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SAFT AMERICA LITHIUM SULFUR DIOXIDE BATTERY (P/N 38303301) FOR FLYRT APPLICATION: PERFORMANCE DISCHARGE TEST REPORT

BY J. A. BANNER P. B. DAVIS E. R. PEED C. S. WINCHESTER

RESEARCH AND TECHNOLOGY DEPARTMENT

AUGUST 1991

NAVAL SURFACE WARFARE CENTER
DAHLGREN DIVISION • WHITE OAK DETACHMENT
Silver Spring, Maryland 20903-5000

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FOREWORD

The Battery Technology Group of the Electrochemistry Branch (Code R33) of the Naval Surface Warfare Center, White Oak Detachment, was tasked by the Countermeasures Group of the Naval Research Laboratory to execute a series of performance discharge tests on a lithium/sulfur dioxide (Li/SO_2) battery. The battery was designed and assembled by SAFT America (P/N 38303301) for use in the Flying Radar Target (FLYRT) Demonstration Program. The preliminary battery tests were designed to determine the ability of the battery to fulfill the electrical requirements of the FLYRT payload package. These requirements include a power requirement of a nominal 600 watts for 10 to 12 minutes and a loaded voltage within the range of 66 to 100 volts. This report details the tests performed, the results generated, and the conclusions and recommendations based on these results.

Approved by:

Carl E. Mueller

CARL E. MUELLER, Head
Materials Division

ABSTRACT

The Battery Technology Group of the Electrochemistry Branch (Code R33) of the Naval Surface Warfare Center, White Oak Detachment, was tasked by the Countermeasures Group of the Naval Research Laboratory to execute a series of performance discharge tests on a Li/SO_2 battery. The battery was designed and assembled by SAFT America (P/N 38303301) to be used for the Flying Radar Target (FLYRT) Demonstration Program. The preliminary battery tests included discharge tests designed to determine the ability of the SAFT America battery to deliver a nominal 600 watts for 10 to 12 minutes within the voltage range of 66 to 100 volts. The battery was tested insulated in some cases to determine the effects of an adiabatic environment on its performance. The battery exceeded the goals set for power and lifetime in all tests. However, events consistently occurred at the end of battery life that raised safety concerns with the present battery design. Data were also analyzed for voltage delay characterization; no serious voltage delay problems were evident.

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ILLUSTRATIONS

INTRODUCTION

The Electrochemistry Branch (Code R33) of the Naval Surface Warfare Center, White Oak Detachment (NSWCWODET), was tasked by the Naval Research Laboratory (NRL) to conduct battery performance discharge tests on four specialized lithium/sulfur dioxide (Li/SO_2) battery packs designed and assembled by SAFT America, Inc. The performance requirement for this battery is a nominal 600-watt discharge for 10 to 12 minutes within the voltage range of 66 to 100 volts.

BATTERY DESCRIPTION

The battery (P/N 38303301) contains 33 nominal "1.25C" size SAFT America Li/SO_2 cells (P/N L030SH) connected in series to produce an open circuit voltage of 99 volts. The cells are arranged in four columns of eight cells each, with the thirty-third cell placed perpendicularly on one end (see Figure 1). Each string of eight cells is independently packaged in a shrink wrap tube. The four 8-cell subassemblies are held in place by lines of hot melt glue between adjacent cell columns and a covering of shrink wrap around the entire battery. Each cell has a coined metal vent on the bottom of the cell can. The cells were less than 2 years old.

The battery contains three safety devices, an electrical fuse, a thermal fuse and a diode. The diode is located in the positive lead of the battery, and the two fuses are located in the negative lead. The batteries tested were assembled by SAFT America at their Valdese, North Carolina, plant.

It is anticipated that the thermal environment which the battery will experience in the Flying Radar Target (FLYRT) vehicle will be extreme. The design constraints of the payload and the vehicle indicate that the battery will discharge in an adiabatic manner. Additionally, because of nearby high thermal rejection electronics, the battery will be a potential heat sink for the thermal environment of the payload. To simulate this scenario, some of the discharge tests were performed on batteries wrapped in insulation.

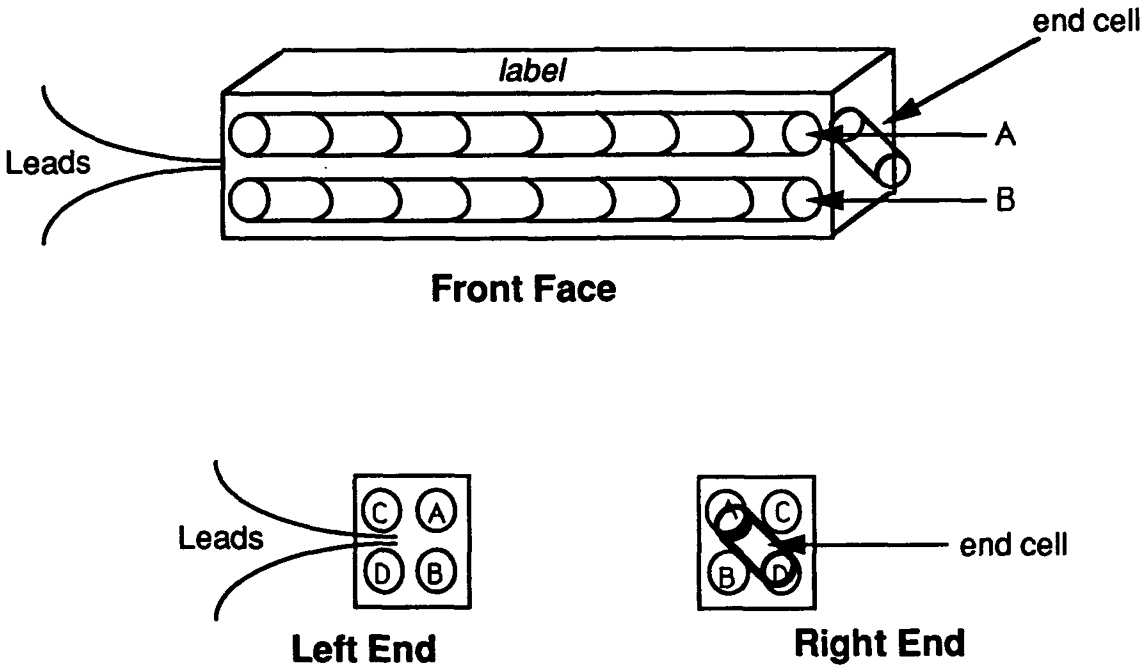

FIGURE 1. SCHEMATIC OF Li/SO_2 BATTERY

TEST ONE

TEST DESCRIPTION

The first test was a constant current discharge at 6 amperes. The test was performed at room temperature and the battery was not insulated. The temperature of the battery was monitored using five K-type thermocouples taped on the battery. The test circuit is illustrated in Figure 2. The performance goal for the battery at a 6-ampere discharge rate was 10 to 12 minutes above 66 volts. The test was continued into voltage reversal to evaluate safety performance issues.

TEST RESULTS

The battery met the performance goal of 12 minutes and continued discharging benignly for an additional 28 minutes before ventings began. The discharge curve for this test is presented in Figure 3. The battery delivered a nominal 530 watts for a total of 40 minutes, with an average voltage of about 86 volts. At the end of the discharge, some of the cells were entering voltage reversal. The battery sustained voltage reversal for approximately 1 minute before cell venting began.

The initial event consisted of several benign, muted ventings in which cells released pressure through their vents with a popping sound. The gases escaped through the battery shrink wrap with little or no physical damage. Within 5 minutes, however, a cell near the end of the battery (where the thirty-third cell is located) vented violently, accompanied by a lithium fire which transitioned into a carbonaceous fire. The carbonaceous fire was identified by the coloration of the flame and is attributed to consumption of the acetonitrile electrolyte. The shrink wrap was burned away exposing some of the cells. The ventings and fires spread to adjacent cells, and over the period of approximately 1 hour, all of the cells vented and burned. Some cells were physically separated from the battery pack by the force of the ventings.

Inspection after the fire showed that six or seven cells had been detached from the battery. All of the cells had vented and were severely corroded. Some cells appeared to have vented through the glass to metal seal, however, most vented from the coined vent. The postmortem analysis revealed that the cell closest to the output leads did not vent. This cell possessed an open circuit voltage (OCV) of 2.92 volts at the time of the postmortem analysis.

Although this summary indicates that the battery reached end of life in a spectacular fashion, it should be reiterated that the battery discharged safely for three times the desired life, and did not fail violently until several cells were forced into voltage reversal.

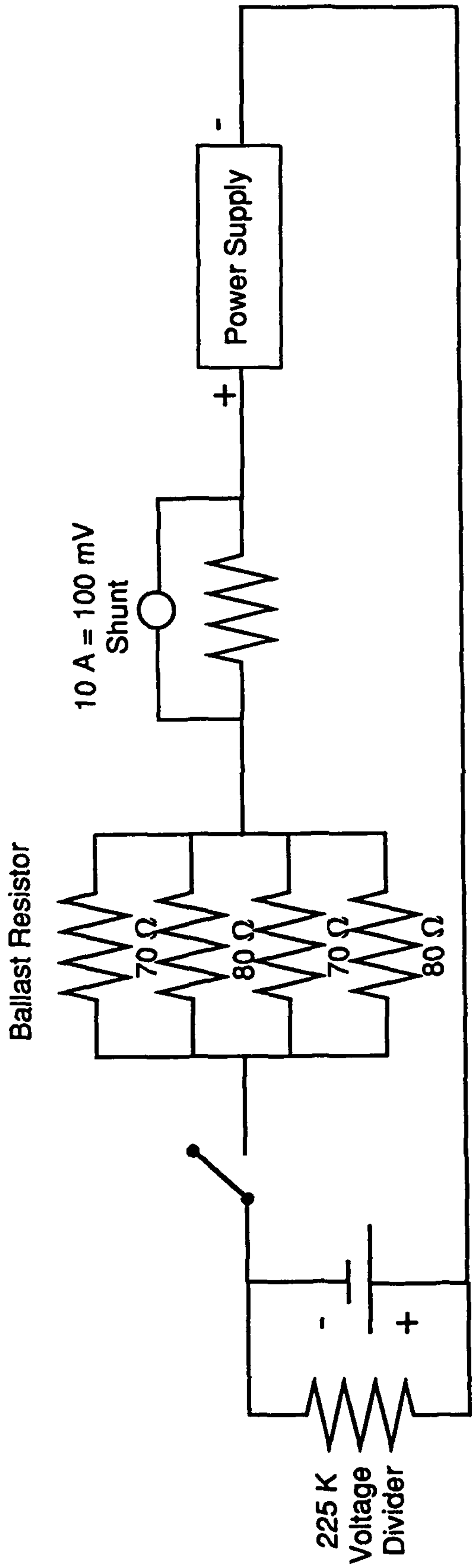

FIGURE 2. TEST CIRCUIT FOR 6-AMPERE CONSTANT CURRENT DISCHARGE (TEST #1)

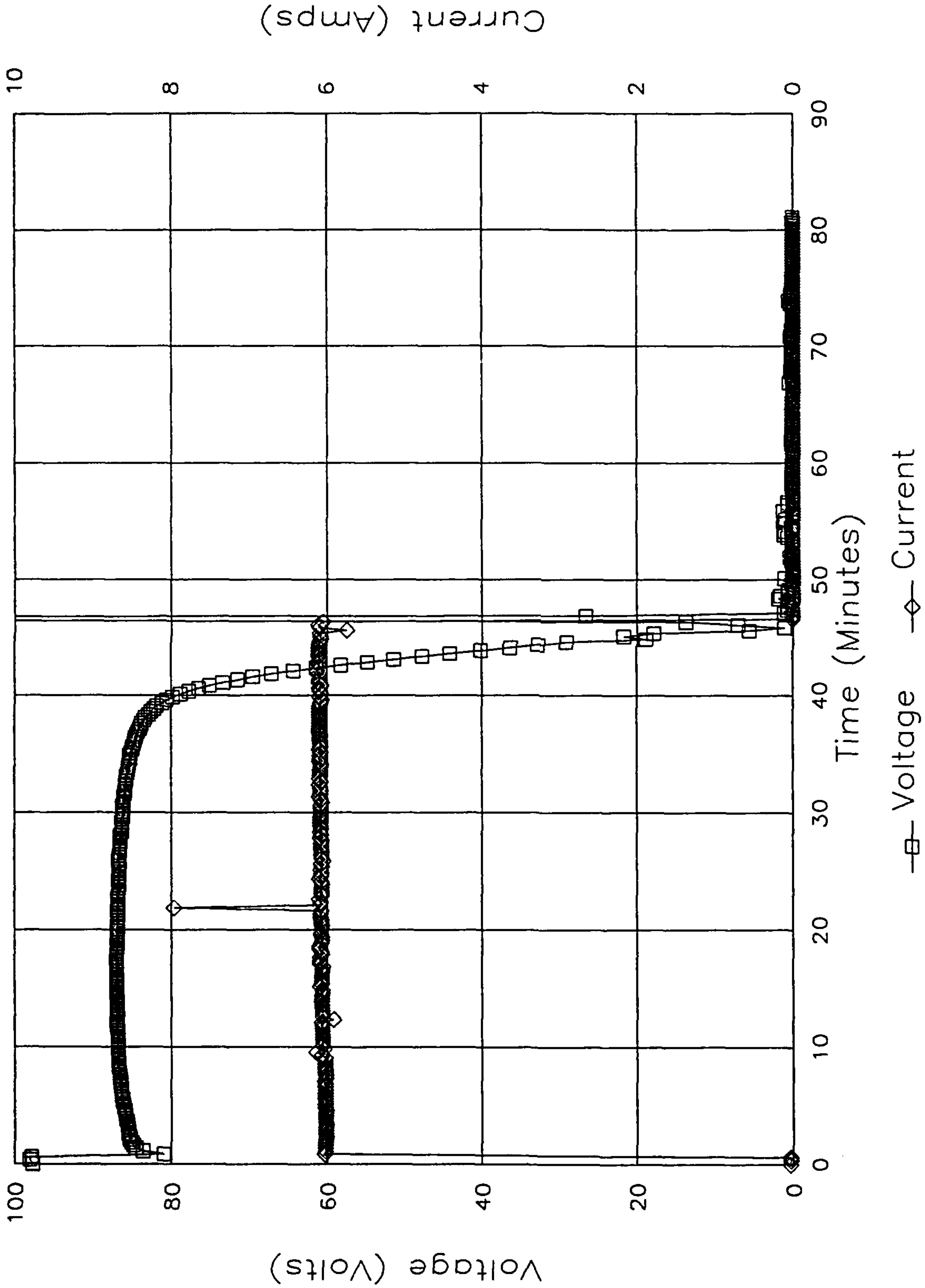

FIGURE 3. CONSTANT CURRENT DISCHARGE AT 6 AMPS

TEST TWO

TEST DESCRIPTION

The second test was a constant current discharge at 8 amperes. This test was also performed at room temperature, however the battery was insulated with two layers (each layer was approximately 1 inch thick) of Fiberfrax™ insulation secured by fiberglass tape. The battery was insulated to simulate an adiabatic discharge condition. Six K-type thermocouples were taped onto the surface of the battery (underneath the insulation) to monitor the temperature of the battery during the test. The test circuit is illustrated in Figure 4. Because the battery performed so successfully during the 6-ampere test, the performance goal chosen for the constant current discharge at 8 amperes was also 10 to 12 minutes.

TEST RESULTS

The discharge curve for this test is presented in Figure 5. Although the discharge curve shows a voltage drop initially, the battery delivered about 660 watts over a lifetime of 20 minutes at an average voltage of 82.5 volts. Thus, the battery met and exceeded all of its performance requirements in this test.

The first event was a muted, benign vent which occurred 18 minutes into the discharge. The electrical load was disconnected at this time, but because of the heat held in by the insulation, the battery went into thermal runaway, venting violently 2 minutes later and burning for over 45 minutes. The ventings were accompanied by lithium and carbonaceous fires. As in the first test, the fire began at the end of the battery by the thirty-third cell and propagated to the other end.

The Fiberfrax™ insulation did not burn, so the cells were held in their configuration by the two layers of insulation and the fiberglass tape. The postmortem analysis revealed that all the cells were severely damaged, with most venting through the vent, but with some venting through the glass to metal seal. At least two cells vented through holes in the cell case as well as through the vent area. However, the cell cases did not fragment. The nickel tabs and connectors were corroded by the sulfur dioxide and the intense heat of the fire.

From this test, it is possible to conclude that although the battery could perform for the required life of 12 minutes at a rate of 8 amperes under adiabatic conditions, the potential for thermal runaway resulting in extensive battery venting accompanied by fire is increased under these circumstances.

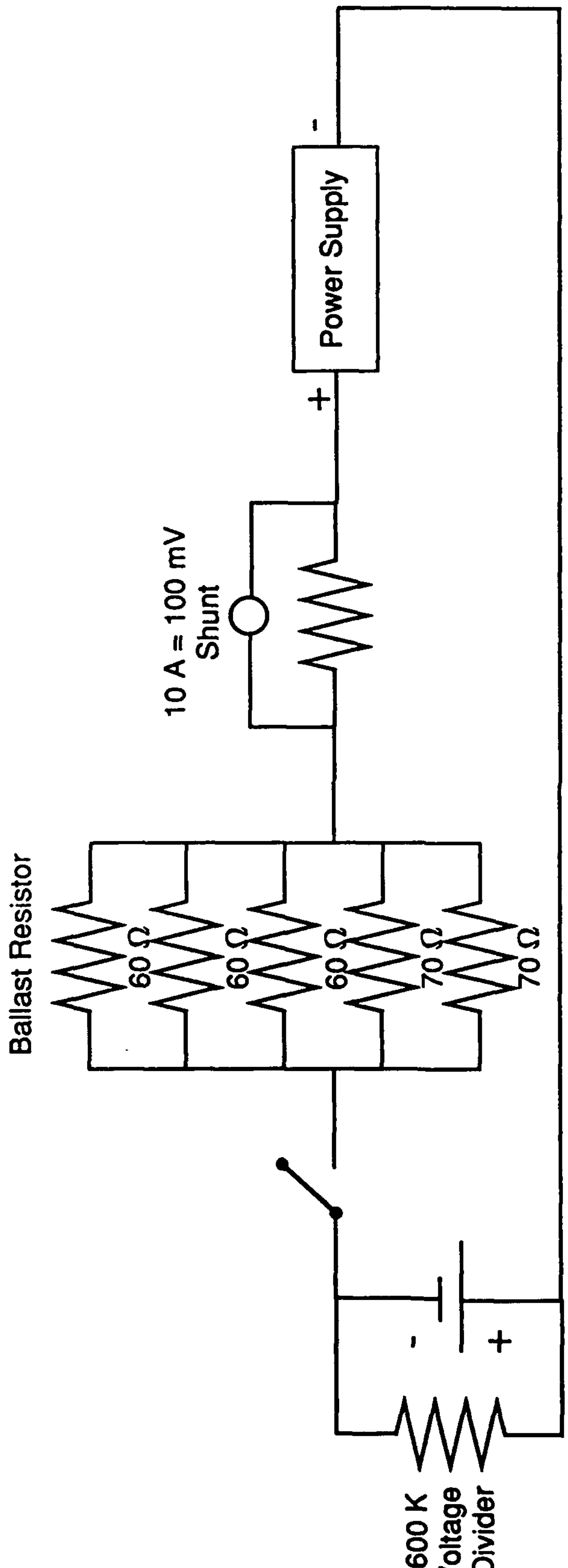

FIGURE 4. TEST CIRCUIT FOR 8-AMPERE CONSTANT CURRENT DISCHARGE (TEST #2)

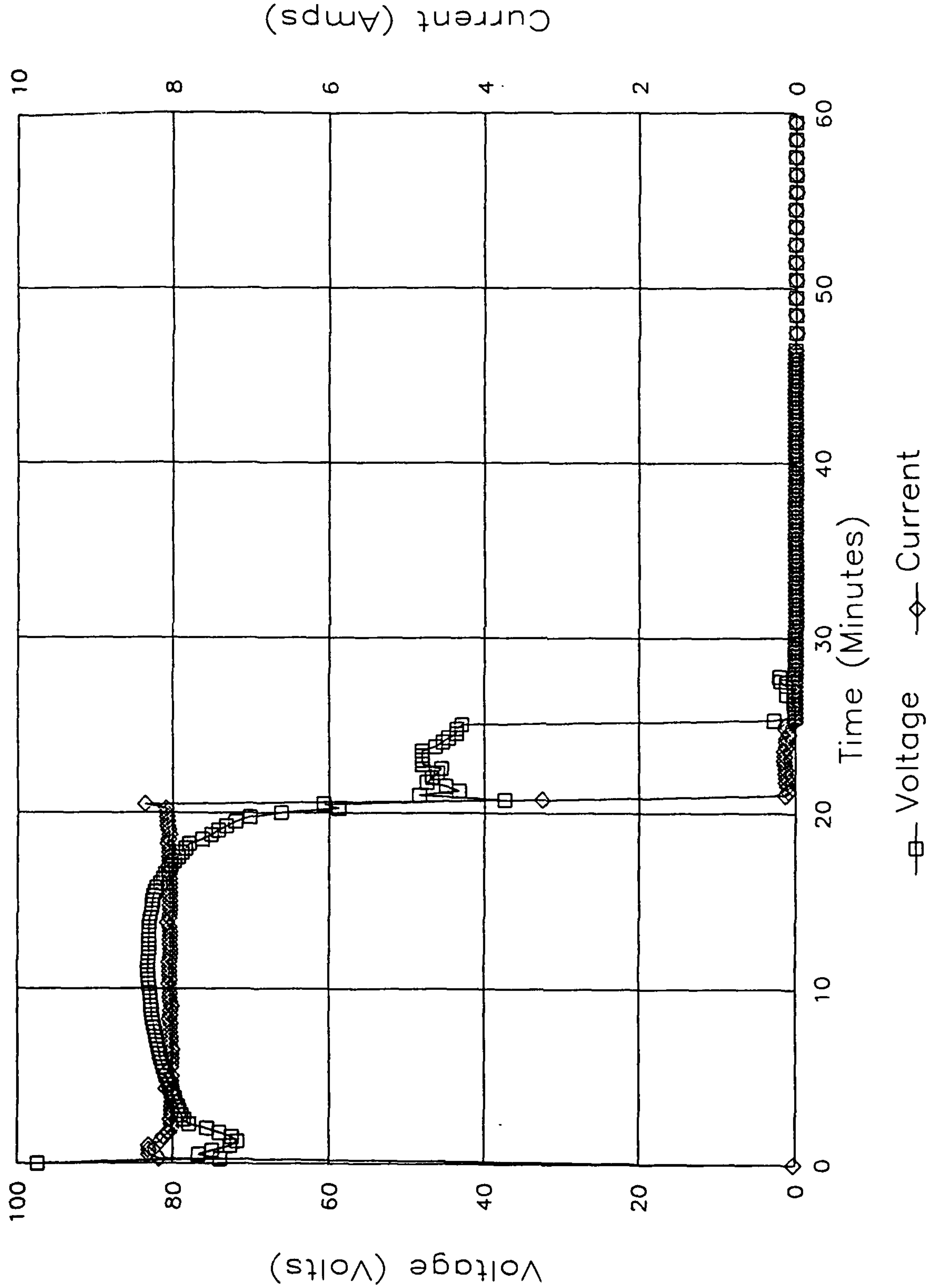

FIGURE 5. CONSTANT CURRENT DISCHARGE AT 8 AMPS

TEST THREE

TEST DESCRIPTION

During the initial setup for this test, it was discovered that the battery pack as received had one or more vented or leaky cells. This was determined because a strong smell of SO_2 was detected upon opening the sealed, transparent bag which held the battery. A closer inspection of the battery was made in an effort to determine which cell or cells had leaked. The gray shrink wrap was removed, but the cells could not be exposed further without the risk of short circuiting them. From what was visible, it was not possible to locate the faulty cell(s). There was also no more evidence of SO_2, either visual or olfactory.

Based on the supposition that a leaky cell represented a cell with decreased capacity, it was decided that the battery should be discharged resistively at a low rate. This allowed the faulty cell(s) to be forced into reversal and subsequent failure by the balance of cells in the battery assembly. This was accomplished by subjecting the battery to a resistive discharge at 5.5 amperes. The battery temperature was monitored using six K-type thermocouples taped to individual cells. The test circuit is illustrated in Figure 6.

TEST RESULTS

The discharge curve for this test is presented in Figure 7. The test was ended after an apparent single venting occurred 35 minutes into the discharge. The battery delivered about 481 watts during this time, with an average voltage of about 87.5 volts.

A postmortem analysis of the battery was performed to determine if the safety devices functioned. Initial inspection of the battery pack revealed that the positive lead was severed into two pieces at the point where the diode was located. Upon disassembling the pack, a single vented cell was located directly beneath the point where the positive lead was severed. Neither the electrical fuse nor the thermal fuse appeared to have functioned. It appears that the cell which had leaked SO_2 had suffered a capacity loss and was forced into reversal by the stronger cells in the series. It subsequently vented directly onto the positive lead, severing it and ending the discharge.

TEST FOUR

TEST DESCRIPTION

The final test was a resistive discharge at 8.75 amperes. The test was performed at room temperature and the battery was insulated in one layer of Fiberfrax™ to simulate the adiabatic nature of the application. Battery temperature

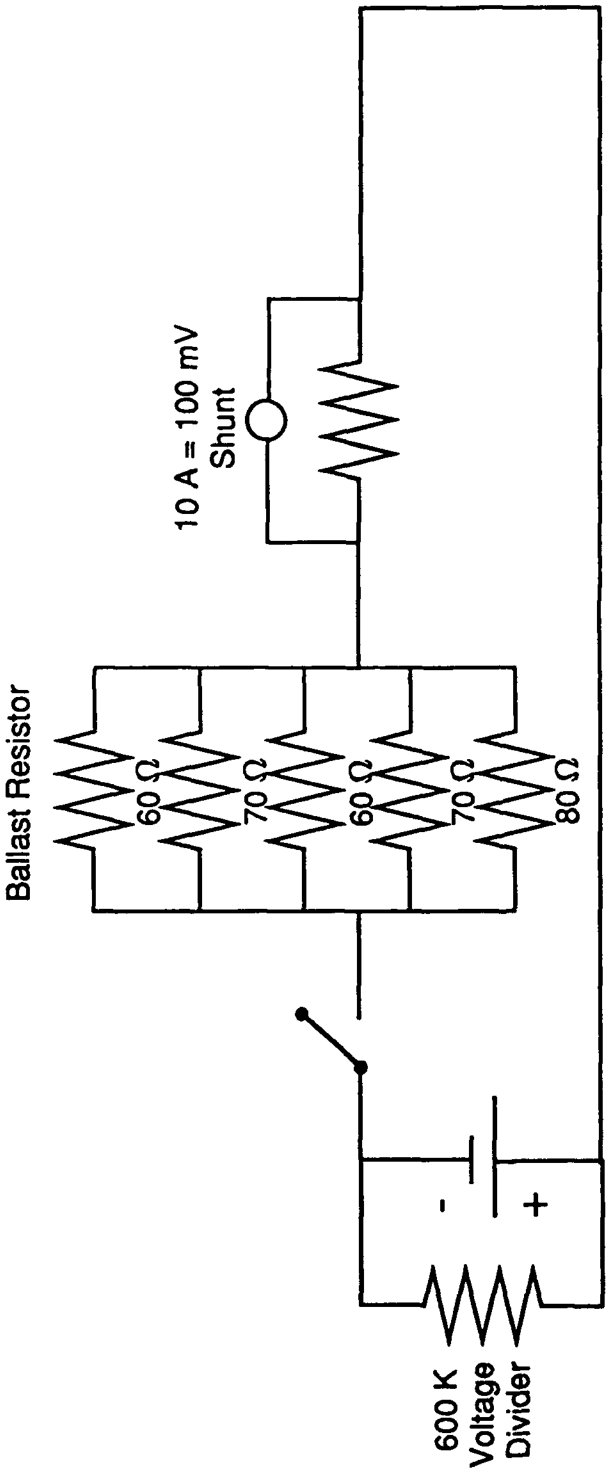

FIGURE 6. TEST CIRCUIT FOR 5.5-AMPERE RESISTIVE DISCHARGE (TEST #3)

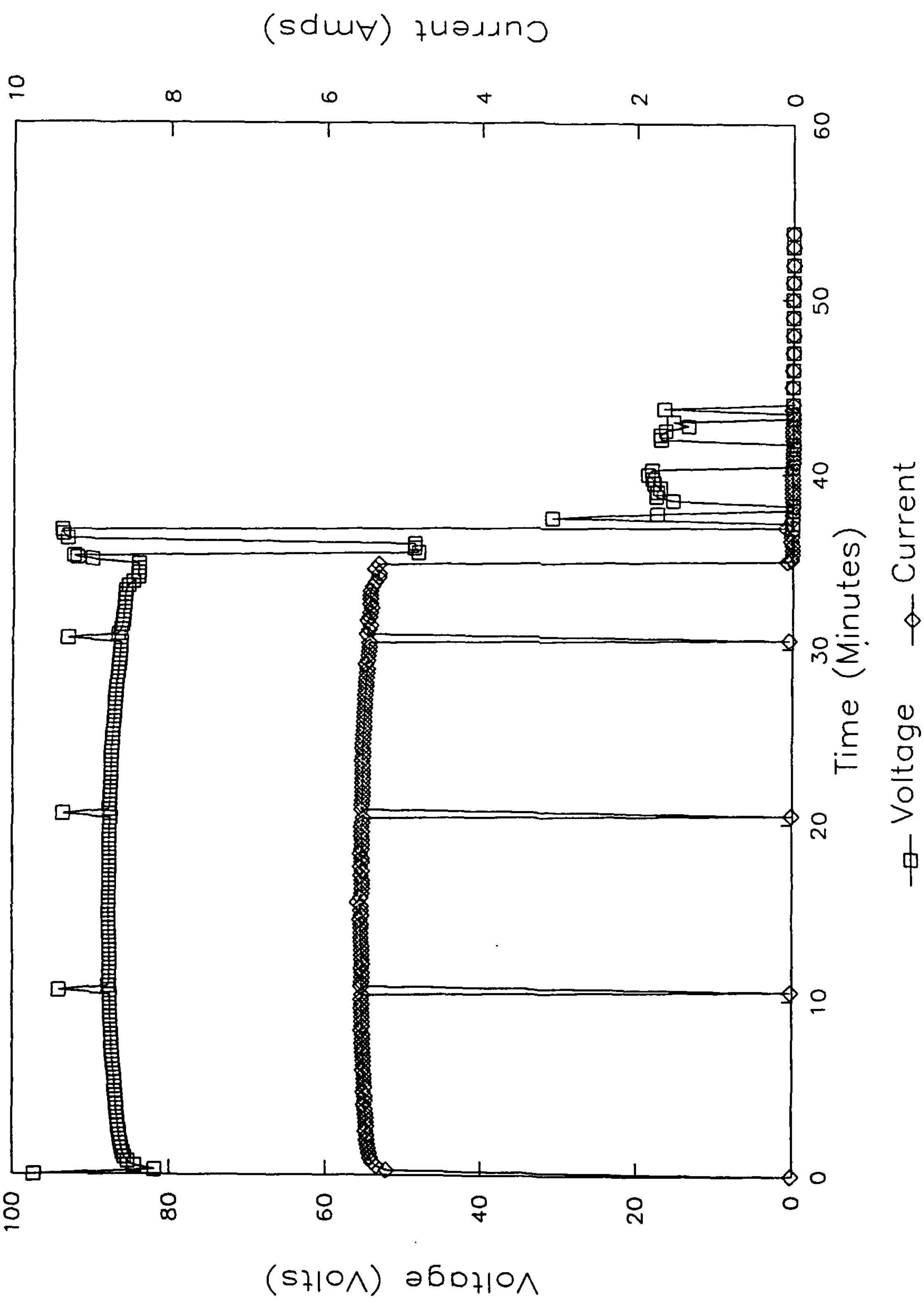

FIGURE 7. RESISTIVE DISCHARGE AT 5.5 AMPS

during the test was monitored using six K-type thermocouples taped to the surface of the battery (underneath the insulation). The test circuit is illustrated in Figure 8. The goal of this test was to determine if an event or venting would occur at the end of battery life without the cells being pushed into voltage reversal by either a power source in the circuit or the presence of a weak cell.

TEST RESULTS

The discharge curve for this test is presented in Figure 9. The battery discharged successfully for 22 minutes. The voltage curve is relatively flat, and the battery delivered about 721 watts at an average of approximately 82.5 volts in 22 minutes. This performance exceeds all of the requirements for the application. As before, the insulation allowed sufficient thermal buildup so that cells vented violently near end of life, causing both lithium and carbonaceous fires. These fires were similar to the results in the second test. The condition of the cells after the fire burned out was also similar to the postmortem results of test two. Most cells vented through the coined metal vent, but a few vented violently through the glass to metal seal and two through the cell case. All of the cells were severely corroded.

From the results of this test, it was concluded that discharging this battery to end of life in an adiabatic environment will lead to a failure involving violent venting and fires. However, the battery is able to safely perform for the required lifetime of 10 to 12 minutes and deliver more than the required 600 watts during that time.

VOLTAGE DELAY ISSUES

BACKGROUND

Voltage delay is a passivation layer phenomenon associated with most active batteries, particularly those batteries subjected to long-term storage or high extremes of temperature and specifically to those exposed to the combination of both conditions. The phenomenon is associated with the formation of anodic films. Voltage delay is manifested by a high apparent cell resistance which decreases the cell voltage to lower than expected levels upon load application and maintains the polarized condition for several seconds to several hours before voltage recovery occurs.

Voltage delay in lithium anode/sulfur dioxide cathode batteries is associated with the formation of a layer of tightly packed lithium dithionite ($Li_2S_2O_4$) crystals on the lithium anode surface. This layer is a by-product of SO_2 reaction with the lithium metal anode. The rate of film formation and its characteristic density and thickness are increased by extreme (>40°C) temperature. This passivation layer serves a beneficial purpose in that it is the primary mechanism that allows the Li/SO_2 chemistry to withstand prolonged storage at elevated temperatures without extreme loss of capacity. However, significant voltage delays may be expected if the film becomes too thick.

Breakup of the film, sufficient to allow substantial current flow (>0.1 mA/cm^2) with low polarization, can be caused by either impact shock (external mechanical

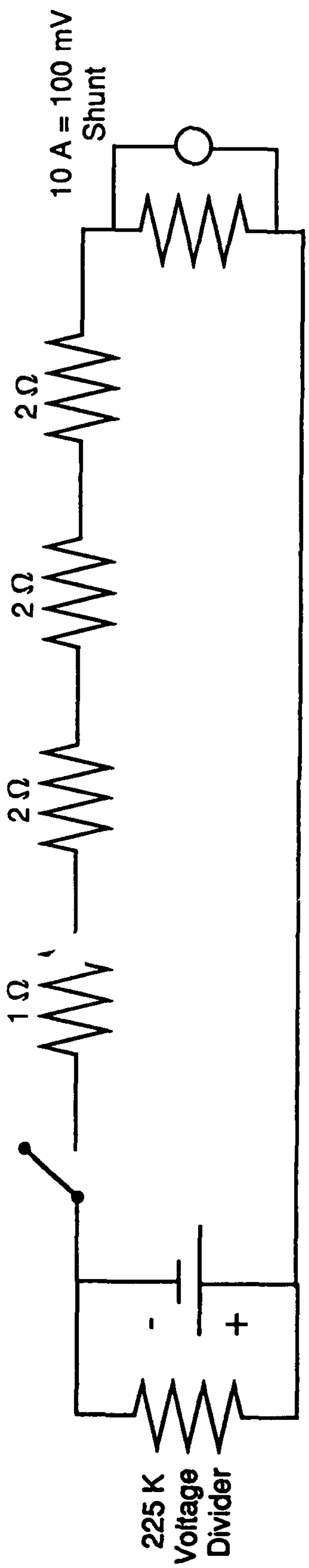

FIGURE 8. TEST CIRCUIT FOR 8.75-AMPERE RESISTIVE DISCHARGE (TEST #4)

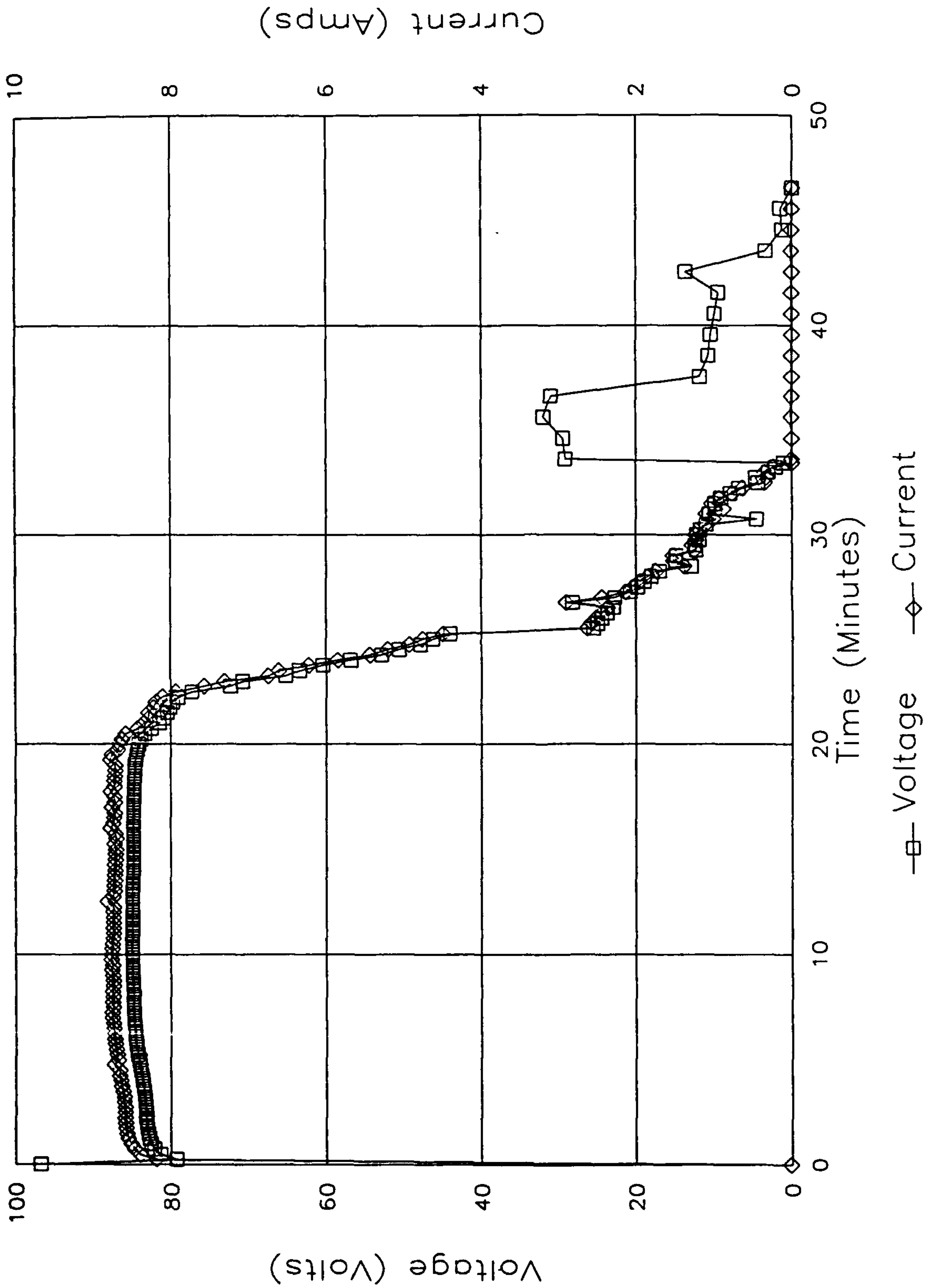

FIGURE 9. RESISTIVE DISCHARGE AT 8.75 AMPS

disruption of the film layer) or by electrochemical discharge of the anode through the micropores of the film. Sustaining a moderate discharge load on a battery/cell will cause breakup of the passivation layer. "Wake-up" loadings, typically using a "slow-blo" fuse in a low resistance (short) circuit have often been effective in the breakup of the passivation layer allowing immediate discharge above minimum voltages.

VOLTAGE DELAY IN PRELIMINARY TESTING

The four battery packs (consisting of 33 Li/SO_2 cells in series) were discharged by turning on the load abruptly, without precursor loading or "wake-up" loading being applied to the battery packs. Minimal voltage delay was observed on the four battery pack tests, and in all cases, battery voltage did not drop below the specified minimum voltage for the application (66 VDC). For three of the tests, cell/battery recovery took less than 1 minute to reach stable voltage plateaus.

However, as depicted in the accompanying voltage-time traces for the battery tests, the voltage required several minutes to stabilize in the second test (see Figure 5). This voltage curve exhibits an anomalous double-dip followed by recovery. The battery discharged in this test required slightly more than 2 minutes to attain stable discharge voltage. This double-dip behavior may be associated with the overall lower performance from the 8.0 ampere discharge test than that observed from the 8.75 ampere discharge test (test four – see Figure 9). The voltage dip behavior may be indicative of a weak cell in the series string or of improperly stored cells.

Discharge testing was conducted at ambient temperatures (25°C) under different current drain rates (5.5 to 8.5 amperes) with reasonably fresh (<2-year old) cells that had presumably not been exposed to abusively high temperature storage. If testing had been conducted with cells under cold, preconditioning extremes (-40°C to 0°C), with old cells and/or with cells that had undergone long-term high temperature storage, the voltage delay could have been severe, perhaps dropping to less than 0.1 VDC/cell (< 3.0 VDC/battery) until the passivation layer breakup occurred.

CONCLUSIONS AND RECOMMENDATIONS

The four tests performed on the 33-cell Li/SO_2 battery designed and assembled by SAFT America for NRL reveal that the battery can meet the performance discharge criteria set forth by NRL for their FLYRT application. However, the violent behavior of this battery at end of life raises clear safety concerns. The results from the fourth test show that voltage reversal of the whole battery pack at end of life is not necessary to induce violent venting and fire. Heat buildup is sufficient to cause safety hazards and limit performance. It is also obvious that the safety devices as they exist in the present design are insufficient, and that some design changes will be necessary to improve battery safety.

Based upon the voltage delay behavior of the four preliminary tests performed, moderate to warm precondition temperature should have little impact on the performance of the batteries, providing that future payload batteries use fresh cells of known storage history. Cold preconditioning of the batteries, as may be expected under demonstration flights scenarios, may cause excessive voltage delay.

Self-heating of the cell stack under adiabatic discharge load conditions will aid in alleviating the cold condition effects on battery performance, after the battery recovers from the voltage delay. Alternatively, usage of a wake-up pulse application to the battery stack would be considered to assure rapid start-up of the battery pack. Electrical wiring schemes for applying the wake-up current pulse should be external to the safety devices in the battery circuit.

Performance of the battery pack in an adiabatic environment might not be possible if the pack is preconditioned above 60°C. Above 60°C, the temperature increase of the battery pack would be sufficient to cause the thermal fuse to function. Should the fuse fail to operate, as experienced during this test program, the battery would cease performance as the cells went into thermal runaway.

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13. ABSTRACT *(Maximum 200 words)*

The Battery Technology Group of the Electrochemistry Branch (Code R33) of the Naval Surface Warfare Center, White Oak Detachment, was tasked by the Countermeasures Group of the Naval Research Laboratory to execute a series of performance discharge tests on a Li/SO_2 battery. The battery was designed and assembled by SAFT America (P/N 38303301) to be used for the Flying Radar Target (FLYRT) Demonstration Program. The preliminary battery tests included discharge tests designed to determine the ability of the SAFT America battery to deliver a nominal 600 watts for 10 to 12 minutes within the voltage range of 66 to 100 volts. The battery was tested insulated in some cases to determine the effects of an adiabatic environment on its performance. The battery exceeded the goals set for power and lifetime in all tests. However, events consistently occurred at the end of battery life that raised safety concerns with the present battery design. Data were also analyzed for voltage delay characterization; no serious voltage delay problems were evident.

14. SUBJECT TERMS
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