the cell voltage at 60 sec. The H-21 cell data are even more striking. Three T-cells have no voltage delay after 208 hr at 71°C. The fourth has a voltage delay of less than 4 sec. The cell voltage at 60 sec is the same observed for the H-20 T-cells. Apparently no significant passivation occurred between 136 and 208 hrs. Figure 7 and 8 show the individual voltage delay tests for H-20 and H-21. Figure 9 shows a comparison of the anode polarization of H-21 T-cells and H-26 T-cells. These data further illustrate the improved performance of the H-21 T-cells.

The characteristics of the complete cell discharge to 2.0V are also improved for the H-20 and H-21 T-cells. Table 2 contains some pertinent discharge data and Figure 10 shows the voltage curves for T-cells from H-10, 20 and 21. Again, an improvement is clearly evident. The estimated Li utilization to 2.0V is only about 10% less than we have observed for fresh Li anode discharges (9). The average discharge current and the mid-discharge voltage are much better than for the H-10 T-cell.

Three major changes were made in the preparation of these cells. The specific change or changes which are responsible for this improvement are presently being investigated.

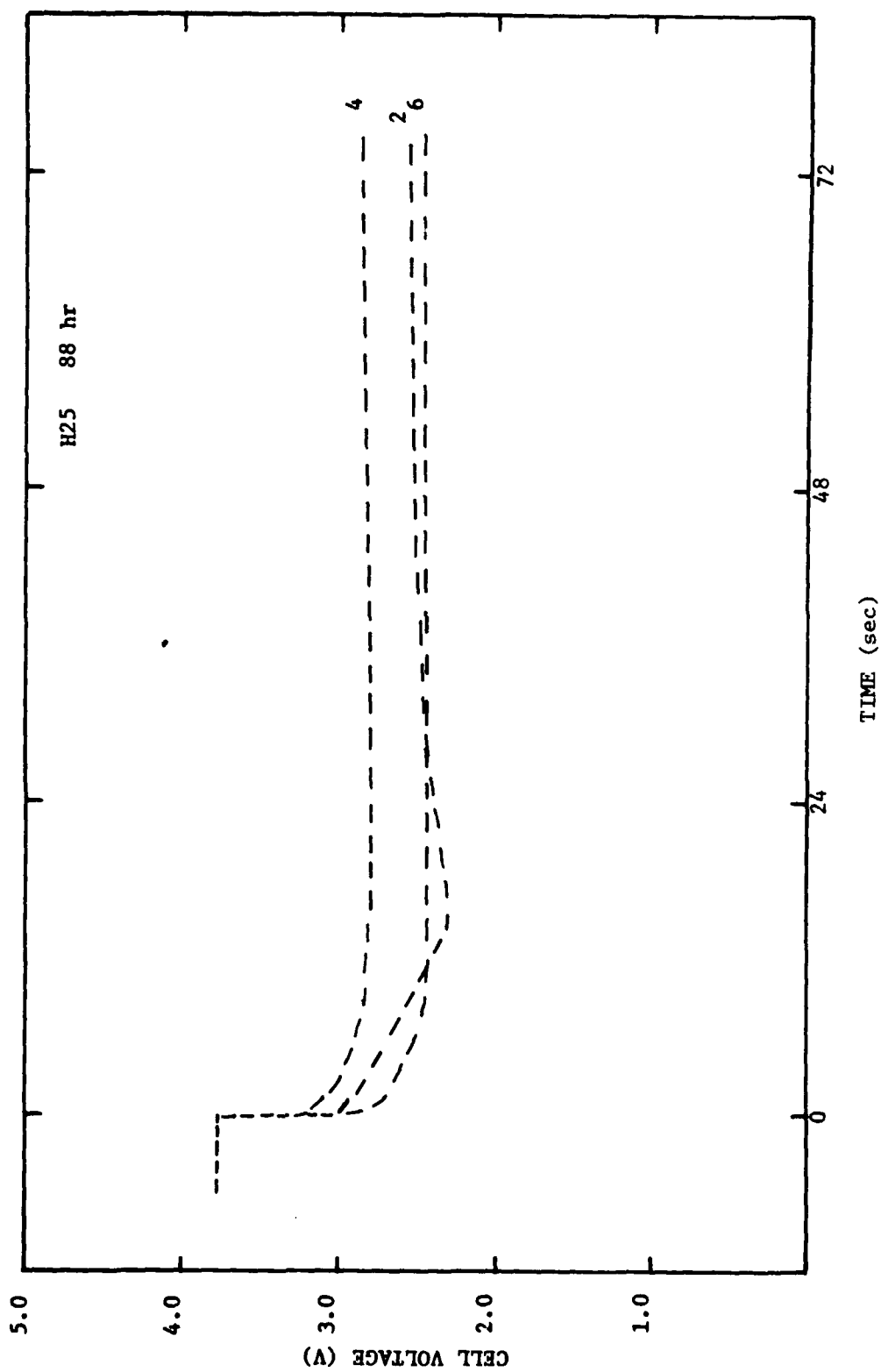


Fig. 6: Initial polarization of Li anode/SOCl₂ cells with 480G (v1 cm²). H19 was stored 88 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

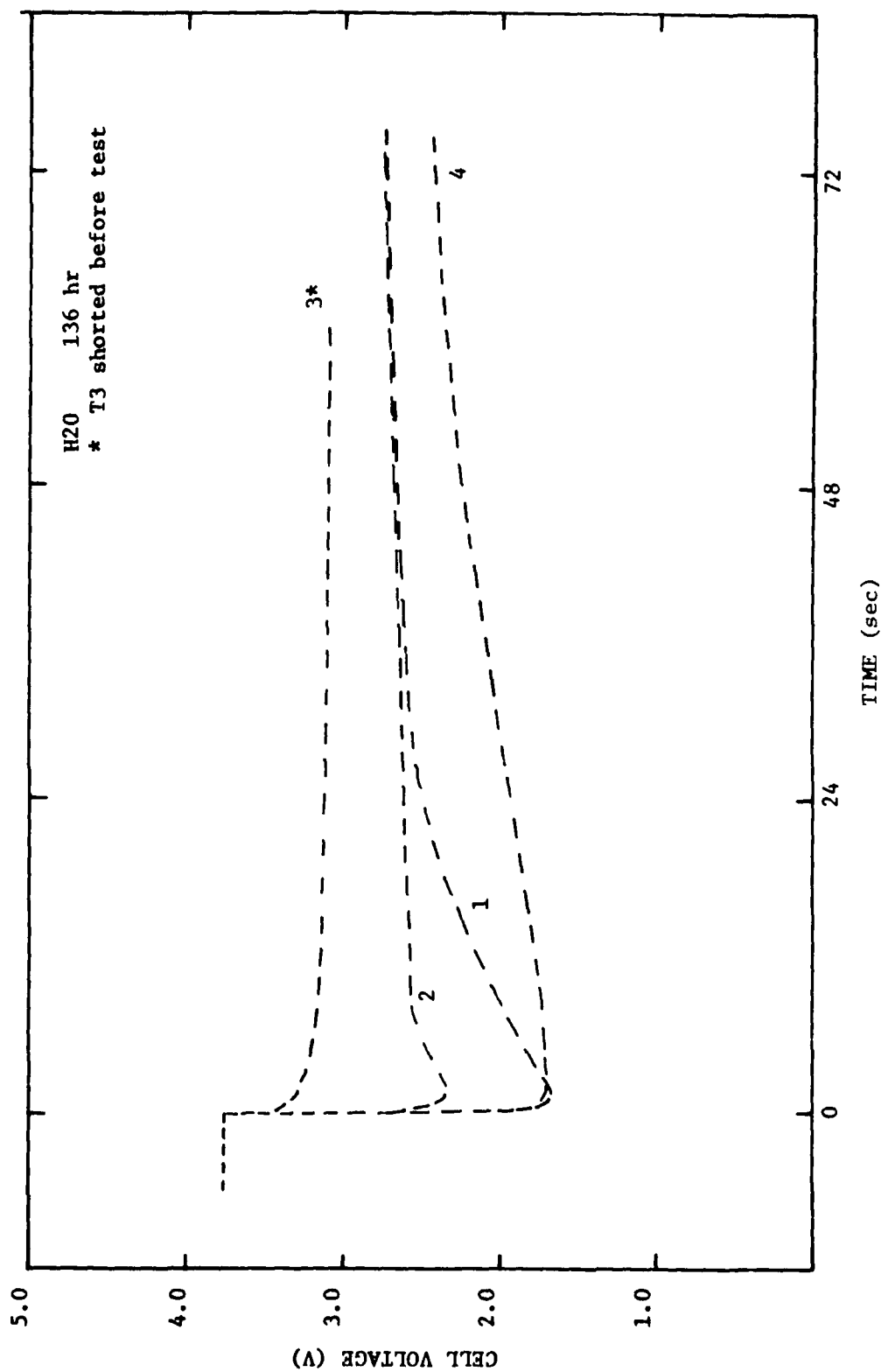


Fig. 7: Initial polarization of Li anode/SOCl₂ cells with 480Ω (∞1 cm²). H₂O was stored 136 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

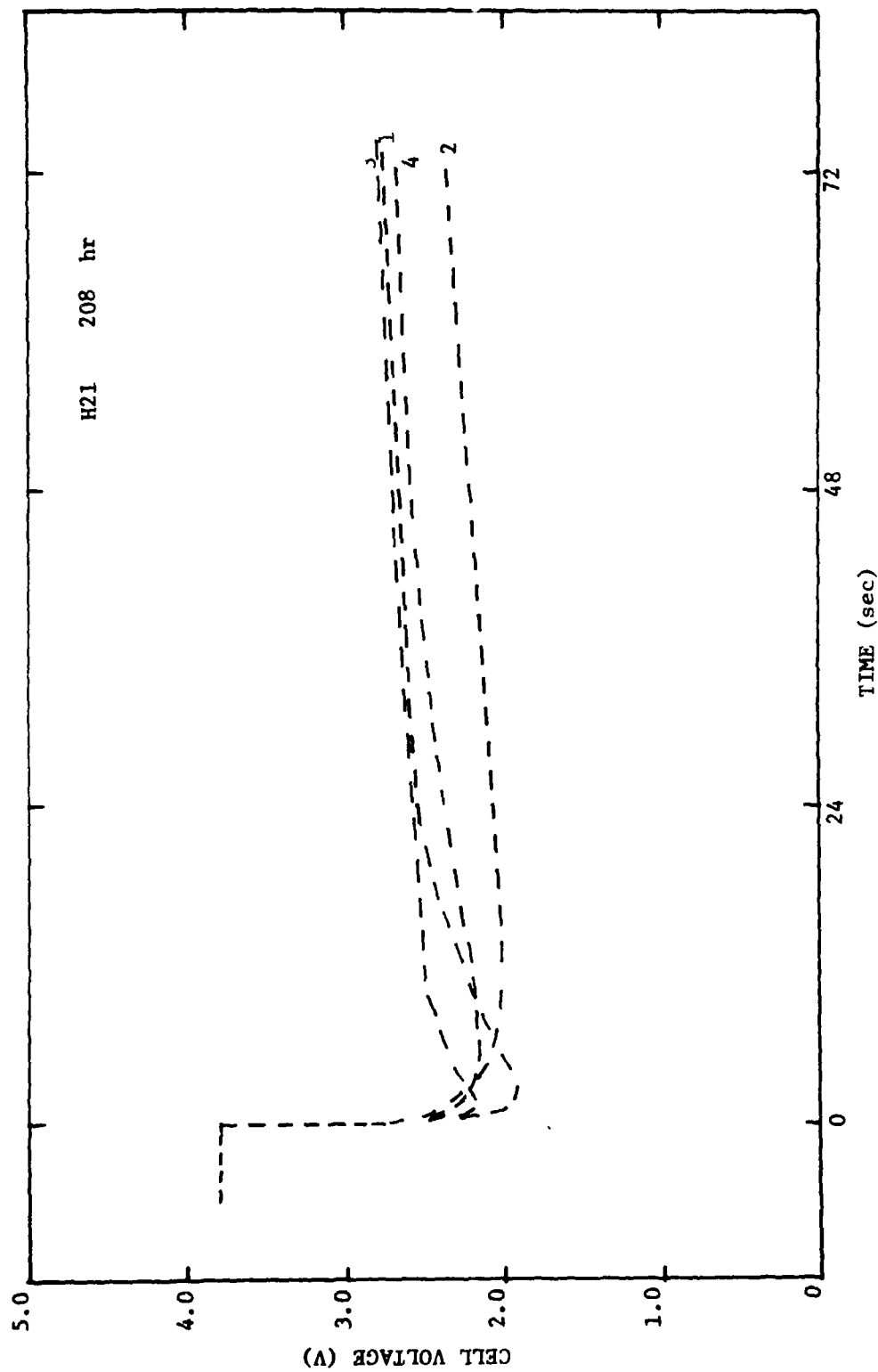


Fig. 8: Initial polarization of Li anode/SOCl₂ cells with 480Ω (≈1 cm²). H21 was stored 208 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

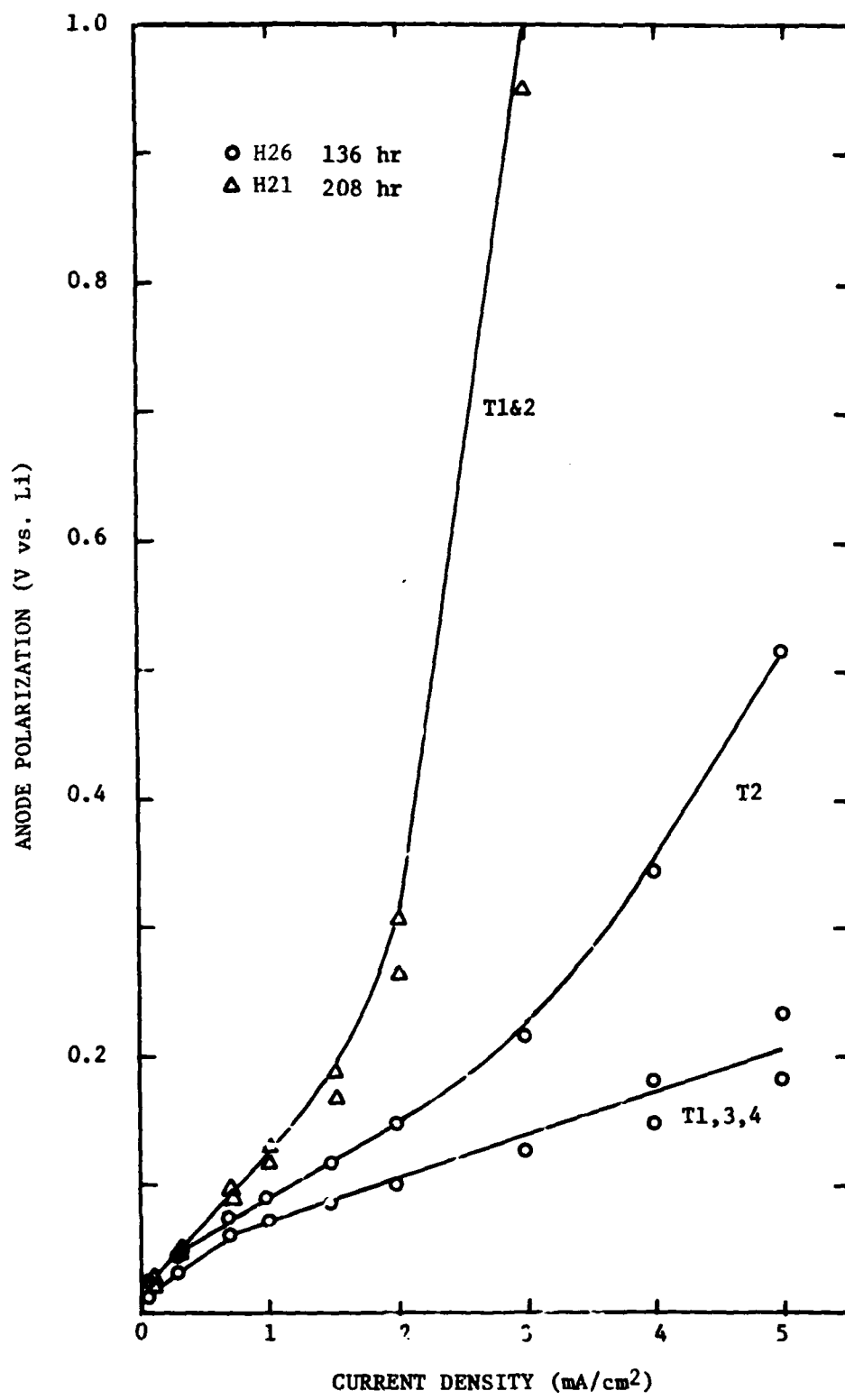


Fig. 9: Anode polarization of Li/SOCl_2 cells, H26 was stored 136 hr with type A electrolyte and H21 with type E.

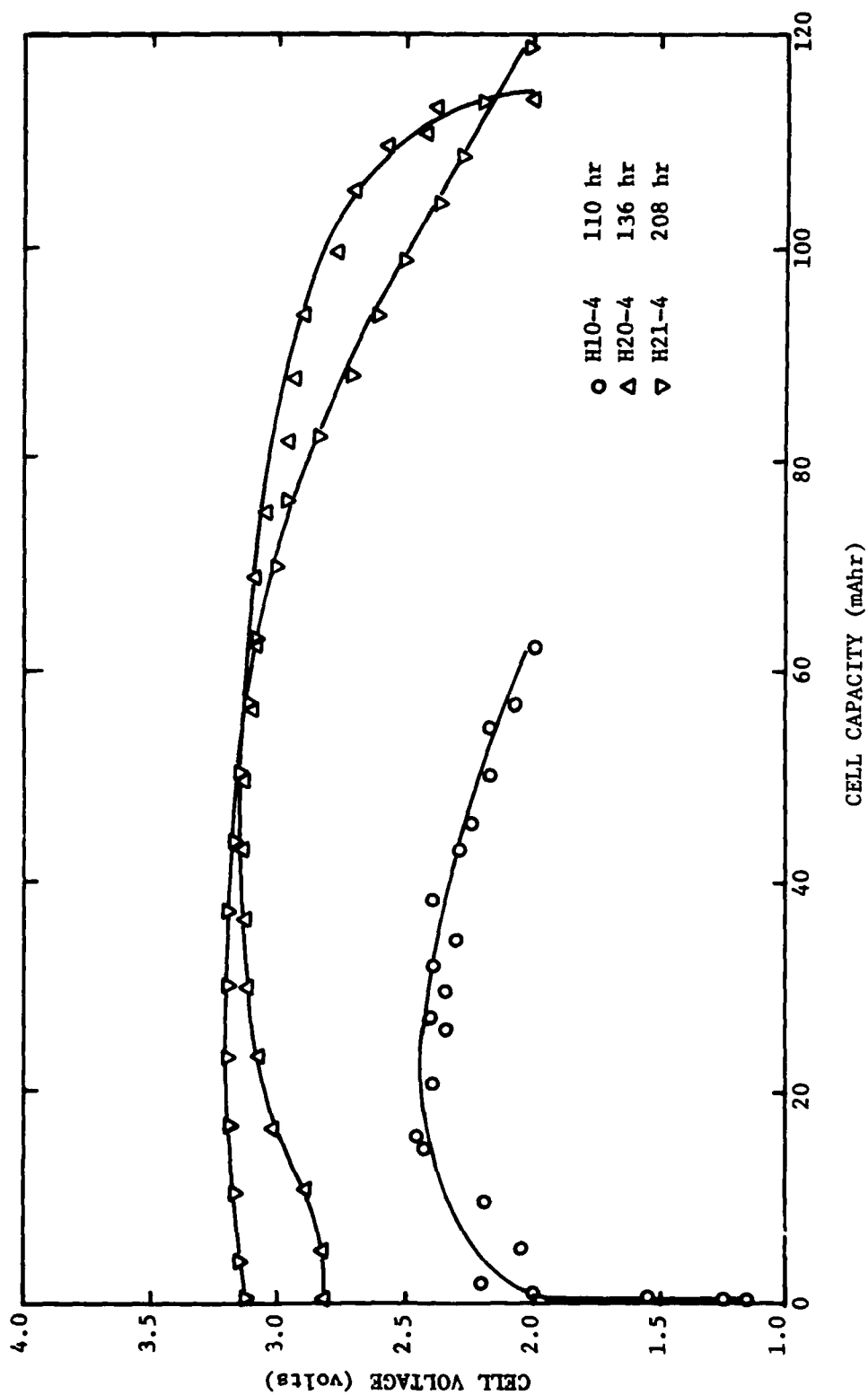


Fig. 10: Potential of Li/SOCl_2 cells discharged through 4800 ($\sim 1 \text{ cm}^2$) at 25°C after storage at 71°C .
H10 used type A electrolyte and H20 and 21 used type E.

IV. ELECTROCHEMICAL CHARACTERISTICS OF LI ALLOY ANODE/SOCl₂ CELLS

We have continued to explore the effect of modifying the negative electrode on the voltage delay and depression. In a previous quarterly report we reported test results on the discharge characteristics of 9 fresh Li alloys as anodes in complete SOCl₂ cells (9). These were Li/Al(5 at.%), Li/Ag(5 at.%), Li/Au(2 at.%), Li/Cd(5 at.%), Li/Cu(4 at.%), Li/Mg(5 at.%), Li/Pb(3 at.%), Li/Sn(3 at.%) and Li/Zn(10 at.%). Eight of these proved to be acceptable anodes but the Li/Mg(5 at.%) did not discharge satisfactorily. The Li/Sn(3 at.%) was also tested by storage at 71°C. It showed no improvement over the Li anodes. During the present quarter we have tested 3 additional fresh alloys. These are Li/Bi(5 at.%), Li/Mg(1 at.%) and Li/Si(4 at.%). We have also tested each of the twelve alloys except Li/Sn at least once after storage at 71°C.

A. Cell Discharge of Fresh Li Alloy Anodes

The alloys were tested as negatives in complete Li/SOCl₂ cells. These tests were to establish the base line performance of the materials to determine the effect of storage. The alloys tested were Li/Bi(5 at.%), Li/Mg(1 at.%) and Li/Si(4 at.%). All were obtained from Foote Mineral. The assembled cells were immersed in 1.5M LiAlCl₄/SOCl₂ electrolyte sufficient to cover and saturate the electrode package. A Li reference electrode was inserted into the solution for following the anode potential. The cells were discharged through a constant load of 480Ω and the potential was monitored. Cell capacities were calculated by piecewise integration of the discharge curve.

The results of the cell capacity measurements to 2.00V cutoff are shown in Table 3. The cells were anode limited. In Table 3, we also estimate the Li utilization efficiency. It is a general estimate, because it is based on the assumption that Li is the only species oxidized during discharge. Any contribution to the cell capacity from the alloying element will increase the anode efficiency. Data for Li metal anodes are included for comparison.

Figures 11-13 show the discharge curves. Included are the anode potentials vs a Li reference. The data are presented as a fraction of the total discharge to make intercomparison more convenient. Approximately the same current density was observed in all cases. Also included in the figures is the discharge curve of pure Li metal. Two of the Li/Si cell anodes failed before the 2.0V cutoff was reached, and the Li/Bi shows some voltage depression past the 50% point. Nevertheless, these Si alloys appear suitable for further testing.

TABLE 3
Li Alloy/SOCl₂ Cell Discharge Capacities

	OCV (Volts)	MDV (Volts)	Capacity (Coul)	Efficiency ^a (%)
<u>Li</u>				
32-52	3.75	3.30	161	80.0
32-81	3.68	3.20	153	75.9
<u>Li/Bi</u>				
77-8	3.75	3.16	272	65.5
77-9	3.76	3.15	301	72.4
<u>Li/Mg(1 at.%)</u>				
32-120	3.88	3.15	374	81.0
32-122	3.68	3.14	374	81.0
<u>Li/Si</u>				
32-117	3.80	3.23	330	105.0
32-119	3.83	3.27	326 ^b	104.0
77-10	3.50	3.26	351 ^b	112.0

^aEfficiency based on Li as only species oxidized.

^bAnode failed with cell voltage at 2.5V.

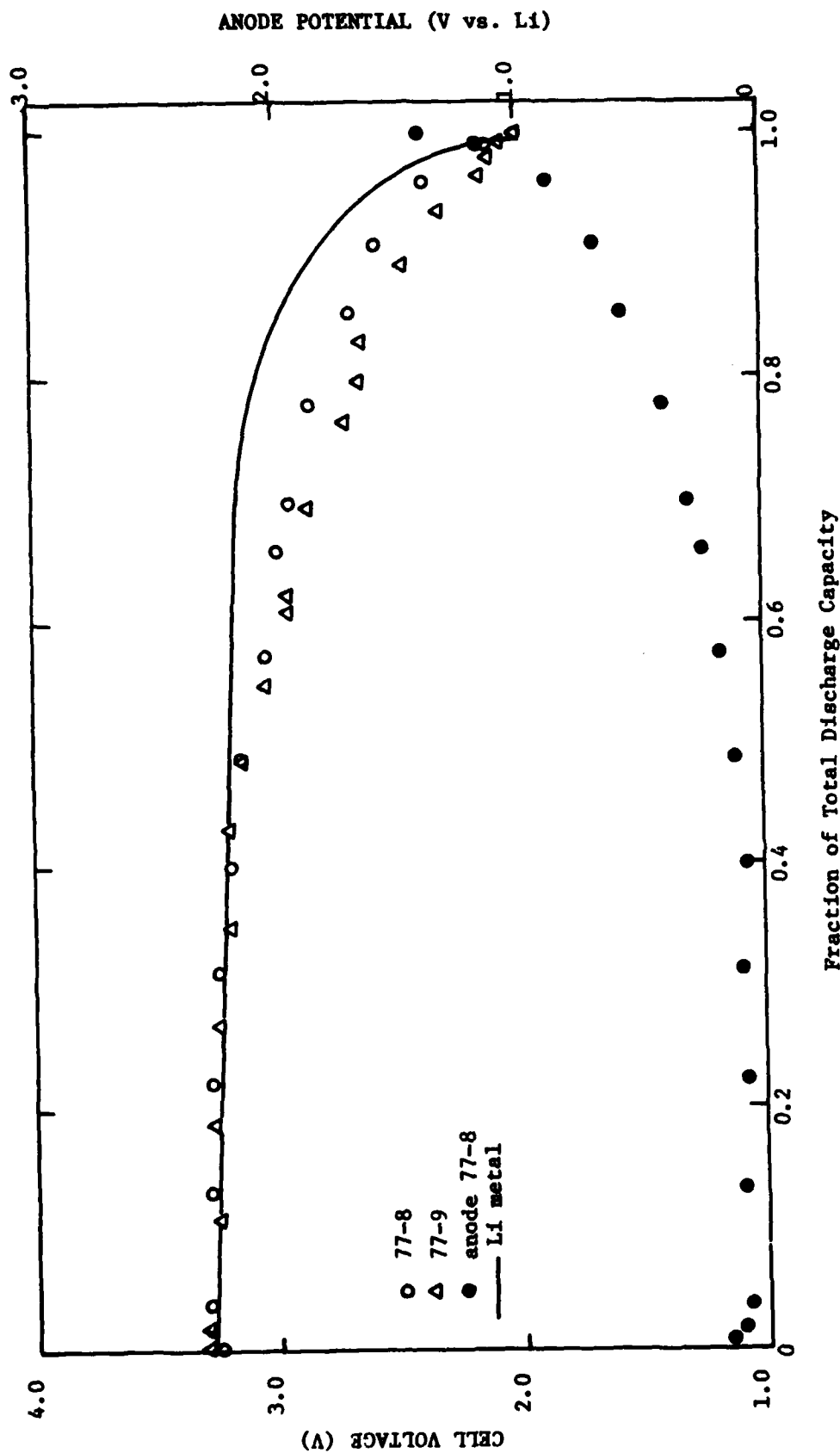


Fig. 11: Discharge potential of Li/Bi(5 at.%) alloy anode, SOCl_2 cells discharged through 480Ω ($\sim 6 \text{ mA/cm}^2$) at 25°C .

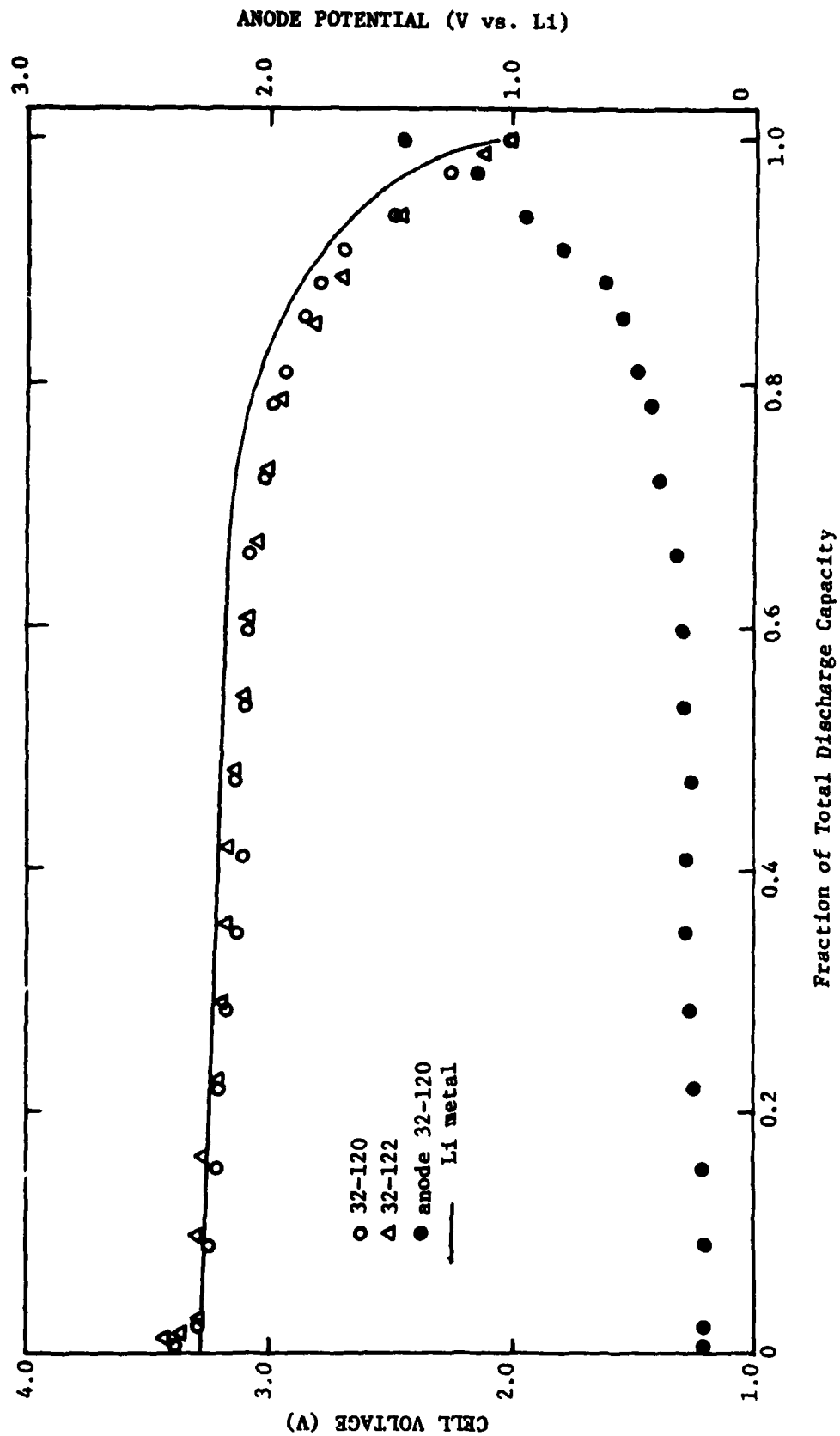


Fig. 12: Discharge potential of Li/Mg(1 at.%) alloy anode, SOCl₂ cells discharged through 480Ω (26 mA/cm²) at 25°C.

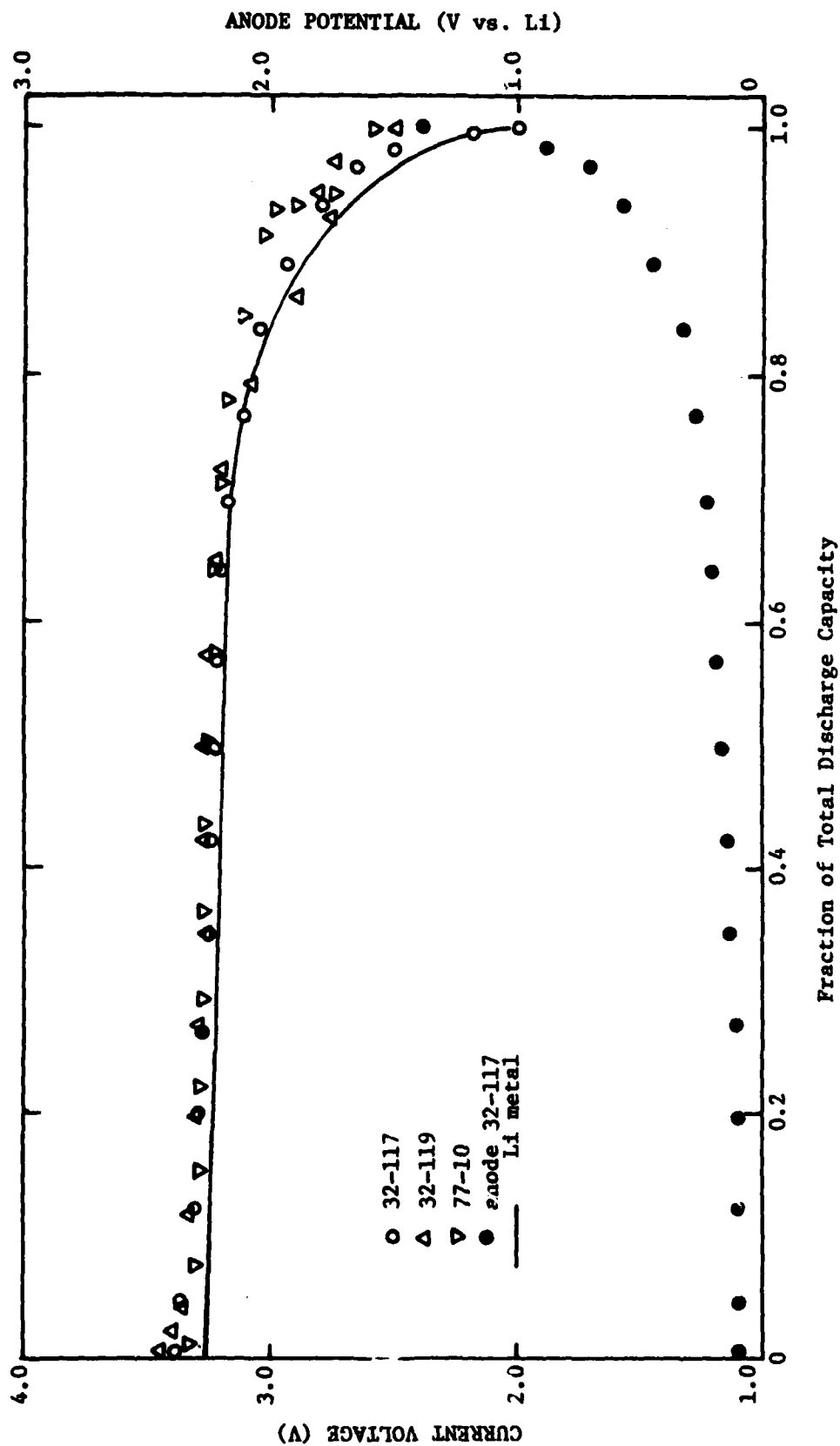


Fig. 13: Discharge potential of Li/Si(4 at.%) alloy anode, SOCl_2 cells discharged through 480Ω ($\sim 6 \text{ mA/cm}^2$) at 25°C.

The Li utilization efficiency of the Li/Bi alloy is in the range of the alloys tested previously at this current density (6-7 mA/cm²). The Li/Mg(1 at.%) efficiency is equivalent to that of pure Li. This is not surprising in view of the alloy composition. This alloy is markedly different from the Li/Mg(5 at.%) alloy, which polarized strongly and gave very poor Li utilization with the 480 Ω load.

The Li/Si alloy appears to have a Li efficiency greater than 100%. This clearly indicates Si is being oxidized as well as Li. This is the first direct evidence of an alloying element oxidizing in the SOCl₂ electrolyte that we have seen. Recalculation of the anode utilization based on both Li and Si, and assuming a 4 electron oxidation of Si, yields 90.1%, 89.2% and 96.0% for the 32-117, 32-119 and 77-10 cells, respectively. These indicate almost complete utilization of the anode and perhaps are the reason for the sudden anode failure in two of the cells. The phase diagram for the Li/Si binary system indicates that the anode material is a mixture of Li₄Si and metallic Li (15). Since the discharge potential closely approximates that of pure Li, this suggests that Li₄Si is oxidized as a compound at a potential close to the Li potential. The available thermodynamic data indicate that elemental Si is not oxidizable at this potential. SiCl₄ is the most likely discharge product. Its free energy of formation at 298K is -148 kcal/mol (1.60V), which compares unfavorably with that of LiCl, which is -90 kcal/mol (3.90V) (16). Further, recently presented data (17) show that at ~400°C, Li/Si alloys with high Li content, i.e., Li₅Si, Li₂₂Si₅, oxidize at only a few tens of millivolts positive of Li.

The Li/Si(4 at.%) alloy appears to offer a practical improvement in the Li/SOCl₂ anode utilization ~92% vs ~78% for pure Li at 6-7 mA/cm² with no penalty in equivalent weight. For a 4 electron oxidation, the Si equivalent weight is 7.02 g/eq vs 6.94 for Li.

B. Electrochemical Characteristics of Li Alloy/SOCl₂ Cells after 71°C Storage

The Li alloys were tested in the same manner as the Li/SOCl₂ cells (Section III). After storage they were tested for voltage delay and depression with a 480 Ω load, followed by a galvanostatic test and, finally, another test with a 480 Ω constant load.

Table 4 presents the test conditions and some of the results of the tests. Storage times ranged from 69 to 207 hr. Type A electrolyte was used in all cells but one, H26, where type D was used. Table 4 also contains the cells voltages at 60 sec after the initial application of the 480 Ω load. The voltage listed is the average voltage for all T-cells, either three or four. The spread between cells in some cases was quite large, e.g., H12, H15, and H24. The choice of the 60 sec cell voltage is somewhat arbitrary but it does summarize the pattern of results.

TABLE 4

Test Conditions and Results for Li Alloy Anode/SOC12
T-Cells Stored at 71°C

<u>Cell</u>	<u>Anode</u>	<u>Hrs Storage at 71°C</u>	<u>Cell Voltage At 60 sec, 480Ω Load^b</u>
H23	Li/Ag(5 at.%)	111	2.40 ± 0.27
H12	Li/Al(5 at.%)	70	1.85 ± 0.50
H24	Li/Au(2 at.%)	111	1.80 ± 0.55
H32	Li/Bi(5 at.%)	207	0.21 ± 0.04
H15	Li/Cd(5 at.%)	69	1.81 ± 0.74
H28	Li/Cd(5 at.%)	158	0.79 ± 0.29
H16	Li/Cu(4 at.%)	69	2.55 ± 0.38
H19	Li/Mg(1 at.%)	89	2.81 ± 0.04
H25	Li/Mg(1 at.%)	88	1.43 ± 0.24
H26 ^a	Li/Mg(1 at.%)	136	1.18 ± 0.11
H13	Li/Mg(5 at.%)	72	0.55 ± 0.15
H31	Li/Pb(3 at.%)	207	0.20 ± 0.07
H29	Li/Si(4 at.%)	158	0.74 ± 0.19
H14	Li/Zn(10 at.%)	72	2.01 ± 0.02

^aType D electrolyte was used, all others used Type A.

^bError limits are average deviation.

Correlation of Passivation with Storage Time

It has been apparent qualitatively that anode passivation increases with storage time at 71°C, as evidenced by voltage delay and depression data. A quantitative description would provide a more rigorous basis for data correlation. We have obtained an empirical correlation between cell voltage and storage time using the average cell voltages of the T-cells from one H-cell. These voltages were measured at the same time after the application of the 480Ω load of the initial test for voltage delay. Figure 14 illustrates the correlation for cell voltages at 60 sec. Choosing to take the average at 60 sec is arbitrary, but the same procedure applied between 6 and 96 sec yields similar results. The averages of the T-cells from an individual H-cell varied, depending on which time was chosen (i.e., 6 sec, or 18 sec, etc.), but the general pattern remained the same. Linear least squares analysis yields slopes between -0.014 and -0.020 V/hr on storage. The data point for H13 (Li/Mg(5 at.)) is included in Figure 14, but not in the mathematical analysis: Li/Mg(5 at.%) alloy anodes showed inadequate performance in fresh cells. Hence its performance in storage cell H13 is sufficiently inferior to the other materials to preclude its use in the mathematical analysis.

The data for H20 and H21 (Figure 14) illustrate most clearly our previous conclusion that the method of preparation used for these cells does improve their performance. They are clearly superior to the average performance, and are worth further study.

The base line data suggest that storage times between 150 and 200 hr as the most economical in terms of maximizing data output. The cells are sufficiently passivated by this time that any improvements will be easily noted. Longer storage times would not significantly increase the resolution.

Voltage Delays

Table 5 summarizes the voltage delay measurements for the alloy anode cells. There are several interesting features of these data. A large variability is evident between T-cells of the same H-cell at storage times around 70 hr, e.g., H12, H15, and H16. H13 (Li/Mg(5 at.)) and H14 (Li/Zn) are exceptions. These are discussed below. Figure 15 illustrates this variability for H16 (Li/Cu). The data for H12 and 15 are similar in this regard. The data may suggest that film build-up is inhomogeneous over the anode surface. Some of the anodes still have film areas which are thin or porous enough to be disrupted and to expose fresh metal surface on discharge. Our previous measurements show that the unobscured area necessary to maintain the observed currents at moderate anode polarization is small. For example, an Al alloy anode at +1.5V vs Li can support a minimum of 150 mA/cm² (8). At a cell voltage of 2.0V (~1.5V anode polarization) the cell delivers ~4 mA which indicates only ~2.5% of the anode area need be

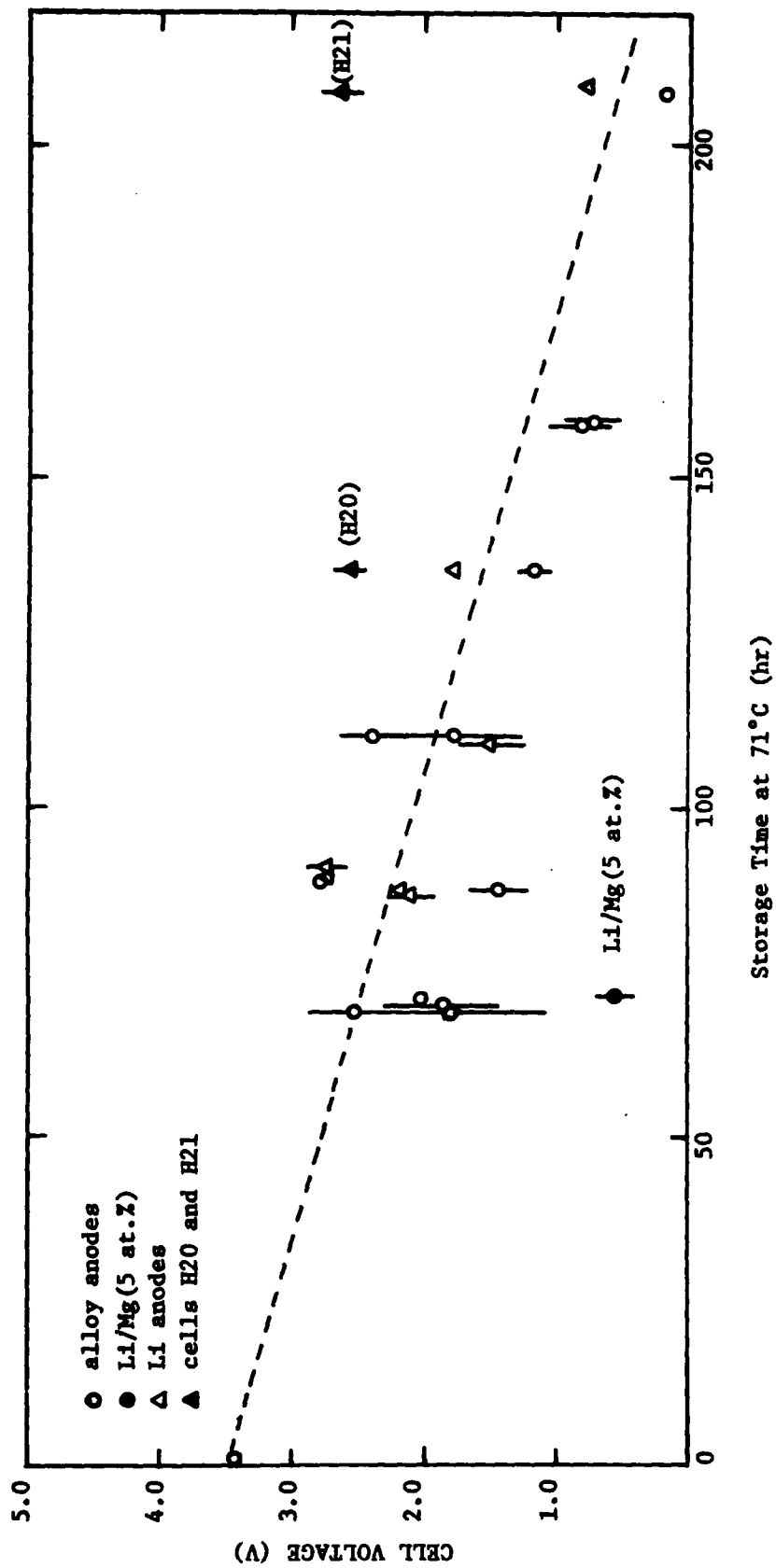


Fig. 14: Cell potential at 60 sec of initial polarization vs storage time. ----- linear least squares lines ($+dv/dt = -0.014$ V/hr).

TABLE 5

Li Alloy/SOCl₂ Cell Voltage Delays After Storage at 71°C

<u>Cell</u>	<u>Anode</u>	<u>Hrs at 71°C</u>	<u>Delay (sec)^a For T-Cell</u>			
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
H23	Li/Al	111	-	41	59	19
H12	Li/Al	70	x	x	o	x
H24	Li/Au	111	23	32	x	x
H32	Li/Bi	207	x	x	x	x
H15	Li/Cd	69	x	o	62	x
H28	Li/Cd	158	x	x	x	x
H16	Li/Cu	69	x	o	o	x
H19	Li/Mg(1 at.%)	84	o	o	o	o
H25	Li/Mg(1 at.%)	88	x	x	x	-
H26	Li/Mg(1 at.%)	136	x	x	x	-
H13	Li/Mg(5 at.%)	72	x	x	x	x
H31	Li/Pb	207	x	x	x	x
H29	Li/Si	158	x	x	x	x
H14	Li/Zn	72	48	48	6	48

- a) x - greater than 72 sec
 o - no delay
 - - no cell

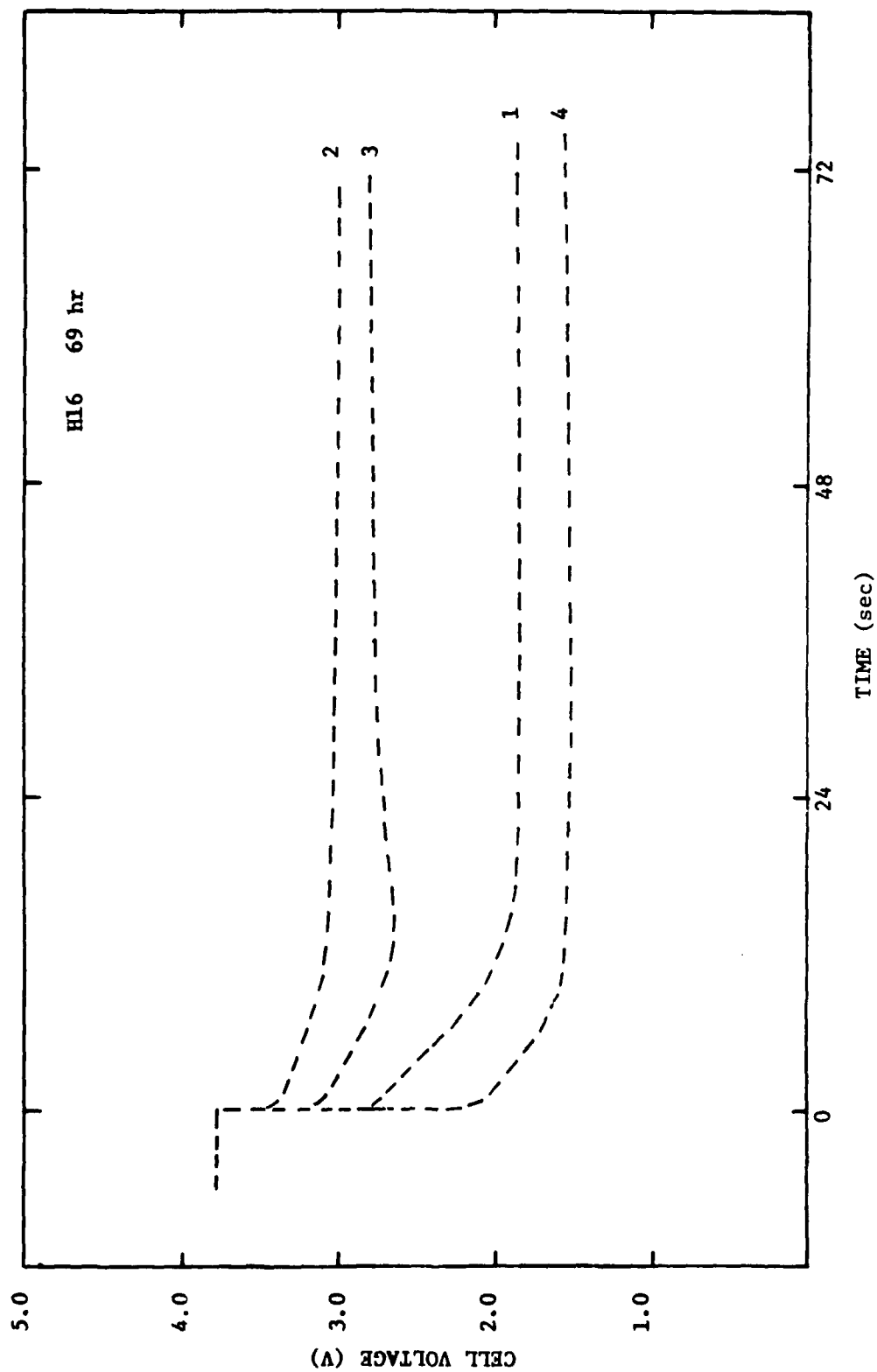


Fig. 15: Initial polarization of Li/Cu(4 at.%) anode, SOCl₂ cells with 480Ω (≈1 cm²). H16 was stored 69 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

active. It is then not surprising that some large variability can exist. The variability probably decreases with storage time because the film thickens sufficiently to prevent its ready disruption.

The Li/Mg(5 at.%) shows inherently poor performance both as a fresh electrode and after storage. It has been eliminated as a candidate for future testing.

The Li/Zn alloy showed very consistent behavior between the four cells tested. With the load applied the cell voltage dropped to $2.0 \pm 0.1V$ and remained there (Figure 16). This consistency is unusual and distinguishes this alloy from the others stored similar lengths of time. The Li/Zn alloy was further distinguished by its anode polarization. The general pattern is distinctly different than any other alloy tested. Figure 17 reproduces the anode polarization for the T-cells of H14 (Li/Zn) and H16 (Li/Cu). The Li/Cu pattern is similar to that discussed previously (Section III, Fig. 3) for Li metal anodes. Three of the T-cells show a gradual increase in polarization with increased current density and then show a distinct rapid increase beyond a "transition" current density. One of the cells does not have this latter feature. This cell originally showed no voltage delay and only a small voltage depression, and we would not expect to reach a severely polarized state at the current density used. The Li/Zn anodes show a sharp increase in polarization at low current density but then increase only gradually. These data suggest that Li is not the species being oxidized. We considered the possibility that heating of the alloy alone (e.g., due to recrystallization) is responsible for the behavior on storage. This possibility was tested by discharging a fresh Li/Zn anode T-cell after the alloy had been heated for 168 hr in argon at 71°C. This anode showed identical behavior to an alloy stored at room temperature.

Improved Li Alloy Anode Performance after Galvanostatic Test

The initial voltage delay and depression of Li alloy T-cells is essentially equivalent to Li metal anode T-cells when prepared under identical conditions. Although they do not present immediate relief to the passivation problem, test results from three of the alloys suggest the possibility of modifying the anode surface to facilitate removal of the passivating film. The three alloys are Li/Ag, Li/Cu and Li/Mg(1 at.%). The results are illustrated in Figures 18-22. These figures present the results of the initial passivation test (480 Ω load) and the same test conducted after the galvanostatic test.

For Li itself, and most of the alloys, the difference between the two tests is small. Figure 18 (Li anodes) shows a plateau at 2.5V in the second test but the cell voltage quickly drops back to the original level. The transition is probably due to concentration polarization. Figure 19 (Li/Si alloy) shows similar behavior. There is slight improvement during the first

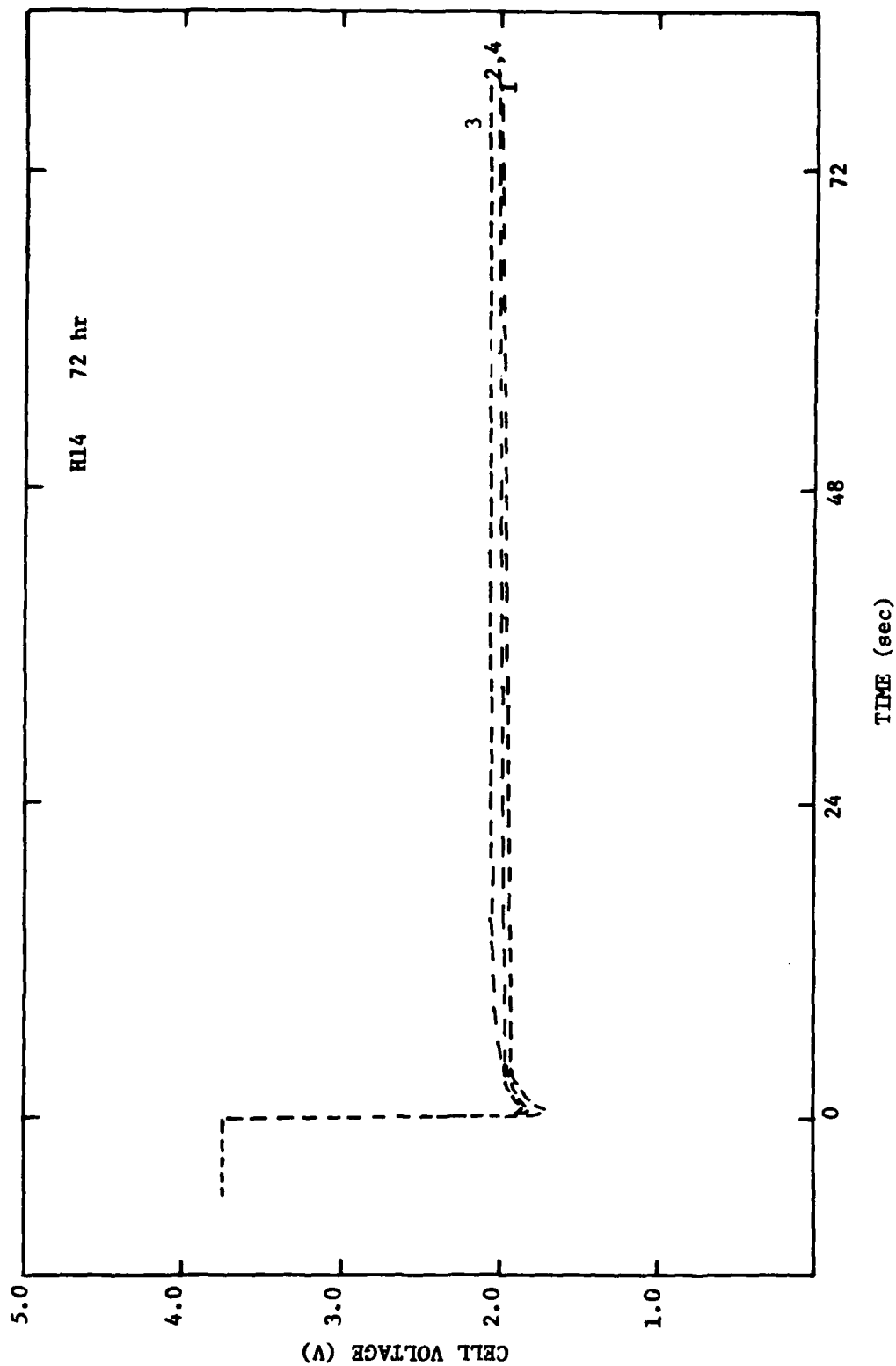


Fig. 16: Initial polarization of Li/Zn(10 at.%) anode, SOCl_2 cells with 480Ω ($\sim 1 \text{ cm}^2$). H14 was stored 72 hr at 71°C with LiCl saturated 1.5M $\text{LiAlCl}_4/\text{SOCl}_2$.

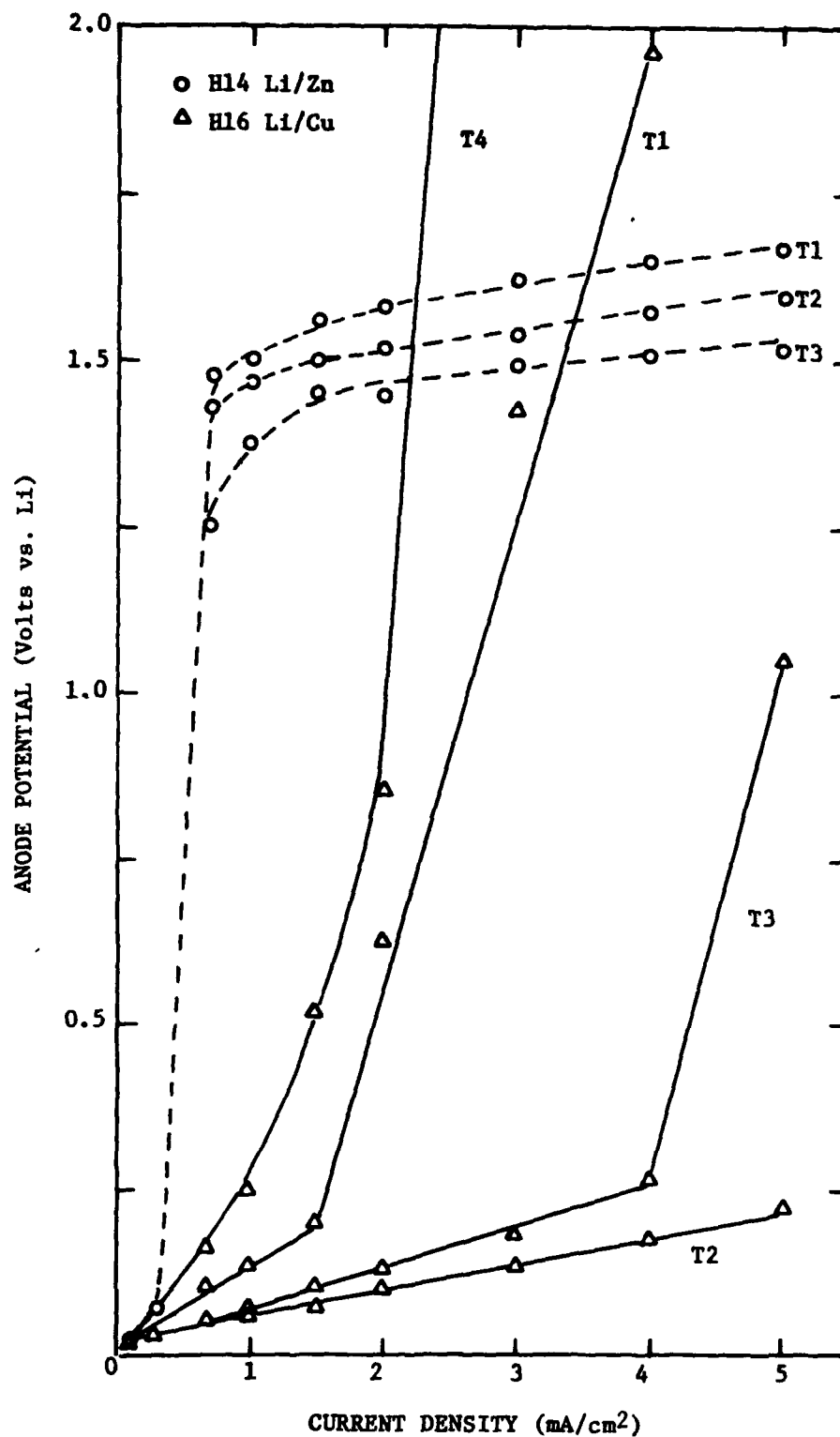


Fig. 17: Anode polarization of cells H14 and H16 after storage at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

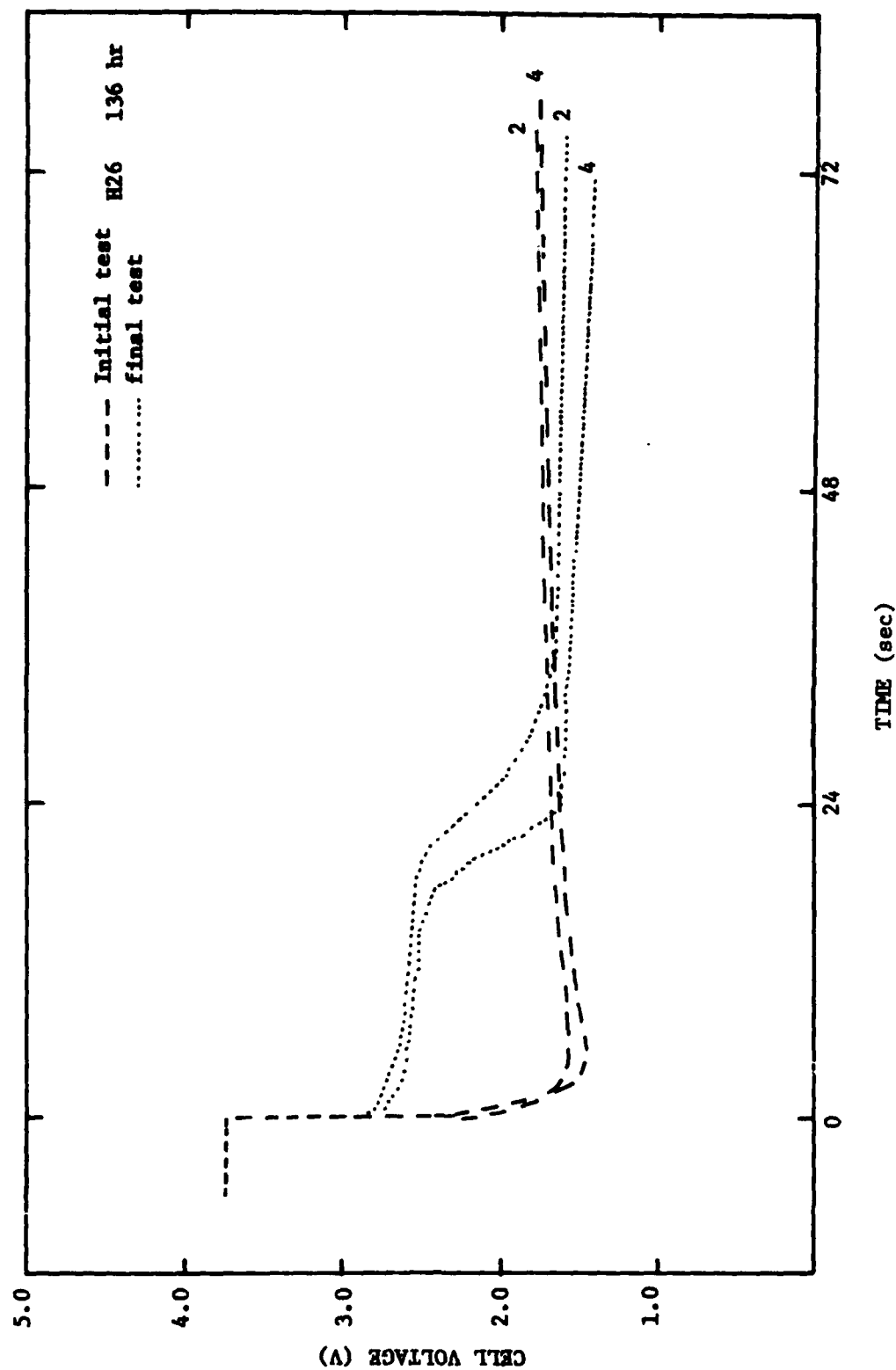


Fig. 18: Initial (---) and final test (.....) polarization of Li anode/ SOCl_2 cells with 480Ω ($\sim 1 \text{ cm}^2$). H26 was stored 136 hr at 71°C with LiCl with $1.5\text{M LiAlCl}_4/\text{SOCl}_2$.

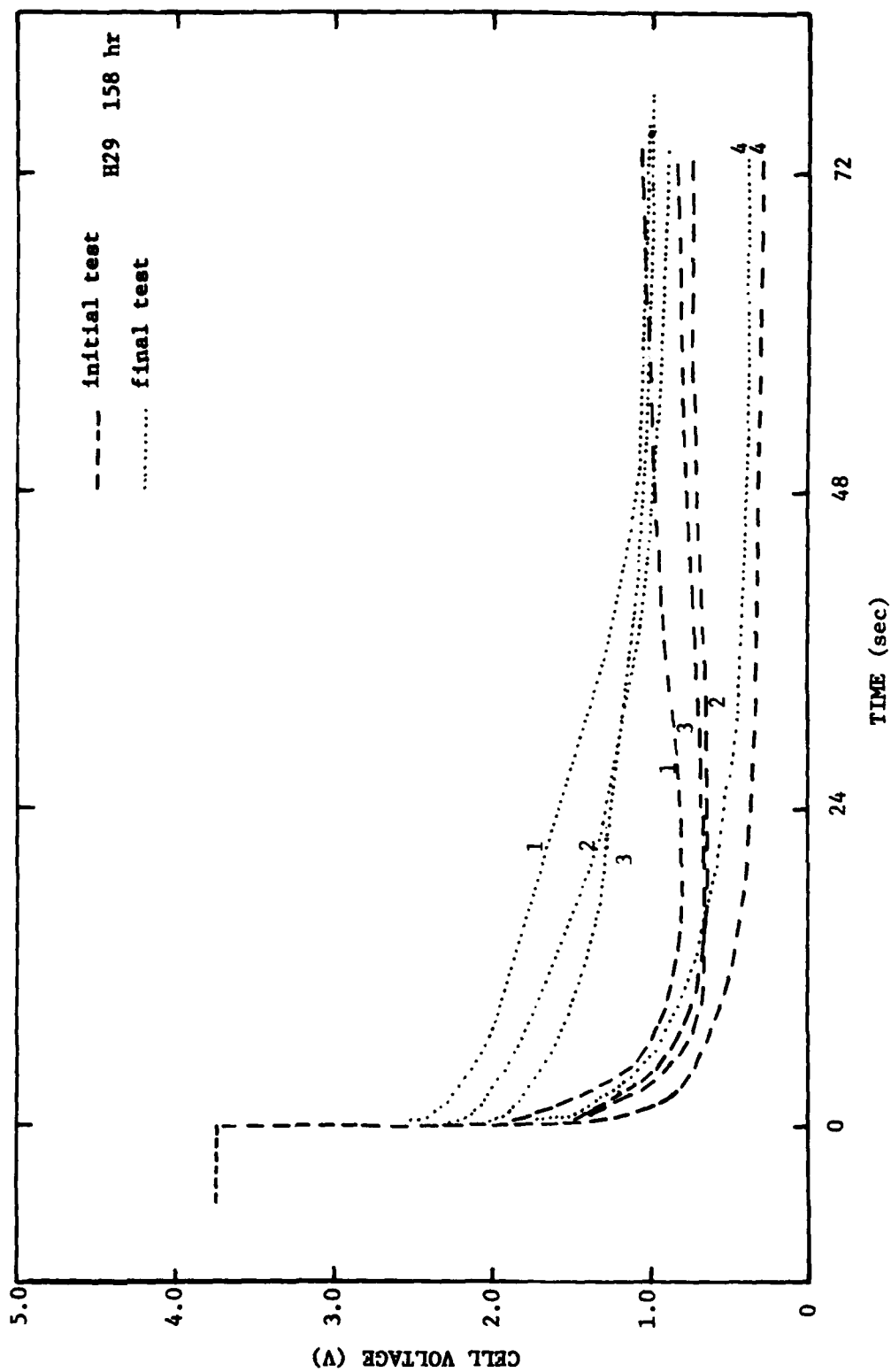


Fig. 19: Initial (---) and final test (.....) polarization of Li/Si(4 at.%) anode/SOCl₂ cells with 480Ω (0.1 cm²). H29 was stored 158 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

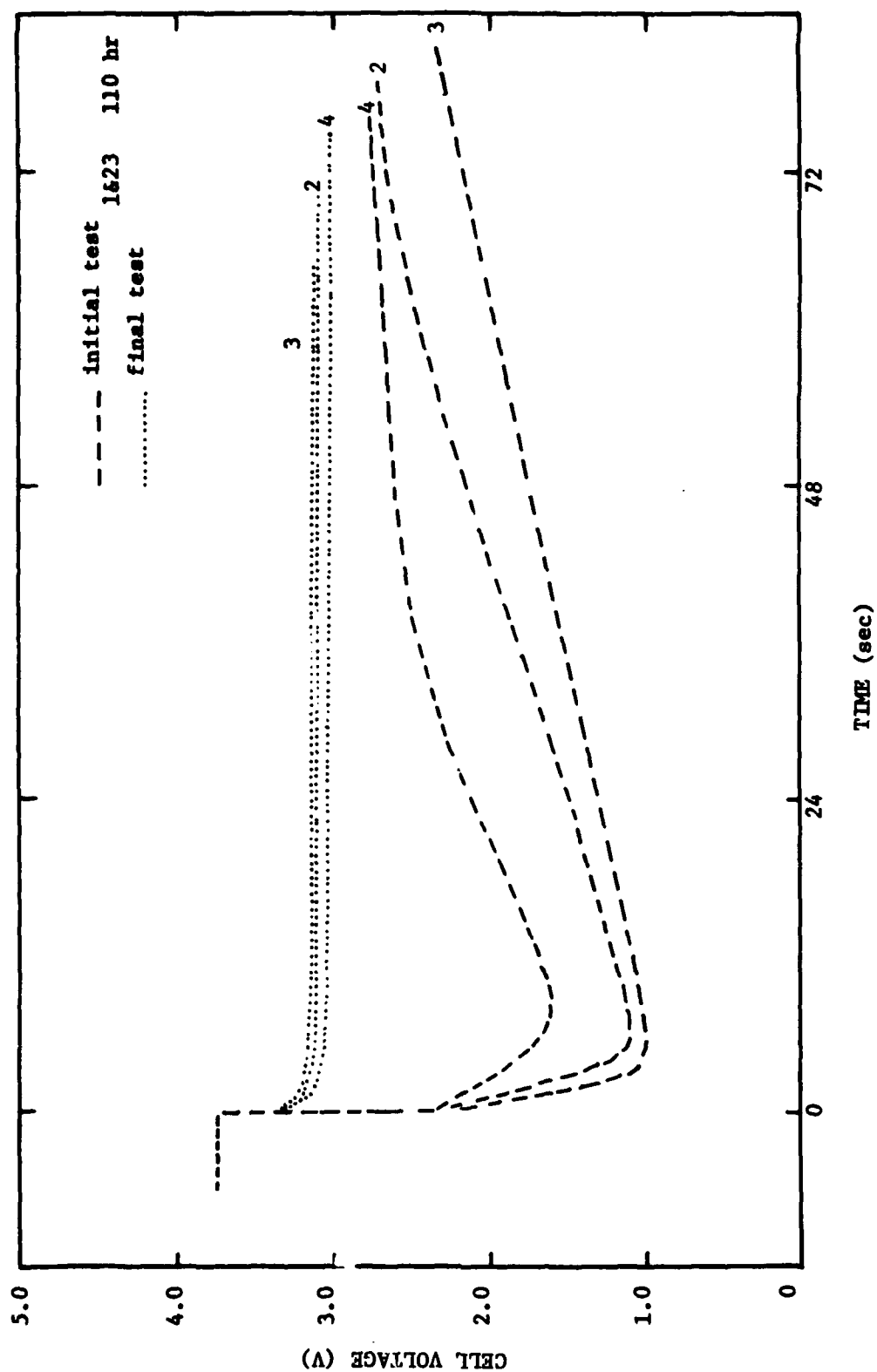


Fig. 20: Initial (---) and final test (.....) polarization of Li/Ag(5 at.%) anode/SOCl₂ cells with 480Ω (≈1 cm²). H23 was stored for 110 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

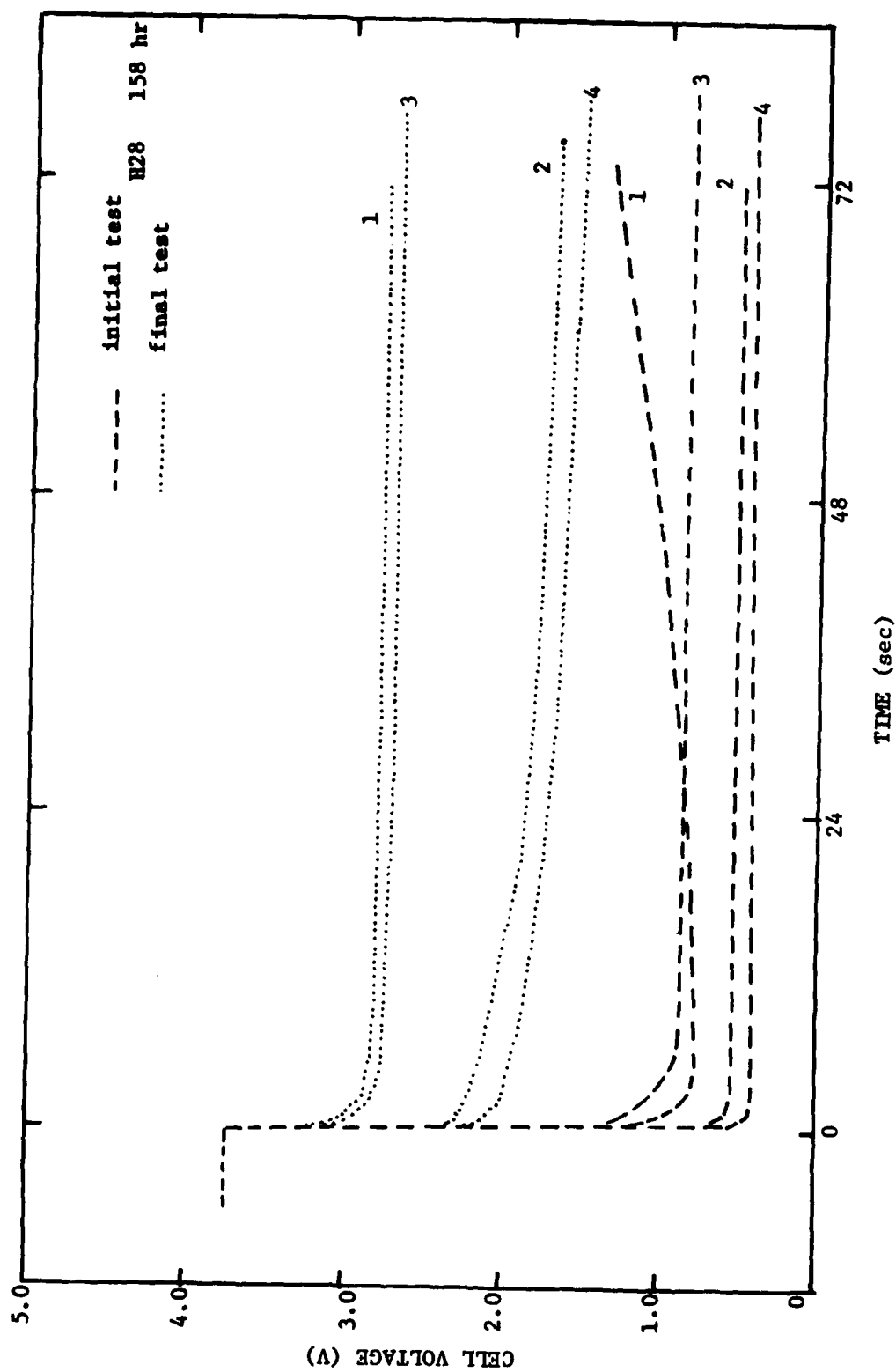


Fig. 21: Initial (---) and final test (....) polarization of Li/Cd(5 at.%) anode/SOCl₂ cells with 480Ω (~1 cm²). H28 was stored 158 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

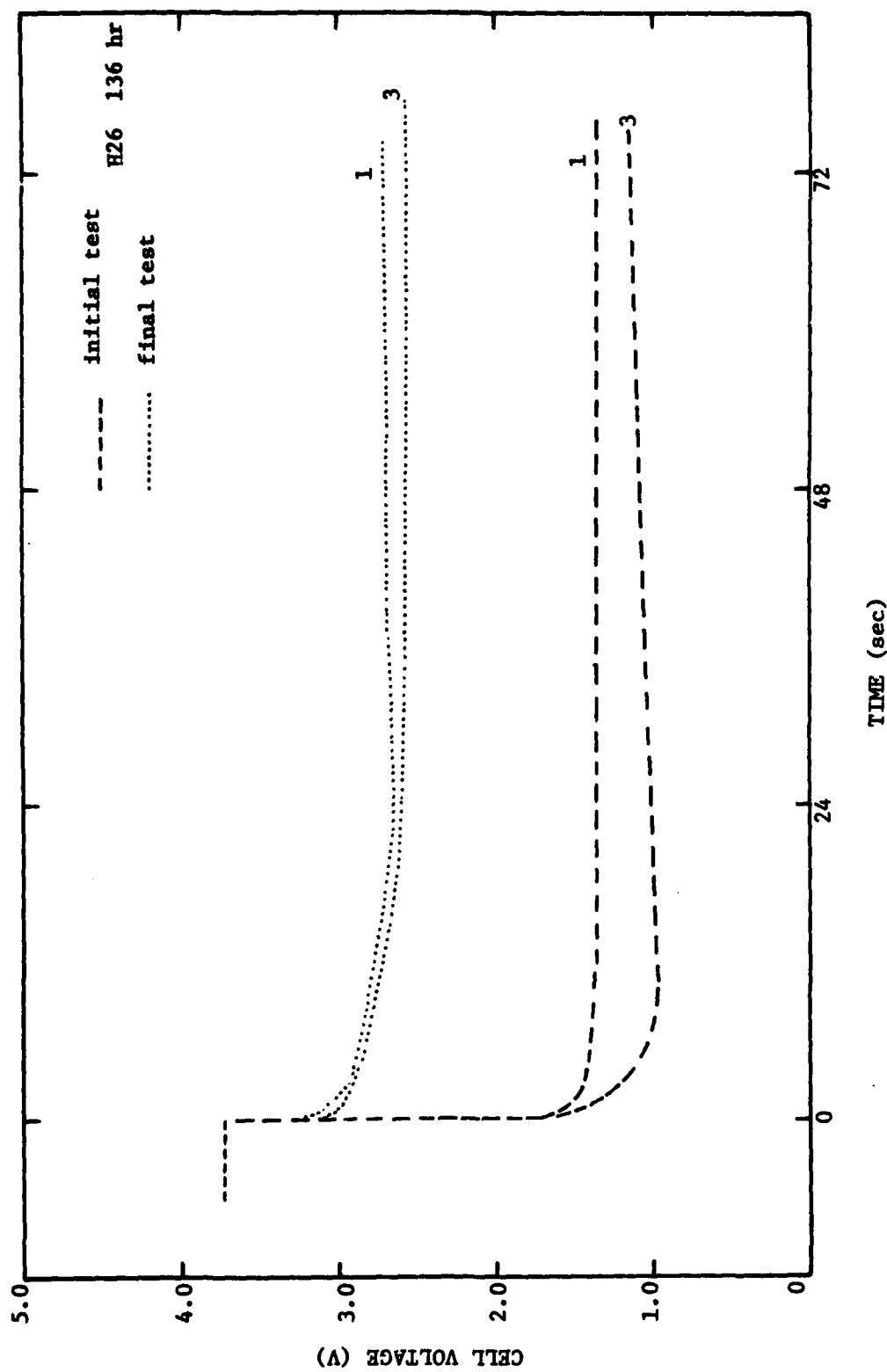


Fig. 22: Initial (---) and final test (....) polarization of Li/Mg(1 at.%) anode/SOCl₂ cells with 480Ω (0.1 cm²), H26 was stored 136 hr at 71°C with LiCl saturated 1.5M LiAlCl₄/SOCl₂.

24 sec, but the cell voltages rapidly converge with those measured initially. The behavior of the above mentioned 3 alloys is considerably different, however. There is significant improvement in the cell voltage in the second test. The Li/Cd and Li/Mg alloys (Figures 21 and 22) have improved by a volt or more. Test data for the other Li/Mg and Li/Cd cells (H25 and H15) show similar improvements.

The Li/Ag alloy cell voltages (Figure 20) improved significantly during the initial constant load test, stabilizing at 2.7-2.8V after 150 sec. After the galvanostatic test, their cell potentials improved to acceptable levels, with values between 3.0 and 3.2V. The galvanostatic test results compare favorably with fresh Li anodes. Figure 23 compares the two. The Li/Ag anodes are polarized only about 50 mV more positive than fresh Li.

These data for the three alloys suggest improvement on the passivation problem can be sought in modifying the anode surface. Further work along this line appears worthwhile, particularly with the Li/Ag alloy.

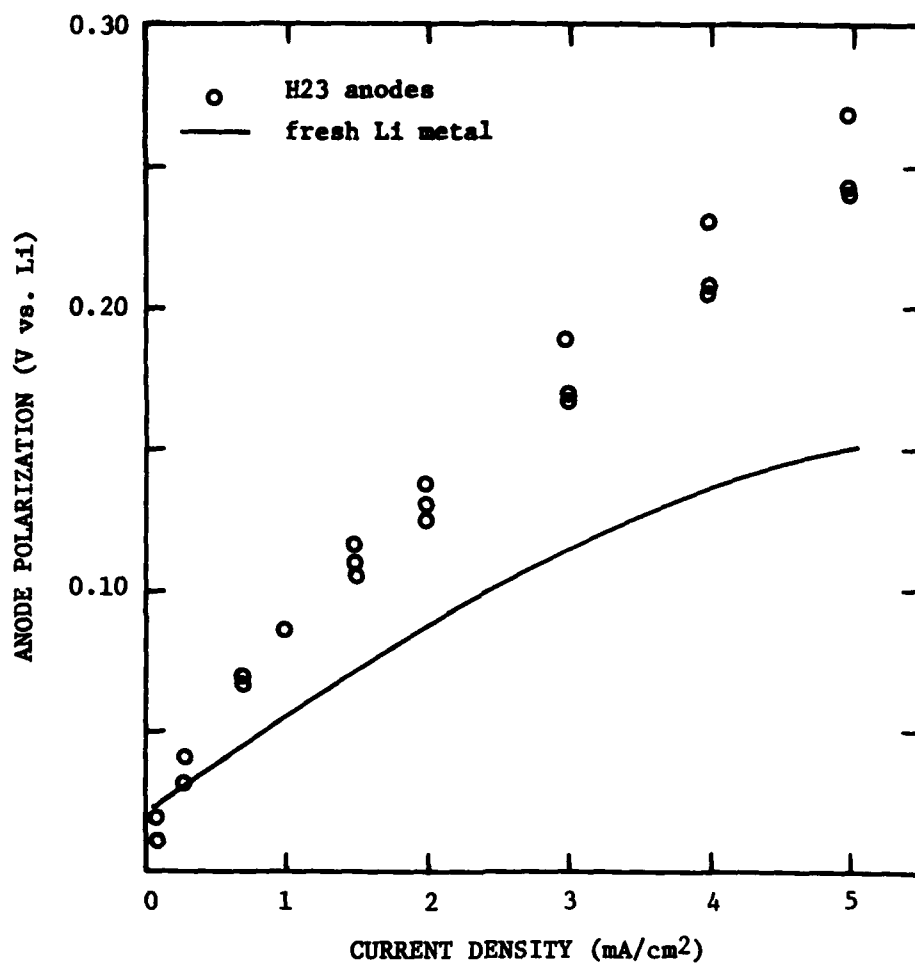


Fig. 23: Anode polarization of Li/Ag(5 at.%) anode/SOCl₂ cells stored 110 hr at 71°C and tested at 25°C.

V. SUMMARY AND FUTURE WORK

Our primary effort is centered on the problem of uncontrolled film growth on Li during storage at 71°C. This results in severe voltage delay and depression in the Li/SOCl₂ cell. Investigation of this problem has included electrochemical characterization of fresh Li alloys and of both Li and Li alloy anodes after storage at 71°C. We have in addition measured the solubility of SO₂ in 1.5M LiAlCl₄/SOCl₂ and in pure SOCl₂.

The solubility of SO₂ derives its importance from the potential hazard of accommodating it in discharged cells. At 25°C the SO₂ mole fraction in 1.5M LiAlCl₄/SOCl₂ was 0.19 (~3M), confirming our previous gas chromatographic results. At 0°C the SO₂ mole fraction was 0.50. The solubilities in phase SOCl₂ were slightly lower. These data indicate that high concentrations of SO₂ in the solution can be accommodated with only moderate pressure increases.

Three more Li alloys were tested as anodes in Li/SOCl₂ cells: Li/Bi(5 at.%); Li/Mg(1 at.%); Li/Si(4 at.%). All three had voltage characteristics similar to Li discharged under the same conditions (~6 mA/cm²). This brings the total number of alloys tested to 12. The Li/Bi and Li/Mg alloys had Li utilization efficiencies of 65-80%, which is typical of alloys previously measured. 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 investigation of passivating film growth was continued. Further evidence was obtained on the deleterious effect of LiCl saturated electrolyte. Based on these results, all subsequent testing used electrolyte saturated with LiCl at 71°C. This provides both a more realistic and accelerated test condition. In connection with this work the solubility of LiCl in 1.5M LiAlCl₄/SOCl₂ at 71°C was measured. It is in the range 0.092 to 0.156M. This high solubility appears to result from a chemical reaction.

Storage tests with SOCl₂ from two sources, MC/B (TX535) and Eastman (246), show no marked difference between them.

A remarkable improvement in performance has been observed in cells prepared with chemically pre-treated components and assembled in a specially controlled atmosphere. The electrolyte (1.5M LiAlCl₄) was pre-treated by heating for 140 hrs at 71°C with Li foil (4 cm²/ml). The glass fiber

separators were pre-treated by heating 140 hrs with Li metal in SOCl_2 . The cells were assembled in a glove bag. A constant flow of argon was used to prevent the accumulation of deleterious vapors (e.g., SO_2 and HCl). Three cells were tested after 136 hr at 71°C . One had no voltage delay and two had voltage delays of less than 30 sec. Four cells were tested after 208 hrs at 71°C . Three cells had no voltage delay and one had a voltage delay of 4 sec.

Eleven Li alloys were tested after storage at 71°C . Storage times ranged from 70 to 207 hrs. The alloys were: Li/Ag(5 at.%), Li/Al(5 at.%), Li/Au(2 at.%), Li/Bi(5 at.%), Li/Cd(5 at.%), Li/Cu(4 at.%), Li/Mg(1 at.%), Li/Mg(5 at.%), Li/Pb(3 at.%), Li/Si(4 at.%) and Li/Zn(10 at.%). 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 at.%), showed less passivation after testing. This indicates the possibility of anode surface modification for reduced voltage delay and depression. The Li/Mg(5 at.%) alloy has been eliminated from any future testing because of its inherently poor performance. An empirical relationship between storage time and cell voltage was established. This appears useful for both data evaluation and experiment design.

Future work will continue into finding practical solutions to the passivation problem. Two promising lines have been opened by this quarter's results; cell assembly under ultrapure conditions and use of alloys which "clean up" during discharge. Both of these lines will be investigated further. The specific causes of the improvement in the pre-treated cells will be investigated. Extended testing of these cells will also be undertaken. This technique will also be used with Li alloy anode cells, with particular emphasis on the Li/Ag, Li/Cd and Li/Mg(1 at.%) alloys.

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