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JAN 71 F GOEBEL, R MCDONALD, G YOUNGER F33615-77-C-2021
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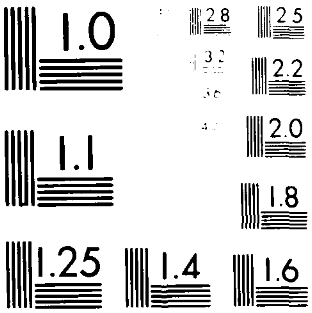

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LITHIUM INORGANIC ELECTROLYTE BATTERY DEVELOPMENT

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GTE PRODUCTS CORPORATION
Sylvania Systems Group
Strategic Systems Division
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January 1981

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Final Report for Period June 1977 to September 1980

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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This effort encompassed experiments, development, experimental cell/battery fabrication in sizes from 5AH to 10,000AH capacity, and testing in sufficient depth and detail to make significant progress toward the objective of providing safe and reliable Lithium Inorganic Electrolyte Primary Battery Technology.

Data is presented on storage degradation abnormal cell operation performance at low temperatures passivation, hazards analyses and Deactivation/Disposal.

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Each of these categories is discussed in its own section in the report.

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1.0 INTRODUCTION

This contract effort (under Air Force Contract No. F33615-77-C-2021) encompassed experiments, development, experimental cell/battery fabrication, and testing in sufficient depth and detail to make significant progress toward the objective of providing safe and reliable lithium inorganic electrolyte primary battery technology.

Investigations were made into Storage Degradation, Abnormal Cell Operation, Performance at Low Temperatures, Passivation, Preliminary Hazard Analysis, and Deactivation and Disposal. Each of these categories is discussed in its own section of this report.

This final report details the various investigations made, results obtained, and conclusions drawn. Program recommendations made in Section 8.0 of this report include a follow-on program to continue the development of the Half-C cell, leading to its qualification.

2.0 STORAGE DEGRADATION

2.1 INTRODUCTION

For the purposes of this study of Li/SOCl cells, capacity is defined as the number of ampere-hours delivered by a cell of DD bobbin design at 3.0 volts. Thus, cells that run marginally near or below 3.0 volts are considered to have low capacity, even though substantial capacity remains at lower voltage.

The purpose of these tests was to determine the effect of long-term storage and elevated temperature on capacity retention in $Li/SOCl_2$ cells, both cathode-limited and anode-limited.

2.2 EXPERIMENTAL

Electrolyte was prepared in the usual way with attention given to minimizing traces of metals, organics, and hydrolysis products. Special electrolytes prepared to minimize voltage are described in subsection 5.2.

The cells used for these tests were standard DD bobbin cells with sufficient lithium to produce either anode- or cathode-limited behavior. Three cells were tested at each combination of storage temperature and time. Data collection methods and instrumentation are given in subsection 5.2.

2.3 RESULTS

The baseline capacities for these DD cells are 9.4 and 28.7 Ah for the anode and cathode limited cell respectively, down to the 3.0-volt cutoff. These represent averages of 20 cell discharges each.

Figures 1 and 2 show capacity loss for lithium-limited and cathode-limited DD cells, respectively. After 35 weeks of room temperature storage, this type of cell has lost three to five percent capacity. However, this high loss rate is not expected to continue in a linear fashion over longer periods. Microcolorimetric data on small cells indicate that lithium corrosion rapidly decreases in the first three months of cell life.

Figure 1 shows a 50-percent capacity loss in lithium-limited DD cells after only eight weeks of storage at 55°C. Figure 2 shows a 50-percent decrease in capacity for cathode-limited cells under the same circumstances

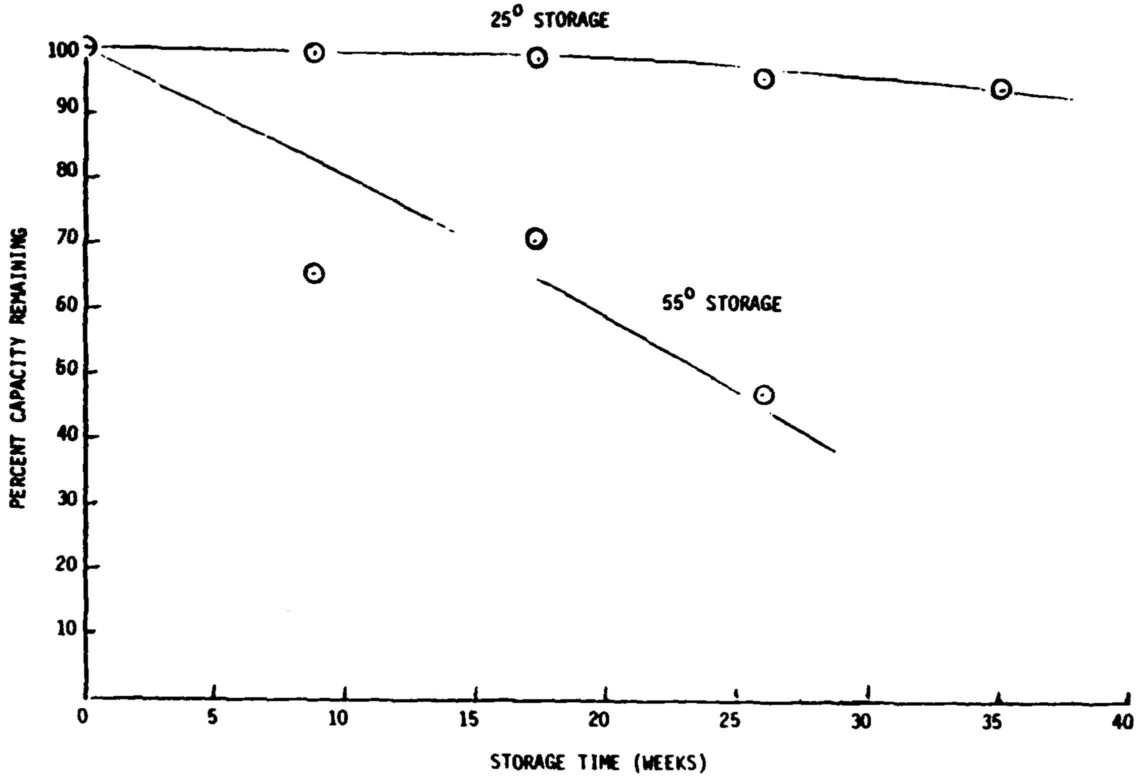


Figure 1. Capacity Loss in Lithium-Limited DD Cells After Storage at 55°C

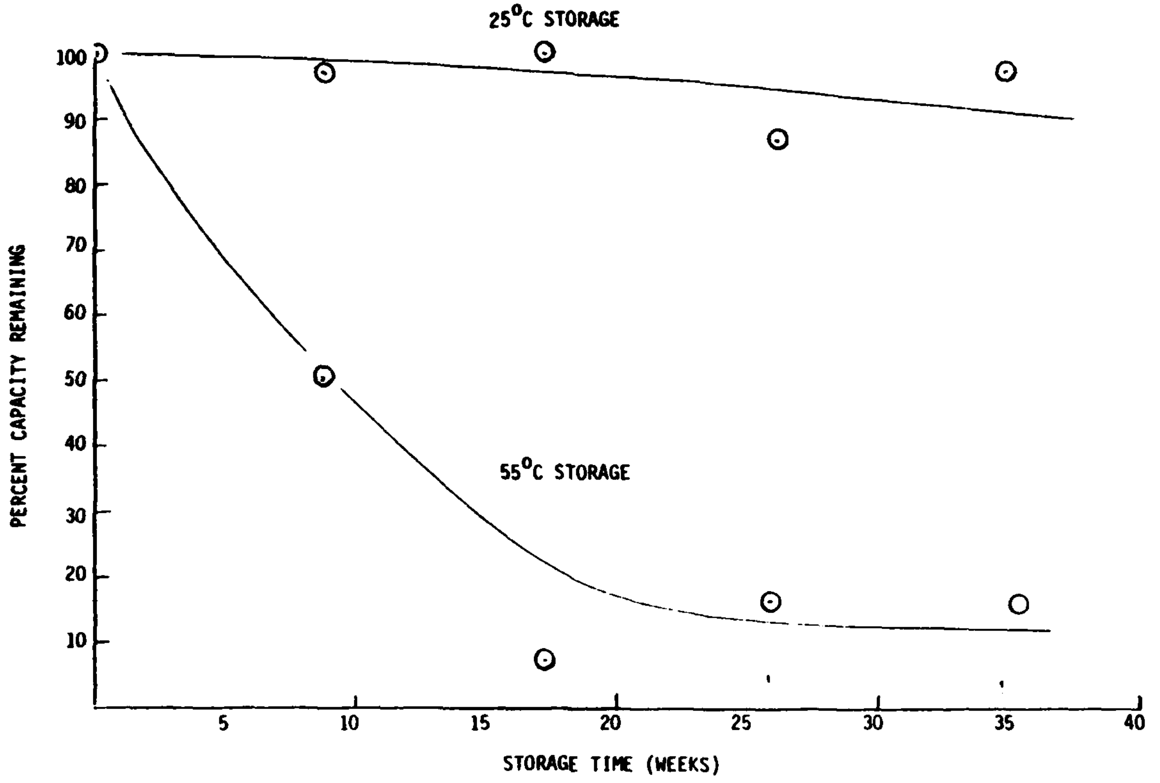


Figure 2. Capacity Loss in Cathode-Limited DD Cells After Storage at 55°C

after 24 weeks. Since an almost five-fold excess of lithium is used in cathode-limited cells, no capacity loss is expected if only lithium corrosion were responsible. Two explanations are offered for this phenomenon.

It is now known that one of the separator paper binders currently used (polyvinyl alcohol) reacts over extended periods with electrolyte. The products of this reaction may increase the resistance of the separator paper, causing the cells to run at lower voltage and to reach the 3.0-volt cutoff prematurely. The second mechanism involves the recrystallization of LiCl in cathode pores from the surface of lithium. It is known that the LiCl film on lithium grows at elevated temperatures due to recrystallization and crystal growth. The $LiAlCl_4$ salt in the electrolyte provides the medium for this process. Thus, LiCl may be continually dissolving at the anode and redepositing at the cathode.

The effect of the voltage delay additives on capacity retention of lithium-limited cells for various 55°C storage times is shown in Figure 3. The calcium and sulfur dioxide additives only deteriorate high-temperature capacity retention, both in SO_2Cl_2 and $SOCl_2$ solvents. However, the 1.8M $LiAlCl_4$ in SO_2Cl_2 showed remarkably good capacity retention up to 22 weeks at 55°C. This finding is of interest since it was felt previously that chlorine from SO_2Cl_2 decomposition

$$SO_2Cl \rightleftharpoons SO_2 + Cl_2$$

would quickly consume all lithium. Chlorine gas does consume lithium when bubbled through $SOCl_2$. Evidently, either the SO_2Cl_2 decomposition is not extensive, or the SO_2Cl_2-formed passive film is impermeable to the chlorine formed.

2.4 CONCLUSIONS AND RECOMMENDATIONS

There are several promising directions to explore in improving high-temperature storability through chemical means. SO_2Cl_2 and So_2Cl_2/$SOCl_2$ mixed electrolytes should be tested further. Lowering the $LiAlCl_4$ concentration will decrease SO_2 solubility and conductivity but may significantly decrease capacity loss on storage by decreasing LiCl recrystallization on the anode and possibly in the cathode.

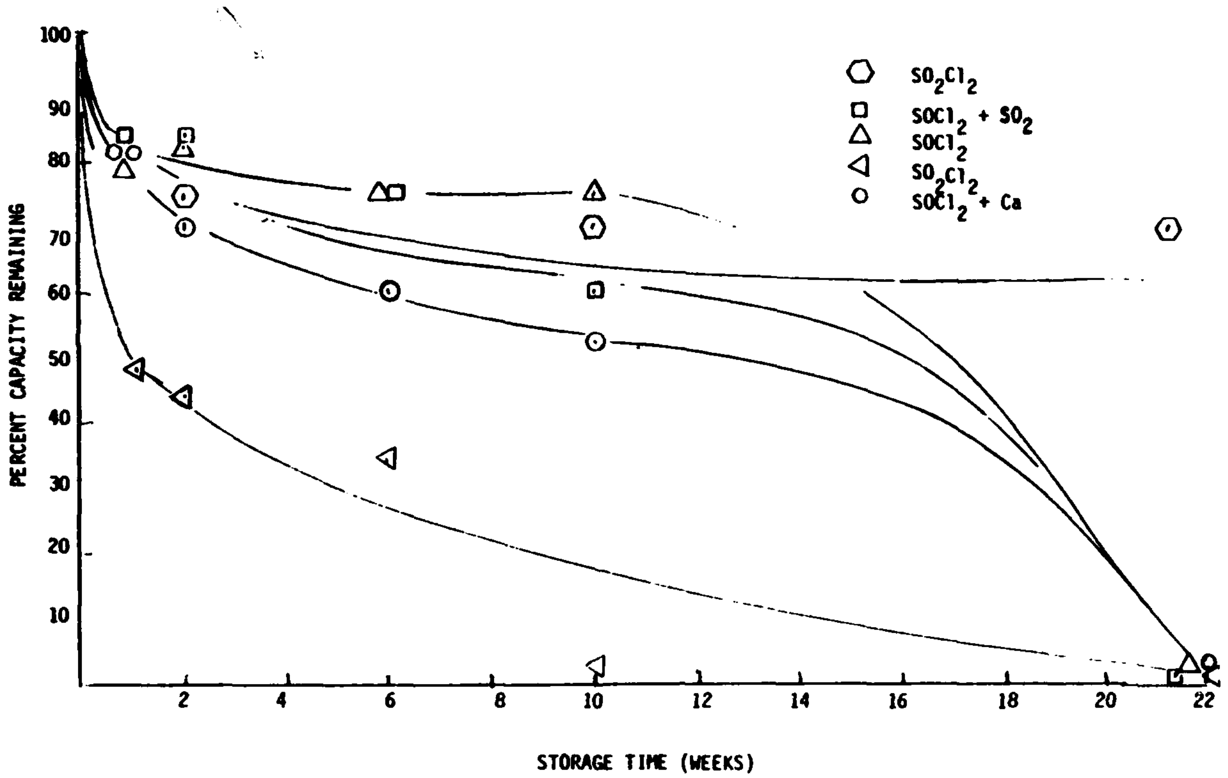


Figure 3. Capacity Loss of Lithium-Limited D Cells After Storage at 55°C

3.0 ABNORMAL CELL OPERATION

Investigations were made by conducting abuse/environmental tests and deactivation/disposal on both cylindrical and prismatic cells. Tests were conducted on cylindrical D and DD cells and on prismatic 2,000 and 10,000 ampere-hour cells. These tests are summarized in this report with the results realized.

Detailed test reports on both types of cells have been previously submitted under this contract. GTE Sylvania Document Number 00-1319104 dated 18 October 1978, covers cylindrical cell tests. GTE Sylvania Document Number 00-1319105, dated 8 May 1979, covers prismatic cell tests.

3.1 CYLINDRICAL CELLS

The 13 different environmental and abuse tests conducted on cylindrical cells were:

a. Discharge to 3.0 V cutoff
b. Salt immersion
c. Discharge at excessive rates
d. Abusive charging
e. Puncture
f. Crush
g. Overheating
h. Drop
i. Vibration (bounce)
j. Shock
k. Incineration
l. Thermal shock
m. Deactivation and disposal

3.1.1 Discharge to 3.0 V Cutoff

Twenty-four cells were discharged at the rate of $1 mA/cm^2$ to the 3.0 V cutoff line. Connectivity for discharge is shown in Figure 4. The group included the following types of cells:

a. 12 each of the standard size D cells, lithium-limited (LL)
b. 5 each of the double D size cells, lithium-limited (LL)
c. 7 each of the standard size D cells, carbon-limited (CL)

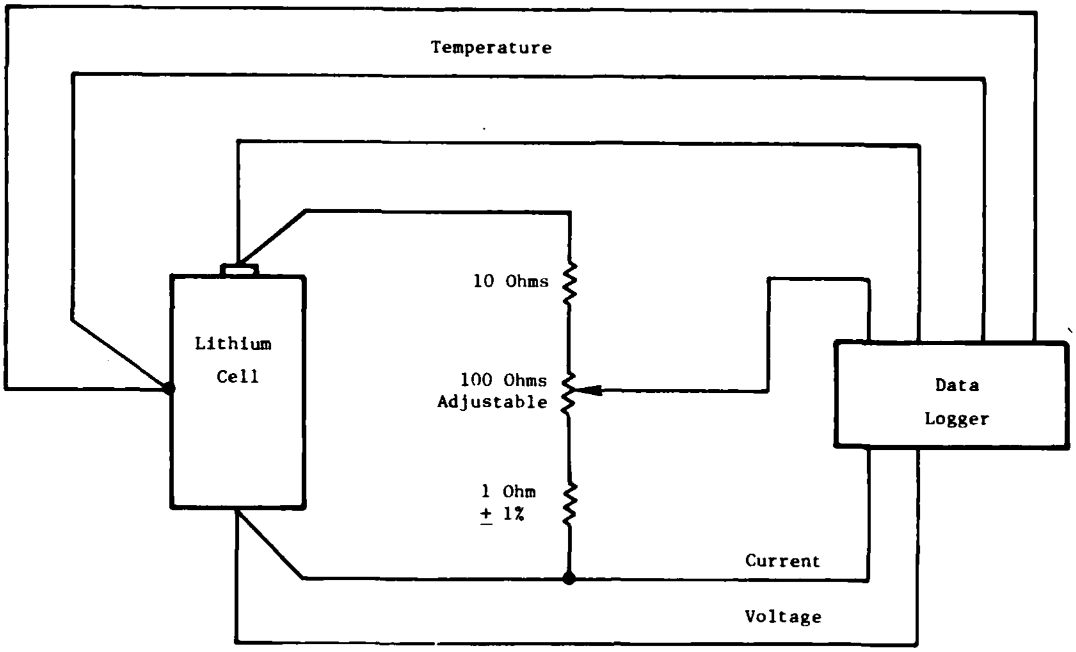


Figure 4. Discharge to Cutoff Connectivity

The average capacity obtained from lithium-limited D cells was 4.75 Ah, with the high and low values being 5.67 Ah and 4.42 Ah, respectively. The theoretical capacity of these cells, based on the amount of lithium used, was 4.4.2 Ah with the possible variation of ± 5 percent from one cell to another, due to nonuniformity in the thickness of lithium foil. The resultant average cell capacity, obtained to 3.0-V cutoff line, represents approximately 84 percent of the theoretical capacity of lithium present. Obviously, this figure would be different for different discharge rates applied, and also for different voltage cutoff lines. The total exhaustion of lithium, and therefore the theoretical capacity, could be reached only at diminishing discharge rates at the end of discharge and on discharge to approximate 0.5 V. The average capacity obtained with the five DD lithium-limited cells, relative to that obtained in standard D cells, could only be ascribed to a greater accuracy in cutting lithium.

The carbon-limited cells in the standard D-size delivered an average of 12.74 Ah, with the high and low values of 13.42 Ah and 11.49 Ah, respectively. The capacity obtained at lower discharge rate or to a lower cutoff line would have been significantly greater, since the cathode polarization is not so sudden as the disappearance of lithium in the anode-limited cells. The average capacity obtained with these cells under the present discharge conditions are considered very high. Table 1 summarizes the results obtained in this test.

TABLE 1

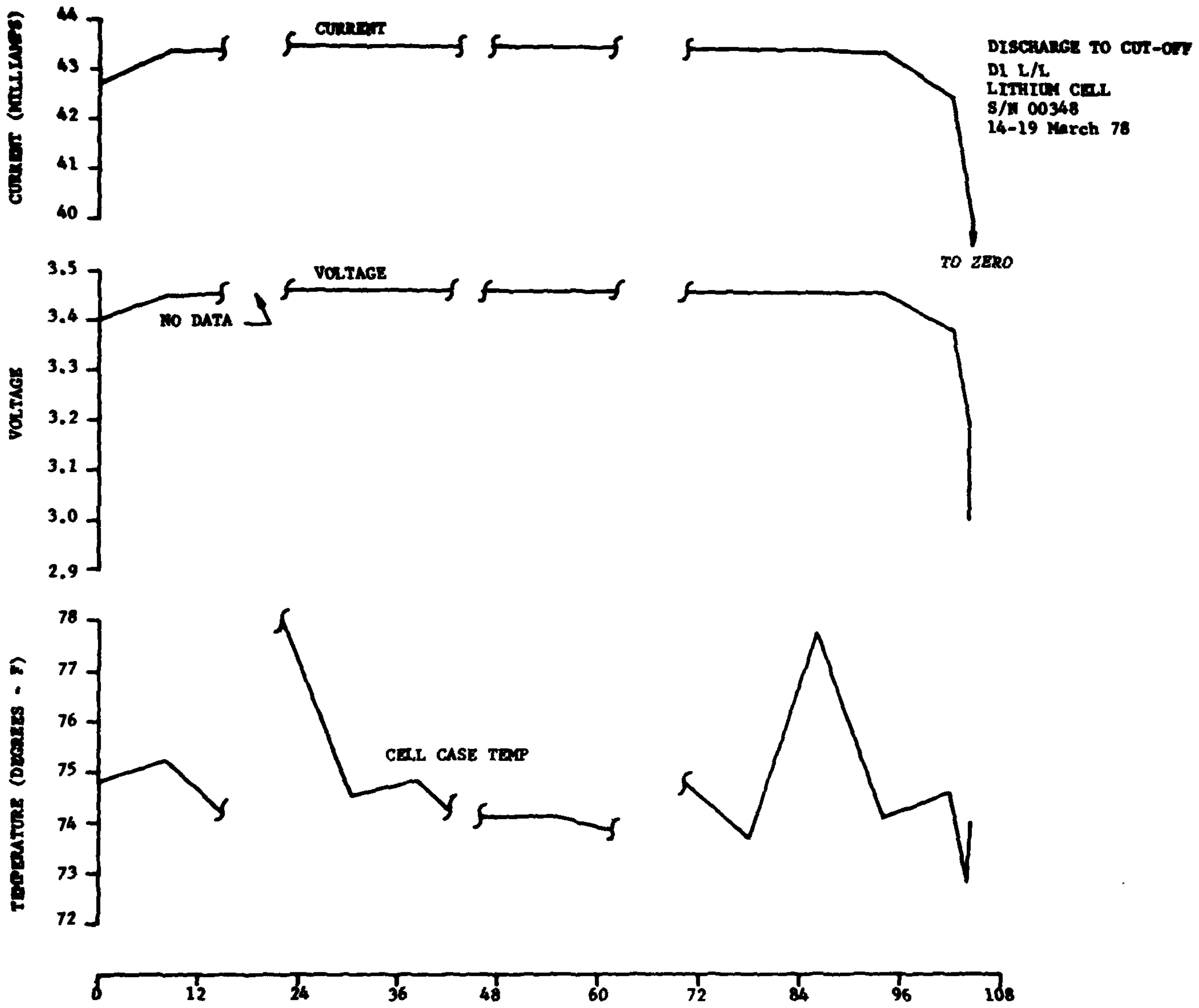
DISCHARGE CAPACITY

	Capacity at 1 mA/cm^2 to 3.0V(Ah)			
Type of Cell	High	Low	Average	2% Aver. Theor.
D,LL	5.67	4.42	4.75	84
DD,LL	10.12	9.45	9.66	92
D,CL	13.42	11.49	12.74	--

Discharge curves for typical lithium-limited and carbon-limited cells are shown in Figures 5 and 6, respectively.

3.1.2 Salt Immersion

One standard D size cell, lithium-limited, was subjected to the salt immersion test for 24 hours in three-percent sodium chloride solution. No leakage was observed from the cell during the test period. The change in the ph of the salt solution from 4 to 6 during the test cannot be ascribed to leakage (the change in case of leakage would have been in the opposite direction). The corrosion of the plus terminal must have been the result of an anode dissolution of the terminal material, caused by the electrolysis of the test solution by voltage of the cell itself. A further proof of the electrolytic process taking place outside the cell is the cell voltage drop to 3.44 V measured imediately after the test. The cell recovered to the full 0 CV of 3.66 V after cleaning, washing, and standing in the air to dry.



DISCHARGE TO CUT-OFF
D1 L/L
LITHIUM CELL
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Figure 5. Discharge to Cutoff - Lithium-Limited Cell

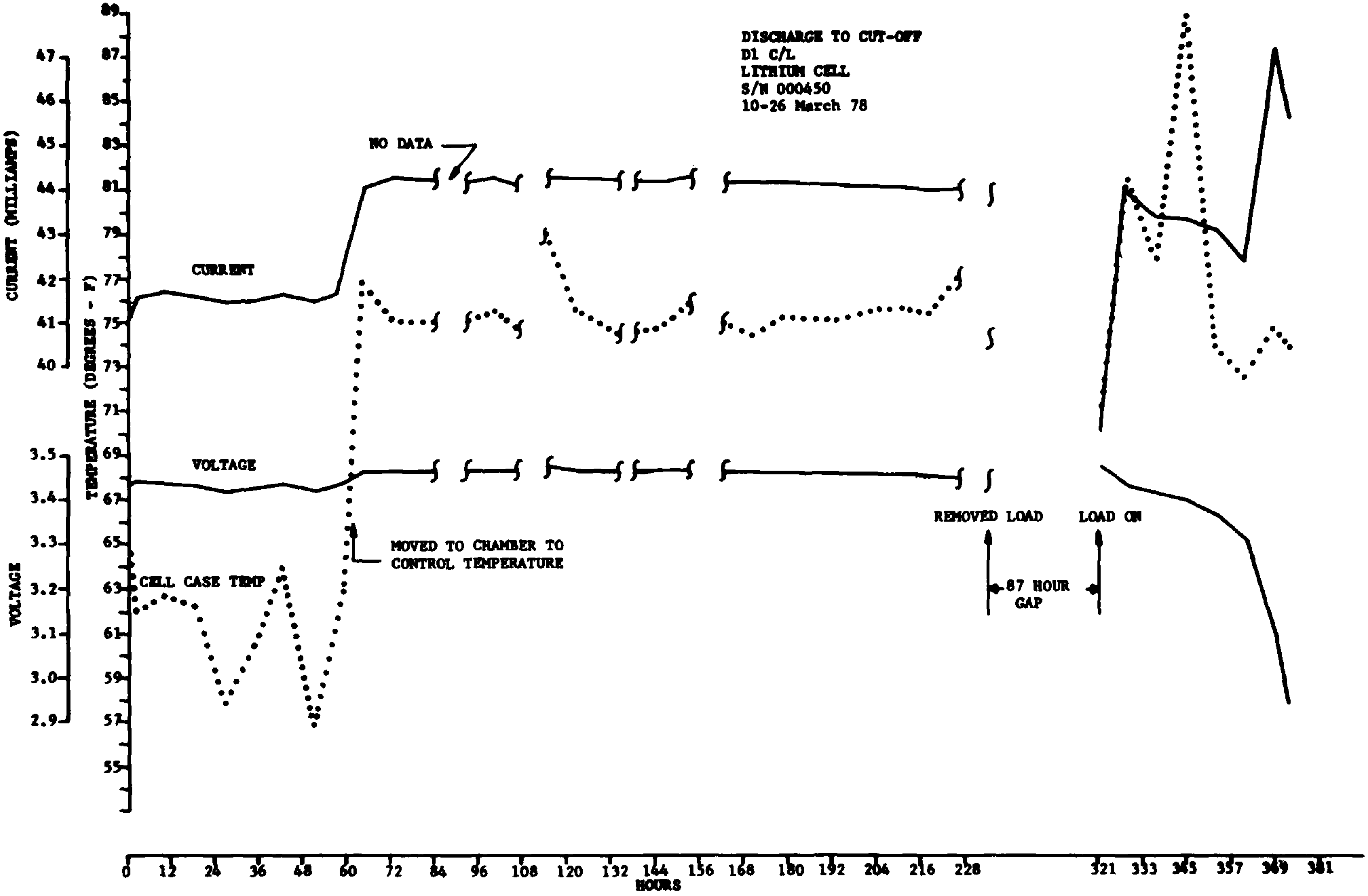

Figure 6. Discharge to Cutoff - Carbon-Limited Cell

3.1.3 Discharge at Excessive Rates

Eight standard-size D cells were subjected to an excessive discharge rate by shorting them through a 100-A, 50-mV shunt. Following is a list of types of cells used, in fresh and discharged states, one each at 25°C and 55°C:

a. 2 cells, D, LL, fresh
b. 2 cells, D, CL, fresh
c. 2 cells, D, LL, discharged
d. 2 cells, D, CL, discharged.

No venting, rupture, or explosion was observed during the tests with any of the eight cells, The maximum temperature of 106°C was achieved, seven to eight minutes from the beginning of discharge at the skin of the fresh cell, which was thermally equilibrated at 55°C in a closed test chamber prior to discharge. The maximum discharge current was 7 A after one minute of discharge for fresh cells. The values were lower for all cells that were tested in discharged states or at the temperature of the test chamber of 25°C. A slow decrease in the discharge current, accompanied by the drop in temperature, were observed after these maxima were passed .

3.1.4 Abusive Charging

Charging tests were performed on standard size D cells of the following types:

a. Constant current charging: 2 each, D, LL, fresh
   2 each, D, LL, discharged
b. Constant voltage charging: 2 each, D, LL, fresh
   2 each, D, LL, discharged.

Two different charging regimes were applied to both fresh and previously discharged cells, one at constant voltage of 4.1 V and the other at a constant current of 44 mA. The discharge current and the cell's case temperature were monitored during the constant current charging. The tests were carried out for several hours in each of the tests, i.e., until the cells reached stable conditions.

The charging of fresh cells under either of the two charging conditions (Figures 7 and 8) showed a slow increase in temperature of 0.5°C/hour. The

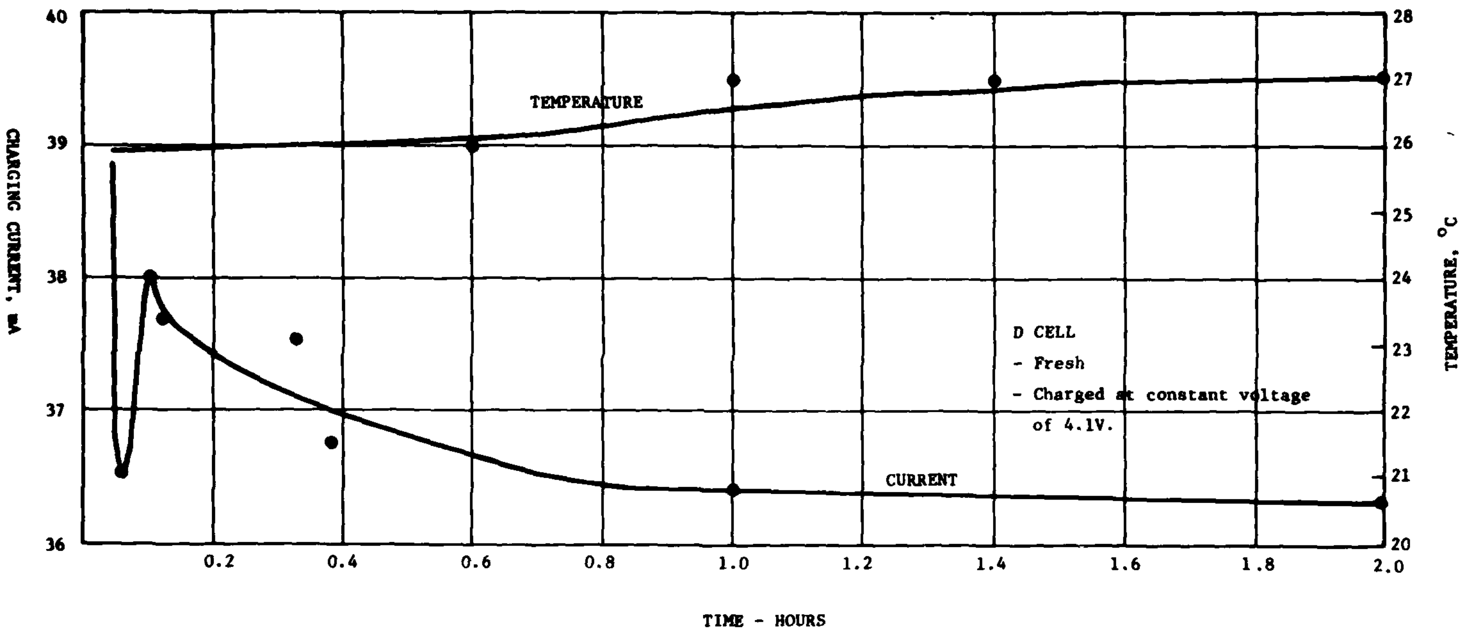

Figure 7. Constant Voltage Charging of Fresh Cell

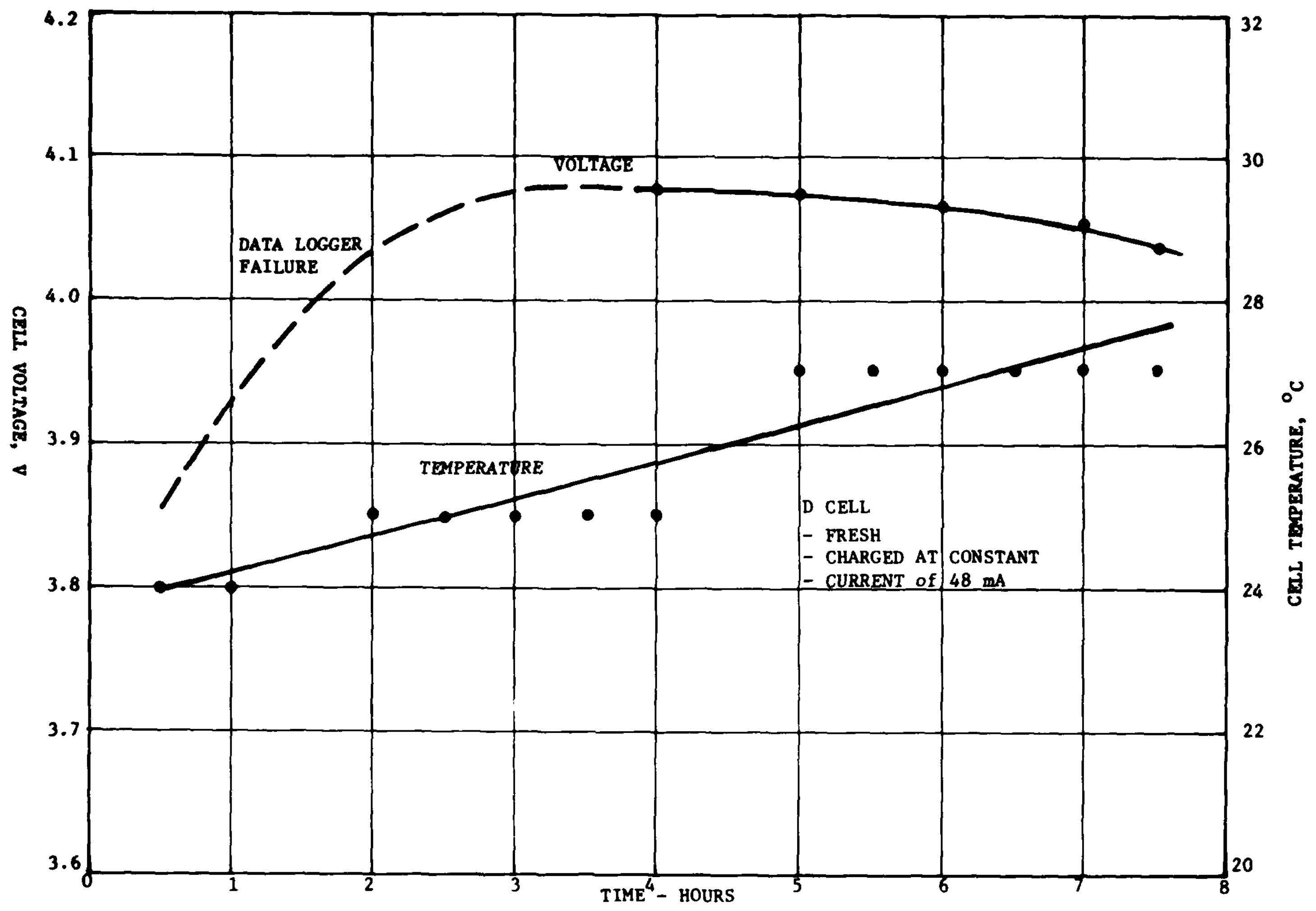

Figure 8. Constant Current Charging of Fresh Cell

two charging regimes did not differ significantly as far as the electric characteristics of cells are concerned. Under the constant voltage of 4.1 V, the high charging current over 100 mA decayed rapidly and stabilized below 20 mA, while under a constant current of 44 mA the charging voltage remained between 4.0 and 4.1 volts over a period of eight hours. A slight difference in the steady-state charging conditions, following the initial period, can be attributed to individual differences in the geometry of the cells, as related to the cell's ability to recombine the products of charging formed on the two electrodes. Of the two cells tested under each of the charging conditions, only one was represented in each of the diagrams, since there were no substantial differences in the behavior of the same type of cells tested under the same charging conditions. Charging of the discharged cells under each of the two charging conditions is shown in Figures 9 and 10, respectively.

The constant voltage charging of discharged cells showed much higher charging current than those observed in charging of the fresh cells, with a slight initial difference in the behavior of the two cells tested (Figure 6). As a result, the rate of temperature increase was much greater, amounting to 2°C per hour over a period of five hours. A slow leveling off in the temperature increase with time is probably influenced by both of two factors: the cooling rate and the reduction of the charging current. The constant current charging of discharged cells closely resembled the charging of fresh cells under the same conditions. A steady increase in the cell's case temperature of 0.5°C/hour was also observed with these cells.

No rupture, leakage, bulging, or explosion was experienced with any of the cells used in the course of the abusive charging test.

The experience gained in these tests agrees with the observations made during the charging tests with the 2,000-Ah rectangular cells, as well as with the observations reported by others (Honeywell, Mallory, Power Sources Conference, Atlantic City, NJ, June 1978). The tentative explanation is that the chlorine generated on the cathode and fresh lithium generated on the anode during charging combine quickly forming LiCL, so that the cumulative effect of charging is just the formation of heat within the cell, corresponding to the heat of reaction of chlorine and lithium, with some contribution of ohmic heating due to the internal impedance of the cell.

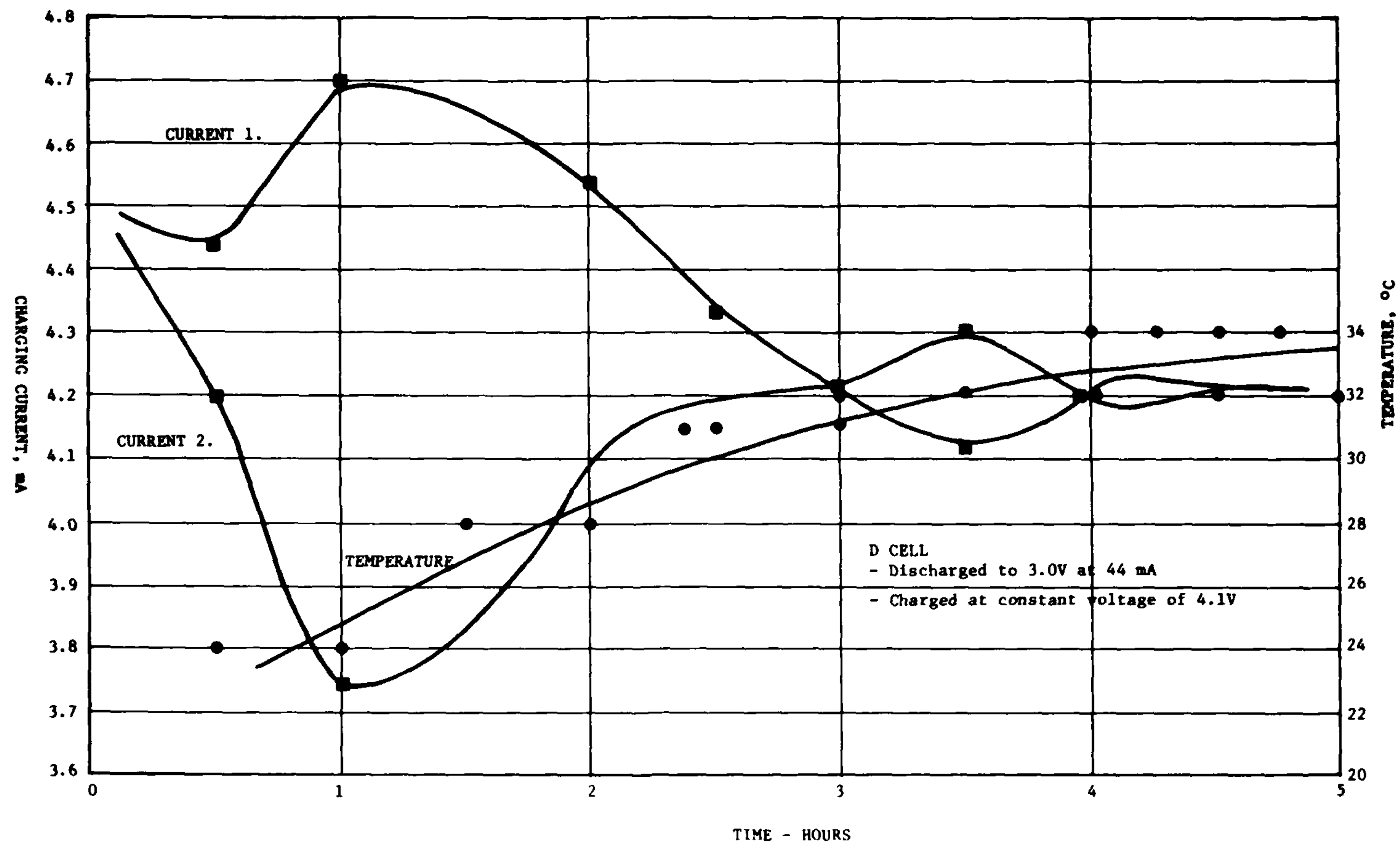

Figure 9. Constant Voltage Charging of Discharged Cell

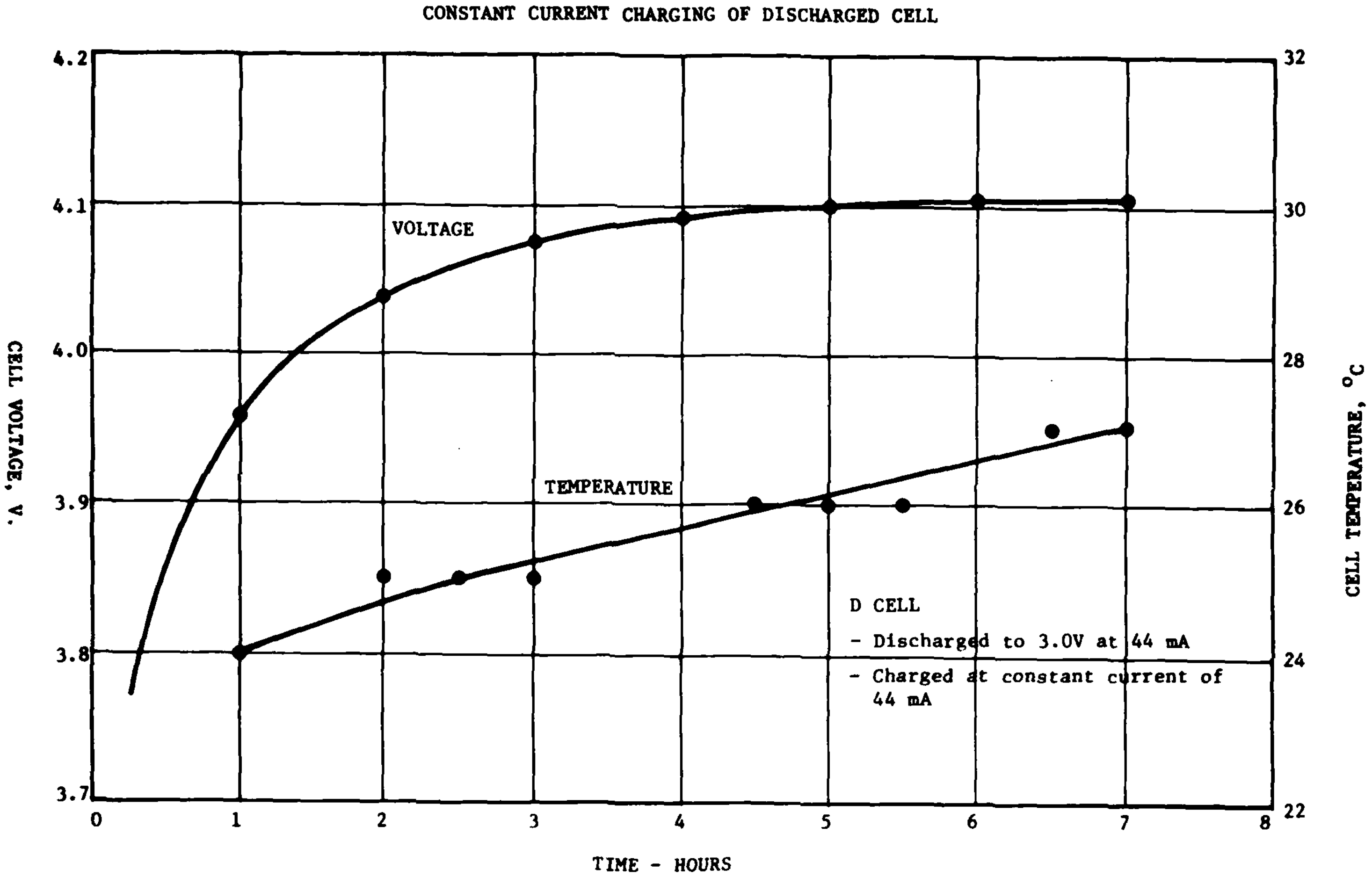
CONSTANT CURRENT CHARGING OF DISCHARGED CELL

Figure 10. Constant Current Charging of Discharged Cell

3.1.5 Puncture

Five cells of the following type and discharge status were subjected to a puncturing test:

a. 1 each, fresh, D, CL, room temperature
D, LL, room temperature
b. 1 each, discharged D, CL
D, LL
DD,LL

The cells were punctured with an electric drill perpendicular to the side, 1/4-inch deep, or until short circuited. No venting, rupture, or explosion was observed. The maximum cell case temperature was 75°C for a fresh DD cell punctured at the ambient temperature of 15°C, 20 minutes after the puncture. Lithium-limited cells discharged at 1 mA/cm^2 to 3.0-V cutoff showed only one to two degrees C increase in temperature, four to five minutes after puncture. The carbon-limited cells, discharged under the same conditions, showed an increase in temperature of 10 to 12 degrees C, 10 to 15 minutes after puncture. Figures 11 and 12 show the discharge characteristics of discharged and fresh lithium-limited cells.

3.1.6 Crush

Three cells were subjected to a crush test, one each of the following:

a. D, CL discharged
b. D, LL, discharged
c. D, LL, fresh.

No venting or explosion was observed. The cells were crushed by pressing the middle of the can sideways until an internal short circuit was developed. The fresh cell developed the internal short circuit one minute after the beginning of the test and under the force of 900 pounds, as indicted by a sudden drop in voltage. The beginning of an increase in the cell temperature of 55°C was reached 16 minutes from the beginning of the test. The discharged cells did not develop short circuit upon crushing and did not show any increase in temperature. Upon rupture under the crushing force (in the area of the glass seal), a light white vapor was observed, probably originating from the hydrolysis of the $SOCl_2$ vapors in contact with humid air.

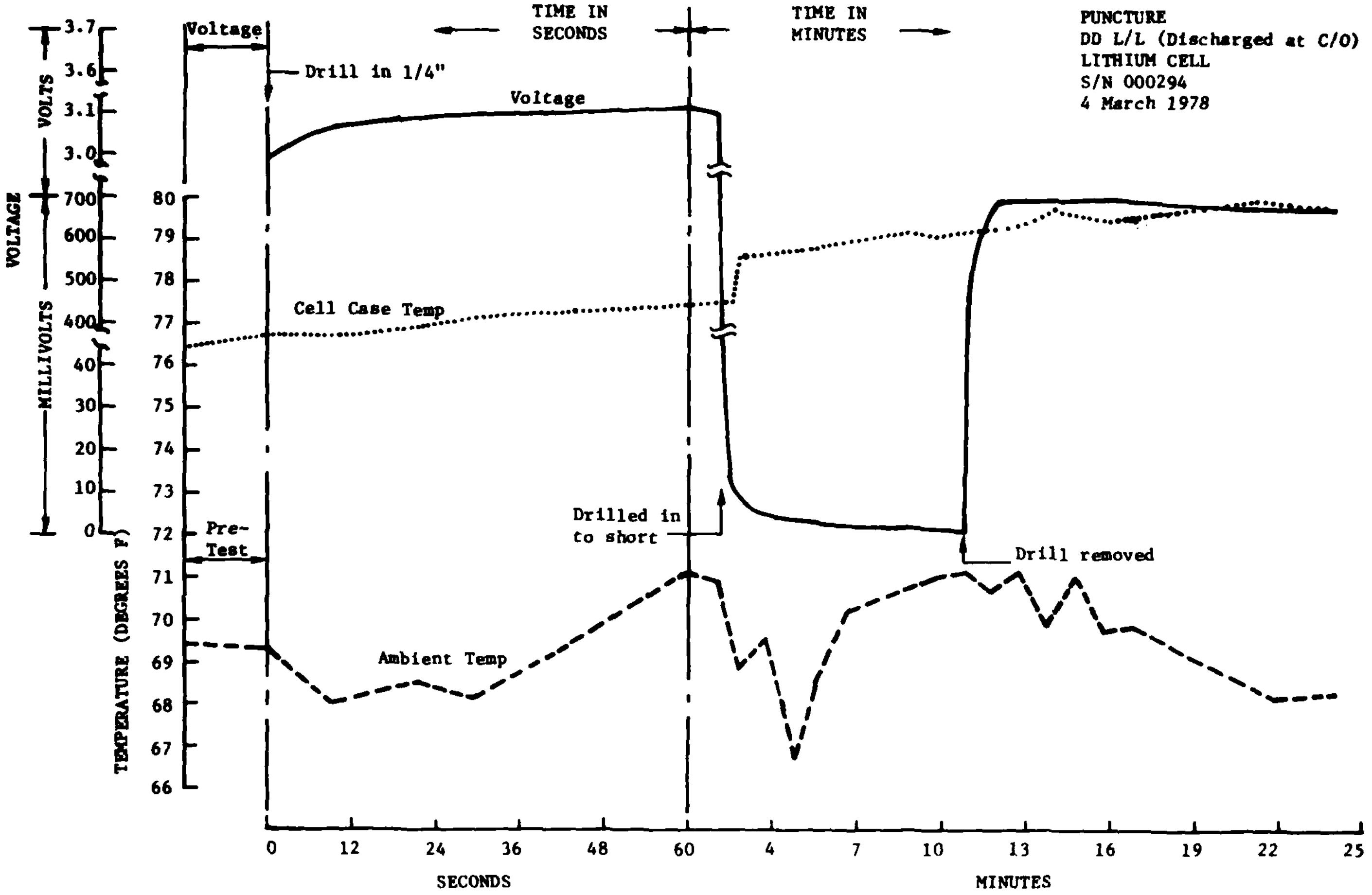

Figure 11. Discharge Characteristics - Discharged Lithium Cell

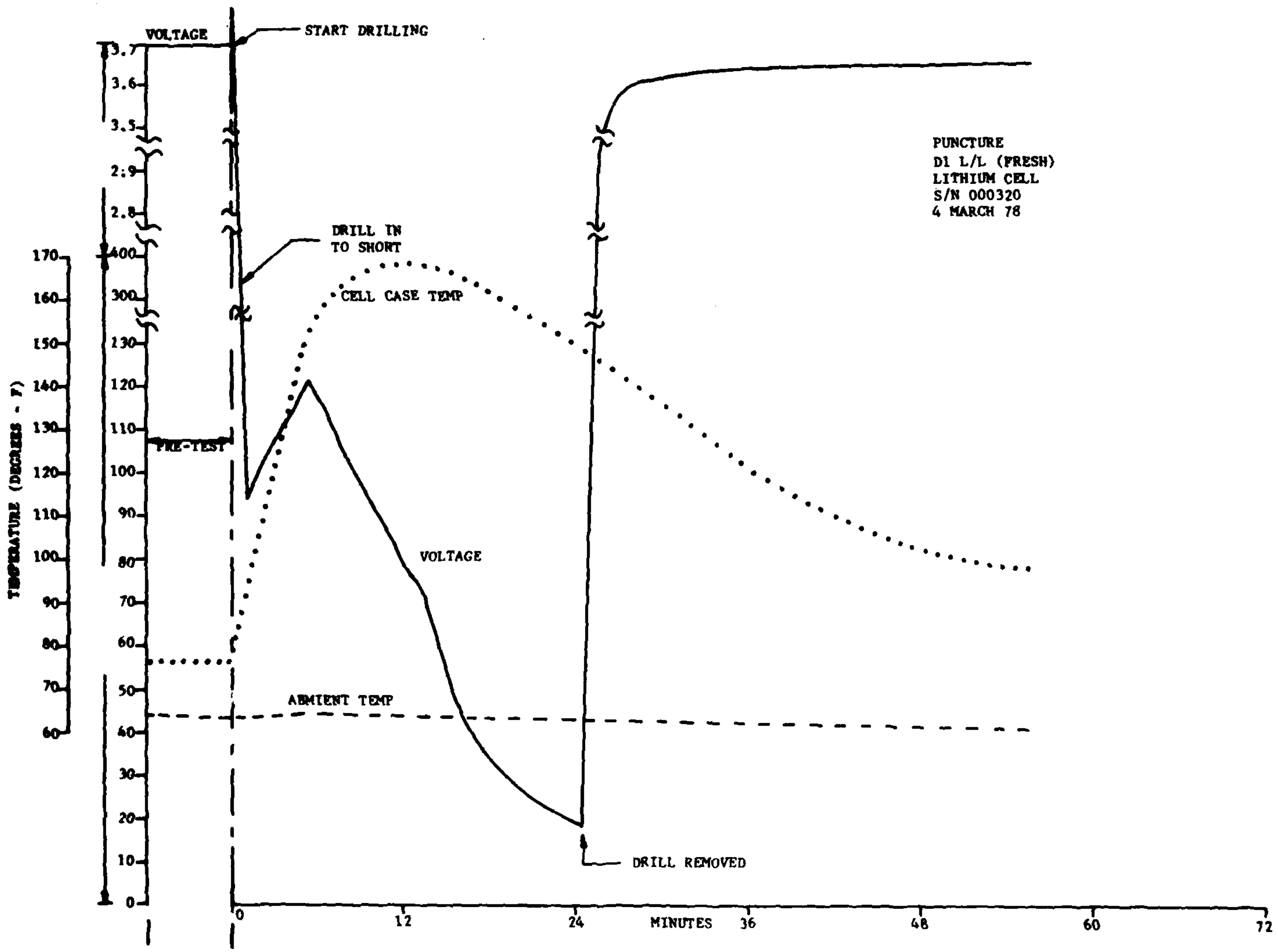

Figure 12. Discharge Characteristics - Fresh Lithium Cell

3.1.7 Overheating

Five cells were subjected to the overheating test in an oil bath placed on the hot plate. Following were the types of cells used in the test.

a. 1 each, fresh D,LL and DD,LL

b. 1 each, discharged D,CL; DD,LL; and D,LL

The overheating test was performed by dropping the cell into preheated oil (115°C) and maintaining the same oil temperature for one hour. Both fresh cells, as well as the carbon-lmited discharged cell, maintained full open circuit voltage throughout the test. Both lithium-limited discharged cells showed fast deterioration of the voltage upon heating. They did not show recovery upon cooling, suggesting that the residual lithium, left after discharge, was consumed in a direct chemical reaction during the overheating test, resulting in permanent loss of the cell's open circuit voltage. None of the cells vented, ruptered, or exploded.

3.1.8 Drop

Two cells of the standard size D, LL, one fresh and one discharged, were subjected to a six-foot drop. The open circuit voltage was measured before the drop test and then monitored for 40 minutes after the drop, along with cell skin temperature. No venting, bursting, or explosion occurred as a result of the drop. Also, no change in either the open circuit voltage or cell skin temperature was observed.

3.1.9 Vibration (Bounce)

The vibration test was conducted in accordance with MIL-STD-810C, Method 514.2, Procedure XI, Part 2, using four cells:

a. 1 cell, DD, LL, fresh

b. 1 cell, D, LL, fresh

c. 1 cell, DD, LL, discharged

d. 1 cell, D, LL, discharged

The cells were tested on the machine designed to meet the MIL SPEC requirements mentioned above. The test duration was 90 minutes in horizontal position, followed by 90 minutes vertical, for each of the four cells. No change in the cells' skin temperatures and open circuit voltages were observed. The specimens did not leak, vent, rupture, or explode.

3.1.10 Shock

The shock tests were conducted using four cells of the following types:

a. 1 cell, DD, discharged
b. 1 cell, D, LL, discharged
c. 1 cell, DD, LL, fresh
d. 1 cell, D, LL, fresh.

The shock pulses were terminal sawtooth shape, 100 milligrams in magnitude and six milliseconds in duration. The shock machine was a drop-impact type with a table weight of approximately 1500 pounds. The impact material consisted of cone-shaped lead pellets designed to produce a particular shock pulse. Typical discharge curves for lithium-limited cells are shown in Figure 13.

Each cell's open circuit voltage and skin temperature were monitored during the test. No change in temperature or voltage was observed. The cells did not leak, rupture, vent, or explode.

3.1.11 Incineration

The incineration test was conducted using three cells, one each of the following types:

a. 1 cell, D, LL fresh
b. 1 cell, D, LL discharged
c. 1 cell, D, CL, discharged.

The cells were incinerated in the flames of burning diesel oil, the temperature of which was well in excess of the melting point of lithium. The fresh cell exploded during this test as expected. Both of the discharged cells vented through the positive terminal as expected.

The test results suggest that a fast spontaneous reaction was initiated between the cell's active components as a result of heating to a high temperature, leading to an explosion. The discharged cells, with a minimal amount of active components left after discharge, expanded slowly during the heating until the cell's top was sufficiently distorted to crack the glass and open the cell to the atmosphere.

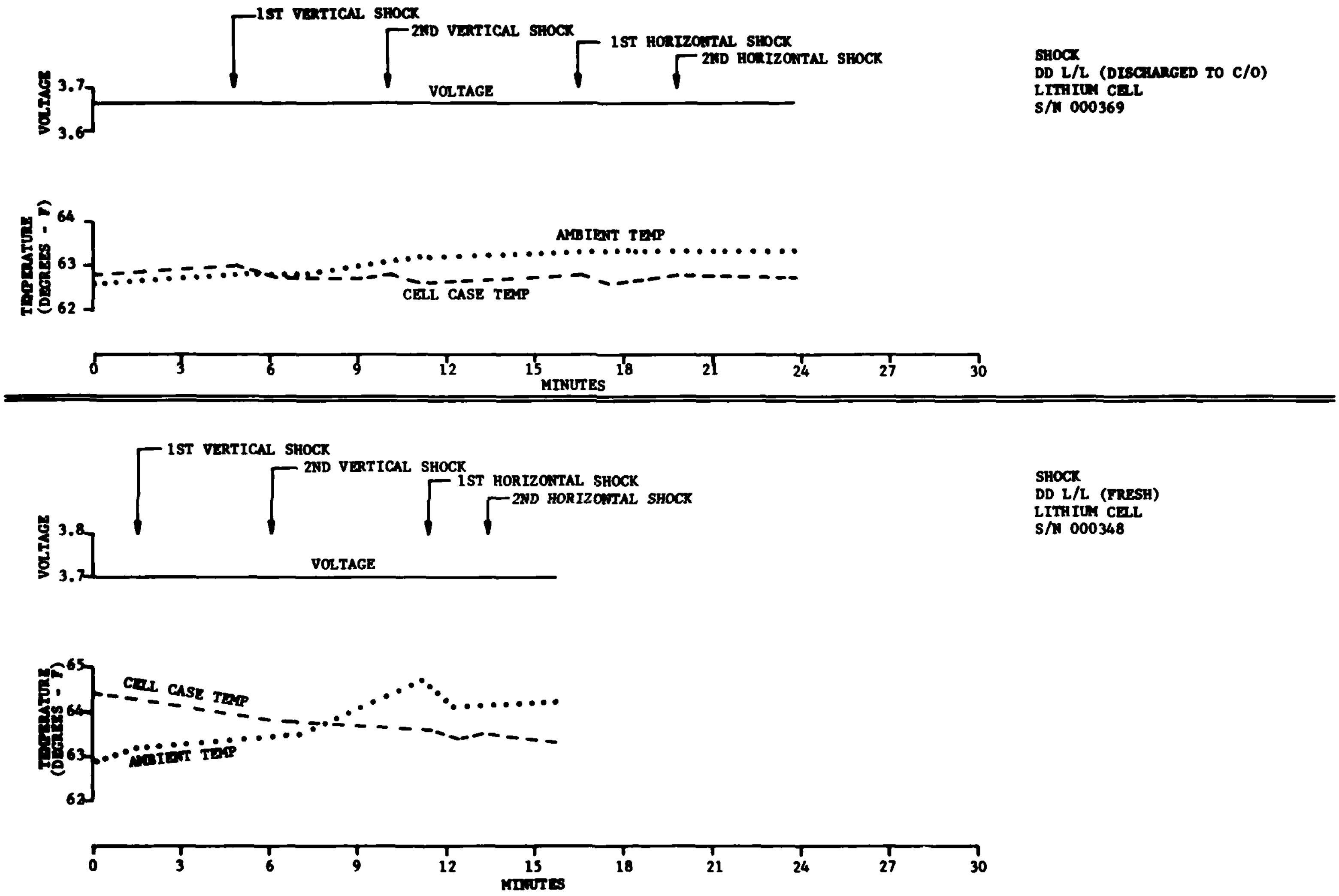

Figure 13. Discharge Curves for Lithium Cell Shock Test

3.1.12 Thermal Shock

Thermal shock tests were conducted using three cells, one each of the following types:

a. 1 cell, D, LL, fresh
b. 1 cell, D, CL, discharged
c. 1 cell, D, LL, discharged.

The thermal shock test was conducted in accordance with MIL-STD-810C, Method 503.1. The cells were equilibrated for four hours inside a chamber at 63°C and then, within a maximum of five minutes, transferred to another chamber and equilibrated at -54°C, where they were left for another four hours. The open circuit voltage and the temperature of the cells were monitored throughout the test. The cycle was repeated two more times.

The cells did not leak, vent, rupture, or explode. The lithium-limited discharged cell showed a drop in its open circuit voltage, most likely due to the disappearance of residual lithium at the high temperature of the cycle (same phenomenon as in overheating tests). The other two cells did not show any change in their open circuit voltage after the test relative to values established before the test.

Discharge curves versus the thermal shock profile are shown in Figures 14 through 16.

3.1.13 Deactivation and Disposal

Three different categories of cells were subjected to deactivation tests, depending on the state at which they were following the tests:

a. Physically undamaged cells
b. Physically damaged cells with ruptures and leaks
c. Debris of exploded cells.

A hole 1/4 inch in diameter was drilled in the bottom of undamaged cells before deactivation. After that, all three categories were deactivated in the same manner by submerging them into a water solution of a neutralizing agent, namely sodium bicarbonate. Two weeks were allowed for the cells to deactivate before the neutralized debris were buried. All cells used in these tests were accounted for. With the exception of the few taken back to GTE, all were deactivated and disposed of.

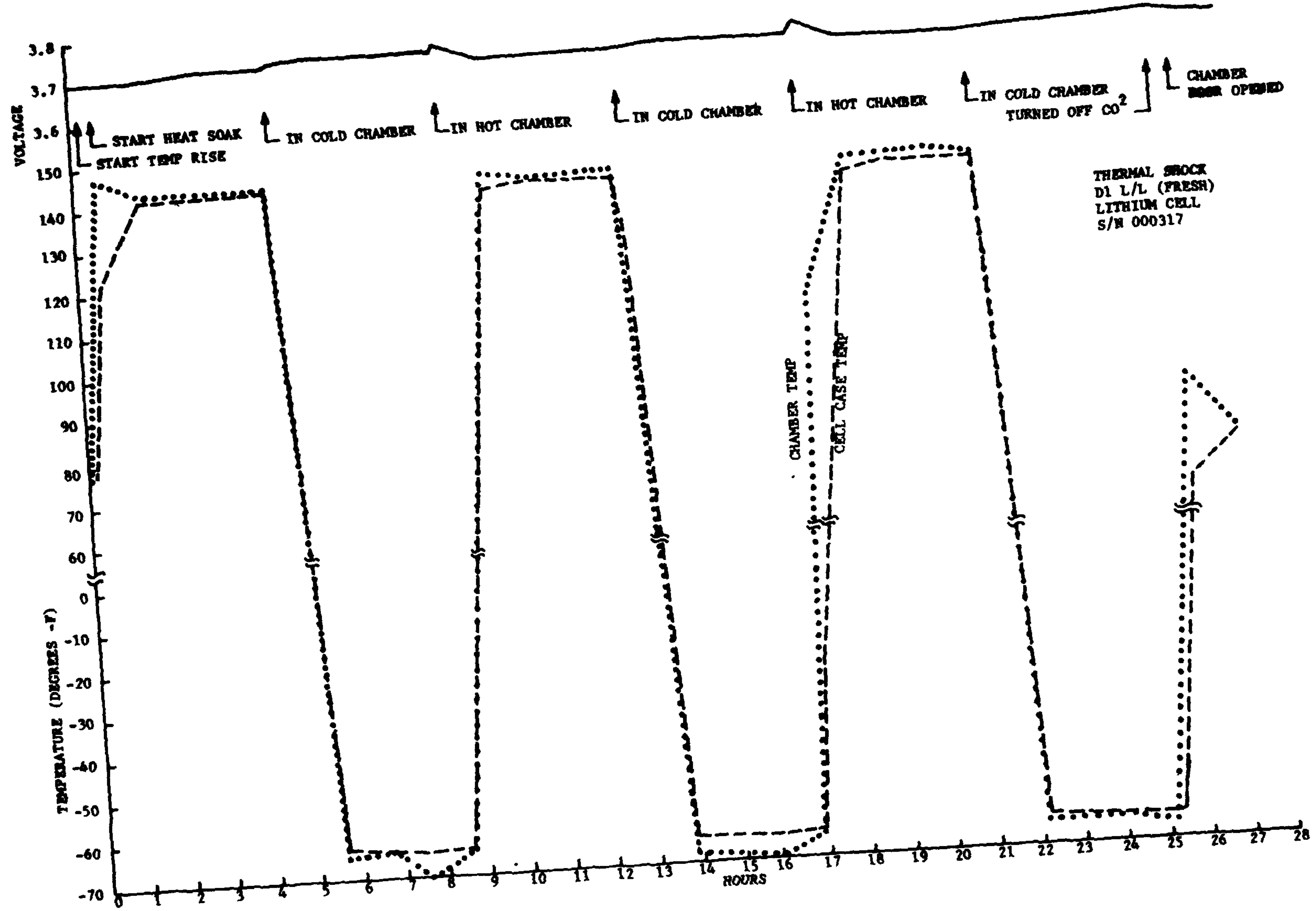

Figure 14. Discharge Curves for Lithium-Limited Cell (Fresh) - Thermal Shock Test

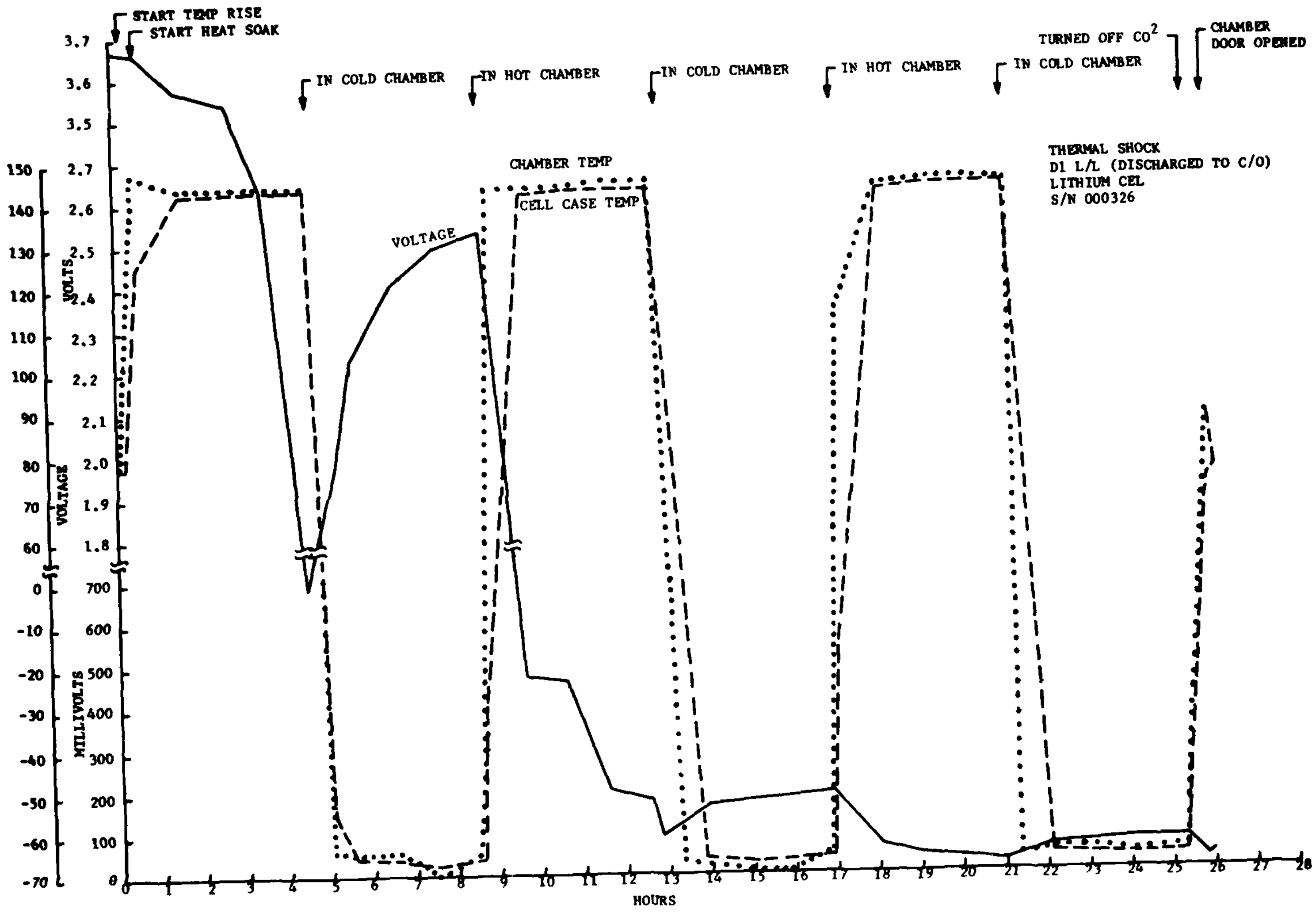

Figure 15. Discharge Curves for Lithium-Limited Cell (Discharged) - Thermal Shock Test

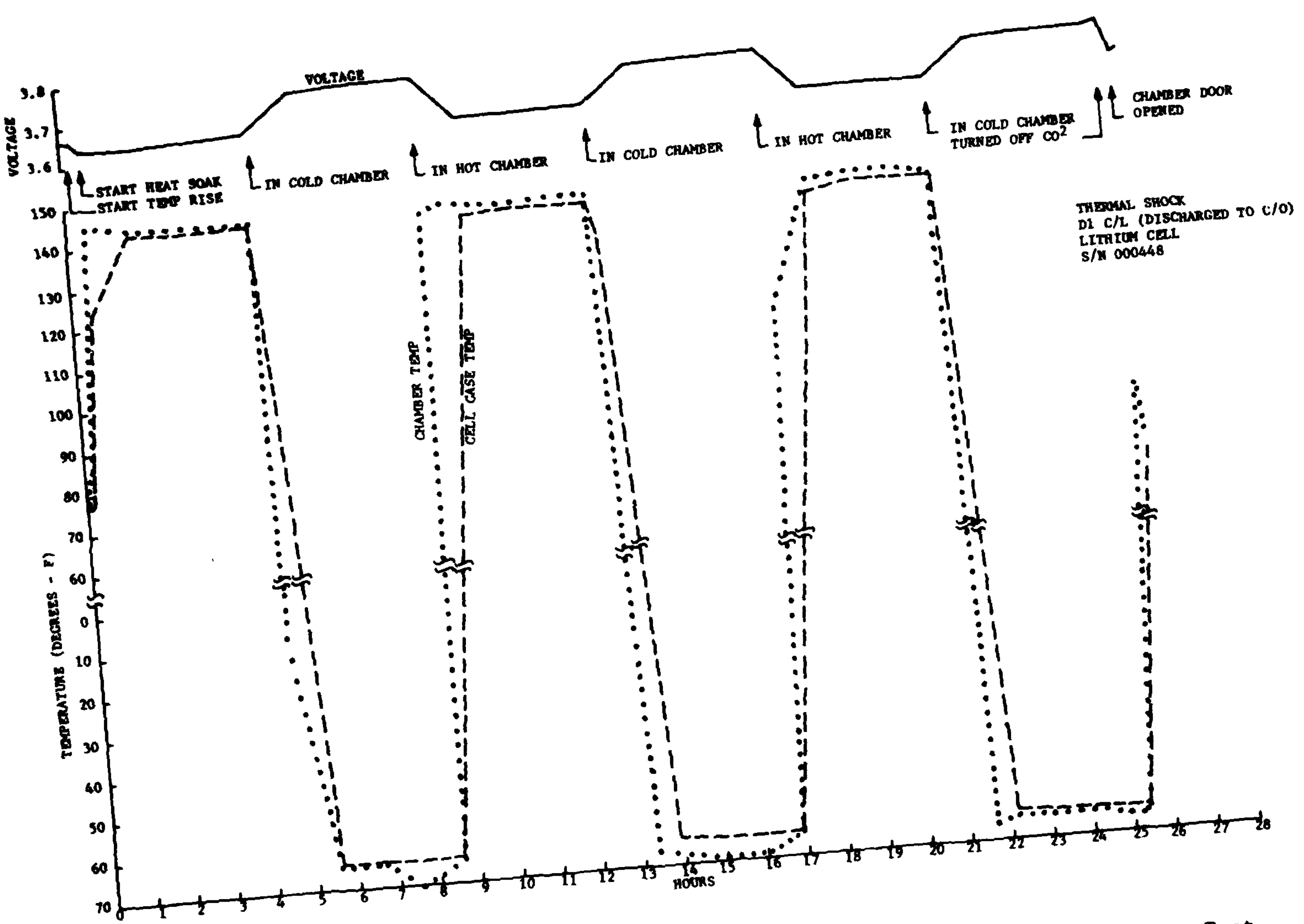

Figure 16. Discharge Curves for Carbon-Limited Cell (Discharged) - Thermal Shock Test

3.2 PRISMATIC CELLS

This subsection presents the results of the investigations conducted on large prismatic lithium thionyl chloride cells, both 2,000 and 10,000 ampere-hour capacity. The intent of the investigation was to maintain the high energy density with the incorporation of features that improve safety in handling, operating, and disposal of the cells.

Some of the abusive tests performed were a "first" for large prismatic cells. It was therefore necessary to design and conduct this test program to prove that in addition to maintaining proper open circuit voltage following the abusive tests, there was no loss in discharge capacity.

Table 2 presents the design of the prismatic test program and correlates test type with size/type of cell and start state of discharge. The test flow and results for the 2,000 ampere-hour cells are presented in Figure 17. The test flow and results for the 10,000 ampere-hour cells are presented in Figure 18.

3.2.1 Discharge Performance

One objective of this program was to establish the practical limits of the energy density and power density obtainable with the prismatic cells in general, and also the reduction of the energy density, if any, resulting from the inclusion of various safety features with the cell design.

Many of the discharge tests conducted under this program may have been a part of another test that included a predischarge, while some other discharge tests were conducted with the specific purpose of establishing if the tests would meet the capacity requirements claimed by the design.

The operating characteristics of prismatic cells were reestablished at the design drain rates using the 2,000-Ah cell and the 10,000-Ah cell. Figures 19 and 20 show the constant load discharge curves at room temperature for a 2,000-Ah (2K-W) and a 10,000-Ah cell (10 K-F), respectively. The respective discharge rates were 8 A and 40 A, in proportion to the expected discharge capacity of the cells.

TABLE 2

PRISMATIC TEST PROGRAM (Page 1 of 2)

TEST GROUP	TEST TYPE	CELL TYPE *	STARTING STATE OF DISCHARGE
Discharge Performance	Discharge At Constant Load	2K-W 10K-F	Fresh
Mechanical Abuse	Abuse Tests With Dummy Cell	2K-D 10K-D	
	Shock Tests	10K-F	Discharged to 0V
		10K-W	Fresh
	Vibration Tests	2K-W	Fresh
		10K-F	Discharged to 0V
		10K-W	Discharged to c/o
		10K-W	Fresh
	Tip	10K-W	Fresh
		10K-W	Discharged to c/o
	Puncture	10K-W	Discharged to c/o
Thermal Abuse	Thermal Shock	2K-W	Fresh
	Temperature Soak	10K-W	Fresh
	Flammability	2K-W	Fresh
	Overheat	2K-W	Fresh
	Temperature Altitude Test	2K-W	Fresh
	Low Temperature Storage	10K-W	Fresh
Electrochemical Abuse	Overdischarge	2K-W	Fresh
	Excessive Discharge	2K-W	Fresh
		2K-W	Fresh

* W=Welded Cell F=Flanged Cell D=Dummy Cell

TABLE 2
PRISMATIC TEST PROGRAM (Page 2 of 2)

MECHANICAL ABUSE		CELL SIZE
Shock Test	100G	10K
Vibration Test	5G (5-50 Hz) 2G (50-2000 Hz)	10K 2K
Tip Test	Free Fall on Edge	10K
Puncture Test	Internal metal-to-metal short circuit	10K
THERMAL ABUSE		
Thermal Shock	54°C to 63°C	2K
Temperature Soak	@ -54°C for 15 days	10K
Flammability	15 second flame impingment	2K
Overheating Test	Oil immersion @ 121°C	2K
Temp/Altitude	-54°C to +65°C @ 40K ft.	2K
ELECTROCHEMICAL ABUSE		
Excessive Discharge	12 milliohm short on 2 2.6 milliohm short on 1	2K 10K
Overdischarge	Constant current for 150% of capacity	2K

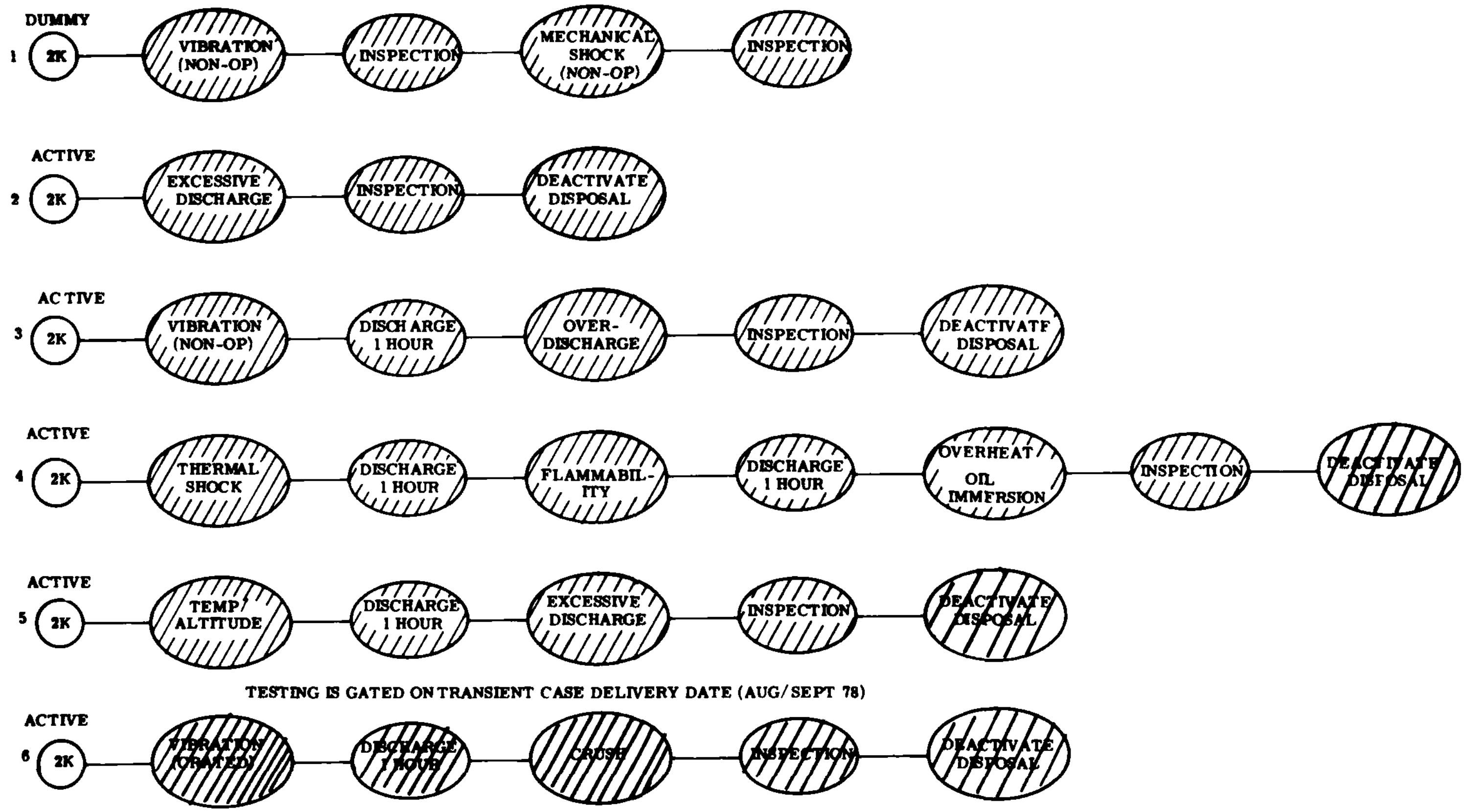

Figure 17. Test Flow and Description - 2,000-Ah Prismatic Cells (Sheet 1 of 2)

SPECIMEN	TEST	CONDITION	RESULT
#1 (Dummy)	Vibration (Non-Op)	Transportation 5 g's (peak) 5-50 Hz 2 g's (peak) 50-2000 Hz	Structural integrity maintained during and after vibration (3 axes).
	Shock (Non-Op)	Transportation 100 g's, shock spectra	Structural integrity maintained during and after shock (3 axes).
#2	Excessive Discharge	External Short Circuit (@ +25°C)	200 Amp external short circuit. Temp/Pressure leveled off. No venting occurred. NO HAZARDOUS CONDITIONS.
#3	Vibration (Non-Op)	Transportation 5 g's (peak) 5-50 Hz 2 g's (peak) 50-2000 Hz	Electrical and structural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS.
	Overdischarge	Discharge thru zero volts (Reversing of Polarity)	150% discharge at the nominal discharge rate. NO HAZARDOUS CONDITIONS.
#4	Thermal Shock	-54°C/+65°C (5 min. transition)	Vented at 6.9 PSIG, + 65°C NO HAZARDOUS CONDITIONS.
	Flammability	15 sec. flame impingement (MIL-STD-202)	Does not result in explosive-type fire. NO HAZARDOUS CONDITIONS.
	Overheat	Immersed in +121°C Oil (Boiling of Electrolyte)	Cell vented as expected. NO HAZARDOUS CONDITIONS.
#5	Temperature/Altitude	-54°C @ 40,000 ft. +65°C @ Amb. Atmos.	No venting occurred. NO HAZARDOUS CONDITIONS.
	Excessive Discharge	External Short Circuit (@ +25°C)	200 Amp. external short circuit. Temp/Pressure leveled off. No venting occurred. NO HAZARDOUS CONDITIONS.

Figure 17. Test Flow and Description - 2,000-Ah Prismatic Cells (Sheet 2 of 2)

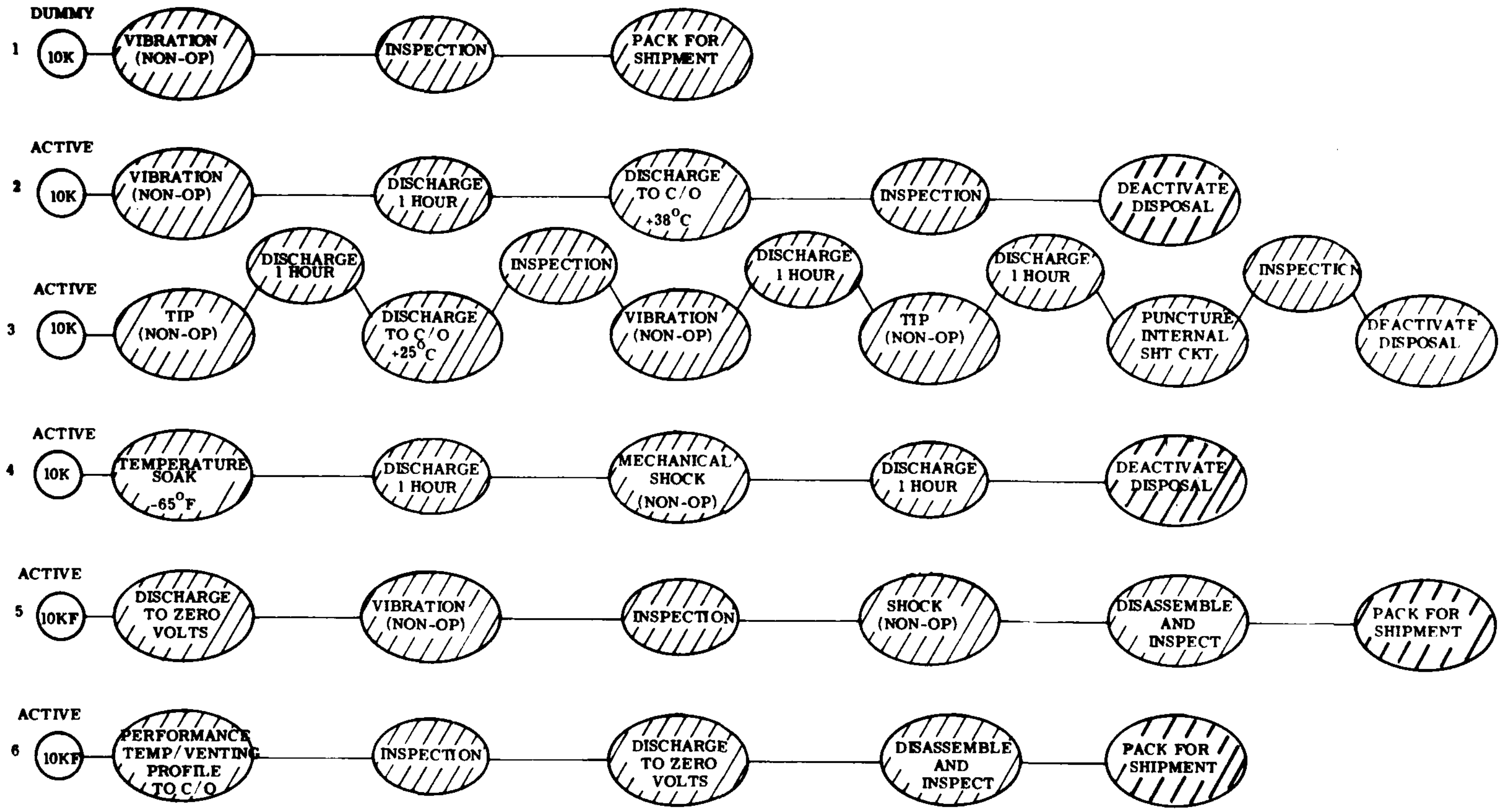

Figure 18. Test FLow and Description - 10,000-Ah Prismatic Cells (Sheet 1 of 3)

SPECIMEN	TEST	CONDITION	RESULT
#1	Vibration (Non-Op) Dummy	Transportation 5 g's (peak) 5-50 Hz 2 g's (Peak) 50-2000 Hz	Structural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS.
#2	Vibration (Non-Op)	Transportation 5 g's (peak) 5-50 Hz 2 g's (peak) 50-2000 Ha	Electrical and structural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS
	Discharge to C/O	36 Amp Rate @ 38°C	Preliminary analysis indicates temp/press. rise within design criteria. Full data analysis in process. NO HAZARDOUS CONDITIONS.
#3	Tip	Cell tipped over from its normal upright position to each of its largest sides.	No rupture or case deformation. Cell performance not affected after tip. NO HAZARDOUS CONDITIONS.
	Discharge to C/O	36 Amp Rate @ 25°C	Preliminary analysis indicates temp/press. rise within design criteria. Full data analysis in process. NO HAZARDOUS CONDITIONS.
	Vibration (Non-Op) (Discharge State)	Transportation	Electrical and struttural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS.
	Tip (Discharge State)	Cell tipped over from its normal upright position to each of its largest sides.	
	Puncture (Internal Short Circuit)	Cell puncture perpendicular to center of largest side to a depth of midway.	Internal short circuit effective excess of 2 hours. Max. internal indicated 4.2 PSI temp rise minima + 2° to +3°C. NO ADVERSE CONDITIONS NOTES. NO HAZARDOUS CONDITIONS.

Figure 18. Test FLow and Description - 10,000-Ah Prismatic Cells (Sheet 2 of 3)

SPECIMEN	TEST	CONDITION	RESULT
#4	Low Temperature Storage	$-54^{\circ}C$/15 Days	Performance not affected after extended period of time at low temperature.
	Shock (Non-Op)	Transportation 100 g's, shock spectra	Electrical and structural integrity maintained during and after shock (3 axes). NO HAZARDOUS CONDITIONS.
#5	Discharge to Zero Volts ($+25^{\circ}C$)	Discharge to C/O 36 Amps Discharge C/O to Zero at 18 Amps	Preliminary analysis indicates temp/pressure rise within design criteria. Full data analysis in process. NO HAZARDOUS CONDITIONS.
	Vibration (Non-Op) (Discharge State)	Transportation 5 g's (peak) 5-50 Hz 2 g's (peak) 50-2000 Hz	Electrical and structural integrity maintained during and after vibration (3 axes). NO HAZARDOUS CONDITIONS.
	Shock (Non-Op). Discharge to Zero Voltage	Transportation 100 g's, shock spectra	Electrical and structural integrity maintained during and after shock (3 axes). NO HAZARDOUS CONDITIONS.
#6	Temp/Venting Profile to C/O @ $+25^{\circ}C$	70% of capacity @ 36 Amps, remaining 30% @ 18 Amps. No load condition after C/O @ $+150^{\circ}F$ storage.	Preliminary analysis indicates temp/pressure rise within design criteria. Full data analysis in process. NO HAZARDOUS CONDITIONS.

Figure 18. Test Flow and Description - 10,000-Ah Prismatic Cells (Sheet 3 of 3)

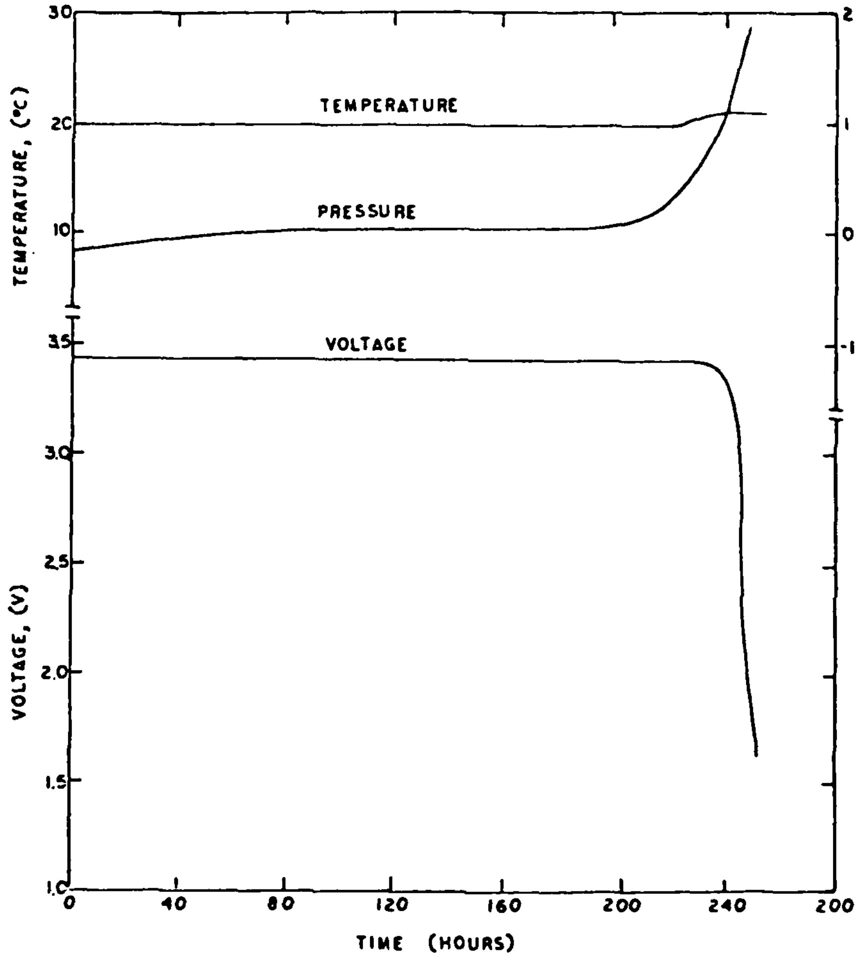

Figure 19. Constant Load Discharge 2,000-Ah Cell, 0.44 Ohms

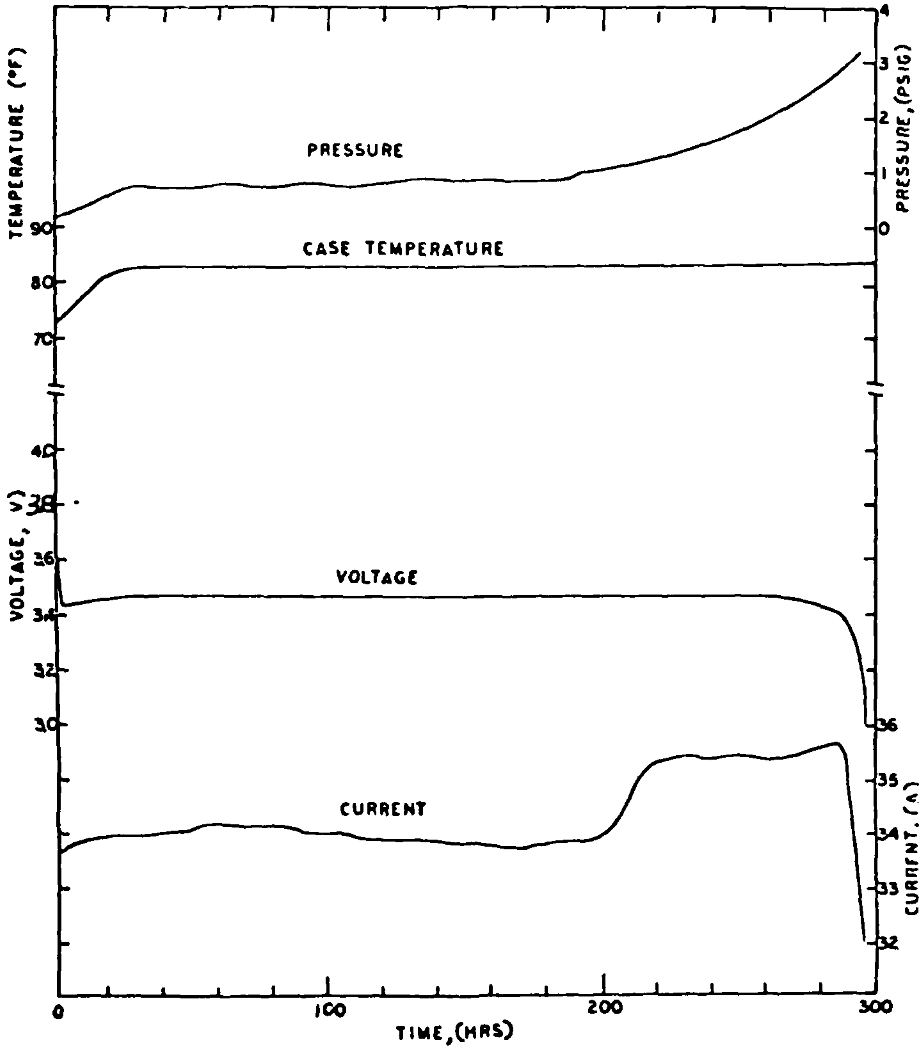

Figure 20. Constant Load Discharge 10,000-Ah Cell

These figures show very stable operating voltages of each of the cells throughout the entire active life of the cells. The end of life is signalized first by a slight increase in temperature and pressure (a few degrees and a few psig, respectively) as the polarization of the cell begins. The drop in voltage at the end of discharge is usually very sudden with this electrochemical system, more so with the anode-limited cells and with the cathode-limited cells with thin cathodes (below 0.050 inch).

The 2,000-Ah cell tested here delivered exactly 1976 Ah at the voltage of 3.43 V to a cutoff voltage line of 3.00 V, thus resulting in the energy of 6778 Wh. The cell in question was equipped with extra insulating plates and extra thick container walls, so that the realistic energy density could not be estimated. However, based on the internal volume occupied by the electrode structure and the extra electrolyte on top of the structure (586 cubic inches), the structure produced an energy density of 11.5 Wh/cubic inch. Obviously, this is far below the maximum energy density obtainable from an optimized 2,000-Ah cell and must be considered as a study figure produced in the course of a more complex experiment.

The 10,000-Ah cell delivered exactly 10,030 Ah at the voltage of 3.5 V to a cutoff voltage line of 3.00 V. This amounted to 35,105 Wh in a volume of 2874.5 cubic inches, or to the energy density of 12.6 Wh/cubic inch. The figure is valid for a welded cell, using the overall cell dimensions and disregarding the fact that the present test was conducted in a flanged cell for practical reasons. Many safety features, overdesigned and incorporated in this cell, were responsible for the reduction of the effective energy density, but were used for the same reason mentioned above for the 2,000-Ah cell. The same cell was used in a variety of mechanical abuse tests (see Table 2) for the first time. The probability of accident could not be estimated in advance, so the cell had to be made as safe as possible for those first tests.

3.2.2 Mechanical Abuse

Limited experience in abusive testing and hazardous behavior of large cells showed that following events such as an internal short circuit at explosion, it is difficult to establish the cause of the hazard. Distortion, overheating, and corrosion of hardware components, loss of electrolyte by leakage or evaporation, and loss of cathode and anode materials that might have been involved in initiating the hazardous behavior complicate the analysis of the event. For these reasons, abuse tests were conducted first with a dummy cell, in which one or more of the active components would be substituted with inactive ones that were similar in physical characteristics but incapable of hazardous behavior.

3.2.2.1 Dummy Cell Tests

Two dummy cells were built, one each of the 2,000-Ah and 10,000-Ah sizes. It was decided to use the real cathodes as the most fragile component of the electrode structure. In order to simplify the incorporation of short circuit sensors, as well as the transport of the dummy cells to the test site, it was decided to substitute a nonflammable material for lithium. Polyethylene sheets of equal thickness, clad with copper on one side, were used. All other components, such as separators, insulators, plate interconnectors, etc., were kept the same as in real cells.

Three types of sensors were incorporated into the cell structure before the test: short circuit sensors, accelerometers, and strain gauges.

The dummy cells, one each of the 2K and 10K sizes, were subjected to mechanical shock test with a terminal sawtooth shaped pulse, 100G in magnitude and 6 milliseconds in duration. The pulse was applied twice in each of the three axes, with both pulses in two axes applied to the cell in upright position and one pulse in X and Y axes for cells in each of the upright and upside-down positions.

The same cells were subjected to vibratory motions over a frequency range of 5 to 50 Hz at 5 G, limited to 0.8-inch double amplitude and 50 to 2,000 Hz at 2 G peak. The frequency range of 5 to 2,000 to 5 Hz was traversed at a rate of one octave per minute. The vibratory motion was separately applied to each of the three mutually perpendicular (orthogonal) axes of the lithium cell. The following parameters were monitored and recorded: cell positive terminal cell case response, accelerometer, and strain gauge responses.

The 2K cell withstood the shock and vibration tests with no visible or detectable damage either to the casing and connectors or to the electrode structure. No part of the case reached the yield point at any time during the shock and vibration tests. The accelerometers indicated a slight relative motion of the electrode plates, low enough in magnitude so that it did not cause either tear of separators or erosion of the carbon plates discussed below. The short circuit indicators showed no contact established either between the cell terminals or between each of the terminals and the cell case.

The tests with the 10K cell were conducted under identical dynamic conditions as those established for the 2K cell. The strain gauges showed that no part of the cell casing reached the yield point at any time during the shock and vibration tests.

The two groups of accelerometers (internal and external) showed different effects of the shock and vibration. The external accelerometers indicated the vibration of the case walls in X (or Y) direction, during the shock and vibration tests along Z axis. The bottom and top of the case showed similar vibration with the maximum amplitude obviously in the center of each plane. The internal accelerometers showed a small relative motion of the plates in the electrode assembly. They also showed a cumulative motion of plates relative to the case wall, proportional to the distance of the plates from the wall. This cumulative effect resulted in a bow formation with a minimum total motion of the center plate during the vibration tests along the Z axes.

The short circuit indicator installed to monitor the contact of cathodes to the cell case showed a short circuit. Post-mortem inspection indicated that the carbon of one of the end cathodes was extruded under pressure over the edge of the side insulator plate, tearing the separator and making contact with the wall of the case. This experience suggested that a perfect line-up must be achieved of all plates of the electrode stack before it is placed in the container.

3.2.2.2 Live Cell Tests

Two full-size 10,000-Ah cells were subjected to the mechanical shock tests, one in the fresh state and one in the fully discharged state.

Figure 21 shows the typical result of the test performed with the 10K flanged cell previously discharged to 0 V. There was no visual evidence of leakage of the electrolyte. The post-test cell width measurement was 11.650 inches, compared with 11.375 inches baseline data. The open circuit voltage was 0.1823 V. No change in pressure or temperature was observed.

The cell was moved to a site suitable for cell disassembly. It was then disassembled, inspected, and packed for shipment.

Figure 22 shows the typical results of the shock test performed with the 10K welded cell in fresh state. Prior to the shock test, a one-hour discharge test was performed verifying that the fresh cell was functioning properly. The cell was then subjected to the shock test in each axis twice. A one-hour discharge test was performed after each shock in a given axis. In each case the cell indicated normal operation during the one-hour discharge following the shock tests.

A load was applied initially for three minutes, whereupon the output voltage of the cell showed a value of 3.30 V, rather than the 3.45 V expected. The load was removed and the cell recovered to 3.6 V.

The load was reapplied and a similar indication occurred, an out-of-specification voltage of 3.30 V. The load was removed, and the cell recovered to 3.6 V. Again a load was applied, and after one hour, the cell's operating voltage was 3.18 V, unacceptable with respect to normal operation.

The post-test analysis indicated that one possible explanation is that a portion of the stack lost good electrical conductivity with the bus, thus reducing the number of plates participating in discharge, and therefore causing a larger voltage drop under load.

Four cells were subjected to vibratory motions over a frequency range of 5 to 50 Hz at 5 G, limited to 0.8-inch double amplitude, and 50 to 2000 Hz at 2 G peak. The frequency range of 5 to 2,000 to 5 Hz was traversed at a rate

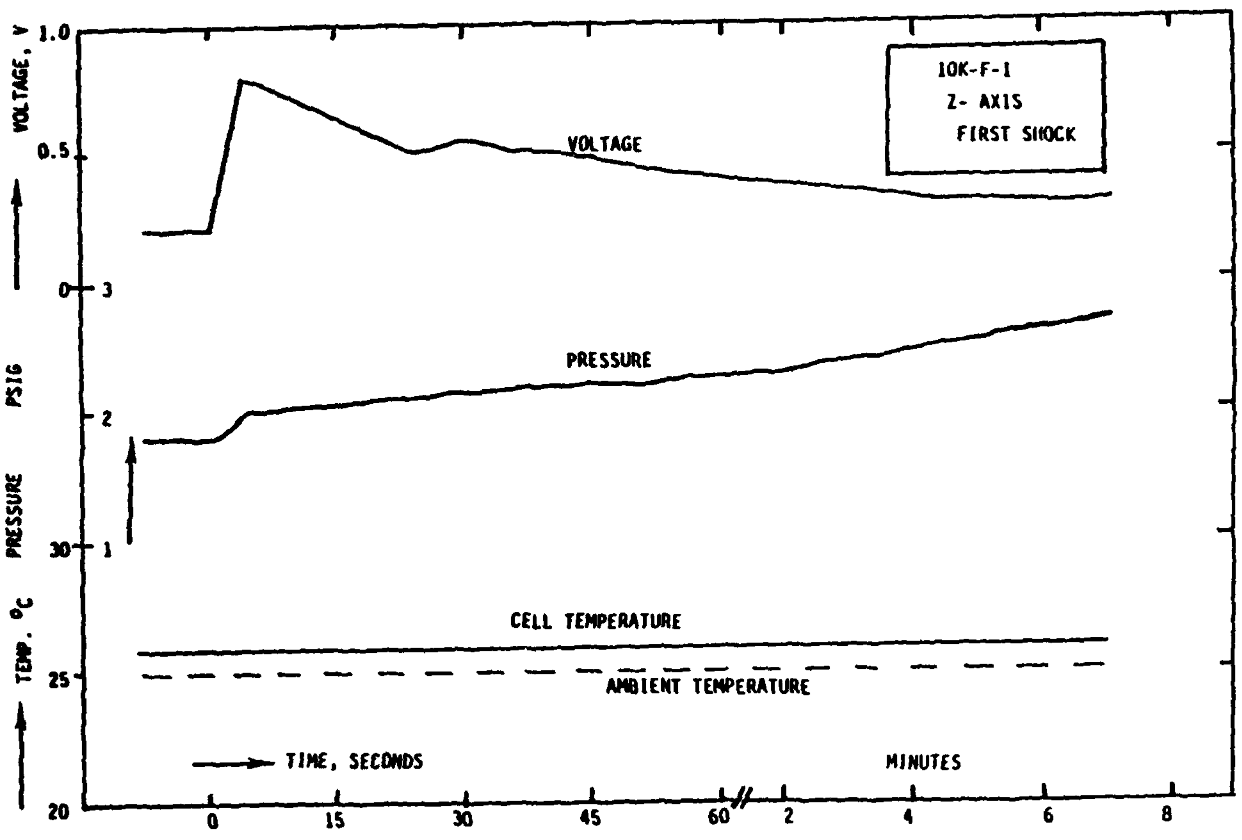

Figure 21. Shock Test of Live Flanged 10K Cell

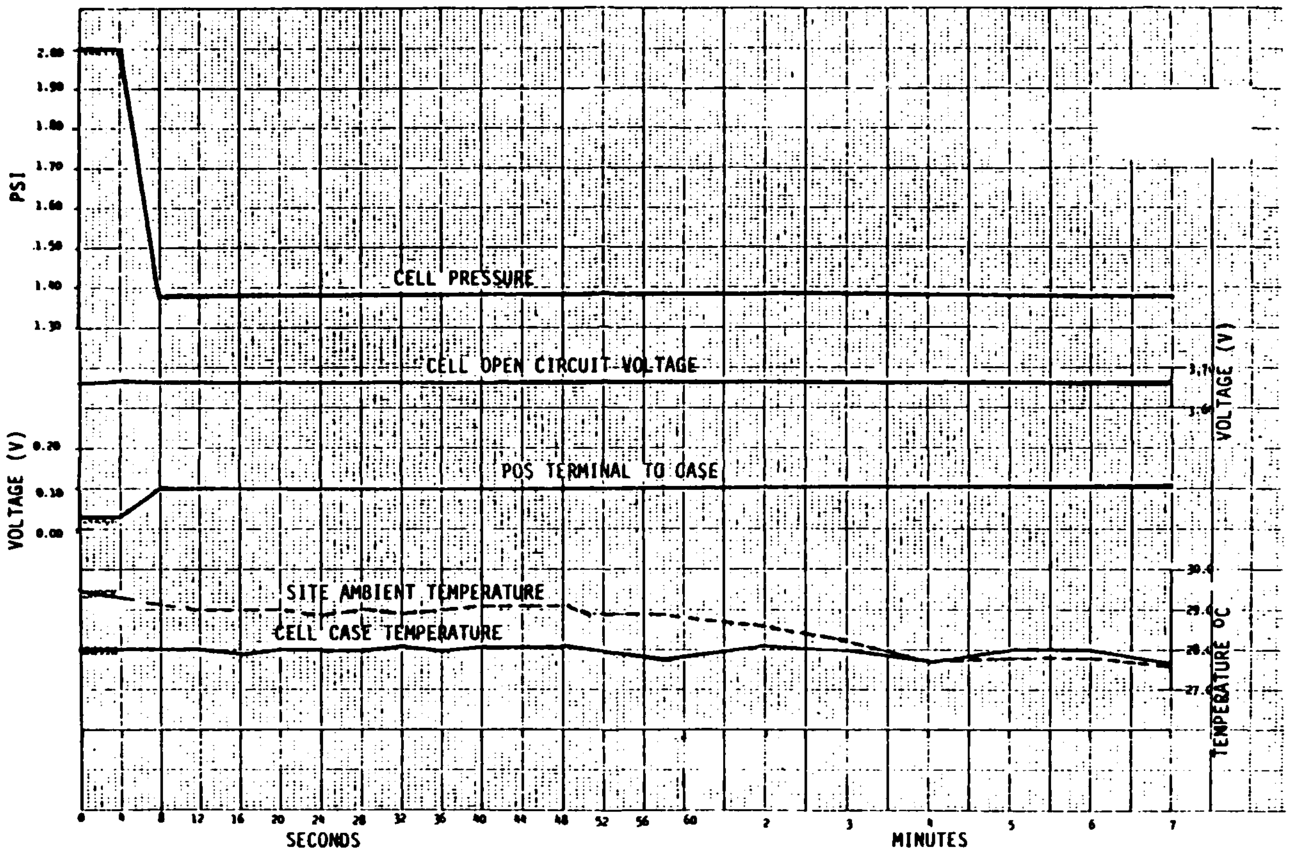

Figure 22. Mechanical Shock Test Results (First Shock)For 10,000-Ah Cell

of one octave per minute, a test period of 16 minutes per axis. The vibratory motion was separately applied to each of the three mutually perpendicular (orthogonal) axes of the lithium cell. Case temperature cell voltage, and cell internal pressure were recorded throughout the vibration test.

For reasons of safety and with the purpose of acquiring initial test data on large cells, the first one of the full size, the 10K cell, was completely discharged to zero volts before it was subjected to the vibration test. Being a lithium-limited cell by design, it was assumed that it contained no lithium prior to the vibration test. The test was performed in all three directions (X, Y, Z),while the voltage, the pressure, and the temperature were monitored continuously. The post-test inspection revealed no visible evidence of damage or deformation. The open circuit voltage of 0.2634 V observed at the end of the test showed, as it should have, no presence of lithium in the cell. The test results are shown in Figure 23.

Another 10K cell was discharged at the nominal rate of 34 A to the cut-off voltage line of 3.0 V before it was subjected to the vibration test. Although lithium-limited by design, the cell at the end of discharge to the cut-off voltage line still contained an unspecified amount of lithium spread over the anode screens, as evidenced by the quick recovery of the voltage to the open circuit value upon discontinuation of the discharge.

One 10K cell was subjected to the vibration test in fresh state. A one-hour discharge at 34 A was conducted before the test and after the vibration in each of the directions in order to verify the proper discharge performance of the cell. The test results are shown in Figure 24.

The open circuit voltage, the case temperature, and the cell's internal pressure were monitored for the duration of the vibration. No change was observed in any of the three parameters as a result of vibration.

There was no visible evidence of damage or deformation at the completion of the test. The cell was later discharged to cut-off at 36 A discharge rate and inspected. No visible damage was noted. The cell was then deactivated (discharged to 0 V) and deposited in a deactivation well.

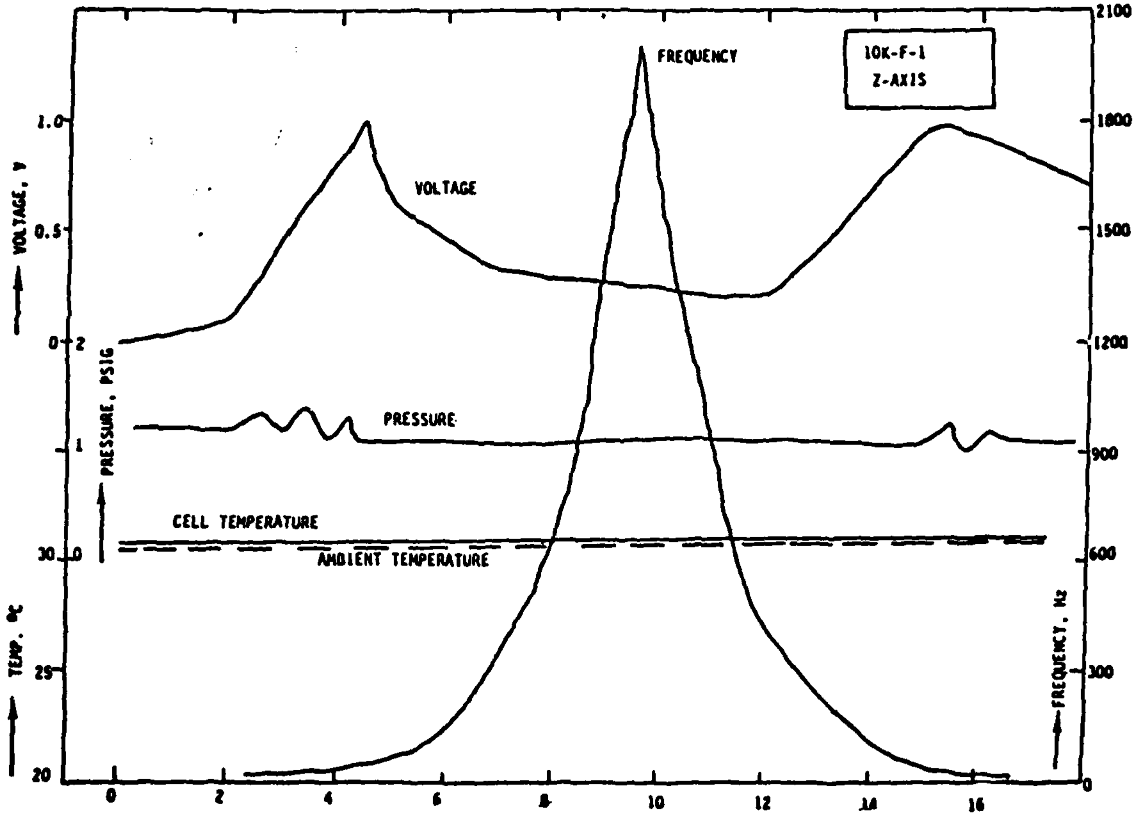

Figure 23. Vibration Test Results, Discharged 10,000-Ah Cell

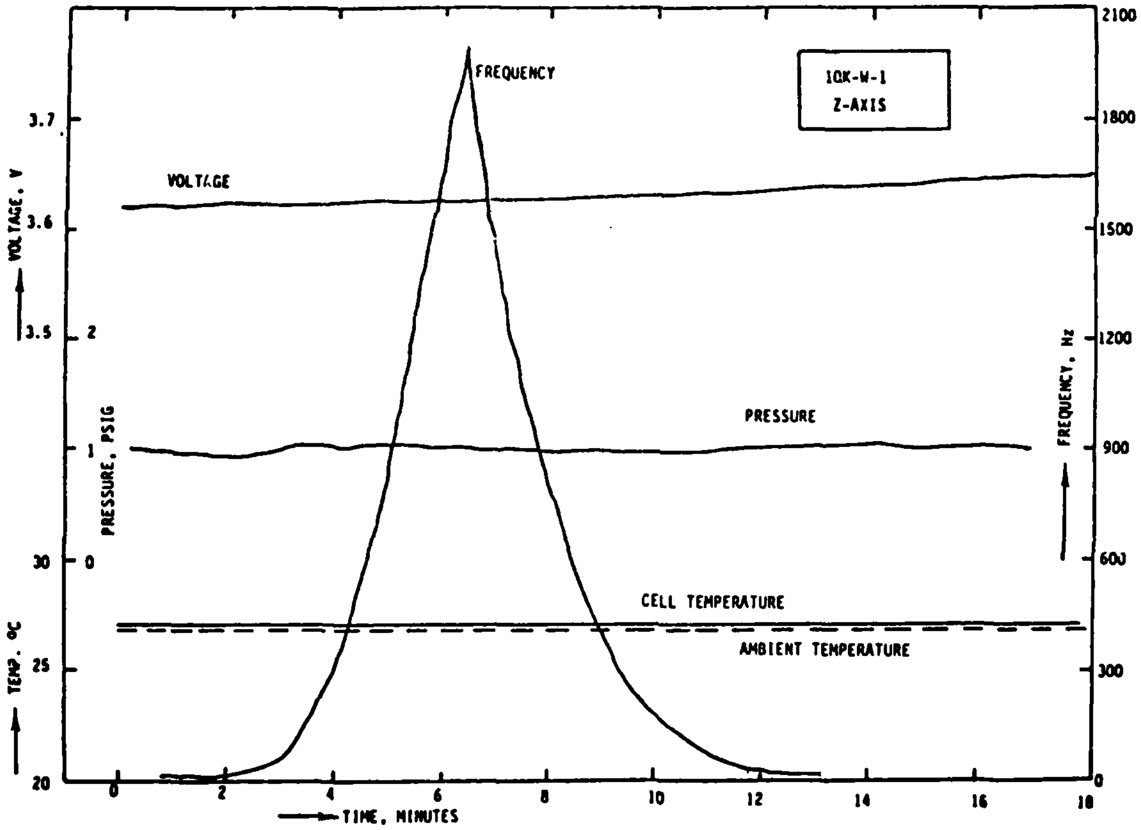

Figure 24. Vibration Test Results, Fresh 10,000-Ah Cell

3.2.2.3 Tip Test

One 10,000-Ah cell was subjected to a tip test both in the fresh and in the discharged state.

Figure 25 shows typical results of the tip test (both surfaces) for the fresh 10K cell. The cell continued to operate in a normal manner after the tip tests. There was no evidence of electrolyte leakage. The post-test cell width measurement was 11.685 iches compared to pretest measurement of 11.663 inches. Open circuit voltage was 3.67 V.

No rupture or case deformation was observed. The performance of the cell was not affected after the tip test. No hazardous conditions occurred.

3.2.2.4 Puncture Test

A 10,000-Ah cell was subjected to the puncture test after discharge to cut-off voltage value of 3.0 V at 34 A. The purpose of this test was to determine the type and magnitude of hazardous conditions created in a discharged to cut-off cell by penetrating the cell wall in the direction perpendicular to electrodes and creating an internal metal-to-metal short circuit between the metal substrates of the anode and cathode. Specifically, this test was to demonstrate whether a discharged 10,000-Ah cell still has enough energy (as does a freshly activated cell) to heat the metal-to-metal short circuit area high enough to cause a spontaneous reaction and cell rupture.

The discharged to cut-off 10K cell was penetrated perpendicular to the center of its largest side with a remotely operated 1/4-inch diameter drill bit. The depth of penetration was four inches, resulting in a metal-to-metal internal short, as evidenced by a sharp drop in terminal voltage.

The open circuit voltage immediately dropped from 3.65 to 3.45 volts and ocntinued to decrease gradually over the next 60 minutes until the cell reached its 3-volt cut-off level. At this point, the 1/4-inch diameter drill bit was removed. The maximum cell temperature recorded during the test was 32°C, indicating a three-degree rise and a maximum pressure of 4.2 psi.

Puncturing a discharged 10,000-Ah prismatic cell to a depth sufficient to create an internal metal-to-metal short will not result in an explosion.

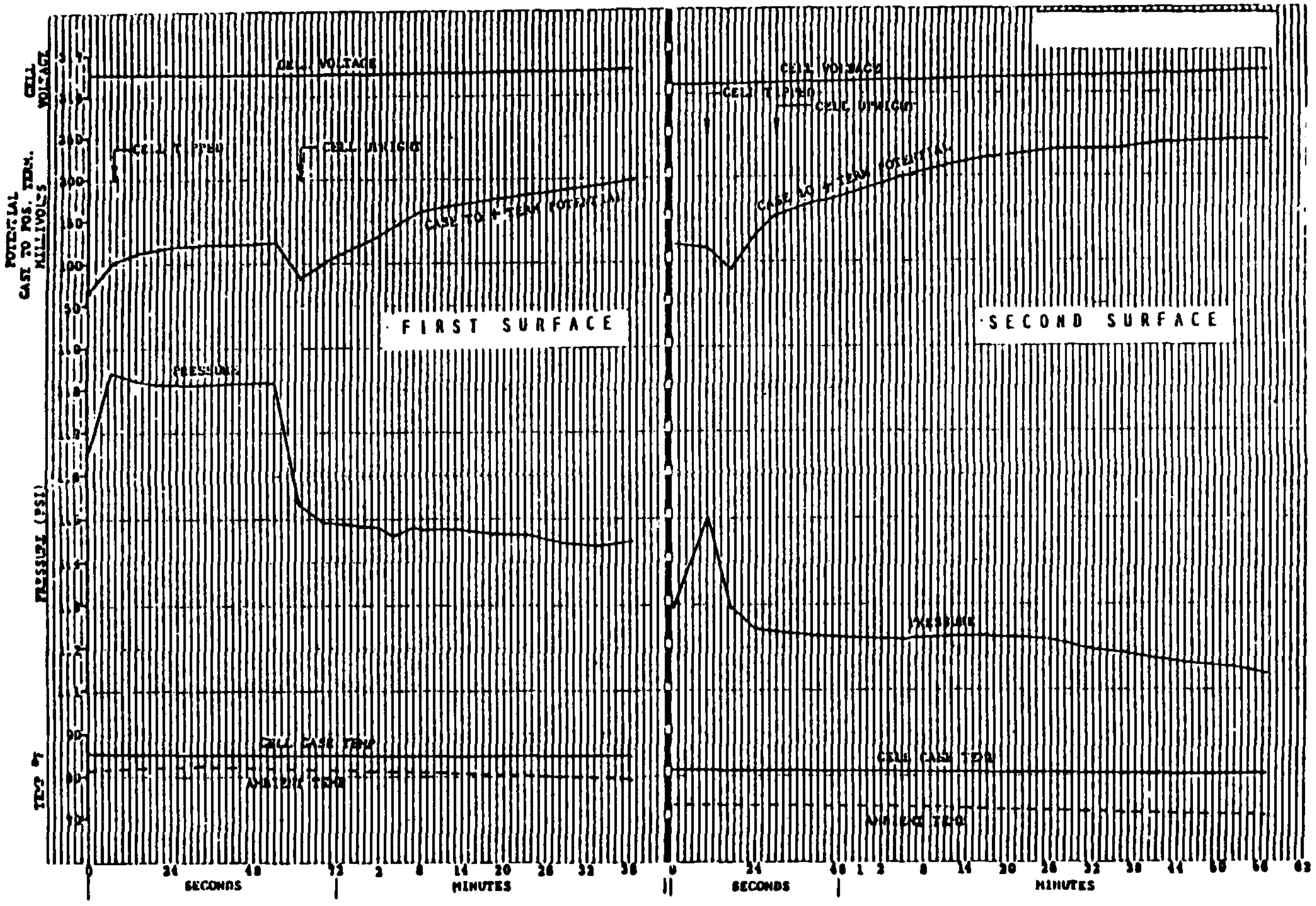

Figure 25. Tip Test Results for 10,000-Ah Cell

3.2.3 Thermal Abuse

3.2.3.1 Thermal Shock

The thermal shock test was performed on one 2,000-Ah prismatic cell to demonstrate the resistance of the basic prismatic design to the anticipated sudden changes in temperature and the possible adverse effects, if any, of the sudden temperature changes upon the discharge performance of the cell.

Figure 26 shows the results of the thermal shock test. The cell was held in each of the two temperature chambers for hours, and the cycle was repeated three times. The open circuit voltage, the cell's case temperature, and the internal pressure were monitored for the entire period of the thermal shock test. Following the thermal shock test, the cell was allowed to equilibrate at room temperature before the one-hour discharge test was performed to determine the effect, if any, of the thermal shock on the performance characteristics of the cell. The same one-hour discharge test was applied to the cell prior to the thermal shock test, for comparison.

The internal pressure of the cell varied between -7 psig and +7 psig, dependent on whether the cell was going through the cold or hot part of the thermal shock cycle. No change in the discharge performance of the cell was observed as a result of the thermal shock test. No leakage, rupture, venting, or explosion was observed during the thermal shock test.

3.2.3.2 Temperature Soak

A deep-freezing test over an extended time period was performed on one prismatic cell for the purpose of demonstrating if such a treatment would affect the discharge performance at ambient temperatures. The low temperature was not expected to affect the electrolyte, since it was still far above its freezing point, but proof was needed that all the other components and subassemblies are unaffected by an extended exposure to low temperature.

To verify that the cell functioned properly, the cell was discharged at a rate of 36 A for a period of one hour following the deep freeze test. The cell continued to operate with the same performance as before the test. The performance of the cell was not affected after the extended exposure to a low temperature.

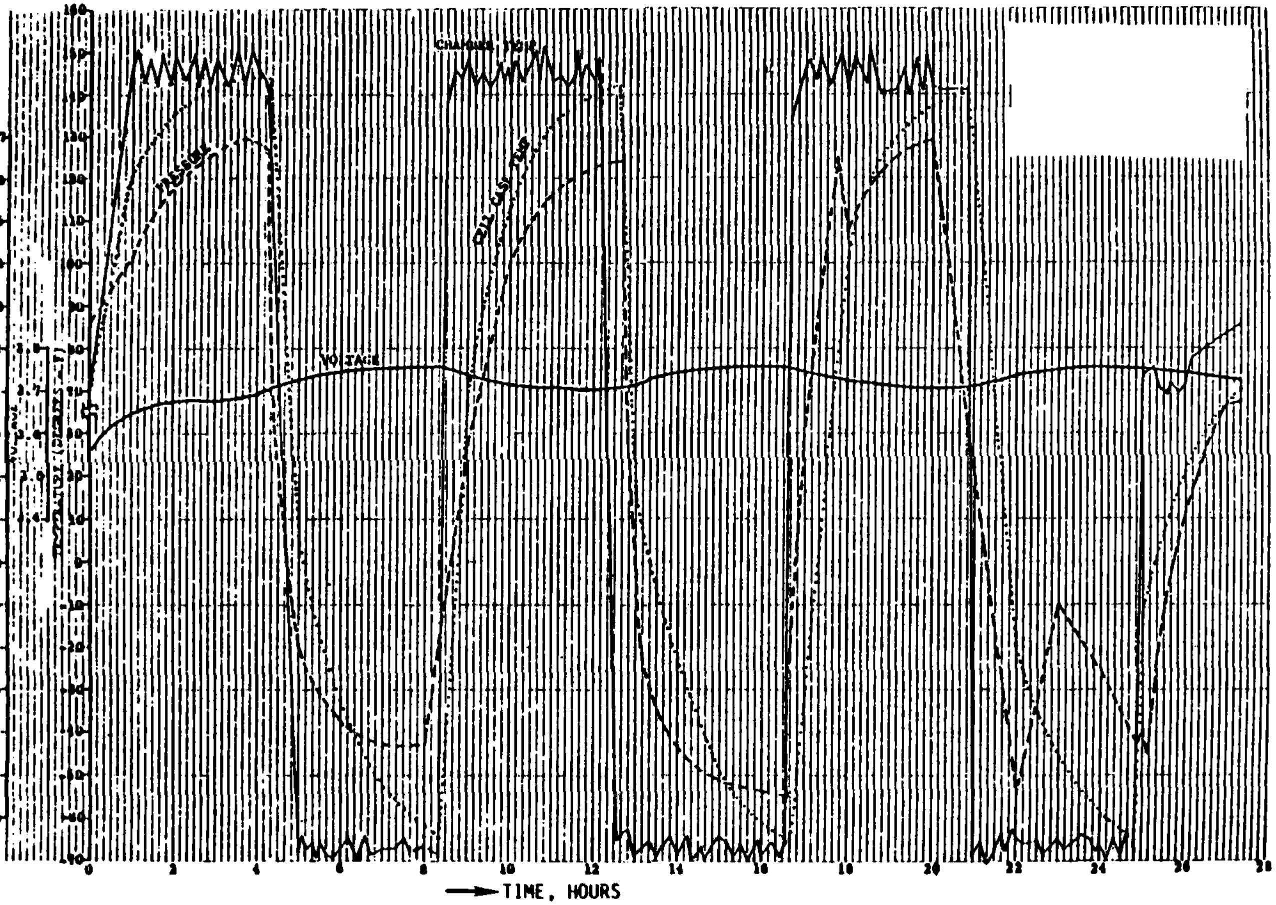

Figure 26. Thermal Shock Test Results for 2,000-Ah Cell

3.2.2.3 Flammability

The thermal abuse test often includes a short-term exposure to flame. A test was performed to demonstrate not only that the exterior of the cell is not flammable, but also that the short-term exposure to flame would not seriously change the vital signs of the cell (open circuit voltage, pressure temperature) and its discharge performance after the test.

The flammability test was applied to one cell of the nominal capacity of 2,000 Ah by remotely applying a flame from torch for 15 seconds. The open circuit voltage, the cell's case temperature on the flame side, and the internal pressure were monitored during the 15-second test and 24 hours following the completion of the test.

No change was observed in the cell's open circuit voltage, the internal pressure, or the case temperature on the wall opposite the flame side. The case temperature on the flame side climbed to 98°C in the 15 seconds of test, and returned to the temperature of the opposite wall over the period 35 minutes following the flame test.

3.2.3.4 Overheating

The resistance of thionyl chloride cells to overheating had to be experimentally established, since overheating accompanies many other mechanical and electrochemical abusive treatments. Although the components of the fresh cell are considered stable at elevated temperatures up to a point of a phase change (such as the melting of lithium), the hardware components and subassemblies may also be affected to the point where they could initiate other forms of abuse, such as short circuit, leakage, etc.

The open circuit voltage changed only in the range expected, corresponding to the increase in temperature. It settled down at the initial full value, after cooling of the cell to room temperature following the test.

The cell's case temperature trailed closely the temperature of the oil in the bath.

The internal pressure of the cell climbed slowly to 6.3 psig during the oil heat-up period in the first hour of thetest. At this pressure, the cell vented into a scrubber, but the pressure contiued to climb thereafter, as the temperature of the bath icreased, reaching a maxium of 23 psi 45 minutes after the oil bath temperature maximum was achieved. The pressure steadily declined over the last four hours of the test in spite of the constant temperature of the bath oil.

The scrubber temperature climbed, following the venting point, from 35°C to 105°C, when a slow, steady cooling of the scrubber started, reaching 40°C at the end of the test.

Upon cooling to approximately 45°C following the test, the cell's internal pressure reached -12.6 psig, which was expected, based on the fact that the cell lost some of its electrolyte during the venting.

No leakage, rupture, or explosion occurred as a result of the overheating.

3.2.3.5 Temperature/Altitude

The temperature/altitude test was performed using one cell of nominal capacity of 2,000 Ah. The cell was subjected to this test in a temperature altitude chamber. The chamber pressure was changed from ambient to that equivalent to a 40,000-foot altitude (2.7 psi), after the chamber temperature was changed from ambient to -65°F. This temperature change was accomplished in one hour. These conditions were maintained for 50 hours thereafter. The pressure was then changed to ambient over one hour, and the temperature was raised to 65.5 _2°C over a period of four hours. These conditions were also maintained for 50 hours thereafter. Finally, the chamber temperature was allowed to equilibrate with the ambient over the period of four hours.

No change of the cell's open circuit voltage was observed, other than expected, due to the change in temperature. The performance characteristics of the cell were established through a one-hour discharge period following the test, and they do not appear different from those established through the same type of discharge test prior to the test. The cell temperature and the scrubber temperature followed closely the temperature of the chamber. The cell pressure followed the pressure in the chamber closely at low temperature and showed a value of approximately +2 psig during the high temperature period following the low temperature test. The cell was then discharged for approximately one hour to confirm that it functioned properly after the temperature/altitude test. Proper operation was verified.

3.2.3.6 Temperature Vent Profile

A 10,000-Ah prismatic lithium cell was subjected to a temperature vent profile test to determine the venting system characteristics as a function of cell pressure and temperature.

The temperature vent profile test data are shown in Figure 27. After 170 hours of discharge at a 35-ampere rate and at a chamber temperature of 26°C, the load was removed. The internal cell pressure had reached 4.2 psia.

The chamber temperature was increased to 38°C over a four-hour period with the load removed. The internal cell pressure steadily increased, and at 5 psi, the vent valve cracked open. The maximum internal cell pressure reached was 7.1 psi, at which point the vent valve was full open. The flow rate was calculated to be 0.35 cubic foot per hour for approximately 10 hours and then decreased to zero as the cell pressure decreased.

After 24 hours, the 35-ampere load was applied for 15 hours, during which time the cell pressure reached 7.9 psia and the vent flow rate peaked at 0.45 cubic foot per hour. The scrubber pressure was also increasing at this time, indicating partial plugging in the vent system.

The test was discontinued to change the scrubber and vent valve, as well as to change the data logger, which appeared erratic.

The test chamber temperature was increased once again to 38°C with no load on the cell. Cell pressure increased to 3.8 psi at this point. The 36-ampere load was applied and the cell pressure reached 5.6 psi in approximately 10 hours. The pressure remained constant at the valve for the next 70 hours until the 3.0 volt cutoff was reached. Erratic pressure data indicated that possible venting occurred during the early portion of this final discharge at a very minimal flow rate.

This test indicated that the vent valve flow rate does maintain a constant internal cell pressure as designed.

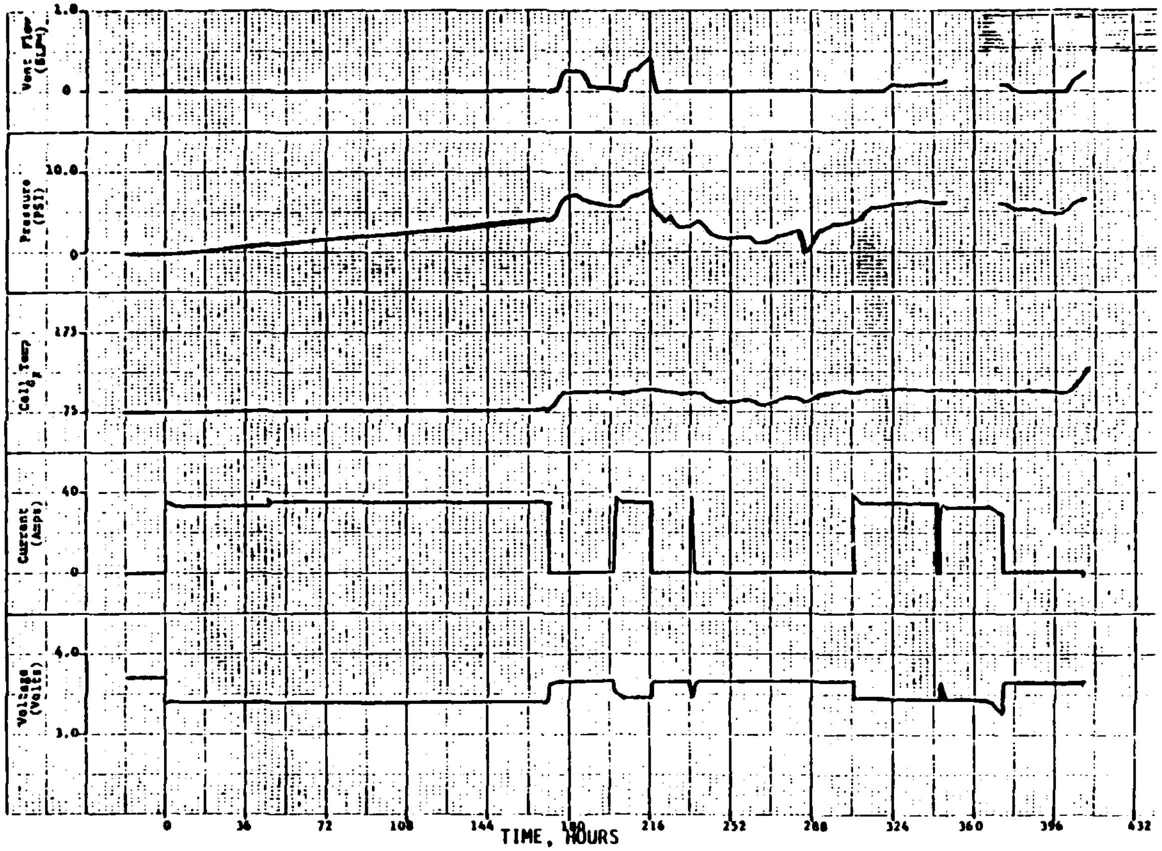

Figure 27. Temperature Vent Profile Test Results for 10,000-Ah Cell

3.2.4 Electrochemical Abuse

Primary chemical power sources, in general, are subject to abuse in all situations where either an excessive demand for power is made or the source is driven by another source at excessive rates in either charging or discharging direction. Some of them, such as the solid state batteries, can withstand considerable abuse, due to their high internal impedance. They respond to an excessive power demand by a strong polarization and, in fact, assume the diffusion-limited mode of operation in which a maximum discharge rate is achieved. For the same reason of high internal impedance, they cannot easily be driven at considerable rate by the external power sources. The high-rate primary power sources, such as lithium batteries with high surface area electrodes, can meet very high power demands, but will develop high internal temperature due to the voltage drop across the electrode structure.

The consequences of the internal overheating will depend on the energy density and the design of the cell. The lithium batteries with high surface area electrodes can support the excessive discharge rate for a long period of time, due to their high energy density. They are also made with much stronger closures so that they do not burst early enough to discontinue the temperature rise. As a result, they reach high temperature and pressure before the container bursts, and thus explode with considerable violence. The same type of cells made with low surface area electrodes will resist the high power demands in a fashion similar to the solid state cells; they will show some increase in internal temperature, depending on the power demand, but will proceed to discharge without visible external change.

Typical applications for large primary cells fall into the category of low surface area cells. However, for practical reasons, they are made in prismatic form, with the prismatic containers much more sensitive to internal cell pressure than the customary cylindrical containers.

3.2.4.1 Overdischarge Test

The cell of the nominal capacity of 2,000 Ah was subjected to a full discharge at a constant current of 8 A, followed by an overdischarge equivalent to 50 percent of the capacity obtained on discharge. The cell voltage, the discharge current, the internal pressure, and the case temperature were monitored for the duration of discharge and overdischarge. The test lasted for a total of 380 hours. In the period of overdischarge, the voltage remained at a constant value of 1.7 V for almost the entire period. The test results are shown in Figure 28.

No leakage, rupture, or explosion occurred during the discharge test.

3.2.4.2 Excessive Discharge (Short Circuit) Tests

Figure 29 shows the results of the short circuit test for a 2K cell. The cell sustained a peak current of 250.3 A without leakage, rupture, or explosion. The design or intended drain rate during normal operation is 8 amperes.

The voltage of the cell, the discharge current, the temperature of the case, and the internal pressure of the cell were monitored for the duration of the test. The test under load lasted in excess of five hours, in which period the cell voltage dropped from 3.67 V open circuit to 2.38 V immediately upon applying the load, then gradually increased to a maximum of 2.73 V one hour from the beginning of discharge, before it started a gradual decline to a minimum of 0.29 V. The open circuit voltage was fully restored upon removal of the load at the end of the test.

The results of the short circuit test with the 10,000-Ah cell (TD-010005) are shown in Figure 30. A current of approximately 700 A was maintained for almost two hours above 2 V, before a gradual and then sudden drop in both the current and the voltage were observed. The removal of the load after the sudden drop of voltage showed a full recovery of the open circuit voltage, but no capability of the cell to deliver any appreciable current. No leakage, rupture, or explosion were experienced during this test.

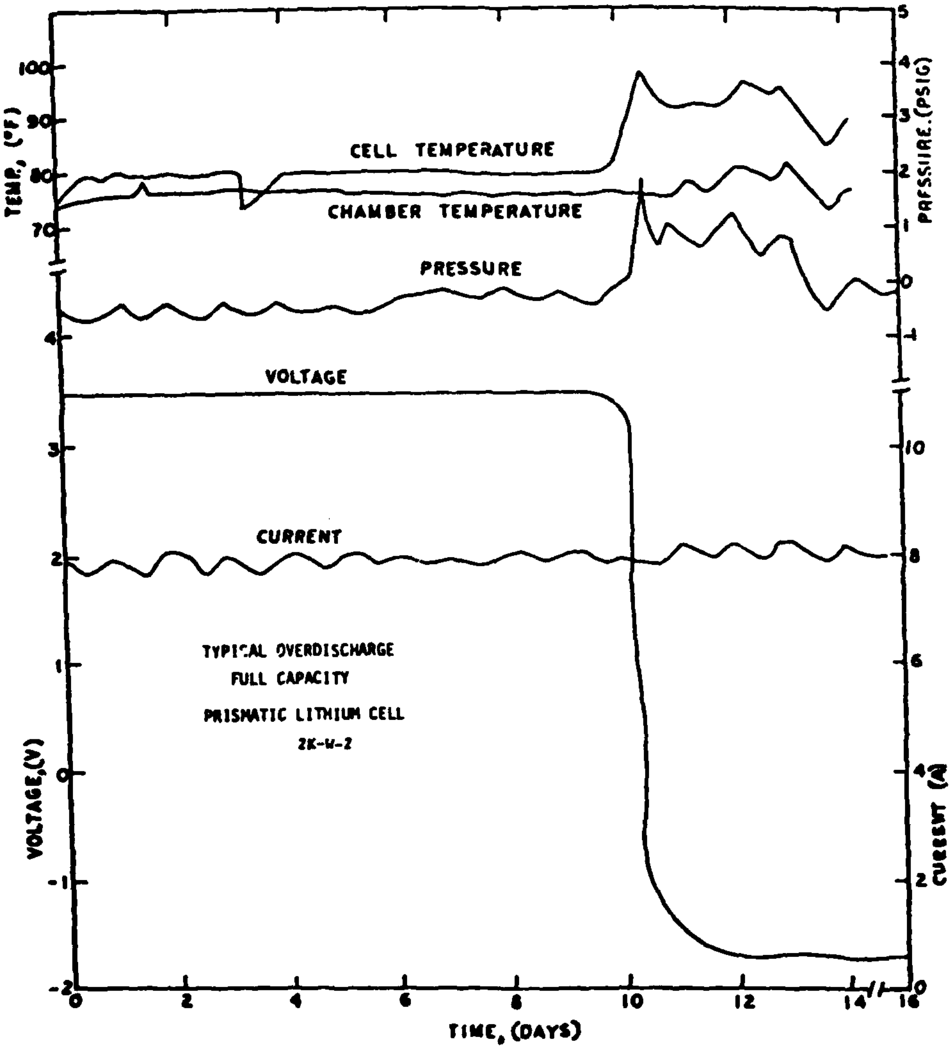

Figure 28. Overdischarge Test Results - 2,000-Ah Cell

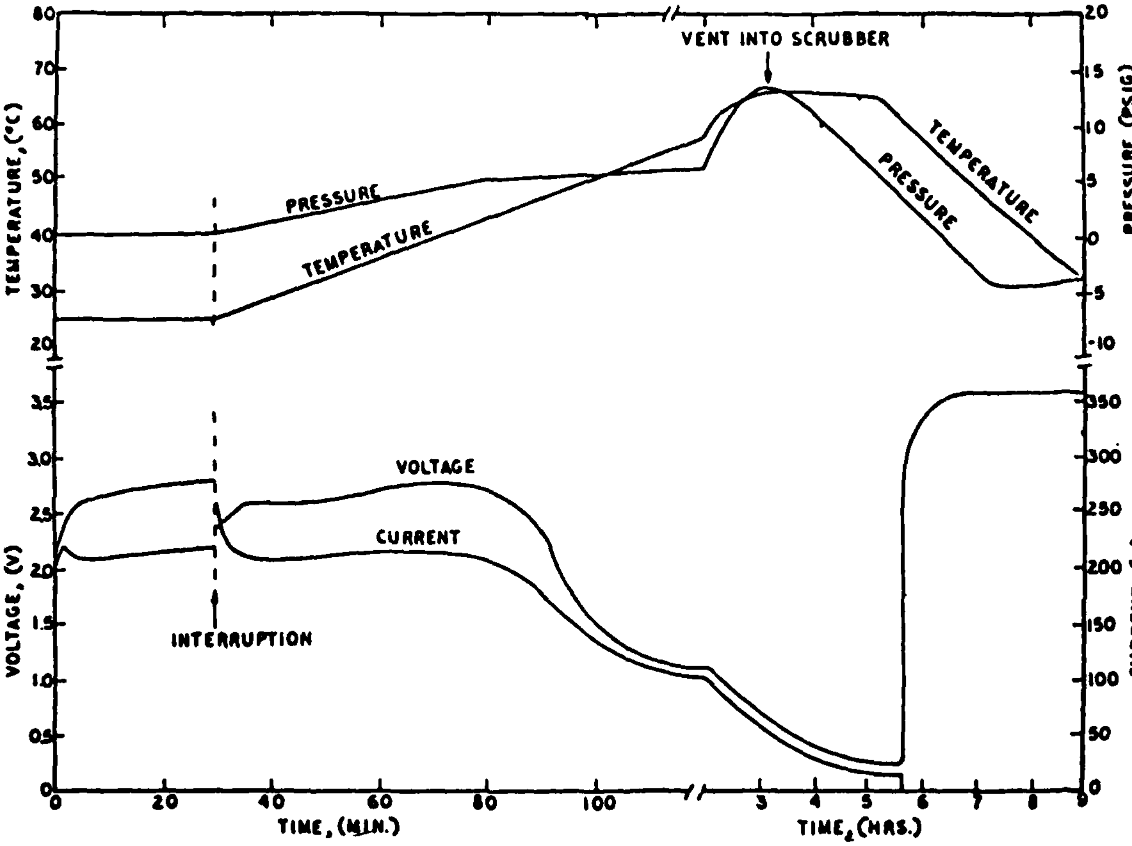

Figure 29. Short Circuit Test Results for 2,000-Ah Cell

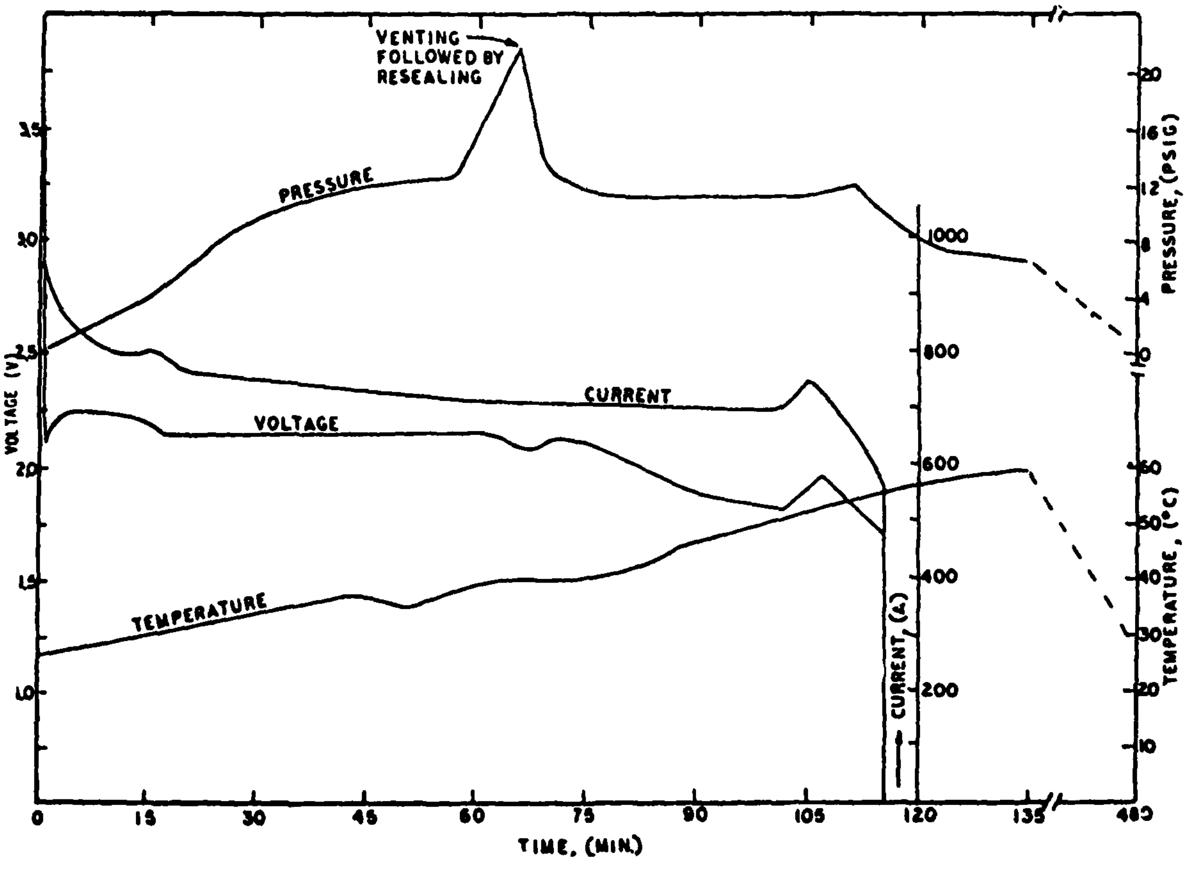

Figure 30. Short Circuit Test Results for 10,000-Ah Cell

4.0 LOW TEMPERATURE

4.1 PURPOSE

The purpose of this program is to develop a small cell (half-C) capable of powering the so-called man pack radio even at temperatures of -40°C. The desired capacity at -40°C is 25 percent of the room temperature.

4.2 GENERAL

It is established that $LiSOCl_2$ cells can be used over a very wide temperature range. However, at -40°C, the reaction mechanism is limited by the kinetics of the system, which have a diminishing effect on the rate capability of the cell.

Methods to overcome some of the low temperature problems are to increase the surface area of the electrodes and the catalytic activity of the materials involved. For that reason, modifications on the carbon were introduced to reduce the polarization effect of the cathode. The spiral-wound electrode structure was chosen over the standard bobbin-type design for improved electrode surface area. However, the maximum geometrical electrode surface area obtainable with the wound structure is approximately 65 cm^2. This requires a current density that exceeds 2 mA/cm^2 to meet the man-pack radio requirements. Tests indicate (see interim report) that at the 1-mA/cm^2 rate, the 3.0-volt capacity was extremely low; sometimes -40°C temperature capacity could only be obtained below 3-V operating voltage.

In view of these problems with the spiral-wound design, the multi-electrode disc cell was developed. In this new design, disc type anodes, cathodes, and separators are stacked under compression within the cylindrical container (see Figure 31). All plates are connected in parallel and provide a total surface area of 112.5 cm^2, nearly twice the surface area of the equivalent wound structure.

The discharge rate for the man-pack radio is 300 mA. This value can be achieved in the half-C configuration by using thinner electrodes. However, at present, the lithium suppliers cannot manufacture lithium in thicknesses less than 0.005 inch. Each disc has its own current collector to reduce the IR losses across the electrodes to a minimum, which results in a more uniform

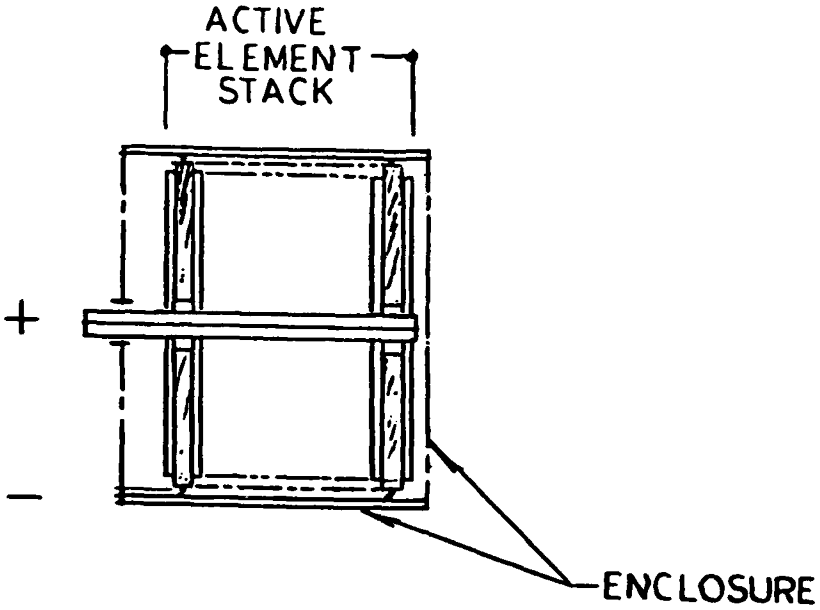

Figure 31. C Cell Disc Stack Design Schematic

and better material utilization than realized with the jelly-roll configuration cell. In addition, the thermophysical properties of the disc design should be much better, since each cathode is heat-sinked over its total periphery to the can.

4.3 DATA

Wound C cell performance (Table 3) and cell voltage characteristics (Figures 32 through 35) are included from the interim report for comparison with disc cell results. Table 4 includes data on all disc cells tested and Figures 36 through 56 show each cell's discharge characteristic.

TABLE 3

HALF-C WOUND CELL TEST RESULTS

TEMPERATURE °C	CURRENT DENSITY mA/cm^2	DISCHARGE CAPACITY (AH) to a voltage cutoff line of 3.0	2.0	1.0	TEST NO.
25	1	1.91	2.10	-	1
		1.97	2.10	-	2
	3	1.46	1.70	-	3
		1.86	1.97	-	4
-40	1	0.7	0.96	1.00	5
		0.0	0.94	1.27	6
	3	0.0	0.164	1.0	7
		0.0	0.308	0.79	8

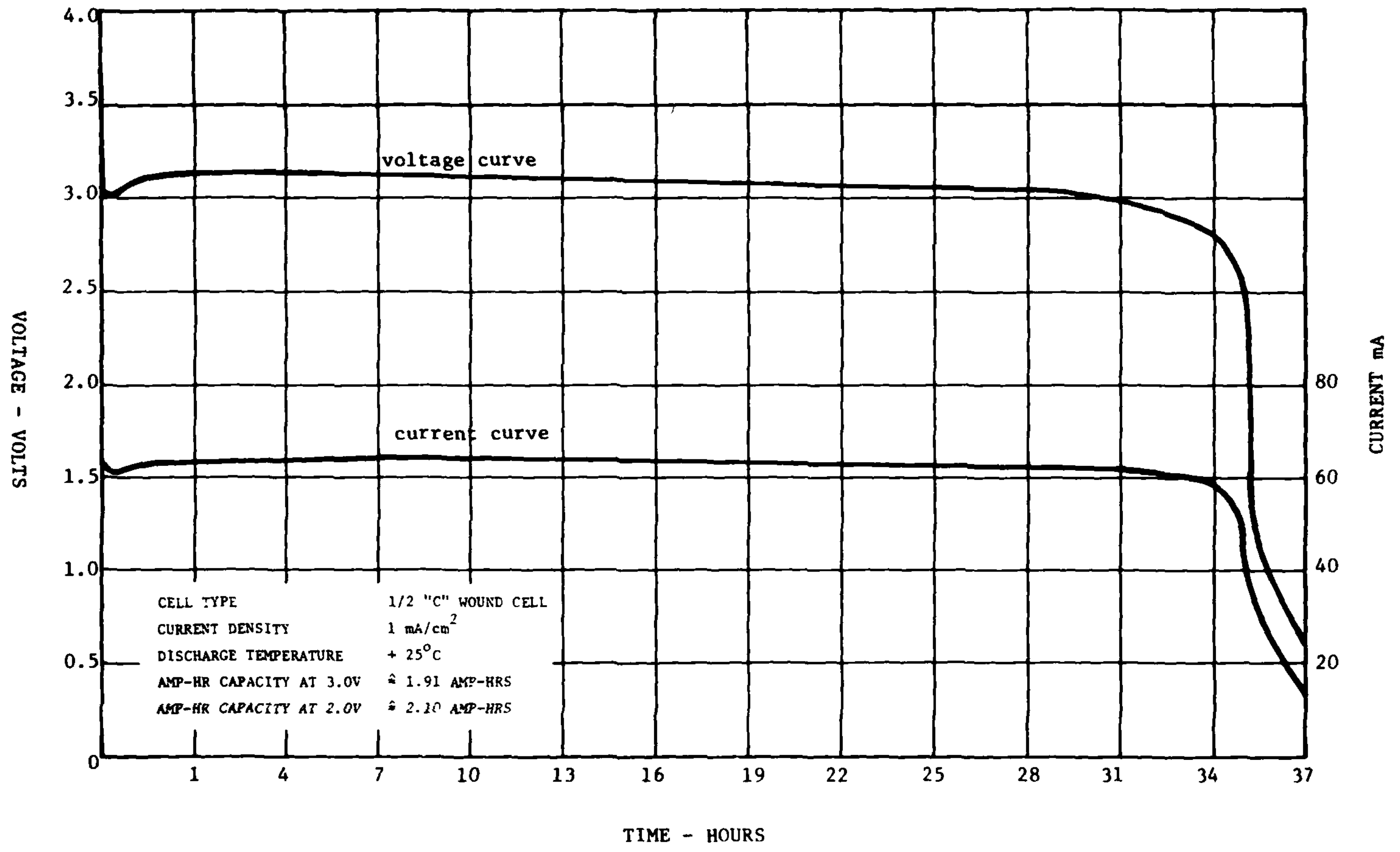

Figure 32. Discharge Results - Wound Cell (1mA/cm^2 at +25°C)

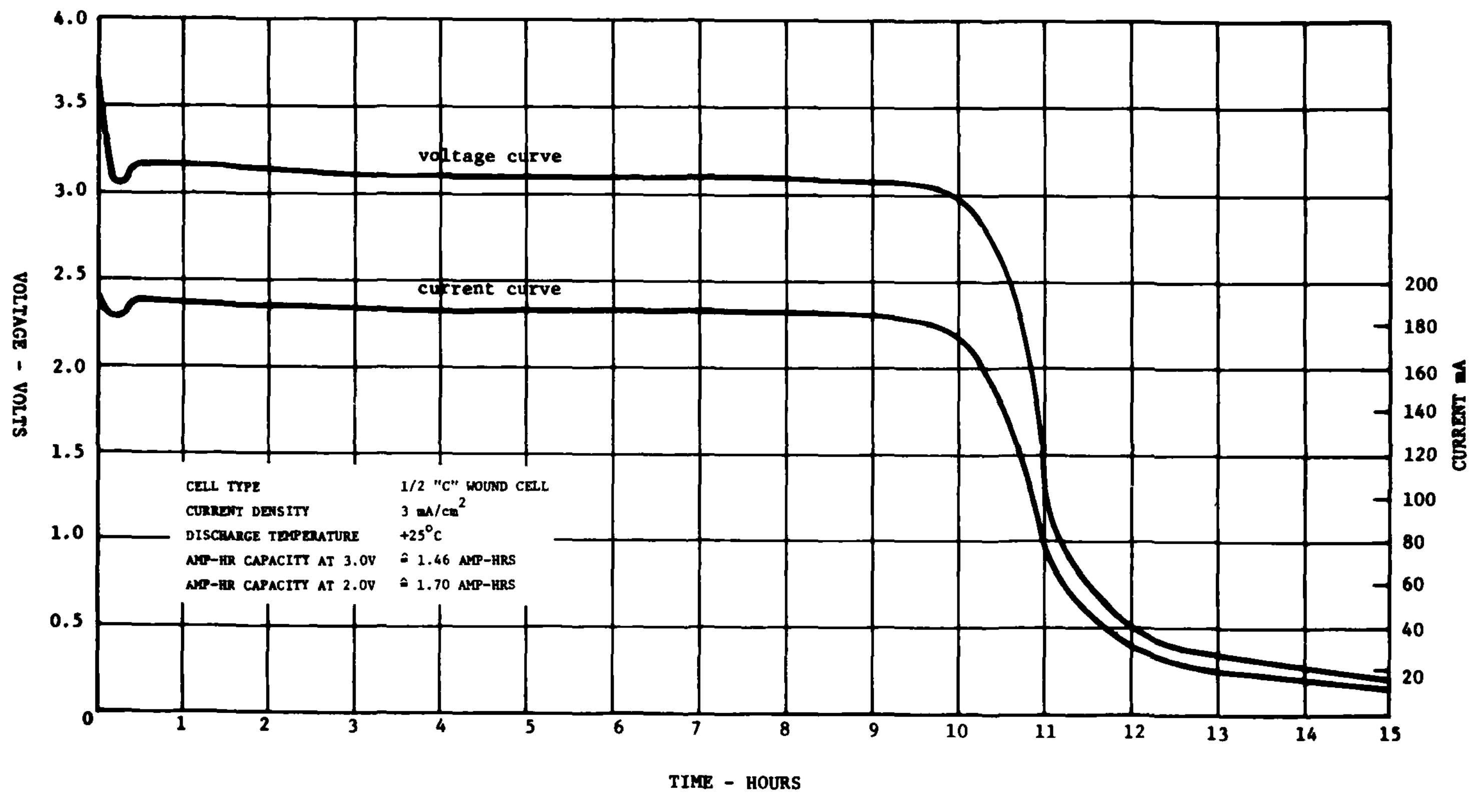

Figure 33. Discharge Results - Wound Cell (3mA/cm^2 at +25°C)

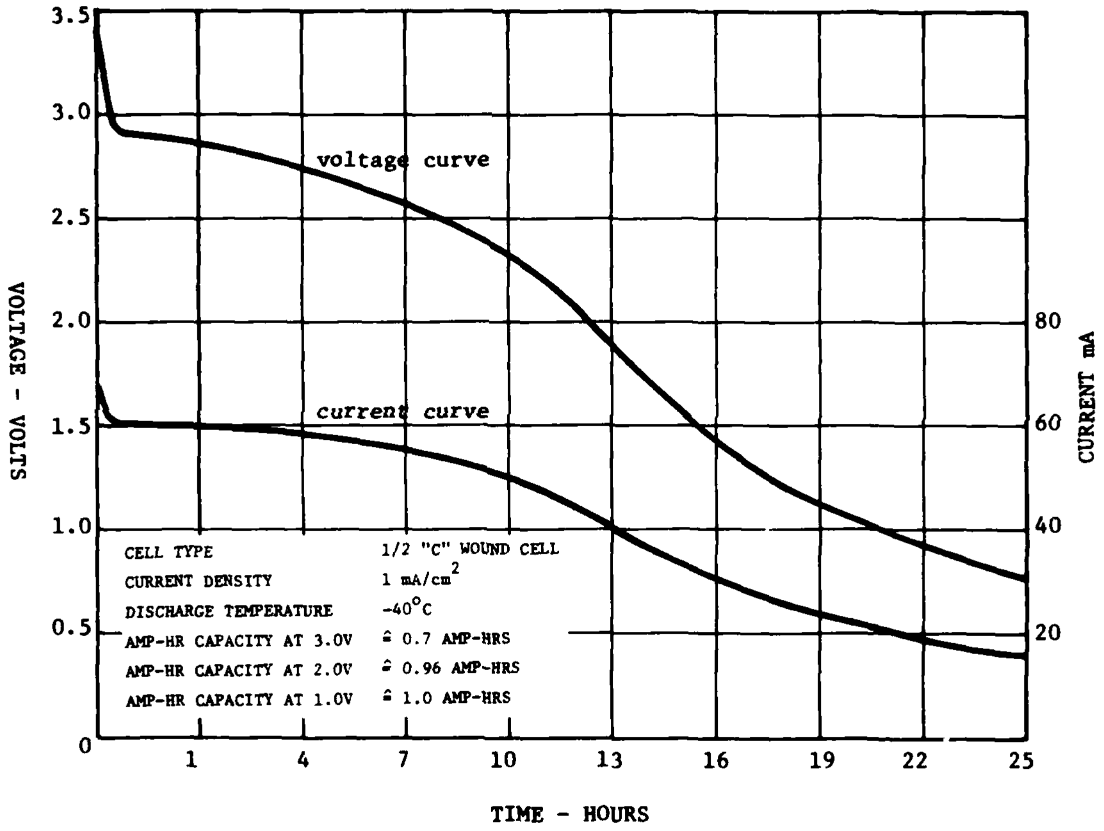

Figure 34. Discharge Results - Wound Cell (1 mA/cm^2 at -40°C)

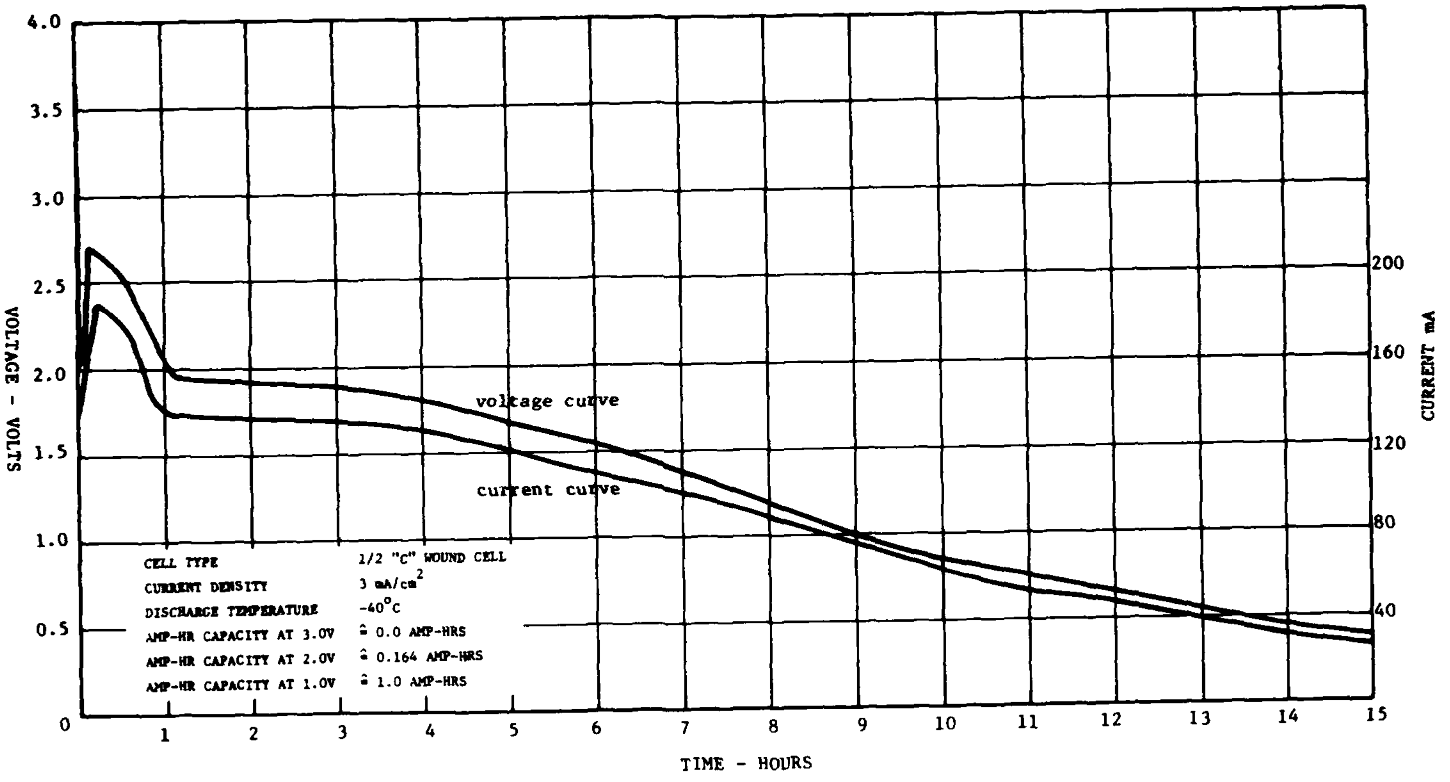

Figure 35. Discharge Results - Wound Cell (3 mA/cm^2 at $-40^{\circ}C$)

TABLE 4

DISC CELL DATA

(Page 1 of 2)

CELL NO.	NO. OF ELEM[1]	ELEM. THICK		CUMULATIVE THICKNESS				ACTIVE AREA	CARBON MIX	ELECT TYPE	TEST COND.	DISCH RATE	CURR. DENS.	CAPAC. 3.0V	CAPAC. 2.66V
		ANODE	CATHODE[2]	ANODE	CATHODE	SEPAR[3]	STACK	(c m^2)				(A)	(m/A/cm^2)	Ah	Ah
24	1	0.016	0.010	0.032	0.020	0.012	0.066	7.5	STAND.	$SOCl_2$	R T	0.0075	1	0.168	0.172
25a	1	0.016	0.007	0.032	0.0135	0.012	0.0595	7.5	STAND.	$SOCl_2$	R T	0.0075	1	0.1369	0.1505
26	1	CELL	FAILED					7.5		$SOCl_2$					
27a	1	0.016	0.007	0.032	0.014	0.012	0.060	7.5	STAND.	$SOCl_2$	-38°C	0.0075	1	0.014	0.0403
28	1	CELL	FAILED							$SOCl_2$					
29	1	0.016	0.010	0.032	0.019	0.012	0.065	7.5	STAND.	$SOCl_2$	-42°C	0.0075	1	0.0205	0.057
30	1	0.016	0.011	0.032	0.022	0.012	0.068	7.5	MOD.	$SOCl_2$	R T	0.0075	1	0.2153	0.2208
31	1	0.016	0.010	0.032	0.020	0.012	0.066	7.5	MOD.	$SOCl_2$	-43°C	0.0075	1	0.025	0.060
32	1	0.016	0.011	0.032	0.022	0.012	0.068	7.5	MOD.	SO_2Cl_2	-40°C	0.0075	1	0.101	0.110
33	1	0.016	0.010	0.032	0.020	0.012	0.066	7.5	STAND.	SO_2Cl_2	R T	0.0075	1	0.2002	0.2101
34	1	CELL	FAILED					7.5	STAND.	SO_2Cl_2	-40°C	0.0075	1	0.00	0.0691
35	1	0.016	0.009	0.032	0.018	0.012	0.064	7.5	MOD.	SO_2Cl_2	R T	0.0075	1	0.2045	0.2155
36	1	0.016	0.010	0.032	0.020	0.012	0.066	7.5	MOD.	SO_2Cl_2	-40°C	0.0075	1	183 Total	0.209 Total
37	10	0.016	0.007	0.160	0.137	0.120	0.437	75	STAND	SO_2Cl_2	R T	0.075	1	1.3981	1.547
38	10	0.016	0.010	0.160	0.1955	0.120	0.4955	75	MOD.	SO_2Cl_2	-40°C R T	0.075	1	1.522 Total	1.821 Total
39	10	0.011	0.010	0.110	0.1985	0.120	0.4485	75	MOD.	SO_2Cl_2	-35°C R T	0.075	1	1.44 Total	1.66 Total
40	1	0.011	0.010	0.022	0.019	0.012	0.055	7.5	MOD.	SO_2Cl_2	R T	0.0375	5	0.1645	0.1856
41	10	0.011	0.0096	0.110	0.1925	0.120	0.4425	75	MOD.	SO_2Cl_2	R T	0.075	1	1.618	—
42	1	0.016	0.010	0.032	0.020	0.012	0.066	7.5	MOD.	$SOCl_2$	R T	0.0375	5	0.0758	0.1251
43	15	0.011	0.010	0.165	0.2975	0.180	0.6125	112.5	MOD.	SO_2Cl_2	-40°C+ R T	0.1125	1	2.06 Total	2.32 Total
44	1	0.011	0.010	0.022	0.020	0.012	0.056	7.5	MOD.	$SOCl_2$	R T	0.0075	1	0.0694	0.0924
45	15	0.011	0.0105	0.165	0.317	0.180	0.697	112.5	MOD.	$SOCl_2$	R T	0.5625	5+1	1.56 Total	2.483 Total
46	1	0.011	0.010	0.022	0.020	0.012	0.056	7.5	MOD.	$SOCl_2$	R T	0.0075	1	0.1857	0.1958
47	1	0.011	0.0095	0.022	0.019	0.012	0.055	7.5	MOD.	SO_2Cl_2	R T	0.0075	1	0.208	0.214

TABLE 4

DISC CELL DATA

(Page 2 of 2)

CELL NO.	NO. OF ELEM.[1]	ELEM. THICK		CUMULATIVE THICKNESS				ACTIVE AREA	CARBON MIX	ELEC. TYPE	TEST COND.	DISCH RATE	CURRENT DENS.	CAPAC. 3.0V	CAPAC. 2.66V
		ANODE	CATHODE[2]	ANODE	CATHODE	SEPAR	STACK[3]	(cm^2)				(A)	(mA/cm^2)	Ah	Ah
48	5	0.011	0.0105	0.066	0.1075	0.060	0.243	37.5	MOD.	$SOCl_2$	-40°C R T	0.0375	1	0.318 Total	0.556 Total
EC00001	15	0.011	0.010	0.165	0.300	0.180	0.675	112.5	MOD.	SO_2Cl_2	R T	0.1125	1	2.235	2.365
49	3	0.011	0.0095	0.044	0.057	0.036	0.099	22.5	MOD.	$SOCl_2$	R T	0.0225	1	0.603	0.639

NOTES:

1 ONE ELEMENT INCLUDES: TWO CATHODE DISCS AND TWO HAVE ANODES AND ONE CATHODE SUBSTRATE (.002" THICK)

2 THIS IS THE AVERAGE THICKNESS FOR EACH CATHODE DISC.

3 THIS MEASUREMENT INCLUDES THE THICKNESS OF ONE CATHODE SUBSTRATE PER ELEMENT.

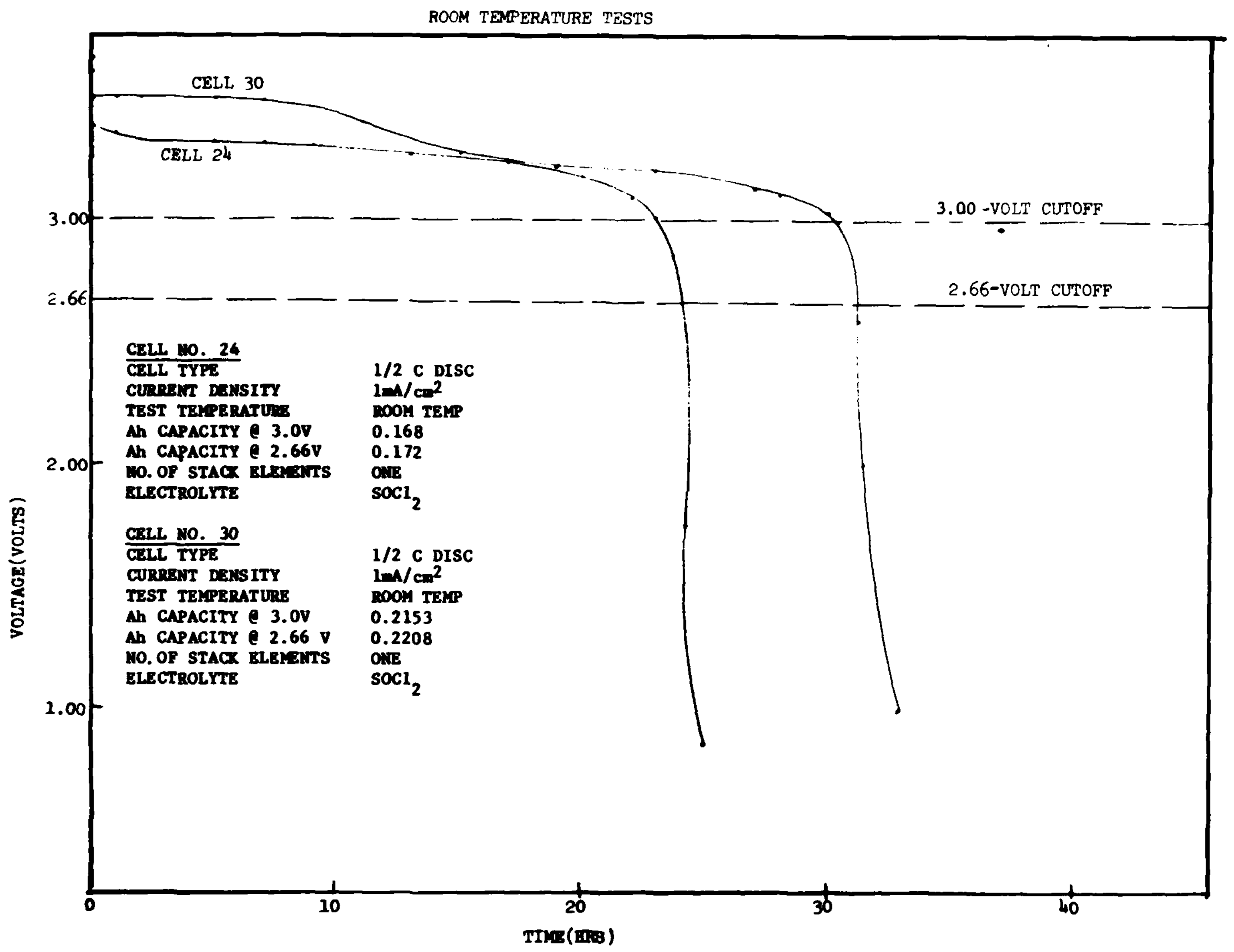

Figure 36. Discharge Results - Cells 24 and 30

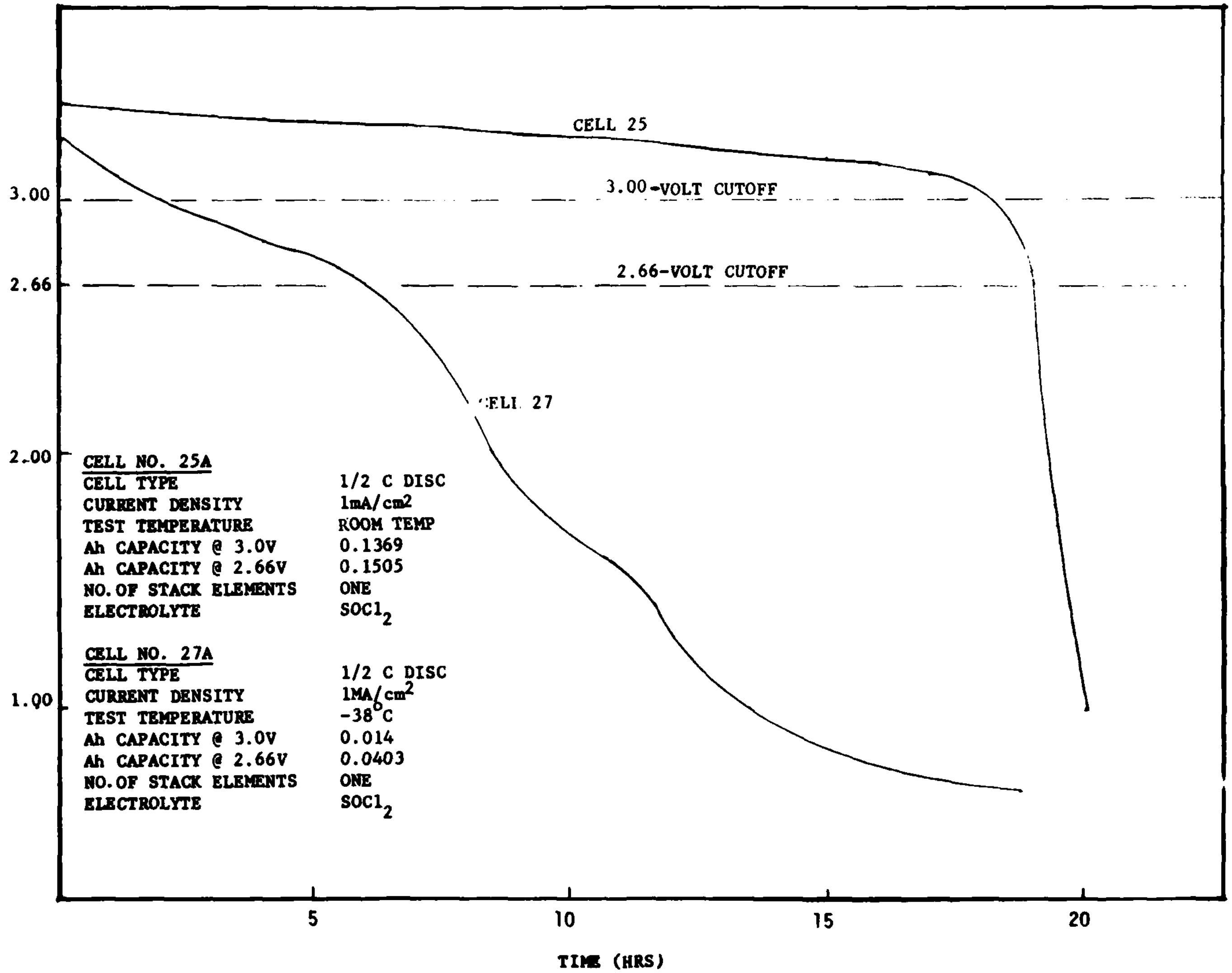

Figure 37. Discharge Results - Disc Cells 25A and 27A

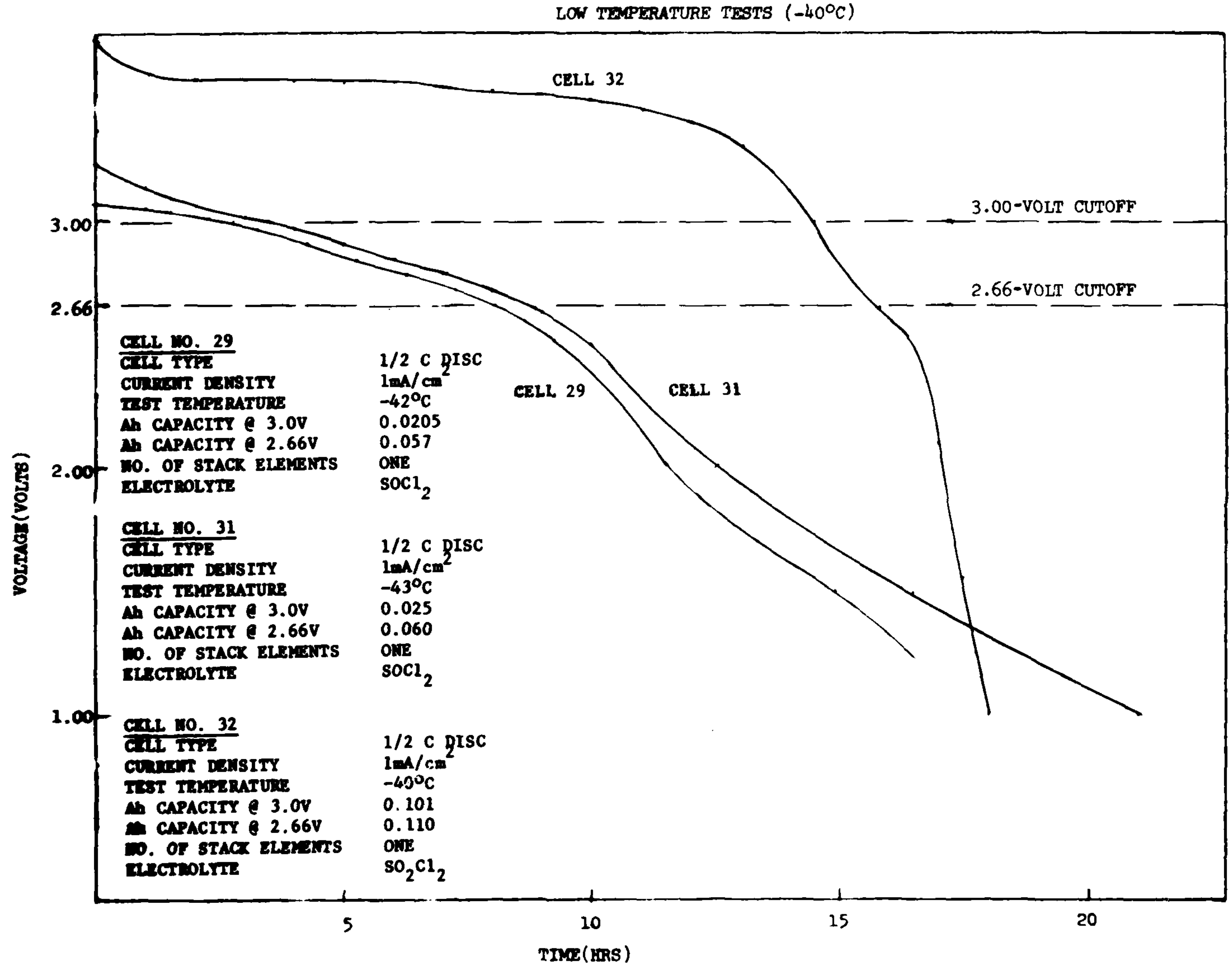

Figure 38. Discharge Results - Disc Cells 29, 31, and 32

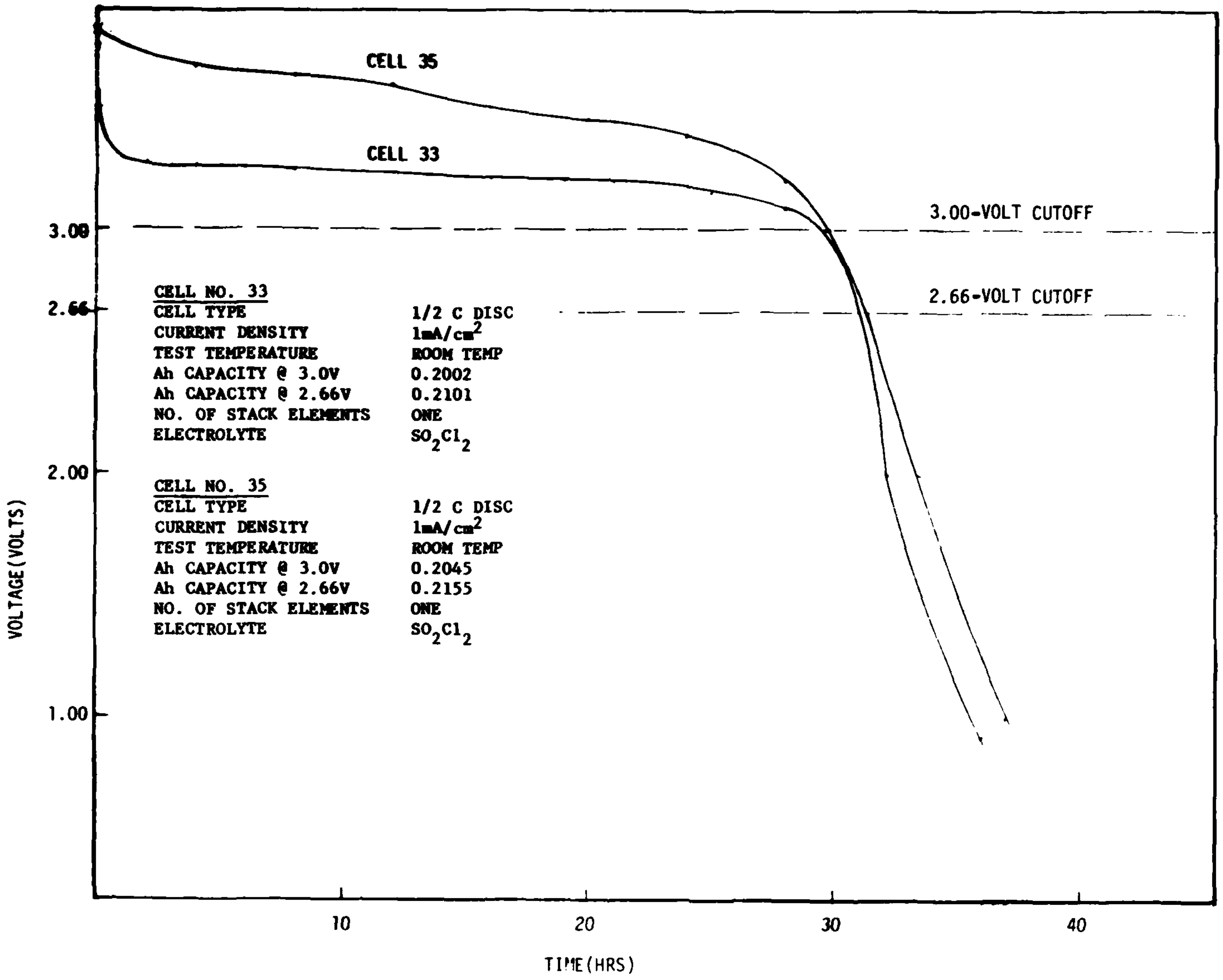

Figure 39. Discharge Results - Disc Cells 33 and 35

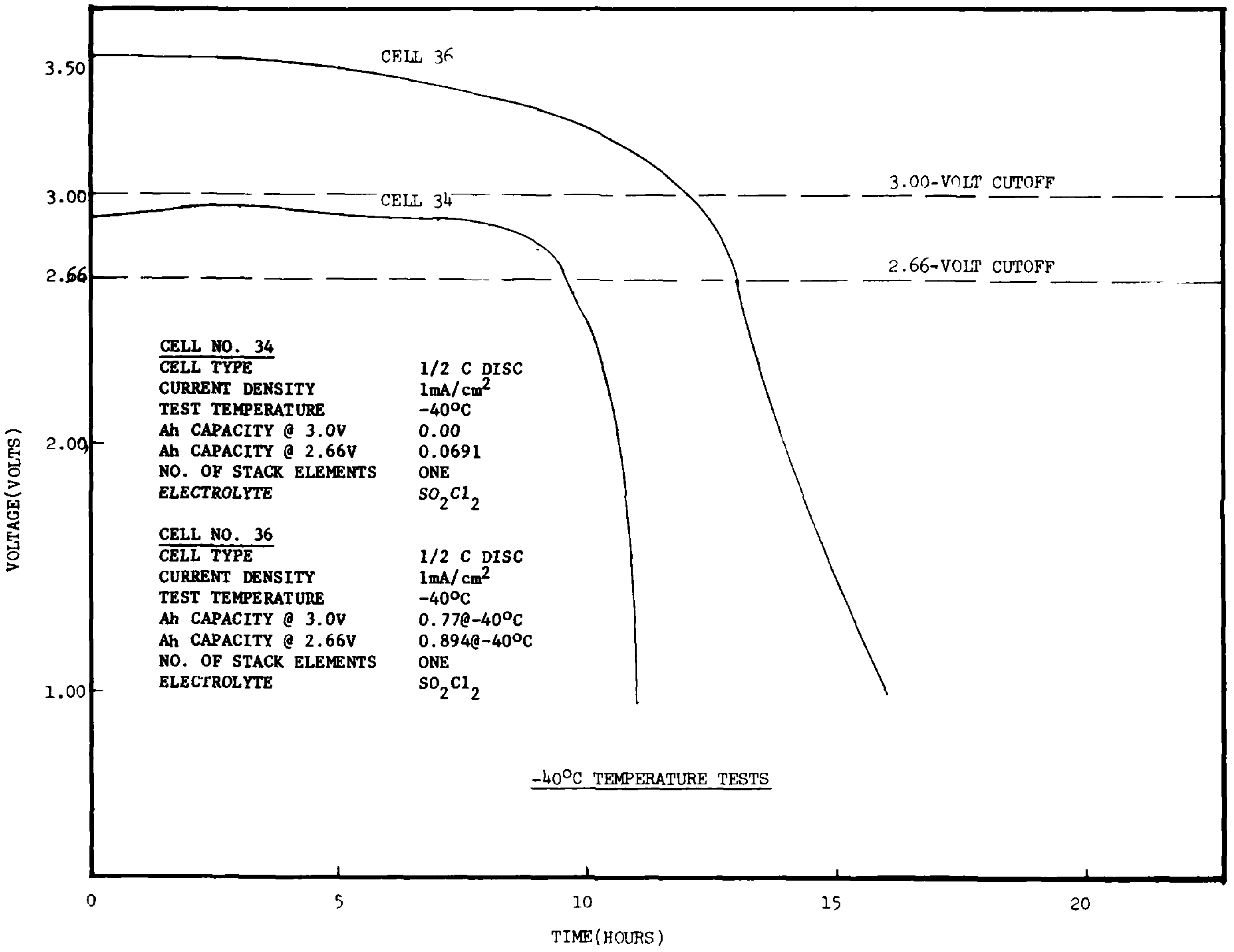

Figure 40. Discharge Results - Disc Cells 34 and 36

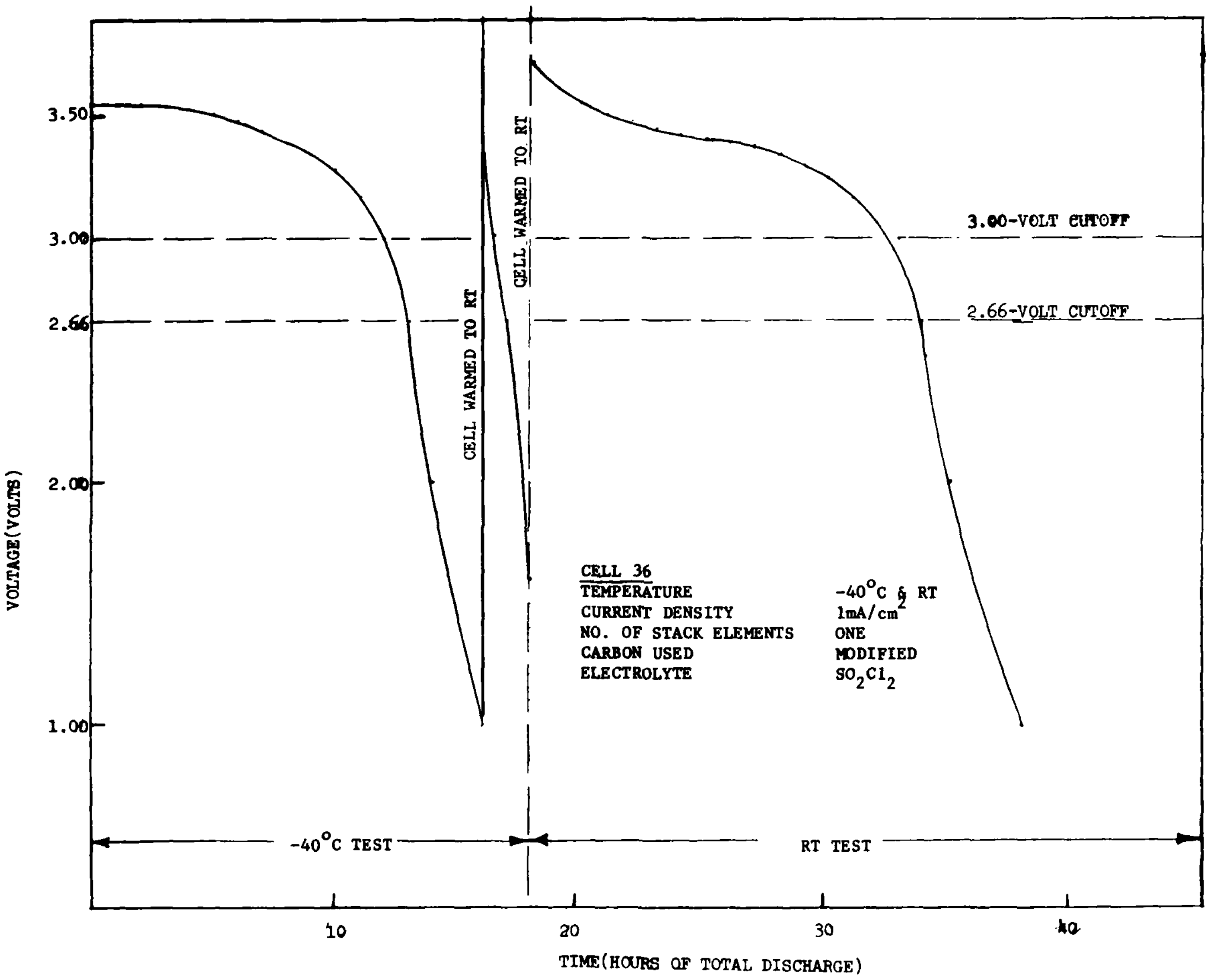

Figure 41. Discharge Results - Disc Cell 36

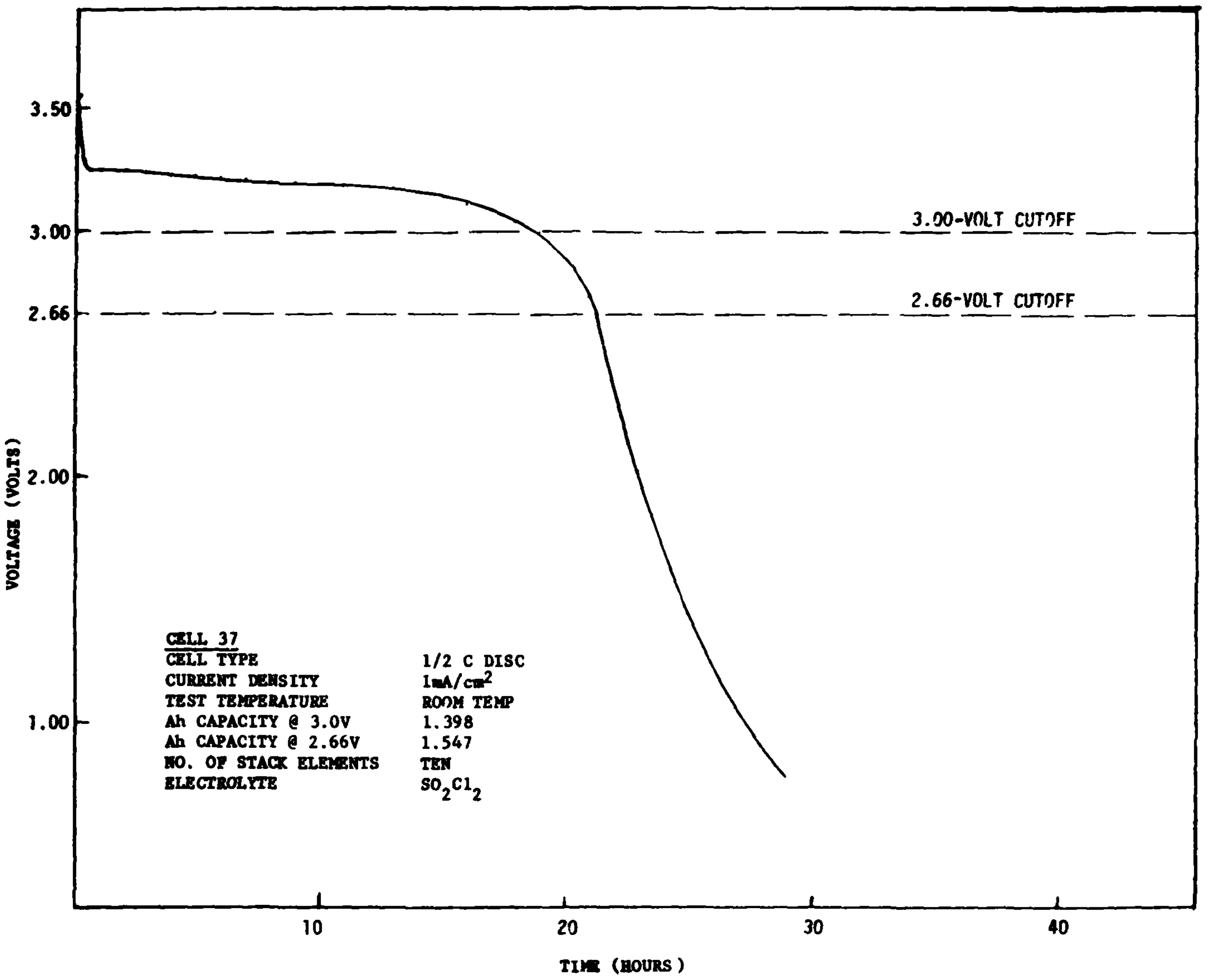

Figure 42. Discharge Results - Disc Cell 37

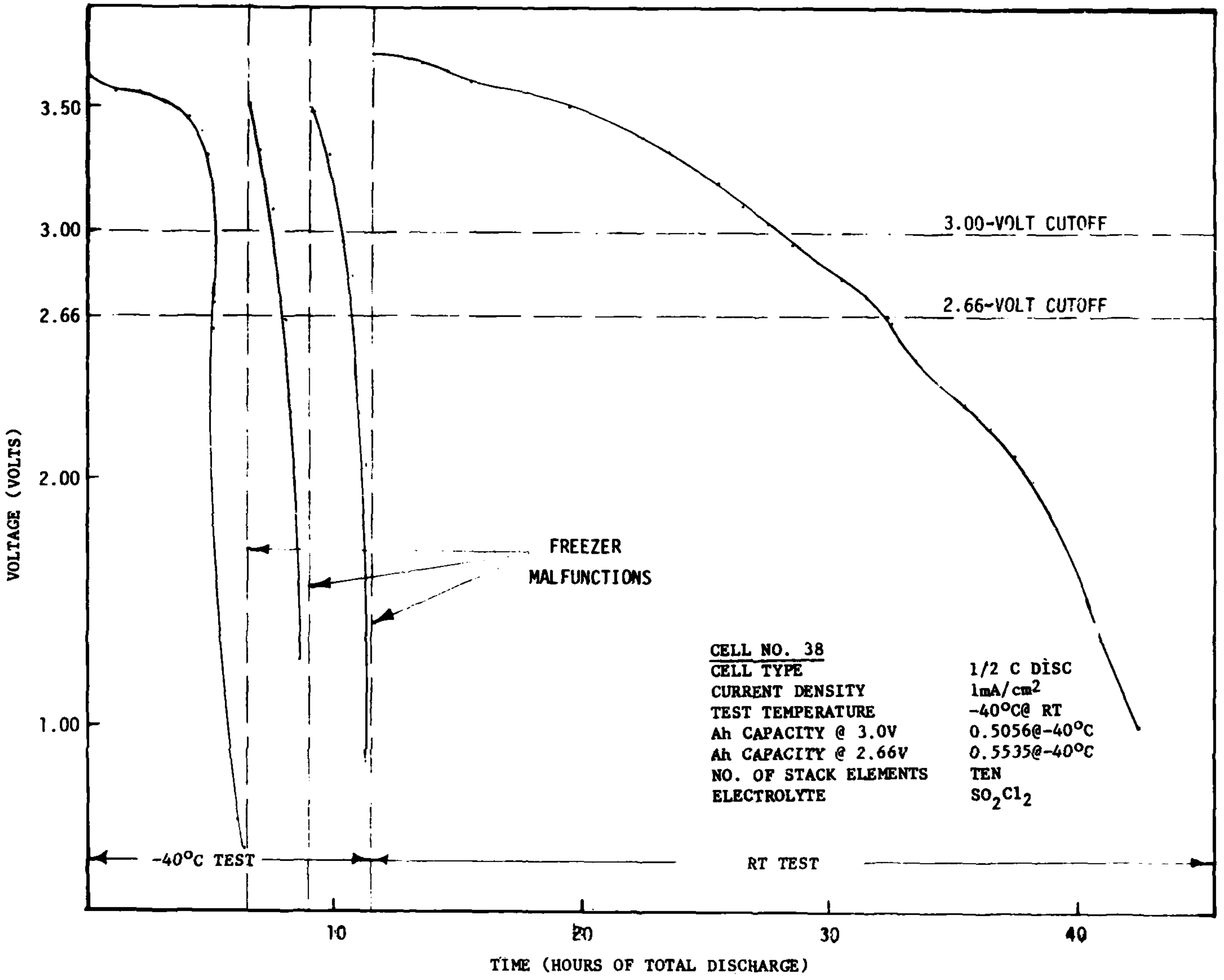

Figure 43. Discharge Results - Disc Cell 38

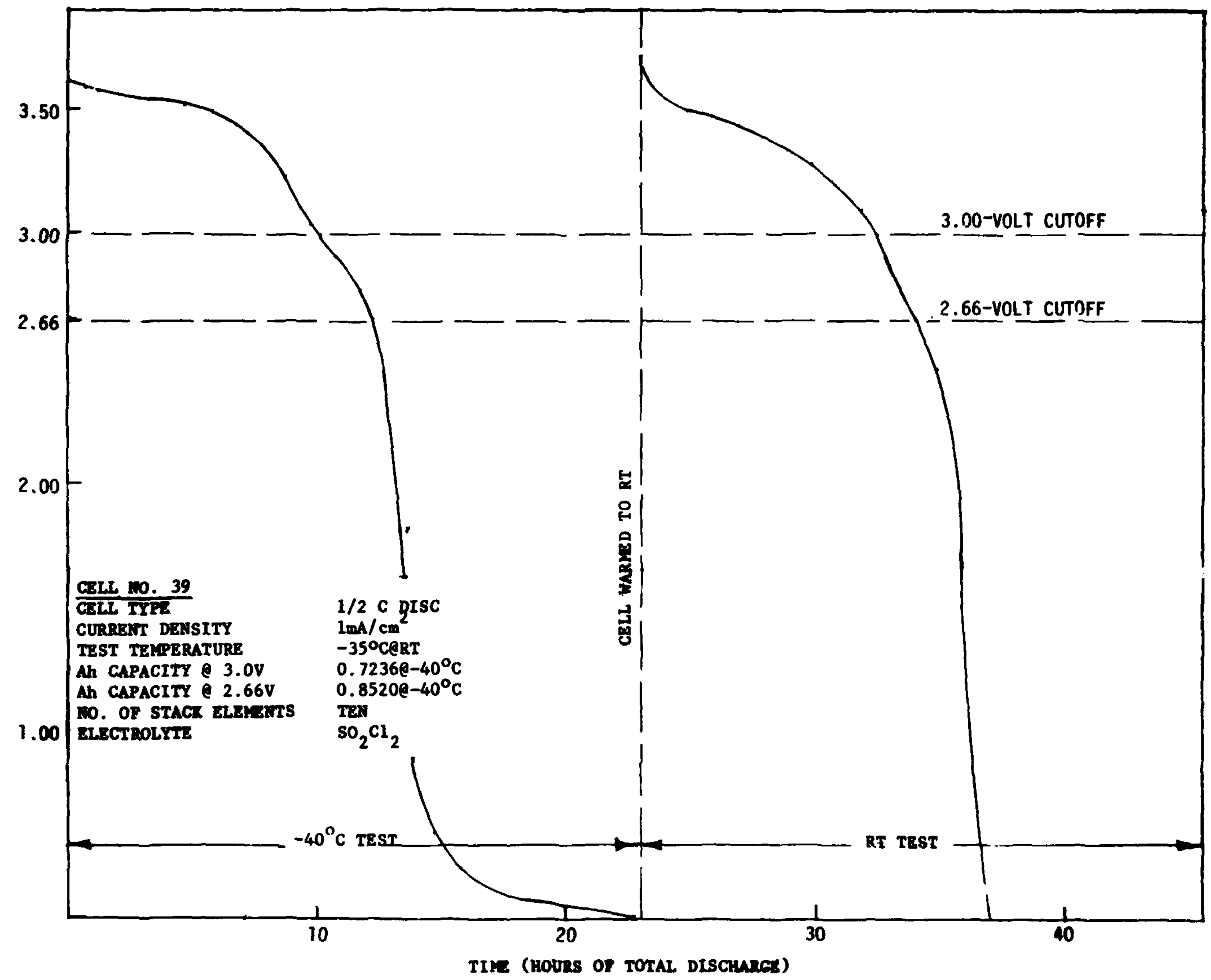

Figure 44. Discharge Results - Disc Cell 39

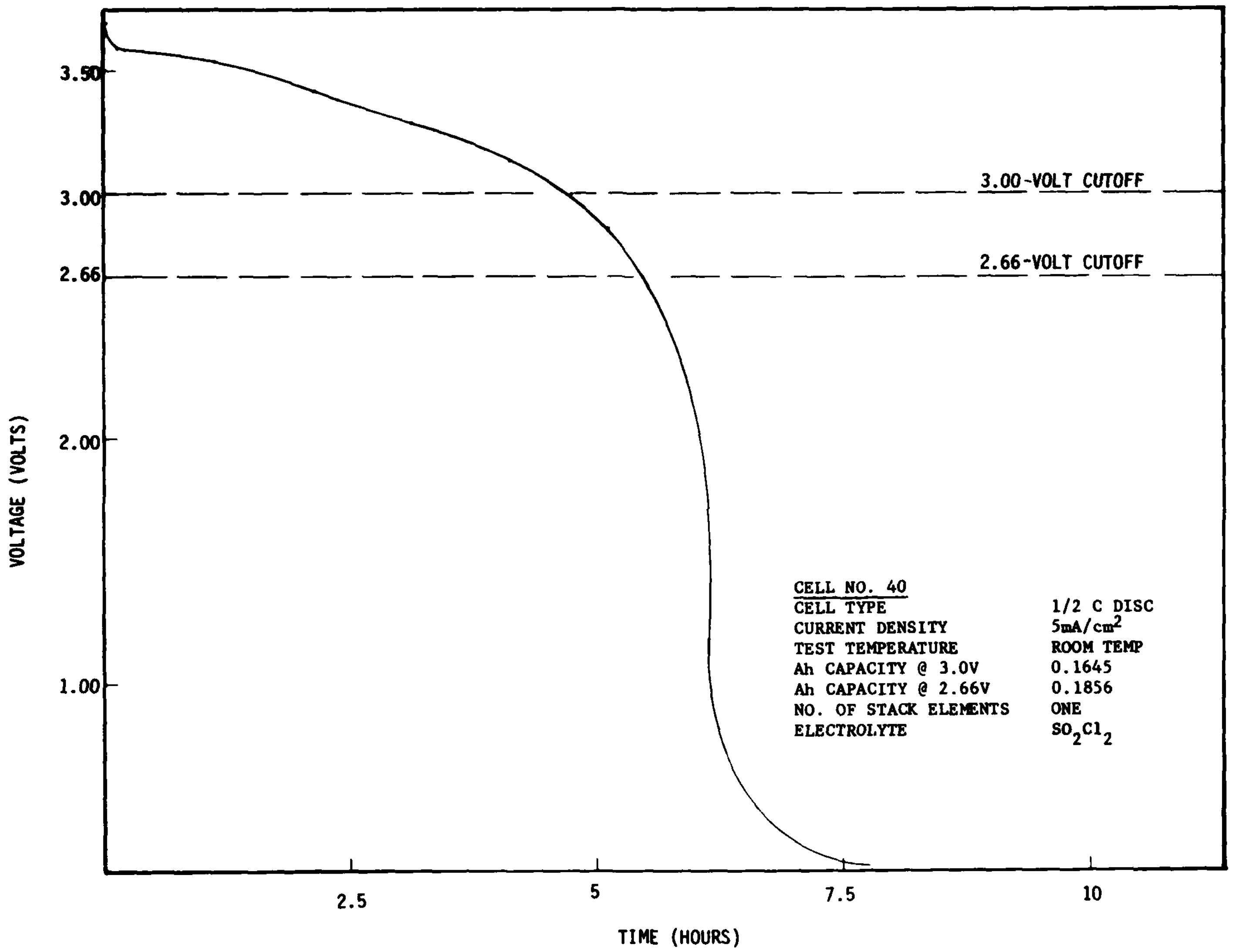

Figure 45. Discharge Results - Disc Cell 40

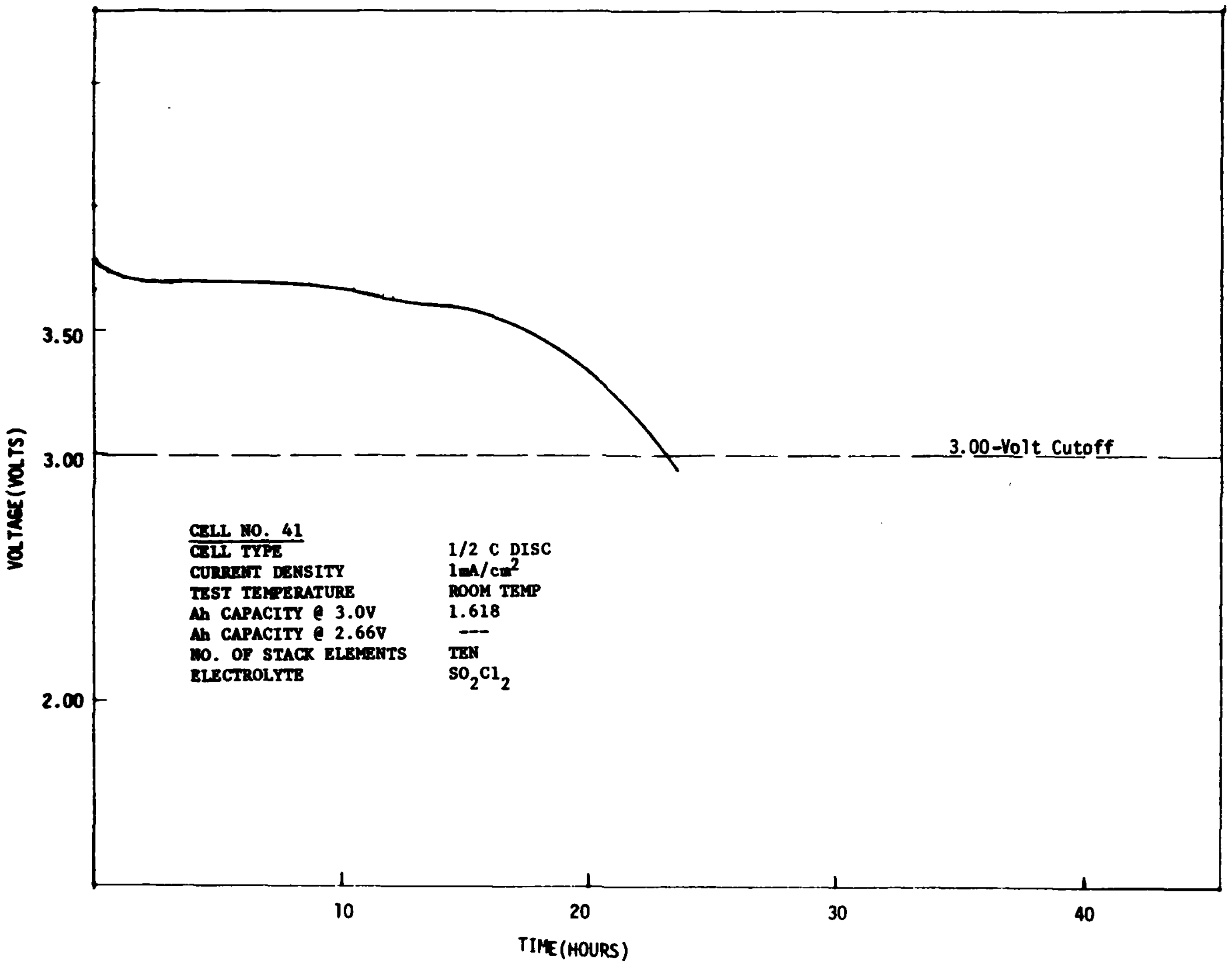

Figure 46. Discharge Results - Disc Cell 41

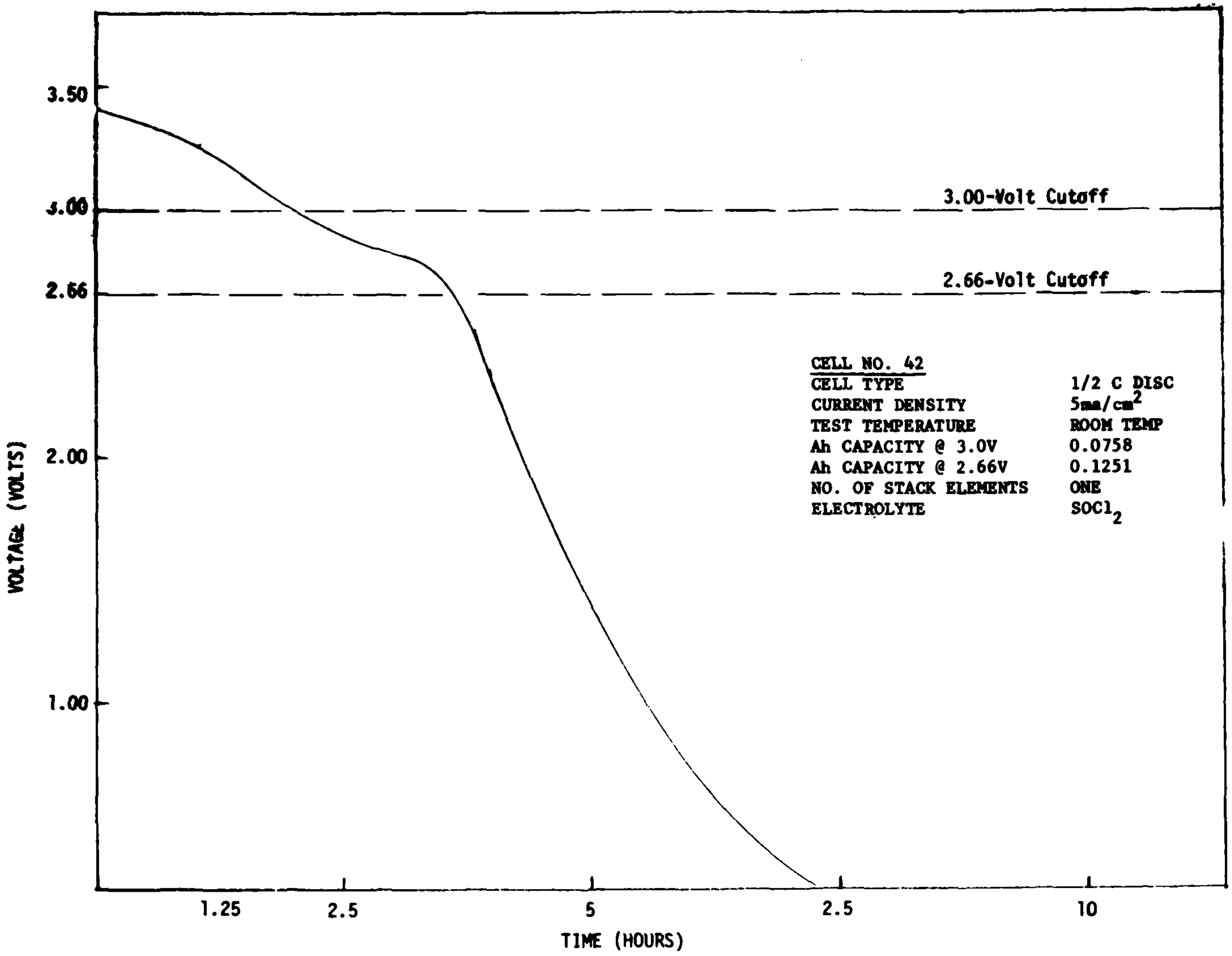

Figure 47. Discharge Results - Disc Cell 42

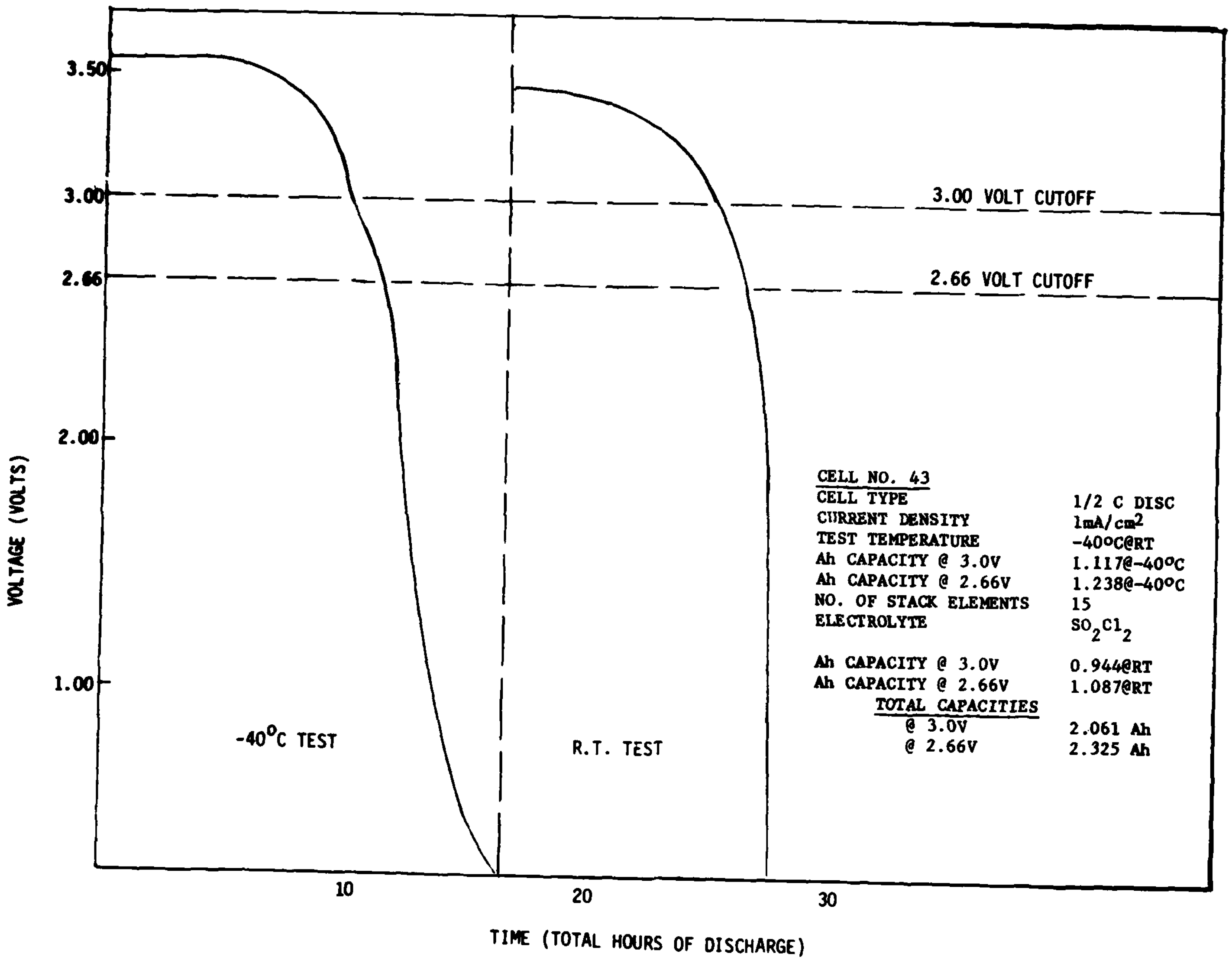

Figure 48. Discharge Results - Disc Cell 43

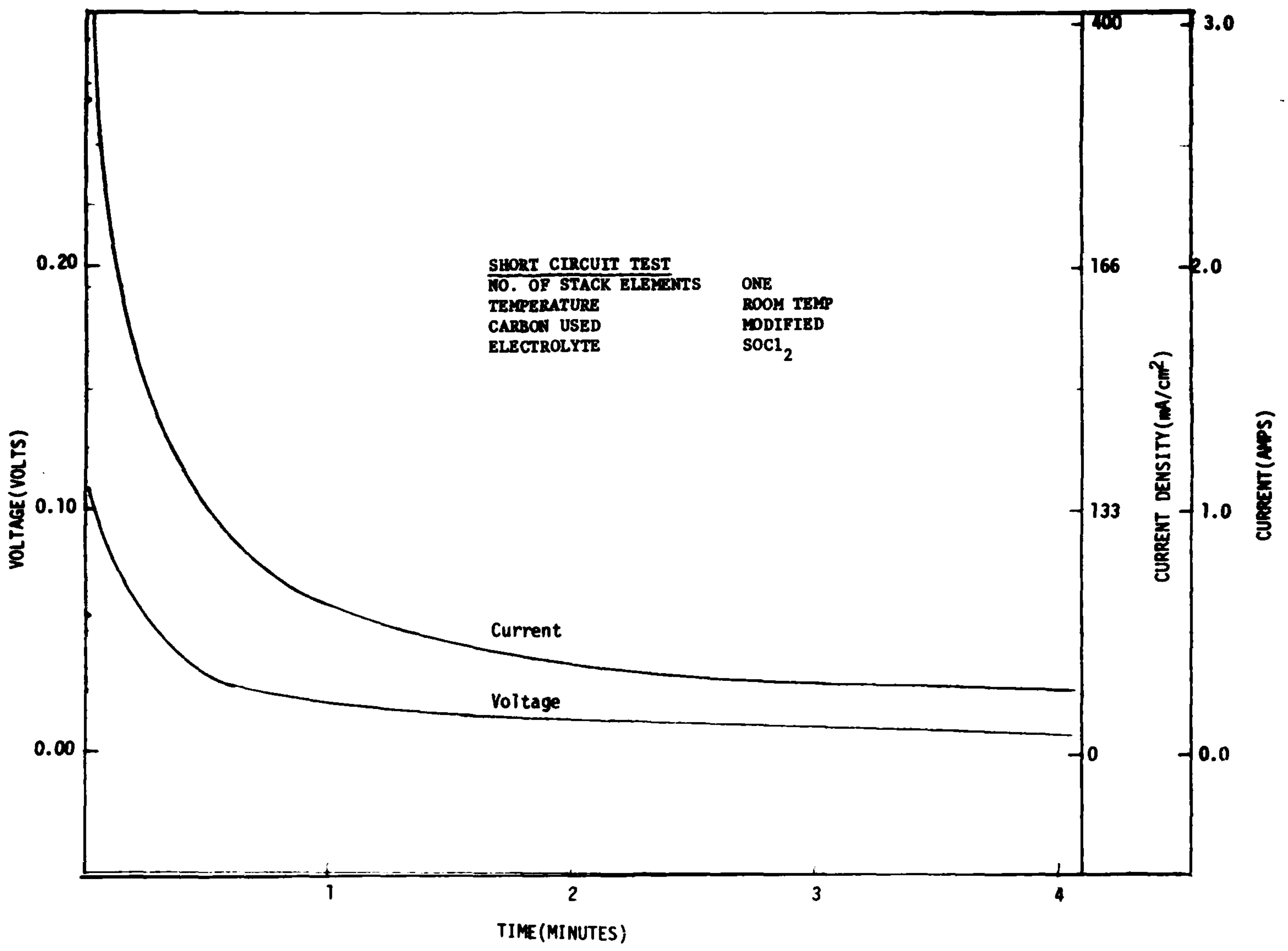

Figure 49. Discharge Results - Disc Cell Short Circuit Test

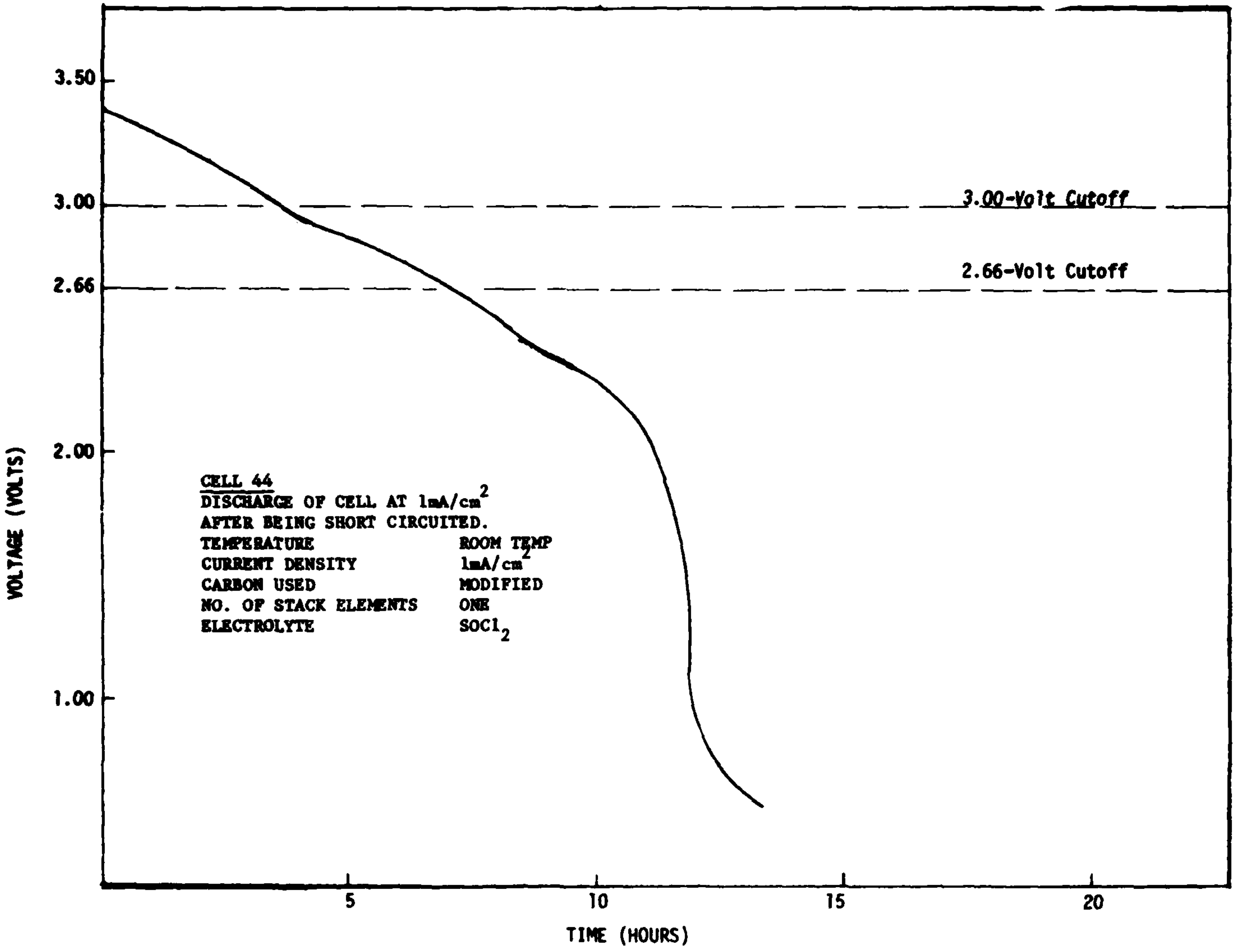

Figure 50. Discharge Results - Disc Cell 44

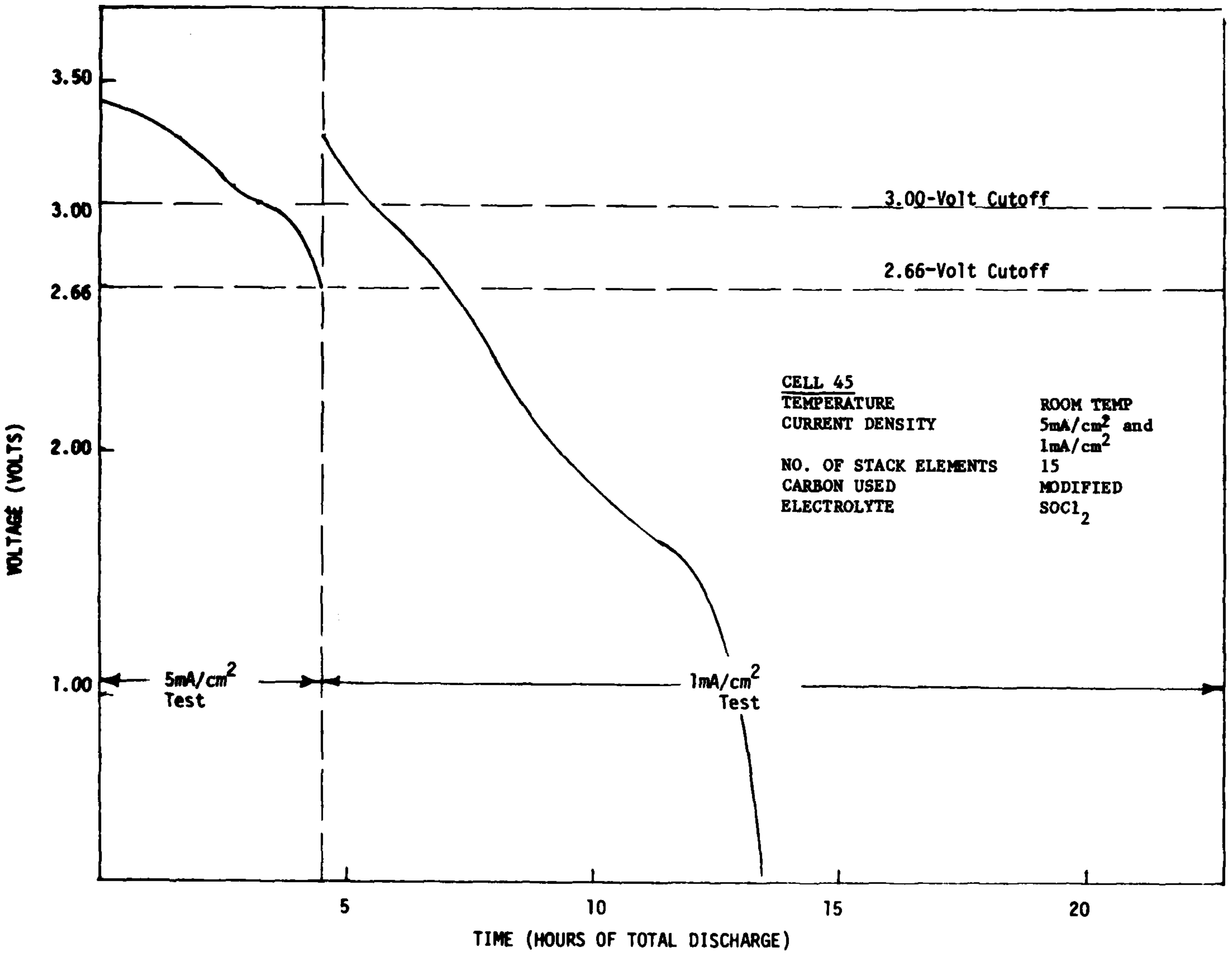

Figure 51. Discharge Results - Disc Cell 45

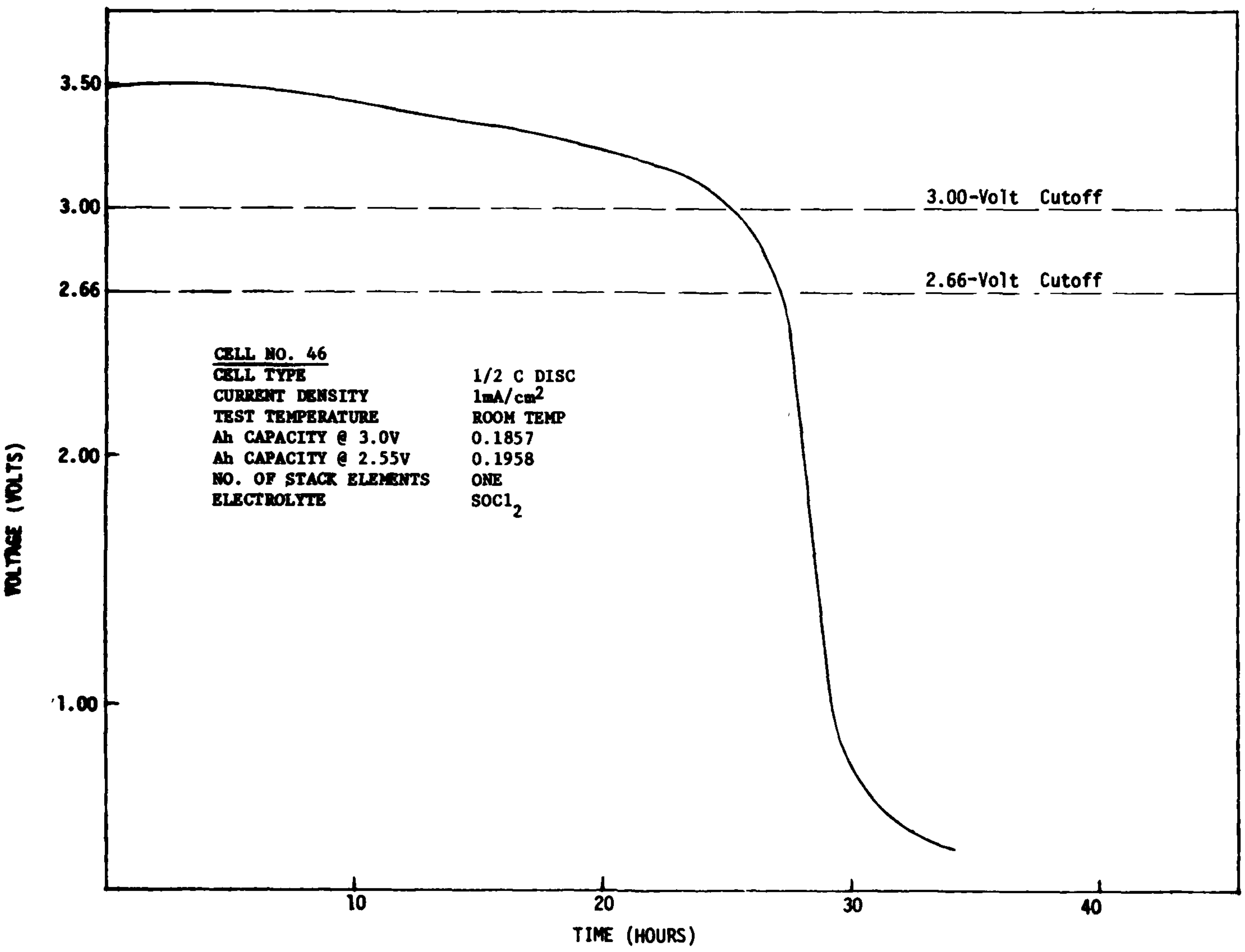

Figure 52. Discharge Results - Disc Cell 46

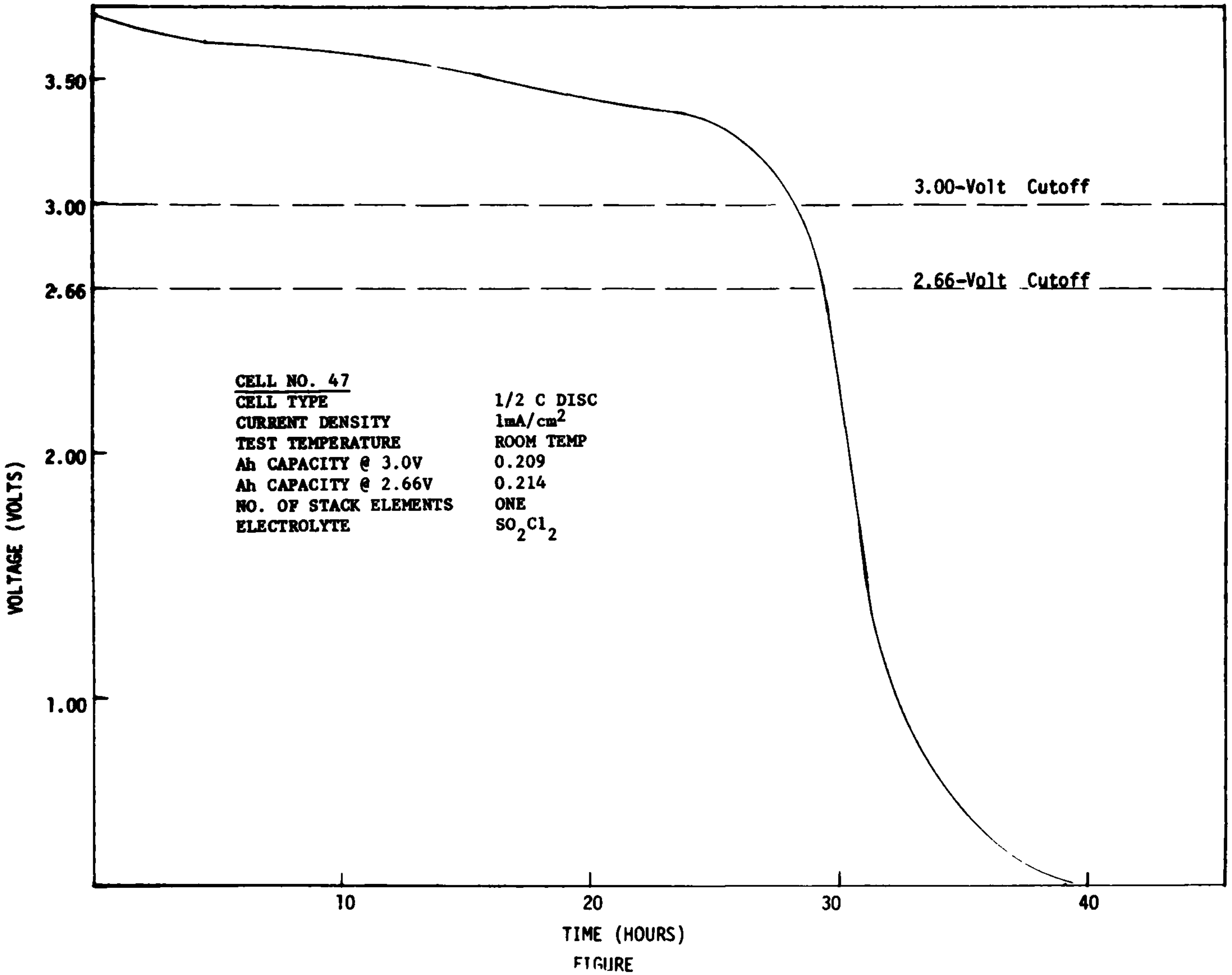

Figure 53. Discharge Results - Disc Cell 47

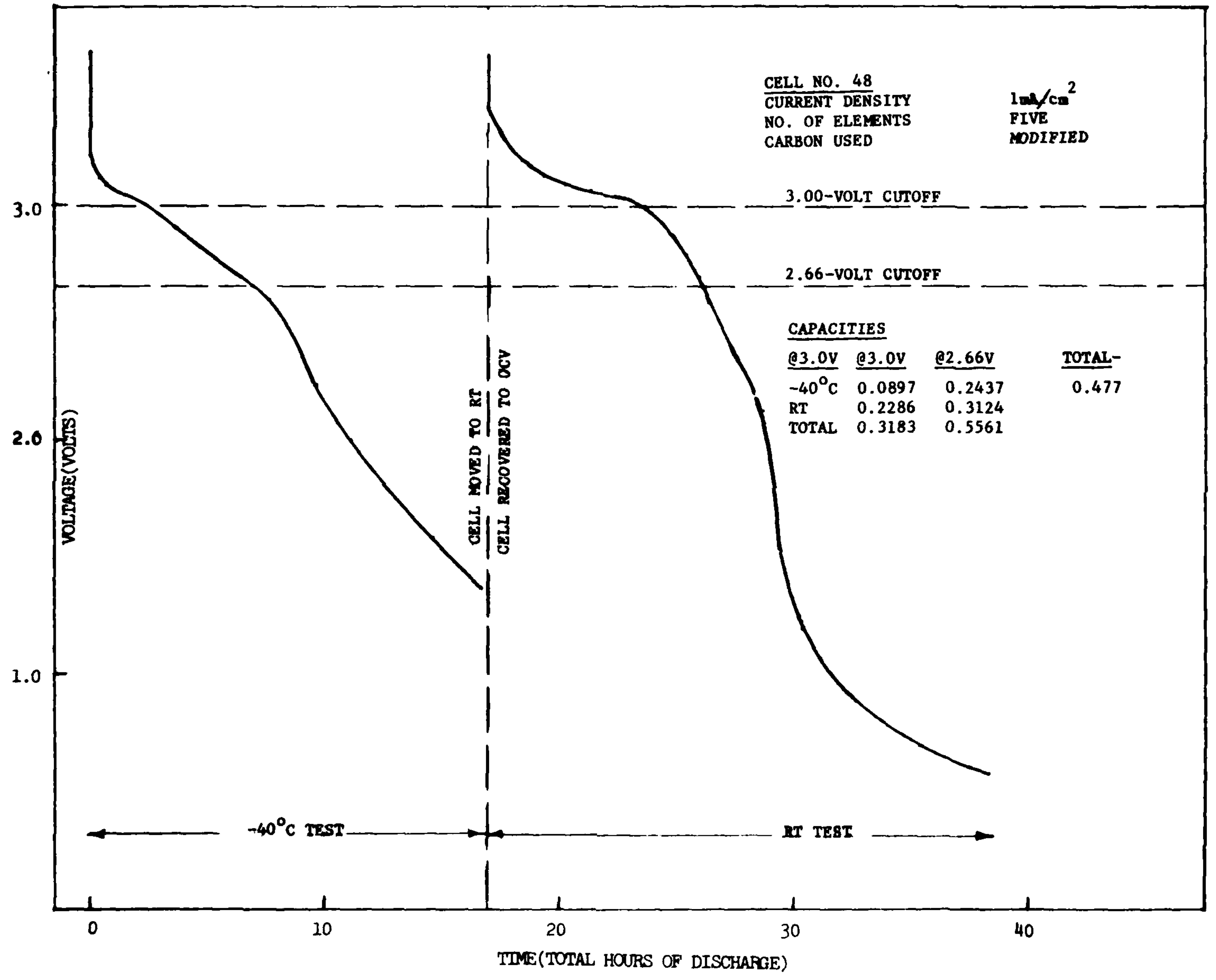

Figure 54. Discharge Results - Disc Cell 48

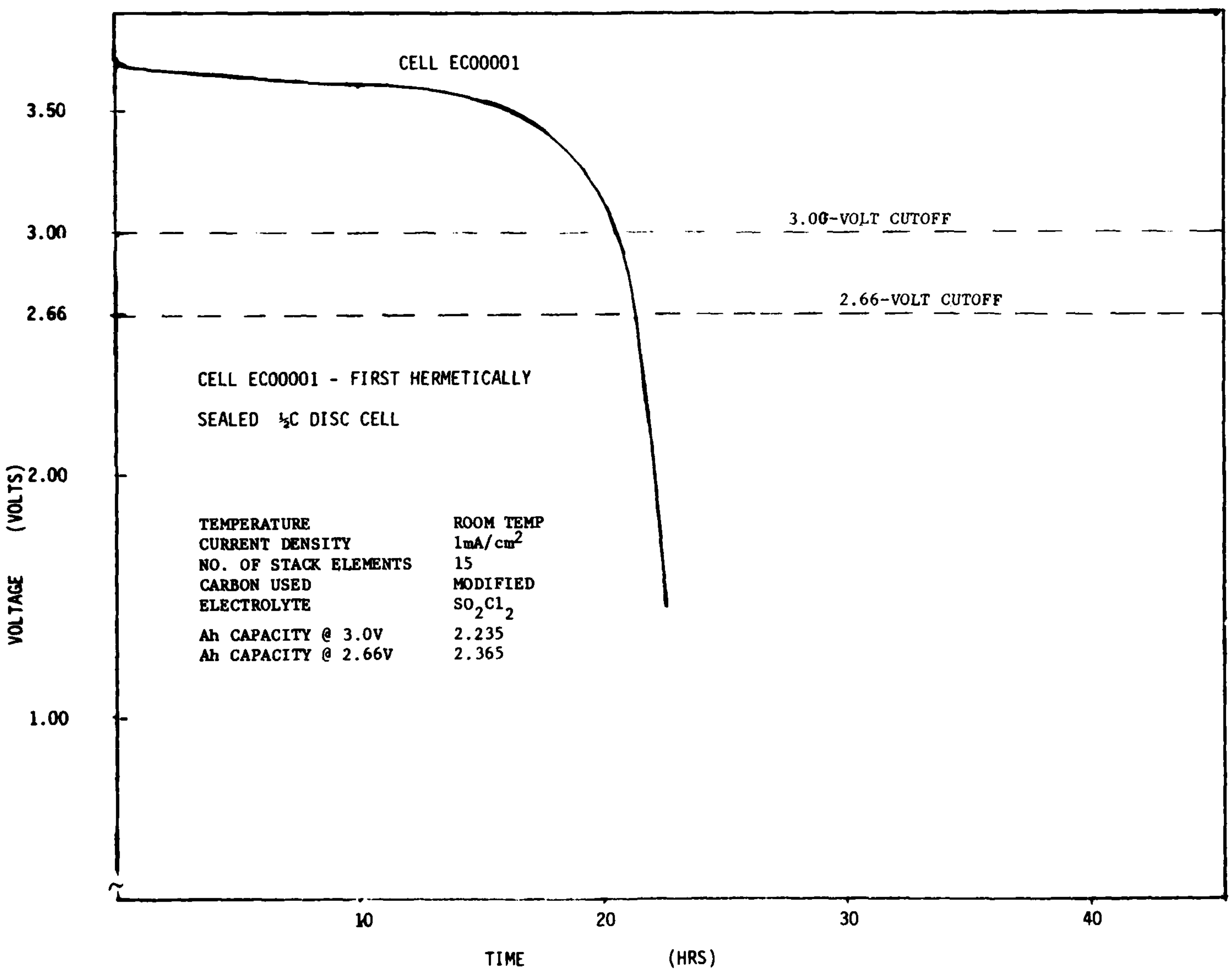

Figure 55. Discharge Results - Disc Cell EC00001

AD-A098 711   GTE PRODUCTS CORP NEEDHAM HEIGHTS MA STRATEGIC SYSTE--ETC F/G 10/3
LITHIUM INORGANIC ELECTROLYTE BATTERY DEVELOPMENT.(U)
JAN 71 F GOEBEL, R MCDONALD, G YOUNGER   F33615-77-C-2021
UNCLASSIFIED   AFWAL-TR-80-2121   NL

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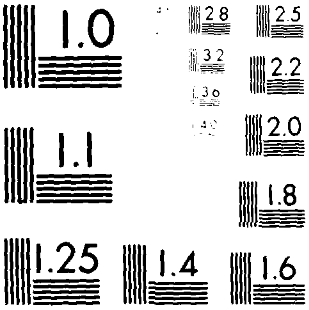

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

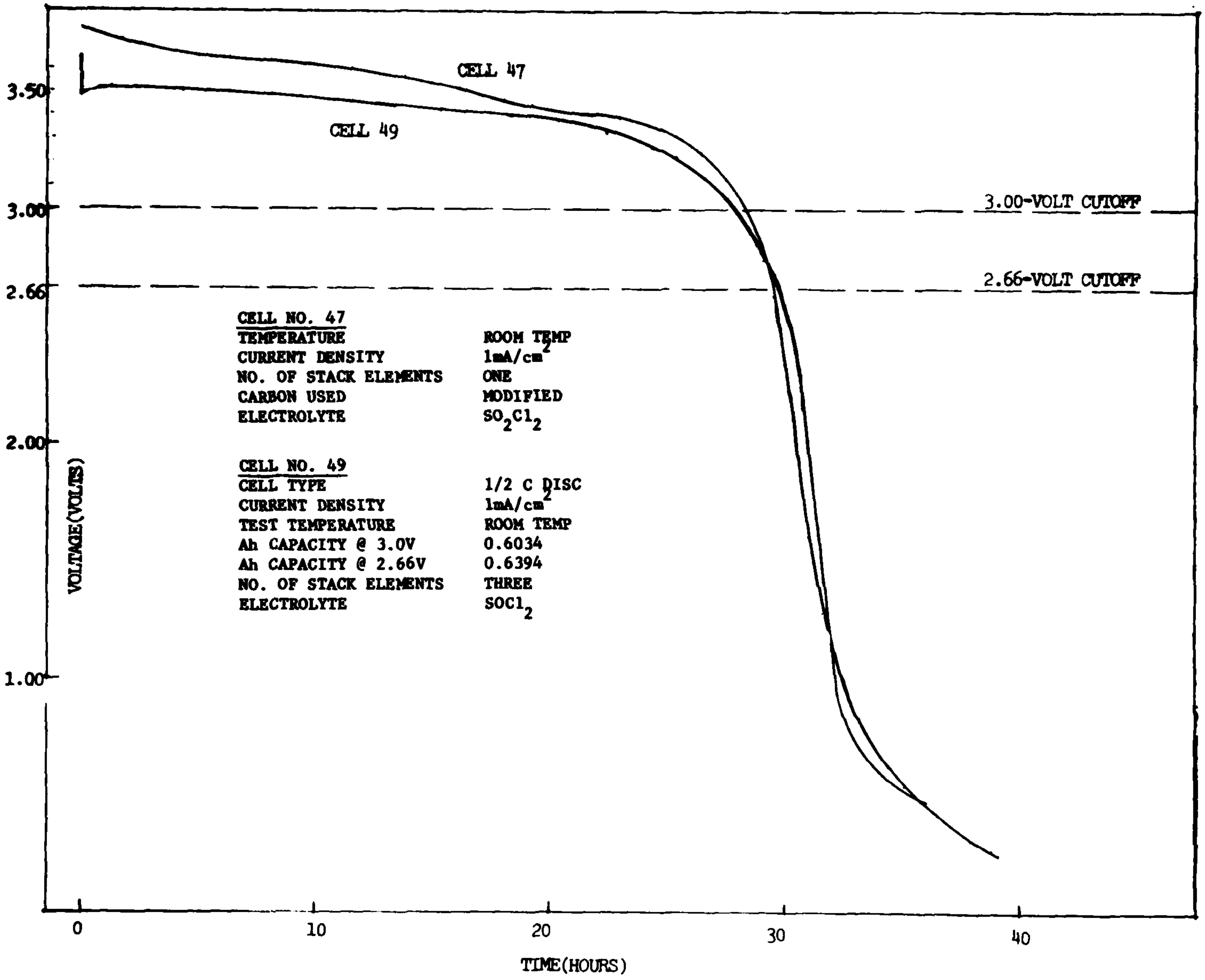

Figure 56. Discharge Results - Disc Cells 47 and 49

The capacity obtained from disc cells with $SOCl_2$ discharged at 1 mA/cm^2 at -40°C to 3.0-volt cutoff was 11.6 percent of the room-temperature capacity and 33 percent for cells using SO_2Cl_2. Capacity to 2. 0 volts cutoff was 40 percent for both electrolytes. These cells were warmed to room temperature (RT) after -40°C testing and then discharged. The total capacity obtained from these cells, at both -40° and RT, was 98 to 100 percent of the total capacity obtained from an identical cell discharged at RT only (Figures 41, 43, 44, 48, 51, and 54). Disc cells were also discharged at 5 mA/cm^2 at RT. The capacity to 3.0-volt cutoff was 70 percent, and to 2.0 volt cutoff was 86.8 percent, of the cells discharged at 1 mA/cm^2 and RT. The voltage cutoff requirement for the man-pack radio is 2.66 volts. The capacity of the cells discharged to 2.66 volts at -40°C was approximately 38.5 percent of room temperature capacity for both electrolytes.

Two abuse tests were performed: a shock test on cell EC00001 (hermetically sealed with a total stack), and a short circuit test on cell No. 44 (single element). The shock pulses applied to cell EC00001 were terminal peak sawtooth in shape, 100 g in magnitude, and six ms in duration. The cell was subjected to two shock pulses in the longitudinal axes (one in each direction) and two shock pulses in the transverse axes (one direction). Throughout the test, the cell's open circuit voltage showed no significant change or indication of physical damage. This cell was then discharged at RT at 1 mA/cm^2 to verify normal performance (Figure 54).

The short circuit test was conducted on a single element cell (No. 44). The initial current was 3.18 amperes (424 mA/cm^2). This figure, if compared to a full stack, would be 47.7 amperes. This amount of current would burn out the internal contacts before a hazardous level would be reached. The short circuit test characteristics are shown in Figure 49. After the short circuit test, the cell was discharged at 1 mA/cm^2. This is shown in Figure 50.

4.4 CONCLUSION

During the course of the program, it could be demonstrated that with a multi-disc half-C cell, the requirements to power a man-pack radio at -40°C can be met if thinner lithium anode material could be procured from the supplier. At -40°C, the cell delivered never less than 30 percent of its room temperature capacity, and upon recovery to room temperature , most of the remaining capacity could be obtained above 3.0-volt operating voltage. This performance was demonstrated with $SOCl_2$ and SO_2Cl_2 electrolyte using modified carbon material. The disc-type electrodes permitted to double the role capability by increasing the geometrical electrode surface area within the same volume occupied by a jelly-role configuration.

Sufficient amounts of data have been obtained to qualify the electrochemical performance of the new disc design for its application. In addition, a short circuit test on a fractional stack and a shock test on a complete hermetically sealed half-C cell were completed. However, to assure the safe operation of the cell, a more complete test program needs to be conducted. Additional cells have to be built for a better statistical evaluation.

5.0 PASSIVATION

5.1 INTRODUCTION

Passivation in Li/$SOCl_2$ cells consists of the surface reaction of lithium directly with thionyl chloride to produce a film of lithium chloride (LiCl). This film prevents the complete and rapid reaction of lithium and thionyl chloride at moderate temperatures. On discharge of a cell, lithium ions must be conducted through this film from the lithium metal anode to the electrolyte solution. The ionic conductivity is affected by film morphology, porosity, thickness, crystallinity, and the presence of trace elements.

Under certain conditions, the passive film may grow to a thickness sufficient to retard ionic flow. When a cell is first placed on load, a thick film of LiCl on the lithium anode will cause a delay before normal operating voltage is obtained. This delay is often accompanied by a voltage drop, the magnitude of which is a function of applied discharge rate, storage time, storage temperature, and cell physical and chemical design.

The purpose of the tests described below was to establish the baseline voltage delay behavior of single and double D cells (D and DD) at 25°C and 55°C after various storage periods.

5.2 EXPERIMENTAL

Lithium-limited D cells of the bobbin configuration were used to study passivation. Both voltage delay and capacity were measured for cells stored for various lengths of time up to 20 weeks at 25°C and 55°C. Voltage delay is defined as the time required for the cell to reach 3.0 volts with an applied current of 2 mA/cm^2. Capacity is defined in ampere-hours for a cell discharged at 1 mA/cm^2 to a 3.0-volt cutoff.

Temperatures were maintained within ± 3°C. Voltage, current, and temperature were recorded using a Fluka Datalogger.

$SOCl_2$ electrolyte was prepared in the usual way to reduce trace amounts of water, metals, and organics. The conductive solute was 1.8M $LiAlCl_4$. $SOCl_2 + SO_2$ was prepared by addition of 1.0M SO_2 to the $SOCl_2$ electrolyte. $SOCl_2$ + Ca electrolyte was prepared by addition of 0.5M Ca $(AlCl_4)$ to the $SOCl_2$ electrolyte. SO_2Cl_2 electrolyte was prepared in a manner similar to $SOCl_2$ electrolyte using 1.8M $LiAlCl_4$ as the conductive salt.

5.3 RESULTS

None of the electrolyte combinations showed voltage delay when discharged freely at room temperature. An initial set of 55°C storage results shown in Table 5 were tainted by the suspicion that the electrolytes used were wet. Additional storage tests were conducted at 55°C using freshly prepared dry electrolyte. The results proved to be like those obtained initially. The two sets of results are shown in Figure 57. Each point represents the average of three to five tests.

Figure 58 shows average discharge curves for the second (dry electrolyte) set of cells after five months storage at 55°C. Each curve is an average of five cell discharges. An error bar showing the average deviation is included on each curve.

Figure 59 shows voltage delay results after storage at 55°C for five months.

TABLE 5

VOLTAGE DELAY IN D CELLS STORED AT 55°C WITH VARIOUS ELECTROLYTES

Electrolyte Type	Baseline Capacity Delay (Ah)	Month 1 Capacity Delay (Ah)	Month 2 Capacity Delay (Ah)
$SOCl_2$	5.112	3.891 0.2 sec	4.472 1.8h
	5.182	4.928 0.8 sec	1.821 2.0h
	5.012	4.218 1.2 sec	3.157 2.0h
$SOCl_2 + SO_2$	5.151	5.066 2h 1m 11s	4.750 2.0h
	5.054	4.600 1 16 45	5.768 2.0
	5.172	5.117 - 19 20	4.143 1.6
$SOCl_2$ + Ca	5.132 0.31 sec	4.055 0	2.17 2 hrs
	4.949 0.37 sec	4.035 6s	1.90 56m 10s
	5.009 0.50 sec	4.616 0	2.18 50m 51s
SO_2Cl_2	4.8	1.98 1m 29s	4.10 --
	4.9	2.10 29 sec	4.35 --
	4.6	2.00 34 sec	4.52 --

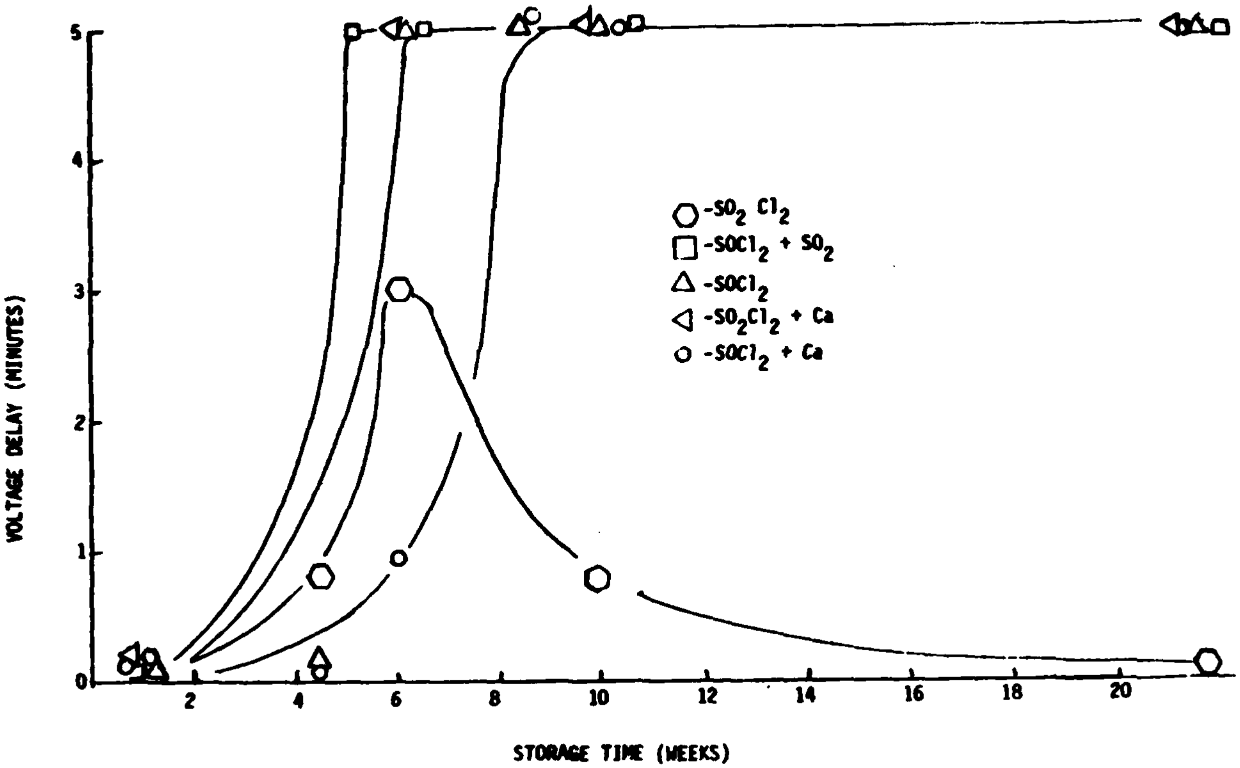

Figure 57. Voltage Delay Following Storage at 55°C

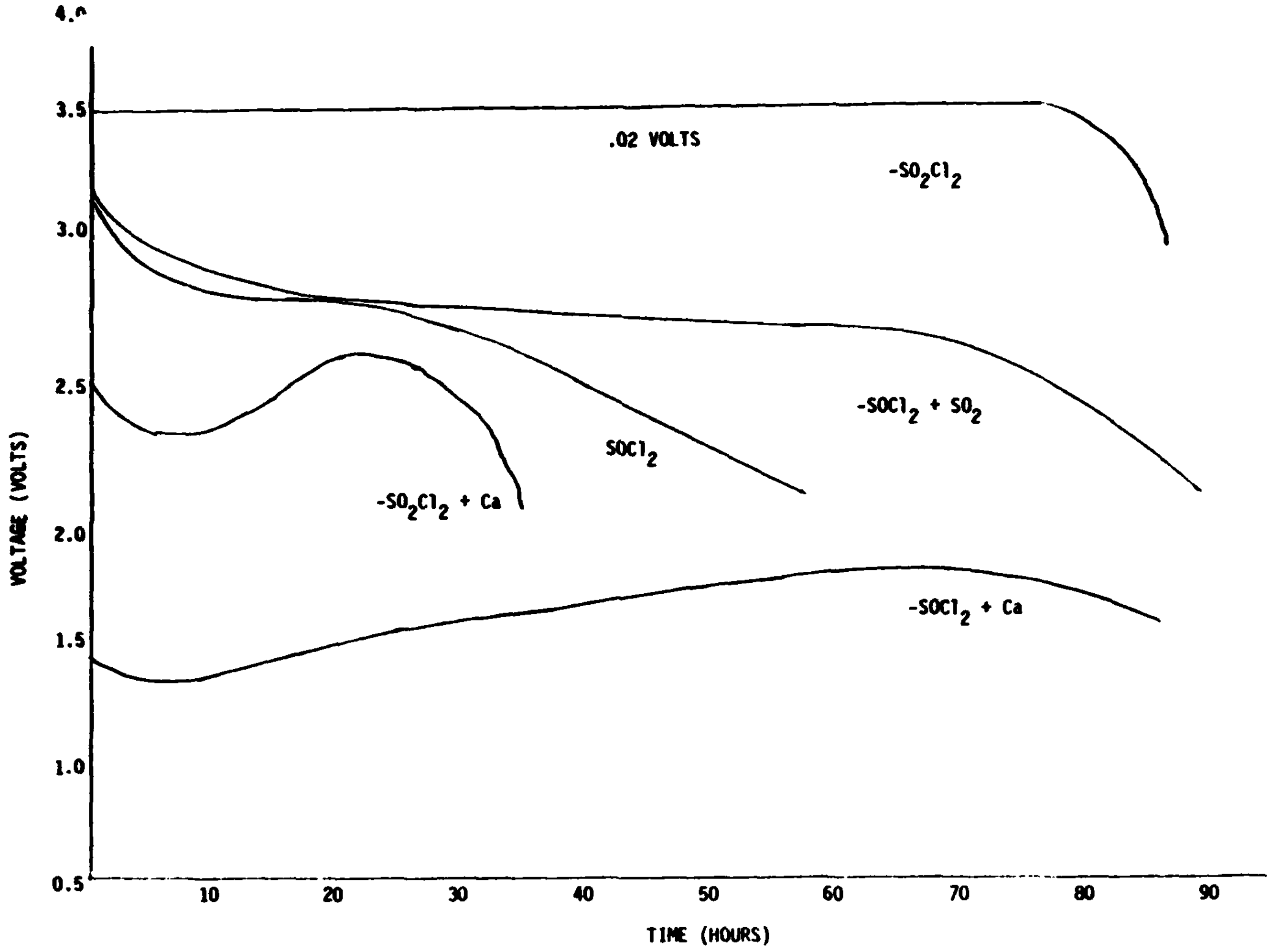

Figure 58. Discharge Profiles After Five Months at 55°C

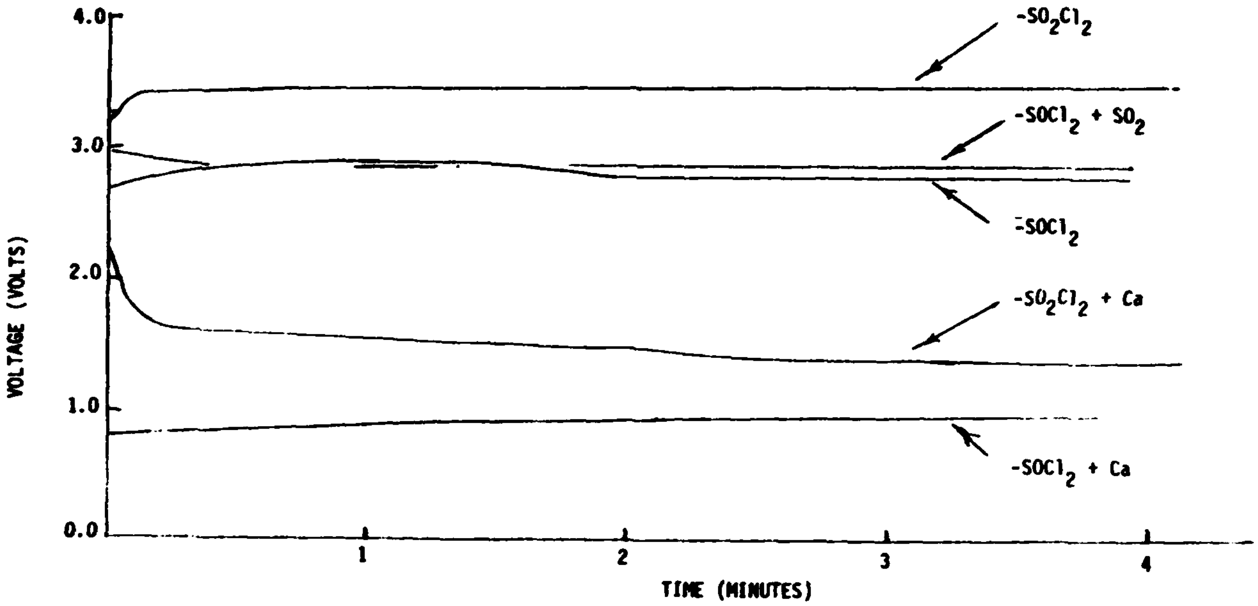

Figure 59. Voltage Delay After Five Months at 55°C

5.4 DISCUSSION

The $SOCl_2$, SO_2Cl_2 + Ca, and $SOCl_2$ + SO_2 electrolytes showed similar voltage delay effects. In fact, the $SOCl_2$ + SO_2 electrolyte produced higher voltage delay than the former two at 55°C storage for one month (Table 5). The $SOCl_2$ + Ca electrolyte showed significantly lower voltage delays after 55°c storage times up to six weeks.

The best results were obtained from the electrolyte containing 1.8M $LiAlCl_4$ in SO_2Cl_2 with no additives. This was due in part to the higher running voltage of SO_2Cl_2 cells. However, the low voltage delays after 10 and 22 weeks of 55°C storage clearly showed superior performance of the passive film.

Several points should be kept in mind in interpreting these results. The test discharges were all continuous. It is probably true that cells discharged intermittently will behave differently. In particular, the effect of the SO_2 additive will be much less on voltage delay for a cell started after being discharged to some extent, since SO_2 is generated during discharge. Furthermore, the length of time between discharges, especially at elevated temperatures, will affect the voltage delay observed.

Ideally, the best electrolyte for low voltage delay should be one that quickly and uniformly forms a thin ionically conductive passive film on lithium. The rate of recrystallization of this film should be as slow as possible, since this is the principle mechanism of film growth and cracking. Lastly, the electrolyte should consume as little lithium as possible in forming this film.

The results of this work indicate that pure $SOCl_2$ is superior to pure $SOCl_2$ or combinations of these electrolytes with calcium or sulfur dioxide. The $SOCl_2$ + Ca, which shows low voltage delay after 55°C storage, apparently accomplishes this through contrival dissolution of the passive film and lithium metal, as was discussed in Section 2.0.

5.5 CONCLUSIONS AND RECOMMENDATIONS

In view of the high capacity loss of $SOCl_2$ + Ca electrolyte, only the 1.8M $LiAlCl_4$ So_2Cl_2 electrolyte is recommended for further testing as a low voltage delay electrolyte. The effect of intermittent discharge and the extent of SO_2Cl_2 decomposition need to be cosidered. Mixtures of $SOCl_2$ and SO_2Cl_2 electrolyte should also be considered, especially for low temperature applications.

6.0 PRELIMINARY HAZARD ANALYSIS

6.1 INTRODUCTIONS

A system preliminary hazard analysis was performed, in accordance with paragraph 5.8.2.1 MIL-STD-882 dated 15 July, 1969, to identify the hazards and define any risks involved in using the lithium thionyl chloride cell.

6.2 METHOD OF ASSESSMENT OF IDENTIFIED HAZARDS

The identified hazards matrix of Table 6 specifies a Real Hazard Index number for each of the hazards listed. This Index is the product of Hazard Severity Value and Hazard Probability Value, and has been used as a guide in ranking potentially hazardous conditions. Hazard Severity categories with values are listed in Table 7. Hazard Probability categories with values are listed in Table 8.

6.3 GROSS HAZARD TYPES

Safety in handling, transportation, discharging, and disposal is of prime importance. Potential Gross Hazards, which cannot be tolerated during test or operations, are as follows:

EX = Explosion
F = Fire
T = Toxic gases
C = Corrosive liquids
EL = Electrical Hazards
O = Other

These hazards are defined as follows:

a. Explosion (EX): An internal lithium-to-metal short resulting from out-of-specification conditions can cause a high current drain in the area of metal contact. This internal short could cause heating sufficient to melt lithium (186°C) in a localized area, which in the presence of thionyl chloride could result in an explosive reaction in a cell sufficient to rupture the cell case structure with possible mishaps to adjacent equipment or personnel.

TABLE 6

IDENTIFIED CATEGORIES I AND II HAZARD MATRIX

Hazard Reference Number	Hazard Category	Est. Probability	Real Hazard Index	LITHIUM POWER SOURCE GROSS HAZARD TYPES						
				Explosion	Fire	Toxic Gases	Corrosive Liquids	Elec. Hazards	Other	
PHA1-1	I	D	12	EX	F	T	C			Safety Concern
PHA1-2	I	D	12		F			EL	O	Safety Concern
PHA1-3	I	D	12	EX	F	T	C			Safety Concern
PHA1-4	II	E	6		F					
PHA1-5	II	E	6		F					
PHA1-6	I	D	12	EX	F	T	C			Safety Concern
PHA1-7	II	D	9			T	C			
PHA1-8	II	D	9			T	C			
PHA1-9	I	D	12	EX	F	T	C			Safety Concern (same as 1-8)

TABLE 7

HAZARD SEVERITY

CATEGORY		SEVERITY VALUE
I	Catastrophic. May cause death or system loss.	4
II	Critical. May cause severe injury, severe occupational illness, or major system damage.	3
III	Marginal. May cause minor injury, minor occupational illness, or minor system damage.	2
IV	Negligible. Will not result in injury, occupational illness, or system damage.	1

TABLE 8

HAZARD PROBABILITIES

Description Word	Level	Specific Individual Item	Higher System Level	Prob. Value
Frequent	A	Likely to occur frequently.	Continuously experienced.	6
Reasonably Probable	B	Will occur several times in life of an item.	Will occur frequently.	5
Occasional	C	Likely to occur sometime in life of an item.	Will occur several times.	4
Remote	D	So unlikely, it can be assumed that this hazard will not be experienced.	Unlikely to occur but possible.	3
Extremely Improbable	E	Probability of occurrence cannot be distinguished from zero.	So unlikely, it can be assumed that this hazard will not be experienced.	2

b. Fire (F): Lithium can be ignited from explosion above or alone in the presence of air (by exposure to water) and become a primary source of fire, which can propagate to a secondary fire of surrounding materials.

c. Toxic Gases (T): Thionyl chloride ($SOCl_2$) liquid is a basic constituent of the electrolyte. Sulfur dioxide (SO_2) is a product of the discharge process and is dissolved in the electrolyte. Electrolyte boils at 180°F at atmospheric pressure, and is a highly toxic liquid with an industry recommended threshold limit value of five parts per million in air. Sulfur dioxide also has an industry recommended threshold limit value of five parts per million in the air.

d. Corrosive Liquids (C): Thionyl chloride will attack most metals and most plastics and, when combined with moisture, will generate hydrochloric acid (a strong corrosive acid).

e. Electrical Hazards (EL): Extremely high current drain, if shorted between terminals or plus to system structure, can result in damage to equipments, electrical fire, and burns.

6.4 HAZARDS MATRIX

The identified hazards matrix, Table 6, lists hazards identified for Categories I and II and indicates as a safety concern those with a Real Hazard Index of 12 or more.

Descriptions of the Hazard Reference Number on Table 6 are:

PHA 1-1	External overheating
PHA 1-2	External burning from shorted terminals
PHA 1-3	Internal cell short circuit caused by handling abuse
PHA 1-4	Unauthorized cell disassembly and exposure to air
PHA 1-5	Internal short circuits caused by disconnected or broken electrodes during disassembly
PHA 1-6	Case rupture leading to release of toxic and corrosive materials or lithium reaction
PHA 1-7	Venting during discharge and neutralization
PHA 1-8	Leaking of corrosive and toxic materials due to problems with manifold
PHA 1-9	Penetration of shipping container and enclosed cell(s)

7.0 DEACTIVATION AND DISPOSAL

Deactivation of cells must be done through several different operations if the goal of the procedure is reclamation of materials and cell subassemblies. However, in order to carry out the operations with highest efficiency and minimum efforts, the cells must be divided into several categories according to the type of design, state of assemblage, state of discharge, etc. Classes of cells that might have to be deactivated are shown in Figure 60.

It appears from the table that there may be six different types of cells, each type requiring different series of treatment steps, leading through deactivation to a complete reclamation of all materials and subassemblies. The treatment steps involved for each of the eix classes of cells to be processed are summarized in Table 9. The steps will be further discussed below, with a particular emphasis on neutralization and reclamation as procedures that might involve several substeps before they would yield reusable materials or subassemblies.

7.1 DISCHARGE

The electrochemical discharge could sometimes be used as a first step in deactivating cells. Obviously, it would be applicable only to operable cells, carbon-limited or lithium-limited, that were not previously discharged. This step reduces the amount of active materials present in the cell and could reduce the degrees of violence, should a mistake be made in handling the cells during deactivation. On the other hand, the discharge is associated with elimination of costly materials such as lithium, and results in formation of lithium salts that would be reprocessed into lithium only through a series of costly operations. There is an obvious economic advantage in avoiding this step, but, for safety reasons and until the process is well established, this step should be practiced on all operable cells prior to other deactivation steps.

Obviously, discharge will have different effects on the cells, depending on whether they are constructed as carbon-limited or lithium-limited.

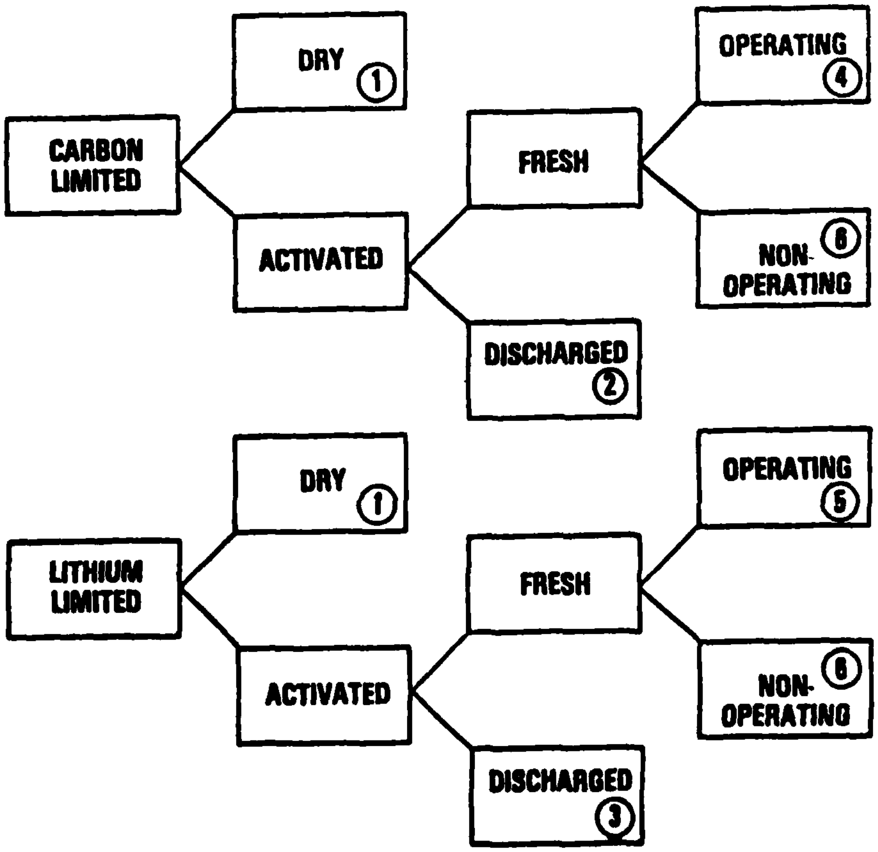

Figure 60. Classes of Cells to Be Activated

TABLE 9

TREATMENT STEPS FOR EACH CELL CLASS

CLASS OF CELLS	DEACTIVATION PROCEDURES					
	DISCHARGE	POST DISCHARGE	EXTRACTION	DISASSEMBLY	NEUTRALIZATION	RECLAMATION
① C.L.DRY L.L.DRY	–	–	–	X	–	X
② C.L.D.	–	–	X	X	X	X
③ L.L.D.	–	–	–	X	X	X
④ C.L.F.O.	X –	X –	X X	X X	X X	X X
⑤ L.L.F.O.	X –	X –	– X	X X	X X	X X
⑧ C.L.N. L.L.N.	–	–	X	X	X	X

In the case of lithium-lmited cells this step leads to a complete elimination of one of the components (lithium); in the case of the carbon-limited cells, it only reduces the amount of active materials in general.

7.2 POST DISCHARGE

All operable cells, previously involved in any of the discharge tests, should be subjected to the post-discharge test before any of the other deactivation tests are applied. This step is necessary because most of the standard discharge tests are terminated at a particular voltage cutoff line, signifying the lowest voltage at which they would serve in practice before they were replaced. At the cutoff point these cells may contain more or less of the active components still available for discharge, depending on whether the cells were constructed as carbon-limited or lithium-limited and, also, depending on the rate at which they were discharged.

The lithium limited cells can be brought to a complete discharge in this step, eliminating the last quantity of lithium and, with it, any danger of explosion. In most cases the post-discharge step with these cells is not particularly time consuming and, certainly not costly, since most of the active materials were already eliminated in the previous discharge.

The carbon-limited cells can also be brought to a complete discharge in this step since their "carbon-limited" status was established based on a particular discharge rate. By lowering the discharge rate, and allowing more time for this step, the status of these cells can, in most cases, be changed from the carbon-limited to the lithium-limited one, since the carbon is a nonstoichiometric participant in the discharge reaction, yielding higher capacity when the discharge rate is lower. Moreover, with the experience of the last several years, very few cells will be built carbon-limited, and if they are, the excess lithium capacity will be sufficiently low to permit total exhaustion at lower rates.

From a safety point of view, there is a great advantage in eliminating one of the active components from the cell, prior to any of the other deactivation steps. With lithium absent from the cell, all possible mistakes in handling become less consequential, short of gross negligence such as a direct inhalation of thionyl chloride vapors. For this reason, the post discharge stop should be employed at the least beginning of operation of deactivation facility.

The simplest post-discharge procedure, using a fixed load resistor, is recommended. When the cell's open circuit voltage, (with the load removed) no longer recovers to 3.6 V, the post discharge step of an operable cell can be considered completed.

The incineration of lithium thionyl chloride batteries has proved that an unstable condition occurs when the melting point of lithium (180°C) has been exceeded. In order to avoid a spontaneous reaction from within the cell, care has to be exercised to store/handle/test within the specified temperature ranges (-40°F to 125°F) and discharge rate (1mA/cm2).

8.0 RECOMMENDATIONS

The results of the various test programs conducted on Li/$SOCl_2$ cells under this contract indicate additional improvements in safety and/or performance are attainable. Corporate-sponsored research has generated new electrolyte and cell additives at the laboratory level. Design application of these advancements to Li/$SOCl_2$ cells can improve their performance and safety. Based upon the results of this contract and the new corporate advancements, a program consisting of the following investigations is recommended.

8.1 STORAGE DEGRADATION

There are several promising directions to explore in improving high temperature storability through chemical means. SO_2Cl_2 and $SO_2Cl_2/SOCl_2$ mixed electrolytes should be tested further. Lowering the $LiAlCl_4$ concentration will decrease SO_2 solubility and conductivity but may significantly decrease capacity loss on storage by decreasing LiCl recrystallization on the anode and possibly in the cathode. Also, a new binderless separator material is being developed, which can be evaluated.

8.2 SHORT CIRCUIT PROTECTOR

An additive has been developed that, when added to a cell, will reduce the electrolyte conductivity at high temperatures significantly enough to prevent a thermal runaway condition.

8.3 LOW TEMPERATURE PERFORMANCE

A half-C cell has been developed that provides 30 percent of its room temperature capacity at -40°C. Since this is a high power cell that is to deliver 125 mA continuously, additional abuse testing must be performed to ensure its safe operation under all abusive and environmental conditions.

8.4 VOLTAGE DELAY

In view of the high capacity loss of $SOCl_2$ + Ca electrolyte, only the 1.8m $LiAlCl_4$ SO_2Cl_2 electrolyte is recommended for further testing as a low voltage delay electrolyte. The effect of intermittent discharge and the extent of SO_2Cl_2 decomposition need to be considered. Mixtures of $SOCl_2$ and SO_2Cl_2 electrolyte should be considered, especially for low temperature applications.

In addition, a new electrolyte salt is being evaluated at GTE Laboratories that shows great promise for significantly reducing voltage delay at both room- and high-temperature storage. This electrolyte will also be evaluated.

*U.S.Government Printing Office: 1981 — 757-002/515