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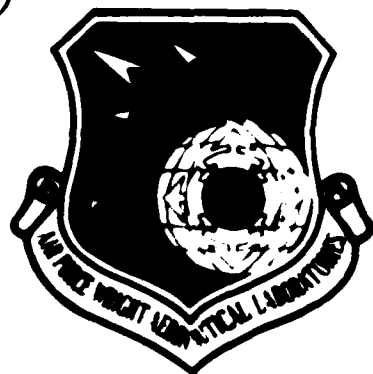
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CALCIUM INORGANIC ELECTROLYTE
BATTERY DEVELOPMENT

R. HIGGINS

EAGLE-PICHER INDUSTRIES, INCORPORATED
ELECTRONICS DIVISION
JOPLIN, MISSOURI 64801

August 1981

FINAL REPORT FOR PERIOD AUGUST 1977 - OCTOBER 1980

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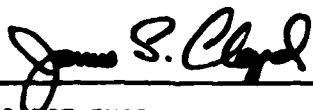
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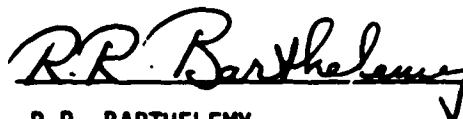
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which is the continuing problem of safety. The problem of response to abuse of Li/SOCl₂ cells primarily results from the reactivity of molten Li, a problem compounded by its low melting point of 180°C. On the assumption that most Group I and II metals are highly reactive in the molten state, the problems might be reduced by using materials with higher melting points. Several Group I and II elements have energy densities near that of Li, such as Na, Ca and Mg; of these three however, only Ca and Mg have acceptable melting points. Ca, though lower in energy density than Mg, is capable of 5.93 WH/cm, has a working voltage of approximately 3.0V, and has a higher melting point than Mg.

These inherent characteristics, as well as preliminary investigations carried out at the Aero Propulsion Laboratory, led to the present work on further development of Ca/SOCl₂. The purpose of this program was to develop experimental hardware, establish preliminary performance, safety, and storage data, and define the magnitude of any potential problems. The hardware size and performance criteria were to be consistent with three potential applications: Life support/rescue equipment, spacecraft power, and standby/emergency power.

The program was carried out in two phases. Phase I consisted of evaluation of basic system characteristics and problems, development of a test cell consistent with life support requirements, and evaluation of the electrical performance, storage, and abuse response of that cell. Phase II consisted of development tests and evaluation of larger hardware for spacecraft and standby power applications. Three cell sizes were used for the majority of this work: A half sized "D" cell rated at 3.5 AH, a 600 AH rectangular cell, and a 7000 AH rectangular cell.

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SECTION I

GENERAL INTRODUCTION

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The use of lithium (Li) anodes with thionyl chloride (SOCl_2) has been vigorously investigated by many researchers during the past decade, advancing from laboratory cells to a viable 400-600 WH/Kg system demonstrated in cell sizes up to 17000 AH. Several improvements in performance have been made during these years, especially with regard to basic problems such as voltage delay due to anode passivation. Improvement in other areas of performance, however, have been more modest, a particular example of which is the continuing problem of safety. The problem of response to abuse of Li/ SOCl_2 cells primarily results from the reactivity of molten Li, a problem compounded by its low melting point of 180°C . On the assumption that most Group I and II metals are highly reactive in the molten state, the problems might be reduced by using materials with higher melting points. Several Group I and II elements have energy densities near that of Li, such as Na, Ca and Mg; of these three however, only Ca and Mg have acceptable melting points. Ca, though lower in energy density than Mg, is capable of 5.93 WH/cm^3 , has a working voltage of approximately 3.0V, and has a higher melting point than Mg.

These inherent characteristics, as well as ~~preliminary investigations~~ carried out at the ~~Aero Propulsion Laboratory, Wright-Patterson AFB,~~ led to the present work on further development of Ca/ SOCl_2 . The purpose of this program was to develop experimental hardware, establish preliminary performance, safety, and storage data, and define the magnitude of any potential problems. The hardware size and performance criteria were to be consistent with three potential applications: life support/rescue equipment, spacecraft power, and standby/emergency power.

The program was carried out in two phases. Phase I consisted of evaluation of basic system characteristics and problems, development of a test cell consistent with life support requirements, and evaluation of the electrical performance, storage, and abuse response of that cell. Phase II consisted of development tests and evaluation of larger hardware for spacecraft and standby power applications. Three cell sizes were used for the majority of this work: A half sized "D" cell rated at 3.5 AH, a 600 AH rectangular cell, and a 7000 AH rectangular cell.

SECTION II

PRELIMINARY SYSTEM INVESTIGATION

1.0 INTRODUCTION

The preliminary system investigation was composed of general evaluation of the performance of the system, using the standard techniques normally applied to Li anode systems. The investigation was divided into three basic areas, one for each major cell component: electrolyte, anode, and cathode matrix. The goal of this effort was to make a preliminary estimate of the problems inherent in the system, develop the cell components to the point that the test of sealed hardware was feasible, and establish a general baseline of performance, which could be expected in later hardware.

The first investigation of Ca/SOCl_2 cells was made in bag cells to evaluate general characteristics, and effects of variations in cell components such as anode cathode matrix, and electrolyte. Included in this work were: anode characteristics, such as surface condition, temper, and configuration; electrolyte effects, such as solute type and concentration, and cathode matrix utilization with respect to carbon type, thickness, density and pore volume. Certain of these conditions were later reevaluated in larger sealed cells.

The majority of this work was done in parallel with the development of the 3.5 AH D/2 cell and was completed early in the program. Work on cathode matrix utilization however, was continued into later stages of the program to support the thicker cathodes required by development of higher capacity cells.

2.0 TEST CELLS

Three basic cells were used to evaluate the system and its components. Bag cells were made using electrodes 3.18 cm square, held in a polypropylene bag and clamped in a restraining fixture. The fixture was placed in a plastic or glass container with feed-throughs for electrical connection. After manually filling the cells with electrolyte the container was flushed with argon and then exposed to several vacuum/pressure cycles to insure complete wetting of matrix and separator. Pressure in the container was controlled using a valve on the cover of the cell container.

The second cell was constructed in a sealed cylindrical container having the volume of a D/2 cell. The cell case was made of type 304 stainless steel, and had a nickel diaphragm vent in the bottom. The cover was also 304 stainless with either one or two glass-to-metal seals and a 0.157 cm diameter tube for activation. The cell case will be described more completely in Section III. The third cell was rectangular, type 304 stainless, with a nickel diaphragm vent, two feed throughs and a fill tube. The cell dimensions were 52 mm X 101 mm X 26 mm. The rectangular cell was used only infrequently to evaluate the thicker flat cathodes used in the 600 AH and 10,000 AH cells.

3.0 ELECTROLYTE

Thionyl chloride for this part of the program, was obtained from Apache Chemical, and was redistilled Hooker material. Aluminum chloride was obtained from Fluka. LiAlCl_4 solutions were prepared at a concentration

of 1.5 molar. $\text{Ca}(\text{AlCl}_4)_2$ solutions were prepared at concentrations of 1.0 molar. Attempts to prepare $\text{Ca}(\text{AlCl}_4)_2$ solutions at greater concentrations than 1.0 molar produced an intermediate species having a mole ratio of 3 AlCl_3 to CaCl_2 , with the excess CaCl_2 precipitating. Final solutions having the expected 2 to 1 mole ratio were later prepared by prolonged stirring of a heated solution with the CaCl_2 precipitate. Electrolyte solutions used during the first part of the program had a hydrolysis product content equivalent to approximately 300 ppm measured with a Perkin Elmer 597 IR spectrophotometer. Later solutions had equivalent water contents approximately of 40 ppm.

Stability of calcium in these solutions was evaluated by storing samples in sealed glass ampules at 22°C and 49°C. Ca stored in SOCl_2 for 30 days darkened slightly during the first 24 hours, then remained the same for the rest of the storage period, both at 22°C and 49°C. Ca stored in solutions of 1.5 molar LiAlCl_4 in SOCl_2 produced variable results. Of 30 test ampules, most exhibited an immediate darkening of the Ca surface, followed by a period during which pitting slowly appeared at isolated points on the surface. The pitting, once begun, progressed during the balance of the 30 days, sometimes covering the entire surface of the sample. Several of the 30 test samples did not exhibit the pitting corrosion. These samples darkened slightly at the beginning of the test, but then remained unchanged for the balance of the 30 days at 49°C. Throughout the test, corrosion of the samples was generally all or nothing. If a single pit occurred, it was followed

by others. There were no instances in which the samples visibly pitted and then stabilized. Control ampules having Li rather than Ca remained unchanged during the length of the test period. Calcium samples stored in 1 molar $\text{Ca}(\text{AlCl}_4)_2$ in SOCl_2 never stabilized, but corroded continually throughout the test. In certain cases, the samples completely disintegrated; however, not all of the $\text{Ca}(\text{AlCl}_4)_2$ solutions were completely neutral, i.e. some of the solutions appeared to be in the intermediate form of 3 AlCl_3 to 1 CaCl_2 and presumably had an excess of AlCl_3 , which reacted directly with the Ca. Ca samples which corroded heavily had a thick white crust over the surface which flaked off as a solid to first make a flocculent solution and eventually collecting on the bottom of the ampule.

The Ca used in preparing these samples was of various forms (nuggets, foil, vapor deposited) and temper, ranging from fully annealed to work hardened. In general the annealed samples appeared more resistant to pitting corrosion than work hardened samples.

4.0 ANODE

Calcium was obtained as pellets from Pfizer Inc., and subsequently vapor deposited onto nickel foil. Other samples were obtained from PMF Alloys in the form of foil, .005 -.010 inches thick. The foil was slightly darkened as received and was extremely hard. Annealing of electrodes was done under a vacuum of approximately $5-15 \times 10^{-3}$ torr after backfilling with argon several times. The foil was then laminated onto expanded nickel grid. The newly work hardened electrodes

were used both in the hardened form and after re-annealing. The calcium surface, which was grey as received, darkened further during annealing. Electrodes were used both with the darkened surface and with a bright surface produced by sanding with emery cloth. Intentionally oxidized electrodes were prepared by exposing finished electrodes to an atmosphere of approximately 23°C and 75% RH for 60 minutes, which completely blackened the anode surface.

A comparison of cells using anodes prepared from annealed and hardened calcium is shown below. The samples were discharged in bag cells through a constant resistive load of 27 ohms.

Workhardened Calcium

<u>Cell #</u>	<u>Anode Thickness</u>	<u>Discharge Time Above 2.0 Volts</u>	<u>Capacity</u>
8	.010 inches	1.50 hours	75 mah
9	.015 inches	1.75 hours	87.5 mah
10	.020 inches	1.70 hours	87.0 mah

Annealed Calcium

<u>Cell #</u>	<u>Anode Thickness</u>	<u>Discharge Time Above 2.0 Volts</u>	<u>Capacity</u>
13	.010 inches	3.50 hours	175 mah
14	.015 inches	3.65 hours	182.5 mah
15	.020 inches	3.72 hours	186

The capacity difference between the work-hardened and annealed anodes was attributed primarily to differences in electrical contact between the anode and collector. The nickel collector did not penetrate

deeply into the workhardened calcium, probably did not break up the surface film on the calcium, and was prone to delamination. By comparison, the softer annealed calcium flowed easily around the nickel during lamination, with the probable effect of good film breakup and a low resistance contact between calcium and collector.

The effect of surface conditions was also evaluated in bag cells. The calcium was in the 'as received' workhardened condition, and was prepared in three forms; the existing finish (medium grey), polished bright, and with an oxide film prepared by exposure to 75% RH atmosphere.

Effect of Anode Surface on Discharge

<u>Anode Preparation</u>	<u>Surface Condition</u>	<u>Discharge Time Above 2.0 Volts</u>
As received	Medium grey	45 Minutes
Polished	Bright	40 Minutes
As received and exposed to 75% RH for 60 Minutes	Black	45 Minutes

The anodes were all .005 inches thick, and the cells were cathode limited. The absence of surface condition effects on discharge was confined in half "D" cells and led to the use of calcium with grey to black surface for most cells throughout the balance of the program.

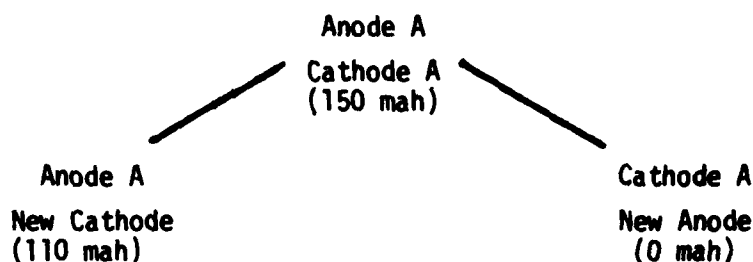
5.0 CATHODE MATRIX

The first cathode used in bag cells was a standard teflon bound acetylene black matrix on an expanded nickel collector. The cathode produced a matrix utilization of approximately 1 AH/cm³ against lithium anodes, however, its capacity when discharged against calcium anodes was much reduced. A comparison of cathodes of various thicknesses was made at three current densities in bag cells.

<u>Cathode Thickness</u>	<u>Capacity and average potential at:</u>		
	<u>2.7 ma/cm²</u>	<u>5.0 ma/cm²</u>	<u>9.6 ma/cm²</u>
1.3 mm	150 mah/2.87	155 mah/2.60	70 mah/2.54
2.5 mm	145/2.80	172/2.70	70/2.55
5.1 mm	156/2.84	170/2.70	72/2.60

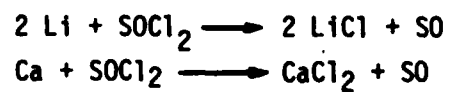
The reduction in capacity with increasing current density was expected; however, nearly the same capacity was produced by each cathode thickness, apparently due to only a surface utilization of each. That the failure was due to cathode, rather than anode, failure was confirmed by test cells having a reference electrode made with lithium wire.

Additional test cells were discharged to a 2.0 volt end potential, then disassembled and the cathodes used to prepare new cells. The spent cathodes produced no additional capacity in the second usage. By comparison, anodes treated to the same substitution produced a second discharge as expected until the calcium was exhausted.



Spent cathodes from cells which had produced 3.5 AH were found to contain 6.8 grams of CaCl_2 . Assuming a reaction for Ca analagous to that proposed for Li, $\text{Ca} + \text{SOCl}_2 \rightarrow \text{CaCl}_2 + \text{SO}$, the quantity of CaCl_2 would be 7.26 grams. The CaCl_2 found in the spent cathodes was the result of a single leaching and was expected to be slightly low.

The overall reduction in capacity when compared to Li controls was consistently 30-40%. If matrix utilization is presumed to be influenced by reactant volume, the reactions of Ca and Li with SOCl_2



would indicate a reduction in capacity of 20% based on the volumes of CaCl_2 and LiCl , $0.96 \text{ cm}^3/\text{AH}$ and $0.77 \text{ cm}^3/\text{AH}$ respectively. The increased loss in capacity may be due to a reduced cation mobility or to the larger physical size of the primary reaction product, CaCl_2 . This possibility is suggested by the fact that a positive correlation was found to exist between matrix utilization and pore diameter.

The effects of various carbon blacks on matrix utilization were also evaluated in bag cells, Figure 1, using each in standardized cathodes of 90% carbon and 10% TFE. Shawinigan carbon black, 50% compressed, consistently produced the best results.

CARBON BLACKS EVALUATED

<u>CARBON TYPE</u>	<u>PARTICLE DIAMETER</u>	<u>STRUCTURE</u>
Shawinigan Acetylene Black	42 nanometer	-
Degussa Corax	28	480
Huber N-339	23	128
Huber N-650	60	125
Huber N-765	23	103
Huber N-326	29	75
Huber N-762	76	65
Huber N-330	29	103
Ashland N-650	68	134
Ashland N-762	74	80
Ashland N-375	26	102
Ashland N-339	22	114
Cabot Monarch 1300	13	121
Cabot Monarch 1100	14	65
Cabot Monarch 880	16	120
Black Perl 1300	13	105
Black Perl 1100	14	50
Black Perl 880	16	110
Vulcan XC72	30	185
Vulcan XC72R	30	178
Regal 336	62	25
Regal 330R	62	70
Mineral Lamp Black 8405		
Mineral Carbon Black C391		
Mineral Water Dispersable Black 8452		

Figure 1. Carbon Blacks Evaluated

SECTION III

3.5 AH/LIFE SUPPORT CELL

1.0 INTRODUCTION

A cylindrical cell having the volume, but not the exact dimensions of a half sized "D" cell was designed to evaluate the basic performance of the system and to fulfill the requirement for a life support cell. This basic cell was first used to evaluate the performance of Ca/SOCl_2 in sealed cells, then as a test vehicle for the development of suitable electrodes to demonstrate the system.

Electrical performance of the cell was evaluated over a temperature range of -29°C (-20°F) to 74°C (165°F) at discharge rates of 50 ma to 1000 ma. Response to environmental stress and abuse was evaluated by exposing the cell to: short circuit, inceneration, reversal, charging, shock, vibration, crushing and puncture.

2.0 EXPERIMENTAL

The half "D" cell volume was chosen because of its appropriate size for the required life support application. The non standard demension of the cell was the result of using existing tooling and cell cases. The overall size of the cell was 30.2 mm (1.188 inches) diameter and 38.1 mm (1.500 inches) long. The bottom end of the cell was modified to accept a 0.05 mm (.002 inches) thick vent diaphragm which opened at approximately 150 psi. The top end of the cell had a fill tube and either one or two terminal feed-throughs having glass to metal seals. The cell was negative. The terminal pin in the cell header was positive. In some cases a lithium reference electrode was included in the cell and was connected to the second terminal pin.

Both case and cover were type 304 stainless steel. The vent diaphragm was Ni 200, and the terminal pin was Ni 52. Cathodes for the half "D" cell were made using 90% Shawinigan carbon black bound with 10% DuPont type 30 TFE. The current collector was Ni 200 expanded screen. The overall dimensions of the electrodes were 25.4 mm (1.00 inch) X 393.7 mm (15.50 inches) X 0.43 mm (.017 inches). The positive current lead was Ni 200 foil 0.05 mm (.002 inch) X 5.1 mm (.200 inches) X approximately 25.4 mm (1.00 inch).

Calcium obtained from Pfizer Inc., was rolled into foil by PMF Alloys. The anode was made by laminating calcium foil onto a current collector of Ni 200 expanded screen and had dimensions of 25.4 mm (1.00 inch) X 0.33 mm (.013 inch) X approximately 432 mm (17.00 inches). The negative current lead was of the same material and dimensions as the positive lead.

The electrodes were separated by one layer of Dexter non-woven glass mat approximately 0.36 mm (0.014 inch) thick. Each cell was filled with 22 grams of electrolyte, which was obtained from Apache Chemical and was 1.4 molar LiAlCl_4 in SOCl_2 . The hydrolysis product content was approximately 50 ppm by IR spectroscopy.

A sketch of the half "D" cell, which had an approximate capacity of 3.5 amperehour, is shown in Figure 2.

3.0 ELECTRICAL PERFORMANCE

The effect of discharge rate and temperature on cell capacity was evaluated by discharging a group of cells under the following conditions.

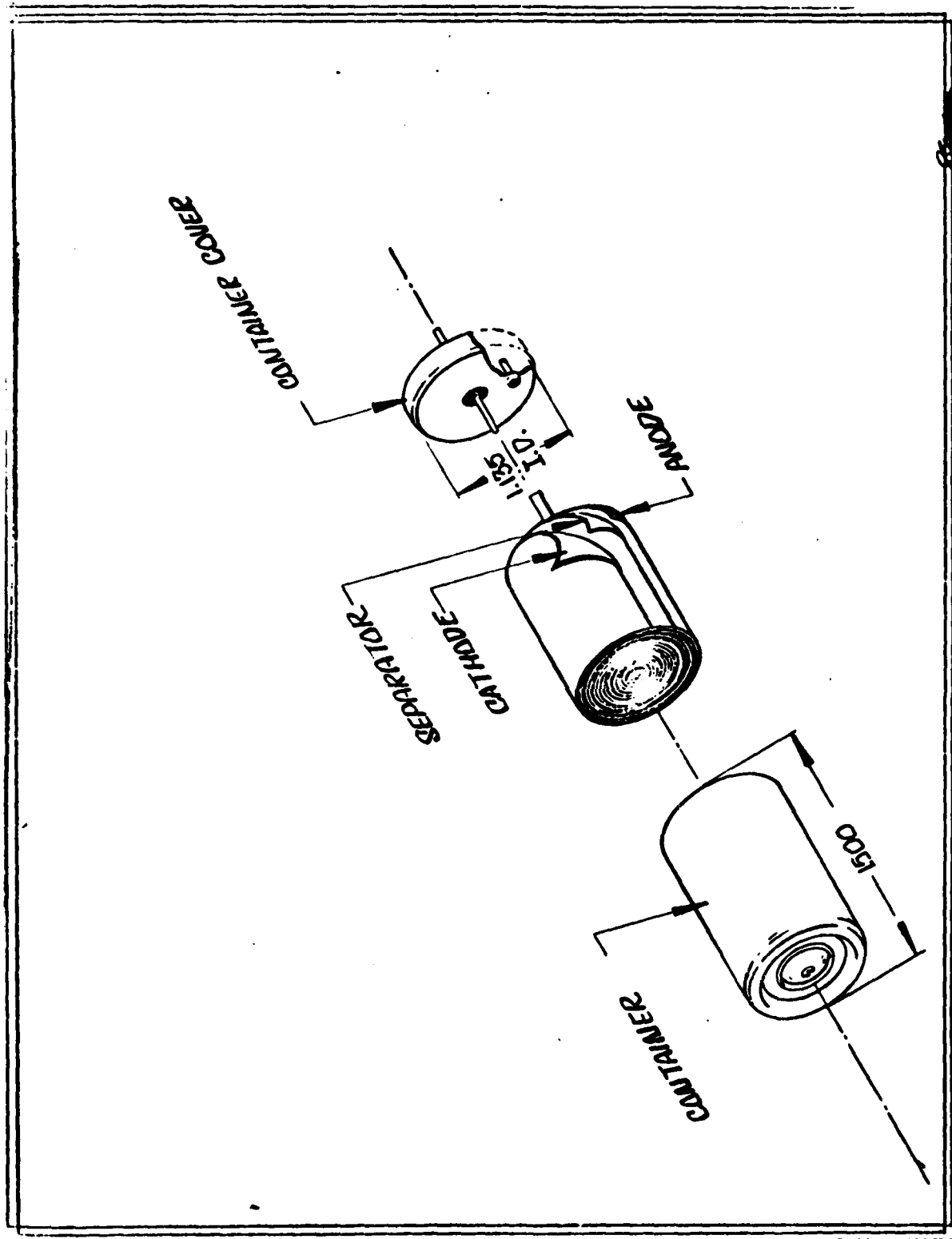


FIGURE 2 Ca/SOCl_2 "HALF-D" CELL CONFIGURATION

50 ma @	-18°C,	24°C,	49°C,	74°C
100 ma @	-18°C,	24°C,	49°C,	74°C
500 ma @	-18°C,	24°C,	49°C,	74°C
1000 ma @	-18°C,	24°C,	49°C,	74°C

Cells were discharged through a constant resistance which provided the referenced current at an end potential of 2.0 volts. Average discharges are shown in Figure 3 through 6. A summary of the data is given in Figure 7. When discharged at -29°C, only those cells at 50 ma produced significant capacity above 2.0 volts. When discharged at 74°C, only those cells below 1000 ma produced full capacity without opening the cell vent due to internal heating. The average capacity produced at the lower rates was 3.5 amphotours.

4.0 STORAGE EVALUATION

Two separate storage tests were performed using the half "D" cell. The first test was made at 24°C and continued for a period of six months. Cells were withdrawn at one, three, and six months, pulsed at 100 ma to observe any voltage delay, and then discharged to a 2.0 volt end potential through a constant twenty ohm load. At monthly intervals, the impedance of each cell was measured using a Hewlett Packard milliohmeter operating at 1000 Hz. After the test was completed it was found that each cell also received a monthly 100 ma pulse for a period of approximately two seconds. A summary of this data is given in Figure 8.

DISCHARGE CURVE AT -18 C

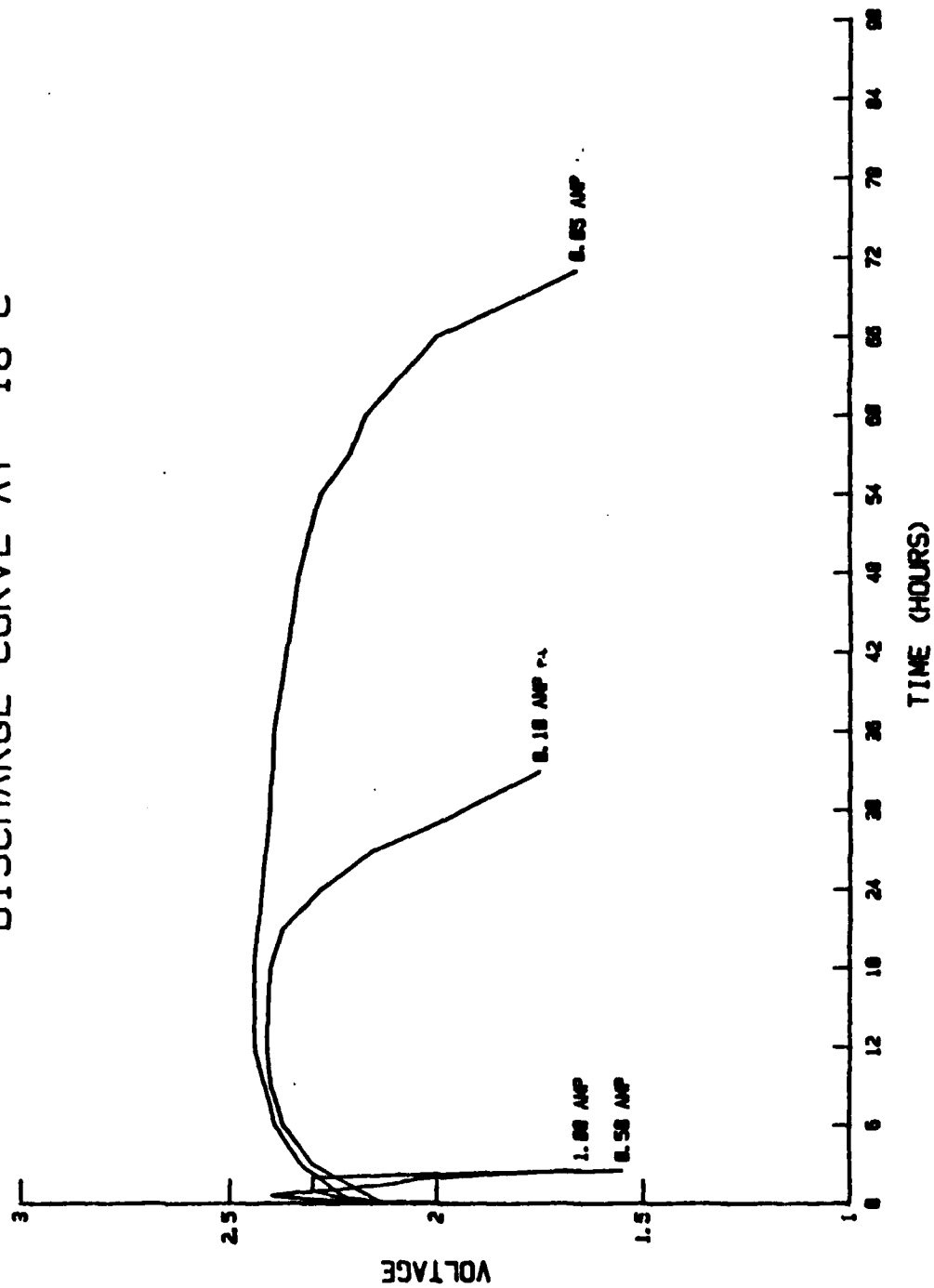


Figure 3. Discharge Curve at -18C

DISCHARGE CURVE AT 24 C

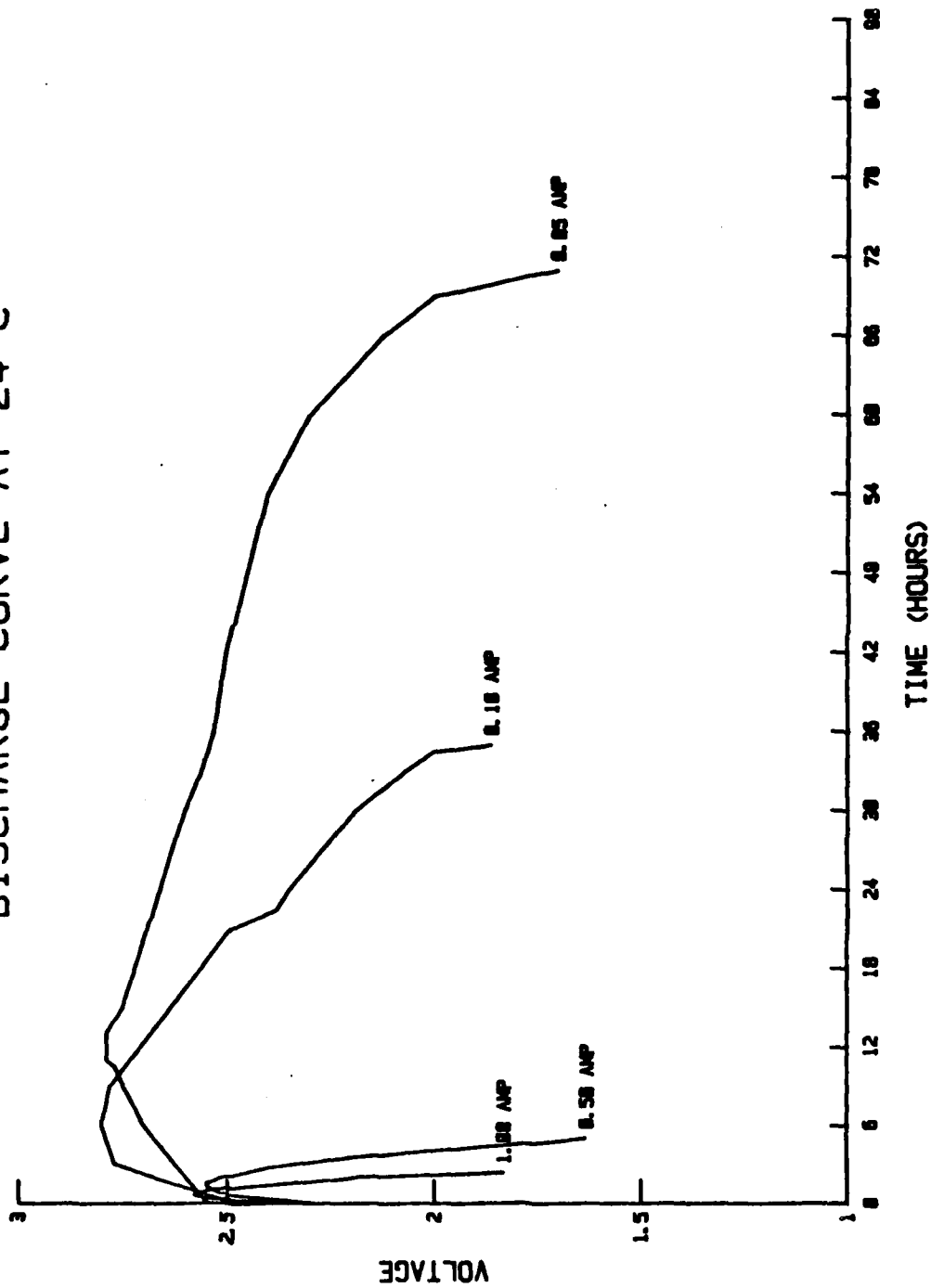


Figure 4. Discharge Curve at 24 C

DISCHARGE CURVE AT 49 C

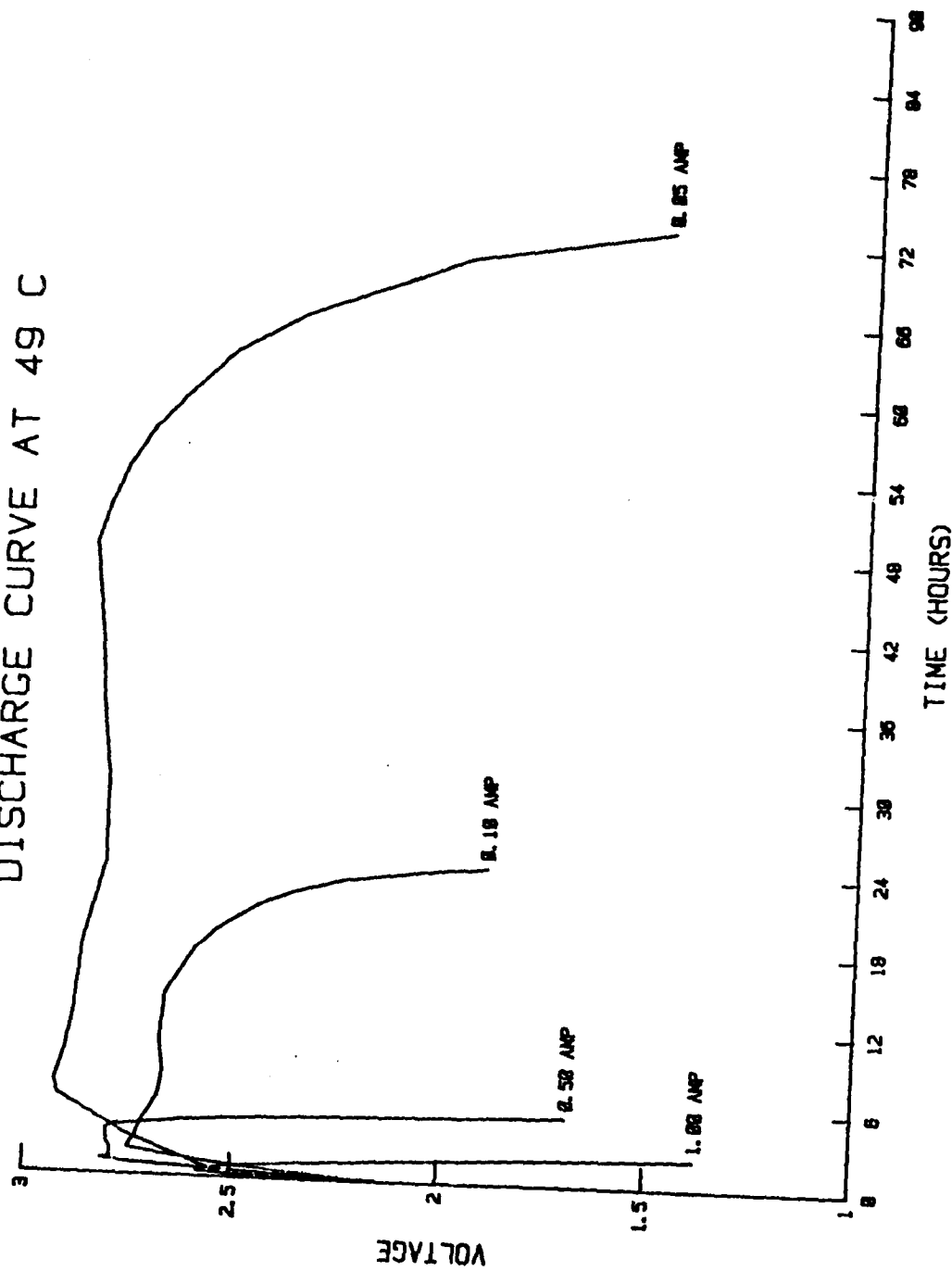


Figure 5. Discharge Curve at 49 C

DISCHARGE CURVE AT 74 C

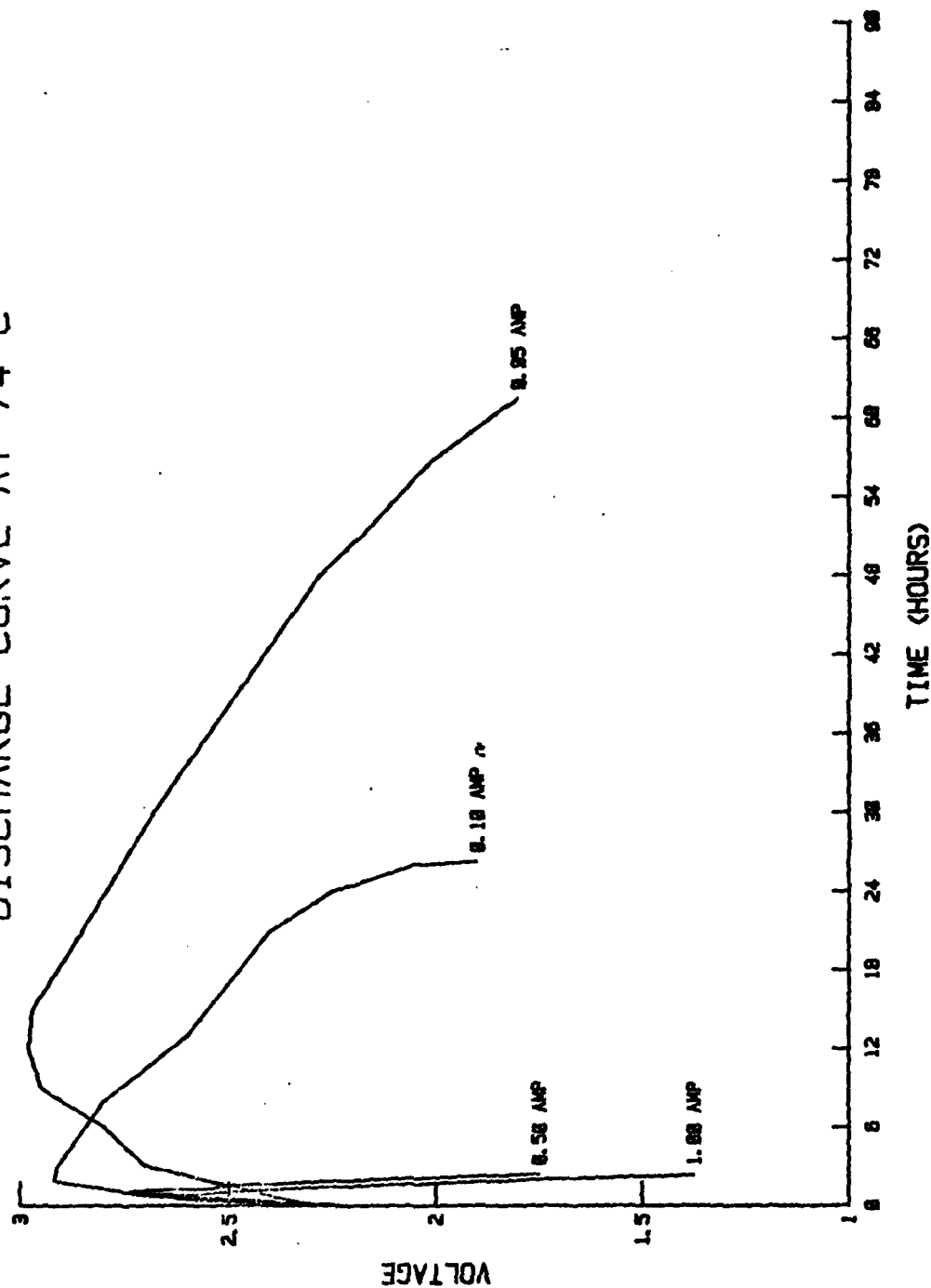


Figure 6. Discharge Curve at 74 C

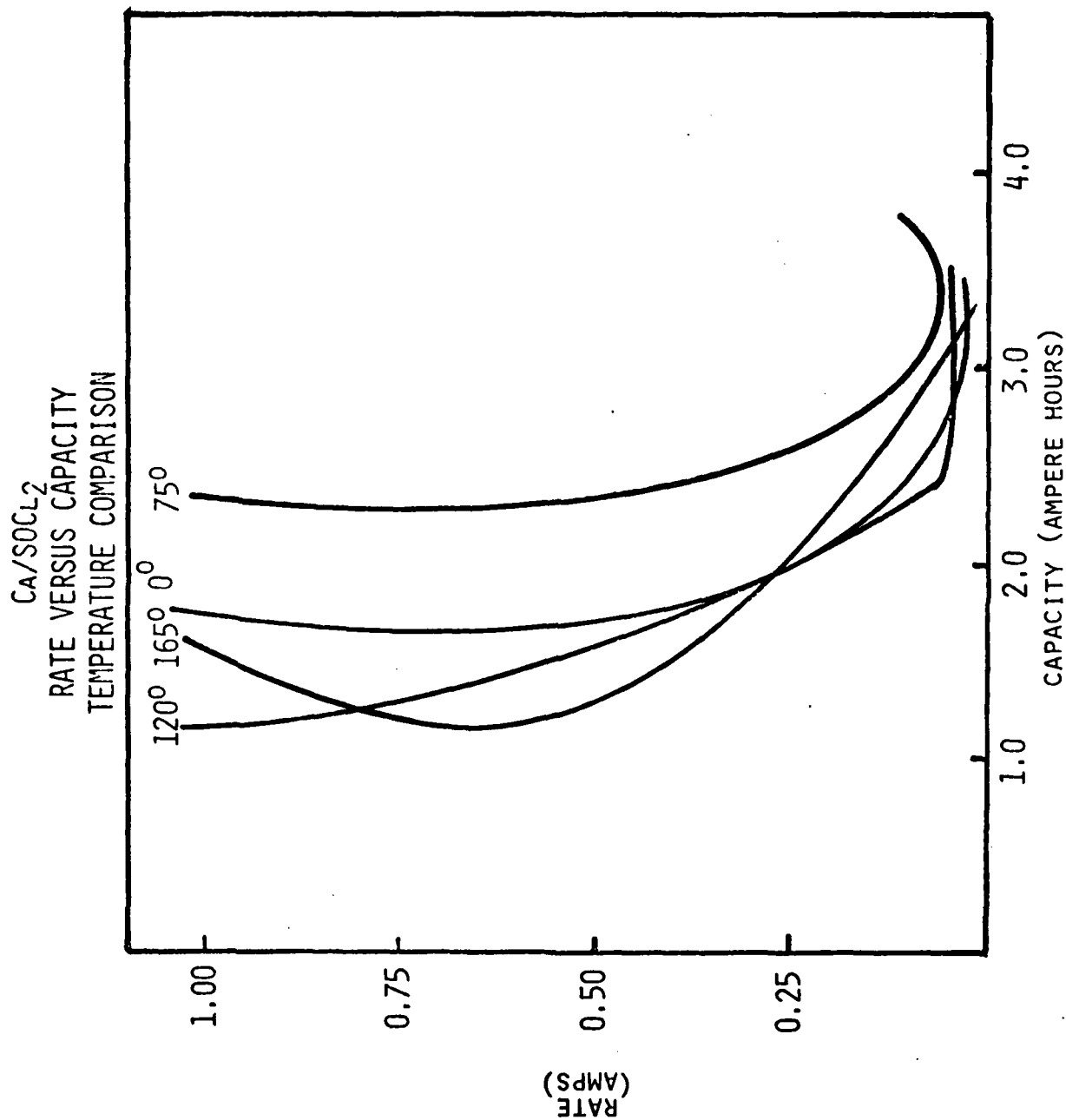


FIGURE 7 Ca/SOCl₂ RATE VERSUS CAPACITY TEMPERATURE COMPARISON

<u>PRELIMINARY STORAGE DATA</u>						
<u>TIME IN STORAGE</u>	<u>SN</u>	<u>OPEN CIRCUIT (Volts)</u>	<u>RISE TIME TO 2.00 (Seconds)</u>	<u>IMPEDANCE (Ohms)</u>	<u>RATE (Amps)</u>	<u>CAPACITY (Ampere Hours)</u>
1 Month	26	3.10	1	.950	.1	3.50
1 Month	27	3.12	1	.900	.1	3.46
3 Months	28	3.10	1	1.80	.1	3.40
3 Months	29	3.09	1	1.75	.1	3.42
6 Months	30	3.10	2	2.30	.1	3.45
6 Months	31	3.10	2	2.35	.1	3.40

Figure 8. Preliminary Storage Data

A second storage test was performed at temperatures of 24°C and 55°C over a period of eighteen months. Cells were removed at monthly intervals and discharged through a twenty ohm load at room temperature. Data from this test is summarized in Figure 9.

Cells used in the second test did not retain capacity as well as those in the first test. After five months storage at 24°C the capacity had dropped from 3.5 AH to 2.0 AH. Five month's storage at 55°C reduced capacity from 3.5 AH to 1.0 AH. During months four and five, cells were removed from 55°C storage which had no capacity.

5.0 ABUSE TESTS

The response of the half "D" cell to various types of environmental stress and abuse was evaluated using approximately 150 cells in the following tests.

- (a) Short Circuit
- (b) Incineration
- (c) Reversal
- (d) Charging
- (e) Shock
- (f) Vibration
- (g) Crushing
- (h) Puncture

The methods and results of each test are given below:

(a) A short circuit test was performed on cells at approximately 15°C - 25°C by shorting the cells through a 100 mv/50 amp shunt. The total resistance of the circuit was not measured. Skin temperature, potential

6 MONTH STORAGE TEST

STORAGE TIME (Months)	STORAGE TEMP. (°C)	CAPACITY (AH)
0	—	3.5
1	24	3.4
1	55	2.1
3	24	2.5
3	55	1.8
4	55	0.6
5	24	2.0
	55	1.0

Figure 9. 6 Month Storage Test

and shunt current from the cell were monitored until the cell vented or the temperature reached a maximum and started to fall. Characteristic results from a cell are shown in Figure 10. Immediately after closing the circuit, cell potentials dipped to less than 100 mv at shunt currents of about 5 amps. Shunt current normally rose to approximately 17 amps within two minutes after shorting. Maximum skin temperature lagged the vent by several minutes and never exceeded 82°C. The cell cases were not deformed before venting and the unrestrained cells were not moved by the vent. Actual venting was often inaudible and was accompanied by little visible liquid or gas.

(b) Incineration of cells was performed by exposing test cells to a propane flame touching the cell surface at the center. The test was performed on cells which were fresh, 50% discharged at 24°C and 50% discharged at -29°C. The cells vented mildly after approximately 1.5 minutes in all cases. The propane flame was continued for a minimum of five minutes after venting with no additional results. There were no noticeable differences in results of the various test samples. Examination of the cells after test revealed that several cell cases had a small hole where the propane flame had touched the cell. The hole is presumed to have opened after venting since all vent products were observed to come from the vent area.

(c) Reversal of cells was done at a constant current of 250 ma. Cells were discharged through a constant forty ohms until reaching 0.1 volts where they were power discharged at 250 ma into reversal. The reversal was continued approximately three hours until the potential required to maintain the current exceeded 20.0 volts. Characteristic results of a cell reversal are shown in Figure 11. In no instance did noticeable venting

Ca/SOCL₂

SHORT CIRCUIT

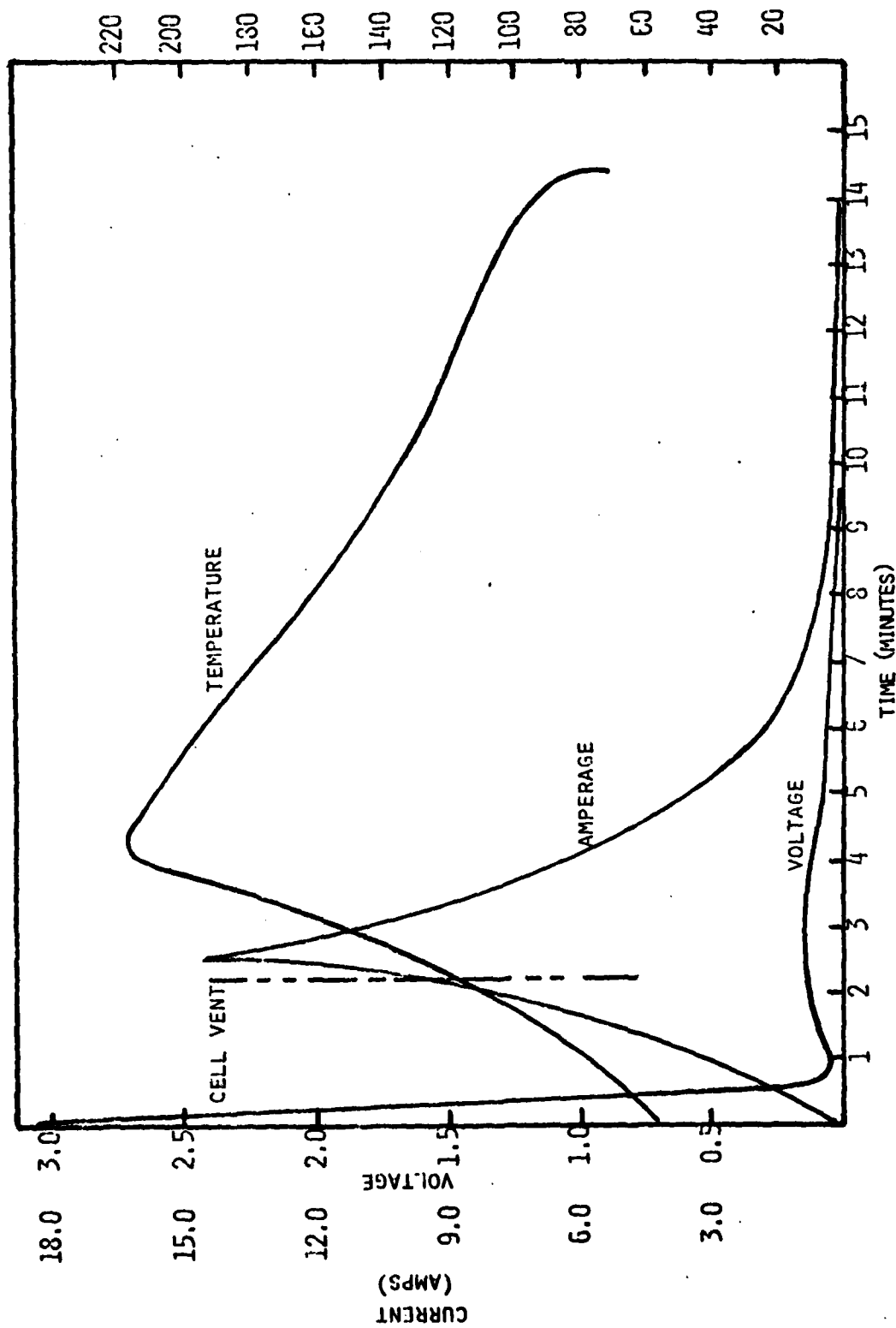


FIGURE 10 Ca/SOCL₂ SHORT CIRCUIT

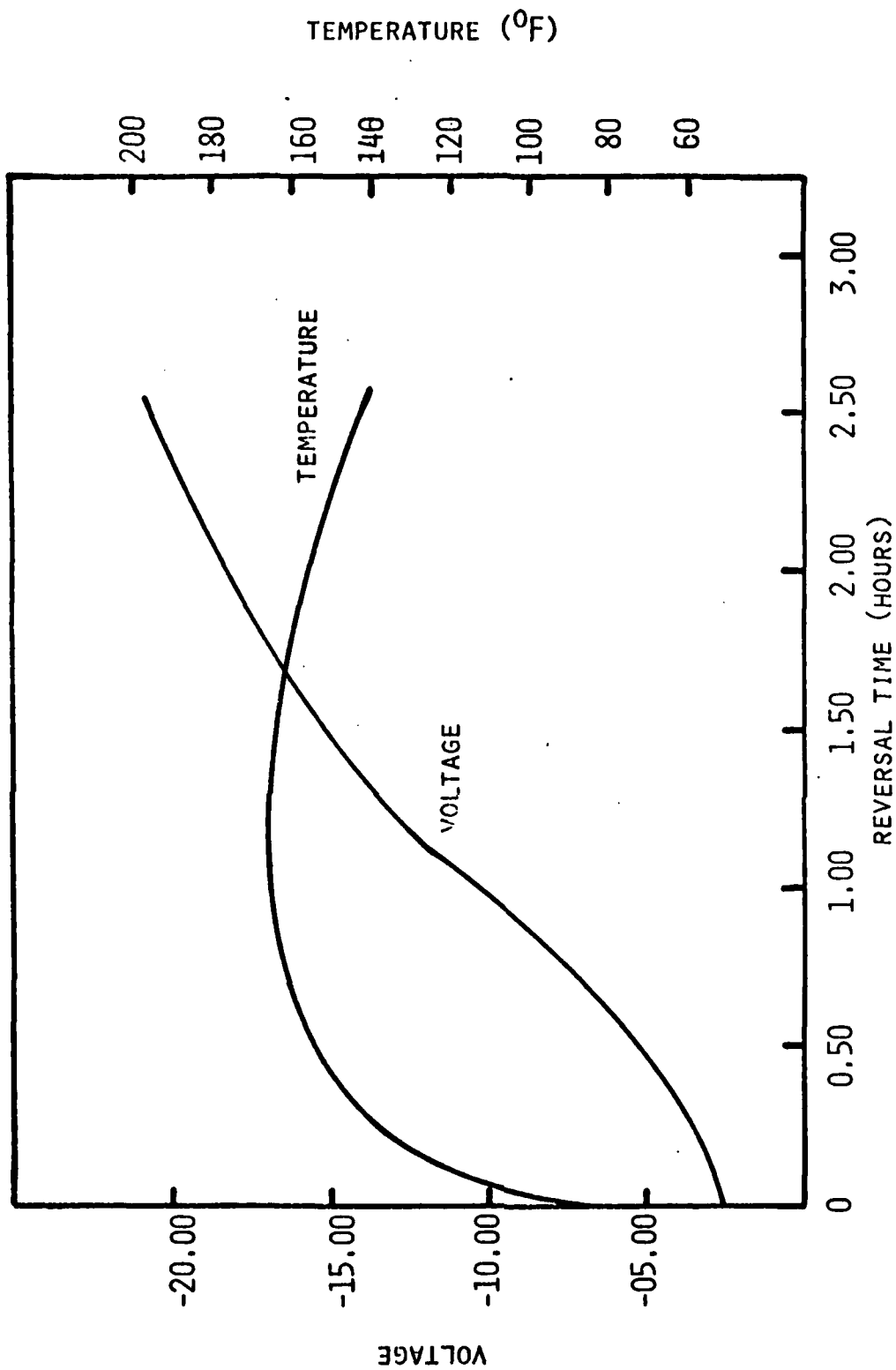


FIGURE 11 Ca/SOCl₂ CELL REVERSAL S/N 69 (FRESH CELL) 0.25 AMP.

occur during reversal; however, in several cases examination of cells after the test revealed a slightly opened vent. A group of cells which were power discharged and reversed at -29°C produced the same results.

(d) Charging of cells was done at both constant potential and constant current using fresh cells, cells 50% discharged at room temperature and -29°C , and cells 100% discharged at room temperature and -29°C . Cells were charged at constant currents were of 50 ma, 100 ma, and 1000 ma, for periods equivalent to 0.5 amp hours capacity. Characteristic results of this test are shown in Figures 12 through 15. Cells charged at constant current did not vent. The highest temperature observed was 38°C . Cells charged at a constant potential of 5.0 volts received up to 1.5 amps and vented at times varying from eighteen to sixty minutes. Fully discharged cells vented quickly, while fresh cells required the longest time. All vents were mild, with a visible spray but no deformation of the case.

(e) Shock tests of 100 g's for 5 msec. were performed in all axis on fresh, partially discharged, and fully discharged cells. No change in open circuit potential was noted during any of the tests; however, discharge of the cells at room temperature through a twenty ohm resistance produced 80% of the normally observed capacity. Teardown of the cell did not reveal a significant change in any cell components.

(f) Vibration (random) in two axis at amplitude up to 15 g's was performed on fresh, partially discharged, and fully discharged cells. Open circuit potential of test cells did not vary during or after vibration; however, as in the shock test, the cells did not produce normal capacity when discharged at room temperature through twenty ohms. The capacity loss was approximately 20%.

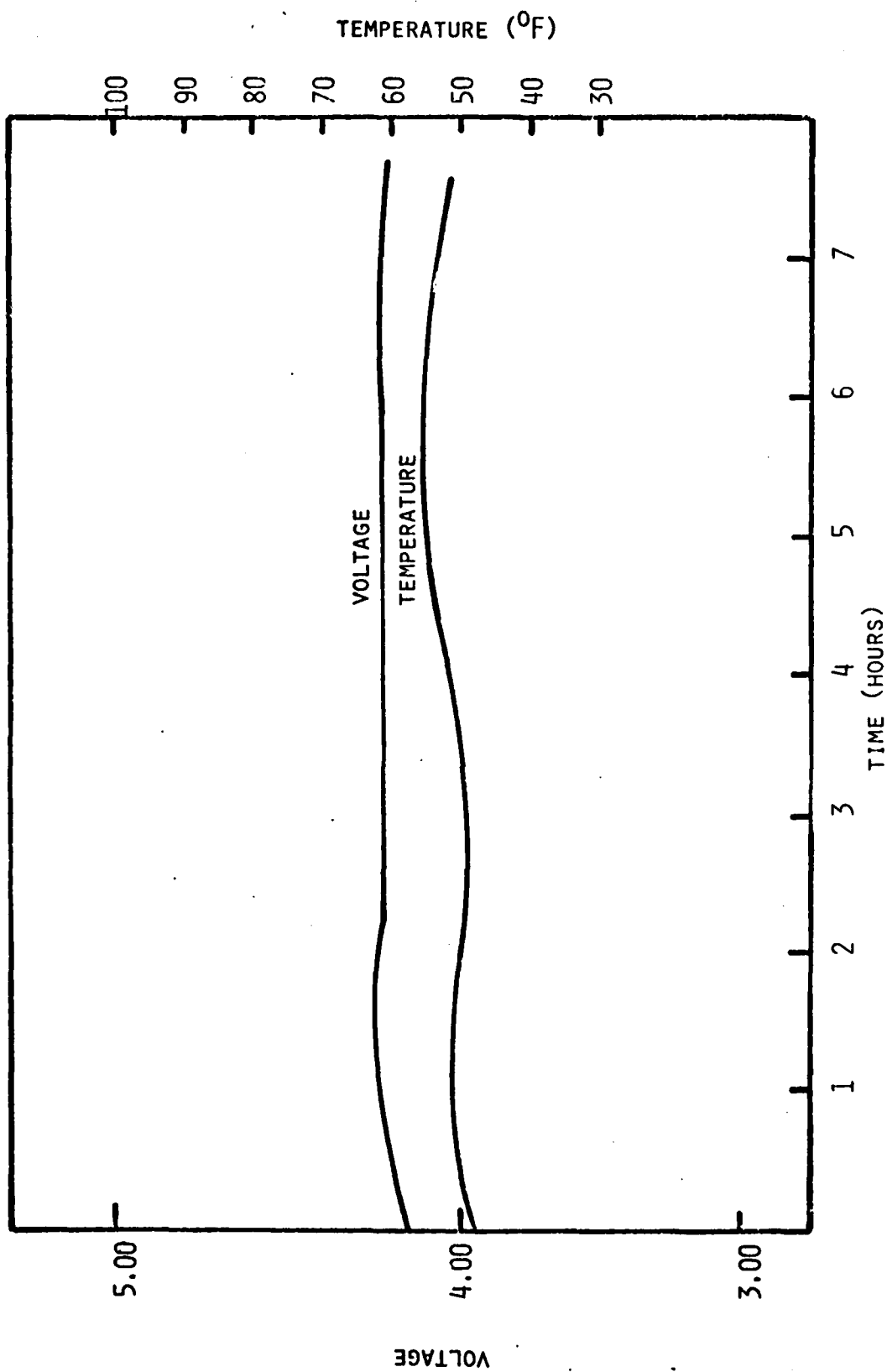


FIGURE 12. Ca/SOCl_2 CHARGING CONSTANT CURRENT 0.05 AMP

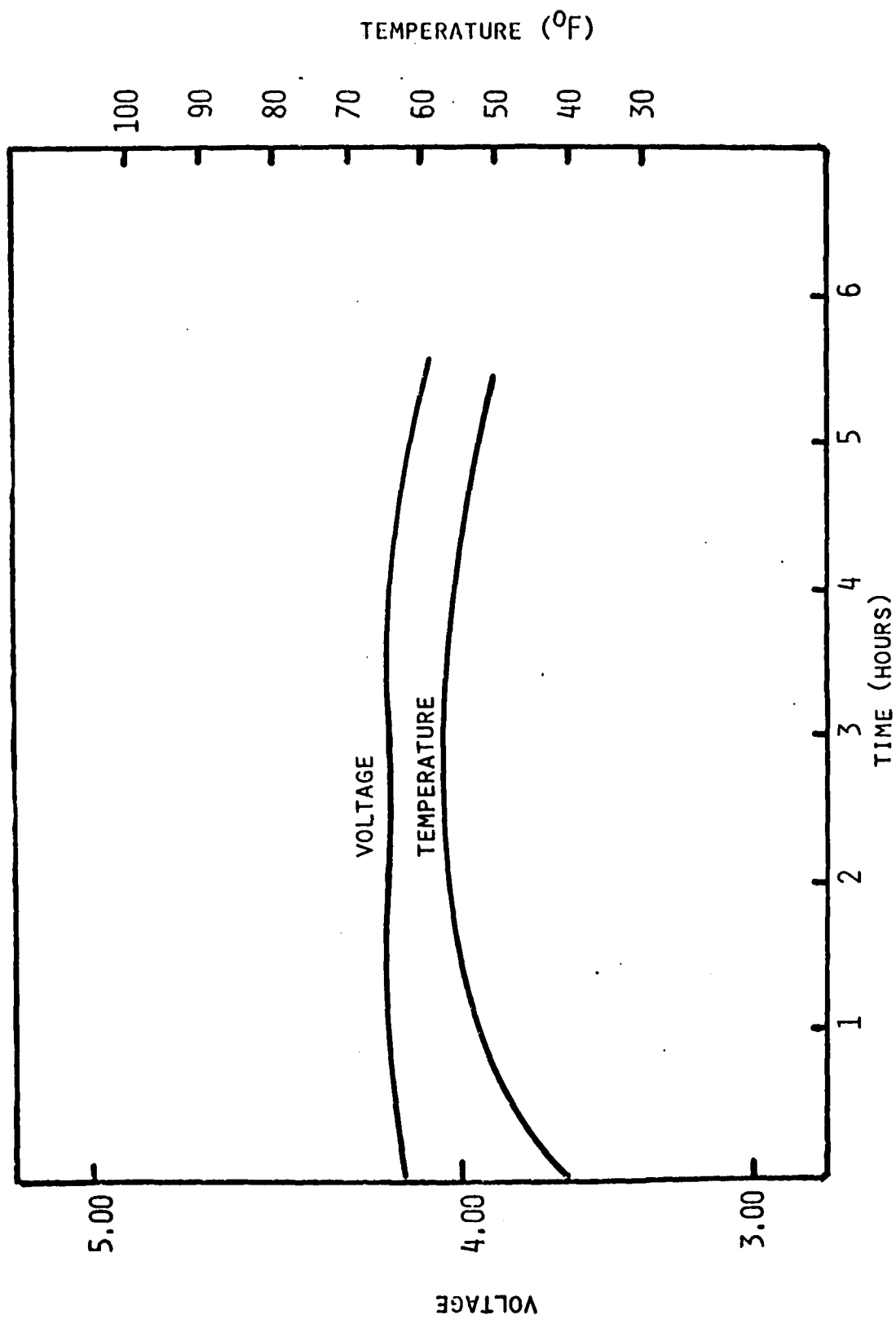


FIGURE 13 Ca/SOCL_2 CHARGING CONSTANT CURRENT 0.10 AMP

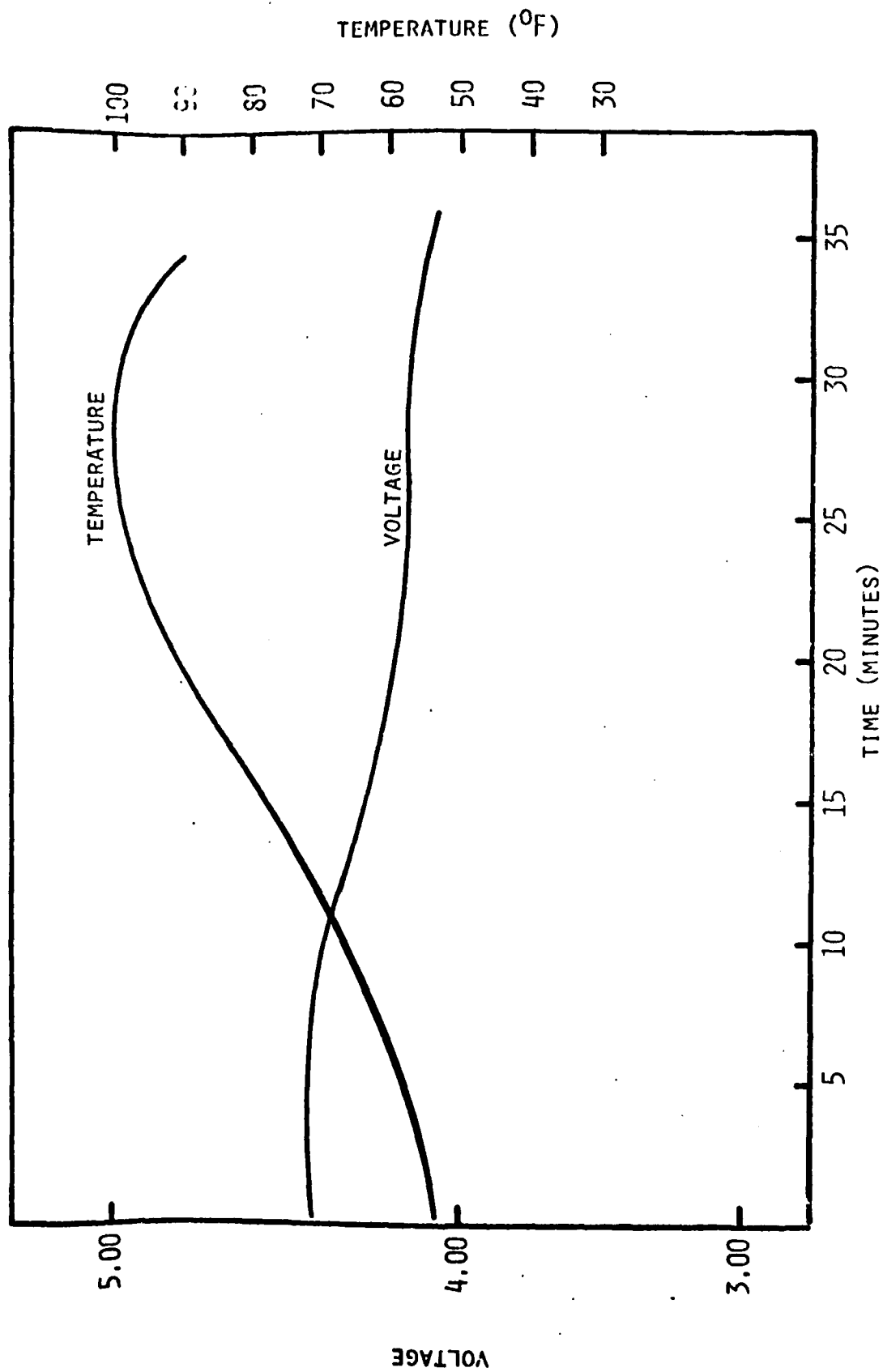


FIGURE 14 Ca/SOCL₂ CHARGING CONSTANT CURRENT 1.00 AMP

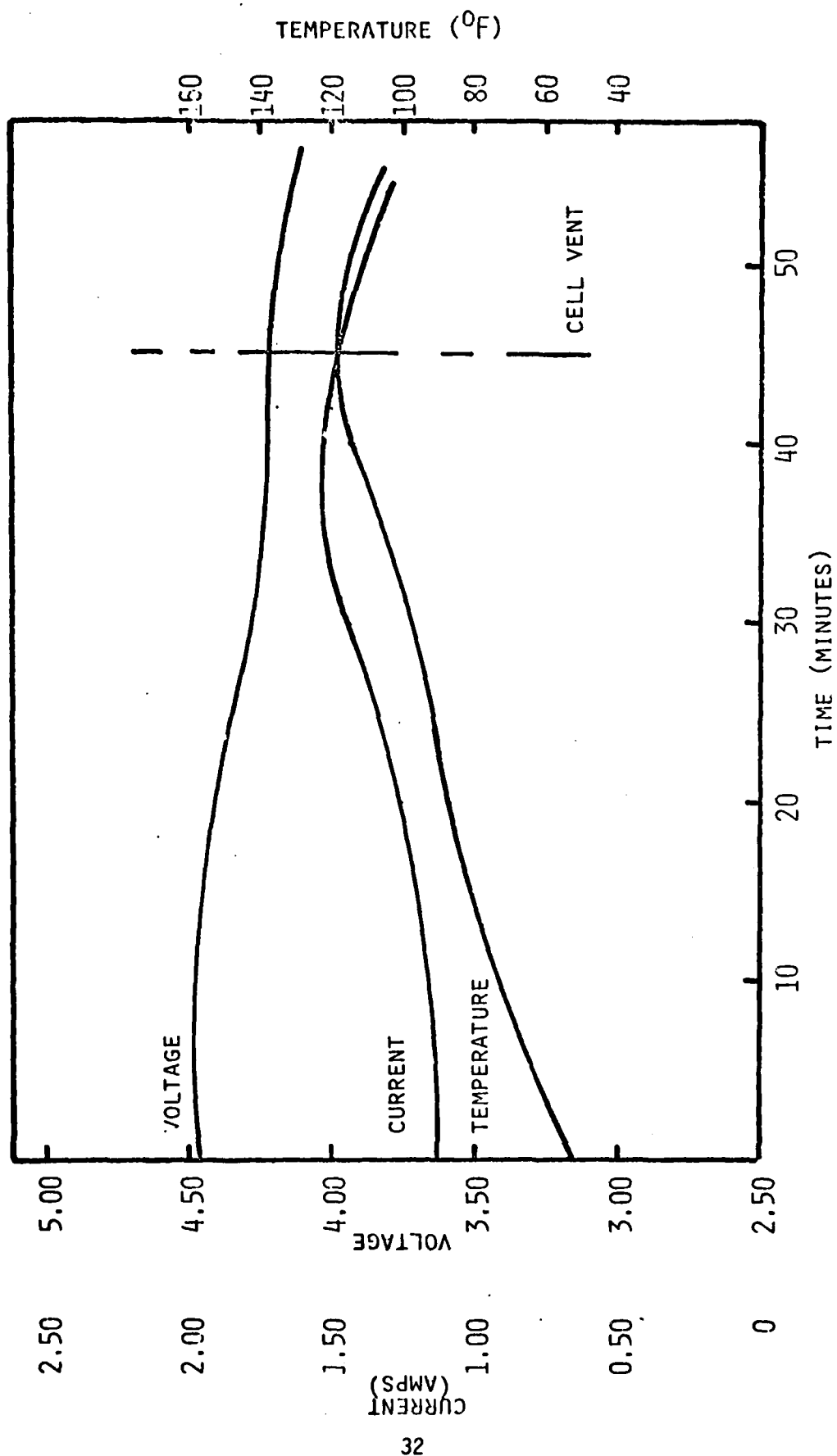


FIGURE 15 Ca/SOCl₂ CONSTANT POTENTIAL CHARGING 5.00 VOLTS

(g) Crushing of the cell case until obvious internal short circuit had been created was performed on fresh, partially and full discharged cells. The cells were crushed with a remotely operated ram, bearing on the side of the cell midway between top and bottom. Certain of the cells were crushed only until a definite voltage drop occurred, such as is shown in Figure 16. In such tests the cell potential normally recovered, and cell temperatures did not change. Other cells were crushed to the limit of the hydraulic ram, which usually resulted in extreme deformation and opening of the cell case. The minimum voltage noted in such tests was 0.6 volts, corresponding to a maximum temperature increase of 5°C.

(h) Puncture of cells was performed using a remotely operated hydraulic ram to force a 16d nail approximately 75% through the side of a cell. The nail was left in place to seal the puncture opening. Cells thus tested included fresh, partially and fully discharged samples, both at room temperature and at -29°C. Results of a typical test are shown in Figure 17. Fresh cells normally vented within 90-120 seconds at skin temperatures of about 82°C. Discharged cells also vented, but required longer than fresh cells.

6.0 DISCUSSION/CONCLUSIONS

The overall results of the 3.5 amp hour tests were that: (1) the cells were capable of adequate energy densities (420 WH/dm³), (2) the cells did not respond to any form of abuse evaluated, and (3) the cells exhibited a wide variation in storage survival. The cell discharges were sensitive to both rate and temperature. The 50 ma rate which produced 3.5 amp hour at 20°C was reduced by 6% at 49°C, and by 23% at 74°C.

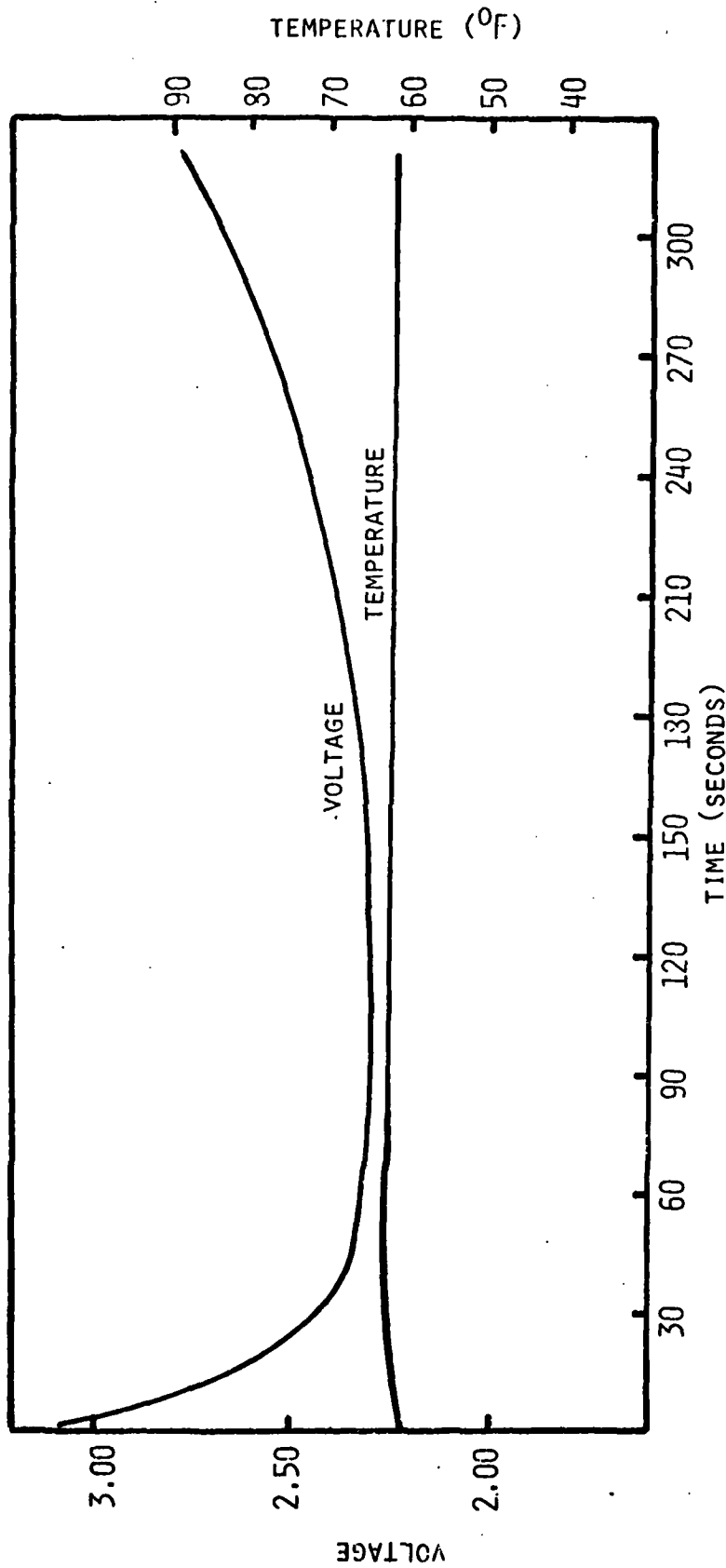


FIGURE 16 Ca/SOCl_2 CELL CRUSHING

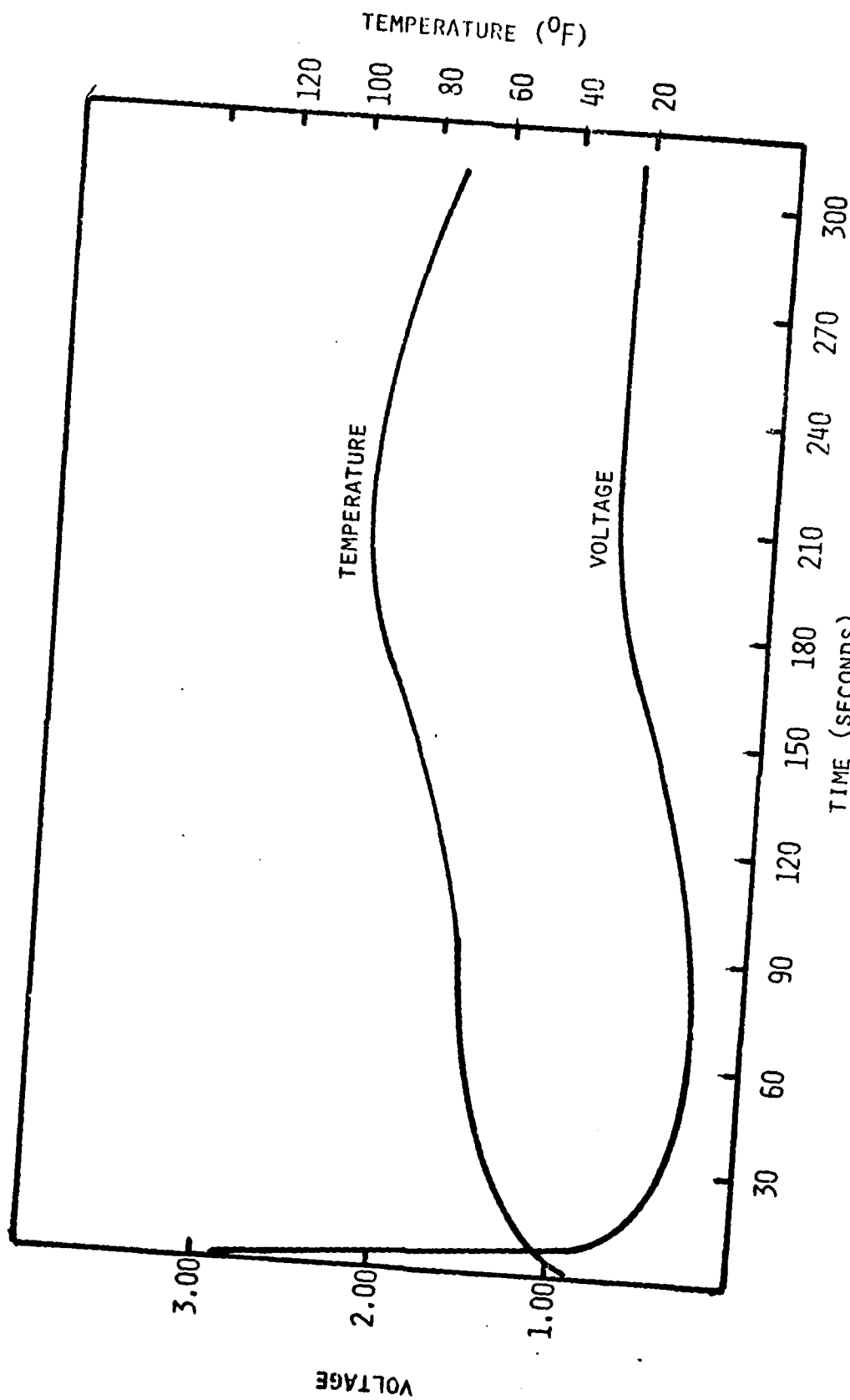


FIGURE 17 Ca/SOCl_2 CELL PUNCTURE

Although this dependence might suggest an accelerated corrosion of the anode, the calcium potential versus a lithium reference electrode remained relatively constant during discharge and failure of cells at all discharge temperatures. Teardown of cells after discharge revealed that the anodes were intact and in good condition.

One of the limitations on cell capacity and rate was the necessity of using very thin cathodes, which were producing the highest matrix utilization at that point in the program. The cathode design developed later in the program, for use in 600 and 10,000 AH cells, was applied to half "D" cells with the same general improvement in energy density as was noted in those cells. Half "D" cells using foam cathodes produced approximately 540 WH/dm^3 at 50 ma when discharged at 20°C .

The storage results, though contradictory from test to test, are consistent with the results of ampule tests of pure calcium in electrolyte solutions. Teardown of cells which failed to survive storage often revealed not just a partially corroded anode, but a completely bare anode collector. As is the case of ampule tests, the corrosion tends to be all or nothing. The test results did not provide any information which would indicate the cause of the corrosion; however, they do indicate that anodes can be made to survive storage without corrosion, although the factors influencing the corrosion are still undefined.

None of the abuse tests performed on half "D" cells produced any condition which was hazardous. The most severe response was that of cells heated with a propane flame; however, even those tests produced only mild venting. Of the approximately 150 cells used in the above

evaluation, none produced any flame from the vent area, or a forceful vent of any kind. The majority of vents were not discovered until after the test had been completed and the cell examined. None of the few low surface area half "D" cells fabricated were exposed to abuse, but it would appear from the existing results that these cells would have even less response.

SECTION IV 600 AH/SPACECRAFT CELL

1.0 INTRODUCTION

A medium sized cell was designed, and evaluated to meet the requirements of Air Force spacecraft power applications, and to provide an intermediate step towards design of the larger ground power cell to follow. The size of this intermediate cell was nominally 600 amp hours. The cell was designed in two versions: High surface area and low surface area. The high surface area (HSA) cells, which were constructed with cathodes 0.50 mm thick and anodes 0.35 mm thick, were used for both electrical performance and abuse evaluation. A second design (LSA) having cathodes 6.35 mm thick and anodes 1.8 mm thick, was constructed after the first group, and was also evaluated by electrical and abuse tests.

The cell tests were duplicated because of the availability, later in the program, of the much thicker cathodes which were better suited to the 600 and 10,000 AH cell designs.

2.0 HSA CELL DESIGN

The HSA cell was designed as a nominally 600 amp hour cell based on electrodes which were similar in thicknesses, and balance, to those used in the half "D" cell. The overall size of the cell was 16.5 cm X 14.0 cm X 17.8 cm. The cell cover contained three terminals held by glass to metal seals, and a diaphragm vent. The vent was a standard one inch NPT fitting made of type 304 stainless and containing a 2.5 cm diameter, scored, blowout disc opening at 150 psi. The vent was fastened to the cell by a threaded stainless fitting welded to the cell cover. Cathodes were 0.5 mm thick, 14 cm wide and 15 cm long. Composition was 90% Shawinigan

carbon black and 10% Dupont type 30 TFE, on a current collector of expanded nickel 200 screen. Each cathode had a nickel 200 tab welded to the positive terminal.

Anodes were 0.35 mm thick, 14 cm wide and 15 cm long, and were made by laminating a solid calcium foil to a current collector of expanded nickel 200 screen. Each anode had a nickel 200 tab welded to the negative terminal.

Separation was 0.35 mm thick Dexter non-woven glass mat, wrapped in a single layer around each cathode. The completed cell contained 56 cathodes and 57 anodes. The cells were filled with 2.5 liters of a 1.4 molar solution of LiAlCl_4 in SOCl_2 . The solution was provided by Apache Chemical, and was based on Hooker SOCl_2 and Fluka AlCl_3 . Each cell contained a referenced electrode connected to the third terminal in the cell cover. The reference electrode in all three HSA cells was calcium.

2.1 HSA Electrical Performance

Three HSA cells were constructed for use in discharge and abuse tests. Of these, one cell was discharged at a constant five amps at a temperature of approximately 16°C . The cell discharged 83 hours above 2.5 volts as shown in Figure 18. Total capacity removed from the cell was 415 amp hours. The failure of the cell at 83 hours was due to the cathode. The anode to reference potential remained relatively constant during the discharge, and did not change appreciably until the cell potential had fallen below 1.0 volts.

2.2 HSA Abuse

All three of the HSA cells were subjected to one or more abuse conditions. Two of the cells, numbers 1A and 2A were fresh during abuse

DISCHARGE CURVE - CELL NO. 3A

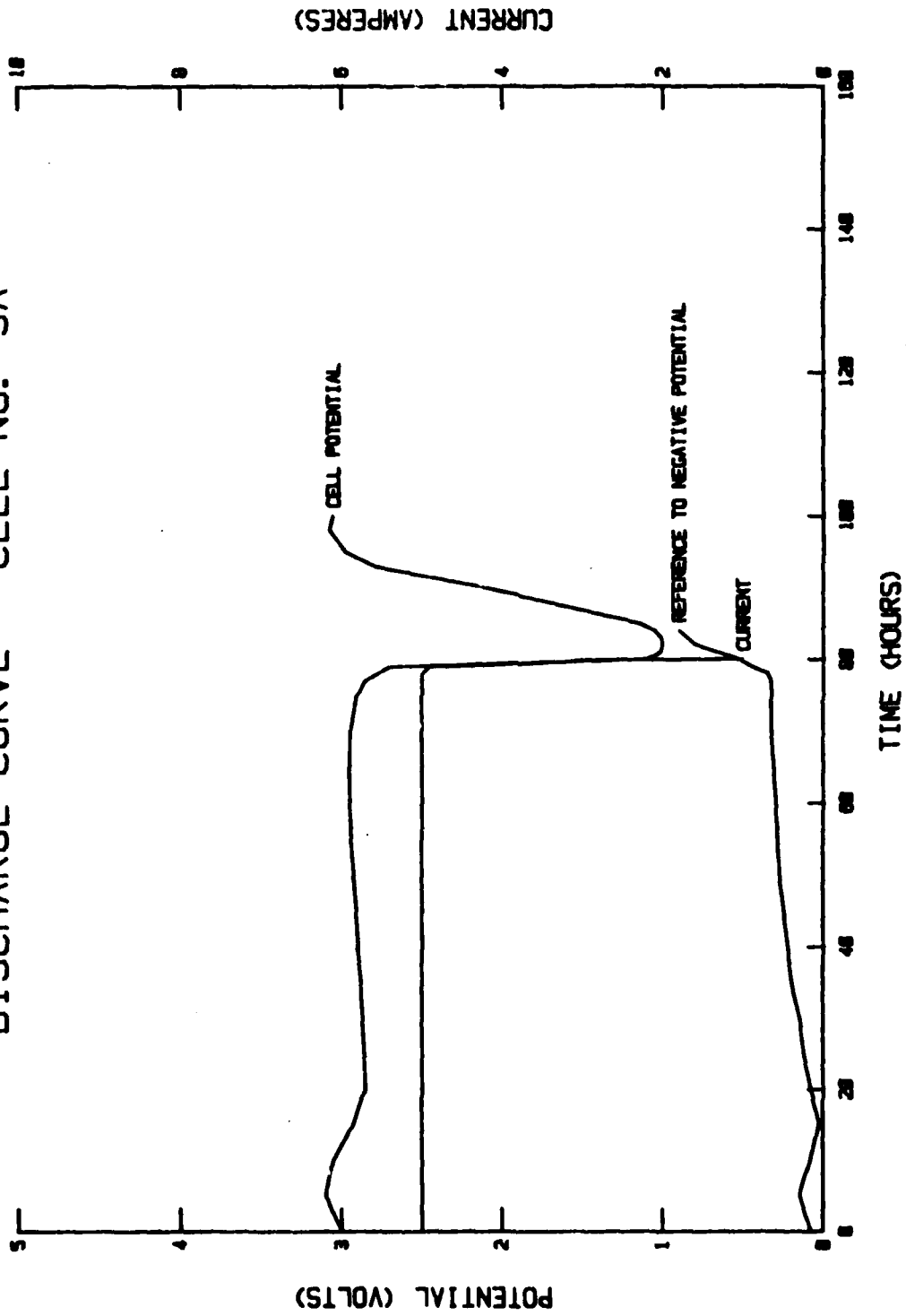


Figure 18. Discharge Curve - Cell No. 3A

tests, cell number 3A, was fully discharged before test. Cell No. 1A, which was the first large cell constructed, was exposed to a succession of abuse conditions, including short circuit, incineration and bullet penetration.

2.2.1 The fresh cell was shorted externally through a 3000 amp, 50 mv shunt and 6.1 meters of 4/0 copper cable. The cell potential dropped immediately from 3.08 volts to 0 volts, with no current flowing through the shunt other than a transient which was not measured. No increase in skin temperature was observed and the cell potential slowly rose from 0 to 0.9 volts over a period of fifteen minutes. All test results indicated that one of the terminals had been burned open by the first current surge. Examination of the cell after this test revealed a burned positive terminal pin; however, the cell had been exposed to other abuse tests before the observation could be made. The cell was then incinerated over a hexane flame large enough that the cell was completely engulfed. Approximately 30 seconds after the incineration began, the cell vented. The flame burned for an additional seven minutes before the hexane was exhausted, with no further damage to the cell.

The cell was allowed to stand with the vent open for a period of approximately 24 hours. The cell was exposed to ambient outside conditions at a temperature of about -7°C during the 24 hours. The cell was then penetrated by a 5.6 mm bullet which passed completely through the cell, but caused no apparent damage other than a 15°C increase in temperature. A second penetration one hour later produced a momentary flash at the point of impact. A third penetration produced a spontaneous fire which burned for approximately five seconds. The force of the flame knocked the cell from its position, burned a hole at the point of the bullet impact

and burned off the vent tube. The anodes were completely consumed by the fire.

2.2.2 Cell number 2A was penetrated by a 16d nail driven by a nail gun. The cell was stabilized at a temperature of 16°C. The nail penetrated about 10 cm into the cell, perpendicular to the electrodes and was left in the cell. The cell potential immediately dropped to 0 volts, then rose to over 3 volts within 5 minutes as shown in Figure 19. The cell potential slowly fell to 180 mv during 150 minutes with a peak temperature on the surface of 64°C, occurring at 110 minutes. The cell vent did not open; however, a small quantity of SOCl_2 was vented continuously during the first 120 minutes from the penetration hole.

Approximately 6 hours after the nail penetration, the cell was incinerated over a hexane flame. The cell vent opened after 30 seconds. Four minutes into the incineration the cell burned in the same manner as Number 1A; however, the bottom of the cell case opened at a weld and the cell was propelled off the incineration oven. As in the previous test, the fire lasted only several seconds and did not cause any fragmentation of the cell. The anodes were completely consumed by the fire.

2.2.3 Cell Number 3A, which was discharged prior to abuse, was later incinerated over a hexane flame for 17 minutes. The cell vented after 7 minutes of incineration, and the cell case deformed noticeably before venting. Examination of the case later revealed that the vent had been filled with two diaphragms rather than one and thus vented at a much higher pressure than normal. The incineration did not produce a calcium fire, therefore, the cell was shot approximately 20 times with a 5.6 mm bullet and then incinerated a second time for a period of 22 minutes, all without effect on the cell.

PUNCTURE - CELL NO. 2A

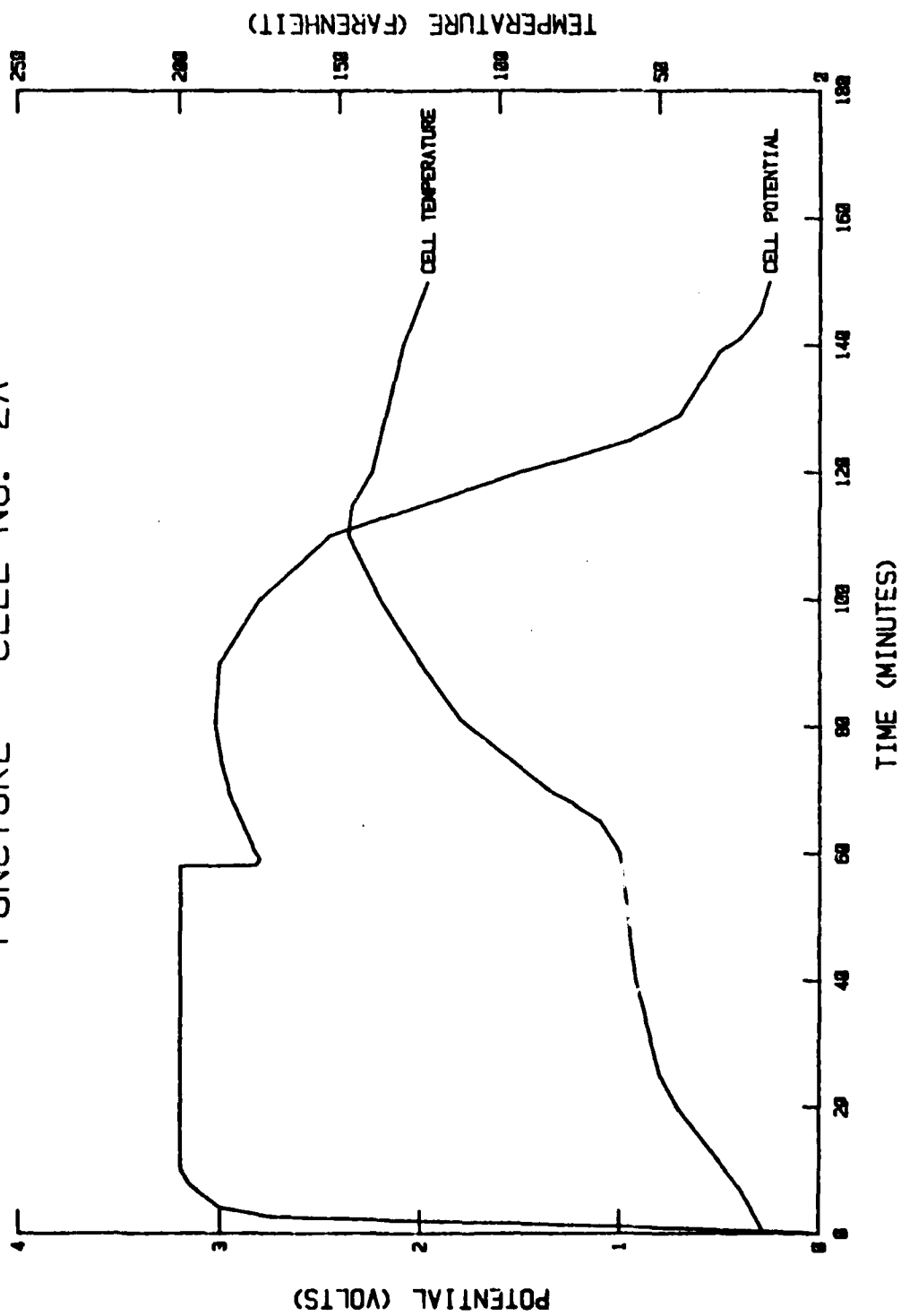


Figure 19. Puncture - Cell No. 2A

3.0 LSA CELL DESIGN

After preliminary test of the HSA design, a thicker cathode became available which had an apparent matrix utilization nearly equivalent to that of the original thin electrodes. The LSA cathodes were 6.35 mm thick, 14 cm and 15 cm in cross section. There were constructed of 90% Shawningen carbon black and 10% Dupont type 30 TFE on a current collector of foamed nickel 200. The anodes were solid calcium foil laminated to a nickel 200 expanded screen. Overall dimensions of the anode were 14 cm X 15 cm X 1.7 mm. Twelve cathodes and thirteen anodes were used in each cell, separated by the same non-woven glass mat referenced in the HSA design.

The cells were filled with approximately 2.5 liters of a 1.4 molar solutions of LiAlCl_4 in SOCl_2 . The solutions were prepared by two sources: Apache Chemical and Lithium Corporation. Both were based on Hooker SOCl_2 and Fluka AlCl_3 . A total of eight such cells were constructed.

3.1 LSA Electrical Performance

Five LSA cells were discharged, at a constant 5.0 amps, at an average ambient temperature of 20°C . The cells were discharged outside and were thus exposed to a true temperature which varied on a diurnal cycle. Reference electrodes were included in all cells; calcium references in cells intended for abuse tests, lithium references in cells intended for discharge. Three of the five cells were filled with 2.4 to 2.5 liters of $\text{SOCl}_2/\text{LiAlCl}_4$ solution provided by Lithium Corporation. The cells, Number 2C, 3C, and 4C, discharged over a period of 98 hours, 98 hours and 95 hours respectively. The capacity withdrawn over the 98 hour period was 490 amp hours to an end potential of 2.0 volts. A plot of a characteristic cell,

2C, is given in Figures 20 and 21. The failure of the cell was similar to all others, in that the potential drop was caused primarily by the cathodes. Anode to reference potentials remained generally constant throughout the discharge.

A plot of internal cell pressure versus discharge time shows essentially no internal pressure for the first 60 hours. During the last 38 hours the pressure increased to approximately 20 psi.

The remaining two cells of the five discharged were filled with 2.4 to 2.5 liters of $\text{SOCl}_2/\text{LiAlCl}_4$ solution provided by Apache Chemical. The cells, numbers 3B and 1C, were discharged in the same manner as those already discussed. Cell Number 3B was found to have a leak at one of the terminals during activation. The cell received approximately 200 ml less electrolyte than intended, and leaked continuously during the discharge, as evidenced by the absence of any internal pressure during discharge, and by a build up of LiAlCl_4 crystals at the point of leakage. This cell discharged 93 hours, thus producing 465 amp hours capacity.

Cell number 1C discharged without incident for 125 hours, producing 625 amp hours. The discharge of 1C is shown in Figures 22 and 23.

All discharged cells were disposed of by remotely opening the vent diaphragm, and immersing the cell into a saturated aqueous solution of Na_2CO_3 .

3.2 LSA Abuse

Three LSA cells were used to repeat certain of the abuse tests which had caused HSA cells to burn violently. All the cells were filled with electrolyte obtained from Apache Chemical.

- 3.2.1 Cell number 1B, fresh was penetrated by a 6.4 mm diameter spike to a depth of 8 cm, perpendicular to the electrodes. After penetration the cell

DISCHARGE CURVE - CELL NO. 2C

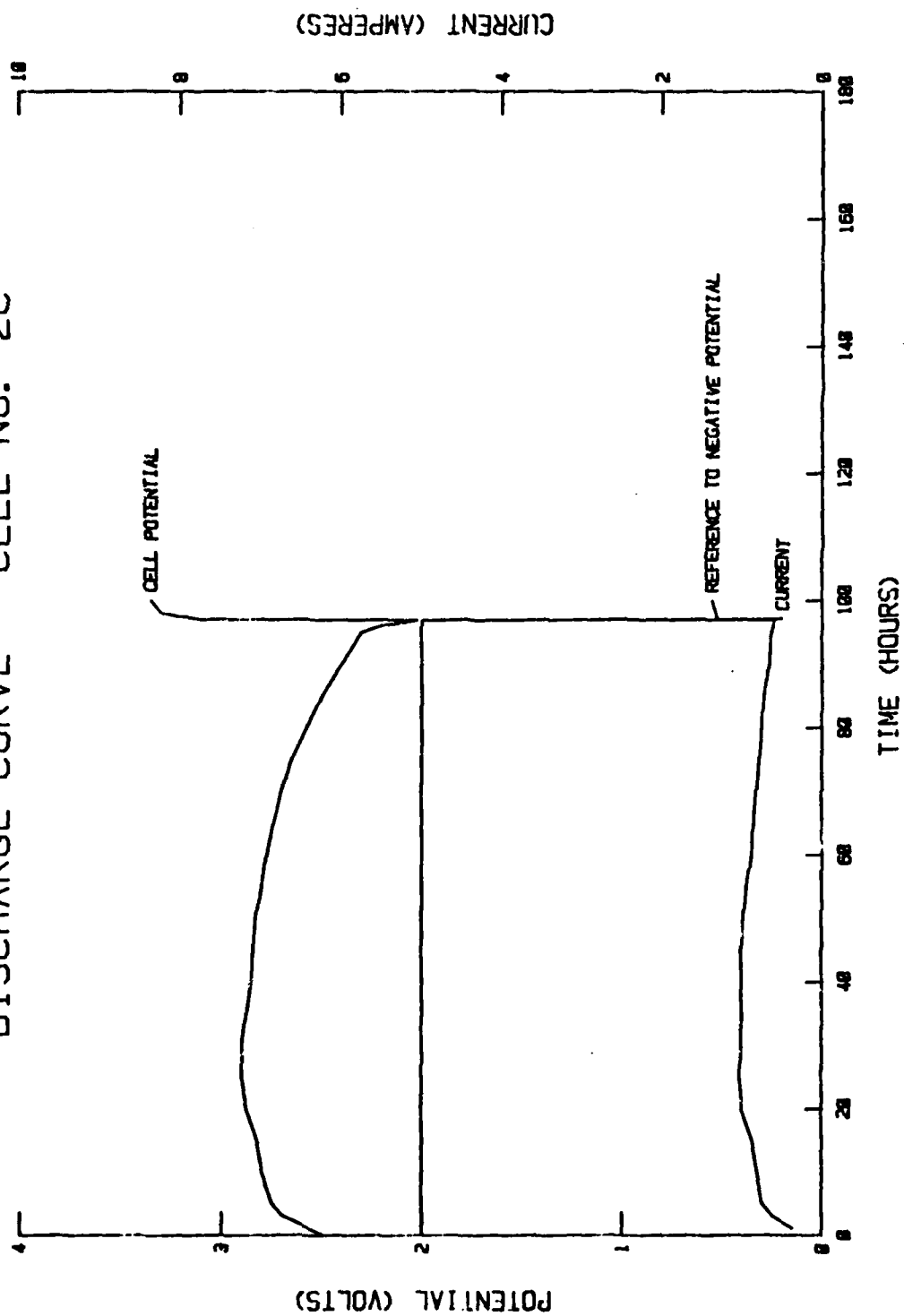


Figure 20. Discharge Curve - Cell No. 2C

DISCHARGE CURVE - CELL NO. 2C

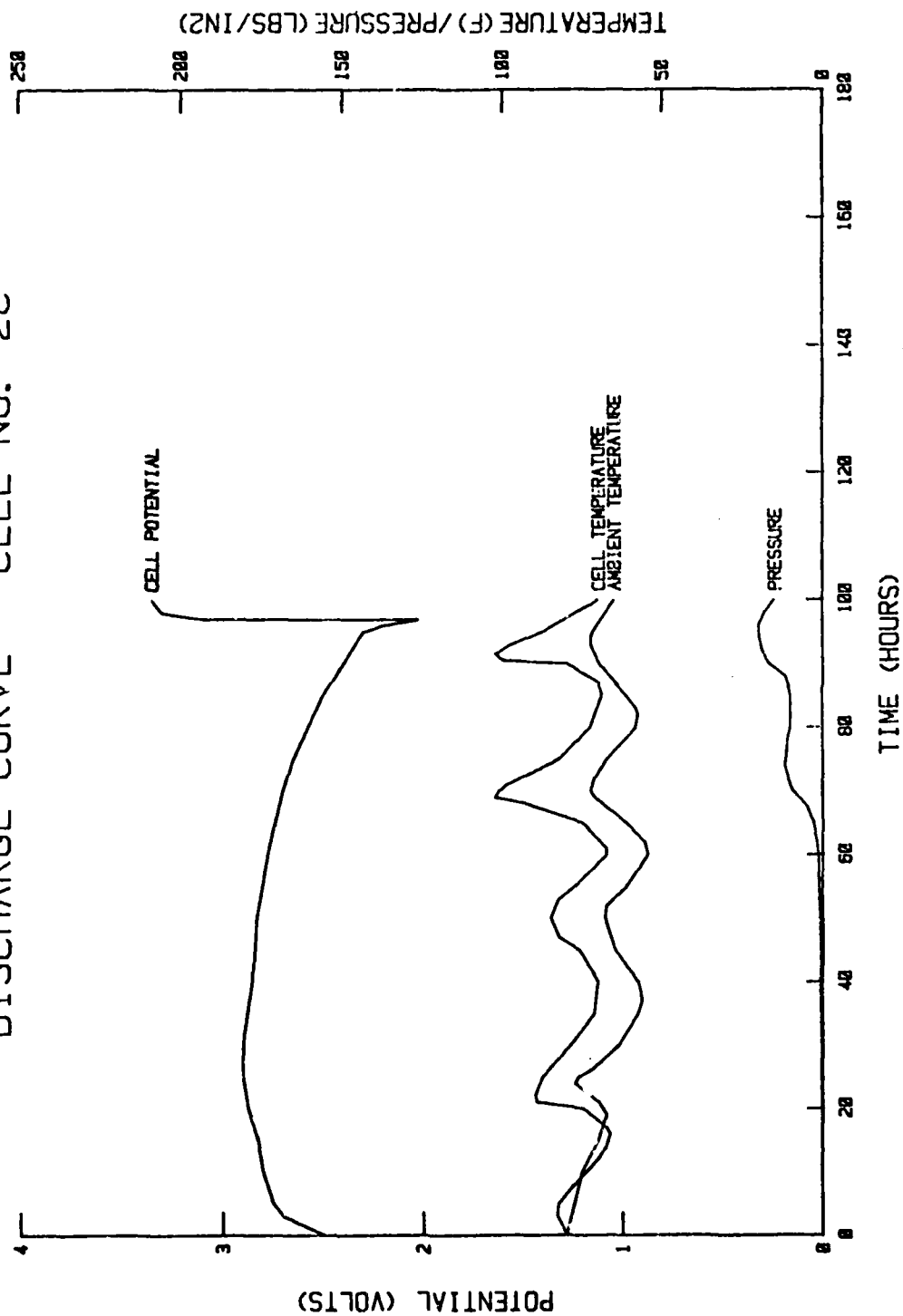


Figure 21. Discharge Curve - Cell No. 2C

DISCHARGE CURVE - CELL NO. 1C

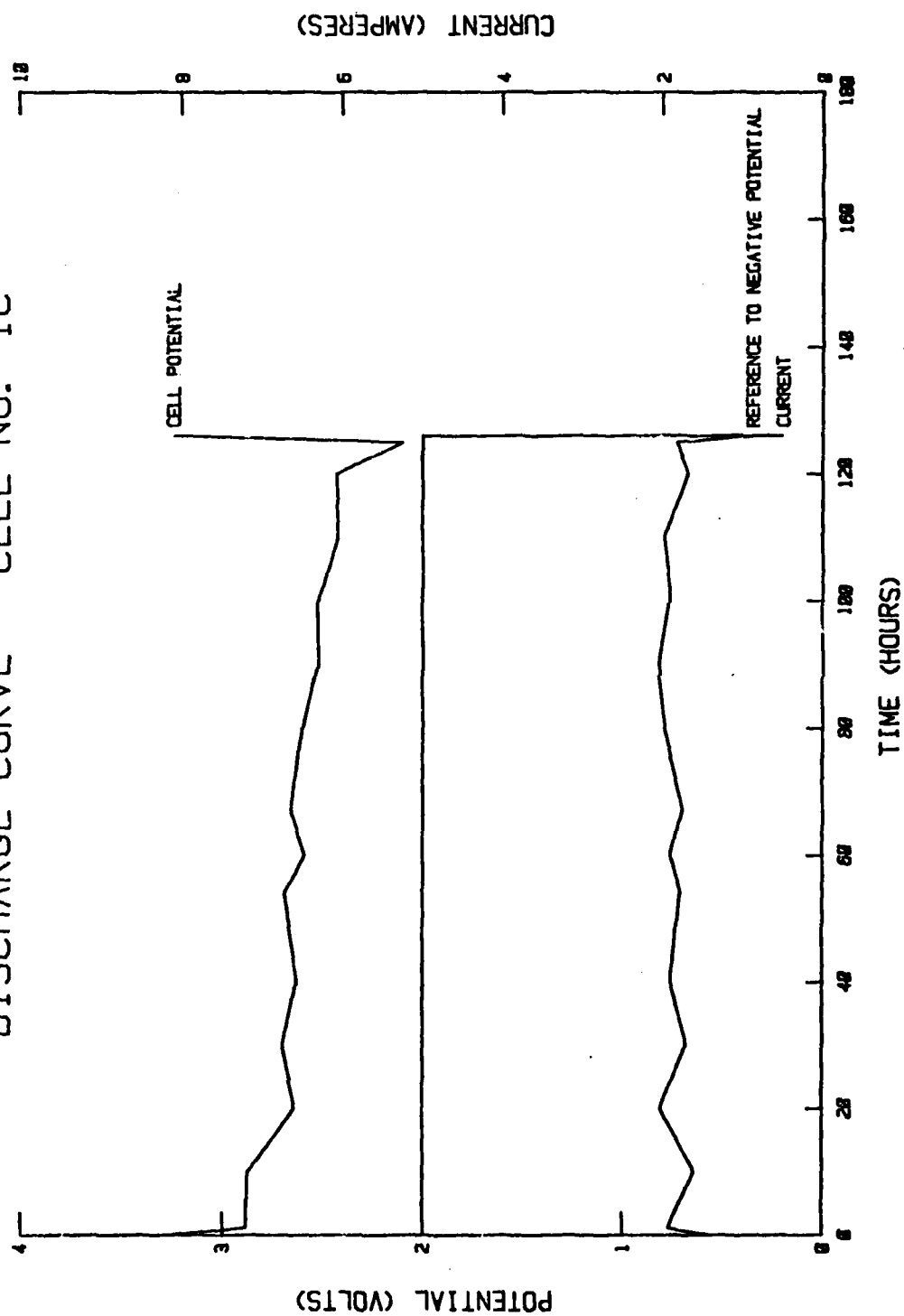


Figure 22. Discharge Curve - Cell No. 1C

DISCHARGE CURVE - CELL NO. 2C

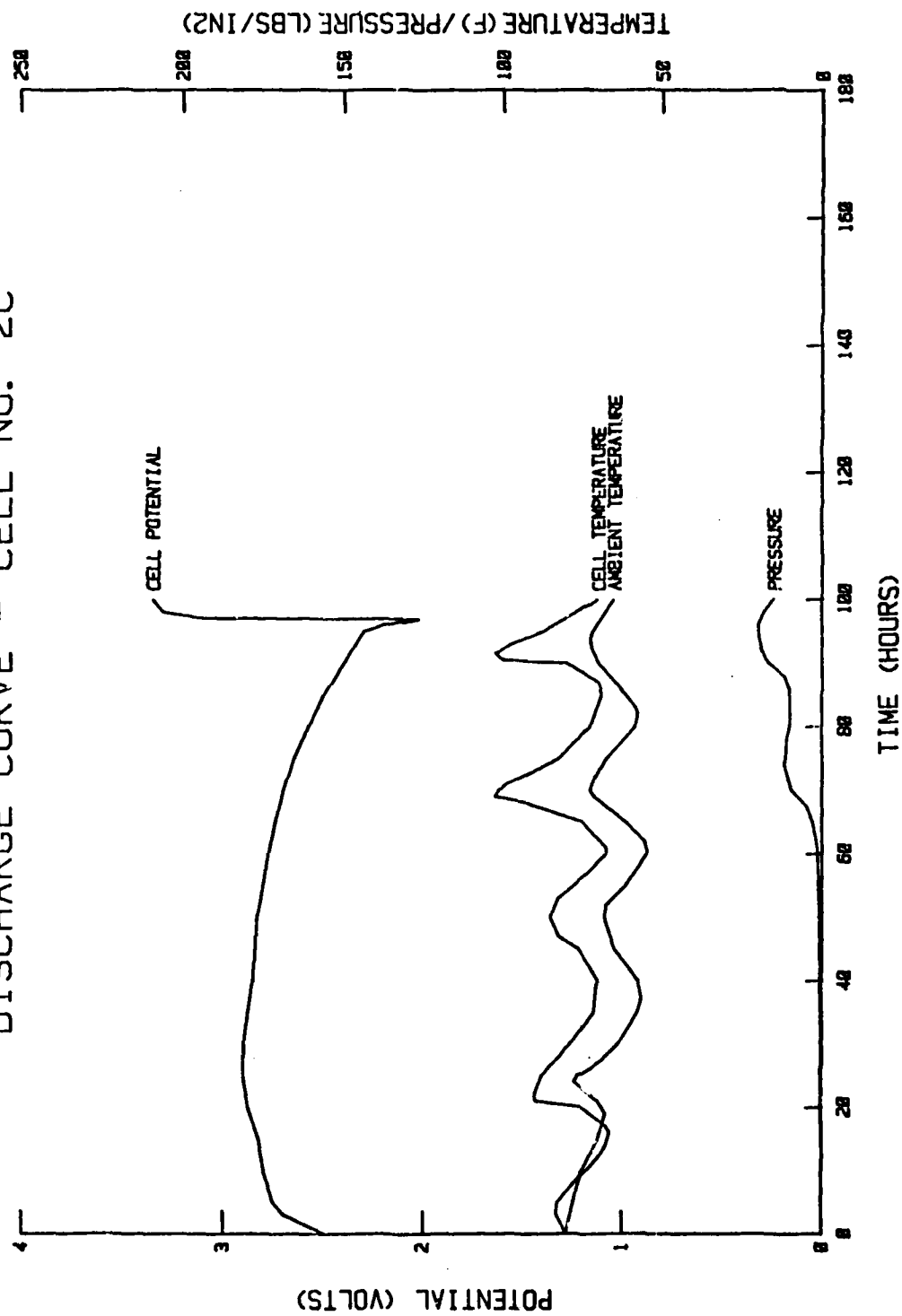


Figure 21. Discharge Curve - Cell No. 2C

DISCHARGE CURVE - CELL NO. 1C

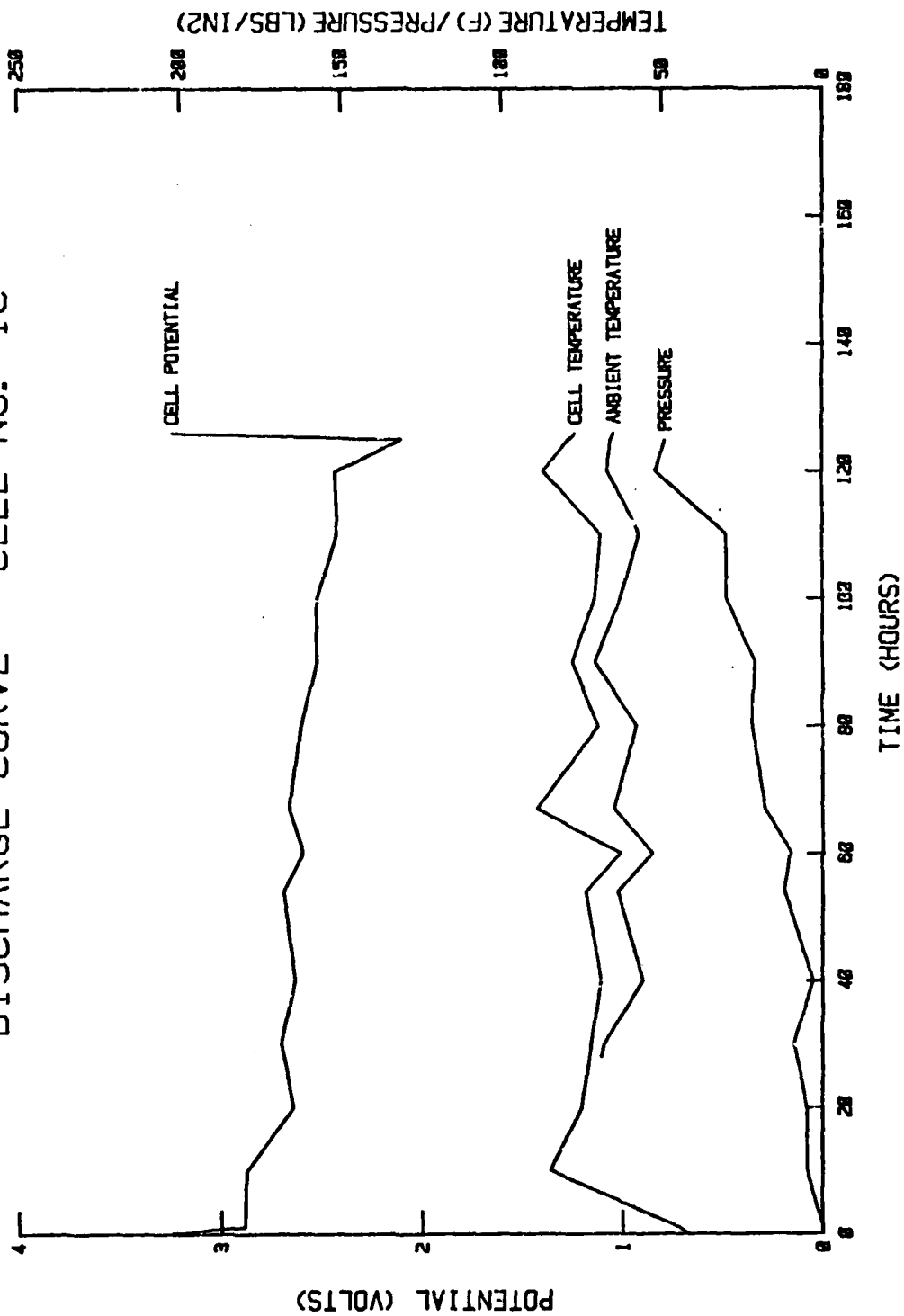


Figure 23. Discharge Curve - Cell No. 1C

potential dropped to 2.5 volts, then rose to 2.93 volts during the next 30 minutes before falling to approximately 300 mv after 60 minutes. The temperature on the skin of the cell reached a maximum of 59°C, 50 minutes after the puncture. Two hours after the test the cell potential was 30 mv and the temperature had only dropped to 58°C. A plot of the cell potential and temperature is shown in Figure 24.

While still at 58°C, the cell was incinerated over a hexane flame for approximately 30 minutes. After 5 minutes exposure to the flame, the cell began burning internally and continued for about 2 minutes; the length could not be exactly determined as the internal fire was only marginally more intense than the hexane fire. Examination of the cell after the test revealed that all anodes had burned.

3.2.2 Cell number 2B, fresh, was also penetrated by a 6.4 mm spike. The cell responded almost exactly as Number 1B, except that the maximum temperature was 80°C. After 76 minutes and at a temperature of 60°C, the cell was penetrated by three 5.6 diameter bullets which passed completely through the cell. Each bullet produced a flash, at the entry point, but the flame did not propagate through the cell. The cell was incinerated over a hexane flame for about 25 minutes after the bullet penetration. The cell responded to the incineration in the same way as did number 1B.

3.2.3 Cell Number 4B, fresh, was shorted through a 3000 amp, 50 mv shunt at an ambient temperature of 20°C. The results of the short circuit are shown in Figure 25. The maximum current observed was 172 amps. After 6 minutes, and at a current of 155 amps the cell terminal failed. The cell potential fell to 0.97 volts immediately after closing the circuit, and fell further to 0.73 volts just before the terminal failed. The maximum temperature observed was 35°C.

PUNCTURE - CELL NO. 1B

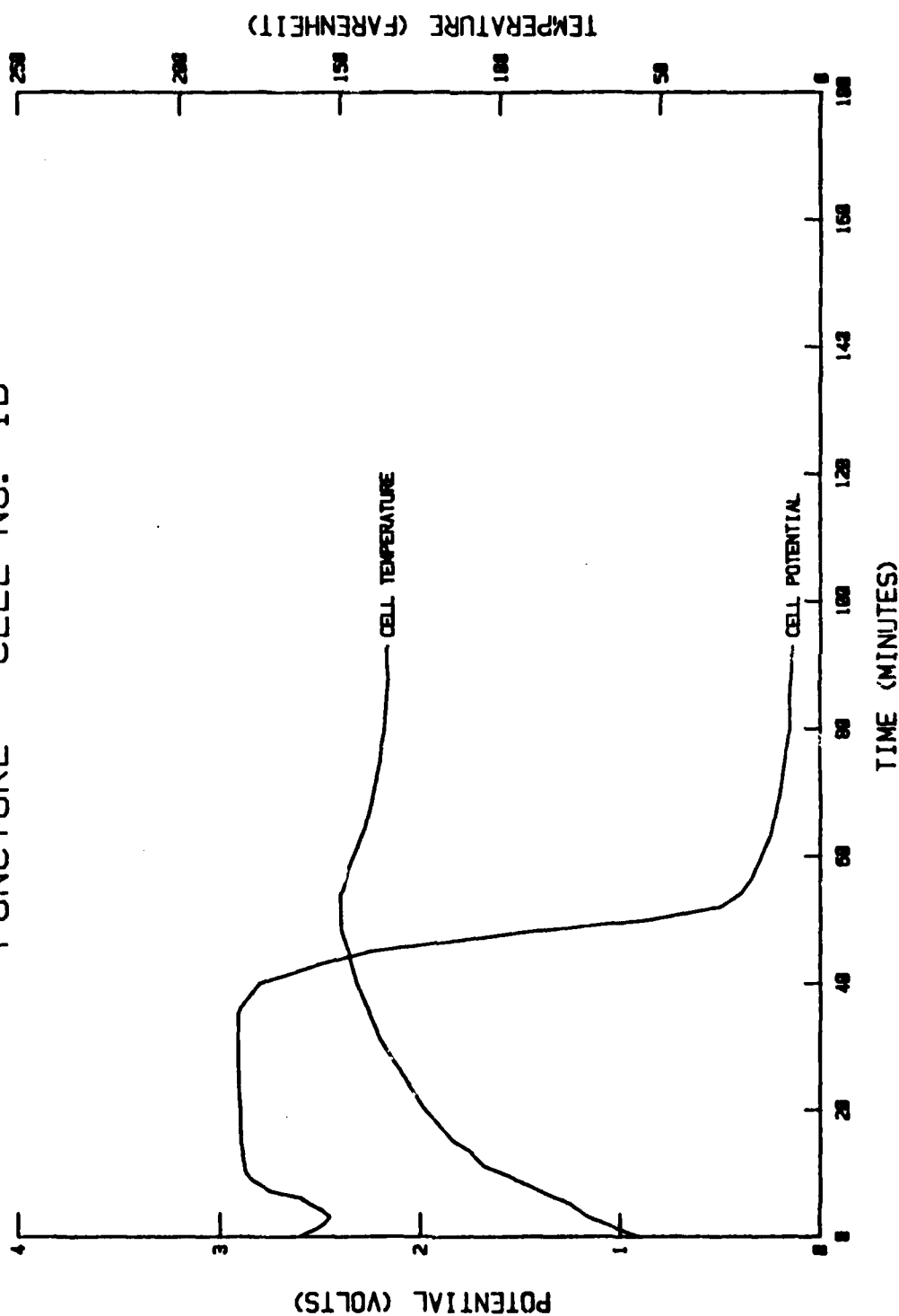


Figure 24. Puncture - Cell No. 1B

SHORT CIRCUIT - CELL NO. 4B

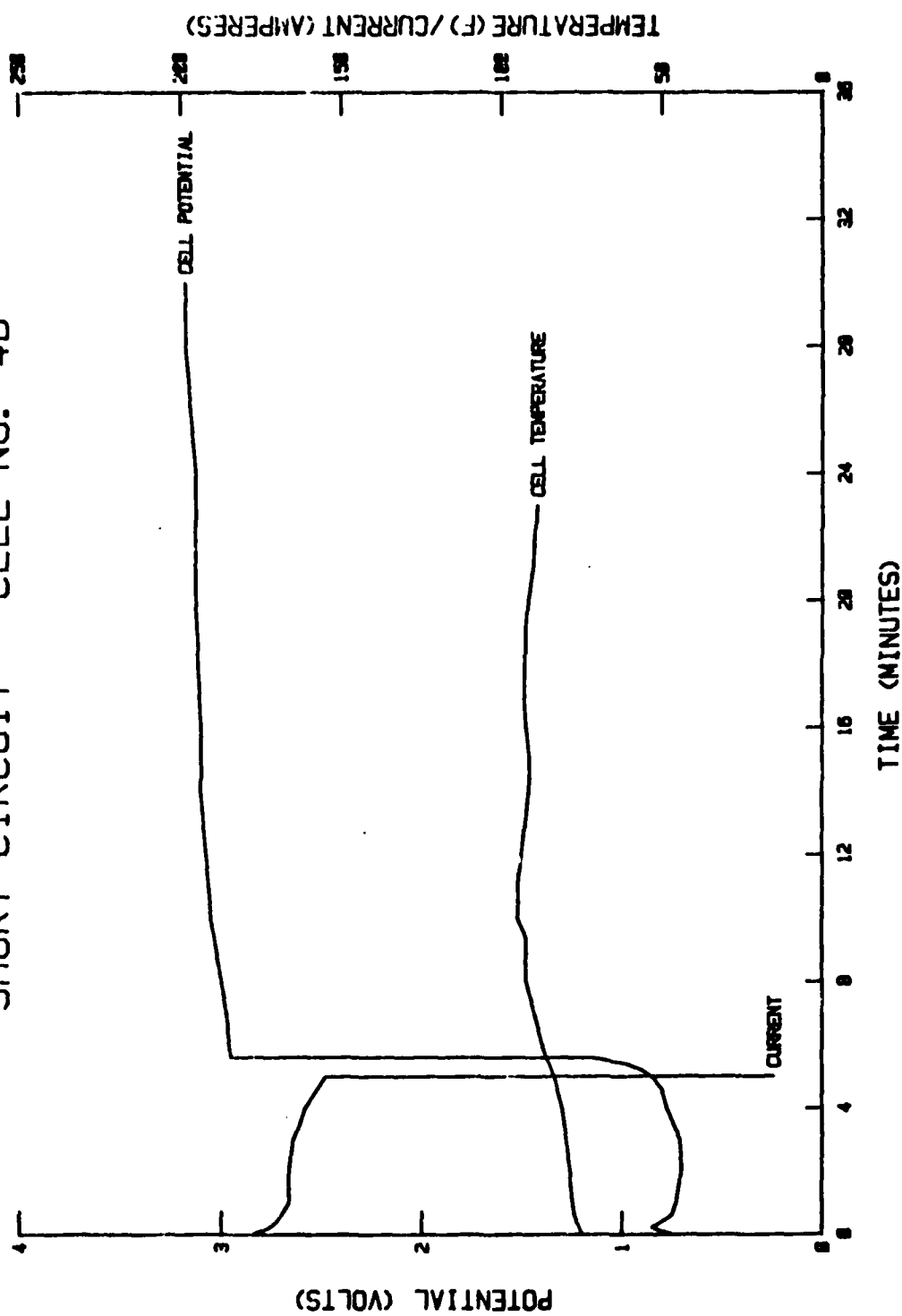


Figure 25. Short Circuit - Cell No. 4B

The cell was later incinerated over a hexane flame for a period of 30 minutes. Four minutes after the start of the test the cell vented. No other response was noted; however, examination after the test revealed that all anodes had burned during the incineration.

4.0 DISCUSSIONS/ CONCLUSIONS

The 600 AH cells were used as a test vehicle to compare the newly developed thick cathodes with the thinner cathodes used earlier in the program. The cells were also the first large cells to be constructed and we therefore emphasized the safety tests to evaluate the practicality of constructing the larger 10,000 amp hour design.

The HSA cells did not produce the same apparent matrix utilization as had been seen in half "D" cells and therefore did not achieve the 600 amp hours expected. Subsequent tests of the same electrodes in smaller rectangular cells indicated that the reduction in utilization occurred in all prismatic cells. Comparison of electrodes recovered from cylindrical and prismatic cells indicated that increased pressure and compaction of the carbon electrode may have been a problem in the prismatic cells; however, looser cell stacks were not evaluated to test the hypothesis.

The LSA cell cathodes, which produced 0.4 AH/cm^3 in small test cells, varied in apparent utilization from 0.3 to 0.4 AH/cm^3 in the 600 amp hour cell. In the discharge of cells 1C-4C, the capacity ranged from 490 to 625 amp hours. The only obvious difference in the cells was the electrolyte source. There were visible differences between the samples from Apache Chemical and Lithium Corporation; however, any differences were the result of process variations, and were not intentional. Comparison of IR spectra of both materials did not reveal any obvious differences.

Comparison of abuse tests in HSA and LSA cells show many similarities, except for the great difference in the intensity of the calcium fire that sometimes occurred. Calcium fires in LSA cells were almost undetectable from normal incineration, whereas the fires in HSA cells were rapid enough to consume all the calcium and were violent enough to move the cells. This difference is assumed to be due primarily to the surface area to volume ratio 5.2 times greater than that of the LSA cell.

In general, no condition of abuse was found which produced a hazardous response from the 600 amp hour cell of the LSA design.

SECTION V.
10,000 AH/STANDBY POWER CELL

1.0 INTRODUCTION

The last cell design to be tested during this program was nominally intended to be of 10,000 amp hour capacity, to meet the application requirements of large standby power sources. Seven cells were constructed to evaluate the abuse response and electrical performance of the cells. The intention of the tests was: to establish whether the larger scale cell would react to abuse as had the 600 AH LSA design or would react as a HSA cell, and whether the 0.4 AH/cm^3 matrix utilization seen in cell number 1C could be reproduced in the scaled up design.

The 10,000 amp hour capacity of the cell was predicated upon an original estimate of a matrix utilization of approximately 0.55 AH/cm^3 , which had been produced in small cells. The 0.4 AH/cm^3 actually observed in 600 AH cells would result in a capacity of 7200 amp hours in the large cell size. In actuality, even this number was reduced due to difficulties encountered in fabricating the large electrodes.

2.0 CELL DESIGN

The 10,000 amp hour cell was in all respects a scaled up 600 amp hour design. The cell case was made of type 304 stainless steel, 28 cm wide, 30.5 cm long and 44.5 cm tall. The container material was 1.6 mm thick. The cell cover was also made of type 304 stainless. The vent used was the same threaded assembly used in the 600 AH design. Three terminals were located in the cell cover, each made of nickel plated copper sealed by a Conax fitting with a teflon sleeve. The terminals of the cell intended for short circuit were 13 mm in diameter, all others were 6 mm

in diameter. A separate fill port was added to the cover which was capped with a threaded 304 stainless steel and teflon valve.

Cathodes for the cell were 27 cm x 36 cm x 6.35 mm, constructed in the same manner as for the 600 amp hour cells. The design was intended to contain 18,000 cm³ of cathode matrix. However, the electrode collector material could not be obtained in the full size required for the cell, and was therefore made by joining several smaller electrodes together using nickel foil. The loss of electrode active matrix caused by the fabrication process reduced the total cathode volume to 16,800 cm³, equivalent to 6700 amp hours at 0.4 AH/cm³. The individual cathodes were joined to the positive terminal by nickel foil, 25 mm wide x 50 mm long x 0.13 mm thick. Anodes were 27 cm x 36 cm x 0.35 mm. The electrodes differed from those used in the 600 amp hour cell in that the calcium foil was used without a current collector.

The electrodes were separated by the same 0.35 mm thick Dexter glass mat previously described. All cells were filled with 25 liters of 1.4 molar LiAlCl₄ in SOCl₂, supplied by Apache Chemical and Lithium Corporation.

A total of eight cells were constructed. Two were used in an undischarged condition for abuse tests. Six were discharged and either disposed of or used in the discharged condition for abuse tests.

2.1 Cell Electrical Performance

Five cells were discharged through a constant resistive load at rates between 50 and 60 amps. Four of the five cells were discharged in open air at an ambient temperature which averaged 38°C during the day and 29°C during the night. The cell temperatures on the skin were normally about 20°C above ambient. The remaining cell was cooled during discharge by immersing in a water bath, which varied in temperature from 27°C to 32°C.

2.1.1 Cell number one was filled with 25 liters of 1.4 molar LiAlCl_4 in SOCl_2 supplied by Lithium Corporation, and was discharged through a resistive load which produced a current of 64 amps at a cell potential of 3.00 volts. The discharge of the cell is shown in Figure 26 and 27. The cell potential reached a maximum of 3.14 volts, then fell to 2.0 volts after 80 hours. Ambient temperature when the discharge began was 36°C . Within 10 hours, the cell temperature, measured on the side of the cell, was 52°C , and reached a maximum of 60°C approximately 40 hours into the discharge.

The approximate capacity withdrawn from the cell was 4400 amp hour.

2.1.2 Cell number two was filled with 25 liters of electrolyte supplied by Apache Chemical and discharged through a resistive load which produced 62 amps at 3 volts. The discharge curve is shown in Figures 28 and 29. After approximately four hours discharge, a 3mm diameter steel cable, which was fastened to the cell as an aid for disposal, fell onto the cell cover shorting the terminals. The cell was shorted for some unknown period of time before the cable was melted and the short removed. The internal pressure caused by the short circuit caused the cell cover to bulge tilting the terminals in such a way that they touched the two brackets which were attached to the cell case to hold the support cable. The cell then shorted intermittently throughout the remainder of the discharge. The cell temperature varied between 41°C - 63°C on a diurnal cycle. Ambient temperatures varied between 21°C and 41°C .

The approximate capacity withdrawn from the cell was 5000 amp hour.

2.1.3 Cell number three was filled with 25 liters of electrolyte supplied by Lithium Corporation and discharged through a .054 resistive load. The

DISCHARGE/REVERSAL - CELL NO. 1

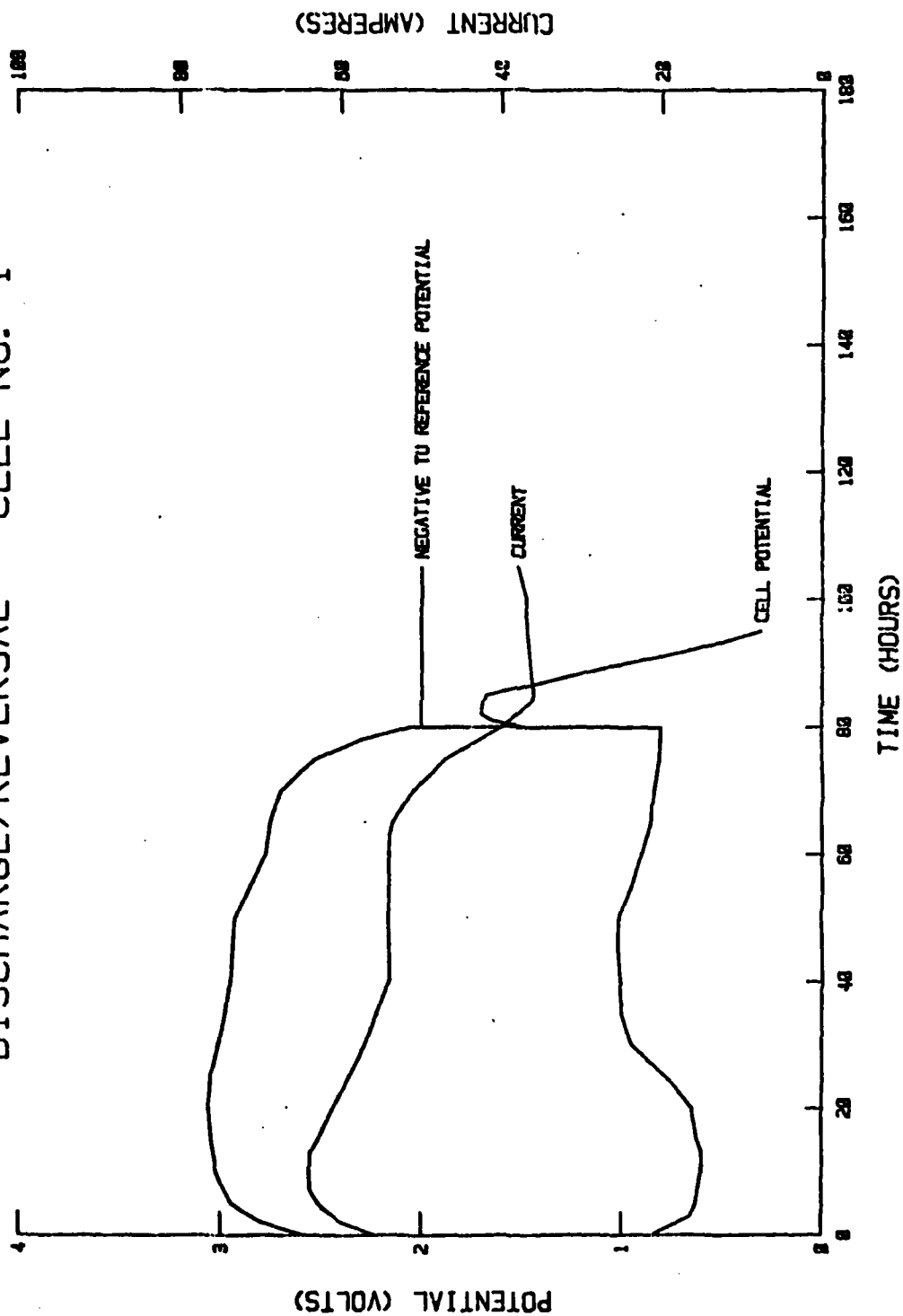


Figure 26. Discharge/Reversal - Cell No. 1

DISCHARGE/REVERSAL - CELL NO. 1

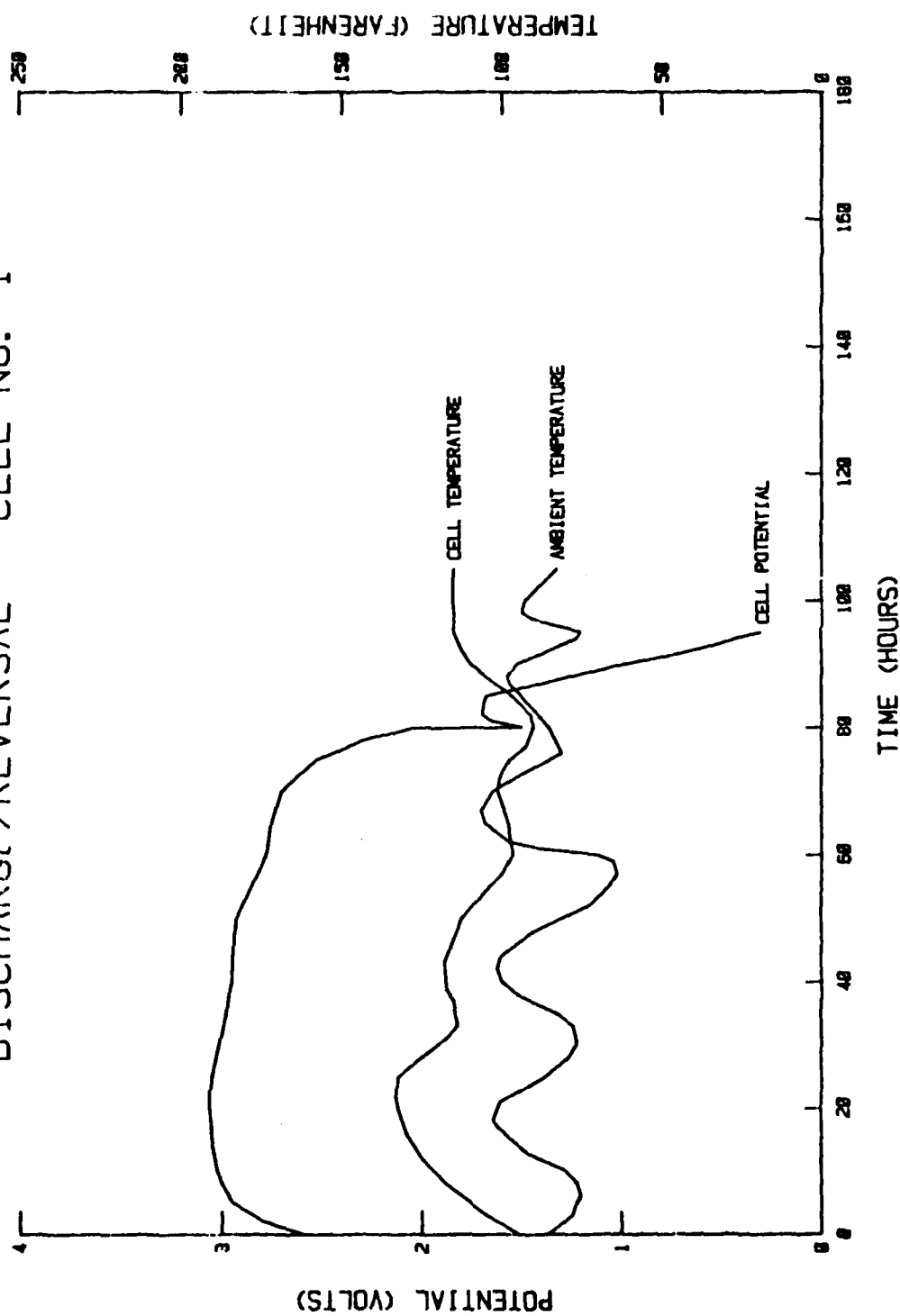


Figure 27. Discharge/Reversal - Cell No. 1

DISCHARGE CURVE - CELL NO. 2

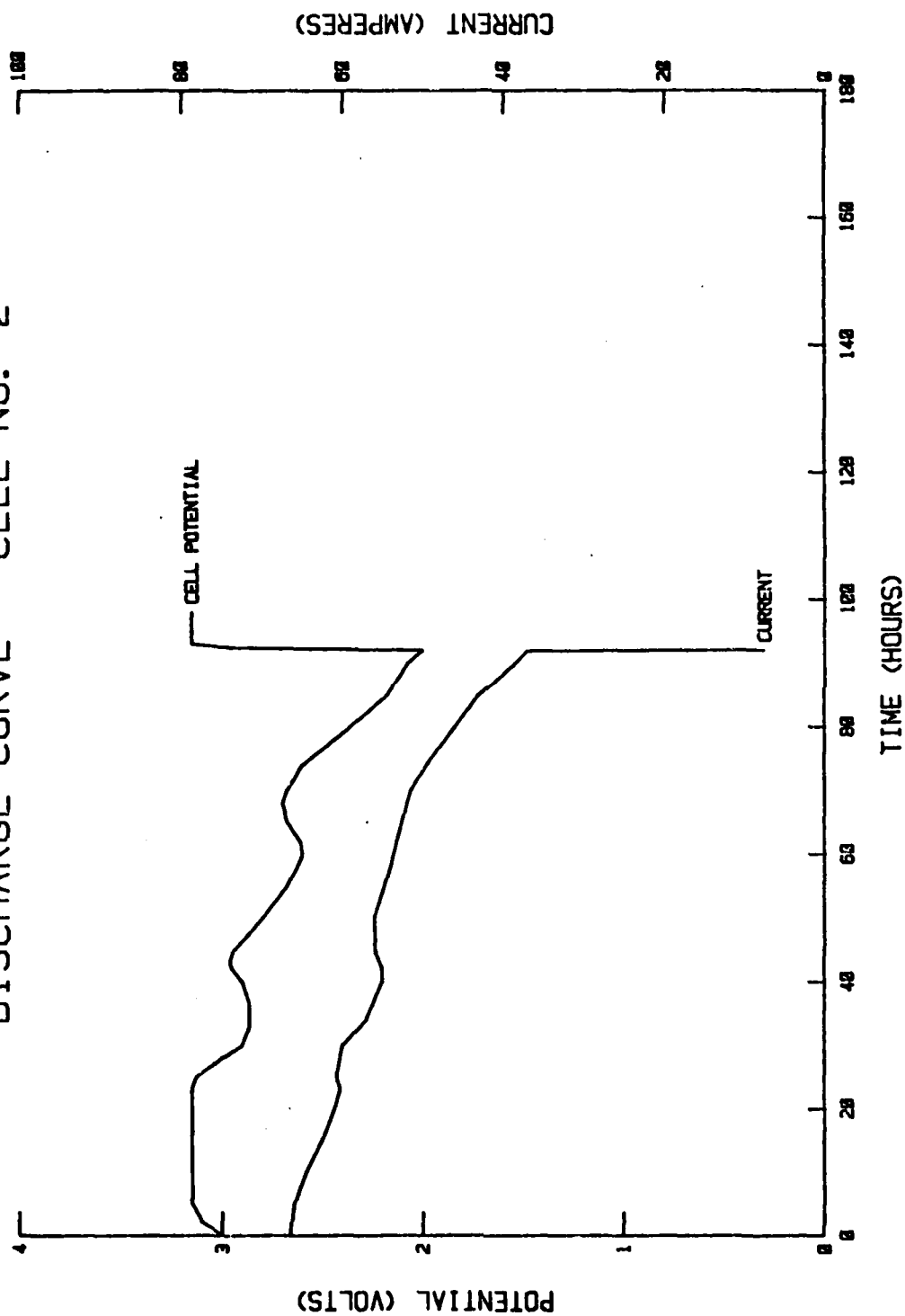


Figure 28. Discharge Curve - Cell No. 2

DISCHARGE CURVE - CELL NO. 2

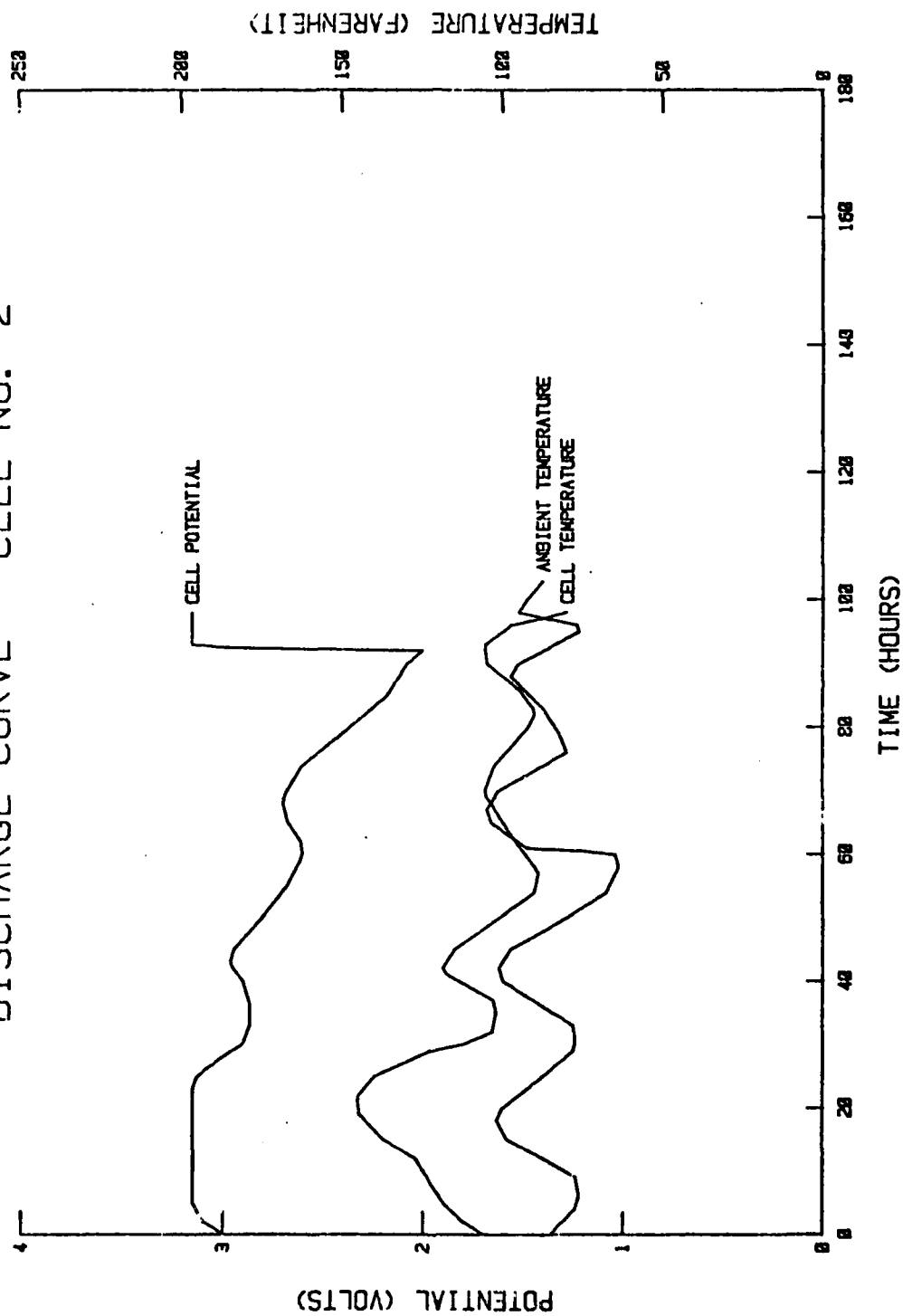


Figure 29. Discharge Curve - Cell No. 2

The discharge is shown in Figure 30 and 31. The cell potential was about 500 mv below normal at the start of the discharge. As the discharge progressed, the cell potential rose to near normal, but only because the cell temperature was much higher than normal. After 23 hours discharge, an explosion occurred, which appeared to be confined to the free headspace above the cell stack. The cell cover was peeled away on three sides, but remained attached on the fourth side, and the electrode stack was expelled intact. The electrodes were scattered around the cell within a radius of approximately ten feet. The cell case was intact and bulged very little. Parts of the glass activation apparatus which were adjacent to the cell were undamaged as were several other pieces of miscellaneous equipment located within one mile of meter of the cell.

2.1.4 Cell number six was filled with 25 liters of electrolyte from Lithium Corporation and discharged through a resistance of 0.034 ohms. This cell was activated and discharge started at the same time as was cell number three. After 20 hours discharge, the cell cover blew off and the electrodes were scattered around the steel intact cell cover. As in the previous occurrence, the electrode stack appeared to have been removed intact. The anodes were not burned, separator and cathodes were intact and not deformed. Essentially all of the electrodes and separator could be accounted for and most were completely undamaged.

2.1.5 Cell number seven was filled with 25 liters of electrolyte from Lithium Corporation and discharged through a 0.034 ohms resistive load. The cell was cooled during discharge by immersing in a water bath which was maintained at about 30°C. Ambient air temperature varied between 21°C and 43°C. Discharge of the cell is shown in Figure 32. Cell discharge lasted 80 hours and the approximate capacity withdrawn from the cell was 6500 amp hours.

DISCHARGE CURVE - CELL NO. 3

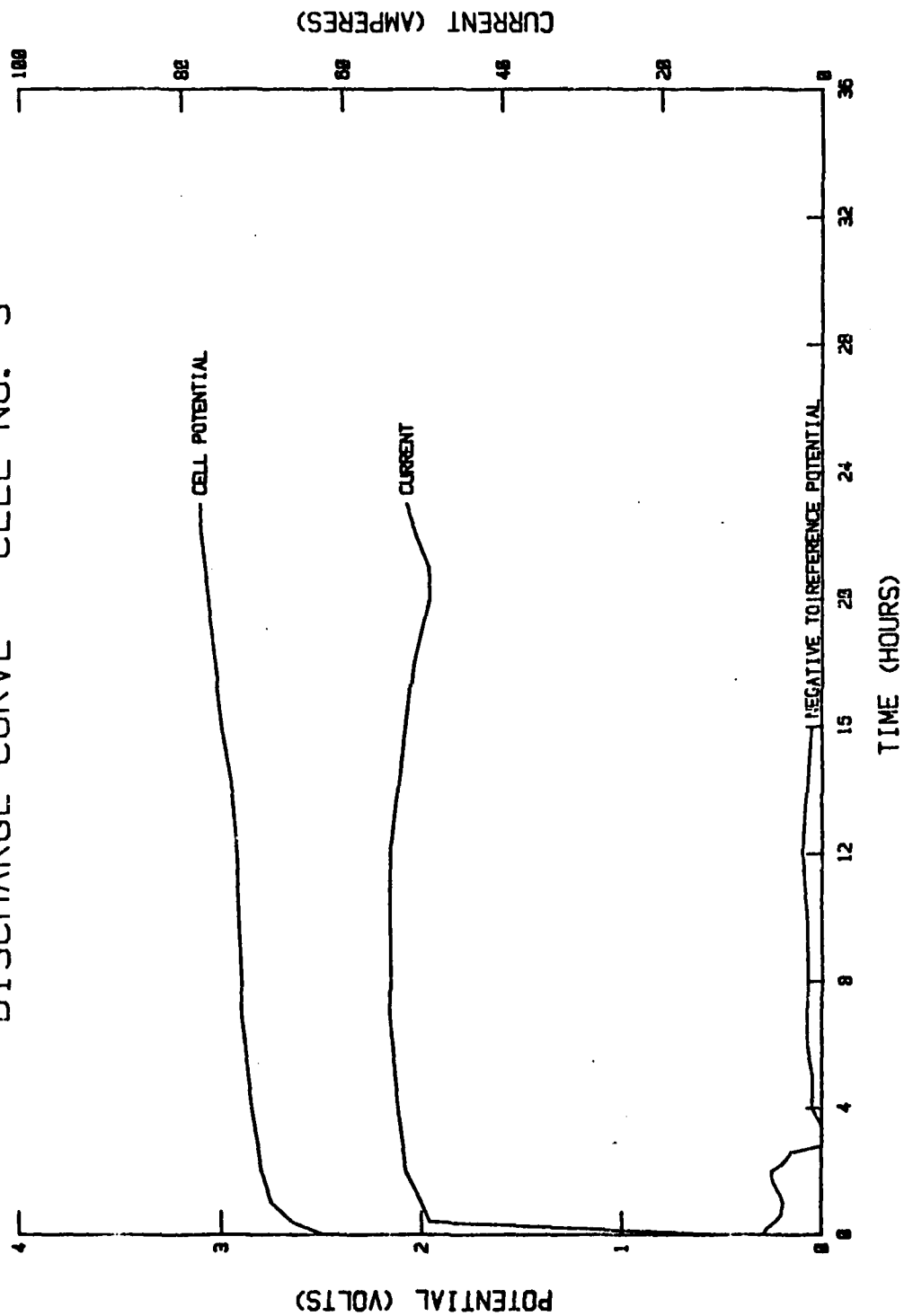


Figure 30. Discharge Curve - Cell No. 3

DISCHARGE CURVE - CELL NO. 3

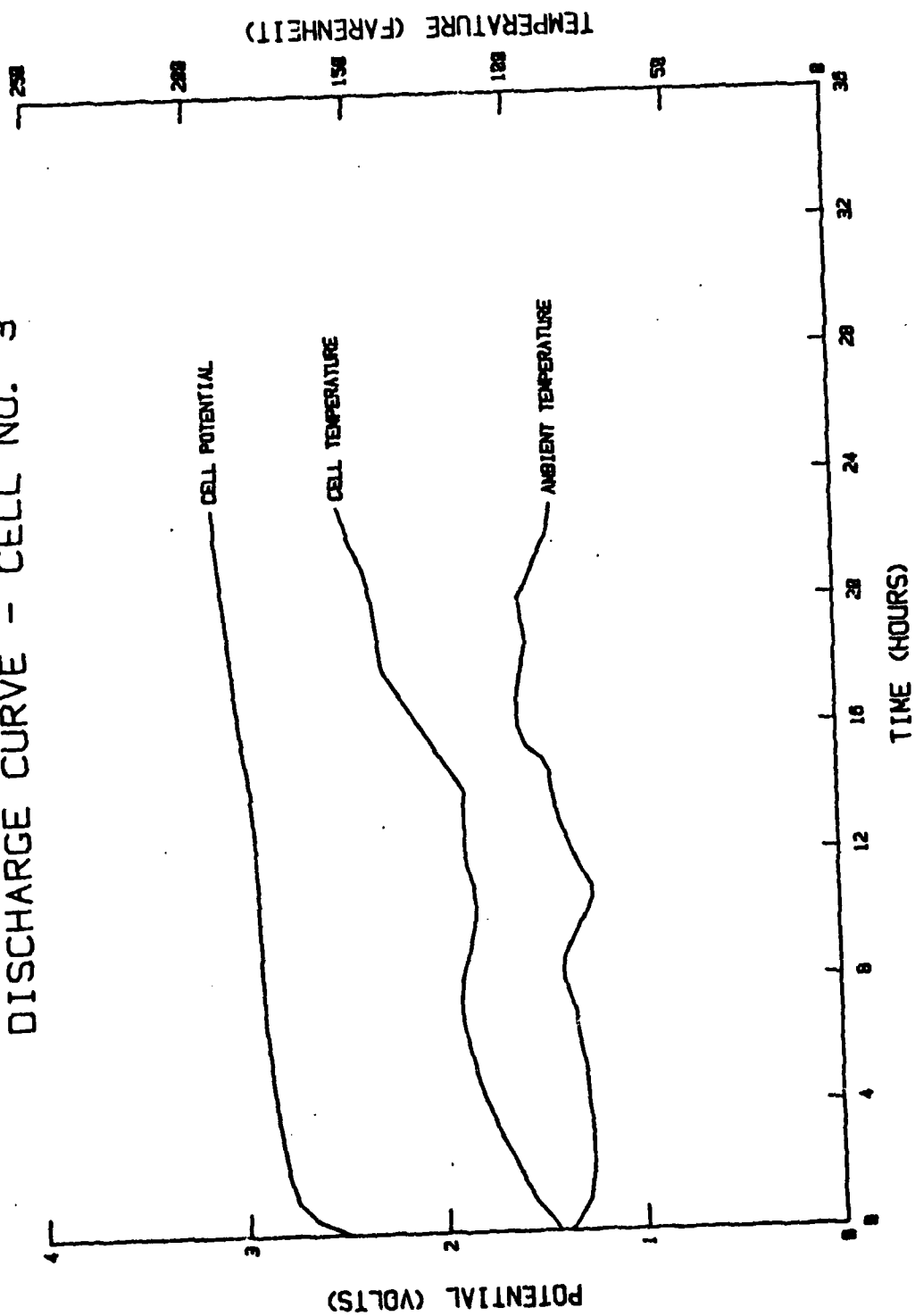


Figure 31. Discharge Curve - Cell No. 3

DISCHARGE CURVE - CELL NO. 7

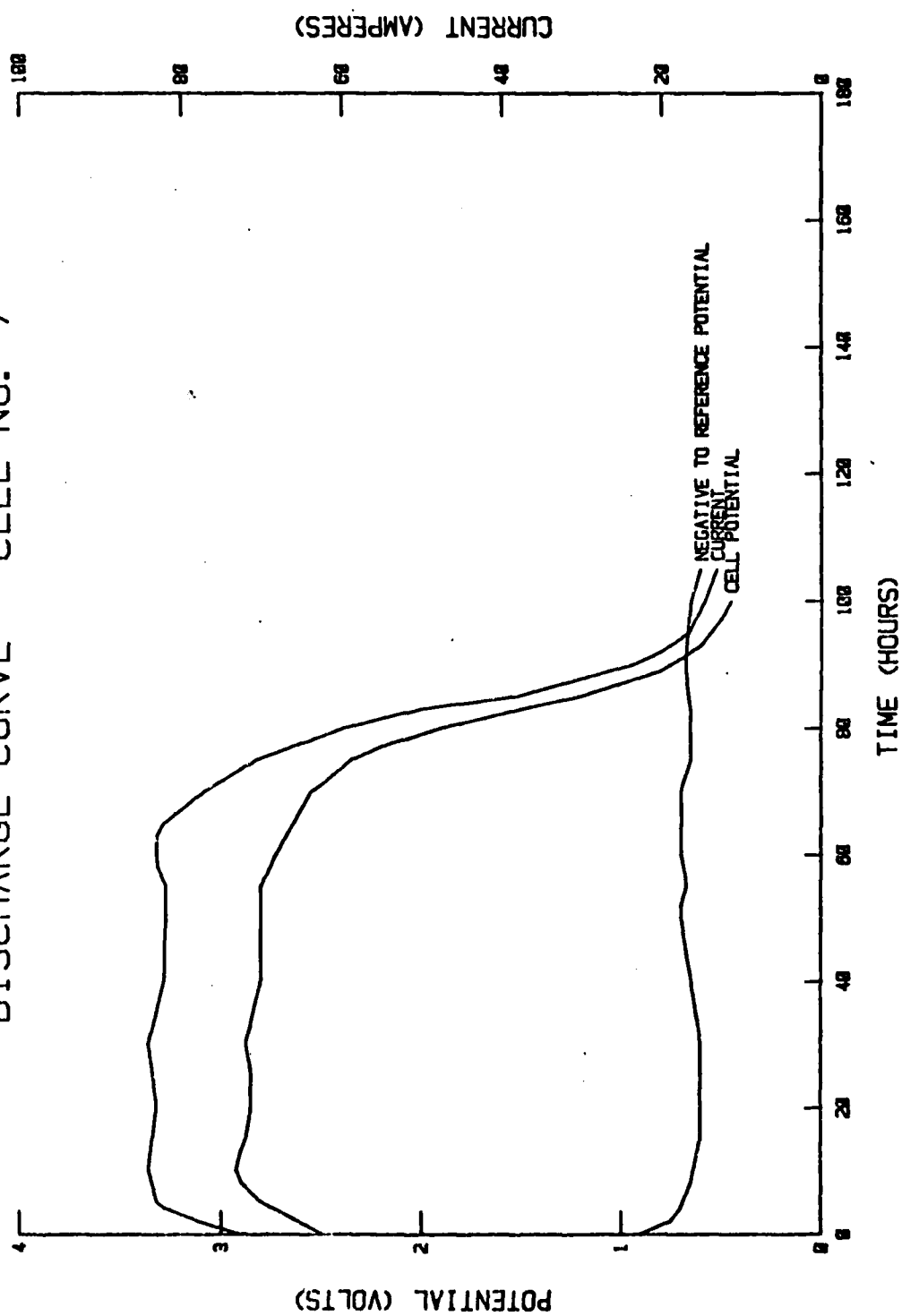


Figure 32. Discharge Curve - Cell No. 7

2.2 Abuse Performance

Three cells were used for evaluation of abuse response. One cell, number one was reversed after discharge. Two cells, number four and five, were used fresh, for short circuit and spike penetration tests. As in other cell tests involving large cells, the test samples were transported dry to the test facility where they were activated. All cells were filled with 25 liters of 1.4 molar LiAlCl_4 in SOCl_2 supplied by Lithium Corporation.

- 2.2.1 Cell number one was discharged to an end potential of 2.00 volts (Paragraph 2.1.1), then power discharged at a constant 50 amps until the cell reversed. After 20 hours of reversal, the cell vented through the diaphragm vent at 150 psi. The cell temperature at the time of venting was 60°C.

No flame was associated with the venting, and the cell was disposed of by immersing in Na_2CO_3 . A plot of the reversal is shown in Figure 33.

- 2.2.2 Cell number four, fresh, was shorted through a 3000 amp 150 mv shunt at an ambient temperature of 24°C, Figures 34 and 35. The cell was connected to the shunt through approximately 6 meters of 4/0 copper cable and a relay. The short was not as low a resistance as had been intended, evidenced by the cell potential of nearly 2.0 volts. The maximum current observed, which corresponded to the maximum potential, was 700 amps, occurring after 55 minutes. The cell temperature at that time was 82°C. After 67 minutes, at a cell temperature of 66°C, the short was removed with no visible effect on the cell.

REVERSAL - CELL NO. 1

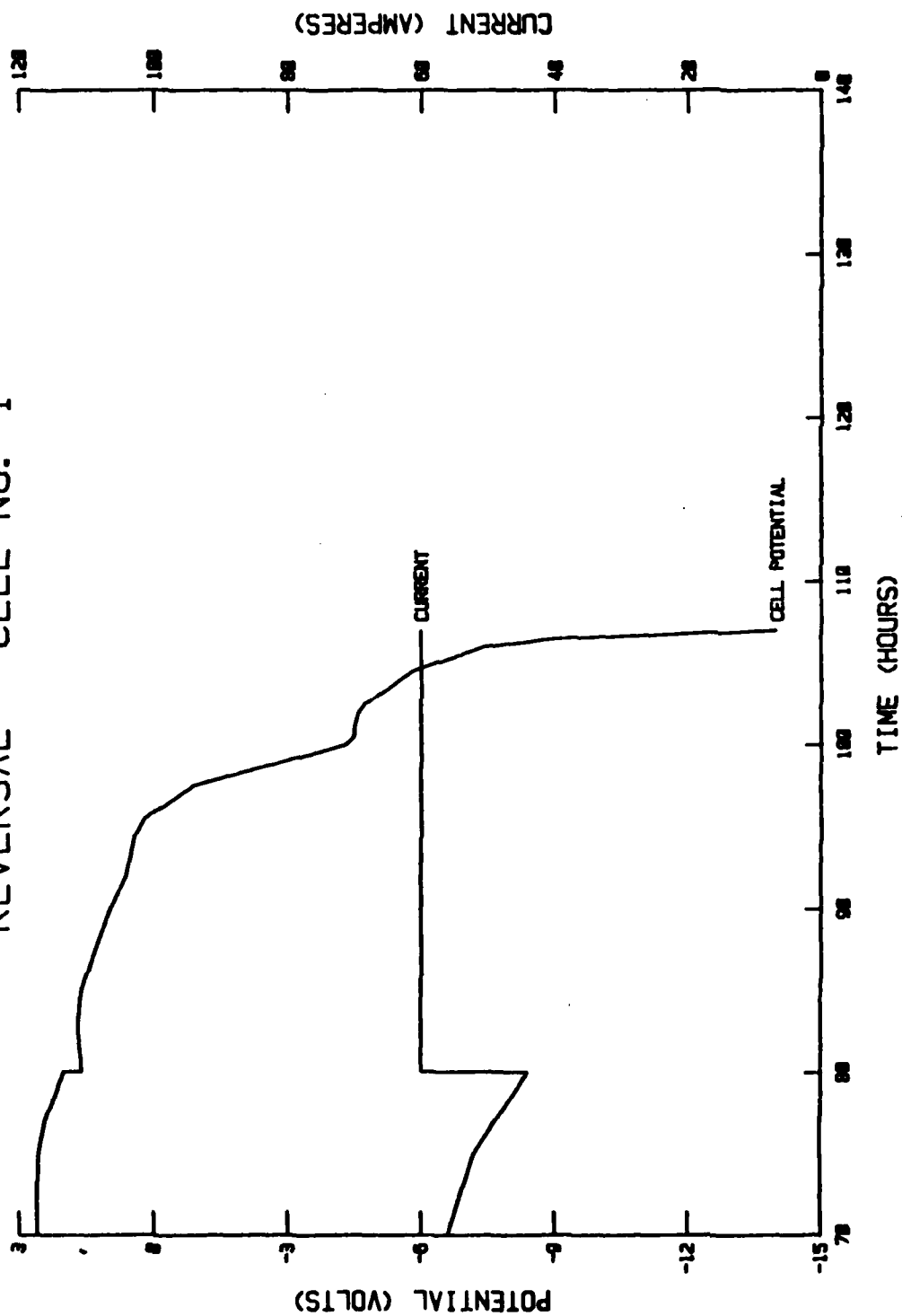


Figure 33. Reversal - Cell No. 1

SHORT CIRCUIT - CELL NO. 4

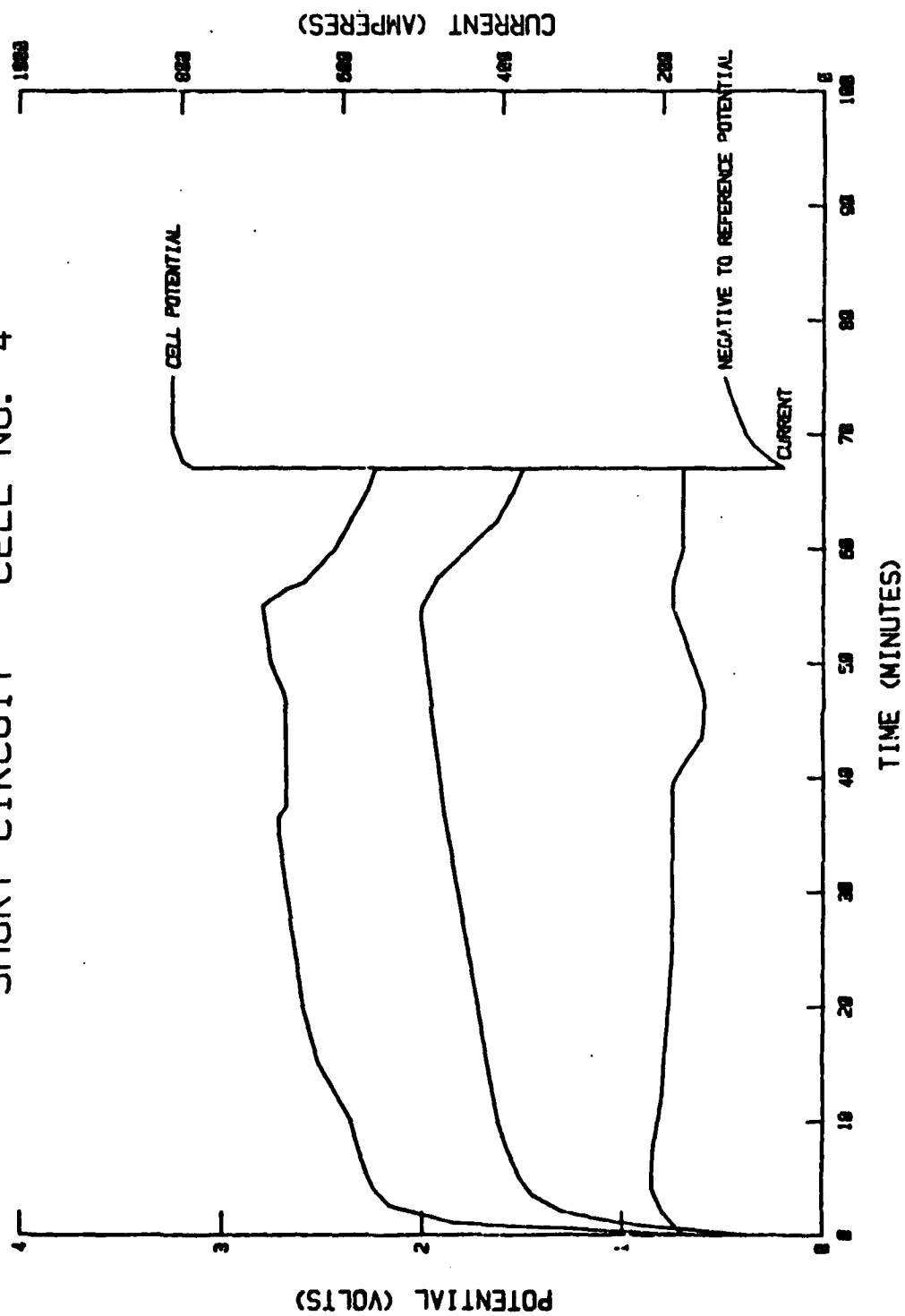


Figure 34. Short Circuit - Cell No. 4

SHORT CIRCUIT - CELL NO. 4

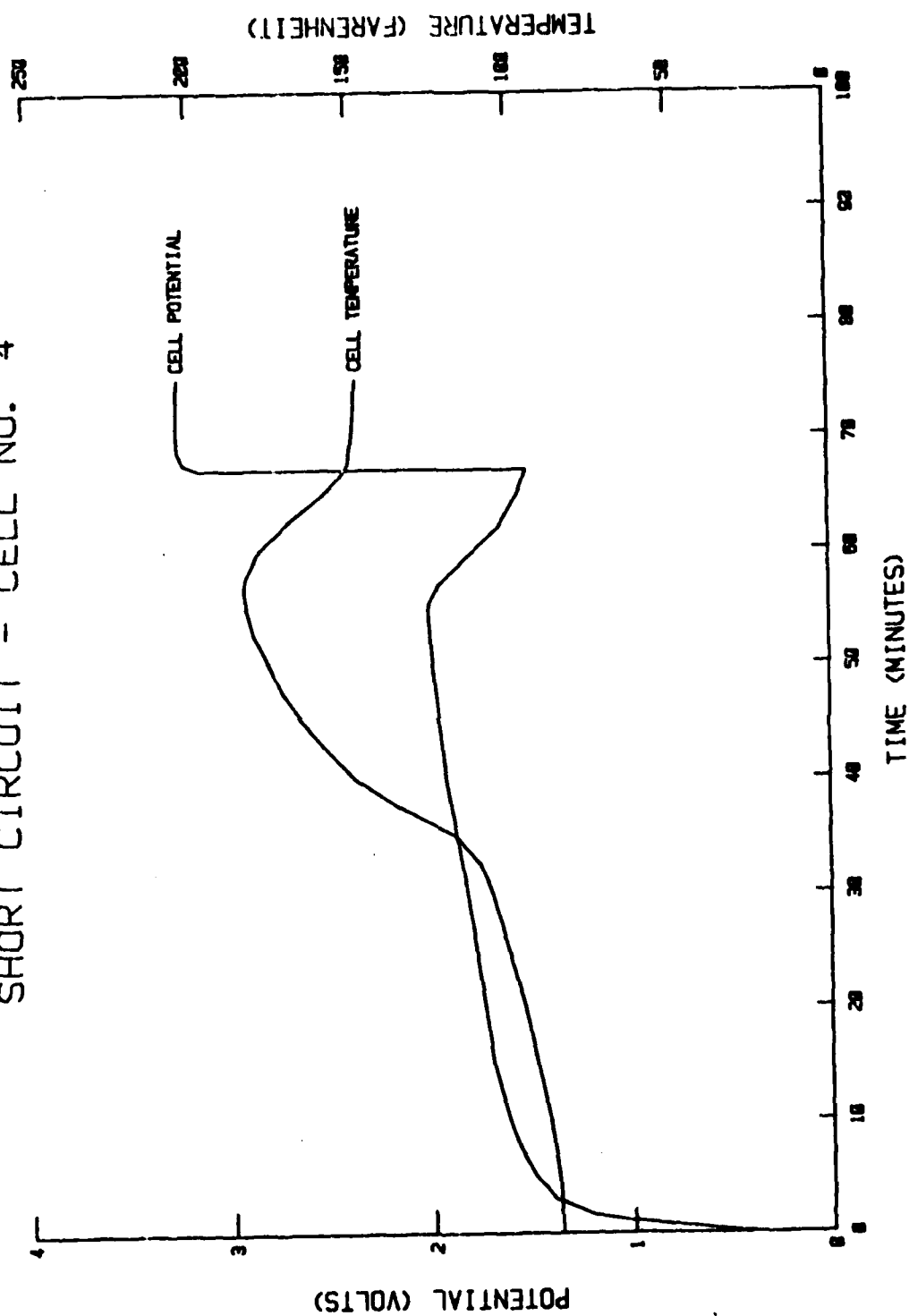


Figure 35. Short Circuit - Cell No. 4

While still at a temperature of 63°C, the cell was penetrated by a 6 mm spike, driven approximately 15 cm into the electrode stack perpendicular to the electrodes. The spike was driven into the cell by a hydraulic ram over a period of about 3 seconds. Upon penetration, the cell potential dropped from 3.2 volts, to 1.75 volts, then rose immediately to over 3 volts, Figure 36. The cell potential gradually dropped to 0.3 volts over a period of 20 hours, after which time the cell was not monitored. The cell temperature during this period dropped continuously from the starting point of 63°C.

2.2.3 Cell number five, was penetrated in the same manner as cell number four, except that the cell was completely fresh prior to the test. The cell response to penetration was almost identical to that of cell number four. Cell potential dropped to 2.20 volt on penetration, then rose to 2.9 volts after 10 minutes. The initial cell temperature was 35°C and rose to a maximum of 82°C. The cell potential, after 85 minutes was 1.01 volts at a temperature of 66°C. While still indicating a temperature of 66°C on the skin, the cell was shot with a 7.8 mm bullet. At the fifth shot the cell started to burn and continued for approximately four minutes.

All cells not destroyed during test were disposed of by shooting them with a 7.8 mm bullet. Certain of the cells, such as number five, required as few as five shots. Normally discharged cells at room temperature required up to twenty shots before fire could be sustained.

PUNCTURE - CELL NO. 4

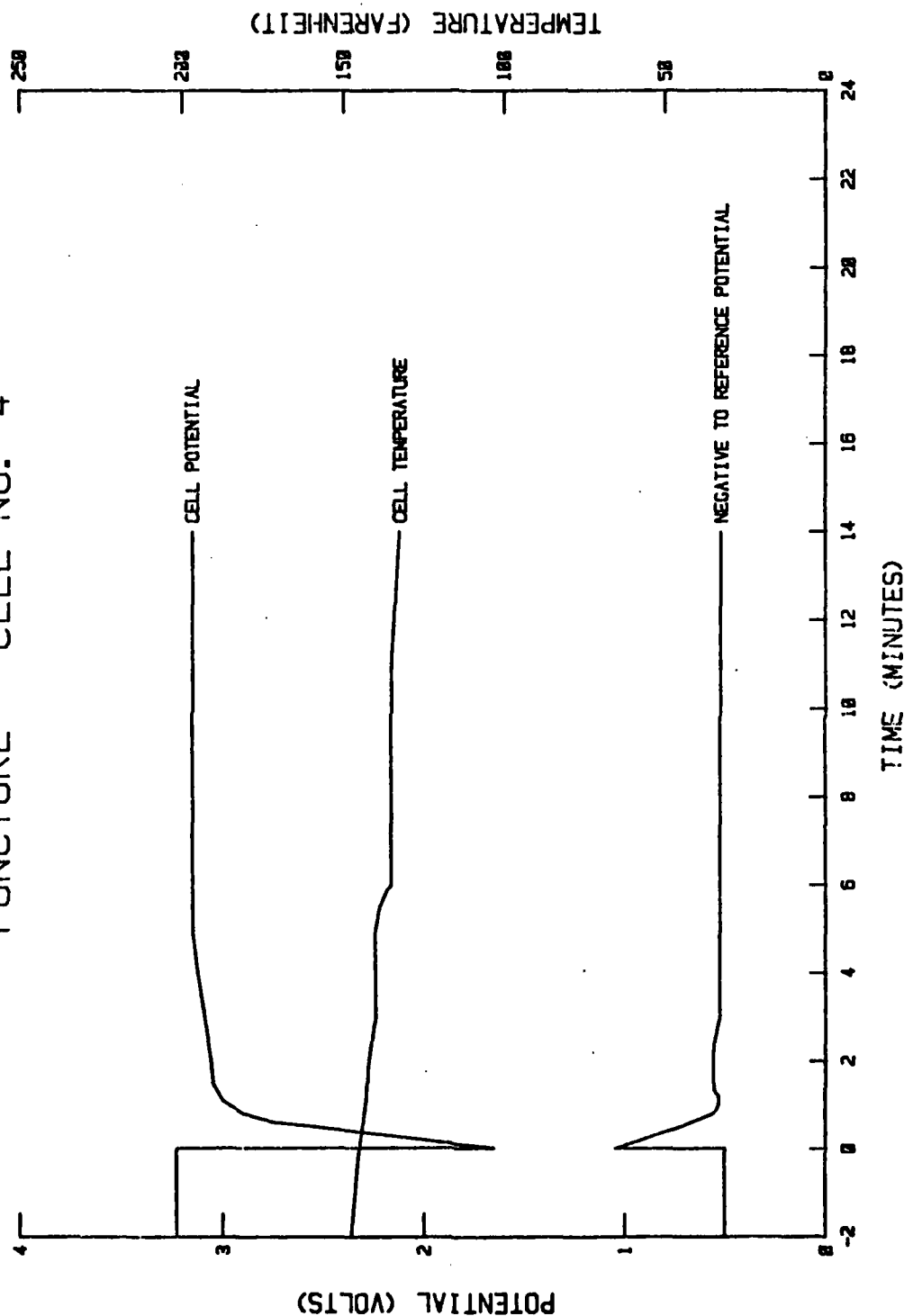


Figure 36. Puncture - Cell No. 4

3.0 DISCUSSION/CONCLUSIONS

Cell numbers 1 and 2 discharged first, were intended to be a comparison between two electrolyte solutions already evaluated in 600 AH cells. Both cells experienced a greater temperature increase than expected, a problem compounded by the high outside ambient temperature. The capacity loss noted earlier in 3.5 AH cells was again apparent. Cell number 1 produced 0.26 AH/cm³ of cathode matrix. Cell number 2 produced 0.30 AH/cm³, despite the temporary short circuit which undoubtedly decreased overall capacity.

Cell number 7, which was cooled during discharge to an approximate temperature of 30°C, produced the greatest cathode matrix utilization, 0.39 AH/cm³.

Cell numbers 3 and 6 both exploded during the first few hours of discharge, after producing 1277 and 1765 amp hours respectively. The cells were activated at the same time, and exploded within three hours of each other. The discharge characteristics of both were unique in that cell potentials were 300-500 mv lower than normal and cell temperatures were about 20°C higher than normal.

The only apparent difference between these cells and the successful discharges was the length of time between activation of the cell and the beginning of discharge. Cells 3 and 6 were both placed on discharge within one hour of activation, whereas the remaining cells were allowed to stand between 3 hours and 24 hours before starting discharge. Both the discharged results and the examination of cell parts after they were thrown from the cell indicate that the cell electrodes were never completely wetted by the electrolyte solution.

The results of abuse tests were similar to those of the LSA 600 AH design in that the cells did not respond in any way to short circuit or puncture. Cells did, however, burn after bullet penetration. Cells normally required up to twenty shots to cause sustained burning. The cell which required only five shots, number five, had just been punctured with a spike and had a skin temperature of 66°C.

SECTION VI.
SUMMARY AND CONCLUSIONS

In summary, during the course of this program, a new couple, Ca/SOCl_2 , has been developed from bag cell stage to the point of demonstration prototypes of 6,500 AH capacity. During this development, several intermediate sized cells were developed which exhibit characteristics unique to high energy density cells.

Half sized D cells were developed which produce approximately the same energy density as Li/SO_2 cells. We were not able to cause a hazardous response from these cells by any means of abuse, including those methods normally used to evaluate Li cell hazards.

A medium sized cell was developed which has a capacity of approximately 600 AH. These cells produced nearly 150 WH/pound without optimization or serious attempts at achieving true electrode balance. The LSA version of the cell could not be made to respond to puncture, short circuit, bullet penetration, or incineration, and appeared completely safe under all conditions of abuse tests.

A large cell, 6500 AH, was developed which demonstrated nearly the same safety under abuse conditions as the small 600 AH cell. The cells did not respond to short circuit, reversal or punctures. The cells did not respond to single bullet penetration, but could be made to burn after multiple shots. The cells were the least efficient of any of these designs with regard to utilization of volume and weight; however, the problem was primarily due to our inability to obtain certain electrode materials in the proper sizes for the prototype cells. Projections of capacity, based on the matrix utilization seen in both 600 and 6500 AH cells, indicate that energy densities in excess of 200 WH/pound should be easily obtainable.

There are two primary areas of development which require additional work. A basic investigation is necessary to evaluate the problem of Ca corrosion, and its dependence on electrolyte salts and material purity. The present work has indicated that Ca can be stable in electrolyte solution, but under undefined conditions.

The second recommendation is for a development effort to balance the electrodes, in a configuration which is compatible with available material sizes. Such a program in conjunction with optimization of electrolyte composition and quantities should demonstrate energy densities nearly equivalent to those of Li/SOCl₂, but with much improved safety.

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