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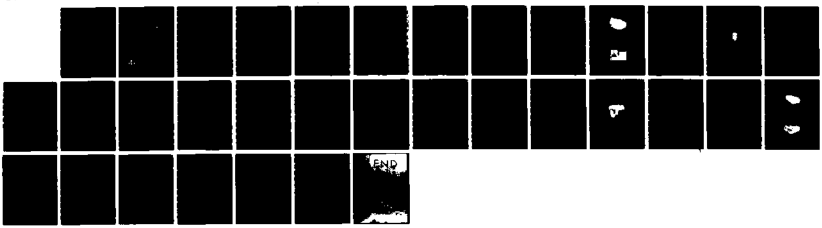

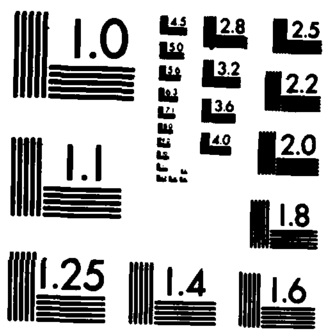
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NSWC TR 83-508

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SAFETY EVALUATION OF AN ELECTRONIC TOTALIZER CONTAINING A Li/(CF)x CELL

BY P.B. DAVIS, R.F. BIS, J.A. BARNES,
S. E. BUCHHOLZ, F. C. DEBOLD, L. A. KOWALCHIK

RESEARCH AND TECHNOLOGY DEPARTMENT

1 NOVEMBER 1983

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A safety review and test program has been conducted on the Electronic Totalizer Model 799806-212 manufactured by Veeder-Root containing the Panasonic Lithium Polycarbonmonofluoride battery (one cell) BR-2/3A. The cell is used for the LCD display of the totalizer.

Tests were conducted on the cell both inside the totalizer and alone. Tests included short circuit, forced discharge into voltage reversal, charging,

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) heat tape, and gas sample collection of combustion products. The tests were run on both fresh cells and partially discharged cells. The forced discharge and charging tests were conducted at both the 250mA and 1 amp level.

No fire or flame was noted during the tests with the exception of the heat tape runs. During heat tape tests fire was noted at 450°C.

FOREWORD

Lithium Poly-Carbonmonofluoride (Li/(CF)x) batteries are used to provide power for the Veeder-Root Electronic Totalizer. This report presents results of a test program to determine if the system is safe for land-base use and to characterize the overall safety of the Li/(CF)x cell. The work presented in this report was sponsored by NAVELEX HQ Code PDE 110-142.

Approved by:

J. R. Dixon

JACK R. DIXON, Head
Materials Division

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CHAPTER 1

INTRODUCTION

A technical evaluation and safety review has been conducted on the Mini LX Totalizer containing a Panasonic BR-2/3A single cell. The purpose of this report is to describe the results of this test program requested by the Naval Electronics Systems Command (as required by Reference 1). The results of some additional tests designed to further characterize the safety of the BR-2/3A cell are also presented. All tests were conducted by the Naval Surface Weapons Center. The tests were conducted to determine if the unit (Electronic Totalizer) was safe to handle, ship, and deploy as configured and to gain general insight into the overall safety of the BR-2/3A single cell.

The Mini LX Electronic Totalizer is made by Veeder-Root of Hartford, Connecticut and is shown in Figure 1. It is to be used in land-based communications to count an impulse generated downline. It is a commercially-available product with a projected LCD life of five years and a projected battery life of ten years. An overhead view of the Totalizer's internal layout is presented in Figure 2. The Panasonic BR-2/3A $Li/(CF)x$ cell is manufactured by Matsushita Electric of Japan. The Panasonic cell is a Lithium anode, poly-carbonmonofluoride cathode cell with a "jelly roll" cylindrical construction, and is depicted in Figure 3. A photograph of the cell is shown in Figure 4. It has an Open Circuit Voltage of approximately 3.2V,[2] a capacity of 1.2Ah and is designed to be used at a $<$ 5mA level.[2] It has a non-aqueous, non-toxic organic electrolyte.[2]

Abuse conditions were generated by:

1) short circuiting of the cell;

2) forced discharge of the cell into voltage reversal with an external D.C. constant current power supply. The tests were conducted at two different discharge rates;

3) heating of the cell to 500°C at rates ranging from 20°C/MIN to 50°C/MIN;

4) charging of fresh and partially-discharged cells with an external D.C. constant current power supply. The tests were conducted at two different charge rates;

5) analysis of gas samples taken from the products of cell incinerations. Incineration was conducted in oxygen, air, and helium atmospheres.

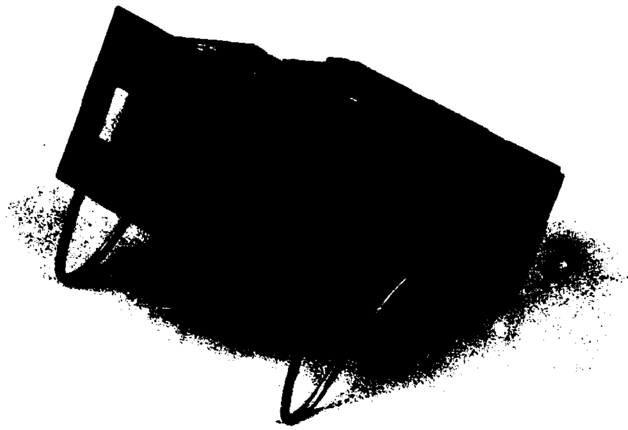

FIGURE 1. PHOTOGRAPH OF ELECTRONIC TOTALIZER

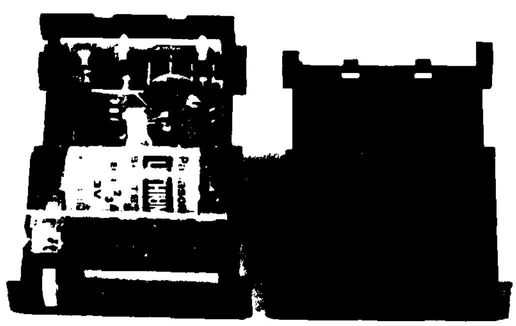

FIGURE 2. PHOTOGRAPH OF INTERNAL LAYOUT OF ELECTRONIC TOTALIZER

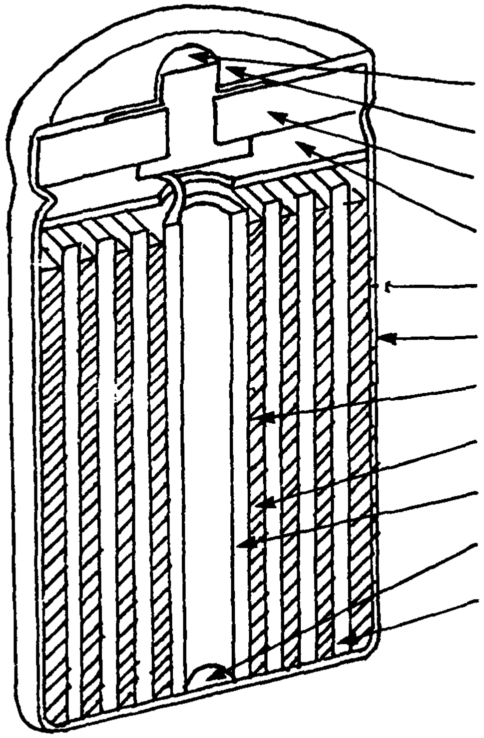

FIGURE 3. CROSS SECTIONAL VIEW OF BR-2/3A BATTERY

FIGURE 4. PHOTOGRAPH OF PANASONIC BR-2/3A CELL

CHAPTER 2

EXPERIMENTAL

The experimental program was conducted as follows:

1) The cell was short-circuited inside the Totalizer with voltage, current, and temperature monitored throughout the run. The test was repeated on the cell alone (total of two tests).

2) Forced discharges of the cell were conducted with a constant current D.C. power supply and were run at both the 250mA and 1 AMP current level (two tests at each rate). At each current rate, one test was run in the Totalizer and one on the cell alone. Current, voltage, and temperature were monitored during all runs. Figure 5 illustrates the circuit used for the tests.

3) Nine heating tests were conducted to 500°C with the heating rates varied from 20°C/MIN to 50°C/MIN. Six tests were run with fresh cells, three inside the Totalizer, and three on cells only. One of the cells was heated to only 300°C. Two tests were run with "dead" cells, one of which was a cell that had undergone forced discharged in a previous test and was only heated to about 300°C. The other was a cell that had been short circuited and was heated in the totalizer to 500°C. The final heating test was conducted only on the Totalizer with no cell.

All heating tests were conducted with Thermolyne heat tape and required the cutting away of about 1/8" circuit board within the Totalizer to accomodate enough room for the heat tape. Battery voltage, temperature, and Totalizer temperature were monitored during runs.

4) Six charging tests were conducted using a constant current D.C. power supply. Four tests were conducted on fresh BR-2/3A cells, with two of the four tests conducted at a 1 AMP charging rate, and the other two runs charged at a 250mA rate. The final two charging tests were conducted on partially discharged cells, with one charged at 250mA and the other at 1 AMP. The partially discharged cells were obtained by discharging at constant current until at least 50% of the capacity was removed. They were discharged and charged at the same current.

None of the charging tests were conducted with the cell in the Totalizer as charging could not take place in the Totalizer. Fresh cells were charged to at least 100% of the cell capacity. Partially discharged cells were charged to full capacity, and then continued to at least an additional 100% of cell capacity. Figure 6 depicts the circuit used for the charging tests.

5) Gas samples were taken and analyzed of all gas products generated by

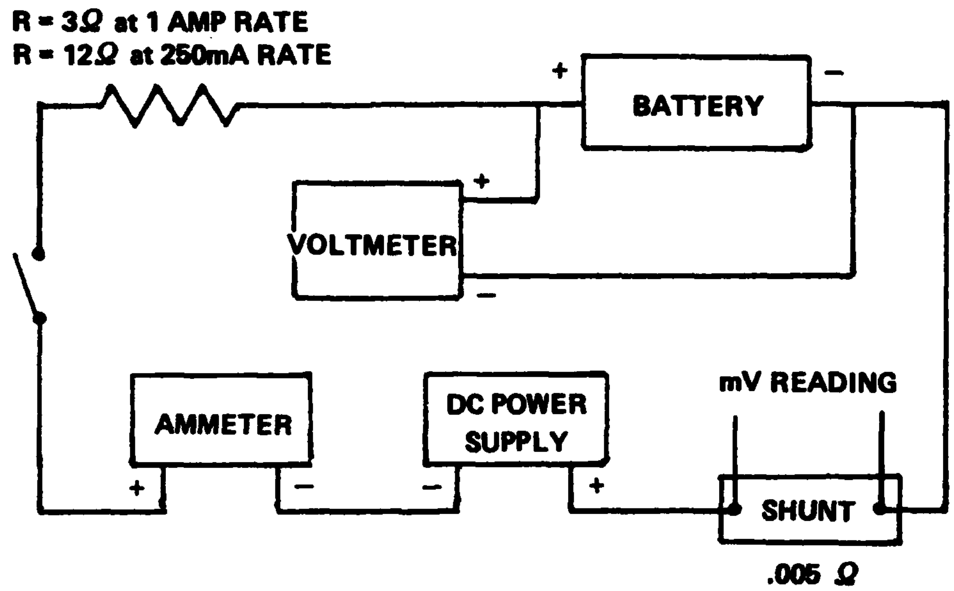

FIGURE 5. SCHEMATIC OF FORCED DISCHARGE CIRCUIT

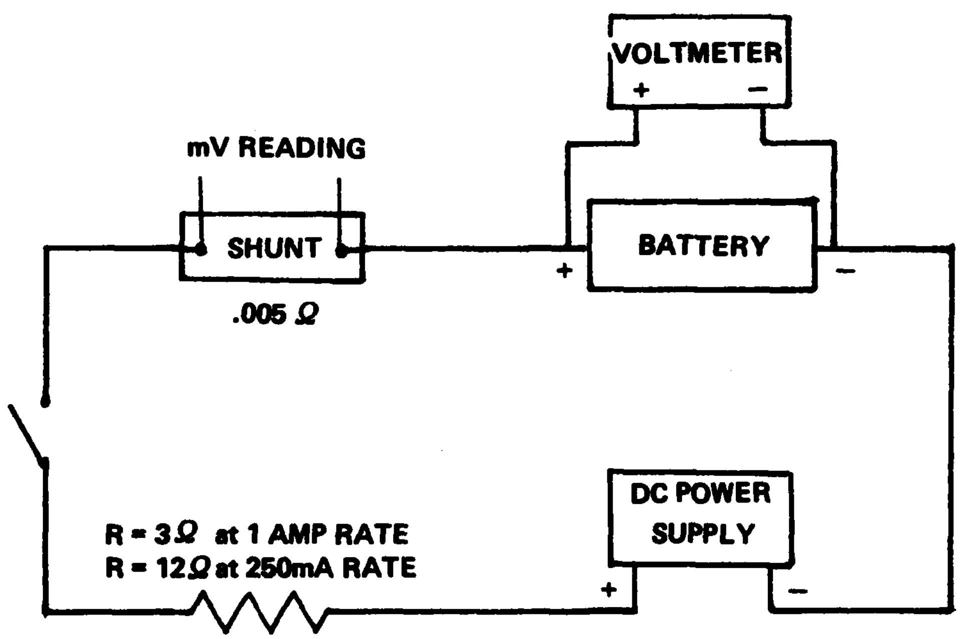

FIGURE 6. SCHEMATIC OF CHARGING TEST CIRCUIT

heating. The cells were placed in a pressure vessel in atmospheres of oxygen, helium, and air at a slight positive pressure (< 5 p.s.i.g). Samples were then heated with heat tape until combustion commenced (approximately 450^{o}C). Then gas samples of the combustion products were taken from the pressure vessel. Voltage, temperature, and internal pressure of the vessel were monitored. The samples were sent to the National Bureau of Standards for analysis.[3]

Temperatures in all of the tests were monitored with type K thermocouples. All reported cell temperatures are cell skin temperatures. The D.C. Power supply used in the tests was a LH 121 made by Lambda Electronics Corporation. The pressure transducer used was a PSI-Tronix model PSI100-250-G1, and had been calibrated for values between 0-150 p.s.i.g.

All tests conducted within the Totalizer required two small modifications of the Totalizer unit to allow data aquisition, but in no way affected the outcome of the tests. The modifications consisted of 1) drilling a small hole on the top of the unit to allow thermocouples and heat tape leads into the Totalizer; 2) soldering of leads from the battery terminals to existing posts leaving the rear of the unit. This was done to facilitate the charging and forced discharge tests and the taking of voltage readings.

CHAPTER 3

RESULTS AND DISCUSSION

Both short circuit tests yielded similar results, and the results of a typical short circuit test is presented in Figure 7. A summary of significant data from both short circuit tests is listed in Table 1. The maximum temperature obtained in both cases was slightly over 130°C, and ventings did not occur. The cell shut itself down in both cases at about two minutes. Cell shutdown occurs when the internal temperature reaches near 130°C and the polypropylene mesh separator apparently fuses. Several weeks after the tests the cells were re-examined and minor leakage was noticed. This was probably due to warpage caused by softening of the plastic top and gasket (one piece) during the high temperatures of the tests. In addition, some minor cracking of the plastic PVC can jacket was noted.

Figures 8 and 9 present the voltage, current and temperature data from the forced discharge tests. Table 2 summarizes the data obtained from all four forced discharge tests. Cells were held in voltage reversal for 100% of cell capacity. Maximum temperature for the 250mA tests was 43°C, and for the 1 AMP tests it was 84°C. No damage to the cell was noticed in any case, and subsequent checks weeks after the tests revealed no cell leakage. As shown in Figure 9, the power supply voltage was turned up at 62 minutes. This was done because the voltage on the constant current power supply had originally been limited to slightly above the cell voltage. When it was apparent that the power supply voltage was limiting the current level during cell voltage reversal, the power supply voltage was increased.

Figures 10 and 11 present the results of the 250mA and 1 AMP charging tests. During both tests "pops" from the cell were heard, and significant smoking occurred. Ventings did occur; and in one test, the top insulation paper was partially pushed out the top during the venting. A photograph of two ventings is presented in Figure 12. Ventings consisted of the pushing of the plastic cap from its seating to allow the release of internal pressure, but in general did not involve fire or flame. However, in one instance at approximately 50 min. into a 1 AMP charging test, a minor and brief fire erupted from the end cap where the cell had vented earlier in the test. This incident occurred on a cell that had been discharged to one half capacity at 1 AMP before commencing charging. No other such incident was noted during any of the charging tests. As can be seen by comparing the data curves, the 1 AMP rate produced much more erratic behavior than did the 250mA rate. In both cases, when the amperage fell from the specified charging rate, the voltage rose to 20 volts. This is due to a power supply limiting voltage of 20. In all cases the PVC outer can jacket was cracked and discolored, but in no test was the steel can affected.

As previously described, a variety of heat tape tests were conducted.

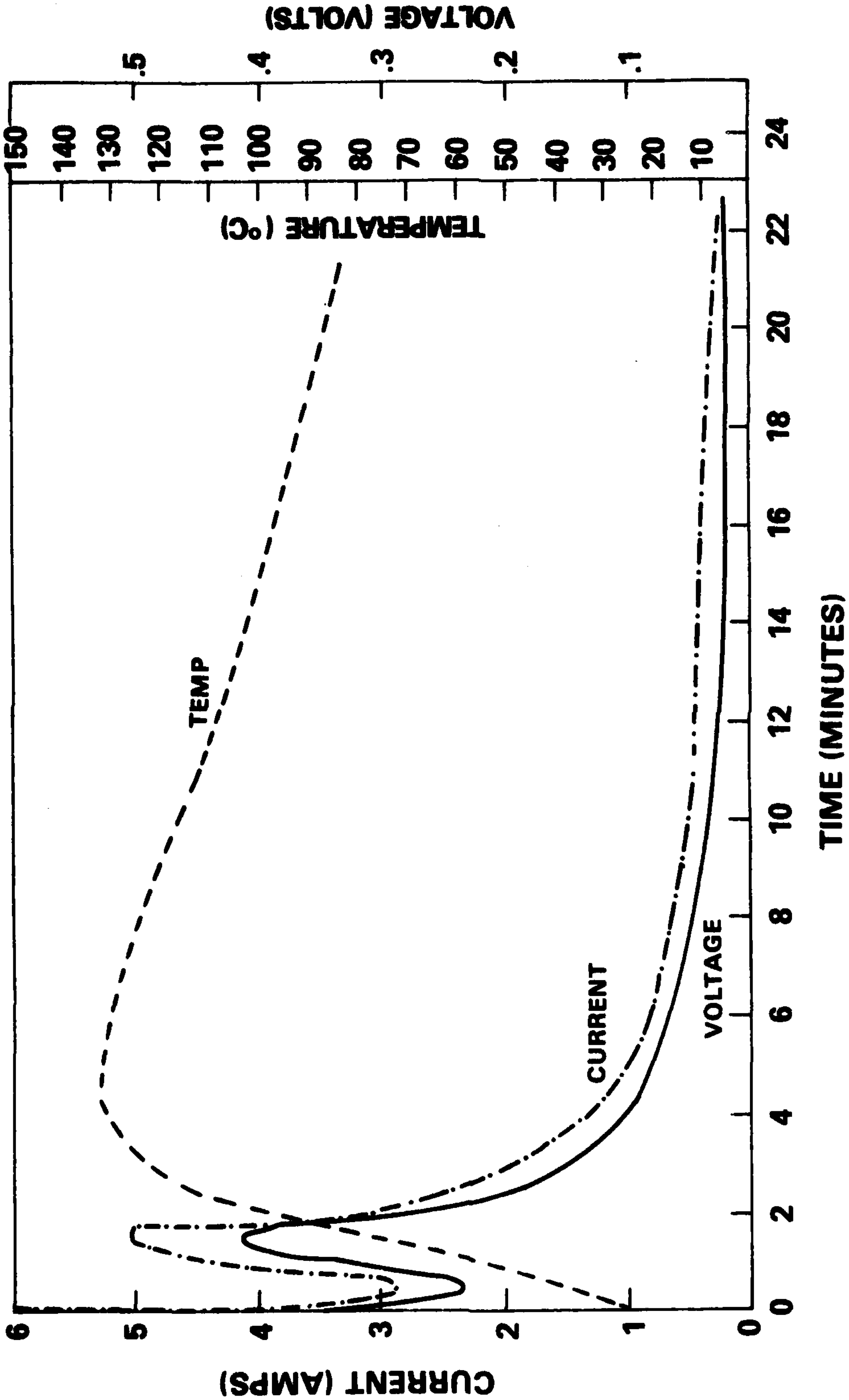

FIGURE 7. SHORT CIRCUIT OF FRESH BR-2/3A CELL IN ELECTRONIC TOTALIZER

TABLE 1. SUMMARY OF SHORT CIRCUIT TESTS

	TEST 1	TEST 2
MAXIMUM TEMPERATURE	134°C	132°C
TIME TO REACH MAXIMUM TEMPERATURE	4.8 MIN	4.7 MIN
PEAK AMPERAGE	5.8 A	5.9 A
BATTERY SHUTDOWN TIME	1.9 MIN	2.0 MIN
BATTERY APPEARANCE	NO CHANGE	
LONG RANGE APPEARANCE	MINOR TO MODERATE LEAKAGE	

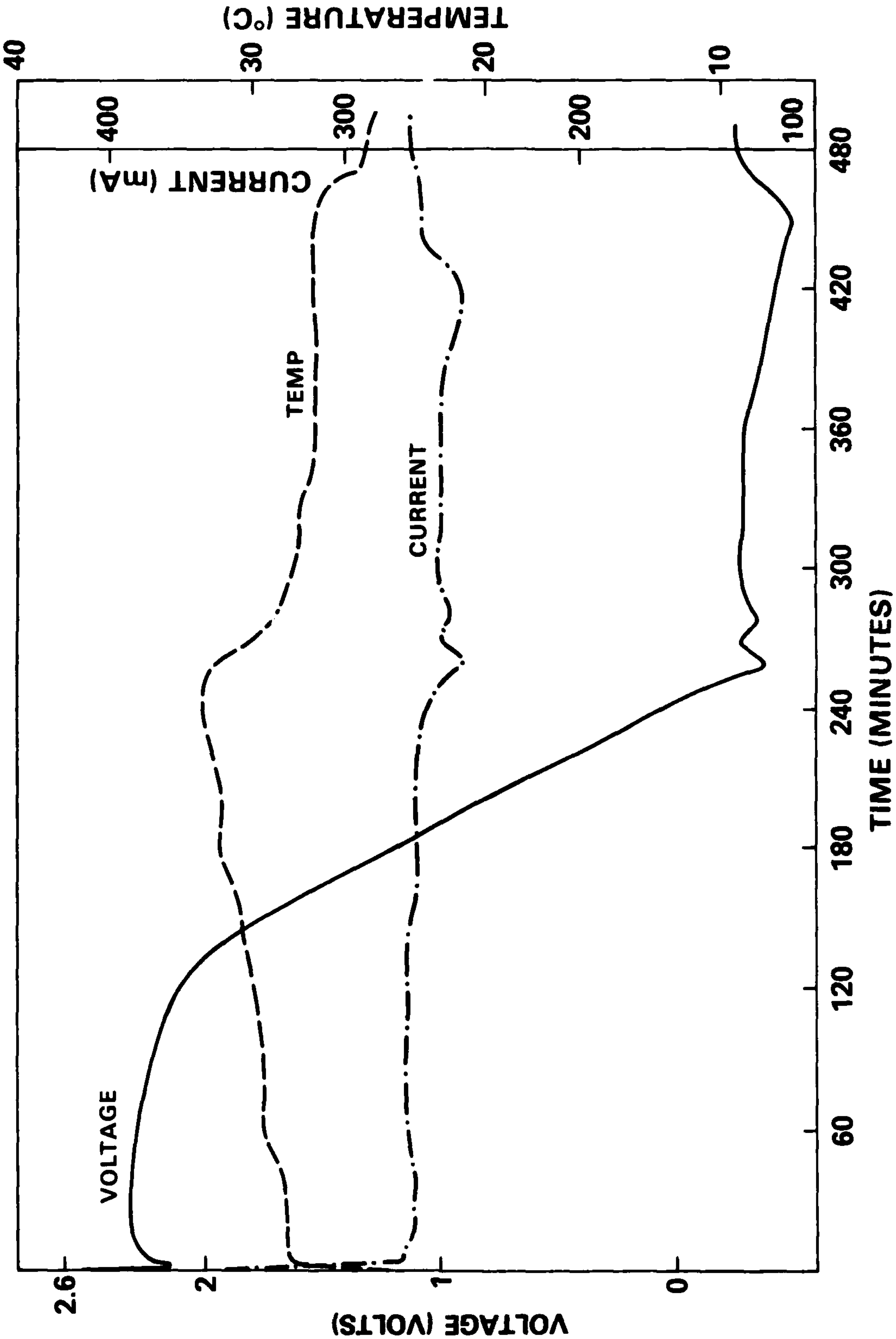

FIGURE 8. FORCED DISCHARGE INTO VOLTAGE REVERSAL ON BR-2/3A CELL (250 mA)

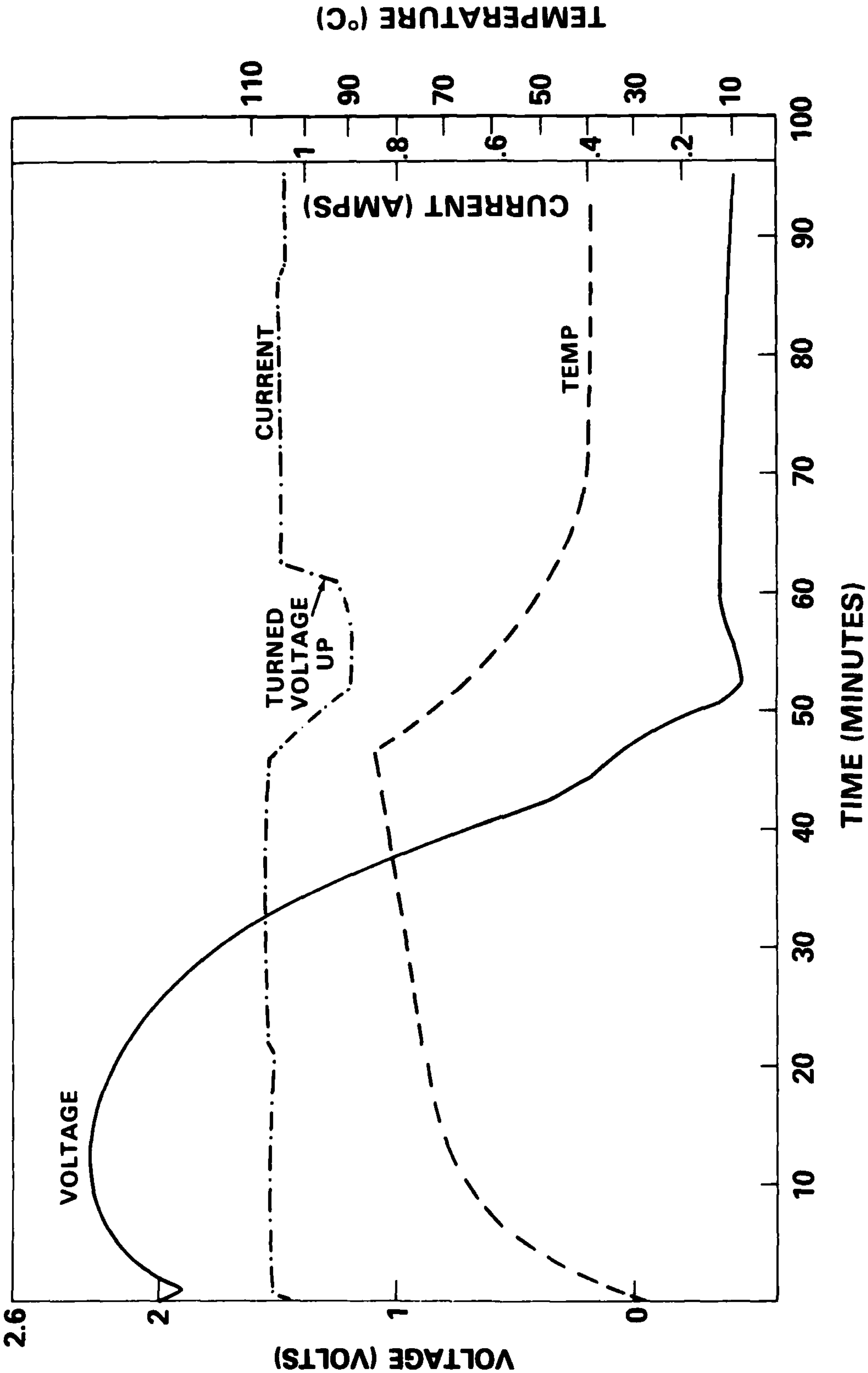

FIGURE 9. FORCED DISCHARGE INTO VOLTAGE REVERSAL ON BR-2/3A CELL (1 AMP)

TABLE 2. SUMMARY OF FORCED DISCHARGE/VOLTAGE REVERSAL TESTS

TEST 1 CELL ONLY } 1 AMP DISCHARGES
TEST 2 CELL IN TOTALIZER } 1 AMP DISCHARGES
TEST 3 CELL ONLY } 250 mA DISCHARGES
TEST 4 CELL IN TOTALIZER } 250 mA DISCHARGES

	TEST 1	TEST 2	TEST 3	TEST 4
CURRENT (AMPS)	1.05 A	0.98 A	250-275 mA	270 mA
VOLTAGE FALLS BELOW 1 VOLT (TIME)	38 MIN	~41 MIN	190 MIN	240 MIN
TIME VOLTAGE REVERSAL REACHED	48 MIN	50 MIN	245 MIN	250 MIN
− VOLTAGE MAXIMUM	−1.0 V	−1.28 V	−0.51 V	−0.99 V
MAXIMUM TEMPERATURE	84°C	82°C	32.1°C	43.4°C
TIME OF MAXIMUM TEMPERATURE	46.5 MIN	~49 MIN	245 MIN	245 MIN
DISCHARGE RATE	1 AMP	1 AMP	250 mA	250 mA

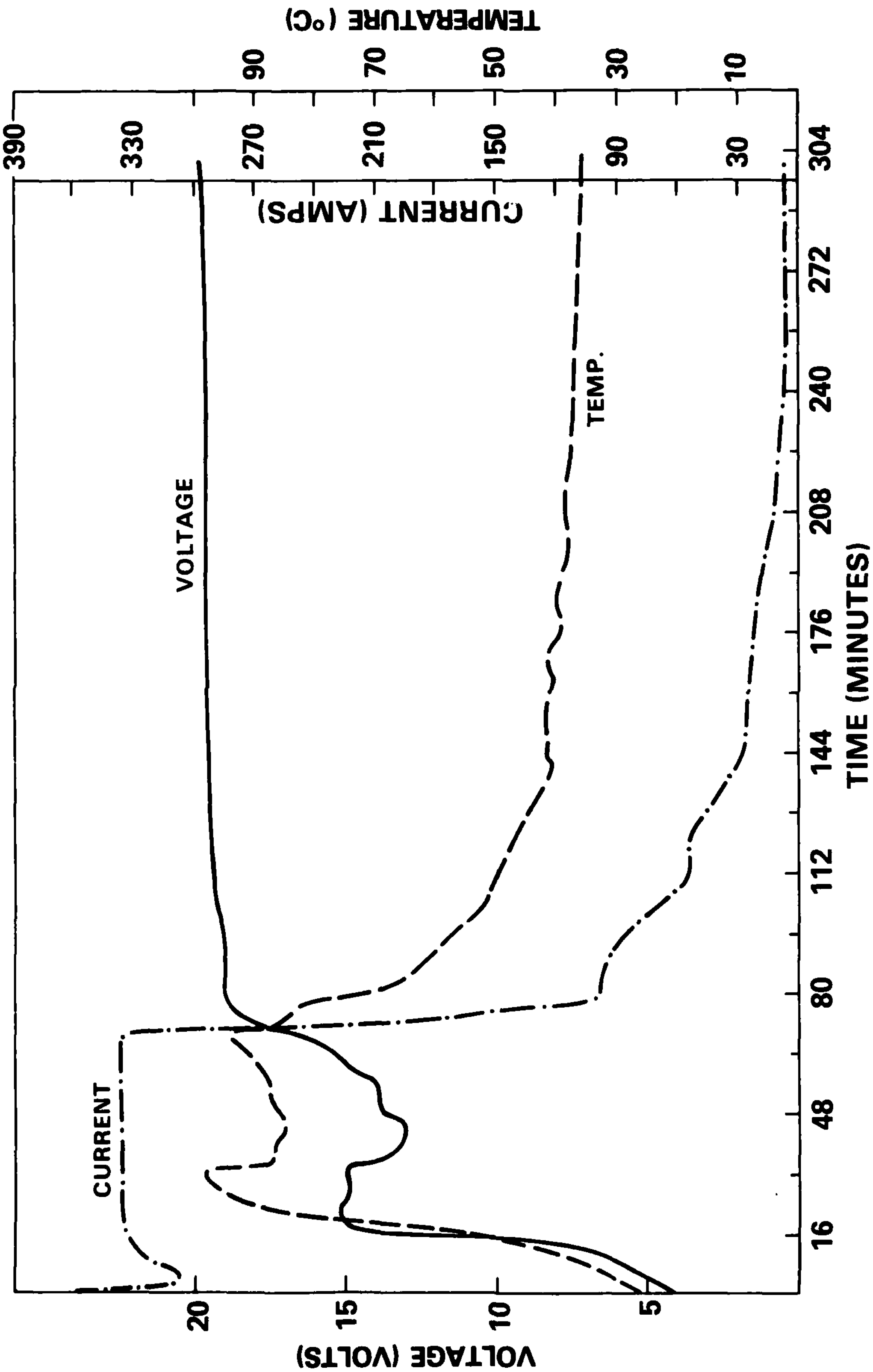

FIGURE 10. 250 mA CHARGING TEST ON FRESH BR-2/3A CELL

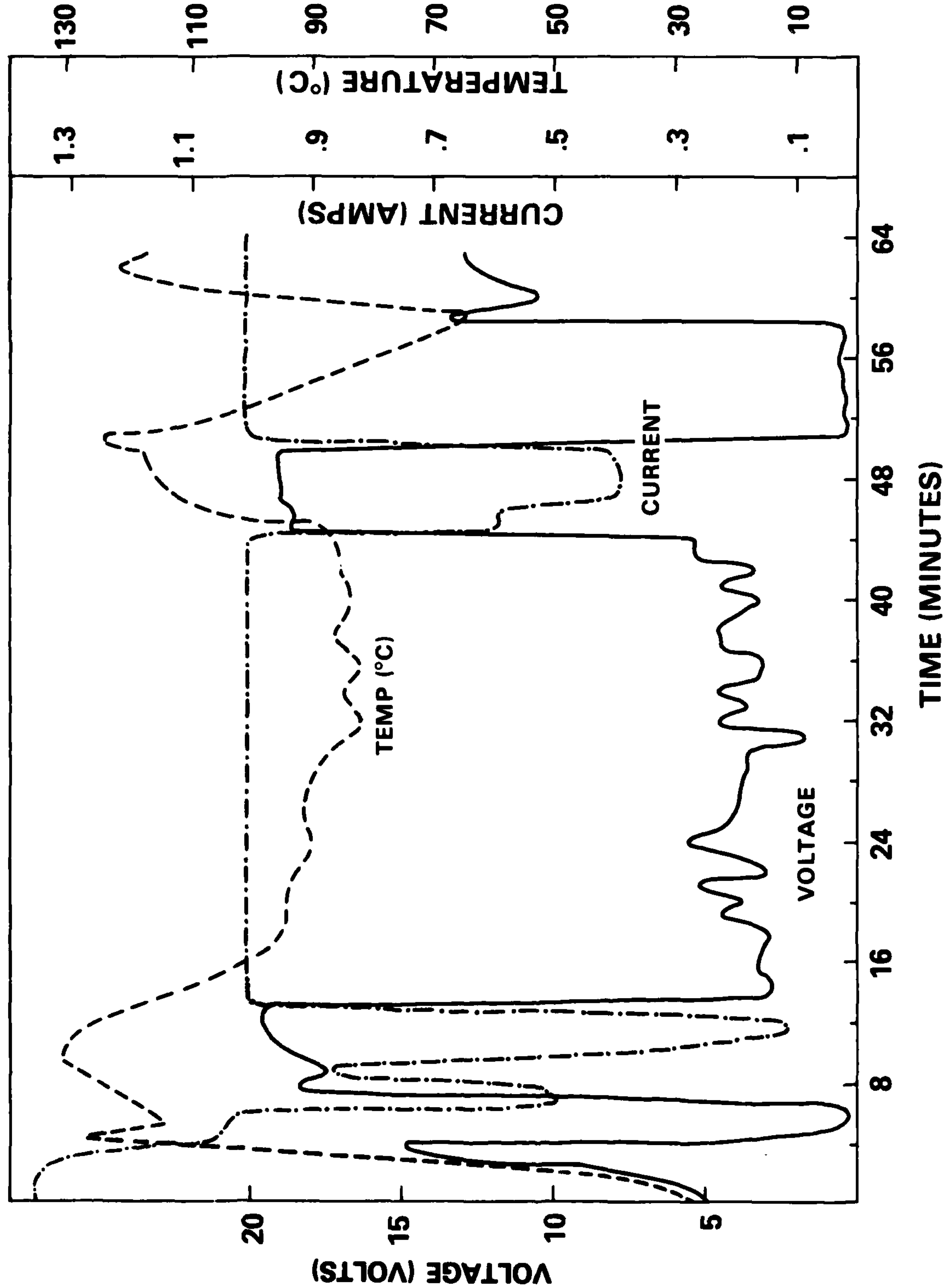

FIGURE 11. 1 AMP CHARGING TEST ON FRESH BR-2/3A CELL

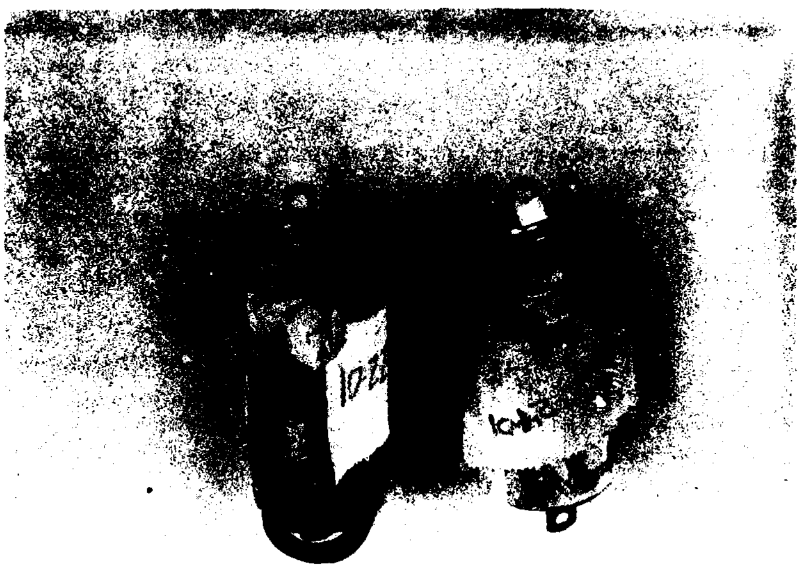

FIGURE 12. PHOTOGRAPH OF TWO CELLS AFTER CHARGING

Those tests that were conducted to only 300°C vented between 200-275°C with loss of voltage, and some minor smoking occurred. Figure 13 presents the typical data obtained for a fresh cell heated to 500°C. On all runs involving fresh cells significant fire and flame erupted between 450-500°C. Initial voltage drop off and venting occurred between 200-275°C. In Figure 13 the temperature rises sharply near 500°C where ignition commenced and a maximum temperature of slightly over 800°C was reached. Those tests on fresh cells conducted in the Totalizer resulted in significant flames escaping from all seams of the Totalizer followed by the Totalizer catching on fire and being totally destroyed. Figure 14 shows the result of the fire on the Totalizer.

Those tests performed on dead cells produced large amounts of smoke at about 450°C, but did not erupt into flames. A test was run on a Totalizer with no cell, but containing a "dummy" cell consisting of a piece of copper tubing wrapped in heat tape and heated to 500°C. This test was designed to determine if the extreme nature of the fire was due only to the battery flames or other internal components and/or plastic erupting into flames. As shown in Figure 15, the tests resulted in some melting and warpage of the Totalizer, but no significant fire or flame was noted. Upon later inspection it appears that some minor charring did occur to the outside case, but at no time was the Totalizer visibly in flames.

As indicated by the manufacturer, the cathode (poly-carbonmonofluoride) is thermally stable up to 400°C. The fact that the majority of incidents (fire or significant smoking) commenced when the battery skin-heat tape interface temperature was approximately 450°C indicates the probable cause of the ignition to be cathode thermal breakdown.

The results of the gas analysis of combustion products is presented in Table 3.[3] The tests were run in a pressure vessel with a volume of 169 $in.^3$, and the maximum pressure developed during combustion was approximately 150 p.s.i.g. (Oxygen atmosphere). Listed in Table 3 for each test are two columns of percentages of the various gases. The first column, labeled battery gas, are the percentages that each individual gas comprises when compared to the total gas attributed to originating from the battery. The second column compares the same individual gases to the total gases in the sample (including gases in the pre-combustion atmosphere). The array of gases is largely comprised of low molecular weight hydrocarbons, some of which are unsaturated (Acetylene, Ethylene, and Propylene). Also present are Fluorocarbons, CO_2, CO, Hydrogen and a low level of Benzene (<1%).

Analysis was completed using Mass Spectroscopy. Species present were identified on the basis of their fragmentation patterns in combination with knowledge of the materials present in a fresh cell. Concentration values were determined from peak intensities which were compared with spectra obtained from standard samples.

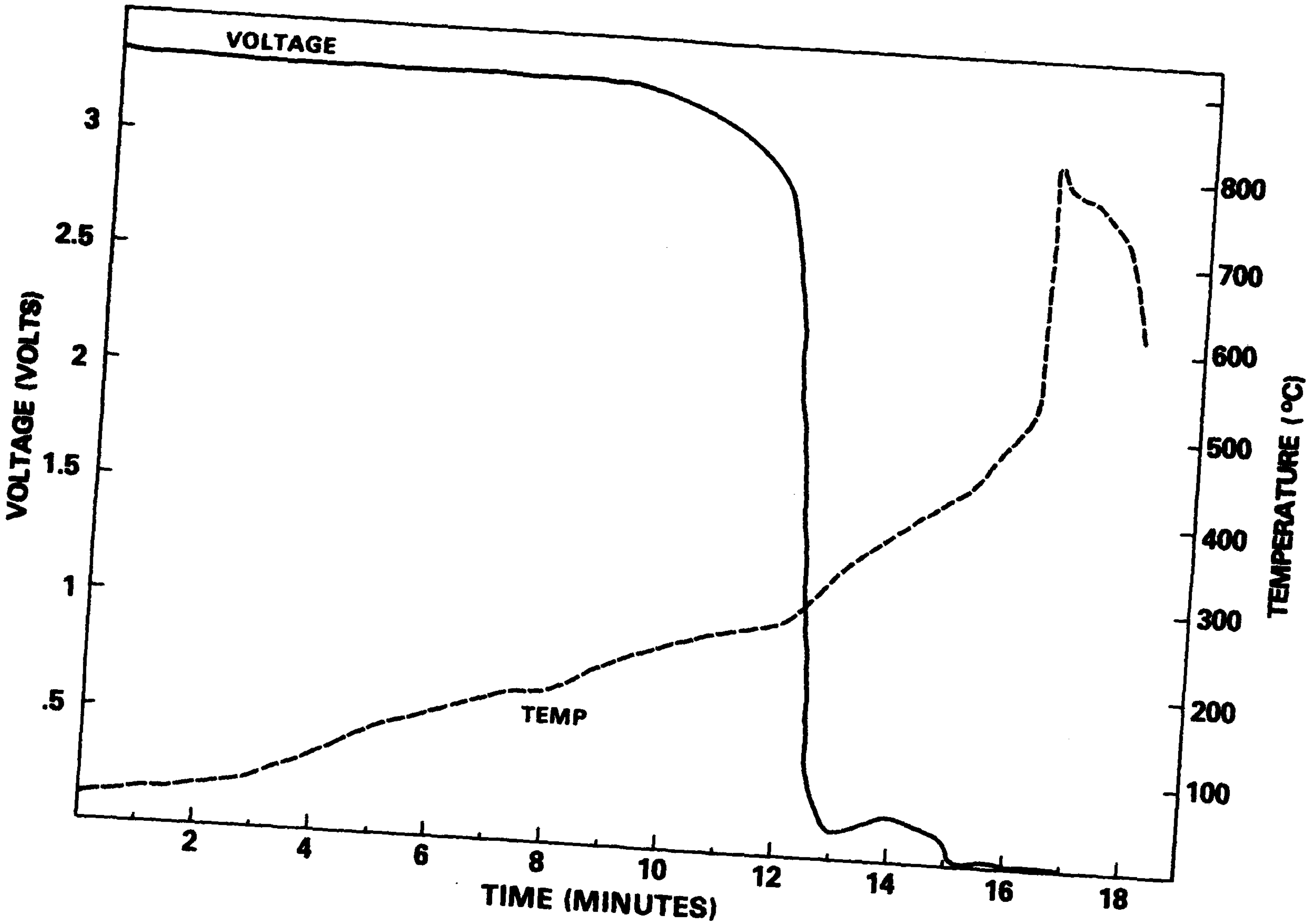

FIGURE 13. HEATING TEST ON BR-2/3A CELL

FIGURE 14. TOTALIZER AFTER HEATING TEST FIRE

FIGURE 15. HEAT TEST OF TOTALIZER WITH NO CELL

TABLE 3. GAS ANALYSIS OF COMBUSTION PRODUCTS AFTER CELL HEATING

	HELIUM ATMOSPHERE		AIR ATMOSPHERE		OXYGEN ATMOSPHERE		OXYGEN ATMOSPHERE	
	Battery Gas	Total Gas	Battery Gas	Total Gas	Battery Gas	Total Gas	Battery Gas	Total Gas
H_2	43.8	10.1	33.2	13.0	16.4	15.2	16.3	15.0
CH_4	12.7	2.9	10.6	4.2	5.7	5.2	5.2	14.8
Acetylene	7.9	1.8	4.0	1.6	1.2	1.1	0.2	0.1
Ethylene	12.1	2.8	10.1	4.0	2.8	2.6	2.1	1.9
CO	6.0	1.4	12.7	5.0	21.0	19.4	30.8	28.2
Propylene	6.6	1.5	3.0	1.2	0.5	0.4	0.6	0.5
CO_2	4.2	1.0	22.5	8.8	50.7	46.9	44.1	40.5
C_xF_x	5.7	1.3	3.1	1.2	1.1	1.0	0.3	0.2
Benzene	0.9	0.2	0.8	0.3	0.5	0.4	0.4	0.3
He	-	73.1	-	-	-	-	-	-
N_2	-	3.5	-	59.6	-	5.0	-	5.7
O_2	-	0.2	-	0.5	-	2.5	-	2.4
Ar	-	0.2	-	0.6	-	0.1	-	0.1

All Figures are Volume Percentages
Volume of Pressure Vessel = 169 $in.^3$

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3. Dorko, William D., "Mass Spectrometric Analysis of Gaseous Off-gas Products of Four Carbon Monofluoride Lithium Batteries," National Bureau of Standards Report of Analysis 553-11-84, Feb., 1984.

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