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EFFECTS OF LONG TERM STORAGE ON AEROSPACE NICKEL–CADMIUM CELL PERFORMANCE

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Summary

A study currently being performed at NASA/Goddard Space Flight Center (GSFC) to evaluate the long term effects of storage on aerospace nickel–cadmium cells is described. A number of 6 A h and 12 A h capacity cells which have been stored in shorted condition for 9 - 11 years at the GSFC have been selected for this study. Of the three tests which have been initiated (initial and final destructive analyses of the test cells, GSFC electrical characterization tests, and life cycling tests) only the GSFC electrical characterization tests have been completed; other tests were scheduled to have been completed by February, 1987. The preliminary electrical performance data from the life cycling test, and chemical composition data from the destructive testing, indicate no anomalous behavior.

Introduction

Investigation of long term storage effects on aerospace nickel–cadmium cell performance is an important topic but it has generated little interest. Although many works have been published on the performance of nickel–cadmium cells, relatively few studies have addressed the effects of prolonged storage of these cells.

This topic is especially important to NASA because we are interested in the reliability of a cell which has been stored for an extended period of time after activation. Cells for a flight project are procured, tested, made into battery packs, and placed in cold storage well in advance of the launch date. Inevitably, because of launch delays, the question of cell reliability as a function of storage time is often asked. Originally NASA/Goddard Space Flight Center (GSFC) placed an arbitrary 18 months age limit on nickel–cadmium cells held in storage for a spacecraft launch; this limit was later extended to 24 - 36 months. At present we at GSFC prefer not to store cells for more than 3 - 4 years after activation prior to the launch date, although there are data supporting storage periods of up to 5 years. With more studies

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on the topic of storage effects we may be able to extend our storage time limit.

A number of studies have addressed the issue of the long term storage effects on nickel–cadmium cells [1 - 13]. Bogner who tested the cells after a 6 month storage at 10 °C reported that the capacity of the cell packs was as good, or better, after storage [2]. Scott has studied the effects of storing batteries, which were shorted and stored at 5 - 10 °C, over a 4 year period. He found no appreciable adverse effect over this time frame and he suggested that the batteries can be stored for up to 5 years when the cells are shorted, and at a fairly low temperature [3]. Similarly, Stanley reported that shorted storage has proved to be effective for up to 5 years without significant degradation [4]. Thierfelder *et al.* reported that the swelling of the positive plates and the decrease in overcharge protection are found to be the life limiting characteristics during prolonged storage [5]. They recommended a maximum cell age of 3.5 years at the time of spacecraft launch for a 7.5 year mission. Brahim *et al.* found that the cells retained a significant efficiency after 5 years of storage [6]. Hobbs *et al.*, however, based on their initial data, suggest that storage effects will constitute a major problem [7]. They later reported reductions in capacity between 1% and 75% after a 3 year storage period depending on the cell model, storage temperature, and storage time [8]. It should be pointed out that the nickel–cadmium cells studied by Brahim *et al.* and Hobbs *et al.* were of commercial grade, not of aerospace quality.

Most of the aerospace cells used in the above studies were manufactured in the 1960s, whereas the cells used in this study were manufactured in the 1970s. The cells used in this study resemble the present day nickel–cadmium cells in characteristics and construction more closely than most of the cells used in the cited studies. Because the cells used in this study were fabricated at a later date, these cells have been manufactured under refined process and improved quality control. Cells used for this study have been manufactured and tested adhering closely to NASA/GSFC specifications [14].

This study was initiated to investigate the effects of long term storage on aerospace nickel–cadmium cells based on electrical acceptance testing, simulated flight conditions in both real time and accelerated time, and destructive analysis. The cells selected for this study have been stored at room temperature under shorted conditions in the laboratory at GSFC for 9 - 11 years. The results from the study will be compared with previous data on these cells: namely, from the initial acceptance data at GSFC, and from the life cycling data on cells from the same lot at the NASA Battery Facility at the Naval Weapons Support Center (NWSC) in Crane, IN. We have selected General Electric (G.E.) 6 A h and 12 A h nickel–cadmium cells for this study because of their relative abundance at NASA, and also because of the availability of their acceptance test data and NWSC life-cycling data. Specific information on these cells is mentioned elsewhere [15 - 20]. The test plans along with the preliminary data were first presented at the 1985 NASA/GSFC Battery Workshop [21, 22].

Test description

For this study, twelve cells were selected from each of the IUE (International Ultraviolet Explorer satellite) 6 A h and 12 A h cell lots at GSFC. Of the 12 cells within a lot, 2 cells underwent destructive analysis at Bowie State College in Bowie, MD following NASA procedures [23]. The remaining 10 cells from each lot were fabricated into two 5-cell packs, one of which was tested at GSFC and the other at NWSC. The steps in the GSFC electrical characterization test are outlined in Table 1. The operating parameters of the NWSC life testing packs are listed in Table 2. The 6 A h test pack is currently undergoing accelerated geosynchronous orbit cycling (GEO), whereas the 12 A h pack is operating at real time low earth orbit (LEO) cycling. These test parameters were deliberately chosen to operate under the same operating conditions as pack 231A for the 6 A h pack, and pack 8G for the 12 A h pack at NWSC [24 - 31]. The specifics of the GSFC and NWSC tests were reported at the 1985 NASA/GSFC Battery Workshop and are available elsewhere [21, 22].

Results and discussion

Only those tests at GSFC have been completed at this time. Therefore, the majority of the discussion will be on the results from those tests.

GSFC electrical characterization tests

Electrical characterization tests as outlined in the Test Description section of Table 1 have been completed on the selected G.E. 6 A h and 12 A h cells. Figures 1 and 2 compare cell capacities at different charge rates and temperatures for the 6 A h and 12 A h cells, respectively. The preliminary indication is that both the 6 A h and 12 A h cells have increased their cell capacities after 9 - 11 years of storage. Moreover, both the cell and third electrode voltages at end-of-charge (EOC) have either remained the same or have increased after the storage period.

The observation that cell capacities increase with storage time is of great concern. Although such observations have been reported by Bogner [2], it is generally believed that cells degrade over a long length of time, principally by degradation of the separator material, nylon. Real time synchronous orbit tests and some LEO tests have shown a gradual increase in the cell capacities during the early cycles of life testing. Such increases may result either from incomplete formation of the positive plates during cell manufacture or from inadequate active "excess charged" negative capacity at the beginning-of-cycling [32]. Scott found that a very large amount of the change is introduced during acceptance testing, and that very little additional changes occur during shorted storage [11]. The tested nickel–cadmium cells have been stored in the shorted state after some 30 cycles of testing in the original acceptance test. These two ideas suggest that

TABLE 1

Steps used in the GSFC electrical characterization tests

Sequence number	Test condition number	Test description	Temperature (°C)	Current	Voltage limits		Test duration (h)	
					Upper limit (V)	Lower limit (V)	Specified	Estimated
1	1	Conditioning charge	25	$C/20$	1.51	0.80	48	—
2	2	Conditioning discharge	25	$C/2$	1.51	0.80	—	3
		Resistive drain	25	—	—	—	—	2
3	3	Conditioning charge	25	$C/10$	1.51	0.80	24	—
4	2	Conditioning discharge	25	$C/2$	1.51	0.80	—	3
		Resistive drain/ temperature stabilization	20	—		—	—	2
5	4	Capacity charge	20	$C/10$	1.51	0.80	24	—
6	5	Capacity discharge	20	$C/2$	1.51	0.80	—	3
		Resistive drain	20	—	—	—	16	—
7	6	Charge retention — open circuit	20	—	—	—	24	—
		Resistive drain temperature stabilization	10	—	—	—	—	2
8	7	Capacity charge	10	$C/20$	1.53	0.80	48	—
9	8	Capacity discharge	10	$C/2$	1.53	0.80	—	3
		Resistive drain/ temperature stabilization	0	—	—	—	—	2
10	9	Overcharge charge	0	$C/20$	1.53	0.80	72	—
11	10	Overcharge discharge	0	$C/2$	1.53	0.80	—	3
		Resistive drain/ temperature stabilization	10	—	—	—	—	2
12	11	Burn-in charge #1	10	$C/20$	1.53	0.80	23	—
13	12	Burn-in discharge #1	10	$C/2$	1.53	0.80	1	—
14	11	Burn-in charge #2	10	$C/20$	1.53	0.80	23	—
15	12	Burn-in discharge #2	10	$C/2$	1.53	0.80	1	—

16	11	Burn-in charge #3	10	*C*/20	1.53	0.80	23	—
17	12	Burn-in discharge #3	10	*C*/2	1.53	0.80	1	—
18	11	Burn-in charge #4	10	*C*/20	1.53	0.80	23	—
19	12	Burn-in discharge #4	10	*C*/2	1.53	0.80	1	—
20	11	Burn-in charge #5	10	*C*/20	1.53	0.80	23	—
21	12	Burn-in discharge #5	10	*C*/2	1.53	0.80	1	—
22	11	Burn-in charge #6	10	*C*/20	1.53	0.80	23	—
23	12	Burn-in discharge #6	10	*C*/2	1.53	0.80	1	—
24	11	Burn-in charge #7	10	*C*/20	1.53	0.80	23	—
25	12	Burn-in discharge #7	10	*C*/20	1.53	0.80	1	—
26	11	Burn-in charge #8	10	*C*/20	1.53	0.80	23	—
27	13	Burn-in capacity discharge	10	*C*/2	1.53	0.80	1	—
		Resistive drain/ temperature stabilization	20	—	—	—	—	2
28	4	Capacity charge	20	*C*/10	1.51	0.80	24	—
29	5	Capacity discharge	20	*C*/2	1.51	0.80	—	3
		Resistive drain	20	—	—	—	—	2

TABLE 2

Operating parameters for NWSC life test packs

	6 A h pack	12 A h pack
Life cycling regime	GEO	LEO
Duration (year, real time)	1	1
Temperature (°C)	10	0
Depth-of-discharge (%)	80	40
Orbit	25 day eclipse	90 min
Charge	$C/10$	$C/1.25$
Discharge	$C/1.5$ (eclipse)	$C/1.25$

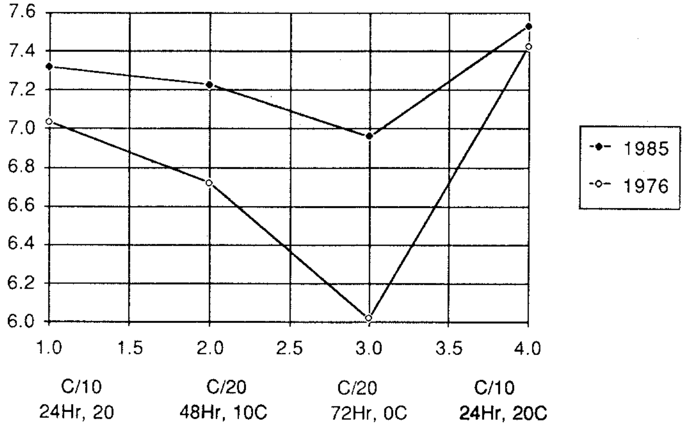

Fig. 1. Comparison of 6 A h cell capacities.

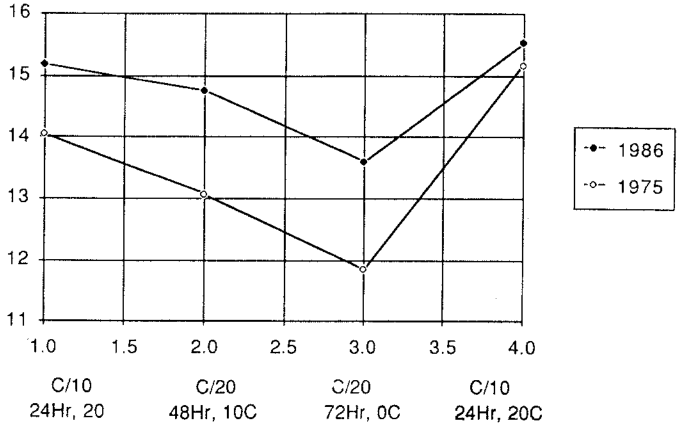

Fig. 2. Comparison of 12 A h cell capacities.

the tested IUE cells are more affected by the GSFC electrical characterization test than by storage. If so, the tested IUE cells may exhibit a slight increase in their cell capacities at beginning-of-life (BOL); we must wait until the life tests are completed to draw any conclusion.

All the 6 A h cells have met the performance specification as outlined in the Cell Acceptance Test Plan [33, 34]. From Fig. 1 it is noted that for either test date, the generally observed cell behavior is that cell capacity increases with cycling time and that the lowest capacity is seen during the overcharge test where the temperature is at 0 °C. For the 12 A h cells, similar behavior was noted (see Fig. 2). Nearly all the plots from the GSFC electrical characterization tests of cell voltage *versus* time and of third electrode voltage *versus* time, exhibited normal cell characteristics.

The third electrode voltage plots for one cell (S/N 014) among the 6 A h cells displayed abnormal behavior, however. This particular cell showed no change in the third electrode voltage for the discharge portion during the second capacity check and during the overcharge test (see Figs. 3 and 4, respectively). For the charge portions of the second capacity check and the overcharge test, the third electrode voltage did not change until the cell was fully charged (see Figs. 5 and 6, respectively). Such behavior for both the charge and the discharge periods are observed in neither the first capacity check nor in the subsequent capacity check or burn-in cycles.

This anomalous behavior of the third electrode is not a cause for alarm. The third electrode voltage is an "unpredictable" parameter. Baer reported that during his testing of the IUE cells, the third electrode voltage test data revealed a very high degree of nonuniformity [20]. His finding was in accord with Scott and Rusta [32] who stated that from the life cycling data and from flight experience the third electrode performance is not reliable over long periods of time. In any case, the third electrode was not utilized to control charge and discharge but rather to provide additional data.

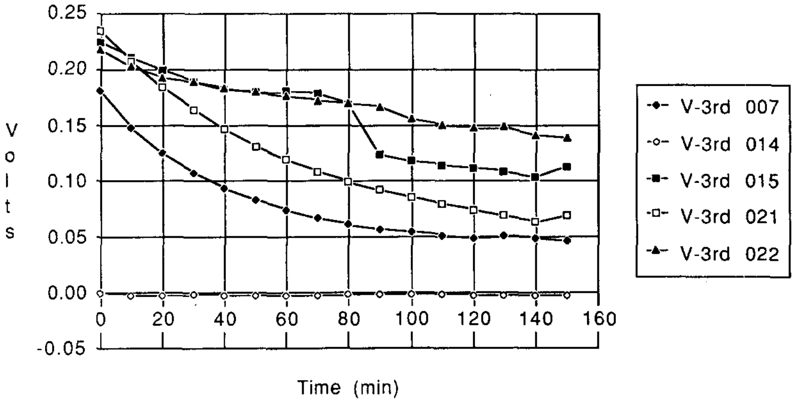

Fig. 3. 3rd Electrode voltage during capacity discharge #2 of 6 A h cells at $C/2$, $T = 10$ °C, Year = 1986.

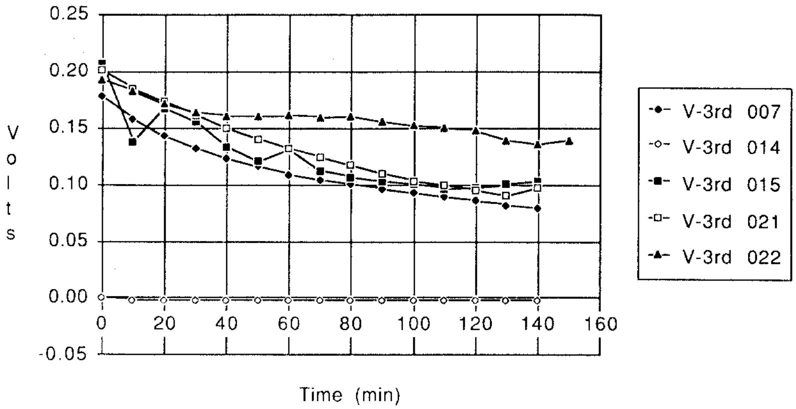

Fig. 4. 3rd Electrode voltage during overcharge of 6 A h cells at $C/2$, $T = 0$ °C, Year = 1986.

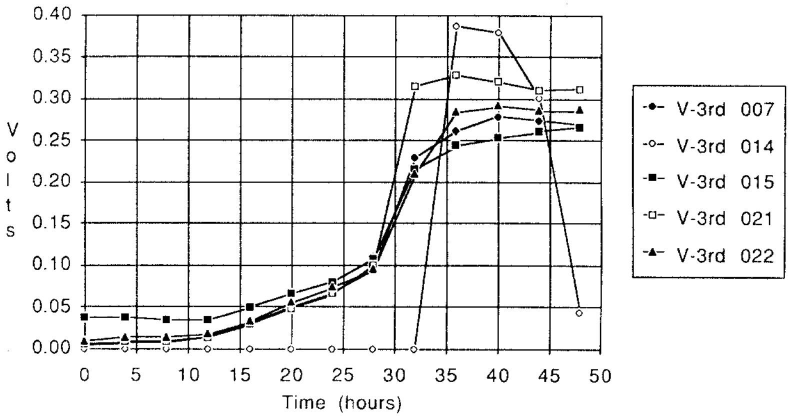

Fig. 5. 3rd Electrode voltage during capacity charge #2 of 6 A h cells at $C/20$, $T = 10$ °C, Year = 1986.

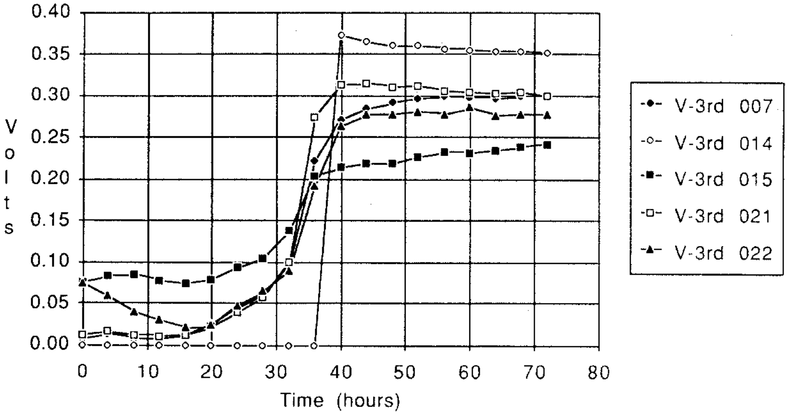

Fig. 6. 3rd Electrode voltage on extended overcharge of 6 A h cells at $C/20$, $T = 0$ °C, Year = 1986.

NWSC life tests

Life tests for both the 6 A h pack and the 12 A h pack were scheduled for completion by February, 1987. As of November, 1986, the 6 A h pack, which is labelled pack 231C at NWSC, has undergone 9 accelerated shadow periods; the 12 A h pack, which is labelled 8I, has undergone about 5000 LEO cycles. The data from NWSC on packs 231C and 8I are plotted in Figs. 7 and 8, respectively. In Fig. 7, pack 231C has completed its eighth shadow period, *i.e.*, equivalent to 4 years of synchronous cycling. The plot of cell capacity for pack 231C is shown in Fig. 9; the cells have not lost any capacity after eight shadow periods. In Fig. 8, pack 8I has completed 4552 LEO cycles. These plots exhibit normal cell characteristics.

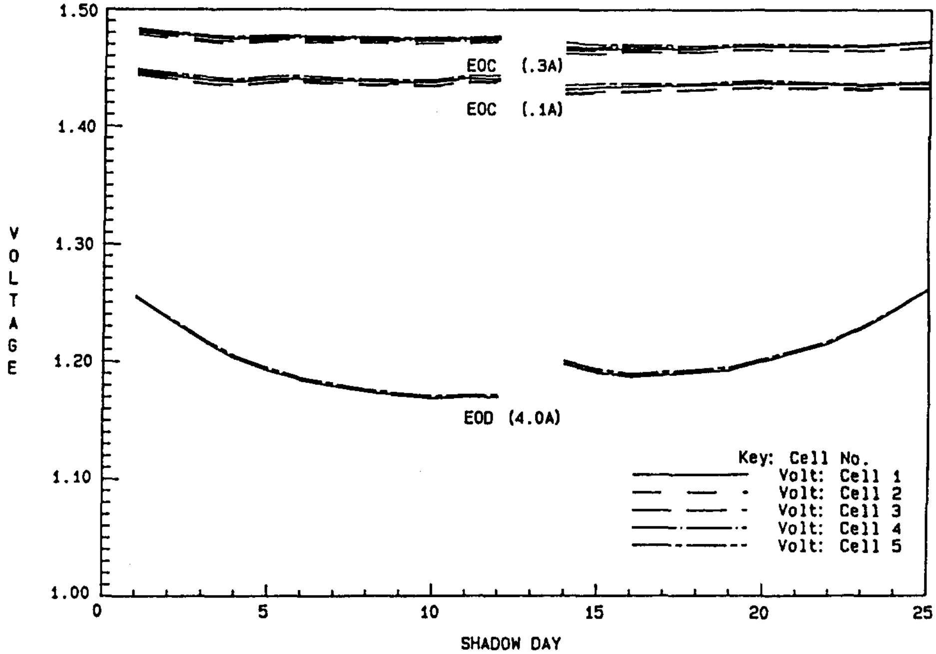

Fig. 7. Pack #231C: accelerated GEO life cycled at NWSC. Pack: 231C; Manf: GE; 6 A h; shadow #8 — cell voltage *vs.* day; cycles: 259 - 283; Temp. (°C): 10; DOD (%): 80; Chg. 0.5 A till 100% return, then 0.3 A for 3 h then 0.1 A to EOC. CX (prior to day 13 every 4th shadow — cells 1 thru 5).

Destructive analyses

At the beginning of this study, four cells were sent to Bowie State College, MD, for destructive analysis; the test analyses show no anomalies. Eight more cells will undergo destructive analysis once the NWSC tests on the cells are completed.

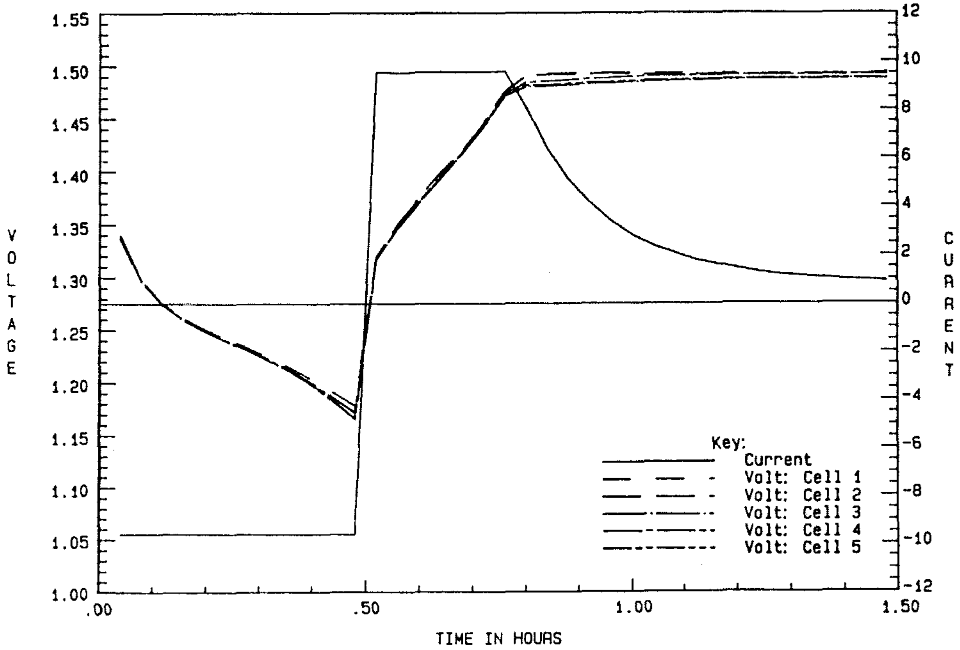

Fig. 8. Pack #8I: LEO life cycled at NWSC. Pack: 8I, Manf: GE; 12 A h; cycle 4552; Orbit: LEO; Temp. (°C): 0; DOD (%): 40; GSFC Vt. Level: 7; voltage limit (v/c): 1.490; Time to Vt. limit (h): #; discharge (amp/h): 9.6/0.48; charge (A/h): 9.6/1.00; A h out: 4.615; A h in: 4.711; C/D ratio: 1.021 EOC (I): 0.90.

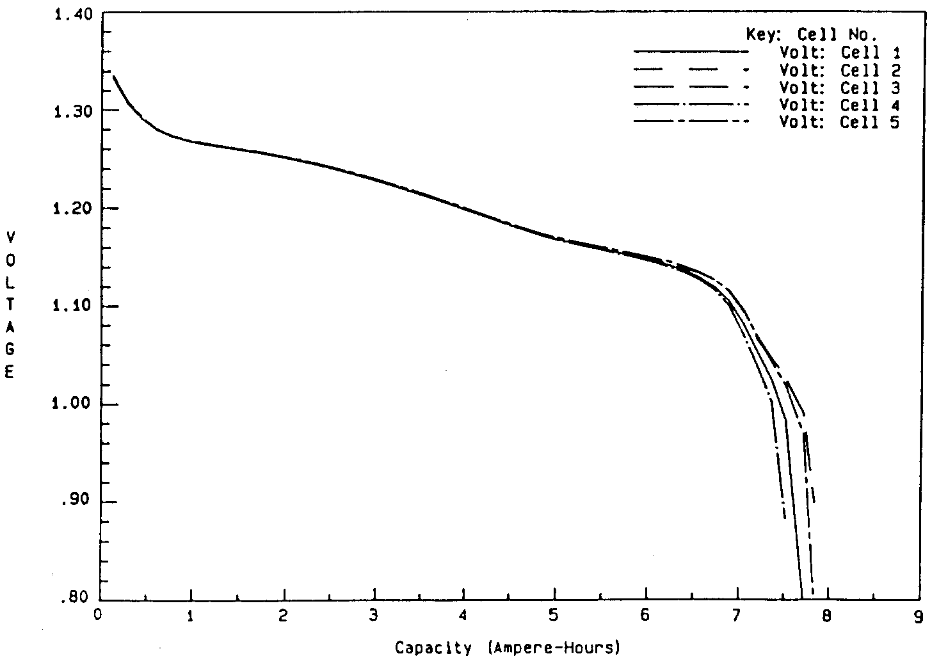

Fig. 9. Pack #231C: capacity check during the eighth shadow period. IUE Pack: 231C; Manf: GE; 6 A h; capacity check — Shadow #8; cycle: 271; temp (°C): 10; rate (A): 4.0; Note: Follows 12th day of shadow period.

Conclusion

This study was initiated to understand better the effects of long term storage on nickel–cadmium cells. The selected cells have passed the GSFC electrical characterization tests; they have been life tested for over 5000 LEO cycles and 9 accelerated GEO shadow periods without failure. Because the tests are still ongoing, no conclusions will be drawn.

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