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Correlation of Design with Performance of Primary Lithium-Sulfur Oxyhalide Cells

H.A. Frank

June 1, 1982

NASA
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ABSTRACT

This document presents results and assessments of a focused literature review of primary lithium sulfur oxyhalide cells. Major emphasis is placed on the effect of component materials and designs on performance (energy density and rate capability), safety, and storage life of these cells. This information is a reference guide for the design of high energy batteries for future use on NASA missions.

SECTION 1

SUMMARY

The objective of the Advanced Primary Lithium Battery Task of NASA RTOP 506-55-55 is to develop primary lithium batteries that operate safely under all conditions while delivering higher energy and longer life than existing primary batteries. The type of lithium battery that appears most attractive and has been selected to meet this objective is based on the lithium-sulfur oxyhalide system (Li-$SOCl_2$ or Li-SO_2Cl_2).

One element of this Task is concerned with development of prototype cells based on this electrochemical system. These cells will a) serve as test vehicles to verify recommendations from the research element of this task on methods to improve safety and life, and b) provide engineering data for the design of optimized cells for flight batteries.

Although lithium-sulfur oxychloride cells are relatively new, a sizeable amount of information has already been published on them. This information was generated primarily by several battery developers and research organizations during the course of government sponsored R & D programs on these cells. Results have been published both in contractor reports as well as publications in the open literature. (Refs. 1 through 28).

In order to avoid duplication of effort and to take advantage of prior findings, this literature was reviewed and assessed as well as JPL's own efforts to date, before beginning development of the prototype cells. Specific areas of interest were the effects of cell materials and design on: a) energy density and discharge rate capability, b) safety, c) voltage delay, and d) storage life.

Results of this review and assessment are presented within this report. Highlights in each of the above areas of interest are summarized below.

Energy Density and Discharge Rate Capability

The most distinguishing feature of Li-$SOCl_2$ and $LiSO_2Cl_2$ cells are their exceptionally high theoretical and practical energy densities. Some versions of these cells have been shown to deliver outputs in excess of 600 W-h/kg. This value of energy density is significantly higher than that of the currently employed aerospace Ag-Zn cell, which can deliver a maximum output near 200 W-h/kg.

As with other types of cells, the energy density of lithium cells is diminished with increased rate of discharge (and corresponding increase in specific power output). This trend is due in some degree to lower discharge voltages and, to a larger degree, to diminished utilization of the active materials at the higher rates of discharge. In the case of lithium cells the utilization problem has been traced to the cathode (typically a Teflon bonded carbon black mix) rather than the lithium anode. Results have shown that energy density of the cells can be markedly increased at the higher rates by: a) decreasing cathode thickness (to a limit), b) use of SO_2Cl_2 (especially with Cl_2 added to this cathodic solvent) in place of $SOCl_2$, c) use of increased number and improved location of cathode current collector tabs, d) use of very high surface area carbon black material for the cathode, e) use of $LiAlCl_4$ electrolyte (which has been found best to date), d) decreasing cathode thickness, and e) using optimum material ratios for the components, especially the solvent-to-carbon ratio. Other factors that have been found to have a lesser but yet measurable effect on energy density at higher rates are: a) using an optimum concentration of $LiAlCl_4$ electrolyte near 1.0 M, and b) using an optimum Teflon content in the cathode (near 10% by weight of the weight of carbon black).

The so-called "spiral wound" or "jellyroll" configuration is well suited for delivering high energy densities at the higher rates of discharge (at least much more so than the so-called "bobbin" design). The "spiral wound" design is not, however, the only configuration that can be employed for this purpose (as one might be led to believe from a cursory examination of the literature). An equally attractive alternate is the parallel plate configuration, with either a prismatic or disc shape.

With current technology, it appears that cells can be designed to deliver an energy density of 300 W-h/kg at a discharge rate approaching the 1-hour rate (with higher energy densities near 600 W-h/kg at very long discharge rates of 100 hours or more).

Safety

These lithium cells have been found on occasion to either vent (expel internal gases and liquids) or to explode, sometimes violently. For this reason the cells have not received widespread use. Only when these phenomena can be eliminated altogether, or at least prevented from occurring, will the cells be employed in a variety of applications, including spacecraft power.

Numerous investigations have been carried out to establish conditions under which the cells vent or explode. These investigations may be divided into two categories consisting of environmental abuse and electrical abuse.

For the case of environmental abuse it was found that the cells do indeed vent or explode under conditions such as crushing, penetration with a nail or bullet, or incineration. These findings are pertinent to terrestrial applications of the cells wherein they may conceivably be exposed to such conditions. The findings are not, however, pertinent to aerospace applications where such conditions can most assuredly be avoided.

For the condition of electrical abuse it was found that the cells can vent or explode under two conditions. These consist of: a) the condition of short circuit or exceptionally high rate of discharge, and b) the condition of overdischarge or reversal. These findings are pertinent for both terrestrial and aerospace applications of the cells since these electrical abusive conditions could arise in either case.

Based on an assessment of the findings of the electrical abuse as well as supporting investigations, the following guidelines are suggested for the safe design and operation of these cells:

a) The cells should be designed and operated in a manner such that internal temperature will never exceed an upper limit during discharge. There is a difference of opinion as to the value of the upper limit and values range from 112°C (the melting point of sulfur) to 179°C (the melting point of lithium). To be on the conservative side, the limit should perhaps be near 100°C. The internal temperature can be estimated with a fair degree of accuracy based on known or projected cell voltage - current characteristics, internal heat generation rates (which can be predicted by equations given herein), thermal mass of the cell, and the thermal environment. For the case of cells designed to deliver very high rates, it may be necessary to provide active cooling. Also, it may be advisable to incorporate a fuse in very high rate cells to limit current and hence internal temperature rise in the event of an accidental short circuit.

b) Li-$SOCl_2$ cells should be designed with a sufficient quantity of $SOCl_2$ such that there is enough of this solvent remaining at the end of discharge to dissolve the product SO_2 gas and thereby keep pressure to tolerable levels of less than about 100 psig (an equation is given for the solubility of SO_2 in $SOCl_2$).

c) Cylindrical case designs are preferable to prismatic case designs since the cylinder can withstand greater pressure.

d) It may be well to incorporate a pressure relief valve in the cells. These should be designed to open at a pressure near 100 psig.

e) Precautions should be taken to avoid the condition of overdischarge or "reversal". All cells in a battery should be designed with a goal of uniform overall capacity, as well as anode-to-cathode capacity ratio. Care should be exercised in handling the cells to insure that one or more of them is not partially discharged and thereby imbalanced from the others. Finally, the depth of discharge should be limited to about 80 or 90% of rated capacity.

f) An extra precaution that may be taken where reversal must be taken into account is to vary the anode-to-cathode capacity ratio by varying the relative weights of the active materials at these electrodes. In the case of Li-$SOCl_2$ and Li-SO_2Cl_2 cells these materials are the lithium and the carbon. (The carbon rather than the solvent usually controls capacity of the cathode). Some claim that cells are less likely to explode on reversal if the ratio is less than 1 (anode limited). Others claim the risk is very unlikely if the ratio is greater than 1 (cathode limited). Reasons for these beliefs are described herein. Most of the experimental data indicates the latter (cathode limited) to be the safest with a ratio of about 1.2/1.

Some investigators add material, such as metallic copper (Cu) or bromine-chloride (BrCl) to $SOCl_2$ cells for safety purposes. Their justification is that these compounds react with product sulfur, which is believed to be associated with the explosions that occur during electrical abuse. Although cells with these additives appear to be safer, there is no conclusive evidence to show that they are safer for the above reason.

Other investigators have suggested the use of additives to decompose suspected explosive intermediates formed during normal discharge. Before seriously considering use of these additives, JPL is first trying to establish the existence of these proposed intermediates and their identities.

Some additional points regarding safety of these cells are as follows:

a) Lithium can react with nitrogen in the atmosphere to form the explosive compound Li_3N. The reaction does not readily occur under good dry-room conditions, but does occur quite rapidly when humidity is increased beyond a few percent. On this basis the humidity in a lithium battery dry room must be closely controlled and exposure time of lithium to the atmosphere be kept to a minimum.

b) Undischarged Li-$SOCl_2$ cells appear to be quite stable over a range of temperatures while partially or fully discharged $LiSOCl_2$ cells exhibit exothermic reactions in the temperature range of 80 to 100°C. This suggests that discharged Li-$SOCl_2$ cells offer more of a safety threat than fresh, undischarged cells.

c) To date there is no convincing evidence to show that Li-SO_2Cl_2 cells are safer than Li-$SOCl_2$ cells or vice versa. It is postulated that Li-SO_2Cl_2 cells are safer because they do not generate any potentially dangerous intermediates (such as SO), or end products which may be generated in Li-$SOCl_2$ cells. JPL is conducting in situ spectroscopic analyses of these systems in order to identify these species and resolve the issue.

Voltage Delay

Like some other types of primary cells, both Li-$SOCl_2$ and Li-SO_2Cl_2 cells exhibit the phenomena of voltage delay. This refers to transient decline and then recovery of cell voltage at the onset of discharge. The time from the start of discharge until voltage recovers to a specified level is designated as the voltage delay time.

Magnitude and duration of the voltage delay has been found to increase with: increase in current density, increase in storage time, increase in storage temperature, and decrease in operating temperature. The magnitude of the initial decline can vary from a few millivolts to 2 or 3 volts, and delay times can vary from a few milliseconds to several minutes.

Although the phenomena are not completely understood from a fundamental point of view, it is known to be associated with a film of LiCl which is formed on the surface of the lithium anode. The film is known to grow with time and its thickness and morphology can be correlated with the magnitude of the delay.

Numerous investigations have been carried out to determine methods for minimizing the delay phenomena. These have met with a fair degree of success and are summarized below.

a) The use of a new lithium-boron electrolyte, $Li_2B_{10}Cl_{10}$, in place of the currently employed $LiAlCl_4$, has been found to markedly reduce delay.

b) The application of one type of film on the surface of the raw lithium has been found to markedly reduce delay. This film is a copolymer comprised of 86% vinyl chloride and 14% vinyl acetate.

c) The application of another type of film on the anode has also been found to minimize delay. This film is comprised of either methyl or ethyl cyanoacrylate.

d) The use of a new electrolyte, $Li_2Al_2Cl_6O$, in place of $LiAlCl_4$, has been found to reduce delay.

e) The addition of SO_2 to Li-$SOCl_2$ cells reduces delay.

f) The addition of some sulfur compounds including S, Li_2S, S_2Cl_2, and SCl_2 are claimed to reduce delay.

g) It is essential to employ very pure solvents ($SOCl_2$ or SO_2Cl_2) in order to minimize delay. Reagent grade solvents are not pure enough for this purpose and will cause significant delays. These must be purified even further by distillation in order to obtain the minimal delays.

h) An operational technique which has been found quite effective in reducing delay consists of subjecting the cell to a short discharge (about 0.25% of its capacity) shortly before it is intended for use.

i) Iron impurities in the cell at levels of 200 ppm cause extremely severe delays. Iron concentration well below this level is required to prevent severe delays. A major source of iron contamination can be the $AlCl_3$, which is one of the starting materials used to prepare the $LiAlCl_4$ electrolyte. The $AlCl_3$ employed must be extremely pure.

Storage Life

Very limited information is available on the storage life capabilities of $Li-SOCl_2$ and $Li-SO_2Cl_2$ cells. This lack of information is attributed to the facts that these cells are relatively new, and also that most of the prior work on these cells has been focused on their performance and safety characteristics.

What little information that is available may be divided into two catagories. The first of these is compatibility type data i.e., stability of materials of construction in the corrosive environment of these cells. The second is accelerated life data obtained by measuring cell capacities after varying periods of storage at elevated temperatures, or by the more recently developed technique of microcalorimetry.

The most important findings regarding stability of materials are summarized below.

a) There are several metals that are suitable as materials of construction for the case, cover, and grids. These metals include nickel, stainless steels (types 302, 304, 306 and 316), nickel plated stainless steels, cold rolled steel, and Inconel.

b) There are a rather limited number of insulating materials that may be employed as a separator, bonding agent, a terminal seal, or for other purposes. These insulating materials include glass, glass fibre mats, Kel-F, and Teflon. Most other rubber and plastic materials are very unstable in the cell environment.

The most important findings regarding the accelerated life tests on these cells are summarized below:

a) There is a great deal of scatter in results of accelerated life tests on what may be called the baseline Li-$SOCl_2$ cells which contain $LiAlCl_4$ electrolyte, carbon black cathodes, nickel grids, and no special additives. Due to this scatter, it is not possible to make a life projection that will cover all of the experimental data. It is, however, possible to make a projection based on the best results reported in the literature. This projection is as follows: $\ln R = \frac{-1.03 \times 10^4}{T} + 32.23$, where R = loss rate in %/month, and T = absolute temperature, K. By application of this equation, one obtains a loss rate of 0.1%/month at 25°C which approximates results obtained in a real-time 2-year life test at ambient temperature.

b) The addition of Cl_2 to Li-$SOCl_2$ cells is found to markedly accelerate their capacity loss rate. Since Cl_2 is a known impurity in $SOCl_2$, the Cl_2 should be removed from the solvent during the purification process.

c) The new $Li_2B_{10}Cl_{10}$ electrolyte, which is effective in reducing voltage delay, may even improve life of Li-$SOCl_2$ cells.

d) The electrolyte, $LiAlCl_4$, must be made with stochiometric proportions of LiCl and $AlCl_3$ or with a slight excess of LiCl. Electrolytes made with an excess of $AlCl_3$ will cause a rapid loss in capacity in an amount equivalent to the excess of $AlCl_3$.

e) The use of BrCl to improve the safety of Li-$SOCl_2$ cells does not adversely affect their storage life.

f) The addition of calcium salts as well as SO_2 to $SOCl_2$ cells tends to diminish their life.

g) The life of Li-SO_2CL_2 cells with $LiAlCl_4$ electrolyte does not appear to be less and may even be greater than life of Li-$SOCl_2$ cells with $LiAlCl_4$ electrolyte.

SECTION 2

INTRODUCTION

One task under NASA RTOP No. 506-55-55 is the "Advanced Primary Lithium Battery Program". Objective of this program is to develop safe, high energy, and long life primary lithium batteries by FY 86. Because of their very high energy density, these batteries will enhance a number of NASA's planned planetary missions by appreciably reducing power system mass. This reduction in mass will improve cost effectiveness of the missions by reducing costly thrust capability and/or permitting increased scientific payload mass, both of which increase the amount of data obtained per unit of mission cost. In addition, these batteries may enable selected missions which are severely mass constrained.

The program is divided into two subtasks, one of which is research oriented and the other of which is engineering oriented. The research subtask is aimed at obtaining a fundamental understanding of the materials and processes that govern some unresolved safety and performance problems with these batteries, and with this understanding to generate methods to insure that they deliver high performance in a safe and reliable manner. The engineering subtask is aimed at developing practical prototype cells that incorporate the above innovations and demonstrating their improved safety and performance by testing them under simulated loads that may be encountered on the spacecraft.

Of the numerous types of lithium battery systems that have been described in the literature, the one that has been selected for this application is the lithium oxyhalide type and in particular the lithium-thionyl chloride ($Li-SOCl_2$) system. As a potentially attractive alternate, the lithium-sulfuryl chloride ($Li-SO_2Cl_2$) system is also being considered. The reasons for narrowing the choice to these two particular candidates are: a) their energy densities are the highest of all lithium batteries (up to 600 W-h/kg); b) they have the potential for supplying power at high rates of discharge (at rates approaching 1 h, and c) there is already some data base to show that completely packaged hardware versions of these cells can already deliver most of the high performance capabilities described above (although not always in a safe manner and not after lengthy periods of storage in excess of 2-3 yrs).

Although the operation of lithium-oxyhalide cells is not yet completely understood from a fundamental chemical and electrochemical point of view, a great deal of practical information is known about the relationship between cell design and performance. These relationships include the effects of factors such as electrode geometries, dimensions, and materials as well as electrolyte materials and concentrations on electrical performance, safety, and life. A great deal of this information has been obtained during the past several years by industrial organizations under government sponsored R & D programs. The information has been published and is available in the form of technical reports as well as publications in the open literature.

In preparation for the prototype cell development subtask of this program, a review and assessment was made of this literature. Pertinent findings from this material were extracted, analyzed, and are summarized within this report. Also included are some related findings of investigations carried out by JPL. The material was organized into four categories which consist of factors that affect: a) energy density and rate capability, b) safety, c) voltage delay, and d) storage life. Most of the material is based on studies of the lithium-thionyl chloride (Li-$SOCl_2$) system which has received most of the attention during the past several years. A limited amount of the material is based on studies of the somewhat newer lithium-sulfuryl chloride (Li-SO_2Cl_2) system. The report should serve as a useful reference guide not only for development of prototype cells but also for general design purposes of lithium oxyhalide cells.

SECTION 3

DESCRIPTION OF CELLS

The cells of concern are commonly referred to in the battery industry as lithium cells with a "liquid" cathode. Like all other electrochemical cells, they are comprised of an anode, cathode, and solvent/electrolyte. In this case the anode is lithium metal, the cathode is the liquid $SOCl_2$ or SO_2Cl_2 solvent in combination with a carbon current collector, and the electrolyte is a lithium salt, which is typically $LiAlCl_4$. The major difference between these and other types of primary cells, aside from the fact that they contain lithium anodes, is that the cathode material is a liquid rather than a solid such as MnO_2 or AgO.

A schematic diagram of two alternative designs of this cell is given in Figure 1 (Ref. 28). The one on the left, designated as the "High Energy Cell", is intended for low current drain applications. This is commonly referred to as the "bobbin" type configuration and is characterized by having very thick electrodes with low internal electrode surface area (since it does not have to deliver much current) and high energy density (since it contains a relatively high percentage of active electrochemical materials and a small percentage of inactive or inert materials). The one on the right, designated as the "High Power Cell", is intended for high current drain applications. This is commonly referred to as the "spiral wound" configuration and is characterized by having very thin electrodes with high internal electrode surface area and high power density (since it is intended to operate at high currents and therefore deliver high power outputs) and somewhat lower energy density than the "bobbin" type (since it contains a higher percentage of inactive inert materials and less active materials than the bobbin type cell).

It should be pointed out that these cells can and have been made with configurations other than the above two. One of these is the so called "prismatic" configuration which is comprised of a stack of alternately spaced rectangular anodes and cathodes. Another is the so called "disc" configuration. This is similar to the prismatic in that it contains alternately spaced anodes and cathodes. The major difference is that the shape of these electrodes is circular rather than rectangular. Both of these configurations can be designed to deliver either high energy or high power as discussed above. The high energy (and corresponding low rate) type is made by employing a small number of thick electrode plates while the high power type is made by employing a large number of very thin electrode plates.

Regardless of the configuration, the cells all employ essentially the same types of materials for the various components. The anode is comprised of lithium metal foil which has been pressure bonded onto a current collector, which is typically a nickel screen or expanded metal grid. The cathode collector is comprised of a Teflon-carbon black mixture that has been bonded on both sides of a screen or expanded metal grid as for the anode. A layer of separator material is located between the anodes and cathodes. This is typically comprised of a non-woven glass fabric material. The cathode solvent is either $SOCl_2$ or SO_2Cl_2, both of which are liquid at room temperature. Electrolyte salt is typically $LiAlCl_4$ which is quite soluble and is dissolved in either of the cathodic solvents. The solvent/electrolyte solution is usually added as a last step in the assembly procedure by a vacuum filling technique. Case and cover are typically made of stainless steel. One of the electrodes, usually the cathode, is electrically connected to the case which serves as one terminal. The other electrode is electrically connected to an insulated feed-through seal, which serves as the other terminal. The cells are hermetically sealed and are usually equipped with some form of a pressure relief device.

SECTION 4

ENERGY DENSITY AND DISCHARGE RATE CAPABILITY

One of the major objectives of this program is to develop cells that simultaneously deliver high energy density and high rate (or correspondingly high power density). From the discussion in Section 3, it would appear that these objectives conflict with one another in that the high energy designs (with thick electrodes) yield low power densities, and the high power designs (with thin electrodes) yield low energy densities. Apparently it would appear necessary to design cells with some intermediate thickness that optimizes both features. This would not be the case if the high energy design (with thick electrodes) were able to operate at very high current densities so as to compensate for its limited electrode area and deliver high currents and power outputs. Under these conditions, however, the voltage of the high energy cell falls to unacceptably low levels well before all of the electrode materials are utilized so that it cannot deliver its inherent high energy. The problem is primarily associated with the positive carbon electrode, the utilization of which is highly dependent on its thickness and current density. (The lithium anode can deliver high current densities with high utilization for a wide range of thicknesses). A key challenge, then, is to develop a cathode that simultaneously delivers high current density and utilization at high thicknesses. A number of investigations have been carried out with this purpose in mind and are described herein.

In addition to properties of the cathode, there are a number of other factors that influence energy density and rate capability. These have also been investigated and are described herein.

4.1 GTE FINDINGS

GTE has obtained data on the effect of cathode thickness on its polarization (voltage-current) and also utilization characteristics (Ref. 1, pp. 1-11). Figure 2 indicates that cathode thickness has a relatively small effect on polarization (and hence rate capability) for a given range of thicknesses. As cathode thickness is increased from 2 to 50 mils, operating voltage is noted to increase by about 0.1 volt over a range of current densities from 0 to about 60 mA/cm^2. Figure 3 shows that cathode thickness does not have much of an effect on utilization (and, hence, energy density) for thicknesses in the range of 0.2 to 1.0 mm (8 to 40 mils). Utilization is noted to decrease about 25% as thickness is increased from 0.2 to 1.0 mm. However, it is noted that utilization increases appreciably as thickness is reduced below 0.2 mm (8 mils). An appreciable increase in utilization of about 50% can be achieved by reducing thickness from 0.2 mm (8 mils) to about .05 mm (2 mils). Alternative types of cathode materials, other than the conventional carbon/Teflon black, have been shown to yield improved polarization and utilization as shown in Figures 4 and 5. Although the material has not been designated by GTE, it is shown in Figure 4 to increase voltage by about 0.3 volts at current densities from 1 to 150 mA/cm^2. Also, in Figure 5, it is shown to markedly increase utilization, especially at moderate-to-low current densities of 1 to 10 mA/cm^2 and for thin, 2-mil thick, cathodes. The effect of electrode spacing on voltage-current characteristics is given in Figure 6. The spacing was varied by changing the thickness of the glass fibre separators between electrodes. Therein it is noted that spacing has a pronounced effect on voltage-current characteristics. For example, at a current density of 300 mA/cm^2, average discharge voltage is noted to increase from 1.2 volts to 2.3 volts as thickness of the separator is decreased from 17.9 mils to 2.7 mils.

In other investigations GTE examined the effect of electrolyte type and concentration on utilization or specific capacity of the carbon cathode (Ref. 2, pp. 262-265). In this study they were comparing the performance of $LiAlCl_4$ and $AlCl_3$ electrolytes for reserve type cells. We are only interested in the $LiAlCl_4$ electrolyte because it can, and is, employed in active cells whereas pure $AlCl_3$ cannot be used in active cells because it causes excessive self-discharge rates for the long term. The lower curve in Figure 9 gives the variation of discharge capacity with concentration of $LiAlCl_4$ in the range of 0 to 4 mols/liter with a 37-μm cathode thickness (1.5 mil). Therein it is noted that capacity exhibits a maximum near $5x10^{-2}$ $mAh/cm^2/\mu m$ at a concentration of 1.5-mol $LiAlCl_4$. Figure 10 gives the same type of relationship for a cell with much thicker electrodes of 950 μm (37 mils). Inspection of the lower curve in this figure for $LiAlCl_4$ reveals a maximum in capacity near $4x10^{-2}$ $mAh/cm^2/\mu m$ at a concentration of 4.0 mols/liter. These results indicate that the optimum electrolyte concentration increases with increase in cathode thickness. As thickness is increased from 1.5 to 37 mils, optimum electrolyte concentration increases from 1.5 to 4 mols/liter.

In another investigation GTE carried out analytical design optimization studies to size the components of spiral wound "D" cells (Ref. 3, pp. 37-42). One important finding of this study was the predicted relation between electrode thickness (anode and cathode) on capacity as shown in Table III. Therein it is noted that as combined thickness of anode and cathode plus two layers of separator is decreased from 2.83 mm (111 mil) to 1.23 mm (48 mil), capacity is predicted to decline from 18.49 Ah to 12.75 Ah. The predicted decrease is attributed to the fact that as electrode thickness is decreased (and length is correspondingly increased) there is a lower ratio of "active material" (carbon and lithium) to "inactive material" (current collectors and separators). Accuracy of the predictive technique was tested by assembling a cell with the indicated dimensions of Cell No. 6 in Table III. The cell was found to deliver 13.4 Ah at 100 mA as compared with a predicted capacity of 14.18 Ah at this current. The discrepancy between predicted and actual capacity is not too large (about 6%) and the predictive technique, therefore, appears to have some merit. Energy density of the above cell was found to be 461 Wh/kg at the current of 100 mA. GTE mentioned in this same study that cell capacity, and hence energy density, declines at higher currents. They pointed out that energy density is high and independent of rate to current densities of 1.8 mA/cm^2. At a current density of 10 mA/cm^2 they find capacity and hence energy density decline to about 75 to 80% of that at the lower current densities.

In a final report from a prior investigation, GTE presented additional findings regarding energy density and rate characteristics (Ref. 5). One series of constant current runs was carried out on cathode limited button cells with a range of cathode thicknesses from 0.023 in. (23 mil) to .052 in. (52 mil) (pp. 19-22). Results are shown in Figure 11 and Table IV. Inspection of Figure 11 reveals specific cathode capacity, in terms of mAh/cm^2, is independent of current density for all thicknesses tested to about 2 mA/cm^2 and that specific capacity for all thicknesses decreases markedly at current densities from 2 mA/cm^2 to 10 mA/cm^2. Inspection of Table IV reveals that the maximum capacity at low currents (<2mA/cm^2) in terms of Ah/g of carbon blend, increases with decreases in cathode thickness from 1.19 Ah/g for 52-mil cathodes to 3.14 Ah/g for 23-mil cathodes. In another series of runs, GTE examined the effect of electrode dimensions on output of spiral wound "D" size cells (Ref. 5). Table V gives the dimensions employed for what are designated as types "A," "B," and "C" designs. These designs are noted to contain progressively shorter and thicker electrode dimensions from "A" to "C", respectively. Each of these was discharged at three different current levels which corresponded to current densities of 0.9 to 3.8 mA/cm^2. Results shown in Table VI revealed a trend toward increased capacity from Designs A to C. For example, at a current density of 0.9 to 1.0 mA/cm^2, capacities were 7.35, 9.45, and 11.38 Ah, respectively, for Designs A, B, and C. For the indicated range of dimensions and current densities, then, the shorter and thicker electrodes yielded higher capacities. This trend might at first appear to be contrary to previous discussions above, where it was pointed out that the thinner electrodes deliver higher utilization. The apparent discrepancy is explained, however, by the fact that cells with the thinner electrodes contain a higher percentage of inactive grid material and hence less active carbon material and capacity.

4.2 HONEYWELL FINDINGS

Honeywell obtained data on the utilization of relatively thick cathodes in cathode-limited cells over a range of operating temperatures (Ref. 2, pp. 247-251). Results of their investigation are given in Table II. Inspection of this data reveals that utilization increases with temperature in the range of 4°C to 43°C, and decreases with thickness in the range of 1.6 cm to 0.45 cm. It is interesting to note that cells with cathode thicknesses as large as 0.81 cm (320 mils) can deliver utilization as high as 2 Ah/g at 24°C. It should be pointed out, however, that the current densities employed in this investigation were quite low, i.e., 0.5 to 1.0 mA/cm^2.

4.3 MALLORY (DURACELL) FINDINGS

Mallory carried out a factorial designed experiment aimed at determining the effect of carbon weight, electrode area, and electrolyte concentration on capacity and energy density of spiral wound "D" size cells (Ref. 4, pp. 493-510). Factors kept constant were the weight of lithium and cathode composition (Shawinigan Black

90% and Teflon 10%). The factorial matrix for the cells is given in Table VII. Results for cell types A, B, and C with 5-6 g of carbon are shown in Figure 12. Therein it is noted that at high rates of discharge (>1.0 amp) cell capacity increased with increasing electrode length and hence area. Capacities of these cells at low rates (<.3 A) ranged from about 13 to 16 Ah. Cell types D, E, and F with 2.5 to 3 g of carbon were found to deliver nearly 8 Ah or about one half the capacity of types A, B, and C. In all of the above cells there was found to be no significant difference in either capacity or rate capability with either 1.0 or 1.8 M $LiAlCl_4$ concentration. It was found, however, that rate capability was diminished for $LiAlCl_4$ concentrations below 0.5 M.

In another parametric study Mallory examined the effects of three variables on performance of Li-$SOCl_2$ "C" size cells (Ref. 6, pp. 5-11). The variables of concern were: a) concentration of $LiAlCl_4$, b) purity or source of $LiAlCl_4$, and c) Teflon content of the Shawinigan Black cathodes. A schematic of the "C" cells employed in these studies is given in Figure 13. Anodes were prepared by pressing .022-in. (22 mil) lithium foil onto nickel Exmet with overall length and width of 7.5 in. and 1.5 in., respectively. Cathodes were prepared by pressing and sintering 1.65 g of a Shawinigan/Teflon mix onto nickel Exmet with overall length and width of 8.0 in. and 1.5 in., respectively. The factorial matrix for this investigation is given in Table VIII. (The only parameter that is not readily apparent in this matrix is the type of electrolyte. The term "LPS" refers to electrolyte that was prepared at Mallory by fusing an equimolar, anhydrous mixture of LiCl and $AlCl_3$ to form $LiAlCl_4$. The term "Foote" refers to $LiAlCl_4$ that was prepared by Foote Mineral Co.) Major findings and conclusions that were drawn from this study are summarized below:

a) Capacity and rate capability increase with decrease in Teflon content of the cathode mix from 30% to 10% as shown in Figure 14.

On this basis, the lowest Teflon content, 10%, yields best performance.

b) Capacity and rate capability are higher for the LPS (Mallory prepared) $LiAlCl_4$ than the Foote Mineral prepared $LiAlCl_4$, as shown in Figure 15. On this basis the Mallory prepared $LiAlCl_4$ yields better performance than the Foote Mineral prepared $LiAlCl_4$. (The method by which Foote prepared the material was not specified in this report. Their process should be investigated for future reference.)

c) Capacity and rate capability show a trend of first increasing, then decreasing as electrolyte concentration is increased from 0.5 to 2.0-mol $LiAlCl_4$ (the Mallory prepared type), as shown in Figure 16. On the basis of the curves shown in this figure it appears that the optimum electrolyte concentration is near 1.0-mol $LiAlCl_4$ in terms of capacity and rate capability.

In this same investigation Mallory fabricated and examined performance characteristics of spiral wound Li-$SOCl_2$ "D" cells (Ref. 6). Details of construction of these cells is given in Section 7.2. Two general types were evaluated in terms of energy density and rate capability. These were designated as the "low" and "medium" rate types. The "low" rate types employed 10 to 15-inch-long electrodes with 0.5-mol $LiAlCl_4$ electrolyte and the "high" rate types employed 20-inch-long electrodes with 1.0-mol $LiAlCl_4$ electrolyte. Energy densities of these cells are given as a function of discharge rate in Figure 27. Maximum capacity of the "low" rate cells was found to be 18 to 19 Ah, which corresponds to energy densities of 1.22 Wh/cm^3 (20 Wh/in^3) and 660 Wh/kg (300 Wh/lb). $SOCl_2$

utilization was about 95-98%. These energy densities were deemed to represent the upper practical limits obtainable in spiral wound "D" cells. The "medium" rate cells were, on the other hand, found to deliver essentially constant energy densities of 0.79 Wh/cm^3 (13 Wh/in^3) and 418 Wh/kg (190 Wh/lb) at discharge rates up to 1.0 amp. Energy densities of these cells were found to drop sharply with discharge rates beyond 2.0 amps. $SOCl_2$ utilization for these cells was found to be in the range of 70 to 75%.

In a follow-on investigation Mallory examined methods for improving energy density of spiral wound Li-$SOCl_2$ "D" cells, especially at the higher rates of discharge (Ref. 13, pp. 4-31). These cells were intended for use in two Army applications including a radio and a laser designator. Most of their work was focused on improving design of the cathode which had been shown to be the component that was primarily responsible for the limitations on energy density and rate capability. In particular, they were interested in examining potential benefits that could be derived from modifying the cathode grid/tab configuration in that the existing configuration (single tab at one end) was known to contribute significantly to internal resistance (which causes lower cell voltages) and non-uniform current distribution (which can result in diminished utilization and capacity). On this basis they proceeded to evaluate cells with eight different cathode grid/tab designs as shown in Figure 28. All of the cathodes were comprised of a mixture of Shawinigan Black with 10% Teflon pressed onto an expanded nickel metal grid. Two different cathode lengths of 20 in. and 25 in. were employed as shown in Figure 28. Cathode widths were 1.75 in. for all designs and thicknesses were 0.025 in. for the 20-in.-long cathodes and 0.01[illegible] in for the 25-in.-long cathodes. Anodes were prepared by pressing lithium onto expanded nickel metal grid. Anode widths were 1.75 in. for all designs and thicknesses were 0.015 in. for the 20-in.-long design and 0.010 in. for the 25-in.-long design. Solvent and electrolyte for all cells was $SOCl_2$ with 1.8-mol $LiAlCl_4$. Performance of the cells with the various cathode designs is given in Figure 28 in terms of short circuit current and in Figures 29 and 30 in terms of voltage-current or polarization characteristics. Inspection of these results reveals that the cathode grid/tab configuration has a marked effect on cell performance. For example, by simply changing location of the single vertical tab configuration from one end (Design No. 1, which has been the standard employed to date) to the center (Design No. 2), the short circuit current is increased more than three-fold and the operating current is increased more than two-fold at voltages between 2.5 and 3.0 volts. Somewhat more moderate additional improvements in performance are noted to result from use of two equally spaced vertical tabs (Design No. 3). Use of an additional horizontal tab across the length of the cathode (Design Nos. 4 and 5) did not yield much improvement in performance. Also, the use of longer 25-in. electrodes (Designs 6, 7, and 8) did not appear to yield much improvement in performance over the shorter (20-inch) electrodes with corresponding configurations (Design Nos. 1, 2, and 3). Based on the above as well as the fact that Design No. 2 was the easiest to assemble, they selected this design and assembled several cells based on it for the above-mentioned application.

The optimized cells were evaluated on special duty cycles for these applications and found to perform significantly better than the previous state-of-the-art cells. For example, the new cells were found to deliver: a) 8 Ah at 10 A and 3 volts, or an energy density of 264 Wh/kg (120 Wh/lb) and, b) 12 Ah at 3 A and 3.3 V, or an energy density of 396 Wh/kg (180 Wh/lb). By comparison, the previous state-of-the-art cells could deliver essentially no output at 10 A and only about 6 Ah at 3 A and 3.0 volts, or an energy density of about 220 Wh/kg (100 Wh/lb).

In the same investigation Mallory examined additional methods to further improve performance of the spiral wound "D" cell and also initiated preliminary development and evaluation of an entirely different disc type cell design (Ref. 13, pp. 17 59). One of the additional methods to improve performance of the "D" cell involved use of additives to the cathode mix. Five such additives were examined at one or more concentration levels. Composition of the additives was not identified in this report. They were, however, referred to as Ni, Cu, Cr, Co, and Mn. This would imply that the additives were comprised of the abovementioned metals although they may very well have been compounds of these metals. In any event, Mallory showed that two of these, Ni and Cu, did show some signs of improving high rate performance of the "D" cells. On the particular duty cycle for this application, they found that use of these additives could increase output up to 22%. The second method examined to improve performance was to reduce electrolyte concentration from the previously employed level of 1.8-mol $LiAlCl_4$. Justification for this change was based on the fact that the 1.8-mol concentration corresponds to the maximum conductivity in the concentration — conductivity relationship and that during the course of discharge, the concentration increases, which results in lower conductivity and, hence, more internal resistive losses. For this purpose they assembled and evaluated cells with 1.4-mol rather than 1.8-mol $LiAlCl_4$. Results, however, showed negligible improvement in high rate performance with the lower concentration of electrolyte. This implies that the high rate capability is influenced more by the cathode and other factors than the electrolyte. Mallory's developmental efforts on the disc type cell were not as comprehensive as those on the "D" type cell in this investigation. Their incentive for examining this configuration was that it has a higher ratio of surface area to volume than the cylindrical "D" size configuration, and should therefore be safer than the "D" configuration in that it will dissipate heat more readily and thereby operate at lower temperatures. This is shown by the expression for the surface-to-volume ratio of a cylinder as follows:

$$R = \frac{\text{Surface Area}}{\text{Volume}} = \frac{2\pi r^2 + 2\pi rL}{\pi r^2 L} = \frac{2}{L} + \frac{2}{r}$$

Where "r" is the radius and "L" is the length of the cylinder

The ratio can thus be increased either by decreasing the length or radius of the cylinder. Fabrication difficulties arise in making a thin narrow cell so that the preferred method is to work with a "flat" cylindrical cell with shorter length. Overall dimensions of the cell that were employed here were 3 in. diameter and 0.9 in. thick. The cell was assembled by sandwiching 40 each disc shaped anodes, cathodes, and separators inside a stainless steel disc shaped can with wall thickness of 0.032 in. Thicknesses of the anodes and cathodes were 0.005 in. and 0.015 in., respectively. Diameter of the electrodes was approximately 2.6 in. The cells employed a glass-to-metal terminal seal with the pin negative and the case positive. The cells were filled with $SOCl_2$ + 1.8-mol $LiAlCl_4$ and overall weight of each cell was approximately 225 g. Despite some problems in reproducibility, Mallory was able to show that this cell did indeed have a very high rate capability. Short circuit current was found to be near 1700 amps. The cell was found to be capable of operating continuously at currents to 100 amps while delivering appreciable energy densities. For example, at a current of 20 amps, the cell maintained an output voltage near 3.0 volts for 1 h with corresponding energy density near 260 Wh/kg (120 Wh/lb). The cell could maintain a potential near 3.0 volts while delivering even higher currents near 100 amps. Due to excessive internal temperature rise the cell could not, however, operate continuously at these very high currents without developing excessive internal pressures that caused it to vent. Although this disc cell configuration has higher heat transfer capability than the "D" cell configuration, its exceptional high rate capability causes its heat generation capability to exceed its heat loss capability. Hence, the cell must be actively cooled at the very high rates of discharge.

4.4 ELECTROCHEM INDUSTRIES FINDINGS

Electrochem Industries indicated that their Li-$SOCl_2$ cells with BrCl additive, as described in Section 5.5, yielded higher capacities than conventional Li-$SOCl_2$ cells (Ref. 9). Their basis for the above is the discharge data for "AA" size Li-$SOCl_2$ cells, both with and without the BrCl additive as shown in Figure 23. Inspection of their product data sheets reveals, however, that this new type of cell with BrCl additive (designated as their type "BCX" cell) does not necessarily have much higher capacity than other types of Li-$SOCl_2$ cells. For example, their "D" size version of this cell (designated as type BCX 72) is listed as having rated capacity of 14 Ah at a current of 175 mA. Comparable "D" size Li-$SOCl_2$ cells from both GTE and Mallory are found to deliver capacities of 12 to 16 Ah at comparable discharge rates to the above. Energy density of this Electrochem BCX cell is near 400 Wh/kg, which is also comparable to the energy densities of the GTE and Mallory cells at the indicated discharge current.

Electrochem Industries has also developed another new lithium cell which is claimed to have higher rate capability than existing Li-$SOCl_2$ cells (12). This new type is based on the lithium-sulfuryl chloride couple (Li-SO_2Cl_2) and contains chlorine as an additive. Construction of this cell is very similar to conventional Li-$SOCl_2$ cells except for the solvent. The anode is made by pressing lithium foil on nickel screen. The cathode is made by bonding a mix of 93% Shawinigan acetylene black and 7% Teflon onto a nickel screen. $LiAlCl_4$ electrolyte is made by fusing an equimolar mixture of LiCl and $AlCl_3$. Electrolyte concentration is 1.1 mol. Chlorine was added to the solvent/electrolyte by condensing it in a liquid N_2/ethanol trap and then adding it directly to the solution. Cl_2 concentration was 0.46 mol. Cells were assembled in the spiral wound configuration employing two layers of a non-woven glass separator between electrodes. Discharge characteristics of "D" size versions of this cell are given in Figure 24 (Ref. 12). Inspection of this figure reveals that output of this type of cell is relatively high, 13 to 14 Ah, and that output is relatively independent of load in the range of 1 ohm to 150 ohm (3 A to 0.02 A). These results are indeed quite impressive, especially the fact that the cells can deliver the high output at the higher rates to 3 A. "D" size Li-$SOCl_2$ cells described by GTE and Mallory are found to deliver outputs of only 6 to 8 Ah at these higher discharge rates. On this basis then, it appears that the Li-SO_2Cl_2 cell with Cl_2 additive does indeed have higher rate capability than Li-$SOCl_2$ cells.

4.5 ERADCOM FINDINGS

The U.S. Army ERADCOM obtained a great deal of useful information on the relationship between properties of carbons and their effectiveness in the reduction of SO_2Cl_2 (Ref. 15). The four different carbons that were employed are listed in Table XVII. Cathodes were prepared from these carbons by mixing them with Teflon and pressing them onto nickel Exmet screens. In all cases the overall cathode length and width were 2.5 cm and 2.0 cm, and thickness was 0.89 mm. These were discharged in SO_2Cl_2 cells with 1.5-mol $LiAlCl_4$ electrolyte and with lithium counter and lithium reference electrodes. Physical properties of the electrodes, including carbon loading, surface area, and porosity, are given in Table XVII. Figure 34 gives the polarization characteristics of cathodes with the four different types of carbons based on geometric surface area. There is noted to be a significant difference in polarization characteristics amongst the four different carbons with the "United" type yielding the highest voltages and the Shawinigan type (most commonly employed in existing lithium batteries) yielding the lowest voltages. When the polarization characteristics are normalized in terms of surface area, however, as shown in Figure 35, the polarization characteristics of all are found to be about the same. Therefore, it appears that polarization characteristics and hence rate capability of all carbons are essentially the same when expressed on a true surface area. Figure 36 gives the capacities of electrodes as a function of porosity of the different carbons. This indicates that capacity (and hence energy density) is directly proportional to porosity and that Shawinigan black, with the highest porosity of 87%, gives the highest capacity. The effect of Teflon content of the cathode mix on output of the cathode is given in Figure 37. The particular carbon employed here was the United type which was shown to exhibit a significantly higher voltage and slightly less capacity than the Shawinigan black and was therefore thought to be more attractive as a cathode material. Results revealed that the cathode output increases and then decreases as Teflon content is increased from 6.7% to 14.3%. Maximum output is noted to occur where Teflon content is 10.7%. This finding is in agreement with that of Mallory in Section 4.3 where it was also shown that cathode output is a maximum with a Teflon content near 10%. Next, ERADCOM carried out a series of runs aimed at determining the effect of electrolyte volume on output of the cathode. Results are given in Figures 38 and 39. Figure 38 gives the discharge curves of the cathodes as a function of the ratio of the volume of electrolyte to the geometric surface area of the cathode. Therein it is noted that as the amount of electrolyte is increased, the operating time and hence capacity is increased. The discharge curves exhibit two plateaus which are typical for Li-SO_2Cl_2 cells. The upper plateau is associated with the reduction of Cl_2 and the lower plateau is associated with the reduction of SO_2Cl_2. They define the output of the cathode to the end of the high plateau as "Q" and the output of the cathode to the end of the lower plateau as "Q'." The data from Figure 38 was reduced and is plotted in Figure 39 in terms of output, mAh/cm^2, versus ratio of electrolyte volume to geometric surface area, ml/cm^2. The output curves are given in terms of both "Q" and "Q'." Also shown in this figure are the percentages of the solvent utilized both for "Q" and "Q'." These results show that output or capacity increases markedly with amount of electrolyte. Output is noted to be essentially 0 mAh/cm^2 until the electrolyte ratio is 0.1 ml/cm^2 as this is apparently the minimum amount required to wet the electrode. Output is noted to increase sharply with amount of electrolyte in the range of 0.1 to 0.4 ml/cm^2. Thereafter, output is noted to increase more slowly with amount of electrolyte in the range of 0.4 to 1.0 ml/cm^2 where output is near 135 mAh/cm^2 for "Q" or full discharge. The solvent utilization, which is the percentage of solvent utilized in the electrochemical reaction, is noted to decrease gradually from 30% to 20% as electrolyte ratio is increased from 0 to 1.0 ml/cm^2. This type of parametric data is very useful in optimizing energy density of a cell with regard to electrolyte-volume-to-carbon ratio. From Figure 39 it would appear that energy density would increase to a point as electrolyte-volume-to-carbon ratio was increased in that specific capacity increases while utilization drops very slowly with increase in this ratio. As specific capacity increases at a lower rate with respect to the electrolyte volume ratio while utilization continues to decline with this ratio, the energy density obviously passes through a maximum with regard to this ratio. Most commercial Li-$SOCl_2$ cells employ a ratio of about 10 to 20 cc/g of carbon which would correspond to a ratio of from 0.15 to 0.30 cc/cm^2 in Figure 39 (the carbon loading for these curves is 0.0146 g/cm^2). This would imply that the optimum volume/area ratio would be near the low end in Figure 39 (i.e., near 0.2 ml/cm^2) with regard to energy density. This may or may not be the case in that this ratio may be employed for reasons other than energy density. Nevertheless, the data in Figure 39 remains useful in showing how energy may at least hypothetically be increased by varying the electrolyte to area (or carbon weight) ratio. Finally, ERADCOM compared the performance of $SOCl_2$ and SO_2Cl_2 solvents in these cells. Electrolyte to area volume ratio was 1 ml/cm^2 in all cases while the $SOCl_2$ cells employed Shawinigan black cathodes and the SO_2Cl_2 cells employed the United carbon black. Results, given in Figures 40 and 41 reveal that the SO_2Cl_2 cells yield appreciably higher voltages and slightly higher capacities than the $SOCl_2$ cells. Therefore, the SO_2Cl_2 cells should yield a somewhat higher rate capability and energy density than the $SOCl_2$ cells.

4.6 JPL FINDINGS

In a prior JPL-sponsored study, Eagle Picher examined methods for improving the rate capability of the existing carbon black cathode (which limits rate capability of the overall cell) (Ref. 27). Their approach consisted of selecting candidate new metals and then comparing their electrochemical polarization characteristics (for the reduction of $SOCl_2$) with those of carbon black cathodes. As part of their initial selection criteria they examined compatibility of several metals with $SOCl_2$ by elevated temperature corrosion tests. Results of these tests are given in Table XX and are discussed in Section 7.4. The most stable metals were then characterized electrochemically by measuring their voltage-current characteristics in a conventional three-electrode cell employing a lithium counter electrode, the working test electrode, and a silver chloride reference electrode (with 1.4-mol $LiAlCl_4$ and $SOCl_2$ electrolyte). As a result of the above two screening test series they concluded that the most promising new cathode metal was gold. This was found to be suitably stable in the electrolyte and to exhibit markedly less polarization than carbon at very high current densities.

In order to take advantage of the high current capabilities of gold to an even further degree, it would be desirable to develop a porous type gold electrode which has high internal surface area per unit weight and volume of electrode. This would enhance the current density to an even larger degree based on geometric surface area. A porous electrode based on pure gold is, however, not feasible because of the exceptionally high cost of gold. A more economical approach would consist of applying a very thin film of gold to a less expensive porous substrate via electrodeposition, vapor deposition, or other technique. With this approach in mind Eagle Picher proceeded to develop and evaluate cathodes based on gold plated porous nickel substrates (the material commonly employed in nickel-cadmium cells). Although the cathodes delivered very high current densities, as anticipated, their specific capacities were appreciably lower than capacities of carbon black cathodes. For example, the specific capacity of the nickel-gold cathodes was found to be 1.15 Ah/cm^3 as compared with 3.23 Ah/cm^3 for carbon black cathodes. In addition to delivering high current and hence high rate capability, the nickel-gold electrodes also delivered high operating voltages which contributes to improved energy density. Their marked low specific capacity however offsets their higher voltage advantage so that their overall energy density is less than that of the carbon black electrodes. This result signified that the high surface area associated with the carbon electrodes is essential for high specific capacity and in turn high energy density. On this basis it was then believed that a most promising cathode would be a carbon black type which has been coated with a very thin film of gold. This type of cathode should simultaneously deliver high current and hence rate capability due to its gold film and high specific and hence energy density due in most part to its high surface area associated with the carbon black and to a lesser degree to its higher voltage, which is also associated with the gold film. Eagle Picher was not successful in developing such a cathode during the course of this rather limited program. One of their major recommendations however was to explore techniques for making a suitable gold-carbon type cathode.

In order to verify the above findings JPL examined the polarization characteristics of the gold-nickel cathodes and compared their performance with that of conventional carbon black cathodes. This work was carried out in glass laboratory cells with a lithium anode, a carbon or gold-nickel reference electrode, and $SOCl_2$ with 1.5-mol $LiAlCl_4$ electrolyte. Results, given in Figure 51, established that the gold-nickel cathodes do indeed yield significantly less polarization than the carbon black cathodes. For example, at a polarization near 0.5 volts (which would correspond to an operating cell voltage near 3.1 volts), it is noted that the nickel-gold cathodes yield a current density of 40 mA/cm^2 while the carbon black cathodes yield a current density of only about 13 mA/cm^2. Under these conditions then, the gold-nickel cathodes yield 300% more current (and hence 300% more rate capability) than the carbon cathodes. These results confirm the findings of Eagle Picher regarding the effectiveness of gold as a cathode material for Li-$SOCl_2$ cells, and also give support to their recommendation for development of improved gold-carbon black cathodes. JPL is therefore planning to pursue development of these cathodes in the near future.

In order to examine the claims of Electrochem Industries on the merits of the Li-SO_2Cl_2 cell with Cl_2 added to the electrolyte, JPL examined the polarization characteristics of carbon cathodes with this particular solvent and Cl_2 additive. This work was carried out in the same type of laboratory cells as described above but with SO_2Cl_2 + Cl_2 instead of $SOCl_2$. Results of these cathode polarization studies are given in Figure 52. Inspection of these curves reveals two significant points. First, it is noted that the polarization characteristics with pure SO_2Cl_2 + $LiAlCl_4$ are lower than those of pure $SOCl_2$ + $LiAlCl_4$ given in

Figure 51. For example, at a polarization of 0.5 volts the current densities with SO_2Cl_2 and $SOCl_2$ are noted to be 35 mA/cm^2 and 13 mA/cm^2, respectively. Therefore, the current and hence rate capability of the SO_2Cl_2 cell is almost 300% that of the $SOCl_2$ cell under these conditions. Second, it is noted that the polarization characteristics of SO_2Cl_2 + Cl_2 are lower than those of SO_2Cl_2 alone. For example, at a polarization of 0.5 volts (which corresponds to an operating cell potential near 3.3 volts), the former yields a current density of 70 mA/cm^2 while the latter yields a current density of 35 mA/cm^2. On this basis the addition of Cl_2 increases the current and hence rate capability of SO_2Cl_2 cells by about 100% under these conditions. These results verify the exceptionally high rate capability of SO_2Cl_2 cells with Cl_2 additive and show that this improved rate capability is a result of diminished cathode polarization with this solvent combination. Further, since Electrochem Industries has shown that cells with this solvent combination yield high capacities at the high rates, it would appear that these are the most attractive from an energy density-rate point of view.

SECTION 5

SAFETY

Numerous safety incidents have been attributed to lithium batteries and cells, especially those with liquid cathode materials. These incidents have ranged from mild venting (expulsion of internal liquids and gases) to violent explosions and fires.

For this reason, this particular type of lithium battery has not been widely distributed and is used only in applications where safety is not a problem or is of secondary importance. For the same reason, these batteries have not heretofore been employed on spacecraft even though they offer exceptionally high performance. Only when the safety problem with these batteries is completely understood and resolved will they be considered for use in space.

Numerous investigations have been carried out to determine the conditions under which the batteries and cells exhibit catastrophic failure and to examine practical means for avoiding the phenomena. Although these studies have not shown why the cells fail from a fundamental point of view, they have at least provided some guidance to the safe design and operation of these cells. Results of these studies are described herein. In addition, there have been other studies of a more fundamental nature to explain why the cells fail under the observed conditions and to suggest possible new means for preventing failure. Although these fundamental explanations and proposed solutions have not been verified, they appear plausible and worthy of consideration. On this basis some of this more fundamental work is also presented herein.

5.1 EIC FINDINGS

EIC examined the effect of anode-to-cathode material ratio on safety of cells for the condition of reversal (Ref. 2, pp. 255-257). This study was carried out on hermetically sealed "C" size Li-$SOCl_2$ cells. They found that all cathode limited cells (where capacity is limited by the amount of carbon rather than the amount of $SOCl_2$ solvent) did not vent or explode during reversal. In these cases, terminal voltage dropped to near 0 volts at the end of discharge and remained at this level during the period of reversal as shown in Figure 7. The constant voltage was attributed to development of internal short circuits caused by plating of lithium metal on the carbon electrodes during reversal, with resultant growth of metallic paths between the anode and cathode. In the case of anode limited cells (where capacity is limited by the amount of lithium), they did however observe explosions on several occasions. With anode limited cells, operating voltage decreased markedly during reversal below -5 volts as shown in Figure 8. The shift in cell voltage was shown to be attributed to the shift in anode voltage as per reference electrode measurements, and the fluctuations were attributed to periodic contacting of residual lithium metal with the anode current collector. As indicated in Figure 8, the cells were observed to explode during reversal without any prior rise in internal temperature.

5.2 HONEYWELL FINDINGS

Honeywell believes that anode limited cells are safer than cathode limited cells because: a) the Li-S reaction is the most likely one to initiate a thermal runaway, and b) anode limited cells contain very small amounts of Li at the end of discharge so that the Li-S reaction cannot readily take place (Ref. 2, pp. 247-251). The fact that little lithium is left in anode limited cells is demonstrated by the results of storage and discharge tests given in Table I. Therein are shown results of discharge tests on cells containing an equivalent of 220 Ah of lithium at currents near 0.35 amp (0.28 mA/cm^2) after various periods of storage to 90 days at 54°C. Inspection of this table reveals that in all cases the anode efficiency (% of theoretical anode utilization) was greater than 90%. On this basis then, there is very little lithium left to react with the product sulfur and there should be little chance of the Li-S reaction taking place in discharged anode limited cells. Honeywell does not make any mention of the safety of anode limited cells during reversal as does EIC above in Section 5.1. On this basis then, it must be assumed that Honeywell's belief in the superior safety of anode limited cells must be qualified with the condition that the cells will not be reversed.

5.3 GTE FINDINGS

In a prior study GTE attributed the major safety problem of high rate cells to thermal effects that result from internal heating (Ref. 3, pp. 37-42). In particular they suggest that a cell will vent or explode when internal heating from the electrochemical reaction raises cell temperature to the melting point of sulfur, 112.8°C, at which the sulfur, which is a product of reaction, reacts with the lithium. By application of principles of thermodynamics and heat transfer they derived an equation relating internal temperature to operating current and discharge time. With this equation they predicted that a "D" cell will explode in 23 minutes if it is discharged at a constant current of 10 amps. In practice they found that when a "D" cell was discharged at 10 amps, it exploded after 28 minutes which is not far removed from the predicted time. On this basis their analyses appear to be quite well founded. Conclusions that follow from this study are: a) that high rate cells be equipped with fuses to limit current to a safe value, and b) that provision be made to cool the cells to limit internal temperature rise.

In another investigation GTE examined means by which a cell may become over-pressurized and hence pose a safety threat (Ref. 8). The means consisted of thermal (due either to exposure to a high temperature environment or to internal generation of heat) as well as a chemical and electrochemical means (gas producing reactions) and combinations of these two means. Several significant conclusions were drawn from these studies. For a sealed undischarged cell the internal pressure is dependent upon the vapor pressure of $SOCl_2$ and the pressure of the entrapped air (from the assembly operation). At 25°C the total pressure is 1 atm and is comprised of 120 mm of $SOCl_2$ and 640 mm of air. At 79°C, the boiling point of $SOCl_2$, the total pressure is 2 atm and is comprised of about 760 mm of $SOCl_2$ and 760 mm of air. At 180°C, the melting point of lithium, the total pressure is estimated to be about 12 atm (200 psig) and is comprised of 9,333 mm of $SOCl_2$ (based on an extrapolated vapor pressure data) and 973 mm of air. For a discharged cell the total pressure is the sum of the above pressures of $SOCl_2$ and air as well as the pressure of SO_2 which is a product of reaction. The pressure of SO_2 in the gas phase is dependent on the amount present (which can be calculated with known depth of discharge and stoichiometry of the reaction), the solubility of SO_2 in the $SOCl_2$ solvent, and the temperature. The solubility of SO_2 in $SOCl_2$ can be obtained by the approximate relationship given by GTE: $\ln X = \frac{(2.147 + 0.184) \times 10^3}{T} - 0.863$ where X = mol fraction of SO_2 in the solvent and T = temp °C. By calculation it can be shown that appreciable pressures (about 5 atm) can result in discharged cells which are at ambient to moderate temperatures (25 to 80°C) and very high pressures (greater than 20 atm) can result in cells which are at higher temperatures (80 to 180°C). GTE further showed how the amount of heat from the electrochemical reaction can be estimated from cell current, voltage and thermodynamic relations and how these relationships can be used to estimate internal temperature rise. From such analyses they show that only moderate temperatures and pressures should result from operation of the cells at low to moderate rates. They do however, point out that excessively high temperatures and pressures can result in cells that are designed to and are discharged at very high rates (or accidentally short circuited). They point out that the heat generation increases markedly as cell voltage declines below 3.0 volts, and that cathode limited cells exhibit longer periods below 3.0 volts than do anode limited cells near the end of discharge. From this point of view the anode limited cells would appear to be safer. GTE also reported that SO_2 can be produced by the reaction between $SOCl_2$ and sulfur, a product of reaction, by the chemical reaction: $2\ SOCl_2 + 3\ S \rightarrow 2\ S_2Cl_2 + SO_2$. They pointed out that this reaction occurs in the temperature range of 150 to 180°C and that it is catalyzed by the presence of $FeCl_3$. Also, they discuss several highly exothermic reactions that can take place between lithium and $SOCl_2$, S, and SO_2 at the melting point of lithium, 180°C, where the protective film no longer separates the lithium from these species. All of the above findings of GTE have the following implications regarding cell design: a) that the cylindrical cell case design is preferable to the prismatic design from a safety point of view in that the cylindrical design can withstand much higher pressures, b) that there should be an adequate amount of $SOCl_2$ present at the end of discharge to dissolve enough product SO_2 so as to keep its vapor pressure to tolerable levels, c) that a cell should be thermally designed such that internal cell temperature is kept below 180°C for the highest anticipated discharge current, d) that anode limited cells are preferable to cathode limited cells, and e) that iron impurities should be kept to a minimum.

5.4 MALLORY (DURACELL) FINDINGS

Mallory examined the use of low pressure vents for preventing explosions in spiral wound "D" cells during the condition of accidental shorting (Ref. 4, pp. 94-114). In earlier work they found that cells equipped with high pressure vents (500-550 psig) always exploded during intentional short circuiting whereas cells with open vents did not explode under these conditions. By equipping cells with pressure transducers and intentionally shorting them, they found that a) internal pressure increased at a relatively moderate rate to 200 psig and then quite rapidly after 200 psig, and b) an explosion occurred shortly after the rapid rise in pressure beyond 200 psig. On this basis they concluded that cells equipped with low pressure vents near 100 psig should not explode. They confirmed this point by shorting cells with these low pressure vents and found that they did not explode. As an extension of this work they examined the use of the low pressure vents in preventing explosions in cells that were forced into the condition of reversal. In this case they found the cells to explode unexpectedly without much rise in temperature or pressure. They therefore concluded that low pressure vents did not prevent explosions in cells that were forced into the condition of reversal.

Mallory also conducted extensive Differential Thermal Analyses on the starting materials, products, and combinations of these in specially designed glass cells (Ref. 6, pp. 116-162). Materials included in these studies were Li, $SOCl_2$, S, Li_2S, Li_2SO_3, H_2O, carbon cathode, glass paper separator, and nickel tabs. The major conclusions from this study were: a) that there are various combinations of materials that react exothermically and that these reactions can lead to thermal runaway, b) that these reactions occur near the melting point of lithium (179°C) and sometimes below this temperature, c) that the exotherms are larger with H_2O present, d) that safe operation should be insured if internal cell temperature is kept below 100°C, e) that special care should be taken to insure that the cells remain hermetically sealed at all times to eliminate contamination with water vapor which can increase the force of an explosion, and f) that the use of additives and inhibitors to prevent explosions remains an open question. In further studies Mallory conducted differential thermal analyses on complete "D" size cells rather than the components of these cells (Ref. 6, pp. 174-196). Therein they found that fresh undischarged cells did not exhibit any exothermic behavior while being heated, but that partially and fully discharged cells exhibited exothermic reactions at temperatures between 80°C and 100°C. They also found that discharged cells that had been heated once did not exhibit exotherms upon heating a second time. They concluded from these studies that a) discharged cells are unstable, b) the instability is attributed to exothermic chemical reactions from the products listed above, or other products such as sulfur-oxygen polymer compounds, and c) that it may be possible to make a discharged cell safe by subjecting it to a controlled heating cycle.

In another series of experiments, Mallory examined the use of design changes to prevent explosions for the condition of reversal (Ref. 6, pp. 207-215). The changes consisted of: a) use of excess lithium, b) use of lithium on both sides of the current collector rather than on one side, and c) use of multiple tabs rather than only one tab on the cathode current collector. Results indicated that all of these innovations tended to minimize, but did not entirely eliminate the possibility of explosion during reversal. It was speculated that the reason why excess lithium is desirable for the condition of reversal is attributed to the fact that it plates out on the cathode to form dendrites, which, in turn, short out the cell internally and enable it to pass the reversal current.

5.5 ELECTROCHEM INDUSTRIES FINDINGS

Electrochem Industries has found that the addition of BrCl to Li-$SOCl_2$ cells renders them safe under essentially all operating conditions including abusive conditions. To demonstrate this point they showed that "AA", "C", and "D" size Li-$SOCl_2$ cells (containing 1.0-mol $LiAlCl_4$ and 14 mol% BrCl) did not vent or explode, during severe conditions of short circuit, reversal, and charging (Ref. 9). Typical results are shown in Figures 17, 18, and 19. During short circuit, as shown in Figure 17, a "D" cell was shown to operate safely even though it delivered a peak current near 18 amps, and achieved a maximum surface temperature near 125°C. During reversal, as shown in Figure 18, a "D" cell was shown to operate safely while intentionally overdischarged at 5 amps for a period in excess of 100 hrs. Finally a "D" cell was shown to operate safely while being charged at a current of 1 amp for a period of over 100 hrs. as shown in Figure 19. Although Electrochem Industries has no direct proof, they believe the safety of their cells is attributed to the fact that BrCl reacts with product sulfur and thereby eliminates the lithium-sulfur reaction which is believed to cause the venting and explosions.

5.6 NAVAL SURFACE WEAPONS CENTER (NSWC) FINDINGS

NSWC carried out a very comprehensive study on the reactivity of Li-$SOCl_2$ cell starting materials, products of reaction, and combinations of these. The reactivity of these materials was examined by Differential Scanning Calorimetry (Ref. 21). This effort was similar to the differential thermal analyses described by Mallory in Section 5.4 but covered a wider temperature range, included more combinations of materials, and yielded somewhat more quantitative results. Their initial work was focused on the three starting materials of fresh cells, including Li, $SOCl_2$, and $LiAlCl_4$ as well as combinations of these. Results revealed that none of these materials by themselves or in combination with any or all others exhibited any exotherms at temperatures to 335°C (their arbitrary cutoff temperature). Thus it appears that these initially present components of an undischarged cell are safe at temperatures even beyond the melting point of lithium. Next, they examined the reactivity of all of the above starting materials as well as the carbon cathode material and various combinations of these with known or speculated products of reaction. Results of these findings are summarized in Table XIX. Inspection of this table reveals several significant points regarding safety of Li-$SOCl_2$ cells. First, it is found that there is no exothermic reaction between lithium and sulfur in the presence of $SOCl_2$ at temperatures below at least 395°C. This finding tends to contradict one of the current beliefs that a cell can exhibit a thermal runaway when its temperature reaches the melting point of sulfur, 112°C, where the lithium will react violently with the product sulfur. Apparently the $SOCl_2$ maintains a film on the lithium which inhibits this reaction. Second, there are found to be no low temperature exotherms of some suspected reactive products or combinations of these with starting materials. Examples are Li_2S, Li_2SO_4, S_2Cl_2, and LiCl by themselves and in combinations with Li, $SOCl_2$, and $LiAlCl_4$. None of these materials, or combinations thereof, gave exotherms below about 400°C. Third, it was found that addition of Cu to the components of Li-$SOCl_2$ cells resulted in an exotherm at the relatively low temperature of 85°C. This finding tends to cast some doubts about the merits of using copper as an additive to Li-$SOCl_2$ cells for safety reasons as suggested by some workers in the field. From this study it would appear that Cu renders the cells less, rather than more safe. Fourth, the results clearly show that the combination of the carbon black in conjunction with Li and $SOCl_2$ is indeed quite reactive. This combination of materials was found to exhibit a strong exotherm at temperatures as low as 40-50°C. This is perhaps one of the most important findings of this study in that it can explain why Li-$SOCl_2$ cells can explode for the condition of reversal. This is attributed to the fact that when cathode limited cells become overdischarged or reversed, the reaction that takes place at the cathode is the deposition of lithium metal onto the carbon according to the reaction: $Li^+ + E^- \rightarrow Li$. Thus, for the condition of reversal an intimate mixture of lithium, carbon, and $SOCl_2$ solvent (which is usually present in some excess) is formed. This combination of materials, as shown above by NSWC, is highly unstable and can exhibit an exotherm at relatively low temperatures of 40°C to 50°C which can be reached quite readily during reversal.

In the same investigation NSWC examined the exothermicity of lithium nitride, Li_3N, and water, both of which could be introduced into cells during assembly in a dry room. (The Li_3N by the reaction of lithium and nitrogen in the atmosphere, and the water if there were lack of humidity control in the dry room). They found that Li_3N and $SOCl_2$ gave the largest exotherm of any combination of materials that they had examined and at a temperature of 130°C. This finding suggests that it is essential to thoroughly examine all raw lithium material that is used in manufacture of cells to insure that it is not contaminated with Li_3N. They found that water contamination does not appear to have any major effect on the exothermicity of the Li-C-$SOCl_2$ reaction. In fact at a water level of 1% they even found some quenching effect on the reaction. This might suggest that moisture control is not critical from a safety point of view.

Finally NSWC examined the exothermicity of a lithium-boron alloy (51% Li and 49% B). Incentive for this work was based on the speculation that as an alloy, the lithium may be less reactive and hence safer than elemental lithium.

Results did not show less reactivity of the Li-B alloy as compared with pure Li. In almost all cases the exotherm temperatures and magnitudes were comparable for pure Li and the Li-B alloy.

5.7 JPL FINDINGS

JPL has carried out two types of thermal investigations aimed at understanding and controlling the safety problems in Li-$SOCl_2$ cells. The first of these involved the use of a calorimeter to measure the heat generation rates in these cells during operation. The second involved the use of a differential scanning calorimeter (DSC) to measure the ignition temperature of various combinations of cell materials.

The specific objective of the calorimeter studies was to obtain data that would be used to develop a model to predict internal cell temperature as a function of operating current and voltage. With this model it would then be possible to establish maximum currents and operating times so as to keep internal temperature below known or suspected upper limits (such as the melting point of lithium, 179°C or the melting point of sulfur, 12°C). In addition, the model could also be used to show how the operating limits could be extended by either improved external heat transfer or modification of cell design so as to improve its voltage-current characteristics.

The cells employed in the calorimeter studies were of the spiral wound configuration with component dimensions, weights, and specific heats as given in Figure 43.

Two theoretical equations are given in Figure 44 for the heat generation rate in cells as a function of cell current and voltage. The first of these is for the general case of any electrochemical cell and incorporates constants that can be determined experimentally (Ref. 24). The second is for the Li-$SOCl_2$ cell in particular and employs previously determined values of the constants (Ref. 24). It should be pointed out that these equations apply to heat from the electrochemical reaction only and not to heat from any chemical reactions that may occur in the cell.

A comparison of the theoretically predicted heat (as per the equation in Fig. 44 for the Li-$SOCl_2$ cell) and the experimentally determined heat (from the calorimeter measurements) is given in Figures 45 and 46 for two different constant current discharge tests on these cells. In both cases it is noted that the experimentally measured heat is slightly greater than the theoretically measured heat. The difference between these two is attributed to heat from chemical reactions (as opposed to heat from the electrochemical reaction).

By combining terms of the second equation in Figure 44 and then iteratively substituting different values for E_{oc} and computing heat generation rates, it is possible to develop a simple empirical equation that fits the experimental data. The resultant equation is given in Figure 47.

Accuracy of this empirical equation was checked by using it to predict internal temperature rise for discharge under adiabatic conditions and then comparing predicted with experimental values. Results for two such runs on these cells are given in Figures 48 and 49. Inspection of these results reveals that the empirical equation yields a fairly accurate prediction of transient temperature rise (within about 5% for most of the indicated operating regimes). On this basis it would appear that this equation predicts actual heat generation rates of Li-$SOCl_2$ cells quite accurately and can be used with a fair degree of confidence in estimating internal cell temperatures over a range of operating conditions and in any thermal environment.

The objective of the DSC studies was to examine if there are any combinations of cell materials that could engage in exothermic chemical reactions and thereby contribute to the safety problem.

The most significant finding of the DSC studies was that the combination of either Li, $SOCl_2$, and C or Li, SO_2CL_2, and C was found to yield a very strong exothermic reaction at very moderate temperatures in the range of 50 to 55°C. This finding suggests potential safety hazards for cathode limited Li-$SOCl_2$ or Li-SO_2Cl_2 cells for the condition of reversal. This is attributed to the fact that under these conditions lithium is electrodeposited on the carbon cathode and since there is always some solvent present we have one of the two potentially reactive combinations listed above (depending on whether it is an Li-$SOCl_2$ or Li-SO_2Cl_2 cell). In either case, if cell temperature reaches 50°C under these conditions (which is not too unlikely since there is some heat generated under these conditions), the DSC results suggest that there may be an exothermic reaction that can trigger a cell explosion.

In order to test validity of this conclusion a previously discharged, cathode limited, Li-$SOCl_2$ cell was placed in the condition of forced overdischarge or reversal (under safe conditions while installed in a concrete test chamber). Results of this test are given in Figure 50. Therein it is noted that while on reversal at a current of 1.0 amp, cell voltage was stabilized at a value of -0.5 volts and internal temperature increased to 40°C, and then diminished during the course of about 270 minutes. At this point the reversal current was increased to 5.0 amp at which voltage declined to a value near -2.1 volts and temperature began to rise. About 10 minutes thereafter with an internal temperature of about 52°C the cell exploded violently. Although these findings are not conclusive, they do lend some support to the above conclusion that cathode limited cells can explode during reversal for the indicated reasons.

In addition to the above, JPL conducted electrical abusive type tests on commercially available Li-$SOCl_2$ cells in order to examine conditions under which they may vent or explode (Ref. 25). The cells were from Altus Co., Palo Alto, Ca. and were designated as their Model No. 250. These were of the disc configuration and contained disc shaped lithium anode and carbon cathode plates, 1.5-mol $LiAlCl_4$ electrolyte, stainless steel cases, and a ceramic terminal seal. Overall dimensions were 6.35 cm diameter and 0.95 cm thick. Cell weights ranged from 72 to 74 gms and nominal capacity was given as 6 Ah. Aside from the above, no further information was supplied by Altus on these cells.

Two major conclusions were reached in regard to safe operating limits of these cells. First,'it concluded that the cells can be discharged safely at high rates up to the 45 minute rate (or 9 amps). At higher rates of discharge, the cells may vent, but do not explode. Second, it was found that the cells can be overdischarged or reversed extensively at rates up to the 30 hr. rate (or 0.2 amps). At higher rates of overdischarge, the cells can vent, but do not explode. Thus it appears that these particular Li-$SOCl_2$ cells can be operated safely over a relatively wide range of operating conditions. Beyond the indicated operating limits the cells do pose the threat of venting but not severe catastrophic explosions. Although neither of these would be acceptable on a spacecraft, it is at least encouraging to know that Altus has apparently eliminated the severe explosion hazard which is the most pertinent to personnel safety during handling and test of these cells. Altus has not disclosed the details of their cell materials and construction, but from the patent literature it is suggested that they may employ copper as an additive (Ref. 26). In this particular patent it is mentioned that copper improves safety of these cells by supposedly combining with product sulfur so as to avoid the exothermic lithium-sulfur reaction.

SECTION 6

VOLTAGE DELAY

Voltage delay is a term that is used to describe the transient voltage profile of cells at the onset of discharge. The profile consists of an initial sharp drop from the open circuit potential to some lower potential followed by a gradual rise to an operating potential. The time for voltage to recover to some arbitrary level, say 2.0 or 2.5 volts, is referred to as the delay time. Magnitude of the initial voltage drop and recovery time have been shown to increase with storage time and temperature as well as current density. The phenomena are exhibited by lithium, magnesium, calcium, and other types of cells.

Half cell studies have shown that the delay is attributed to the anode rather than the cathode. Further studies have shown that it is caused by a passivating film that encases the anode. In the case of $Li-SOCl_2$ and $Li-SO_2Cl_2$ cells, this film has been shown to consist of LiCl.

The delay problem can be very severe with initial voltage drops of 2.0 volts or greater, and recovery times of several minutes to hours. For this reason the delay phenomena can cause severe voltage regulation problems in the power system that employs this type of battery. This applies especially to aerospace power systems wherein voltage deviations outside of certain limits can cause severe equipment malfunctions.

Numerous investigations have been carried out for the purposes of understanding the delay problem and devising practical means to minimize or eliminate the problem. These have met with a fair degree of success and are described herein.

6.1 EIC FINDINGS

In a prior investigation EIC examined two aspects of the voltage delay problem (Ref. 3, pp. 28-30). First, they found that a special pretreatment of the solvent/electrolyte essentially eliminated the delay problem. The pretreatment consisted of storing $SOCl_2$ + 1.5-mol $LiAlCl_4$ in the presence of lithium foil (∿4 cm^2/ml solution) at elevated temperature, 71°C, for an extended time, 140 hrs. Experimental cells which employed this electrolyte exhibited no delay on discharge at 7 mA/cm^2 after storage for 208 hrs. at 71°C. By comparison, cells stored with untreated electrolyte for 80 hrs. at 71°C exhibited delays up to 24 sec. at the same current density, and cells stored for longer periods of 111 hrs. at the same temperature exhibited delay, up to 72 sec., again at the same current density. Second, EIC examined the effect on voltage delay of alloying the lithium with small amounts of other metals. The alloying metals included Ag, Al, Au, Cd, Cu, Mg, Sn, and Zn in amounts to 10 atomic percent. None of the metals showed any marked effect in reducing delay. Li/Ag and Li/Mg did, however, show some improvement over pure Li, in reducing delay.

6.2 HONEYWELL FINDINGS

Honeywell investigated the effect of SO_2 addition to the electrolyte on voltage delay (Ref. 3, pp. 33-37). They found that addition of SO_2 does indeed minimize the voltage delay problem. Cells containing 5 wt % SO_2 were found to exhibit delays less than 100 ms when discharged at 3.3 mA/cm^2 after storage for one month at 74°C. They also found, however, that addition of larger amounts of SO_2 (10 to 20 wt %) caused a marked reduction in discharge capability. On this basis, they concluded that the optimum level of SO_2 addition was 5 wt %.

6.3 GTE FINDINGS

During the course of the storage life tests on the "D" cells described in Section 6.1, GTE also carried out voltage delay tests. These tests were performed by measuring the transient voltage characteristics of the cells at the onset of discharge over a range of currents and ambient temperatures after various periods of storage over a range of temperatures (Ref. 5, pp. 123-131). Results of the voltage delay tests are given in Tables XIII, XIV, and XV. Table XIII gives the delay times (which is the time from the start of discharge to the time when cell voltage recovers to 2.0 volts) after storage of the cells for one month at room temperature. Table XIV gives the delay times after storage of the cells for one month at 55°C. Table XV gives the delay times after storage of the cells for one month at 72°C. Although reproducibility of the results does not appear to be very good, some general trends are apparent. First, there is noted to be a trend toward increase in delay with storage temperature in the range of room temperature to 55°C. For example, after one month of storage and at a current of 1.0 amp (3.1 mA/cm^2) at 20°C, the delay times for room temperature storage are noted to range from 0.5 to 5.5 sec., while the delay times for 55°C storage are noted to range from 20 to 28.5 sec. Second, there is noted, with a few exceptions, to be a trend toward decreased delay at 72°C storage temperature as compared with 55°C storage temperature. This trend applies only at currents of 500 mA (1.5 mA/cm^2) and below, for it was found that cells stored at 72°C could not be discharged at higher currents. Third, there is noted to be a trend toward increased delay time with decrease in test temperature (in the range of +40°C to -40°C) and with increase in discharge current (in the range of 0.1 amp, 0.3 mA/cm^2, to 4 Amp, 12.4 mA/cm^2).

In this same investigation, GTE examined the effect on voltage delay of partially discharging the cells before storage. This was carried out by discharging the cells at 1.0 amp for 1.0 hr. or 1 Ah which is about 20% of the cell capacity. Voltage delays of these cells after one month of storage are given in Table XVI at different test temperatures and currents. Comparison of these results with those in Tables XIII to XV, reveals that the partial discharge markedly reduces delay. To illustrate this point, it was observed that cells discharged at high currents of 11.2 mA/cm^2 (3.6 amps) exhibited delays of 3.5 min. after storage at 72°C whereas all other cells that were not given the prior discharge were found to passivate severely and be inoperable at currents above 1.6 mA/cm^2 (0.5 amp) when stored at 72°C.

In the same investigation, GTE examined the effects of some electrolyte variables on voltage delay. These included use of ultrapure electrolytes and additives to their regular electrolytes. The ultrapure electrolytes were prepared by using triple distilled $SOCl_2$ and very high purity LiCl and $AlCl_3$. The additives included use of excess chlorine as well as sulfur dioxide (each bubbled into the solution until saturated), iron (in the form of $FeCl_3$ at a level of 200 ppm), and finally, use of excess $AlCl_3$ to the extent of 10% greater than the stoichiometric amount required to form $LiAlCl_4$. Voltage delays were measured with all of these electrolyte variations under the same currents, temperatures, and storage times as indicated above. With one exception, the observed delays with these innovations were found to be the same as with conventional electrolytes. The one exception was use of iron additive which was found to markedly increase delay. Cells to which iron had been added showed significant delays when discharged within a few days of assembly and essentially infinite delays after 30 days storage at temperatures from 25°C to 72°C. Clearly, the amount of iron present in the solvent and electrolytes (especially $AlCl_3$) has to be maintained at a very low level to insure that the cells will not exhibit excessive delays.

In this same investigation, GTE presented additional findings to show that the lithium electrode is solely responsible for the voltage delay (Ref. 5). This was demonstrated by showing that: a) the rate of increase of internal resistance with time for a cell with two lithium electrodes was twice that of a cell with one lithium and one carbon electrode, and b) a cell with only two carbon electrodes showed no change in internal resistance with time. (The implication here is that the increase in internal resistance is associated with a build up of a film of nonconductive LiCl on the surface of the lithium electrode. This film is shown to exist and to increase in thickness with time by Mallory in Section 6.4. Also, the findings of GTE suggest the possibility of using impedance to measure age of a cell. This idea has not been suggested in any of the references cited in this report.)

In another investigation, GTE examined the capability of SO_2 and Ca additives in reducing the delay of Li-$SOCl_2$ and also Li-SO_2Cl_2 cells (Ref. 14, pp. 92-98). These were bobbin type "D" cells with 1.8-mol $LiAlCl_4$ electrolyte and with SO_2 and Ca concentrations of 1.0 mol and 0.5 mol respectively (the latter as $CaAlCl_4$) as described in Section 7.1. Their voltage delay in this case was defined as the cell voltage to recover to 3.0 volts (rather than 2.0 volts as in most other work) at a current density of 1 mA/cm^2 after storage for various periods of time at a temperature of 55°C. Voltage delays of cells with the $SOCl_2$, $SOCl_2$ + Ca, and $SOCl_2$ + SO_2 electrolytes were found to deliver similar voltage delays of from 1 sec. to 1 min. after one month, and from 1 to 2 hrs. after two months. Voltage delays of cells with the SO_2Cl_2 + Ca and SO_2Cl_2 + SO_2 electrolytes were no better than any of the above. The best voltage delays were obtained with SO_2Cl_2 alone (without any of the additives except the $LiAlCl_4$). After 22 weeks of storage, the SO_2Cl_2 cells exhibited delays of only about 10 sec.

In another investigation, GTE examined the use of a clovoborate salt, $Li_2B_{10}Cl_{10}$, in place of the commonly employed $LiAlCl_4$ in order to reduce voltage delay (Ref. 11, pp. 129-132, and Ref. 16). Results of voltage delay measurements on "AA" size cells employing this new electrolyte at a concentration of 0.25 mol and also with the standard $LiAlCl_4$ electrolyte at a concentration of 1.8 mol are given in Table XVIII. After two weeks storage at 55°C, it is noted that the cells with the $Li_2B_{10}Cl_{10}$ exhibited markedly less delays than those with the $LiAlCl_4$. For example, it is noted that cells with $LiAlCl_4$ delayed severely with none of them recovering to 3.0 volts during the 1000 sec. test. Cells containing the $Li_2B_{10}Cl_{10}$, however, were noted to recover to 3.0 volts in less than 22 sec. and to exhibit no delay below 2 volts for more than 1 sec.

6.4 MALLORY (DURACELL) FINDINGS

During the course of the storage life tests on the "D" cells described in Section 7.2, Mallory also carried voltage delay tests. These tests were performed by measuring the transient voltage characteristics of the cells at the onset of discharge over a range of currents and ambient temperatures after various periods of storage over a range of temperatures (Ref. 6, pp. 27-52). For fresh cells (less than one week old) they found no delay when discharged at 25°C and at currents from 0.25 to 3.0 amp (0.55 to 6.60 mA/cm^2). When the fresh cells were discharged at low temperatures, however, they did observe some delays, especially at high currents. For example at -54°C, a fresh cell was found to exhibit a delay of 115 sec. at a current of 0.5 amp (1.1 mA/cm^2). At the same temperature and at 3.0 amp, the voltage of a fresh cell was found to remain below 0 volts for more than 50 sec. and to reach 2.0 volts after more than 1000 sec. For aged cells, Mallory found the delays to increase with duration and temperature of storage as well as discharge current. Some typical results that display these trends are given in Table XXI. Inspection of the results of this table reveal that cells do exhibit appreciable delays when comprised of the components described by Mallory in Section 6.2. Further the results establish the trend of increased delay with storage time and temperature as well as discharge current and temperature as indicated above for this type of cell.

In this same investigation, Mallory next examined what they labeled as an "intuitive empirical approach" to minimize the voltage delay with this cell (Ref. 6, pp. 56-58). This consisted of subjecting the cells to a short partial discharge before measuring their delays. The extent of this discharge was from about 0.3 to 0.5 Ah which is a small fraction of the nominal cell capacity of 12 Ah. Results indicated that this technique is indeed effective in minimizing the delay problem. To illustrate this point they showed that a cell, when given such a preliminary discharge, exhibited no delay after storage for 6 months at 72°C and discharged at 0.25 amp at -30°C. At the same storage temperature and discharge temperature and at higher currents (1 to 3 amp) and shorter periods of time (1 to 3 mo.) the cells did exhibit finite delay times. The magnitude of the delay times for these cells were, however, much less than for cells which had not been partially discharged and operated under the same conditions.

Finally, in this same investigation, Mallory examined the effects of some variations of the electrolyte on the voltage delay problem (Ref. 6, pp. 84-92). These consisted of: a) concentration of $LiAlCl_4$ electrolyte, b) addition of S_2Cl_2, and c) addition of SO_2. They found a trend toward reduction in delay with decrease in electrolyte concentration from 1.8 mol to 0.5 mol, but a somewhat longer delay with 0.25-mol $LiAlCl_4$. They suggested an optimum concentration near 0.5-mol $LiAlCl_4$ for minimum delay. They found that addition of 6% S_2Cl_2 did not have any significant effect on delay. The effect of SO_2 addition could not be established because of the leakage problems that it caused during elevated temperature storage.

In another investigation, Mallory employed Scanning Electron Microscopy (SEM) and energy dispersive analysis of x-rays (EDAX) to study the nature of the film on the lithium electrode in a Li-$SOCl_2$ cell environment and the rate of growth of this film during storage over a range of elevated temperatures (Ref. 10). In addition, Mallory measured voltage delay characteristics of lithium electrodes and correlated these delay characteristics with the thickness of the film. The work was carried out on samples of lithium in purified $SOCl_2$ solvent with purified 1.8-mol $LiAlCl_4$ electrolyte. Their major conclusions were: a) that the film is comprised of LiCl, b) that the thickness of the film increases with increasing time and temperature on storage, c) that the voltage delay also increases with increasing time and temperature on storage, and finally d) that there is a direct correlation between film thickness and voltage delay. Evidence to support these conclusions is given in Table XXII which gives the film thickness and voltage delay of samples of lithium stored for increasing periods of time at 55°C. Therein, it is noted that as storage time increases from 154 to 590 hrs., film thickness increases from 4.5 to 45 μM, and voltage delay correspondingly increases from < 1 sec to 30 sec. Another significant finding from this study was that film growth was found to be minimal in pure $SOCl_2$ without $LiAlCl_4$. It was therefore concluded that $LiAlCl_4$ contributes to film growth and voltage delay. On this basis it may be well to search for electrolytes other than $LiAlCl_4$ in order to resolve the voltage delay problem.

6.5 SAFT FINDINGS

In a prior investigation, Saft Co., (from France) reported on the beneficial effects of a new electrolyte, $Li_2Al_2Cl_6O$, in reducing voltage delay (Ref. 7, pp. 348-355). In tests with bobbin cells they found appreciable delays, as observed elsewhere, with conventional $LiAlCl_4$ electrolyte. With 0.5-mol $Li_2Al_2Cl_6O$

however, they found no delay at a current density of 4.8 mA/cm^2 after storage for a period of one month at 70°C. They did not offer an explicit explanation as to why this electrolyte eliminated delay, but merely suggested that the nature of the anion influences the structure of the anodic film, which in turn controls delay.

6.6 UNION CARBIDE FINDINGS

In a U.S. Patent, Union Carbide described effectiveness of a polymer anode film in reducing the delay of $Li\text{-}SOCl_2$ and $Li\text{-}SO_2Cl_2$ cells (Ref. 18). The film is actually a copolymer comprised of 86% vinyl chloride and 14% vinyl acetate. This copolymer is available commercially from Union Carbide and is designated by them as "VYHH". The film is applied by dissolving the copolymer in $SOCl_2$ solvent and then immersing the lithium anode in this solution for about 1 minute. Voltage delays of "C" $Li\text{-}SO_2Cl_2$ cells containing the coated anodes were found to exhibit delays of 1 sec. or less across 20 ohm loads after storage for one month at room temperature. By comparison, the same type of cells without the polymer coated anodes were found to exhibit delays up to 18 sec. under the same conditions.

In another U.S. Patent, Union Carbide described several additives to the electrolyte that are also effective in reducing voltage delay in $Li\text{-}SOCl_2$ and $Li\text{-}SO_2Cl_2$ cells. These are sulfur containing compounds and include elemental sulfur, lithium sulfides such as Li_2S, and lithium halides such as S_2Cl_2 and SCl_2. They cited several examples wherein it was shown that use of these additives at levels from about 5 to 10% by weight of the electrolyte minimized delays to the same order of magnitude as with the polymer film above.

6.7 ALTUS FINDINGS

In a U.S. Patent, Altus Corp., described a novel organic anode coating that was shown to markedly reduce voltage delay in Li-$SOCl_2$ cells. The coating is either methyl or ethyl cyanoacrylate. These are applied by dipping the lithium anodes in either of these organic liquids, assembling a cell with them, and then curing the cell for 12 hrs. at 71°C. Effectiveness of the coating was shown by measuring delays at 5 mA/cm^2 of button cells after various periods of storage at elevated temperature. After storage times of 1, 3, 8, and 21 days at 71°C, cells with the 10 coatings were found to exhibit delays of less than 1 sec., 5 sec., and 20 sec., respectively. By comparison, cells without the coatings were found to exhibit infinite delays (never recovered) under any of the above conditions.

6.8 JPL FINDINGS

In order to substantiate some of the voltage delay claims, JPL conducted its own assessment of the $Li_2B_{10}Cl_{10}$ electrolyte described in Section 6.5 and the vinyl chloride-vinyl acetate film described in Section 6.6 (Ref. 17). Results, shown in Figure 42, revealed that the $Li_2B_{10}Cl_{10}$ electrolyte and the polymer film are indeed effective in reducing delay. After 3 days of storage at 72°C a Li-$SOCl_2$ cell with $Li_2B_{10}Cl_{10}$ electrolyte was found to exhibit a delay of less than 2 sec. at a current density of 10 mA/cm^2. Under the same conditions a cell with the vinyl chloride-vinyl acetate anode film was also found to exhibit a delay of less than 2 sec. By comparison, a Li-$SOCl_2$ cell with conventional $LiAlCl_4$ electrolyte and without the polymer film was found to exhibit a delay of 15 sec. under identical conditions to the above. It is well to point out here that all of the above delay data was obtained on highly purified solvents and electrolytes. Delay times of cells containing improperly purified materials were found to be in the range of 1 to 2 minutes under the same conditions as shown in Figure 42. These results establish that material purification is an essential prerequisite to obtain minimal delay times.

SECTION 7

STORAGE LIFE

Very limited information is available on the storage life capabilities and factors that influence this characteristic of Li-$SOCl_2$ and Li-SO_2Cl_2 cells. This lack of information is attributed to two causes. First, these cells are relatively new and there has been insufficient time to generate real time, long term storage life data. Initial exploratory work on these cells began in the early 1970's. Limited numbers of experimental and demonstration type cells were made and evaluated (including a limited amount of accelerated life tests) beginning in the mid 1970's. Only within the past few years have vendors frozen specific designs of these cells and begun fabrication and evaluation of these (including the initiation of long term storage tests). The second reason for lack of information on storage life is that most of the prior work has been focused primarily on improving safety and performance (including energy density, rate capability, and voltage delay) of these cells. The reason for placing initial emphasis in these areas, especially safety, is that if the cells cannot be shown to operate safely and simultaneously deliver their inherent high performance capability, then it would not be worth pursuing the development of these cells to replace existing primary cells such as zinc-carbon, or zinc-silver oxide cells.

The information that is available on storage life of these cells may be divided into two categories. The first of these may be classified as compatibility type data. This refers to stability of various materials of construction in the very corrosive environment of the lithium-sulfur oxyhalide cells. Results in this category were sometimes obtained by simple corrosion (weight loss) measurements on candidate materials after storage in the solvents at elevated temperature. In other cases the results were obtained by electrochemical techniques involving the measurement of currents between test materials and counter electrodes held at the potential of lithium. The second category of information consists of accelerated life test data on some of the earlier cell designs. These usually consisted of measuring capacity loss rates of cells while on storage at elevated temperature (at which self discharge rates are assumed to be accelerated) and then projecting loss rates and hence capacity of cells stored for given periods of time at ambient temperature. Another accelerated test technique has been developed during the past few years and has been applied to several types of cells including Li-$SOCl_2$ and Li-SO_2Cl_2 cells. The technique involves use of a microcalorimeter to measure the small amount of heat generated in a cell while on stand. The heat generation is attributed to the self discharge reaction so that a quantitative measure of the heat generation can be converted to an equivalent self discharge current. By simply measuring heat generation rate, it is then possible to calculate electrochemical loss rate and residual capacity after any given period of time. Both of these techniques have been employed to project life of some of the earlier designs as mentioned above and some of the newer designs with materials that are intended to improve safety and voltage delay.

The results of the compatibility as well as the accelerated life tests have provided at least some preliminary guidelines with which to establish storage life and factors that influence life of these cells. The most pertinent of their findings are presented herein.

Finally, it is well to mention a few points regarding the merits and uncertainties of the above accelerated tests, as well as some planned JPL work in this area. The merits of accelerated testing are quite well known, i.e., they permit rapid determination of life of the cells and provide a convenient method for rapidly screening candidate new materials and design changes with regard to their effect on life. The major uncertainty of the tests is also well known, i.e., that the mechanism for capacity loss may change with increase in the accelerating factor (temperature) and hence the test results may lead to faulty conclusions. In order to help resolve this uncertainty, JPL is planning studies aimed at establishing the temperature limit below which the mechanism does not change and hence below which the tests must be carried out to yield valid projections. This work will involve use of microcalorimetry as described herein.

7.1 GTE FINDINGS

In a prior study GTE pointed out two possible causes for loss of capacity during storage (Ref. 3, pp 37-42). The first of these is chemical reaction between the lithium anode and $SOCl_2$ solvent. They indicate that the reaction takes place quite rapidly during the very early stages of life and that the process slows to an insignificant rate shortly thereafter. They were not concerned with methods for impeding the reaction in that it consumes only a small and insignificant fraction of the total amount of lithium. The second cause is attributed to electrochemical reduction of $SOCl_2$ on the surface of the anode current collector or cell case which is in contact with lithium, i.e., a short circuited local cell. One factor that was found to influence this second mode of capacity loss is material of construction of the case and collector. Figure 20 gives the current density as a function of time for two different case materials in contact with lithium and $SOCl_2$ at 72°C. The current density, which is a measure of the self discharge rate, is noted to drop sharply after the first few hours for both 304 stainless and cold rolled steel but to level off at a higher current for the stainless. Therefore, the cold rolled steel appears less reactive and should yield better shelf life than the stainless steel. Another factor that is claimed to affect this second mode of capacity loss is electrode geometry (but no details regarding geometric effects are given in this reference).

In a final report from another investigation GTE examined the shelf life of spiral wound "D" cells stored at elevated temperatures (Ref. 5, pp 32-123). These employed lithium-nickel Exmet anodes and Shawinigan Black/Teflon-nickel Exmet cathodes with dimensions given for "Design B" in Table V. Electrolyte was 1.8-mol $LiAlCl_4$ made from oven dried LiCl and sublimed $AlCl_3$. Separator was comprised of .010-in.- (10 mil) thick non-woven glass material. The components were installed and hermetically sealed in .020 (20 mil) thick cold rolled steel cans that were plated with 3 to 4 microns of nickel on their outsides. Figure 21 gives the output of cells of this type as a function of discharge current and temperature to a 2.0 volt cutoff voltage after one month of storage at room temperature.
Table IX gives the corresponding output of these cells after storage for one month at 55°C. Results revealed not much change in output for cells stored at 55°C as compared with cells stored at room temperature at low discharge currents of 0.1 to 0.2 amps (0.3 to 0.6 mA/cm^2). At higher currents the cells stored at 55°C generally gave somewhat lower output than those stored at room temperature.
Table X gives the corresponding output of these cells after storage for one month at 72°C. Results revealed that capacity of the cells had degraded appreciably even at currents of 0.2 amp (0.6 mA/cm^2) and below. Cells discharged at currents of 0.5 amp (1.6 mA/cm^2) and above were found to deliver essentially no capacity in that their voltages dropped rapidly below 2.0 volts at the start of discharge and declined even further during the course of discharge. A notable exception to the above was for cells discharged at 40°C and at currents of 0.2 amp (0.6 mA/cm^2) and below. Capacities of at least some of these cells were noted to be essentially the same as capacities of cells stored for one month at room temperature and discharged at 40°C. These latter results prove that the lithium remains intact during the course of storage. The loss in capacity during storage of these cells cannot therefore be attributed to consumption of lithium. Rather, the loss must

be attributed to other phenomena such as a passivating film on the anode, loss of electrical contact between the lithium and its nickel current collector or loss of contact between the carbon black and its nickel current collector, or possibly some degradation of the solvent and electrolyte. Whether the phenomena responsible for capacity loss are one of the above or some other phenomena, it is well to point out, however, that their effects can be nullified by raising the cell temperature to 40°C. Practical significance of this finding is that it may be worthwhile to investigate heating of aged cells prior to discharge.

As mentioned in Section 6.3, GTE, in this same investigation, examined the use of Cl_2 additive to Li-$SOCl_2$ cells to reduce voltage delay. They found that addition of Cl_2 did not diminish delay but that it did cause severe and rapid loss of capacity. The extent of the loss was much more than could be accounted for by reaction of the known amount of Cl_2 with the lithium anode, i.e., $2Li + Cl_2 \rightarrow 2LiCl$. On this basis it would appear that Cl_2 is very detrimental from a life point of view. Further, since Cl_2 is known to be a contaminant in industrial grade $SOCl_2$, provision should be made to remove it in purifying the $SOCl_2$ for use in Li-$SOCl_2$ cells.

As part of another investigation GTE examined the capacity retention of "DD" size cells as a function of a) anode vs cathode limited design, b) $SOCl_2$ vs SO_2Cl_2, and c) additives used to diminish voltage delay (Ref. 14, pp 2-6). These cells were of the bobbin type configuration and employed highly purified solvents, electrolytes, and additives. They were discharged at a current density of 1 mA/cm^2 for the capacity retention tests. Figures 31 and 32 give the capacity retention of anode and cathode limited $SOCl_2$ cells with 1.8-mol $LiAlCl_4$ at both 25°C and 55°C. Inspection of Figure 31 reveals that the anode limited cells lose less than 5% of their capacity after 35 weeks at 25°C. Based on microcalorimetric studies GTE believes this loss rate at 25°C is not linear with time but diminishes markedly after this time. Therefore, the storage life of these cells is projected to be at least several years at 25°C. At 55°C the cells are noted to lose 50% of their capacity after about 22 weeks of storage. Inspection of Figure 32 reveals that the cathode limited cells also lose about 5% of their capacity after 35 weeks of storage at 25°C and 50% of their capacity after only 8 weeks of storage at 55°C. Since a five fold excess of lithium was used in the cathode limited cells, it is highly unlikely that the capacity loss can be attributed to lithium corrosion. Rather, the mechanism is attributed to recrystallization of LiCl in the cathode pores from the surface of the lithium anode. It is known that a LiCl film grows on the surface of the anode at elevated temperature due to recrystallization and crystal growth. The $LiAlCl_4$ salt provides the medium for this process. Therefore, LiCl is speculated to be dissolving at the anode and depositing at the cathode so as to deactivate the cathode surface. This phenomena would be expected to have a more pronounced effect on capacity loss of cathode than anode limited cells because of the lower initial surface area of the former. The above results indicate that this is the case and give some support to the hypothesis. The results are also in agreement with the earlier studies by GTE above which concluded that the capacity loss cannot be primarily attributed to lithium corrosion.

The effect of some voltage delay additives on capacity retention at 55°C of bobbin type "D" cells employing both $SOCl_2$ and SO_2Cl_2 depolarizers is given in Figure 33. In all cases the electrolyte was 1.8-mol $LiAlCl_4$ and the cells were anode limited. The SO_2 additive was incorporated by adding SO_2 directly to the solvent at a concentration level of 1.0 mol. The Ca additive was incorporated by adding $Ca(AlCl_4)$ to the solvent at a concentration level of 0.5 mol. Inspection of Figure 33 reveals that both the SO_2 and Ca additives have an adverse effect on capacity retention. Also, it is noteworthy to point out that the best capacity retention is obtained with SO_2Cl_2 + 1.8-mol $LiAlCl_4$ without any additives. Capacity of cells with this solvent is noted to drop about 20% during the first week at 55°C and then remain essentially constant for times up to 22 weeks. This finding is somewhat surprising in that it was previously believed that SO_2Cl_2 decomposes readily into SO_2 and CL_2 and that the Cl_2 would react rapidly with the lithium as has been shown to be the case when the Cl_2 is added to $SOCl_2$. The results then imply either that there is not much decomposition at SO_2Cl_2 or that the lithium film in SO_2Cl_2 is more resistive to Cl_2 penetration than it is in $SOCl_2$.

GTE carried out limited storage life tests on cells that employed the new clovoborate electrolyte, $Li_2B_{10}Cl_{10}$, which is effective in reducing voltage delay (Ref. 11, pp 129-132). The tests were carried out on "AA" size bobbin cells employing 0.25-mol $Li_2B_{10}Cl_{10}$ electrolyte and, for comparison, conventional 1.8-mol $LiAlCl_4$ electrolyte. The cells were discharged in the fresh condition (3 days after assembly) and after storage for 2 weeks at 55°C. Results, given in Table XVIII, indicate that storage life of cells with the new clovoborate electrolyte is comparable to, if not slightly longer than, storage life of cells with the conventional $LiAlCl_4$ electrolyte. For example, the average capacity of fresh and aged cells employing $LiAlCl_4$ was found to be 436 and 342 mA-h, respectively (or a loss of 22% during storage). By comparison the capacity of fresh and aged cells employing $Li_2B_{10}Cl_{10}$ was found to be 440 and 391 mA-h, respectively (or a loss of 11% during storage). Thus, it appears that this new electrolyte does not diminish and even appears to slightly improve shelf life.

Electrolytes containing a ratio of LiCl to $AlCl_3$ less than one (those with an excess of $AlCl_3$ over the stoichiometric one-to-one ratio required for $LiAlCl_4$) are preferred for reserve type cells in that they impart higher capacities and rate capabilities than conventional $LiAlCl_4$. Explanation for the improved performance of cells containing $AlCl_3$ rich electrolytes is that the excess $AlCl_3$

reacts with the product LiCl and prevents the latter from precipitating in the pores of the cathode (which has been shown to limit cathode current and capacity). GTE cautions that such electrolytes cannot be used with active cells because the excess $AlCl_3$ will react destructively with the lithium anode (Ref. 2, pp 262-265). Although it was not stated here, this implies that the $AlCl_3$ reacts with the LiCl film on the anode. The film then continues to grow via reaction of Li and $SOCl_2$ and is simultaneously consumed by $AlCl_3$ until the excess of $AlCl_3$ (over the stoichiometric amount) is depleted and then there is no further reaction. On this basis it would then appear that electrolytes containing a LiCl to $AlCl_3$ ratio of one-to-one or greater would be preferable from a life point of view. If this is not the case, then the cells will suffer a loss in anode capacity equivalent to the amount of excess $AlCl_3$ during storage. If the cells are anode limited, then this will be reflected in a direct loss of cell capacity.

7.2 MALLORY (DURACELL) FINDINGS

In a final report of a prior investigation Mallory presented results of material compatibility studies (Ref. 6, pp 4-5). Two types of materials were examined and consisted of: a) metallic materials for use as the cell case, current collectors, etc., and b) insulating materials for use as separators, insulators, sealants, etc. Findings regarding the metallic materials are given in Table XI. Inspection of this table reveals several types of metals, including nickel as well as stainless steel types 304 and 316, that are stable in $SOCl_2$ and are therefore candidate materials of construction for long life cells. Findings regarding the insulating materials are given in Table XII. Inspection of this table reveals relatively few types of insulating materials that are stable in $SOCl_2$ and are therefore candidate materials for long life cells. These insulating materials include glass, Teflon, and Kel-F.

In the same report Mallory presented results of an extensive shelf life test on hermetically sealed "D" size Li-$SOCl_2$ cells (Ref. 6, pp 27-52). These were of the spiral wound configuration with anode and cathode length, width, and thicknesses of 20 in. x 1.75 in. x 0.017 in. and 20 in. x 1.5 in. x 0.019 in., respectively. Nickel was employed as material of construction for both case and cover. Cathode composition was 90% Shawinigan carbon black and 10% Teflon. Electrolyte composition was 1.0-mol $LiAlCl_4$ prepared by fusing pre-dried LiCl with iron and water free (Fluka) $AlCl_3$. Weight of $SOCl_2$ + $AlCl_4$ was 45 gm/cell and weight of carbon was 5.1 g/cell. The cells were stored at temperatures from 25°C to 72°C for periods of time from 1 week to 2 years, and were then discharged at currents from 0.25 amp to 3.0 amp (0.55 to 6.6 mA/cm^2) at temperatures of 25°C and -30°C. Results of this investigation revealed very little capacity loss of the cells for the indicated range of storage times and temperatures. For example, fresh cells were found to deliver outputs near 12 Ah and 8 Ah at currents of 0.25 A and 3.0 A, respectively, at 25°C. After 3 months at 72°C the cells were found to deliver outputs near 10 Ah and 5 Ah at the corresponding currents and temperature. After 6 months at 55°C the cells delivered outputs near 11 Ah and 6 Ah at the corresponding currents and temperature. After 1 year at 45°C the cells delivered outputs near 10 Ah and 6 Ah at the corresponding currents and temperature. Finally, after 2 years at 25°C a cell was found to deliver an output near 6 Ah at 3.0 amp (6.6 mA/cm^2) at 25°C (the data for the output at 0.25 amp (0.55 mA/cm^2) was lost). When the aged cells were discharged at -30°C the cells were found to deliver diminished outputs, as compared with the above, but about the same outputs as fresh cells discharged at -30°C. The major conclusion that can be drawn from these results is that Li-$SOCl_2$ cells, made with the materials and configuration described above, exhibit relatively good storage lives. At storage temperatures up to 45°C they lose no more than about 20% of their capacity for periods up to 2 years. Even at the relatively high storage temperature of 72°C they lose no more than about 25% of their capacity after 3 months. It was found, however, that lengthy storage of the cells, especially at elevated temperatures, did have a pronounced effect on voltage delay. These phenomena are discussed in Section 6.4.

The cells employed in these tests yielded the lowest capacity loss rates of all Li-$SOCl_2$ cells. Results may be used to derive an expression for capacity loss rate under what might be classified as best case conditions. Capacity loss rates at 72°C and 45°C are approximately 8% and 1% per month, respectively. These results are then substituted in and used to determine the constants in an Arrhenius equation of the form: $\ln R = \frac{a}{T} + b$ (where R = loss rate %/month, T = absolute temperature °K, and "a" and "b" are the constants). The resultant equation is $\ln R = \frac{-1.03 \times 10^4}{T} + 32.23$. Employing this equation one finds the loss rate at 25°C is 0.06%/month (which is in fair agreement with the real time test at ambient temperature).

7.3 ELECTROCHEM INDUSTRIES FINDINGS

Electrochem Industries conducted limited storage life tests on AA-size Li-$SOCl_2$ cells with BrCl additive to the electrolyte as described in Section 5.5 (Ref. 9). Results of these tests are given in Figure 22. Curves A and B compare the discharge characteristics of a fresh cell and one stored 3 months at 72°C. Results revealed very little loss in capacity for the cell stored at elevated temperature but somewhat reduced voltage for this cell as compared with the fresh cell. Curves C and D compare the discharge characteristics of these cells across 180 ohm loads (0.75 mA/cm^2) for one stored 3 months at 72°C and for a fresh one. Results revealed essentially the same capacity and voltage levels for the cells at this current density. Finally, curve E gives the discharge characteristics of a cell across a 180 ohm load (0.75 mA/cm^2) after 15 months storage at room temperature. Results revealed essentially the same capacity and voltage characteristics of this cell as compared with a fresh cell at this current density. Comparison of these results with those of GTE and Mallory in the preceding Sections 7.1 and 7.2 reveals that addition of BrCl to $LiSOCl_2$ cells does not degrade and may even improve their storage life capabilities to a limited degree.

Electrochem Industries conducted microcalorimetric studies on "AA" size versions of their Li-SO_2Cl_2 (with Cl_2) cells described in Section 4.4 (Ref. 11). Results of this investigation are summarized in Figure 25. Inspection of this figure reveals that the heat dissipation on stand at 37°C decreases sharply during the first 2 months after fabrication and that the heat dissipation for Li-SO_2Cl_2 cells without Cl_2 is higher than that for Li-SO_2Cl_2 cells with Cl_2. With the assumption that heat dissipation is directly proportional to self discharge, the results indicate a capacity loss of 14% during the first year of storage and a projected 5% loss during the second year for Li-SO_2Cl_2 cells with Cl_2 at 37°C. The loss rates should be less at ambient temperatures.

Finally, Electrochem Industries carried out real time storage life tests on the "AA" size Li-SO_2Cl_2 (with Cl_2) cells described above (Ref. 11). Results shown in Figure 26 indicated a loss of 8% of capacity after one year storage at ambient temperature. These results give some degree of support to the life projections based on the calorimetric studies above. It should be noted, however, that although capacity loss of these cells is very small, they do exhibit lower voltages after storage, especially at the higher currents. On this basis it appears that the $LiSO_2Cl_2$ (with Cl_2) cells exhibit some loss in rate capability with time as do the conventional Li-$SOCl_2$ cells.

7.4 JPL FINDINGS

In 1979 JPL carried out an evaluation of some small button type Li-$SOCl_2$ cells from a new vendor in the field (Ref. 22). Details of construction of these cells were not disclosed. They were, however, known to contain a disc shape lithium anode and carbon cathode, $SOCl_2$ solvent, $LiAlCl_4$ electrolyte, and steel cases. These had a diameter of 1 inch and thickness of 1/8 inch. Nominal capacity of the cells was given as 200 mAh at a current of 10 mA.

The evaluation included a limited amount of accelerated shelf life testing. This was carried out by storing groups of cells at elevated temperatures from 40°C to 100°C and then periodically removing them to measure residual capacity. It was then planned to prepare an Arrhenius plot of "log of capacity loss rate vs 1/temp" so as to project life at ambient temperature. Reproducibility of results was very poor and it was not possible to obtain a meaningful Arrhenius plot. This was attributed to nonuniformity of the cells supplied by the vendor. All the cells stored at 80°C and 100°C vented shortly after being placed in ovens at these temperatures. This indicated that the upper storage temperature limit is less than 80°C for this type of cell. Cells stored at 40°C and 60°C exhibited varying degrees of capacity loss. Those stored at 60°C generally lost more capacity than those stored at 40°C. After 224 days a few cells stored at 40°C delivered capacities near 125 mAh. This corresponds to a loss of 60%/yr at 40°C. By comparison, cells stored at 60°C exhibited capacity loss of about 600%/yr based on shorter periods of storage of 32 days. The capacity loss rates of these cells is much higher than the loss rates of Li-$SOCl_2$ cells from other vendors. The results are not believed to reflect the true shelf life capabilities of the Li-$SOCl_2$ system. Rather, the results suggest a batch of faulty cells from this vendor. This possibility is most likely the case considering the fact that these cells were from one of the first lots of cells that were made by this new vendor.

Currently JPL is exploring an improved method for carrying out accelerated life tests of lithium cells. This involves use of microcalorimetry to measure rate of heat generation on stand which in turn is an indirect measure of the self discharge rate. Experiments are planned to measure heat generation rate on stand over a range of elevated temperatures. The resultant data will then be plotted in the form of an Arrhenius plot of "log Rate vs 1/T." We anticipate a linear relationship up to a certain temperature followed by an inflection in the curve at this point. This will signify that the mechanism of self discharge has changed at temperatures above the inflection point. On this basis we will have established an upper temperature limit for the conduct of accelerated tests. This in turn should provide a more reliable and nondestructive method for accelerated testing of cells, i.e., by obtaining and reducing microcalorimetric data on cells below this upper temperature limit. The technique will then be employed to screen new materials and designs intended to improve life.

Some additional findings that are pertinent to storage life were obtained by Eagle Picher in a prior JPL-sponsored study (Ref. 27). This involved corrosion studies on candidate metals that were being screened as possible substitutes for, or additives to, carbon black in order to improve rate capability (as described in Section 4.6). The corrosion rates of these metals, in terms of mils/yr, were determined by weight loss measurements on samples stored in $SOCl_2$ at elevated temperature, 120°F. Results are given in Table XX. Inspection of this table reveals that there are two metals, niobium and silver, that are apparently completely stable in this environment. Further, it is noted that there are several noble metals, including gold, platinum, and tungsten, that appear to be quite stable with relatively low corrosion rates of less than 2 mils/yr. Finally, it is noted that there are two metals, consisting of copper and aluminum, that are quite unstable with corrosion rates of about 50 to 100 mils/yr. These results are useful in selecting stable new materials of construction for long life cells.

SECTION 8

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Table I. Storage Evaluation Program Results - Anode Limited Cells

	UNITS	CONTROLS				54.44°C STORAGE											
						30 DAY STORAGE				60 DAY STORAGE				90 DAY STORAGE			
CHAMBER NUMBER		W10				W1				W2				W4			
CELL NUMBER		A18	A19	A20	AVG	A1	A2	A3	AVG	A5	A6	A7	AVG	A8	A9	A10	AVG
AVERAGE STORAGE TEMPERATURE	°C	N/A →				132 →				128 →				130 →			
LAST OCV AT DISCHARGE TEMP (1)	VOLTS	3.614	3.655	3.654	3.641	3.707	3.713	3.713	3.711	3.703	3.716	3.716	3.712	3.739	3.739	3.738	3.739
RISE TIME TO 3.111 VOLTS	MIN	N/A →				0	0	0	0	0	0	0	0	0	0	0	0
AVERAGE DISCHARGE TEMP	°C	35.55 →				29.44 →				24.44 →				23.33 →			
AVERAGE VOLTAGE (2)	VOLTS	3.580 →				3.565 →				3.527	3.525	3.529	3.527	3.524	3.525	3.518	3.522
AVERAGE LOAD (3)	AMPS	0.358 →				0.357 →				0.353 →				0.352	0.353	0.352	0.352
TIME TO CUTOFF	HRS	581.0	578.4	578.7	579.4	575 (4) →				583	584	569	578.6	585	578	590	584
CAPACITY DELIVERED	Ah	208.0	207.1	207.2	207.4	205.0 →				205.8	206.1	200.9	204.2	205.9	204.0	207.7	205.9
ANODE EFFICIENCY	%	93.2	92.8	92.8	92.9	91.8 →				92.2	92.3	90.0	91.5	92.1	91.4	93.1	92.2
RETENTION VS CONTROL (AVG)	%	N/A →				98.9 →				--	--	--	98.3	--	--	--	99.1

NOTES
(1) OCV JUST PRIOR TO LOADING
(2) ALL DATA TAKEN TO A 3.111 VOLT CUTOFF
(3) ALL CELLS DISCHARGED INTO A 10 OHM LOAD
(4) ESTIMATED CUTOFF TIME – RECORDER INADVERTENTLY REMOVED FROM THESE THREE CHANNELS PRIOR TO CUTOFF
— ALL CELLS HAVE A NOMINAL ELECTRODE AREA OF 1294 cm^2, NOMINAL CURRENT DENSITY IS 0.28 mA/cm^2
— ALL CELLS HAVE A NOMINAL 0.159 INCH THICK CATHODE, NOMINAL CATHODE MIX WEIGHT OF 112.0 GRAMS WITH A NOMINAL BULK DENSITY OF 0.439 g/cm^3

Table II. Cathode Evaluation Program Performance Summary

	DISCHARGE TEMPERATURE								
	4.44°C			23.89°C			43.33°C		
THICKNESS cm	AVG VOLTS	CAP (Ah)	EFF (Ah/g)	AVG VOLTS	CAP (Ah)	EFF (Ah/g)	AVG VOLTS	CAP (Ah)	EFF (Ah/g)
0.4572	3.508	230.5	1.975	3.545	264.9	2.273	3.567	250.8	2.151
0.8128	3.448	186.5	1.553	3.530	248.4	2.068	3.551	230.4	1.925
1.0668	3.447	150.9	1.306	3.480	194.9	1.694	3.536	239.8	2.079
1.3208	3.425	96.4	1.001	3.469	115.9	1.195	3.503	128.3	1.330
1.6002	3.451	112.9	0.971	3.466	135.5	1.165	3.508	156.2	1.354

Table III. Typical Computer Printout for D Size Cell

L_1 (CM)	L_2 (CM)	L_3 (CM)	L_4 (CM)	T_1 (MM)	T_3 (MM)	T (MM)	D (CM)	Q (AH)	N
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

L_1	..... Length of cathode
L_2	..... Length of first separator
L_3	..... Length of anode
L_4	..... Length of second separator
T_1	..... Thickness of cathode
T_3	..... Thickness of anode
T	..... Total thickness (anode, cathode and 2 separators)
D	..... Mandrel diameter
Q	..... Cell capacity
N	..... Number of turns around mandrel

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Table IV. Maximum Capacities Obtained with Various Cathodes

Cathode Thickness in.	Weight of Carbon Blend mg/cm^2	Maximum Capacity Obtained	
		mAh/cm^2	Ah/g of Carbon Blend
0.023	14	44	3.14
0.034	28	53	1.89
0.052	52	62	1.19

Table V. Electrode Parameters

Design/Electrode		Length Inches	Width Inches	Thickness Inches
A	Cathode	16	1.75	0.023
	Anode	18	1.75	0.010
B	Cathode	14	1.75	0.034
	Anode	16	1.75	0.015
C	Cathode	12	1.75	0.052
	Anode	14	1.75	0.022

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Table VI. Test Results with Different Designs

Design	Discharge Current A	Current Density, mA/cm^2	Time of Discharge Hours	Cell Cap. to 2.0 V Ah
A	1.40	3.90	3.0	4.20
	0.70	1.95	9.5	6.65
	0.35	0.97	21.0	7.35
B	1.20	3.62	7.5	9.00
	0.60	1.81	17.5	10.5
	0.30	0.90	31.5	9.45
C	1.00	3.72	10.0	10.0
	0.50	1.86	26.5	13.25
	0.25	0.93	45.5	11.38

Table VII. The Factorial Matrix for the Empirical Optimization of the Li/SOCl$_2$ Cells

Carbon weight (g)			5–6			2·5–3	
Cathode length (cm)		76·2	38·1	25·4	38·1	25·4	12·7
Cathode thickness (cm)		0·038	0·076	0·114	0·038	0·057	0·114
LiAlCl$_4$ (salt)	1·8 M						
concentration	1·0 M						
in SOCl$_2$	0·5 M						
		A	B	C	D	E	F

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Table VIII. Extended Factorial Matrix for the Optimization Studies

Teflon Content Wt %	LPS Electrolyte Conc. of $LiAlCl_4$				Foote Electrolyte Conc. of $LiAlCl_4$		
	0.5(M)	1.0(M)	1.5(M)	2.0(M)	0.5(M)	1.0(M)	1.5(M)
10%	0.1A	0.1A	0.1A	0.1A	0.1A	0.1A	0.1A
	0.3A	0.3A	0.3A	0.3A	0.3A	0.3A	0.3A
	0.5A	0.5A	0.5A	0.5A	0.5A	0.5A	0.5A
	1.0A	1.0A	1.0A	1.0A	1.0A	1.0A	1.0A
20%	0.1A	0.1A	0.1A	0.1A	0.1A	0.1A	0.1A
	0.3A	0.3A	0.5A	0.3A	0.3A	0.3A	0.3A
	0.5A	0.5A	0.5A	0.5A	0.5A	0.5A	0.5A
	1.0A	1.0A	1.0A	1.0A	1.0A	1.0A	1.0A
30%	0.1A	0.1A	0.1A	0.1A	0.1A	0.1A	0.1A
	0.3A	0.3A	0.3A	0.3A	0.3A	0.3A	0.3A
	0.5A	0.5A	0.5A	0.5A	0.5A	0.5A	0.5A
	1.0A	1.0A	1.0A	1.0A	1.0A	1.0A	1.0A

Table IX. Cell Capacity After One Month Storage at 55°C

Discharge Rate A	Cell Capacity at			
	-20°C	0°C	20°C	40°C
0.1	10.30 8.00	9.30 7.20	10.6 9.6	9.80 9.65
0.2	7.40 4.70	10.00 9.50	10.05 9.00	8.80 8.0
0.5	6.50 5.4	4.45 4.30	7.40 5.75	3.0 7.10
1.0	4.20 1.75	2.00 1.00	8.2 6.6	7.25 6.60
2.0	— —	2.50 1.86	5.40 4.70	6.80 6.40

Table X. Cell Capacity After One Month Storage at 72°C

Discharge Rate A	Cell Capacity at			
	-20°C	0°C	20°C	40°C
0.05	6.40 --	5.40 --	1.75 2.60	8.00 4.00
0.1	7.40 2.30	6.00 6.70	7.40 8.40	8.60 10.50
0.2	4.00 2.75	3.20 4.20	8.6 0	9.80 10.00
0.5	-- --	-- --	-- --	4.00 4.00

Table XI. Compatibility Studies of Metallic Meterial with 1.5 (M) $LiAlCl_4$-$SOCl_2$ Inorganic Electrolyte at 85°C (185°F)

Metallic Materials	Duration of Refluxing at 85°C (days)	Condition of the Samples After Refluxing
Ni Span C	47	Discolored in contact with air No sign of corrosion
AM-350	47	" " " " "
Ni-A	47	" " " " "
52 alloy	47	" " " " "
Ni-(99.5%)	47	" " " " "
Inconel 702	47	" " " " "
Inconel 750	47	" " " " "
Inconel 625	47	" " " " "
Invar	47	" " " " "
K-Monel	47	" " " " "
Incoloy 800	47	" " " " "
304 Stainless	45	" " " " "
316 Stainless	45	" " " " "
Monel 400	45	" " " " "
Inconel 600	45	" " " " "
Inconel 601	33	" " " " "
302 Stainless	33	" " " " "
Molybdenum	33	Remained shiny in air No corrosion
Tantalum	33	" " " "
Niclad steel sheet (edges not covered by Ni)	32	Steel completely dissolved, Ni part intact

Table XII. Compatibility Studies of Insulating Materials with 1.5 (M) $LiAlCl_4$-$SOCl_2$ Inorganic Electrolyte at 85°C (185°F)

Insulating Materials	Duration of Refluxing at 85°C (days)	Condition of the Samples After Refluxing
1) 'Webril' nonwoven polypropylene fabric	47	Complete disintegration
2) 'Celguard' polypropylene film	47	" "
3) Glass filter paper	47	Good, no change
4) Epoxy G-10: Epoxy-filled fiberglass woven fabric	33	Glass fabric OK; Epoxy disintegrated
5) Polypropylene sheet	46	Dark and brittle
6) PVC sheet	46	Complete disintegration
7) CPVC sheet	46	" "
8) ABS sheet	46	" "
9) Plexiglass sheet	33	" "
10) Rulon rod (a type of teflon)	27	Good, no change
11) Kel-P rod	27	Good
12) Teflon rod	27	Good, no change
13) Butyl rubber (60 d)	15	Disintegrated
14) Neoprene rubber (50 d)	15	"
15) Neoprene rubber (70 d)	15	"
16) Silicone rubber	15	"
17) Viton rubber (70 d)	15	Cracked

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Table XIII. Voltage Delay After One Month Storage At Room Temperature

Discharge Temperature °C	Discharge Rate A	Cell No.	Recovery Time to 2.0 V Second
40	0.2	1	0
		2	0
	0.5	11	0
		12	0
	1.0	21	2.0
		22	6.5
	2.0	32	3.0
		31	9.0
	4.0	--	--
		--	--
RT	0.1	3	0
		4	0
	0.2	13	1.0
		14	1.5
	0.5	23	--
		24	2.8
	1.0	33	5.5
		34	0.5
	2.0	45	[illegible]0.0
		44	5.0
	4.0	50	144.0
		51	1260.0
0	0.1	5	2.0
		6	0
	0.2	15	14.0
		16	6.0
	0.5	26	9.0
		28	2.5
	1.0	35	21.0
		36	42.0
	2.0	47	28.0
		46	0
	4.0	25	180.0
		53	60.0

Table XIII. Voltage Delay After One Month Storage At Room Temperature (Contd)

Discharge Temperature °C	Discharge Rate A	Cell No.	Recovery Time to 2.0 V Second
-20°C	0.1	7	2.0
		8	0
	0.2	17	1.5
		18	2.0
	0.5	27	5.5
		28	9.5
	1.0	38	97.0
		39	66.0
	2.0	42	46.0
		48	48.0
-40	0.1	9	120.0
		10	4.5
	0.2	19	3.5
		20	4.5
	0.5	29	21.0
		30	96.0
	1.0	40	115.0
		41	106.0
	2.0	43	201.0
		37	251.0

Table XIV. Voltage Recovery on Discharge After Storage of One Month at 55°C

Cell Number	Discharge Rate mA	Discharge Temp. °C	Time to 2 Volts Seconds
54	100	40	0
55	100	40	0
56	100	RT	0
57	100	RT	0
58	100	0	0
59	100	0	0
60	100	-20	0
61	100	-20	208
62	100	-40	290
63	100	-40	22
64	200	40	0
65	200	40	0
66	200	20	71
67	200	20	216
68	200	0	243
69	200	0	414
70	200	-20	27
71	200	-20	0
74	500	40	0
75	500	40	6
76	500	20	0
106	500	20	41
109	500	0	0
79	500	0	63
80	500	-20	90

Table XIV. Voltage Recovery on Discharge After Storage of One Month at 55°C (Contd)

Cell Number	Discharge Rate mA	Discharge Temp. °C	Time to 2 Volts Seconds
81	500	-20	360
84	1000	40	45
85	1000	40	114
86	1000	20	20
87	1000	20	28 1/2
88	1000	0	Discharge below 2V 64, below 0
89	1000	0	84
90	1000	-20	118
91	1000	-20	103
108	2000	40	816
95	2000	40	270
96	2000	20	321
97	2000	20	324
103	2000	0	174
104	2000	0	408

Table XV. Voltage Recovery on Discharge After Storage of One Month at 72°C

Cell Number	Discharge Rate mA	Discharge Temp. °C	Time to 2 Volts Seconds
130	50	40	0
131	50	40	0
132	50	20	0
133	50	20	0
135	50	0	0
136	50	-20	0
110	100	40	0
111	100	40	0
142	100	20	0
113	100	20	0
114	100	0	0
115	100	0	0
116	100	-20	0
117	100	-20	7200
120	200	40	0
121	200	40	0
122	200	20	138
123	200	20	0
124	200	0	0
125	200	0	0
126	200	-20	0
127	200	-20	0
152	500	40	135
153	500	40	60

Table XVI. Voltage Delay After Storage of Partially Discharged Cells
Time of Recovery to 2.0V Storage Time 30 Days

Cell No.	Storage Temp °C	Current Density mA/cm²	Voltage Delay
121	25	2.8	0
122			0
123		5.6	12 sec.
124			6 sec.
125		11.2	12 sec.
126			12 sec.
127	55	2.8	2 min.
128			1 min. 18 sec.
129		5.6	2.5 min.
130			1 min. 15 sec.
131		11.2	4 min. 25 sec.
132			4 min.
133	72	2.8	2 min. 30 sec.
134			2 min. 48 sec.
135		5.6	2 min.
136			3 min.
137		11.2	3 min. 30 sec.
138			3 min.

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Tabl. XVII. Teflon-Bonded Carbon Cathodes (16% TFE)

Type of carbon	Derivation	Carbon loading* (g/cm²)	BET surface area of carbon: meter² Per gram of carbon powder	Per cm² of electrode geometric area*	% electrode porosity
Shawinigan—50% compressed	Decomposition of acetylene	0.0194	66	1.28	87
Darco-G60	Steam-activation of charcoal	0.0048	301	14.4	84
United XC-6310-4	Decomposition of oil	0.0146	1000	14.6	81
Columbia HR 1070	Decomposition of oil	0.0104	1200	12.5	78

* Based on (length × width) area of electrode, one side.

Table XVIII. Voltage Delay, Capacity, and Capacity Loss in AA Bobbin Cells Containing $LiAlCl_4$ or $Li_2B_{10}Cl_{10}$ Discharged Fresh or After Storage at 55°C for Two Weeks

Cell No.	Minimum Potential (V)	Time to Min. Potent. (sec)	Time to Reach 2V (sec)	Time to Reach 3V (sec)	Potential After 100 sec. (V)	Potential After 1000 sec. (V)	Discharge Load (ohms)	Capacity to 2V (mA-hr)
Stored 2 wk, 55° C								
1.8M $LiAlCl_4$								
86	1.6	30	110	—	1.9	2.7	82	325
10	1.6	40	250	—	1.7	2.5	172	353
87	1.4	50	290	—	1.5	2.6	340	360
14	0.45	20	—	—	0.56	1.3	750	329
0.25M $Li_2B_{10}Cl_{10}$								
93	2.6	<0.5	—	<0.5	3.3	—	82	368
46	2.9	<0.5	—	<0.5	3.4	—	172	409
94	2.4	<0.5	—	21	3.2	—	340	403
100	2.4	<0.5	—	2	3.3	—	750	385
Fresh cells (discharge started at ambient temperature within 3 days of filling)								
1.8M $LiAlCl_4$								
39							82	455
37							172	441
40							340	435
38							750	414
0.25M $Li_2B_{10}Cl_{10}$								
79							82	439
77							172	444
80							340	450
78							750	425

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Table XIX. Summary of DSC Results for Li/$SOCl_2$ System

Reaction	Reactants	Cutoff temperature (°C)†	Transition temperature (°C)‡	
			Endothermic	Exothermic
1	$SOCl_2$	241	212	214
2	$LiAlCl_4$	271	143	—
3	Li + $SOCl_2$	338	176	217, 231
4	Li + $LiAlCl_4$	410	181	137(5)
5	Li + Li_2SO_4	400	181	—
6	Li + S_2Cl_2	343	172	—
7	$SOCl_2$ + Li_3N	346	—	196(70)
8	$SOCl_2$ + Li_2S	278	—	—
9	$SOCl_2$ + C	241	—	—
10	Li + [$SOCl_2$-$LiAlCl_4$]*	329	177	—
11	[$SOCl_2$-$LiAlCl_4$] + S	391	236	—
12	[$SOCl_2$-$LiAlCl_4$] + Li_3N	367	—	132(150)
13	[$SOCl_2$-$LiAlCl_4$] + Li_2S	367	—	—
14	Li + $SOCl_2$ + C	343	180	—
15	Li + $LiAlCl_4$ + C	362	179	137(5)
16	Li + [$SOCl_2$-$LiAlCl_4$] + C	350	—	54, 326(25)
17	Li + [$SOCl_2$-$LiAlCl_4$] + C	302	167	180, 204
18	Li + [$SOCl_2$-$LiAlCl_4$] + C	362	181	85
19	Li + [$SOCl_2$-$LiAlCl_4$] + Cu	408	186	—
20	Li + [$SOCl_2$-$LiAlCl_4$] + S	414	184	395(15)
21	[$SOCl_2$-$LiAlCl_4$] + C + S	384	—	—
22	[$SOCl_2$-$LiAlCl_4$] + C + Cu	408	—	—
23	Li + $SOCl_2$ + LiCl + C	362	187	—
24	Li + $SOCl_2$ + Li_2SO_4 + C	362	181	—
25	Li + [$SOCl_2$-$LiAlCl_4$-1% H_2O + C]	455	180	378
26	Li + [$SOCl_2$-$LiAlCl_4$-SO_2] (satd.) + S	414	180	—
27	Li + [$SOCl_2$-$LiAlCl_4$] + C + Cu	417	177	83(30), 348(25)
28	Li + [$SOCl_2$-$LiAlCl_4$-SO_2 (satd.)] + C + S	408	181	88, 181(75)
29	Li-B alloy + $LiAlCl_4$	369	181	137
30	Li-B alloy + $SOCl_2$	343	182	231, 249
31	Li-B alloy + [$SOCl_2$-$LiAlCl_4$]	343	172	—
32	B + [$SOCl_2$-$LiAlCl_4$]	395	—	—
33	Li-B alloy + [$SOCl_2$-$LiAlCl_4$] + C	391	172	50(30), 322(75)

* Ingredients within the square brackets are a homogeneous solution.
† Temperature at which the DSC linearly programmed temperature scan was terminated.
‡ Figures in parenthesis are the increase in the sample temperature above the linearly programmed temperature.

Table XX. Possible Electrode Materials for High Rate $SOCl_2$ Electrode

CORROSION RATES: (in mils/year)

POSSIBLE ELECTRODE MATERIALS
FOR
HIGH RATE $SOCl_2$ ELECTRODE

MATERIAL	PURITY	CORROSION RATE*
Cadmium	4N85	23.0
Cobalt	4N8	4.1
Copper	5N	103.0
Gold	4N85	.92
Iron	4N85	85.0
Molybdenum	3N85	1.9
Nickel	4N8	1.1
Niobium	4N	No Reaction
Palladium	4N	2.2
Platinum	4N	1.6
Silver	5N	No Reaction
Tungstem	4N	0.97
Stainless Steel		7.8
Aluminum		57.0

*Corrosion in Apache Chemical Co.
1.4m $LiAlCl_4/SOCL_2$ at 120°F.

Table XXI. Voltage Delay of Mallory "D" Cells After Various Periods of Storage

Storage Temp (°C)	Storage Time	Discharge Current (Amp)	Discharge Temp (°C)	Delay (sec)
72	2 wk.	1	25	1000
55	2 wk.	1	25	137
25	1 mo.	1	25	0.5
25	1 yr.	1	25	480
25	2 yr.	3	25	180
72	3 mo.	3	25	1670
72	3 mo.	3	-30	infinite

Table XXII. Film Thickness and Voltage Delay of Lithium Samples Stored for Increasing Periods of Time at 55°C

Storage Time (hrs)	Film Thickness (μM)	Voltage Delay (sec)*
154	4.5	<1.0
267	20.0	10.0
406	50.0	30.0
590	45.0	80.0

*Note: Measured at 15 mA/cm^2 versus a lithium counter electrode

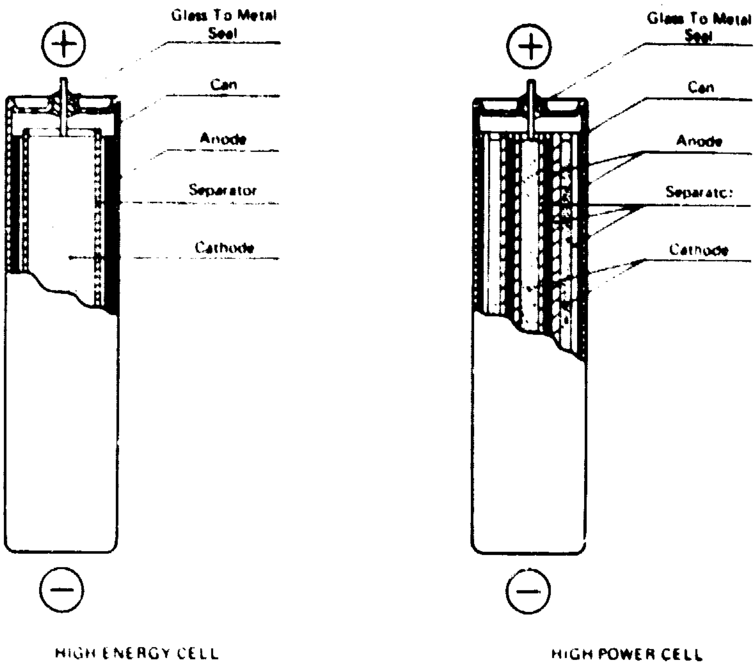

Figure 1. Schematic presentation of cell construction.

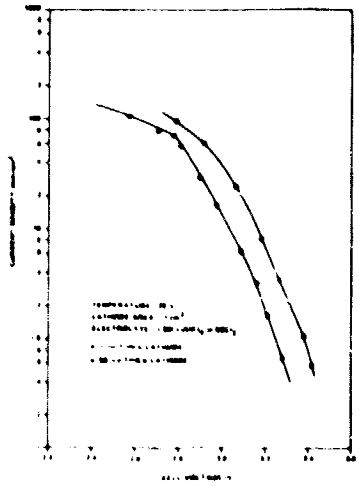

Figure 2. Li/SOCl$_2$ polarization curves with 2 mil and 50 mil cathode thicknesses

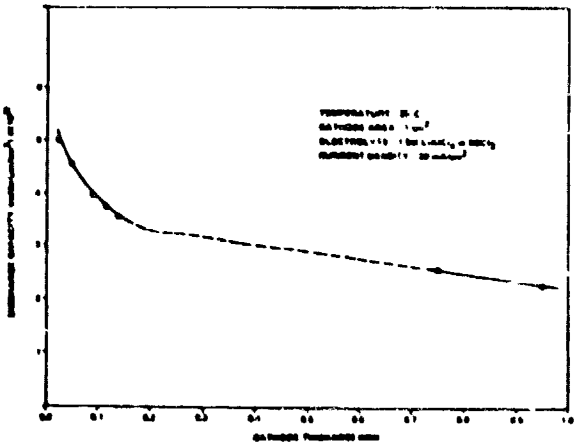

Figure 3. Li/SOCl$_2$ cathode utilization vs cathode thickness

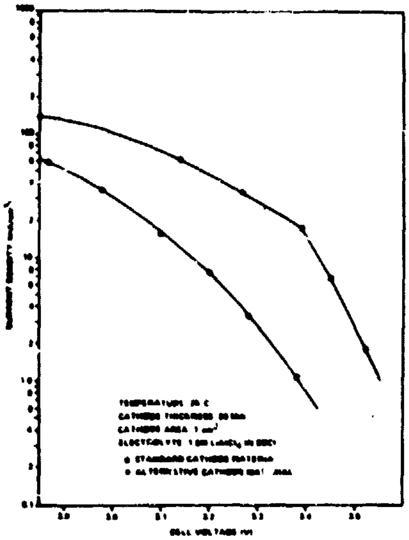

Figure 4. Li/SOCl$_2$ polarization curves with standard and alternative cathode materials

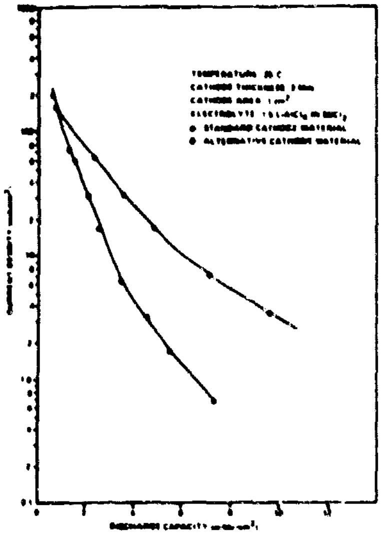

Figure 5. Li/SOCl$_2$ discharge capacity vs discharge rate with standard and alternative cathode materials

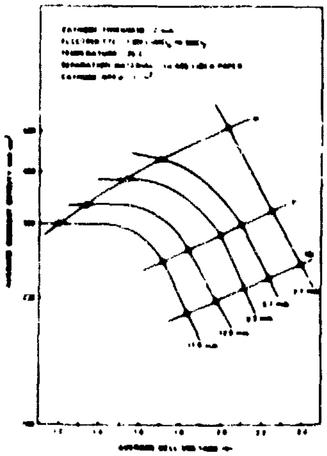

Figure 6. Li/SOCl$_2$ polarization curves with varying separator thickness

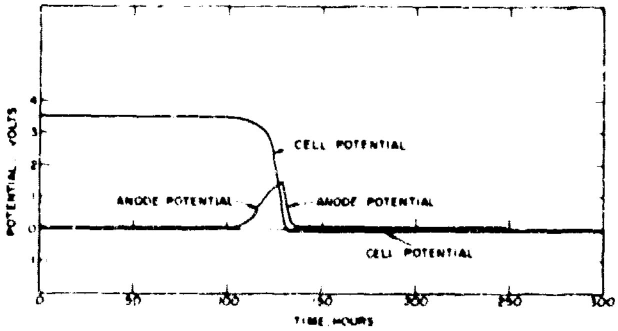

Figure 7. Galvanostatic discharge and overdischarge of spiral wound C-size Li/SOCl$_2$ cell (C-14). Current = 40 mA.

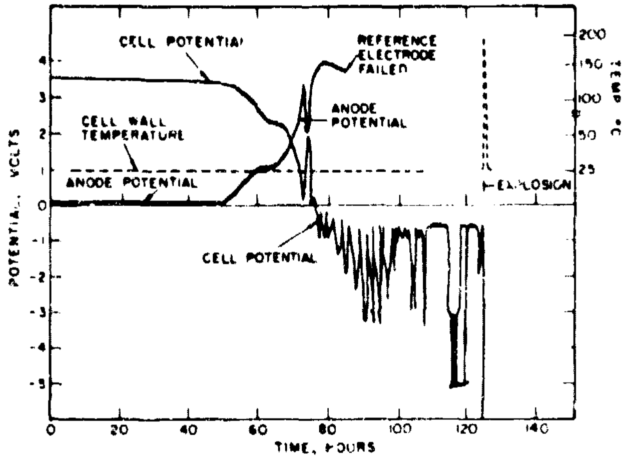

Figure 8. Galvanostatic discharge and overdischarge of spiral wound C-size Li/SOCl$_2$ cell (C-9). Current = 50 mA.

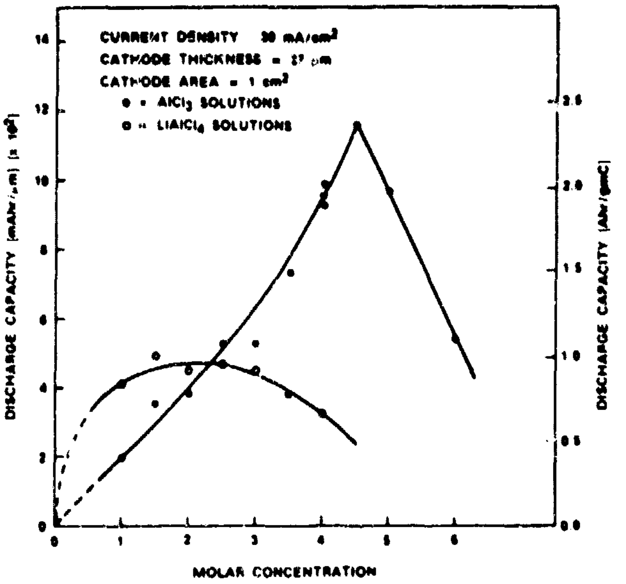

Figure 9. Discharge capacity per unit cathode thickness (for 'thin' cathodes) as a function of electrolyte composition.

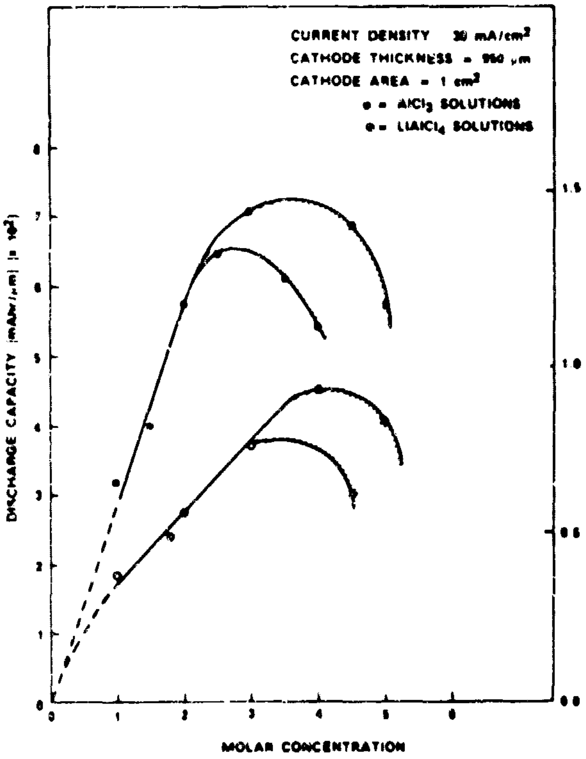

Figure 10. Discharge capacity per unit cathode thickness (for 'thick' cathodes) as a function of electrolyte composition.

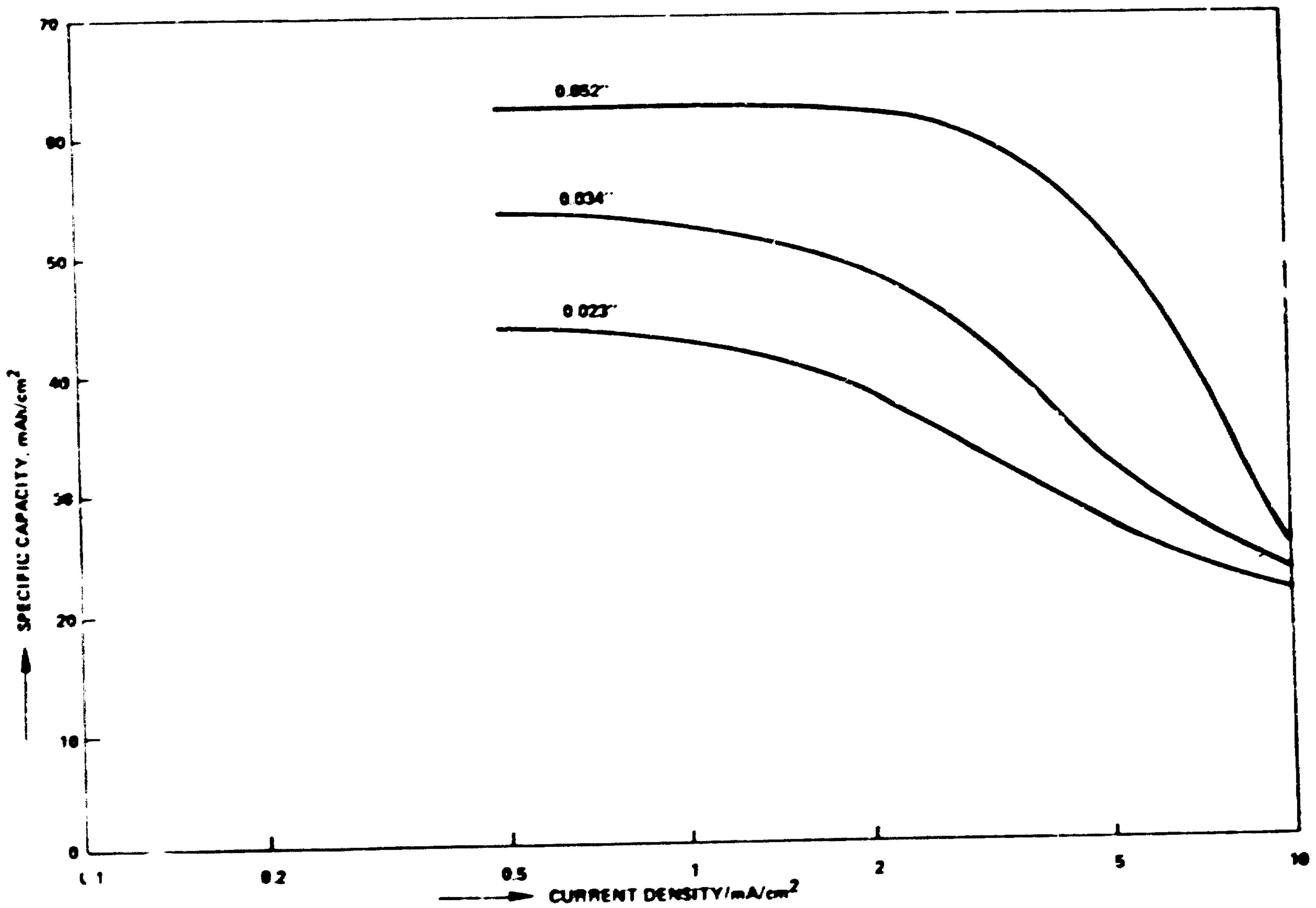

Figure 11. Limiting Specific Cathode Capacity as a Function of Discharge Rate for Various Cathodes

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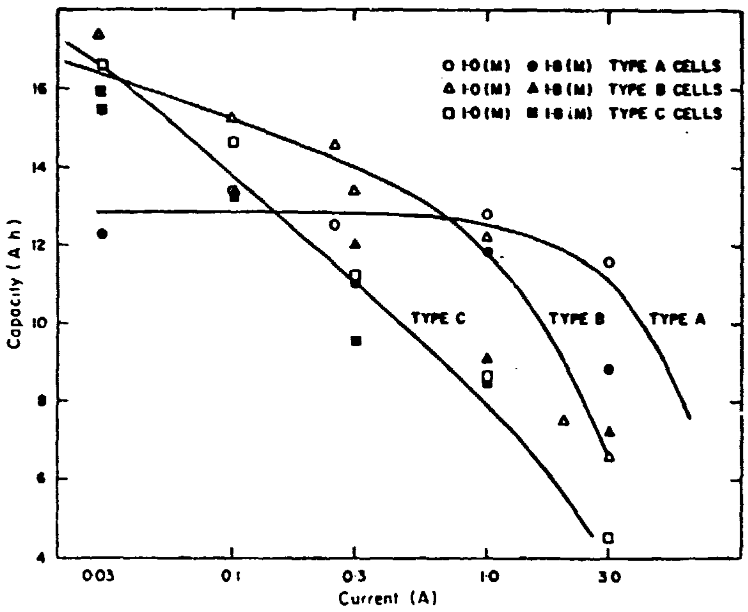

Figure 12. Semilog plots of capacity vs current of type A, B and C cells with 1.0 M and 1.8 M $LiAlCl_4$-$SOCl_2$ electrolyte.

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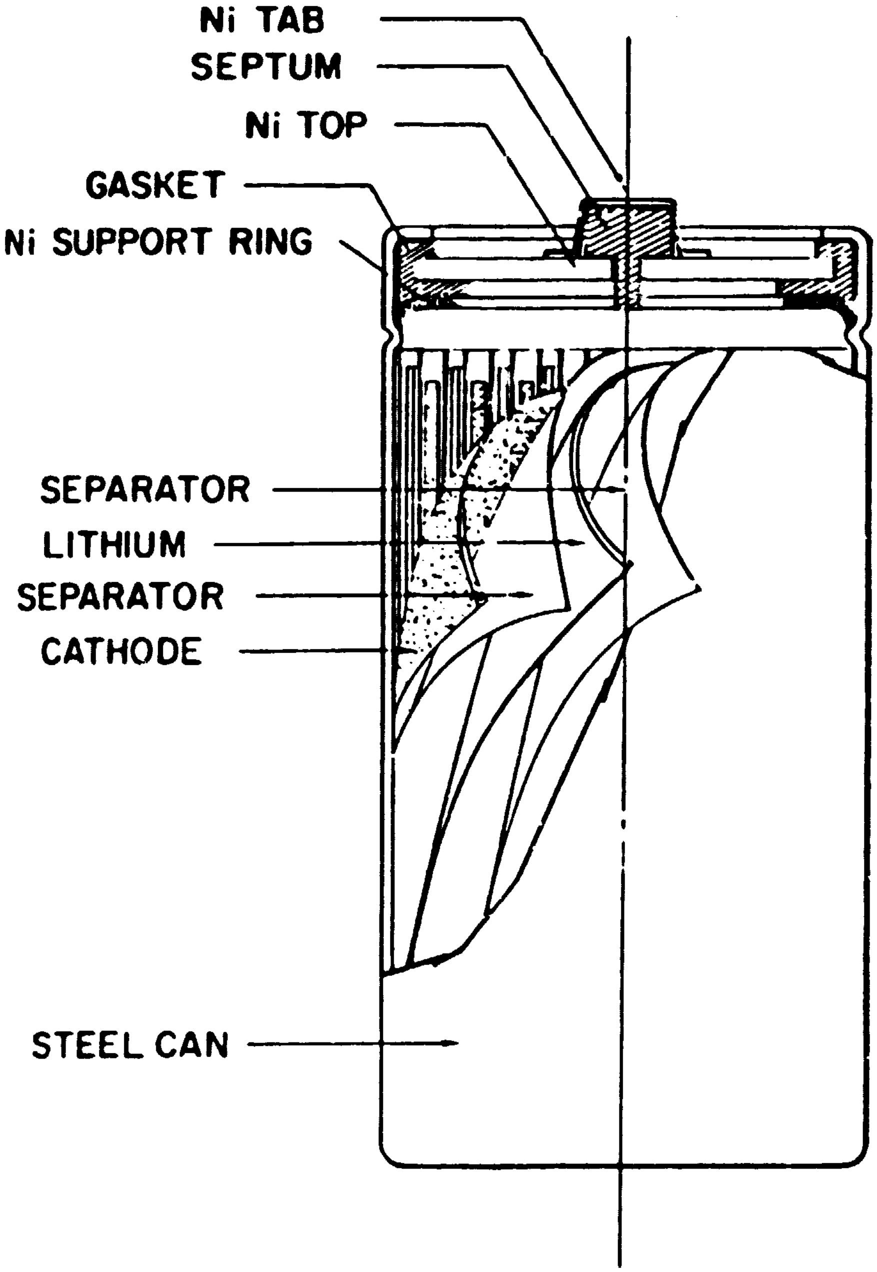


Figure 13. Cut-out View of the Inorganic Electrolyte "C" Cell

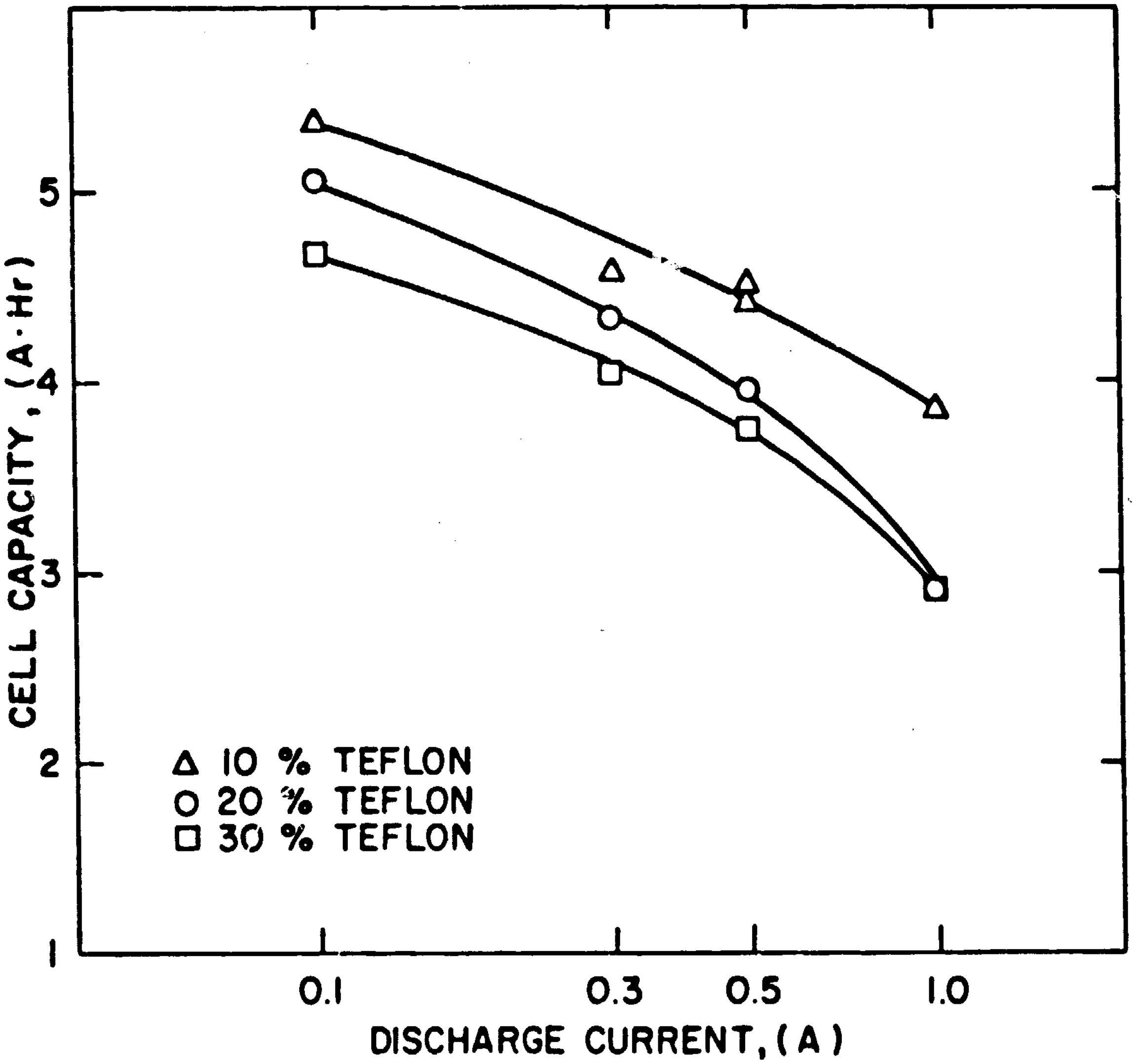


Figure 14. Cell Capacity (Q) vs. Log Current (I) Plots of "C" Cells with 1(M) $LiAlCl_4$ LPS Electrolyte for 10%, 20% and 30% Teflon in the Cathode

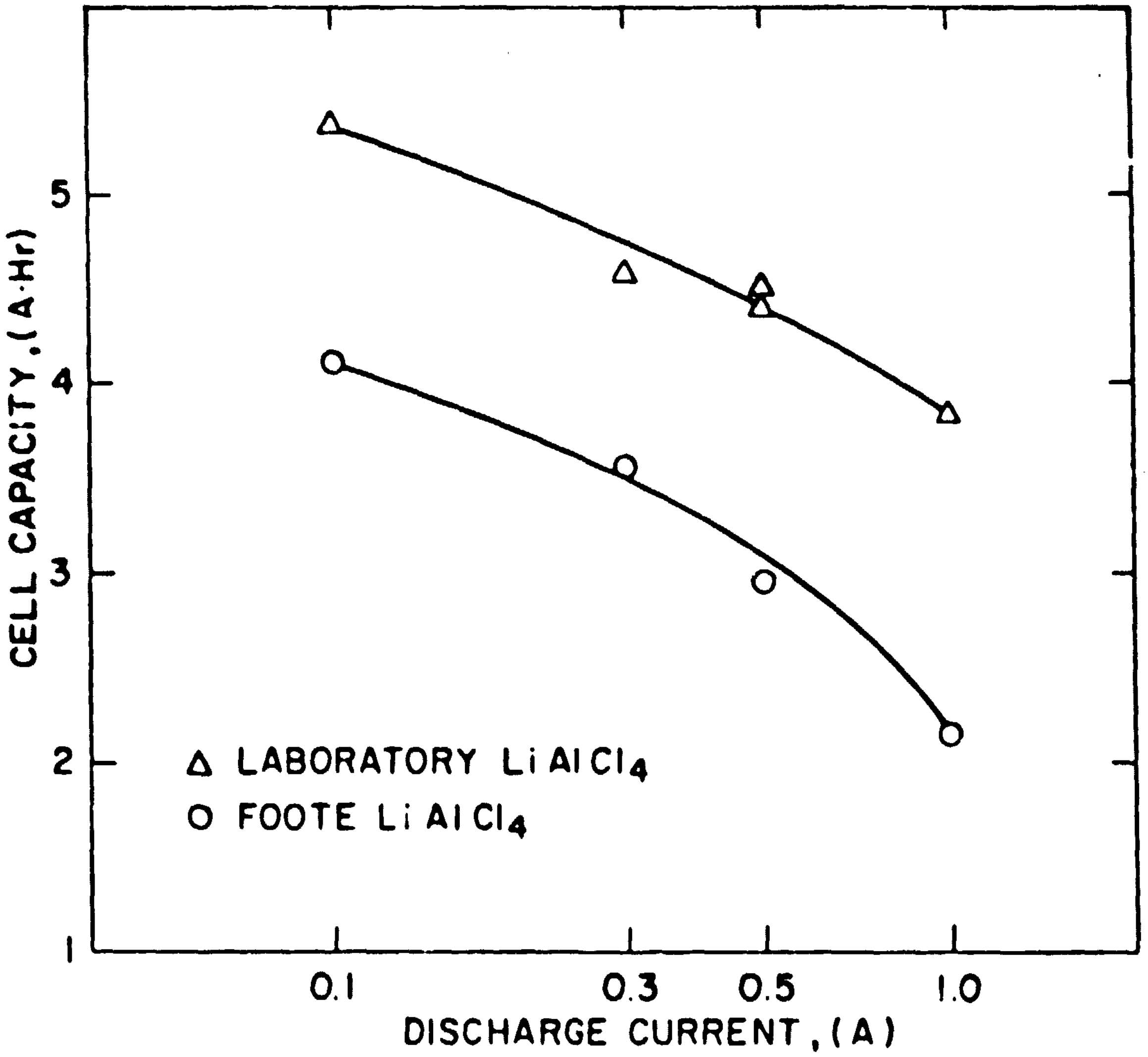


Figure 15. Cell Capacity (Q) vs. Log Current (I) Plots of "C" Cells with 1(M) LiAlCl$_4$ and 10% Teflon for LPS and Foote Electrolyte

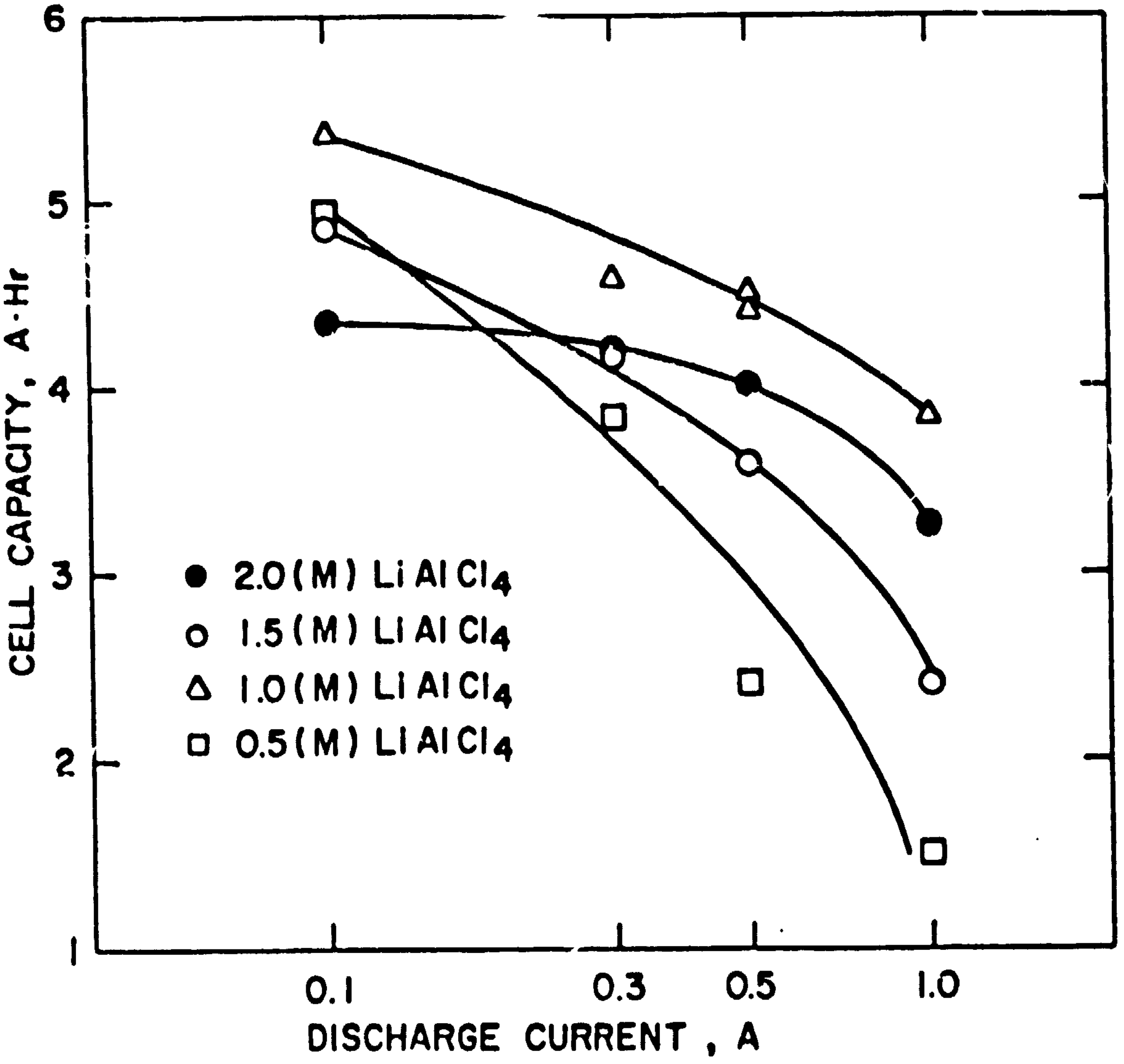


Figure 16. Cell Capacity vs. Log Current Plots of "C" Cells with 10% Teflon in the Cathode at 0.5, 1.0, 1.5 and 2.0(M) $LiAlCl_4$LPS Electrolyte

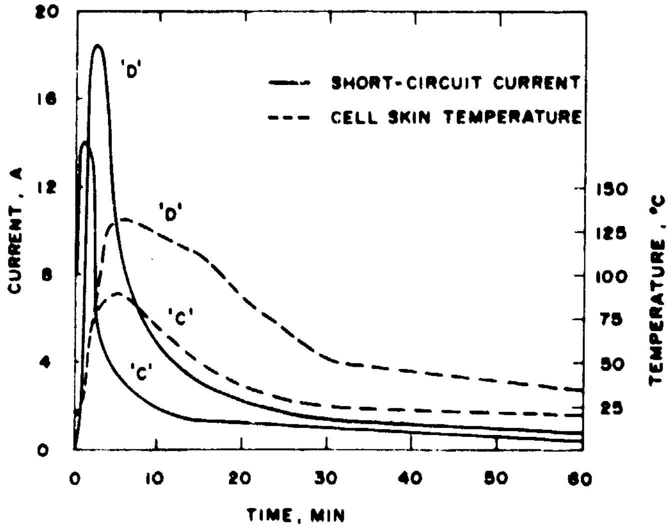


Figure 17. Short-circuit current and skin temperature of C- and D-size Li/BrCl, $SOCl_2$ cells during short-circuit tests.

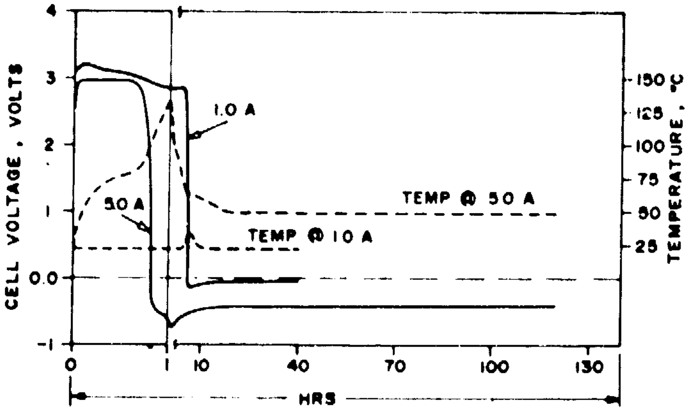


Figure 18. Voltage and skin temperature of D-size Li/BrCl, $SOCl_2$ cells during forced discharge at 1 A and 5 A.

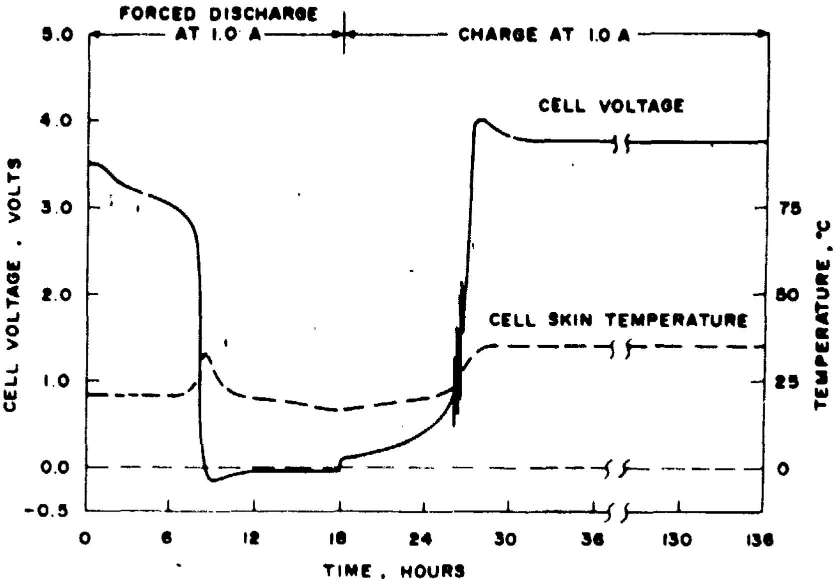


Figure 19. Voltage and skin temperature of a D-size Li/BrCl, $SOCl_2$ cell during forced discharge and charge at 1 A.

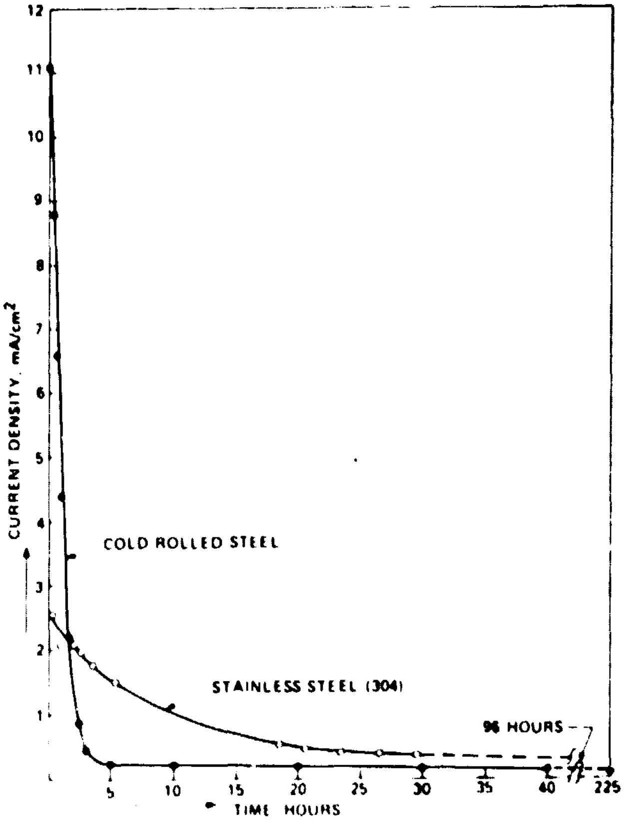


Figure 20. Self Discharge Rate of Anodes in Contact with Stainless Steel and Cold Rolled Steel.

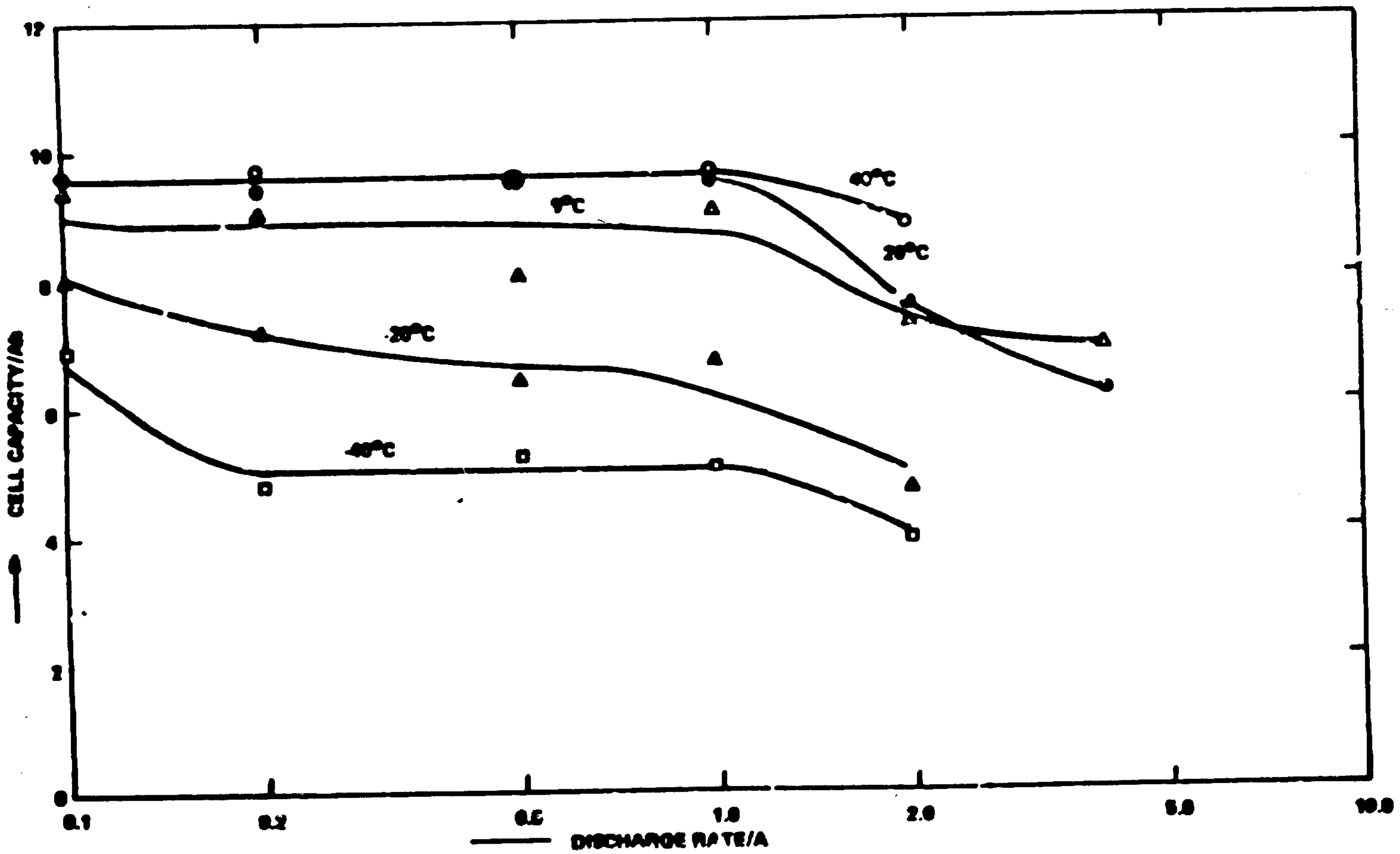


Figure 21. Capacity-Rate Behavior of Lithium/$SOCl_2$ Cells After One Month at Room Temperature

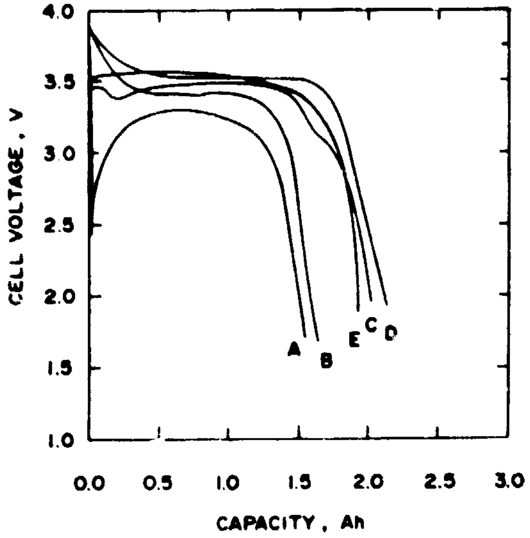


Figure 22. Storage tests for the AA-size Li/BrCl, $SOCl_2$ cells. A, 30 Ω stored for three months at 72°C; B, 30 Ω fresh cell; C, 180 Ω stored for 3 months at 72°C; D, 180 Ω fresh cell; E, 180 Ω stored for 15 months at room temperature.

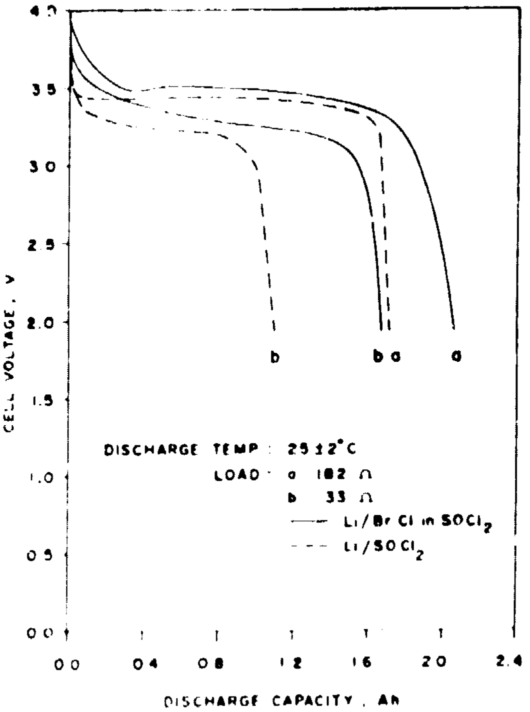


Figure 23. Comparison of the room-temperature discharge characteristics of $Li/SOCl_2$ AA-cells and Li/BrCl, $SOCl_2$ AA-cells.

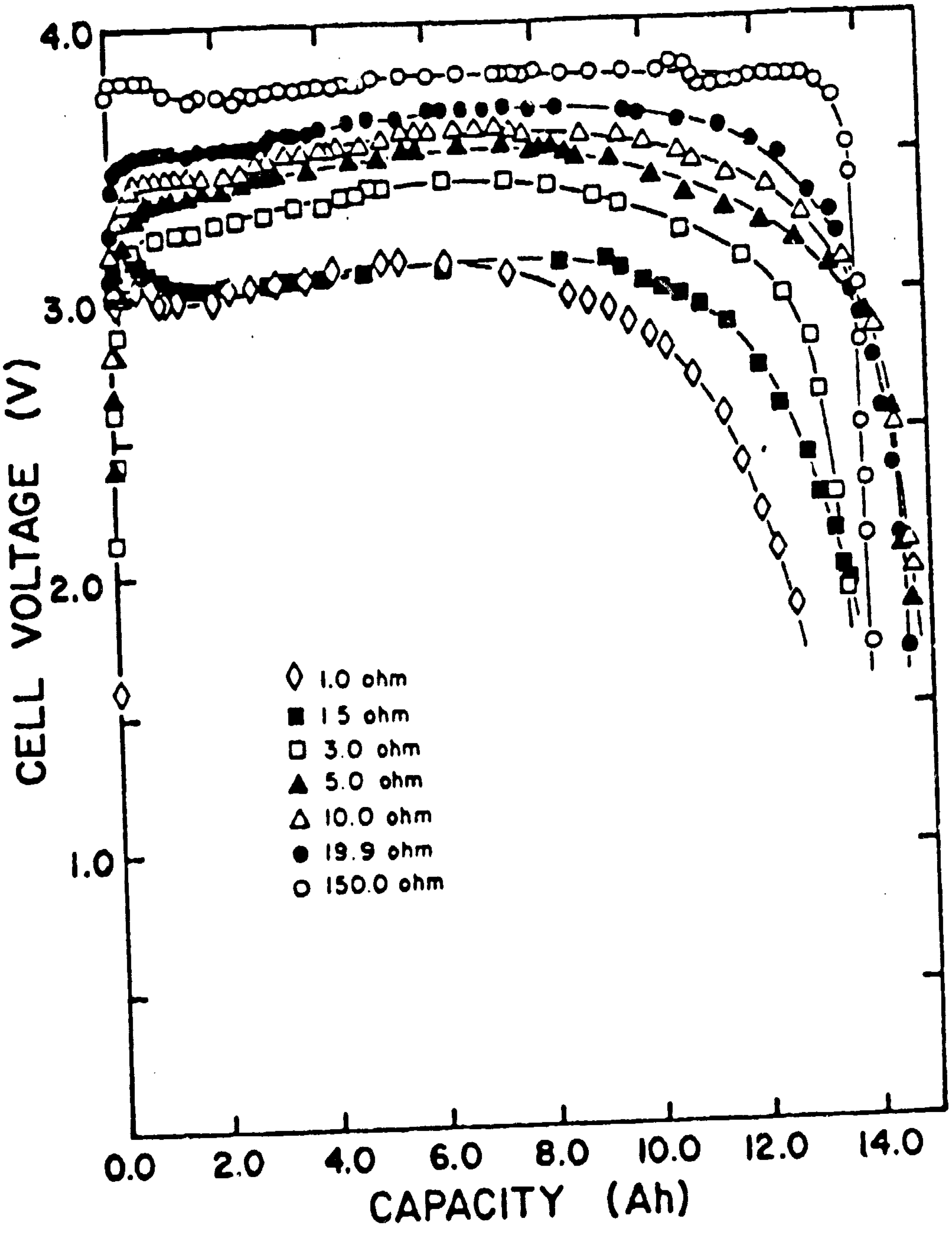


Figure 24. Ambient Temperature (24 ± 3°C) Discharge Curves for D Cells.

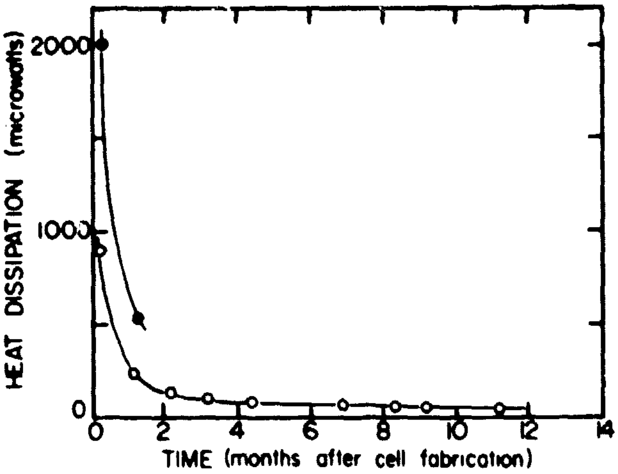


Figure 25. Heat dissipation (microwatts) versus time (months after cell fabrication) for both Li/Cl_2 and Li/SO_2Cl_2 spirally wound AA cells at 37°C. ○ Li/Cl_2 in SO_2Cl_2 and ● Li/SO_2Cl_2.

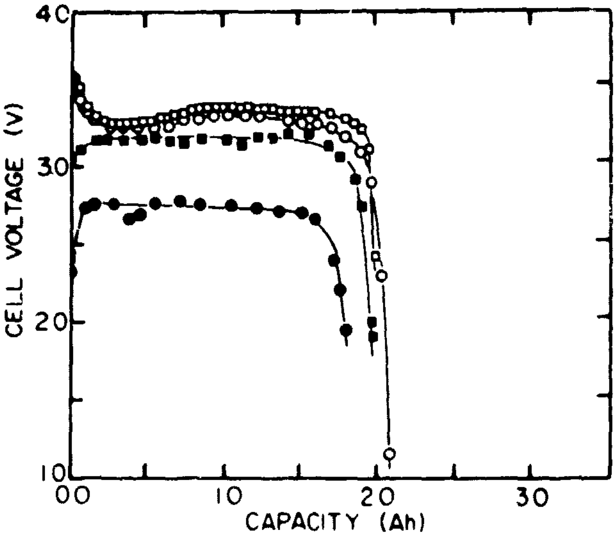


Figure 26. Discharge curves for spirally wound Li/Cl_2 in SO_2Cl_2AA cells before and after storage (1 year under uncontrolled ambient conditions). ○ New cell, discharged at 40 ohms, ☐ New cell, discharged at 75 ohms, ● Cell stored 1 year, discharged at 40 ohms, ■ Cell stored 1 year, discharged at 75 ohms

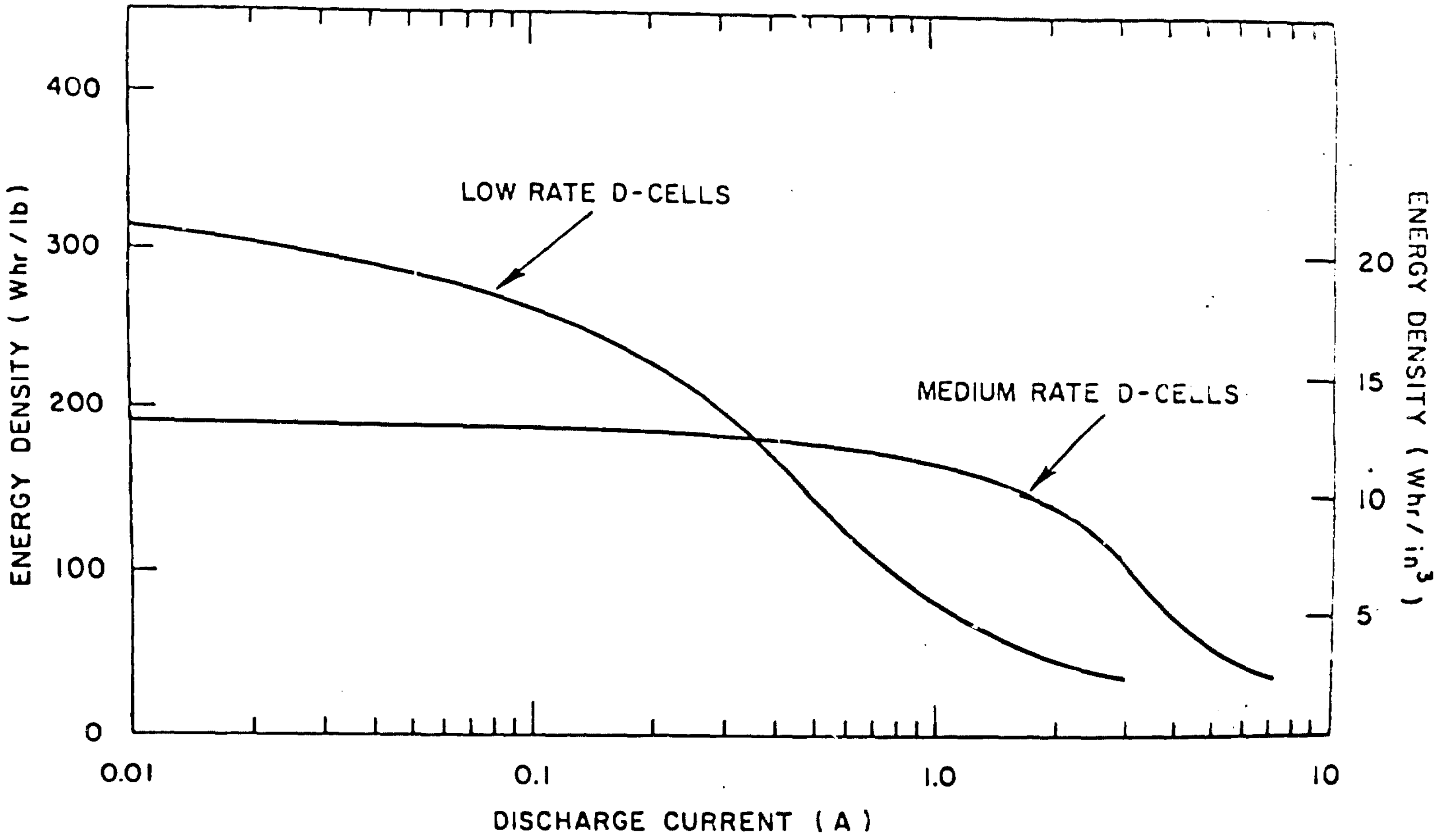


Figure 27. Energy Density-Rate Curves of the Medium Rate and the Low Rate $Li/SOCl_2$ D Cell.

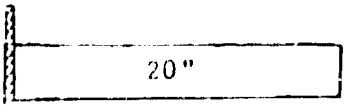
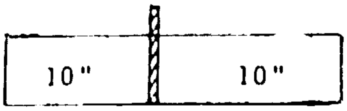
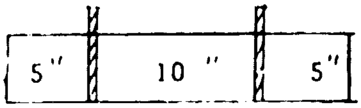
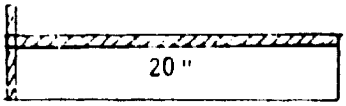
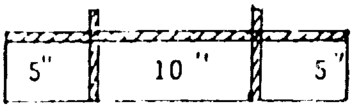
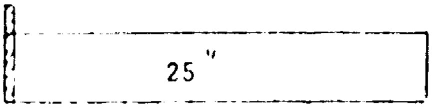
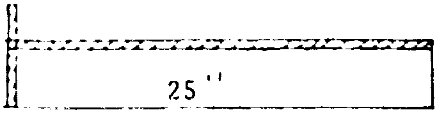
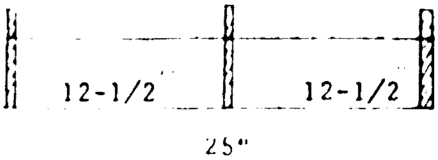
		Maximum Short Circuit	
No.	Cathode Designs	Current (A)	Current Density (mA/cm²)
1.		24	53
2.		76	168
3.		94	208
4.		58	128
5.		98	217
6.		35	62
7.		65	115
8.		104	184

Figure 28. Short-Circuit Currents of Hermetic D Cells With Various Cathode Designs

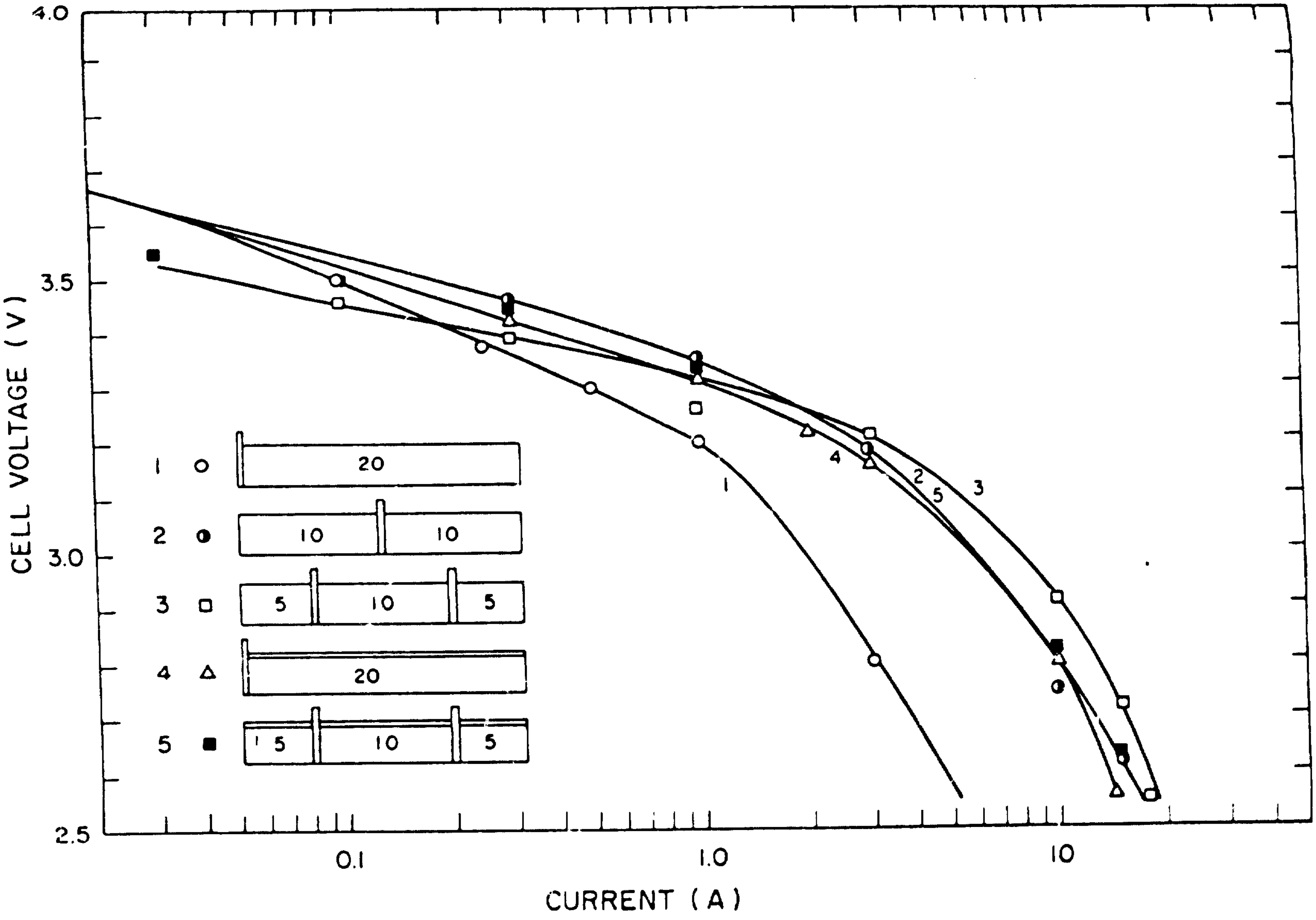


Figure 29. Polarization Characteristics of D Cells with 20 Inch Cathodes of Various Current Collector Designs.

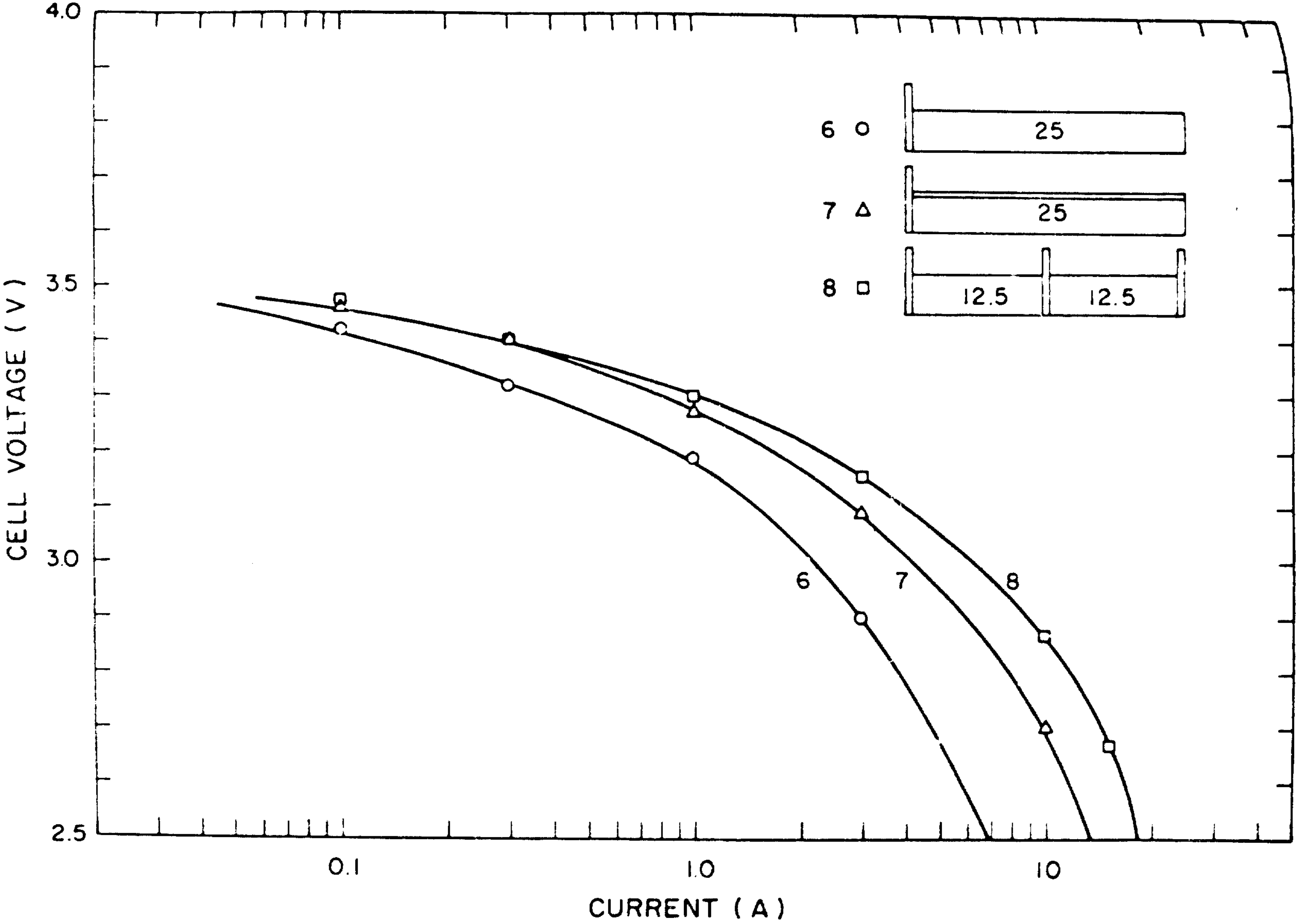


Figure 30. Polarization Characteristics of D Cells with 25 Inch Long Cathodes of Various Current Collector Design.

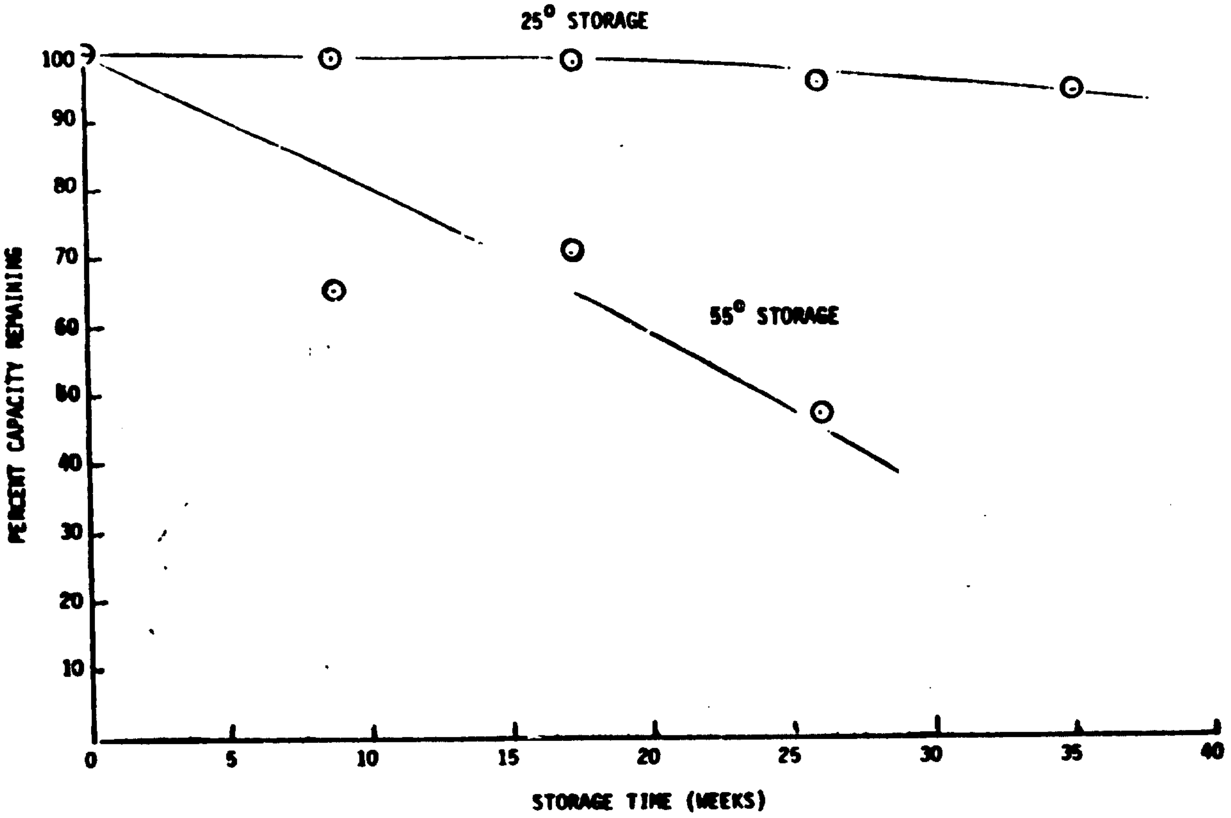


Figure 31. Capacity Loss in Lithium-Limited DD Cells After Storage at 55°C

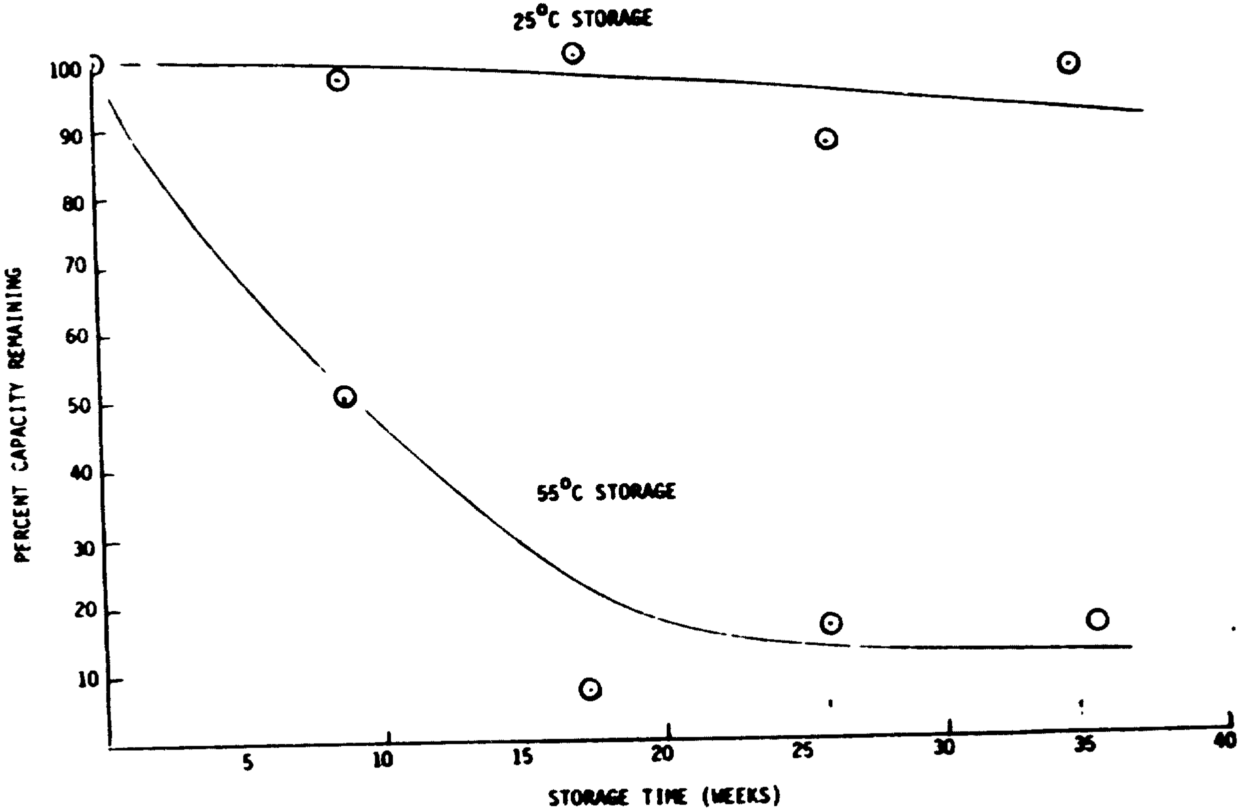


Figure 32. Capacity Loss in Cathode-Limited DD Cells After Storage at 55°C

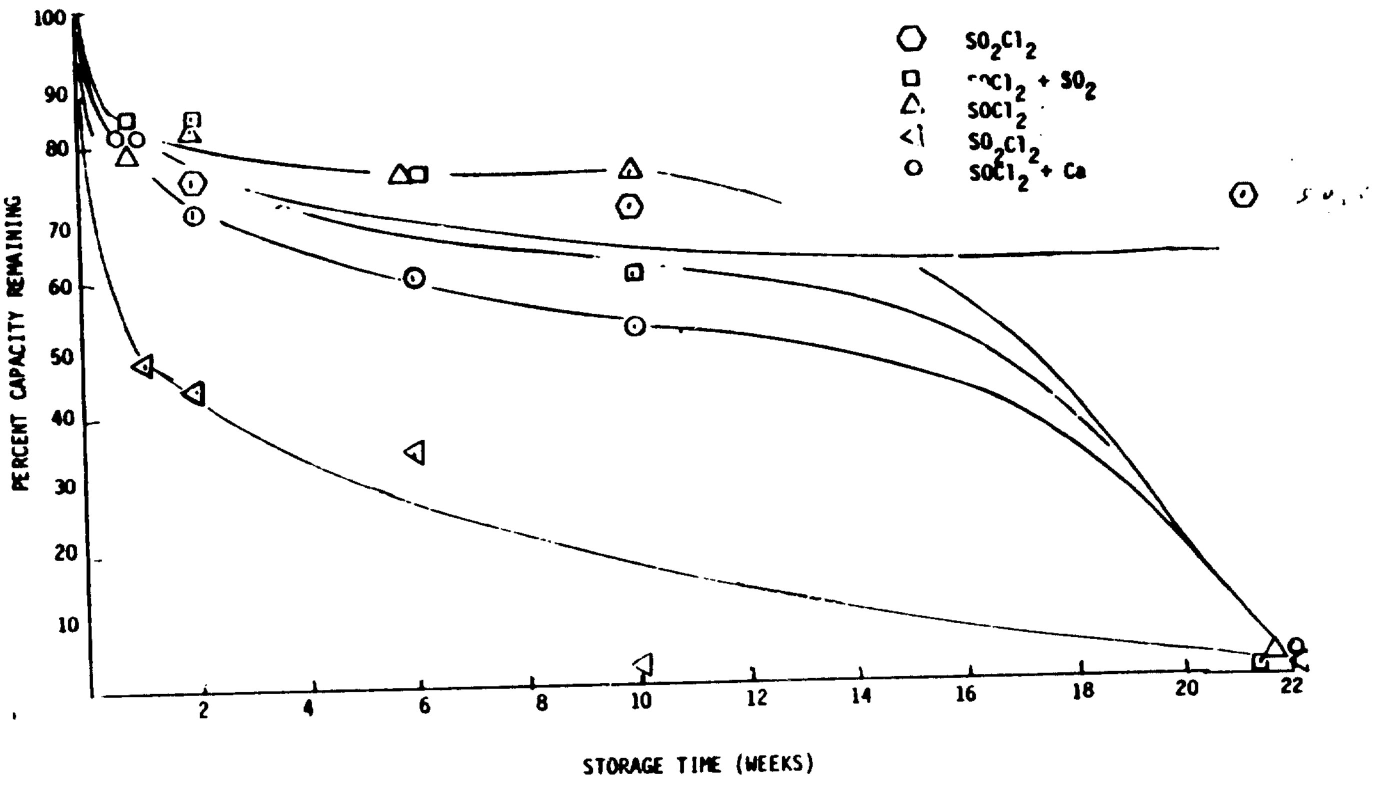


Figure 33. Capacity Loss of Lithium-Limited D Cells After Storage at 55°C

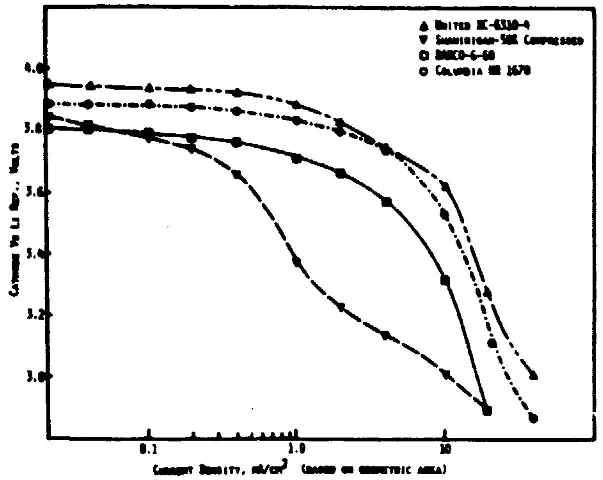


Figure 34. Polarization Curves for Teflon-Bonded Carbon Cathodes (16% TFE, Uncompressed).

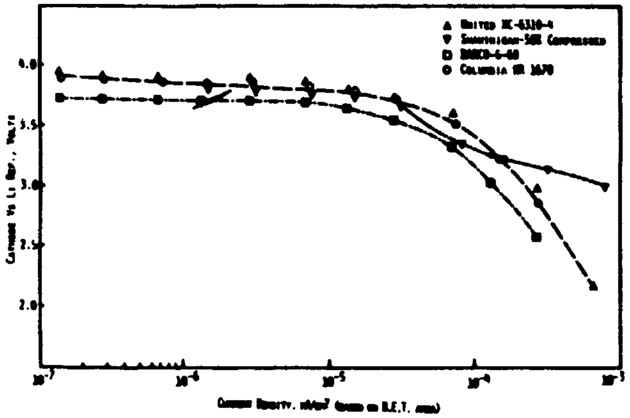


Figure 35. Polarization Curves for Teflon-Bonded Carbon Cathodes (16% TFE, Uncompressed) Normalized with Respect to BET Area.

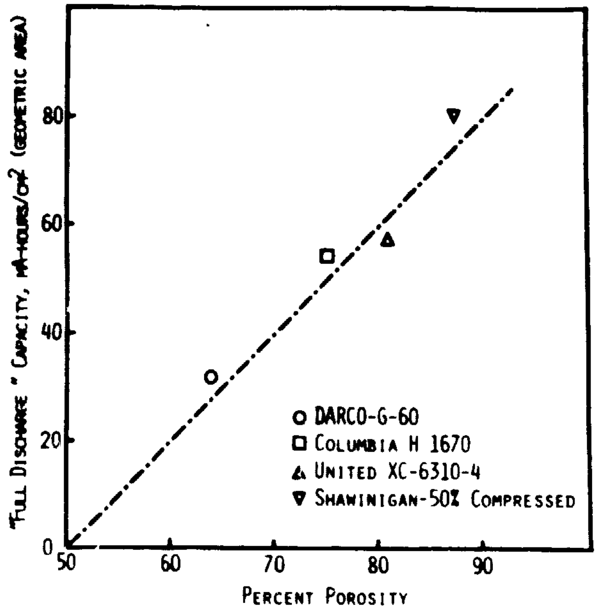


Figure 36. Capacity-Porosity Relationship for Teflon-Bonded Carbon Cathodes (16% TFE, Uncompressed).

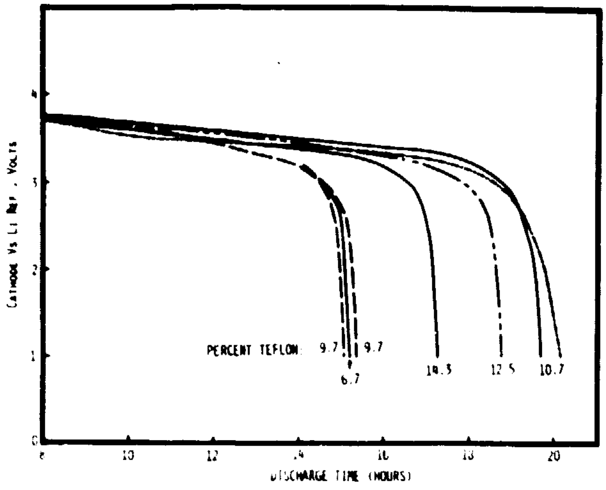


Figure 37. Discharge Curves (1 = 5 mA/cm^2) for Cathodes Formulated with Varying Amounts of TFE (Uncompressed).

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OF POOR QUALITY

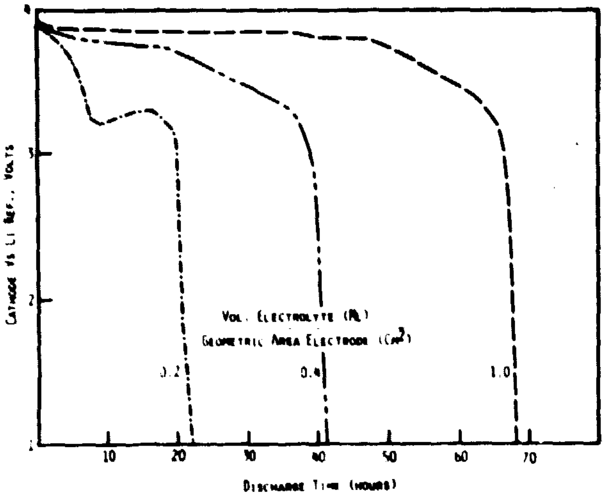


Figure 38. Discharge Curves for Optimized Cathode Using Various Volumes of Electrolyte.

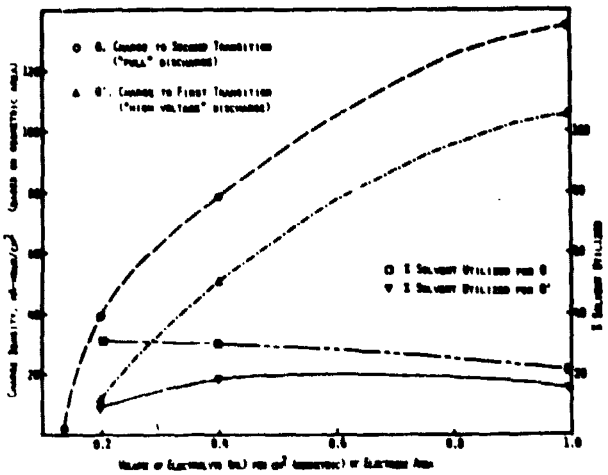


Figure 39. Dependence of Cathodic Charge and Solvent Utilization on Electrolyte Volume.

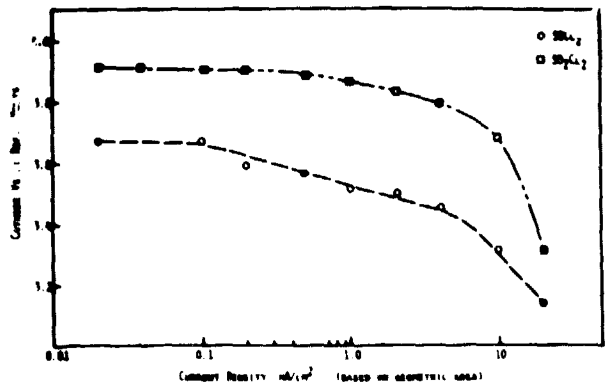


Figure 40. Comparison of Cathodic Polarization Curves for SO_2Cl_2 and $SOCl_2$.

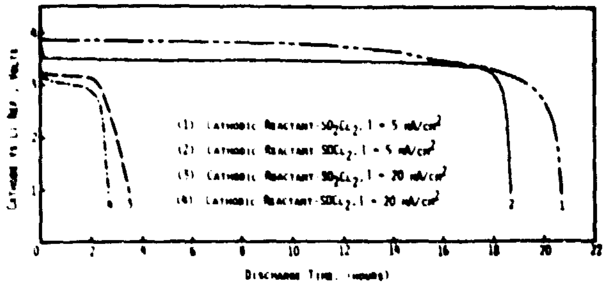


Figure 41. Comparison of Cathodic Discharge Curves for SO_2Cl_2 and $SOCl_2$.

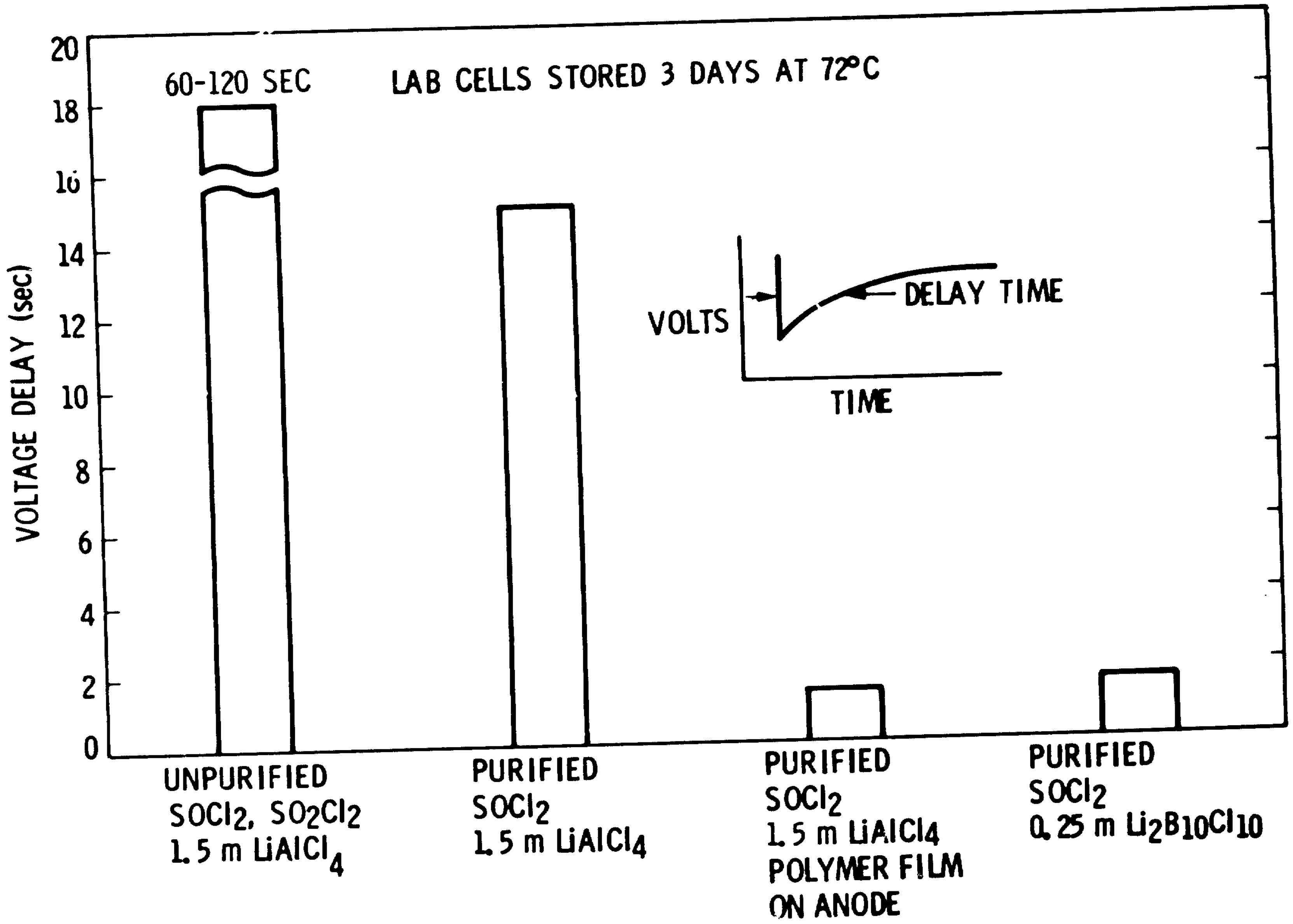
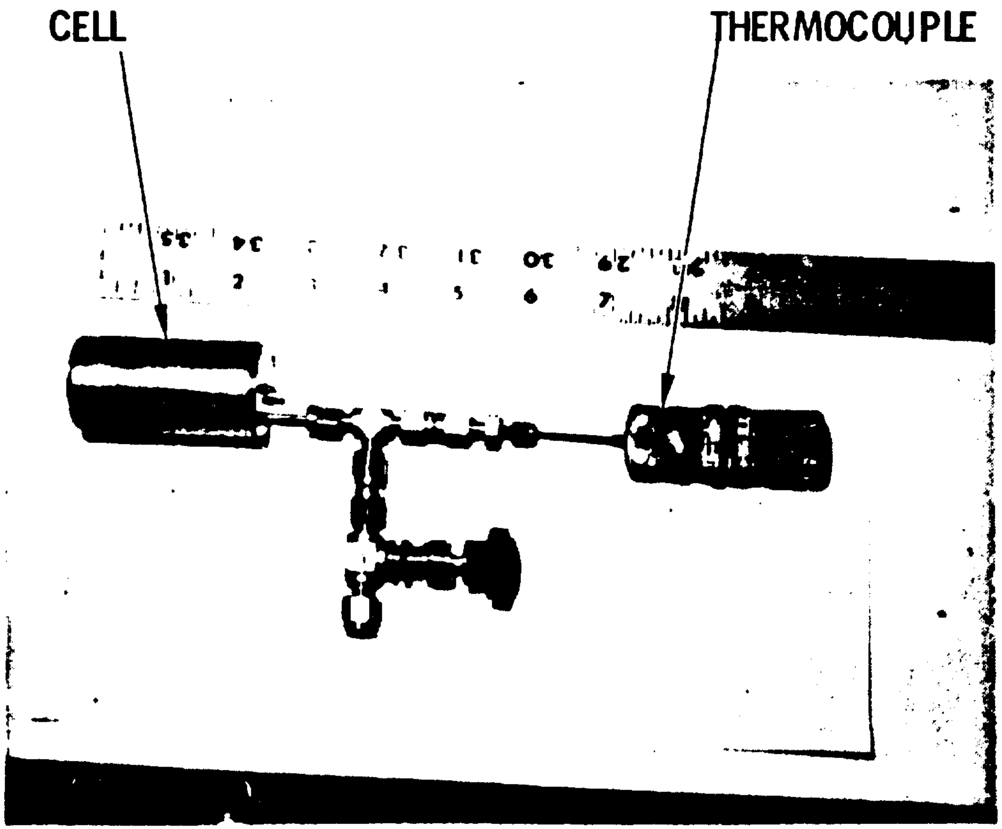


Figure 42. Primary Lithium Battery Task - Voltage Delay Experimentation



COMPONENT	SpHt Cp	WEIGHT gms
Li	0.95	3.7
SAB	0.17	7.6
SS GRIDS	0.12	2.8
GLASS SEP	0.20	0.5
$SOCl_2$	0.24	44.8
LiCl	0.28	1.3
$AlCl_3$	0.19	4.0
TFE	0.25	1.7
SUBTOTAL (STACK)		66.4
SS CASE + COVER		46.1
TOTAL		112.5

NOMINAL CAPACITY = 12.1 AH

THERMAL MASS
OF CELL = 22.71 Cal/°C

ANODE: 6-1/2" x 1-3/4"
CATHODE: 8-1/2" x 1-3/4"
x 0.080"

Figure 43. Experimental Li-$SOCl_2$ "D" Cells

- GENERAL CASE

$$Q = I\,(E_{OC} - E_{op}) - I\,T\,\frac{dE_{OC}}{dT}$$

WHERE: Q = HEAT, WATTS

E_{OC} = OPEN CIRCUIT VOLTAGE, VOLTS

E_{op} = OPERATING VOLTAGE, VOLTS

I = CURRENT, AMPS

T = ABSOLUTE TEMP, °K

$\frac{dE_{OC}}{dT}$ = CHANGE IN E_{OC} WITH T, VOLTS/°K

- FOR $Li\text{-}SOCl_2$ CELLS AT 20°C

$$Q = I\,(3.65 - E_{op}) - I\,(0.316)$$

Figure 44. Theoretical Heat Generation Rates

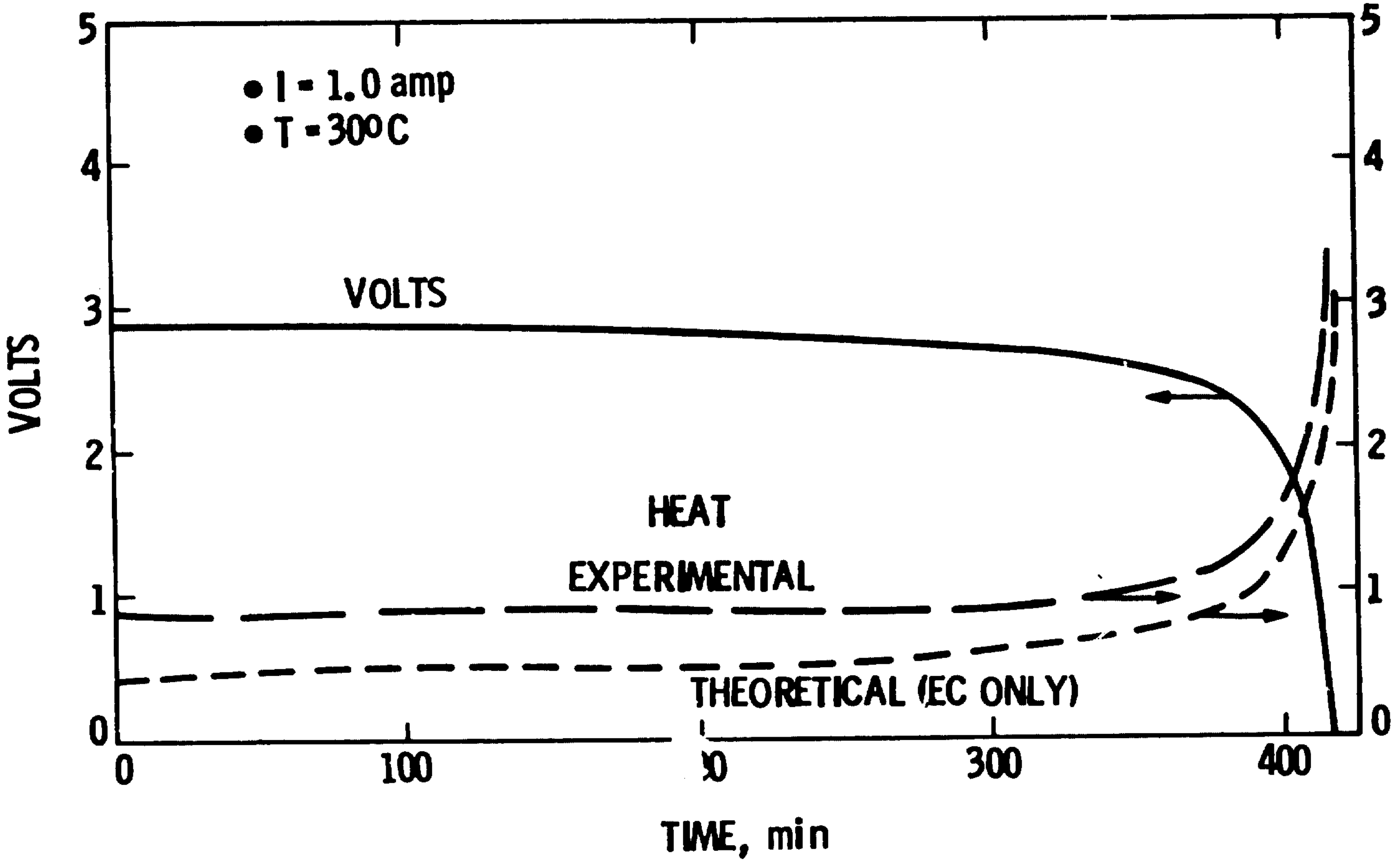


Figure 45. Heat Generation During Constant Current Discharge of "D" Size $Li-SOCl_2$ Cell at 1.0 amp

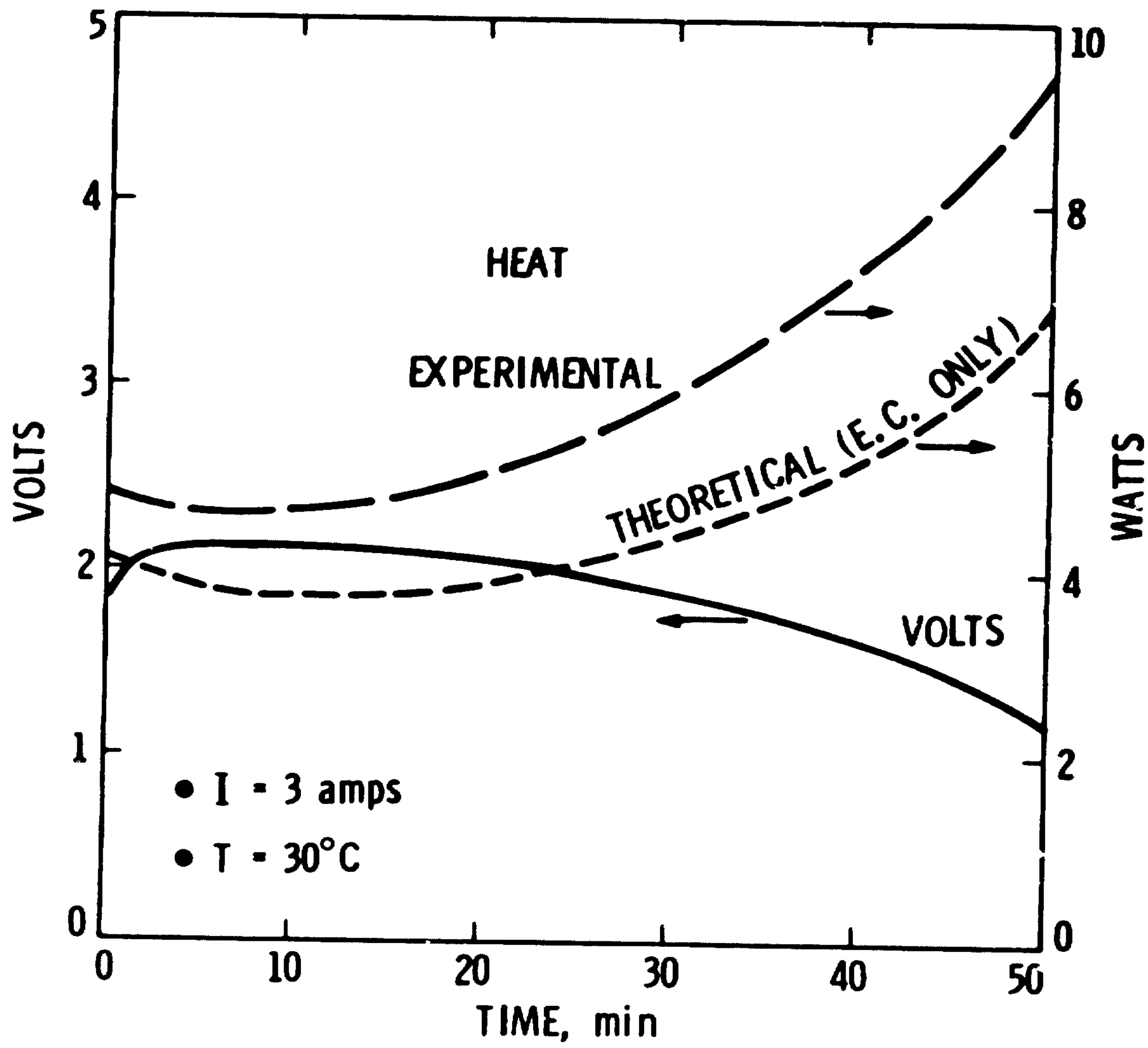


Figure 46. Heat Generation During Constant Current Discharge of "D" Size $Li\text{-}SOCl_2$ Cell at 3 amps

$$Q = (3.7 - E_{op})I$$

WHERE:

Q = HEAT, WATTS

E_{op} = OPERATING VOLTAGE, VOLTS

I = CURRENT, AMPS

Figure 47. Simplified Empirical Equation for Predicting Heat Generation Rates in Li-$SOCl_2$ Cells

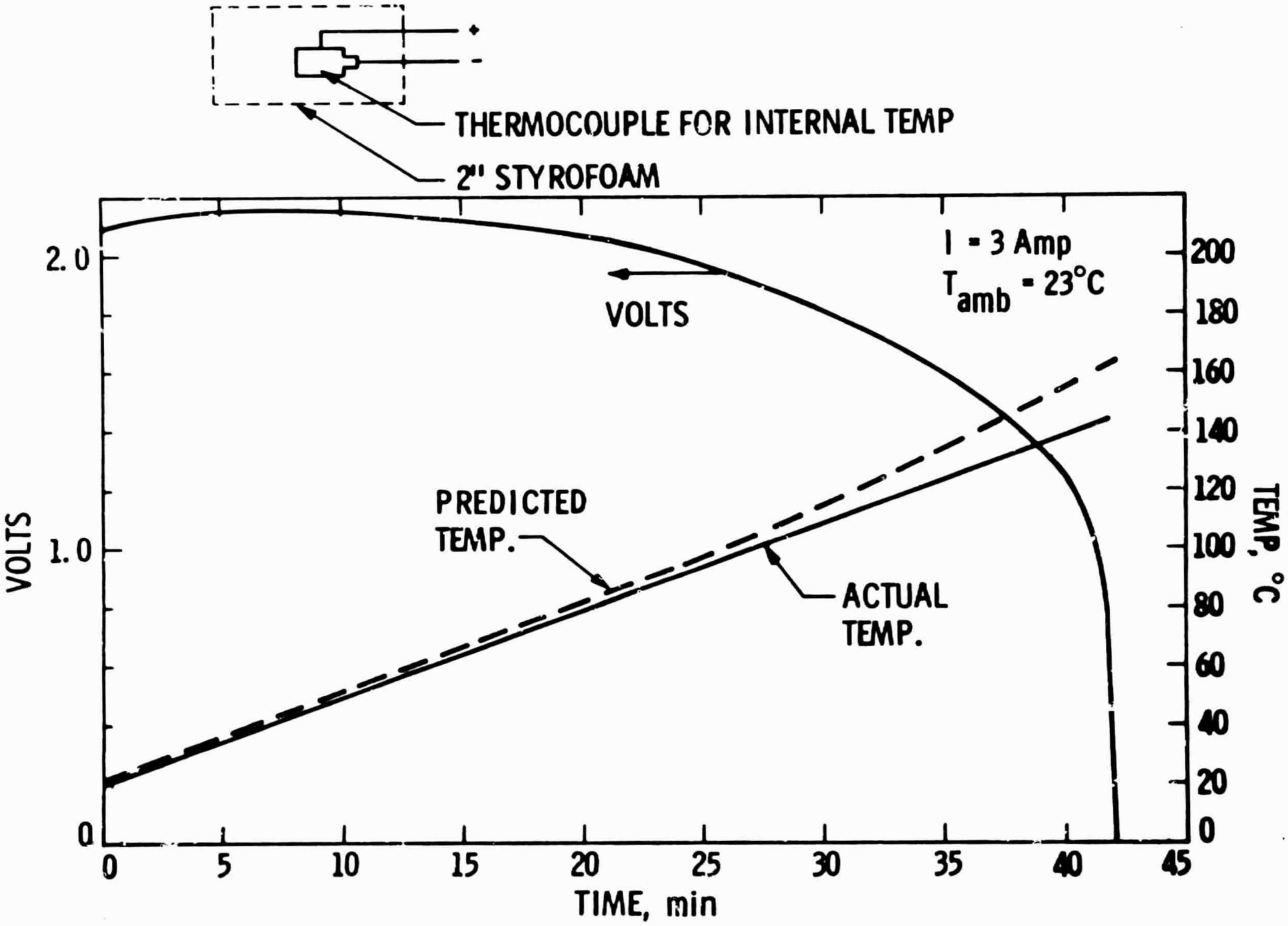


Figure 48. Constant Current Discharge of Li-$SOCl_2$ "D" Cell at 3 amps Under Near Adiabatic Conditions

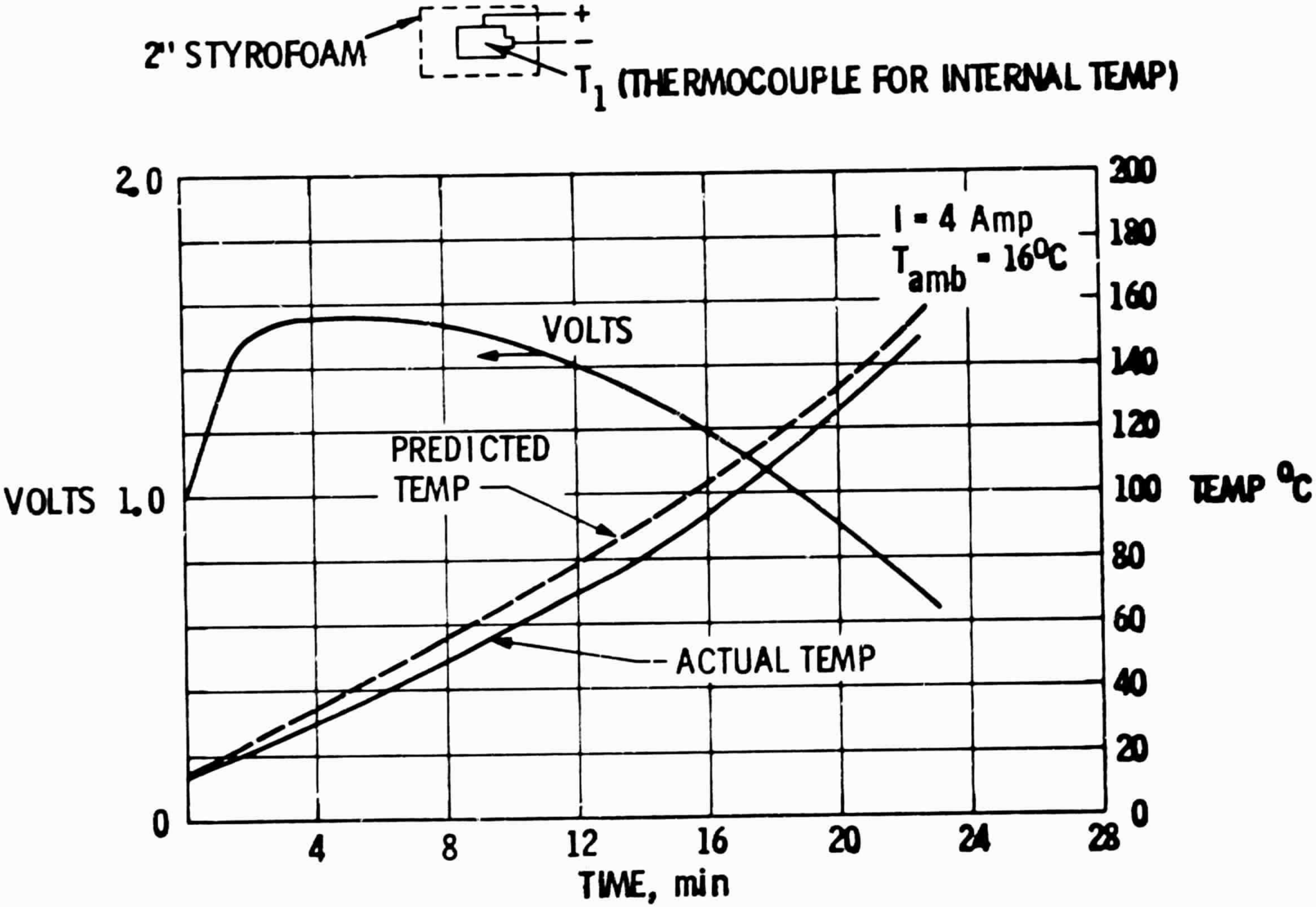
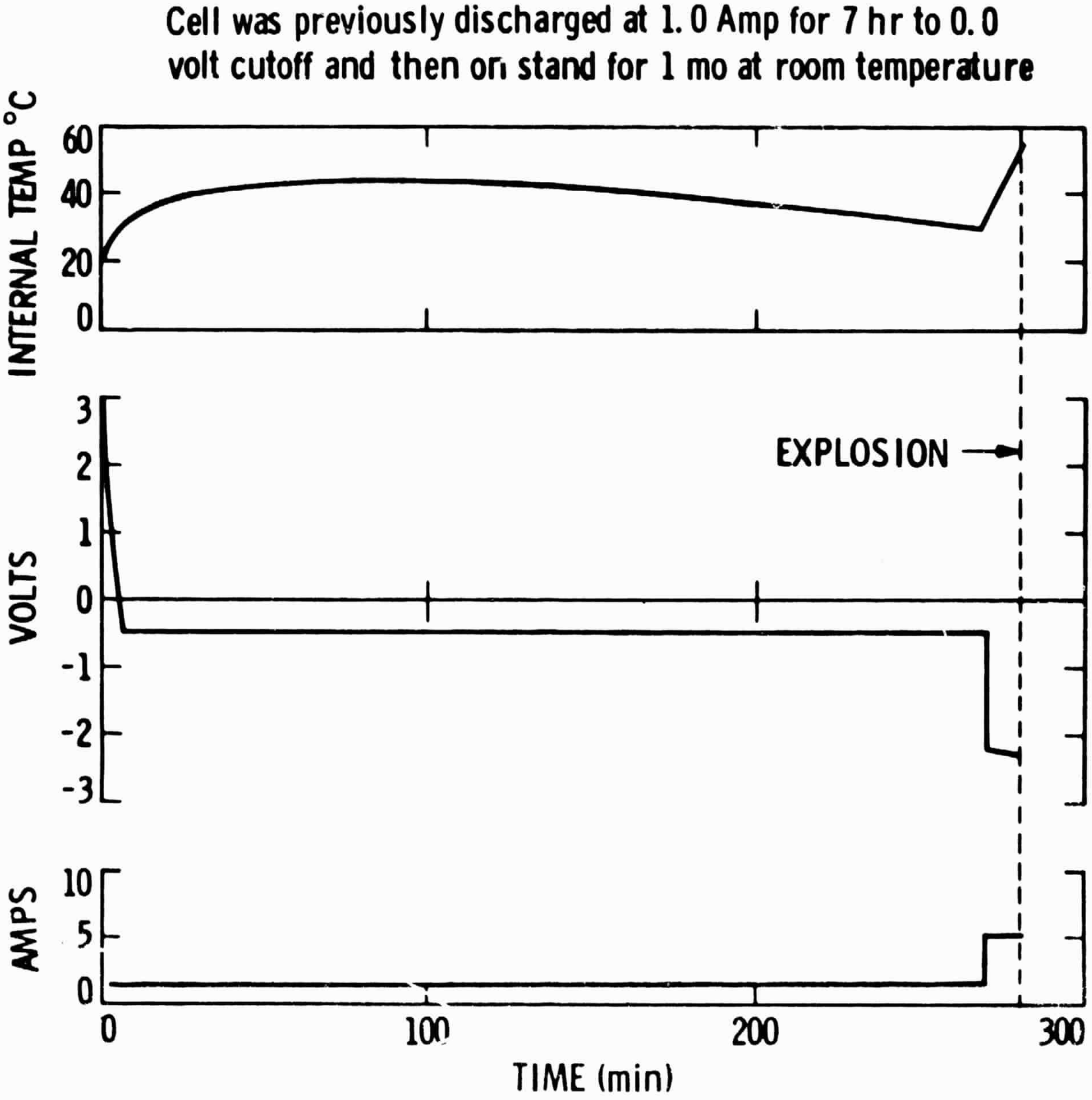


Figure 49. Constant Current Discharge of $Li\text{-}SOCl_2$ "D" Cell at 4 amps Under Near Adiabatic Conditions



Cell was previously discharged at 1.0 Amp for 7 hr to 0.0 volt cutoff and then on stand for 1 mo at room temperature

Figure 50. Forced Overdischarge of $Li-SOCl_2$ "D" Cell

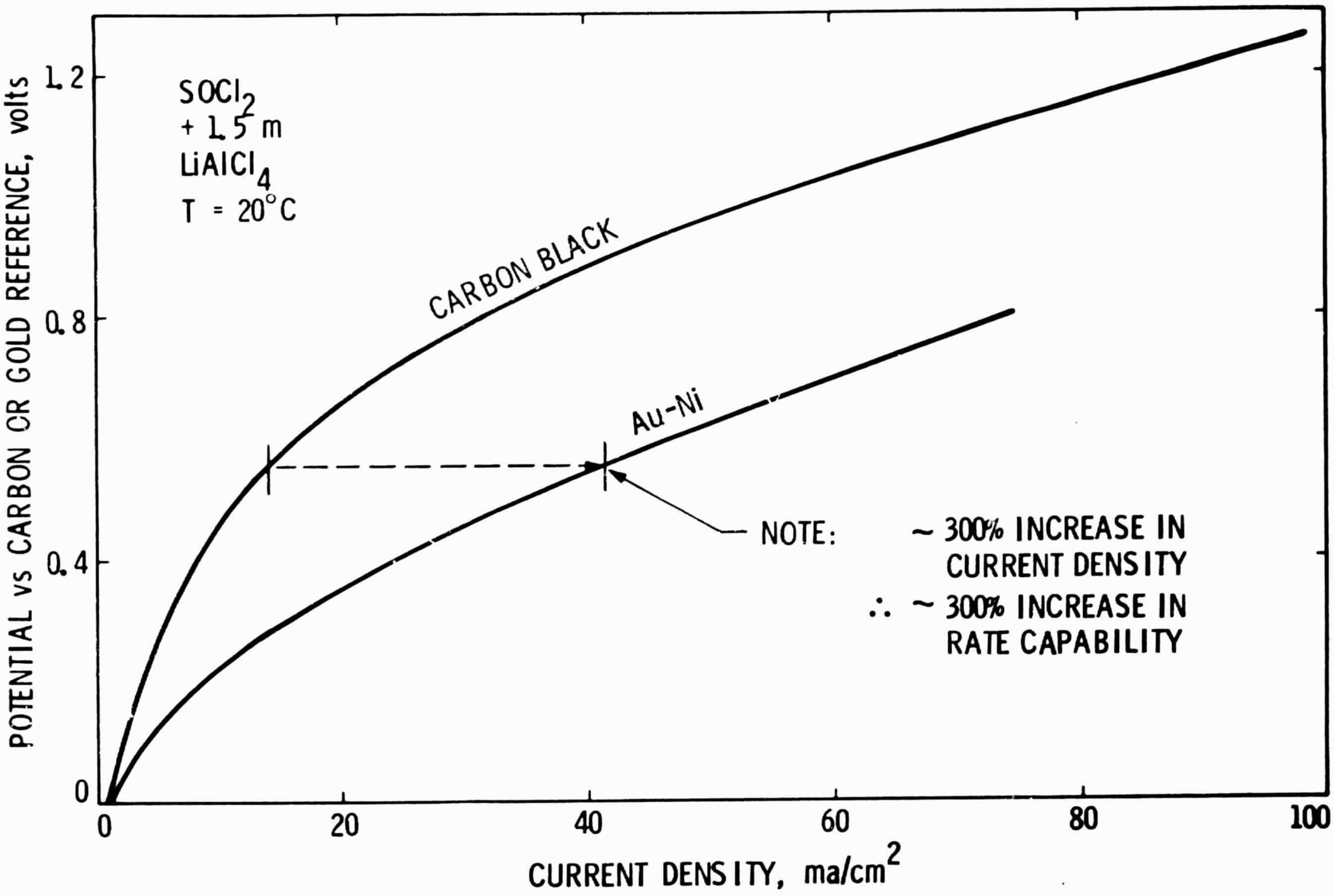


Figure 51. Primary Lithium Battery Task - High Rate Cathodes
Gold Plated Porous Nickel Cathode

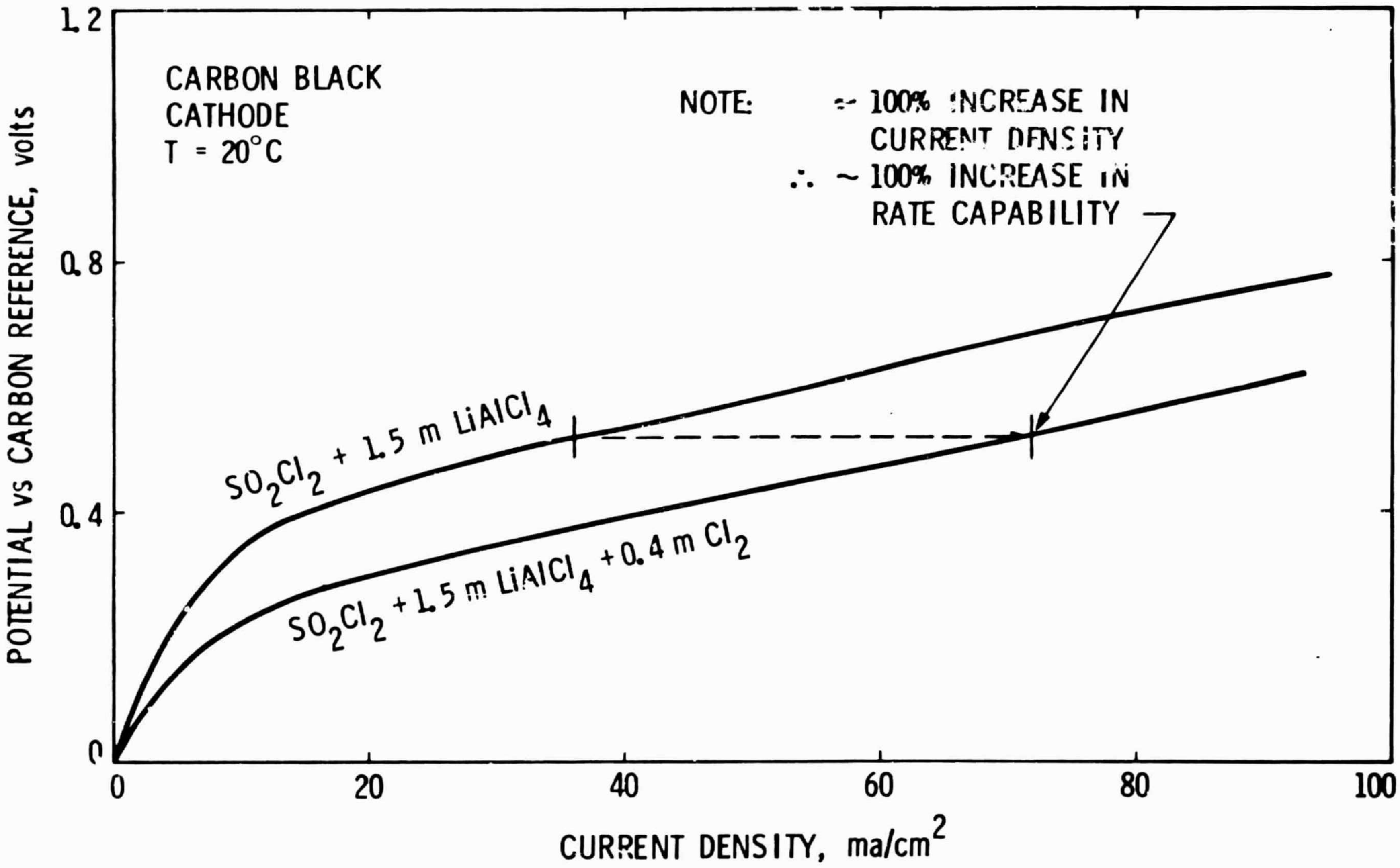


Figure 52. Primary Lithium Battery Task - High Rate Cathodes Addition of Cl_2 to SO_2Cl_2