NASA Technical Memorandum 82638

Qualification Testing of Secondary Sterilizable Silver-Zinc Cells for Use in the Jupiter Atmospheric Entry Probe

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July 1981

NASA

QUALIFICATION TESTING OF SECONDARY STERILIZABLE SILVER-ZINC CELLS FOR USE IN THE JUPITER ATMOSPHERIC ENTRY PROBE

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E-893

SUMMARY

A series of qualification tests were run on the secondary, sterilizable silver oxide - zinc cell developed at the NASA Lewis Research Center to determine if the cell was capable of providing mission power requirements for the Jupiter atmospheric entry probe. The cells were tested for their ability to survive radiation at the levels predicted for the Jovian atmosphere with no loss of performance. Cell performance was evaluated under various temperature and loading conditions, and the cells were tested under various environmental conditions related to launch and to deceleration into the Jovian atmosphere. The cell performed acceptably except under the required loadings at low temperatures. The cell was redesigned to improve low-temperature performance and energy density. The modified cells showed improved performance at all temperatures. Results of testing cells of both the original and modified designs are discussed.

INTRODUCTION

At the request of the NASA Ames Research Center the possibility of using the secondary, sterilizable silver oxide - zinc cell with inorganic separators developed by the Lewis Research Center (refs. 1 and 2) to power the Jupiter atmospheric entry probe was explored. The length of storage time (3 yr) at low temperatures (-10° to 10° C) required of a battery aboard the probe appears to be well within the capabilities of the Lewis-developed silver-zinc secondary cells. These cells have been successfully tested after more than 6 years of storage in a wet but discharged condition at 0° C with less than 10 percent loss in capacity or performance (unpublished Lewis data).

Testing of the 12-ampere-hour secondary, sterilizable silver-zinc cells was conducted in the following three areas according to specifications set by Ames:

(1) The cells were tested to examine their capability to survive radiation to at least 5×10^5 rads without degradation of performance or materials.

(2) Cell performance under various environmental conditions such as ground-handling shock, hoist acceleration, vibration during launch, and deceleration into the Jovian atmosphere was investigated. (These tests were conducted at the Naval Ammunition Depot in Crane, Indiana.)

(3) The cells' performance was assessed under various temperature conditions and at various discharge rates.

This report concerns itself primarily with the electrical tests run under different temperatures at various discharge rates. Results from irradiation and environmental testing are included as an appendix.

The electrical tests consisted of a series of charge and discharge tests and a power profile, representative of mission requirements, run at

N81-30563#

various temperatures (-10° C, 0° C, 10° C, and room temperature). The results of this testing showed the inability of the cells to have sufficient voltage regulation at rates greater than C/2 and at low temperatures, where C is cell capacity. The cell design was modified accordingly with the aim of increasing operating voltage at higher power loads and at lower temperatures and thus increasing the cell's energy density. The electrical tests were repeated on the modified cells. The results of these tests and those on the original cells and the effect of the modifications are discussed herein.

EXPERIMENTAL PROCEDURE

The original 12-ampere-hour cells arrived from the manufacturer filled with electrolyte, sealed, and with two initial formation cycles completed. The formation procedure employed by the manufacturer on these cells consisted of a constant current charge at 0.3 ampere (C/40) to 1.98 to 2.00 volts or 13.5 ampere-hours, whichever occurred first. The cells were then discharged at 1.8 amperes (C/7) to 1.0 volt. The discharged cells were then drained at 0.6 ampere (C/20) to 1.0 volt. After completion of the initial formation cycle the vented cells were heat treated for 24 hours at 100° C in a nigrogen atmosphere. After the heating cycle the cells were cleaned of any electrolyte residue and sealed. A second formation cycle similar to the first was then given to the sealed cells. Since the formation data were not immediately available when the cells arrived, additional formation cycles were run at the Lewis Research Center to determine the cells' capacities. Formation cycles were run with the cells connected in a series circuit. The cells were charged at approximately 0.44 ampere (C/27) based on rated capacities for 30 hours or to 1.98 volts per cell. Discharges were run at approximately 1.75 amperes (C/7) until the first cell in the string reached 1.0 volt; the discharge rate was then decreased to 0.58 ampere (C/20) and the cells were discharged to a cutoff voltage of 1.0 volt. Cells were individually removed from the circuit when they reached the cutoff voltage.

Two basic test regimes were used to evaluate cell performance. The first consisted of a 6-ampere (C/2) discharge (constant current) to 1.0 volt at -10° C, 0° C, 10° C, and room temperture. Here cells were first charged at 0.4 ampere (~C/30) to 1.98 volts (or a cutoff voltage adjusted upward for the tests run at the lower temperature). The cells were allowed to come to equilibrium at each of the temperatures before they were discharged. For this test two or three cells were connected in a series circuit and placed in a freezer at the desired temperatures. Voltages were monitored by strip-chart recorders. Since a manual operation was required to remove a cell from the circuit, and since the cells were isolated in a freezer, the tests were terminated when the first cell in the series reached the cutoff voltage.

In the second test regime the cells were tested for their ability to perform on a power profile representative of mission requirements. The following discharge regime was used for this profile:

Time, min	Current, A
30	1.6
10	.6
10	2.1
27	.6
3.75	2.1
3.75	11.75
Spike	12.6
22.5	11.75

Cells of the original design were tested and evaluated as described above. These cells had insufficient voltage control at rates greater than 6 amperes and at low temperatures. As a result the cells were modified to increase operating voltages at the higher loads and at lower temperatures. The modifications for improving the energy densities were as follows:

(1) The negative electrodes were thinned down.

(2) A positive and a negative electrode were added.

(3) The volume of potassium hydroxide (KOH) was increased.

(4) A thinner asbestos substrate with lower electrical resistivity was used in the separator.

Table I summarizes these specifications for both the original and modified cells. It was also requested that the electrolyte concentration in the modified cells be lowered from 45 percent KOH to 35 percent for improved conductivity. However, this change was not made, and both sets of cells were filled with 45 percent KOH. The cells were prismatic, with the following dimensions: 4.87 by 2.37 by 0.77 inch; cell volume was 9 cubic inches. The cell case was made of 30 percent glass fortified polyphenyleneoxide. Both positive and negative electrodes were placed in asbestos bags that were hand dipped with the NASA-developed inorganic/organic coating (ref. 1).

The modified cells, like those of the original design, were received from the manufacturer filled and sealed and with two formation cycles completed. However, the formation procedure followed by the manufacturer for the modified cells differed significantly from the procedure used on the original cells. Initially the cells were charged at 0.5 ampere (C/30) for 40 hours; no voltage cutoff was employed. End-of-charge voltages ranged between 2.05 and 2.08 volts. The first discharge was run at 3 amperes (C/5) to 1.10 volts. The discharge was followed by a drain at 1.0 ampere to 1.0 volt. The cells were then heat treated at 100° C for 24 hours in a nitrogen atmosphere, degassed, cleaned, and sealed. The second charge was run at 0.5 ampere (C/30) to a cutoff of 1.98 volts; then to increase the ampere-hour input the cells were discharged for 1 hour at 3 amperes, after which the charge was continued at 0.5 ampere, again to 1.98 volts. The cells were then discharged at 3 amperes to 1.25 volts.

As with the original cells the initial formation data were not available when the cells arrived. Additional formation cycles were run on a regime similar to that run on the original cells. The formation procedures for both sets of cells are summarized in table II. The same basic test regimes were run on the modified cells as had been used to evaluate the cells of the original design. In addition a C rate discharge was run on both sets of cells so that energy densities could be compared at various currents. A number of the modified cells were set aside in the discharged state on low-temperature, open-circuit stand storage with capacity and performance checks planned at regular intervals.

RESULTS AND DISCUSSION

The original and modified cells were run through the same series of electrical tests. Since the modified cells had an extra pair of electrodes, their capacity was greater than that of the original cells. The cells were treated as 15- and 12-ampere-hour cells, respectively. To normalize for the capacity difference, the C/2 rate discharges are compared on a time basis.

C/2 Rate Discharges

Figures 1, 2, and 3 compare discharge curves of the original and modified cells at the C/2 rate at 0° C, 10° C, and room temperature, respectively. The operating voltage of the modified cells was better than that of the cells of the original design at all temperatures. As expected, the greatest difference was at 0° C, where the midpoint voltage improved from 1.17 to 1.30 volts. In all cases the modified cells ran for a shorter length of time at the C/2 rate than did the original cells. However, their operating efficiency was comparable with or greater than that of the original cells, and their energy densities were better in all cases. (The curves represent the average of two or three cells; where one cell fell to 1.0 V before the others, the divergence is shown.) The data from the C/2 rate discharges are summarized in table III.

Figure 4 shows a comparison between the energy densities of the original and redesigned Lewis silver-zinc cells at room temperature. Energy density was greater for the modified version of the cell.

Performance was not acceptable at -10° C for either set of cells. The first test run on the original cells was a charge and discharge (at C/2) at -10° C. The cells were charged at the C/16 rate to a cutoff of 2.35 volts (adjusted upward to accommodate the lower temperature). The charge was stopped at 2.35 volts with 9.05 ampere-hours in. The cells were then discharged at the C/2 rate. The discharge was terminated after 19 minutes (1.38 AH out) because all three cells had dropped below 1.0 volt. When the freezer was opened, it was found that two of the three cells on test had blown up. The cells did not charge efficiently at -10° C, and the 2.3-volt cutoff was too high. As a result of this test it was decided to reduce the charge rate from C/16 to C/30 for a more efficient charge at the low temperatures. Since there is no time constraint or charging in the orbital application, the longer charge period should not confound the results.

The modified cells were tested at -10° C. They were charged at C/30. Discharge results at C/2 were again unsatisfactory. All cells dropped below 1.0 volt with 3.25 ampere-hours out. The discharge power profile was not run on either group of cells at -10° C.

Discharge Profile

Cell performance on the discharge profile is shown in figures 5, 6, and 7. Again as with the C/2 rate discharge, the modified cells showed the greatest improvement in performance over the original design at the lower temperatures. At 0° C the modified cells had satisfactory voltage control even at 11.75 amperes for 26 minutes - the end voltage being 1.10 volts whereas the cells of the original design dropped below 1.0 volt almost immediately, recovered, then dropped below 1.0 volt again 12 minutes into the high-rate portion of the profile. Again the redesigned cells showed improved performance at all temperatures.

The poor performance these cells exhibited on both test regimes at the lower temperatures was expected since these cells were designed for lighter loads and because typically silver-zinc cells, as well as many other electrochemical systems, do not operate efficiently at temperatures much less than 0° C. To improve voltage regulation for missions such as that of the probe, a battery heater could be used to raise the battery temperature to at least 0° C and preferably somewhat higher.

Since the modified 12-ampere-hour silver-zinc cells performed acceptably under the various loading conditions at temperatures of 0° C and above, 12 cells were scheduled for low-temperature, wet-stand storage in a discharged state. Here the cells would be stored at 0° C and removed at regular intervals for capacity and performance checks. However, after standing discharged on open circuit at room temperature for approximately 5 months, 11 of the 12 cells developed leaks in the edge seals and the twelfth cell blew up. The buildup in internal pressure that resulted in leaks in the seals and a blown-up cell probably resulted from the initial treatment the cells received at the manufacturer's plant: The cells were given a considerable overcharge during the two formation cycles that were run there. As a result, further testing of these cells was suspended.

APPENDIX - RESULTS FROM IRRADIATION AND ENVIRONMENTAL TESTING

Irradiation Tests

Calculations were made to determine the ranges of high-energy electrons and high-energy protons into the cells. Energy levels of electrons (2.5 MeV) and of protons (41 MeV) were then selected to ensure radiation penetration through the cell case into the components (electrodes, separators, etc.). Likewise, from data supplied by operators of the electron accelerator and the cyclotron, suitable radiation damage rates (rads/sec) were selected.

Three cells were subjected to electron irradiation on each of two sides for 100 seconds at a rate of $2x10^4$ rads/sec, with each cell receiving a dose of $2x10^6$ rads on each side. The procedure was repeated with X-ray (2.5 MeV) irradiation. One of these cells (cell C) was then given an additional dose of electron and X-ray irradiation at a dose rate of $2x10^5$ rads/sec (10 times the original rate) to increase the dose to $2x10^7$ rads. Next, the three cells were subjected to protons at 41 MeV from the cyclotron at a rate of $1.6x10^4$ rads/sec for 150 seconds, giving each side a dose of $2.4x10^6$ rads. Cell C was irradiated for 1200 seconds in the same field, receiving a total dose of $1.92x10^7$ rads to each side. As a final test, cell C was irradiated after a period of recharging at a higher dose rate of $1x10^6$ rads/sec for 960 seconds.

During all irradiation tests the cells were placed under a 1-ohm load, and their voltages and currents were monitored and recorded. Results of these tests are summarized here:

(1) Cells subjected to 2.5-MeV electron irradiation at a rate of $2x10^4$ rads/sec (dose, $2x10^6$ rads) suffered only about 1 percent decreases in voltage and current. This was repeatedly observed in all three cells. No effects were seen from the X-ray irradiation of 2.5 MeV for 100 seconds at $2x10^4$ rads/sec. When subjected to a higher dose rate ($2x10^5$ rads/sec), cell C experienced 7.5 percent drops in voltage and current.

(2) Irradiation of the three cells by 41-MeV protons at a rate of $1.6x10^4$ rads/sec for a dose of $2.4x10^6$ rads produced no observable changes in cell voltages or currents. Increasing the dose on cell C to $1.92x10^7$ rads at the same rate did not change this result.

(3) In the final irradiation test, with cell C subjected to the higher rate of $1x10^6$ rads/sec, the voltage increased by 10.1 percent, and the current increased by about 11 percent. The cell case failed when the dose absorbed by the cell reached a level of about $6.2x10^8$ rads.

After the irradiation tests the two intact cells (S/N 204 and S/N 208) were discharged to 1 volt with a 1-ohm resistor. They were then charged and discharged in the same manner as they were in the formation cycles preceding the irradiation tests (i.e., charged at 0.44 A to 2.0 V or for 30 hr, then discharged at 1.75 A to 1.0 V, then at 0.58 A to 1.0 V). Table IV compares the efficiencies obtained by the cells during the formation cycles before irradiation with those that resulted after irradiation.

The following conclusions were made from the results of the irradiation tests on the 12-ampere-hour secondary silver-zinc cells:

(1) Effects of irradiation on the cells in terms of changes in voltage and current depend more on the rate at which the dose is applied than on the total dose adsorbed.

(2) For dose rates of $2x10^4$ rads/sec and with 100-second exposures to 2.5-MeV electrons or X-rays (total dose, $2x10^6$ rads), effects on cell performance during and after irradiation are negligibly small.

(3) No effects on cell performance can be expected from irradiation by protons of energies as high as 41 MeV when the dose rate is $1.6x10^4$ rads/sec or lower and the total dose is $1.92x10^7$ rads or less.

The total dose anticipated by Ames Research Center for a battery aboard the atmospheric entry probe was stated to be no more than $5x10^5$ rads. The expected dose rates for the probe are orders of magnitude lower than the test conditions.

Environmental Tests

At the Naval Ammunition Depot, Crane, Indiana, three Lewis 12-ampere-hour cells were subjected to (1) an impact shock test (a shock pulse of 20 g's terminal sawtooth of 11-msec duration); (2) a hoist load of 2 g's within 20° of vertical; (3) a sinusoidal vibration at 5 to 26 hertz with 1.3-g peak acceleration, another at 26 to 52 hertz with 0.036-inch double amplitude, and another at 52 to 1000 hertz with 6-g peak acceleration, all at 1/2 octave per minute from 5 to 1000 and back to 5 hertz (four sweeps); (4) the random vibration anticipated during flight in the shuttle orbiter from the mid-fuselage-payload support (as defined in Volume XIV, Revision C, "Shuttle System Payload Accommodations"); and (5) an acceleration of 300 g's in a centrifuge for 75 seconds. The cells were tested in all six directions in their three orthogonal axes except that the cells were not tested "upside down" in the centrifuge. During the tests the cells were discharged at a rate of 3 amperes in the shock and centrifuge tests and at a rate of 1.13 amperes in the longer vibration tests. No loss in performance was noted for any of the cells in any of the tests described. When the cells were opened and their components examined for any physical effects from the environmental tests by NAD Crane personnel, there was no evidence of any physical damage.

Only cells of the original design were run through the irradiation and environmental testing. Cell performance was not affected when the cells were subjected to the environmental conditions and the levels of irradiation that are expected to exist on the probe. Thus, since none of the major elements of the cell design were changed, it was assumed that cells of the modified design would react like the original cells when subjected to environmental and/or irradiation testing.

REFERENCES

1. Bozek, John M.: Structure and Function of an Inorganic-Organic Separator for Electrochemical Cells - Preliminary Study. NASA TM X-3080, 1974.
2. Schwartz, Harvey J. and Soltis, Richard G.: A Versatile Silver Oxide - Zinc Battery for Synchronous Orbit and Planetary Missions. NASA TM X-68036, 1972.

TABLE I. - SPECIFICATIONS ON SILVER-ZINC CELLS

Characteristic	Original cells	Modified cells
Capacity (nominal), AH	12	15
Positive plate thickness, in.	0.018 ± 0.001	0.028 ± 0.001
Negative plate thickness (full), in.	0.096 ± 0.002	0.043 ± 0.002
Negative plate thickness (half plate), in.	----------	0.0235 ± 0.0015
Number of positive plates	4	5
Number of negative plates	3 full	4 full, 2 half full
KOH concentration, percent	45	45
KOH volume, cm^3	37.5	[a]40-42
Substrate thickness, mils	10	7

[a] 45 cm^3 of KOH were initially added to each cell; during the first charge 3 to 5 cm^3 appeared in the overflow tubes and was removed.

TABLE II. - COMPARISON OF FORMATION PROCEDURES USED ON ORIGINAL AND MODIFIED CELLS

Cycle	Original cells (nominal capacity, 12 AH)	Modified cells (nominal capacity, 15 AH)
Formation procedure used by manufacturer		
First charge	Constant current at 0.3 A (C/40) to 1.98 to 2.00 V or 13.5 AH	Constant current at 0.5 A (C/30) for 40 hr; no voltage cutoff
First discharge	1.8 A (C/7) to 1.0 V followed by drain at 0.6 A to 1.0 V; cells heat treated for 24 hr at 100° C in N_2, cleaned, and sealed	3 A (C/5) to 1.10 V followed by drain at 1.0 A to 1.0 V; cells heat treated for 24 hr at 100° C in N_2, cleaned, and sealed
Second charge	Same as first	Constant current at 0.5 A (C/30) to 1.98 V; to increase input cells were discharged at 3 A for 1 hr, then charged at 0.5 A to 1.98 V
Second discharge	Same as first	3A to 1.25 V
Formation procedure used at Lewis Research Center		
Third through fifth charges	Constant current at 0.44 A (C/27) for 30 hr or to 1.98 V	Constant current at 0.55 A (C/27) for 30 hr or to 1.98 V
	1.75 A (C/7) until first cell reached 1.0 V, then current reduced to 0.58 A; cells removed at 1.0 V	2.00 A (C/27) until first cell reached 1.0 V, then current reduced to 0.67 A; cells removed at 1.0 V

TABLE III. - COMPARISON OF AMPERE-HOUR EFFICIENCIES AND ENERGY

DENSITIES AT C/2 RATE

Temperature, °C	Operating voltage (midpoint voltage, V)		Energy density, WH/lb		Ampere-hour efficiency	
	Original	Modified	Original	Modified	Original	Modified
0	1.17	1.30	14.39	18.10	67.7	75.4
10	1.35	1.37	20.44	24.17	95.0	94.5
Room temperature	1.41	1.44	21.35	26.51	84.8	87.8

TABLE IV. - EFFECTS OF IRRADIATION ON CELL EFFICIENCY

Cell	Operation	Before irradiation						After irradiation			
		Cycle 1		Cycle 2		Cycle 3		Cycle 1		Cycle 2	
		Capacity, AH	Efficiency, percent	Capacity, AH	Efficiency, percent	Capacity, AH	Efficiency, percent	Capacity, AH	Efficiency, percent	Capacity, AH	Efficiency, percent
S/N 204	Discharge Charge	12.55 12.49	100.5	13.27 12.96	102.4	12.85 13.23	102.7	13.14 13.23	99.32	13.45 13.34	100.82
S/N 208	Discharge Charge	11.85 12.06	98.34	12.96 12.25	105.8	12.08 13.43	97.80	12.08 13.43	89.95	13.65 13.34	102.32

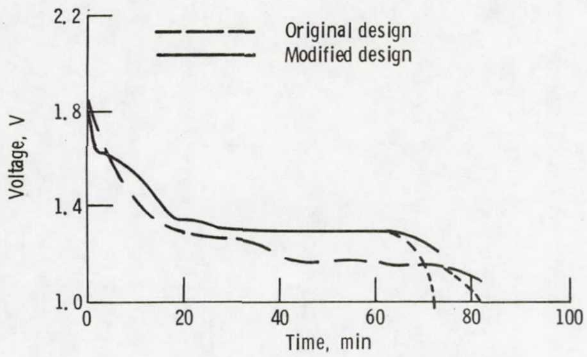

Figure 1. - C/2 rate discharge at 0° C.

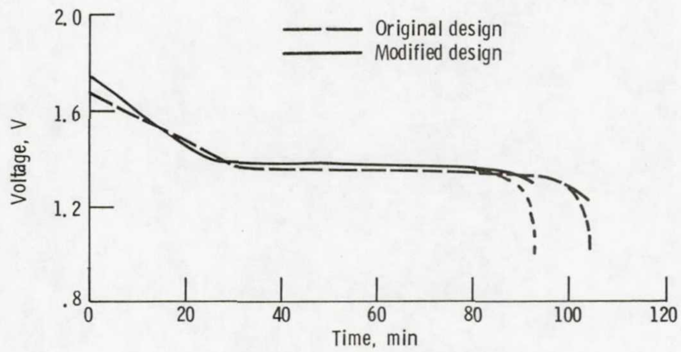

Figure 2. - C/2 rate discharge at 10° C.

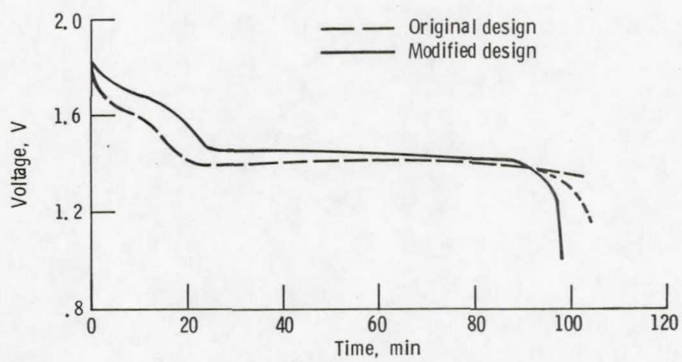

Figure 3. - C/2 rate discharge at room temperature.

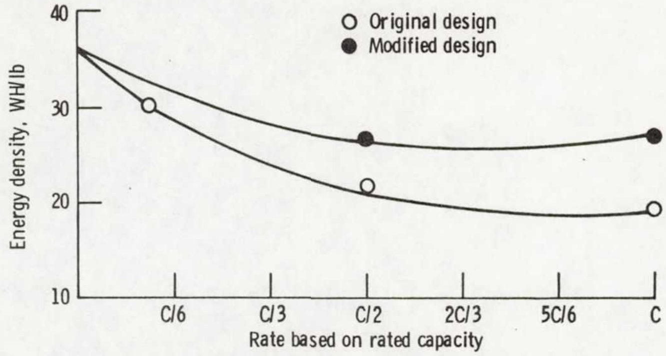

Figure 4. - Comparison of energy densities for cells of original and modified designs at room temperature. (C/2 and C rate discharges from which energy densities were calculated for modified design were run on different cells.)

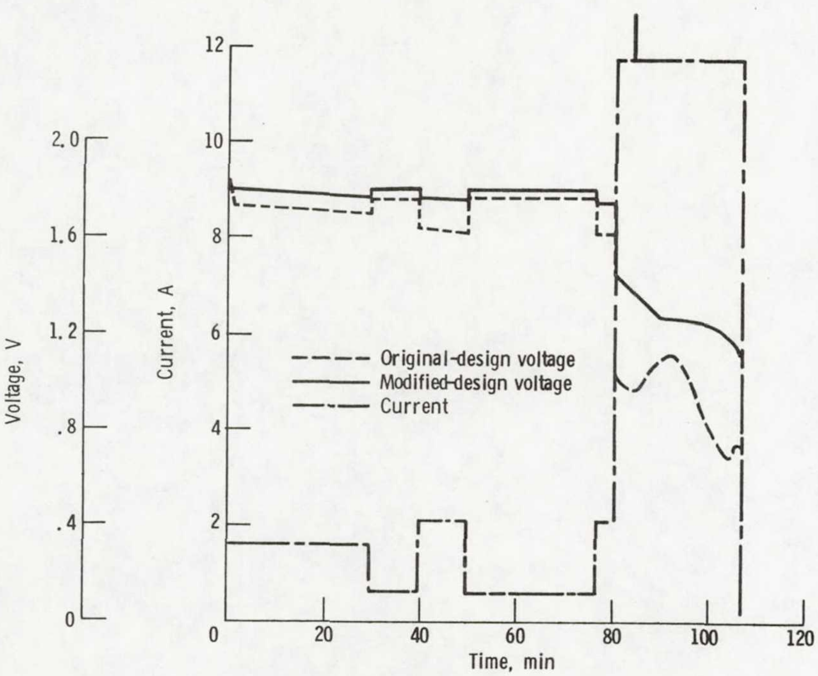

Figure 5. - Discharge profile at 0^{0} C.

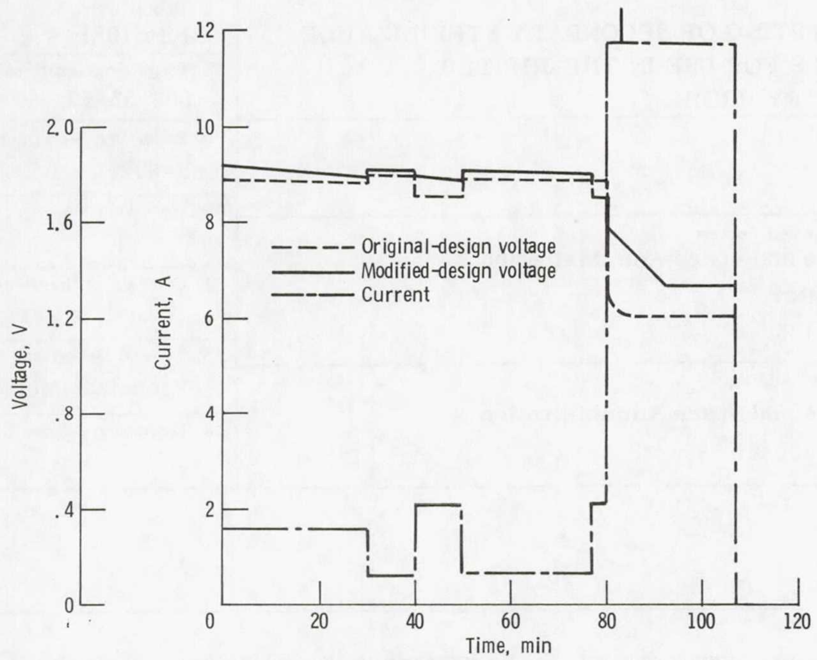

Figure 6. - Discharge profile at 10^0 C.

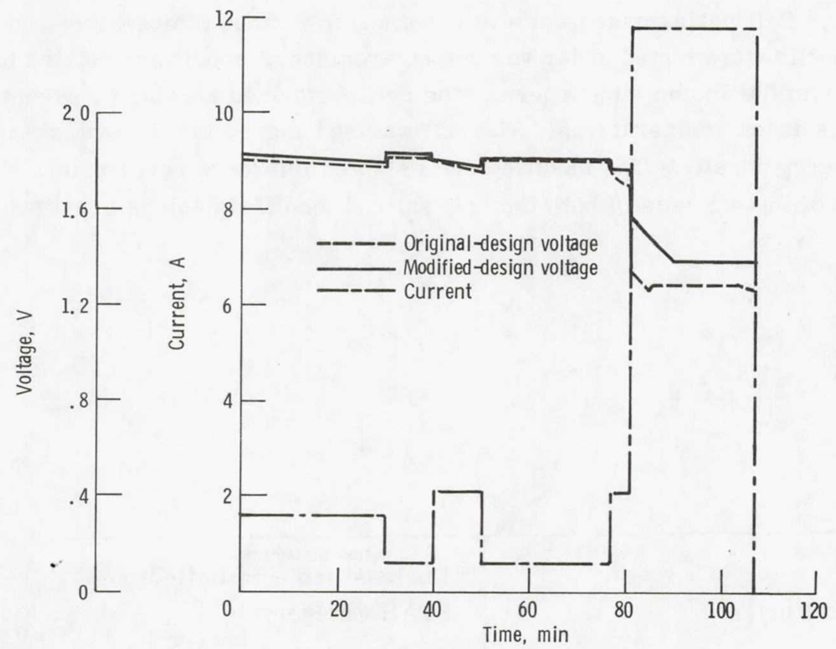

Figure 7. - Discharge profile at room temperature.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-82638		

4. Title and Subtitle	5. Report Date
QUALIFICATION TESTING OF SECONDARY STERILIZABLE SILVER-ZINC CELLS FOR USE IN THE JUPITER ATMOSPHERIC ENTRY PROBE	July 1981
	6. Performing Organization Code 506-55-52
7. Author(s) Michelle A. Manzo	8. Performing Organization Report No. E-893
	10. Work Unit No.
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135	11. Contract or Grant No.
	13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

A series of qualification tests were run on the secondary, sterilizable silver oxide - zinc cell developed at the NASA Lewis Research Center to determine if the cell was capable of providing mission power requirements for the Jupiter atmospheric entry probe. The cells were tested for their ability to survive radiation at the levels predicted for the Jovian atmosphere with no loss of performance. Cell performance was evaluated under various temperature and loading conditions, and the cells were tested under various environmental conditions related to launch and to deceleration into the Jovian atmosphere. The cell performed acceptably except under the required loadings at low temperatures. The cell was redesigned to improve low-temperature performance and energy density. The modified cells showed improved performance at all temperatures. Results of testing cells of both the original and modified designs are discussed.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Alkaline batteries Silver oxide - zinc batteries	Unclassified - unlimited STAR Category 44

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified		

* For sale by the National Technical Information Service, Springfield, Virginia 22161

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