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EFFECTS OF FREEZING ON PRIMARY SILVER OXIDE – ZINC CELLS

by Richard E. Johnson

Lewis Research Center

Cleveland, Ohio

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ABSTRACT

An investigation was conducted to determine the effects of freezing on primary silver oxide - zinc cells. Three freezing rates of 4.77° F/min (2.66 K/min), 0.81° F/min (0.45 K/min) and 0.19° F/min (0.10 K/min) were used. In addition, some cells underwent a slow (28-day) freeze-thaw cycle to -50° F (227 K). No harmful effects were noted, either to the cell itself or its performance.

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SUMMARY

An investigation was conducted to determine the effects of freezing on primary silver oxide - zinc cells. Cells were subjected to various freezing rates and then discharged after being returned to room temperature. Three freezing rates of 4.77° F/min (2.66 K/min), 0.81° F/min (0.45 K/min), and 0.19° F/min (0.10 K/min) were used. In addition, several cells underwent a slow (28-day) freeze-thaw cycle to -50° F (227 K). Voltage, current and cell capacity measurements were made before and after freezing. Microscopic examinations were made of the cell parts. No harmful effects were noted either to the cell itself or its performance.

INTRODUCTION

On October 15, 1967, the batteries of the Surveyor 5 started to deliver current on the Moon after 3 weeks of silence. The cells had retained enough charge through the cold lunar night to permit radio transmission. This event raised questions as to what damage such exposure might cause to the cells, and how much usable capacity still remains after freezing and thawing. Therefore, a program was initiated to determine the effects of freezing on primary zinc - silver oxide cells. The first part of the program investigated three freeze rates, 4.77° F/min (2.66 K/min) 0.81° F/min (0.45 K/min), and 0.19° F/min (0.10 K/min). The second phase dealt with a slow (28-day) freeze-thaw cycle using -50° F (227 K) as the minimum exposure temperature.

First, a number of cells was discharged at room temperature to establish control points for the data. Next, identical cells were activated, then frozen at various rates to determine if the rate of freezing would in any way effect cell structure or performance. A cell was also frozen and thawed 3 times between each electrical test cycle to try to force any structural changes which might be occurring on a small scale to be more apparent.

The objective of the program was to define qualitatively whether damage occurs to cells during the process of freezing and subsequent thawing.

APPARATUS AND PROCEDURE

The tests were performed on a production lot of 20 Yardney PM-5 (primary, manually activated 5 amp-hr) silver oxide - zinc cells. These cells were received in a dry-charged state and stored in a refrigerator until ready for use. This procedure is claimed by the manufacturer to extend the unactivated stand time of the cells to more than a year. In general, 24 hours was the maximum activated stand time required in this program. The cells are rated for 5 ampere-hours but at the current drains used in this program delivered up to 9 ampere-hours. Although they are designated as primary cells, they can be recharged five or more times.

The refrigeration equipment used consisted of a 3-stage 6-cubic-foot freezing unit capable of reaching temperatures as low as -140° F (177 K). The freezer was equipped with a temperature controller which permitted the desired temperature to be held within $\pm 2^{\circ}$ F.

Voltage measurements were recorded by instruments accurate to 0.01 volts. Current was measured with ammeters accurate to 0.005 amperes. Cell discharges were performed using a fixed resistance. A research microscope was used for examining the cells. The magnifications used were 50 to 200 power.

Three cooling rates were investigated, 4.77° F/min (2.66 K/min), 0.81° F/min (0.45 K/min), and 0.19° F/min (0.10 K/min). Three cells were tested at each rate. In general, the first cell was tested through 5 discharge-charge cycles, while the remaining cells were run for 3 to 4 cycles to confirm the result.

The procedure for testing was as follows. Dry-charged cells were activated by removing the vent plug and injecting electrolyte into the cell from a plastic squeeze bottle. Excess electrolyte was removed from around the vent port. After filling, the cell was allowed to soak for 24 hours to ensure penetration of the electrolyte into all parts. The cell was then placed in the deep freeze and its temperature lowered at the desired rate. After freezing, the cells were warmed by standing for 16 hours at room temperature. Next, the cells were discharged through a constant-resistance load, the voltage being automatically recorded and the current visually monitored throughout the discharge of the cell. After discharge the cells were placed on charge for 24 hours at the manufacturer's recommended charge rate of 0.35 amperes. The above procedure was then repeated for the desired number of cycles.

For the 4.77° F/min (2.66 K/min) freezing rate tests, the temperature of the freezer was preset to -140° F (177 K) and then the cell was placed inside. After 45 minutes the cell was removed from the freezer and allowed to stand at room temperture for 16 hours to ensure a complete thaw. Calculations for determination of the freezing rates are included with the data at the close of the report.

For the 0.81° F/min (0.45 K/min) rate tests, the cell was placed in the freezer at room temperature and the freezer was cooled to -120° F (189 K) by placing the control setting at that temperature. This process took 4 hours. For the 0.19° F/min (0.10 K/min) rate tests, the procedure was somewhat different in that the freezer temperature was lowered in 4 distinct steps. First the temperature of the freezer was lowered to 32° F (273 K) and held for 4 hours, then the procedure was repeated to -13° F (249 K) and finally -103° F (197 K) for 4 hours.

In a final series of tests, an effort was made to simulate the conditions which might be seen by a poorly insulated battery on the Moon's surface. This was accomplished by starting at room temperature and lowering the battery's temperature 10° F (5.6 K) each day for 12 days until an arbitrarily selected -50° F (227 K) had been reached. The batteries were held for 4 days at this temperature, and then raised 10° F (5.6 K) per day for 12 days until room temperature was reached. The cells were removed from the freezer, warmed, and discharged. The results were compared with control cells which had been activated and allowed to stand at room temperature for 28 days and then discharged.

RESULTS AND DISCUSSION

The experimental results are listed in table I. The results indicate that, based on electrical performance, no damage to the cells resulted from freezing at any of the rates tested. No significant loss of capacity occurred due to freezing. Charge-discharge efficiencies were high for several operating cycles after low temperature exposure.

One fact that might be mentioned in connection with the freezing rates is that at the fast freeze rate there was a strong tendency for the electrolyte to supercool. For cells cooled at the 0.19° F/min (0.10 K/min) rate or less, supercooling never occurred. However, no differences in performance were detected between cells in which the electrolyte solidified and those in which supercooling occurred.

In a further effort to ascertain whether physical damage was occurring due to freezing of the cells, microscopic examinations (50 to 200 power) were made of several randomly selected cells as received from the manufacturer. The cells were cut open in the dry state and examined. The same procedure was also used for some cells which had been tested for two cycles. The electrolyte was drained off, the cells were opened, and microscopic examinations showed no observable difference between those examined after freezing compared to cells examined as received from the manufacturer.

Following is a series of notes regarding variations in test procedures or abnormalities in performance which were observed. In cell number 6, cycles 3 and 4 were conducted after an activated stand time of two months following cycle 2. No variation in performance was noted. On cycle 3 of the same test, the recorder failed after 3.7 ampere-hours had been discharged from the cell; however, the excellent performance of the cell in cycle 4 indicated that the cell coulombic efficiency must have been between 95 and 98 percent in the previous cycle.

Cell number 7 was frozen three times between each of the three electrical cycles; nevertheless, the performance indicated no adverse changes had taken place in the cell. This test was made when it became apparent that freezing the cells was producing no significant changes, and it was decided to see if some failure could be induced by freezing a cell several times between each charge-discharge cycle.

On cycle number 1, cell number 12 was somewhat lower in output than the other cells. This is impossible to explain on the basis of differences in the treatment of the cell. Therefore, it is concluded that this is simply a manufacturing deviation.

The last series of tests which are listed in table II was an attempt to simulate the variation in temperature which might be experienced by a poorly insulated battery on the lunar surface. As can be seen from the results, no harmful effects were observed.

CONCLUSIONS

1. No damage to the cells as a whole or in part could be found by freezing at any of the rates tested.

2. Microscopic examinations showed no damage to the physical structure of the cells after freezing.

3. On cycling the cells after freezing, the coulombic efficiency never fell below 95 percent on the first three cycles.

4. Supercooling of the electrolyte occurs occasionally in cells frozen at 4.77° F/min (2.66 K/min) rate. It was not observed in cells frozen at the 0.19° F/min (0.10 K/min) rate.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 15, 1968,
124-34-01-09-22.

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TABLE I. - EFFECT OF FREEZING

Cell	Freeze data	Cycle 1				Cycle 2			
		Closed-circuit voltage, V	Discharge current, A	Ampere-hours delivered	Input, (A)(hr)	Closed-circuit voltage, V	Discharge current, A	Ampere hours delivered	Coulombic efficiency, percent
1	Control	1.53	1.60	8.08	4.95	1.56	1.60	4.80	97.0
2	Control	1.54	1.50	8.75	4.80	1.57	1.50	4.74	98.7
3	Control	1.54	1.50	9.00	4.80	1.56	1.50	4.80	100
4	4-hr freeze	1.56	1.60	8.66	4.62	1.57	1.50	4.51	97.8
5	4-hr freeze	1.55	1.55	8.66	4.85	1.56	1.55	4.77	98.5
6	4-hr freeze	1.52	1.60	8.16	4.80	1.56	1.52	4.71	98.5
7	[a]45-min freeze	1.54	1.50	9.00	5.60	1.56	1.50	5.30	94.5
8	45-min freeze	1.53	1.50	8.75	4.80	1.56	1.50	4.68	97.4
9	45-min freeze	1.52	1.57	9.42	4.80	1.56	1.59	4.70	97.9
10	45-min freeze	1.53	1.55	8.53	4.80	1.52	1.45	4.64	96.5
11	16-hr freeze	1.56	1.49	8.94	4.75	1.56	1.50	4.59	96.5
12	16-hr freeze	1.53	1.43	7.55	4.80	1.53	1.50	[a]3.80	-----

[a]Frozen 3 times each cycle.
[b]Recorder failed.
[c]1 week stand.

ɪATE ON CELL PERFORMANCE

Cycle 3					Cycle 4					Cycle 5
Input, (A)(hr)	Closed-circuit voltage, V	Discharge current, A	Ampere-hours delivered	Coulombic efficiency, percent	Input, (A)(hr)	Closed-circuit voltage, V	Discharge current, A	Ampere hours delivered	Coulombic efficiency, percent	
4.95	1.56	1.50	4.87	98.3	4.90	1.56	1.50	4.80	98.0	--------
4.95	1.57	1.50	4.80	97.2	----	----	----	----	----	--------
4.80	1.56	1.50	4.76	99.2	5.00	1.55	1.50	4.38	87.6	--------
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4.80	1.56	1.50	[b]3.70	----	3.60	1.55	1.47	3.42	95.0	--------
4.80	1.55	1.50	4.60	95.8	----	----	----	----	----	--------
4.80	1.56	1.41	4.60	95.6	----	----	----	----	----	--------
4.80	1.56	1.54	4.77	99.3	4.80	1.56	1.60	4.71	98.4	Same as cycle 4
4.80	1.54	1.50	4.10	[c]85.3	----	----	----	----	----	--------
4.75	1.55	1.50	4.13	87.0	----	----	----	----	----	--------
6.00	1.56	1.42	5.68	95.0	----	----	----	----	----	--------

TABLE II. - CELL DISCHARGE DATA 28-DAY

FREEZING CYCLE

Cell number	Closed-circuit voltage, V	Discharge current, A	Discharge time, hr	Ampere hours delivered
1 Control	1.50	2.70	3.25	8.76
2 Control	1.51	2.85	2.85	8.12
3 Control	1.51	2.80	2.92	8.16
4	1.51	2.75	3.08	8.45
5	1.50	2.85	2.80	7.97
6	1.51	2.84	2.70	7.67

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— NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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