

Effect of Storage on Performance of Super Nickel-cadmium Cells

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ABSTRACT

A study was undertaken to examine the capacity maintenance features of SUPER nickel-cadmium cells when stored for extended periods to determine whether the features change when the same kinds of positive plates as that used in nickel-hydrogen cells are used. The cells maintained their capacity when stored at 0°C in the discharged state and at 0°C in the charged state by continuously trickle charging. There was a capacity loss when stored in the open-circuit condition at 28°C. A cycling test at 17% depth of discharge for 2400 cycles using cells stored at various conditions showed that cells maintained good end of discharge voltage regardless of their storage history. However, the EOD voltages of stored cells were lower by 10 mV compared to those of fresh cells. The capacity at the end of the cycling test decreased for the stored cells by 2-7 Ah. The storage related capacity loss is lower for SUPER Ni-Cd cells compared to that of Ni-H₂ cells containing a hydrogen precharge. The results suggest the pivotal role of hydrogen pressure in the capacity loss phenomenon.

INTRODUCTION

The nickel-cadmium battery, introduced in the late mid-sixties as the energy storage device in orbiting satellites has steadily evolved into a reliable power source with excellent voltage maintenance with cycling. This battery has been extensively studied and matters relating to electrode reactions, overcharge and overdischarge, capacity balance between the electrodes, precharge, overcharge protection, electrolyte content and pulse behavior are better understood. However, several questions have arisen in the recent past about capacity stability with cycling, high end of charge voltages and capacity loss when stored for extended periods. The capacity loss phenomenon with extended storage has drawn the attention of the aerospace industry since the battery is expected to be capable of storage for 60 months after fabrication so that launch delays could be accommodated. A related issue is the capacity recovery technique studied by various organizations. There is agreement among various researchers that the capacity loss phenomenon is attributable to the nickel hydroxide positive plates, although, opinions differ about the capacity

fade mechanism. Capacity fading in nickel-hydrogen cells is attributed to cobalt by Zimmerman (1), dehydration by Vaidyanathan (2,3), and platinum hydroxide by Whitely (4).

The capacity fade phenomenon first surfaced in 1986 for nickel-hydrogen cells. Studies showed that cells with aqueous impregnated positive plates, alcohol impregnated positive plates, nickel pre-charge cells and hydrogen precharge cells are susceptible to capacity loss to varying degrees. Attempts to quantify the capacity fade has been unsuccessful since the loss is not a linear function of time and cells that exhibit capacity fading show poor reproducibility in the capacity values from one cycle to the next. Thus, the cells that do not show capacity fading in the beginning of life change their behavior after a combination of inactivity and cycling and vice versa. All this shows that it is difficult to predict capacity fading from looking at the storage conditions. The purpose of this study is to determine whether capacity fading occurs in SUPER Ni-Cd cells which contain electrochemically impregnated plates when stored at various temperatures and in the trickle charge mode. Another objective is to determine the cycling behavior of cells subjected to extended storage. The SUPER Ni-Cd cells contain positive plates similar in structure and composition to that used in Ni-H₂ cells and hence the results of this study would establish the role of hydrogen pressure in capacity fade phenomenon.

Cell Selection

The cells were selected from two different groups of cells manufactured for NASA-Goddard Space Flight center by Hughes/Eagle Picher and their design conformed to the general specifications for a SUPER Ni-Cd cell. The cells contain sintered and electrochemically impregnated positive plates using the alcohol process which are similar to those used in Ni-H₂ cells. The negative plates are sintered and electrochemically impregnated using the aqueous process. The first group of cells were rated at 20 Ah and the second at 50 Ah. Table 1 shows the design features of the cells.

Capacity loss at 0°C storage

A group of 3 cells was stored at 0°C in the discharged open-circuited condition for 30 days and another group of 2 for 60 days. The capacity and average voltage during discharge at 20°C at C/2 were compared before and after storage and are shown in Table 2. The first group after 30 days showed marginal changes in the capacity (to 1V) with one cell showing a small increase, while the total capacity increased 0.7-3%. The second group of cells showed an increase of 6-7.6% in the total capacity after 60 days but with a decrease of 1-2% in the capacity to 1V.

The mid-discharge voltages of the cells are included in Table 2 and they show that after the 30-day storage period the mid-discharge voltage increased by 4-7 mV and after the 60-day storage the increase was 1-8 mV. The changes observed in the capacity and voltage are marginal and the results suggest that the cells maintain their capacity and voltage when stored at 0°C.

Capacity loss in the trickle charge storage

Groups of 3 cells were charged at C/10 for 16 hours and then trickle charged at C/100 for 30 days at 0°C. Table 3 shows the initial capacity and the capacity after 30 days. There was a marginal loss of 1.3-2.7% in the capacity to 1 V and an increase of 2.3-5.3% in total capacity as a result of the trickle charge.

The same cells were then subjected to trickle charge storage for 60 days under the same conditions. Table 3 shows the capacity values after the storage. The cell capacity increased by 0.1 Ah for one of the cells and the other cells showed a marginal loss of 0.1 Ah to 1 V. The total capacity increased by 6-8%.

Table 3 also shows the mid-discharge voltages, which in the case of 30-day trickle charge increased by 3-7 mV. At the end of the 60-day trickle charge, the increase over the initial values was 1-6 mV. The results suggest that trickle charge storage is appropriate for these cells.

Capacity maintenance in a combined 0°C and trickle charge

A group of 5 cells was stored in the following sequence-trickle charge at 0°C for 30 days, open-circuit for 30 days at 0°C, trickle charge for 60 days at 0°C another group in the sequence-open-circuit at 0°C, trickle charge for 30 days at 0°C and open-circuit for 60 days at 0°C. The capacity maintenance values were compared. The capacity to 1 V decreased by 0.4-2.1% and the total capacity increased by 4-8%. The magnitude of change in the capacity to 1 V is not significant, therefore, a technique consisting of open-circuit storage followed by trickle charge or vice versa to store cells is also appropriate.

Capacity loss at 28° C storage

Two 50 Ah cells was stored at 28° C in the open circuit condition for 30 days and the capacity was determined. The cells were then stored for another 30 day at 28°C. The cell capacities were determined and values are shown in Table 5. After the first 30-days the cells showed losses in capacity (to 1V) at 0°,10° and 20° C. However, after the second 30-day storage both the cells showed a loss of 3.4 Ah in capacity in the 20°C test. In the 10°C and 0°C test one cell showed a decline of 0.8 Ah and the other cell showed a marginal increase. The results suggest that the cells are susceptible to capacity loss when stored at 28 C. The reversal of the trend after the first 30-day storage indicates the difficulty in generalizing the capacity loss phenomenon. The mid-discharge voltage showed an improvement for both the cells after the storage periods as shown in Table 5. The storage behavior of Ni-Cd cells at 28°C can be compared to that of nickel precharge and hydrogen precharge Ni-H₂ cells. An earlier study indicated that the 10°C capacity decreased by 23% in 52 days of storage for the nickel precharge cells and by 35% for the hydrogen precharge cells(2). The decline in the 20°C capacity obtained for the Ni-Cd cells is 5.7 % which is marginal when compared to that obtained for nickel-hydrogen cells. This observation brings forth the role of hydrogen pressure in the capacity fading mechanism. Since the cadmium electrode is believed to generate minute quantities of hydrogen that is a function of negative electrode structure, composition, temperature, KOH concentration and age, the Ni-Cd cells are not hydrogen free. Therefore, it is not the presence of hydrogen but it's quantity that is important in capacity fading.

Cycling behavior of cells stored at 0°,10° and 28° C

The initial capacity of 3 pairs of cells was determined first and then the cells were stored a pair at 0°C, another at 10°C and the third at 28°C. The storage sequence consisted of capacity discharge, resistive drain, storage in the open-circuit condition for 3- days, capacity determination, resistive discharge and finally storage for another 30 day. The cell capacities were again determined. A cycling test was started which mimics the load, temperature and charge profile for a low earth orbit satellite. The cells were cycled continuously at 17% depth of discharge with an overcharge of 7% in a regime consisting of discharge for 26 minutes at 20 A and charge at 16 A for 70 minutes. The cells maintained good discharge voltage and after 2379 cycles the value was 1.210-1.213 V for the end of discharge voltage as shown in Figure 1. There was no significant difference in the end of discharge voltage for the cells that showed a loss in capacity as result of storage at 28°C. It is possible that capacity recovery occurred for the cells stored at 28°C as a result of cycling. Figure 1 also includes the variation of end of discharge voltage for a group of fresh cells cycled at 25% depth of discharge. The end of discharge voltages of the fresh cells is higher by 10 mV at every cycle compared to the stored cells in spite of the fact that the depth of discharge is 25% as opposed to 17%. Thus, the storage has an effect on cycling behavior, but quantitatively the effect is marginal. The cell capacities were determined at the end of 2400 cycles and the results are

shown in Table 6. There was a capacity loss of 2-6 Ah for the cells. The cells stored at 28°C showed the maximum decline. The mid-discharge voltage during discharge at C/2 at 10°C was 1.229-1.239 V which represents no change in the behavior. Thus, the limited cycling test data suggests that there is some degradation as a result of storage but the effect of storage on cell performance is marginal. An extended cycling data on the stored cells is needed to verify this observation.

CONCLUSIONS

The results of the study on extended storage of SUPER nickel-cadmium cells suggest the following conclusions;

- cells maintain their capacity if stored at 0°C
- cells maintain their capacity if stored in the trickle charge mode at 0°C
- There is a capacity loss if stored at 28°C, but the decline is marginal compared to that obtained in Ni-H₂ cells, thereby indicating the increased susceptibility of the positive plates to exhibit capacity fading when hydrogen pressure is high.
- Cells stored for 2 months when cycled show marginal decrease in the end of discharge voltage and capacity

REFERENCES

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TABLE 1: CELL DESIGN FEATURES OF THE SUPER Ni-Cd CELLS

Components	Parameters
Rated Capacity	21 Ah and 50 Ah
Activation Date	21 Ah-Spring 1995 50 Ah-Fall 1994
Interelectrode spacing	approximately 10 mils
Electrolyte	31 % KOH-Theoretical approx. 24 % KOH-actual approx. 10 % K ₂ CO ₃ -actual
Separator	Zircar separator coated with PBI
Positive Plates	Alcoholic electrochemically deposited approx. 1.3 g active Ni/cc void volume approx. 100 % plate utilization
Negative Plates	Aqueous electrochemically deposited approx. 12 g Cd/dm ² approx. 70 % plate utilization

TABLE 2: OPEN CIRCUIT 0°C STORAGE- CAPACITIES

ITEM	S/N 38		S/N 45		S/N 58		S/N 66		S/N 79	
	Capacity (Ah) 1.0 V	Mid-DV	Capacity (Ah) 1.0 V	Mid-DV	Capacity (Ah) 1.0 V	Mid-DV	Capacity (Ah) 1.0 V	Mid-DV	Capacity (Ah) 1.0 V	Mid-DV
before	22.9	26.3	23.0	26.1	21.9	25.4	23.0	26.2	22.8	26.2
Open Circuit-0°C		1.230		1.229		1.224		1.223		1.226
	after	22.8	26.5	23.0	26.9	22.4	26.2	22.5	28.2	27.8
		1.233		1.231		1.233		1.231		1.227
				30 days				60 days		

TABLE 3: CAPACITY OF CELLS STORED IN THE TRICKLE CHARGE MODE

ITEM	S/N 38			S/N 45			S/N 58		
	Capacity (Ah) 1.0 V	Total	Mid-DV	Capacity (Ah) 1.0 V	Total	Mid-DV	Capacity (Ah) 1.0 V	Total	Mid-DV
before	22.9	26.3	1.230	23.0	26.1	1.229	21.9	25.4	1.224
Tickle Charge- 0°C-30 days after	22.5	27.1	1.234	22.7	27.5	1.236	21.3	26.0	1.227
Tickle Charge- 0°C-60 days after	22.8	27.9	1.231	23.1	28.2	1.230	21.8	27.0	1.230

TABLE 4: CAPACITY OF THE CELLS AFTER COMBINED 0°C AND TRICKLE CHARGE MODE

ITEM	TEST GROUP A						TEST GROUP B			
	S/N 38		S/N 45		S/N 58		S/N 66		S/N 79	
	Capacity (Ah) 1.0 V	Mid-DV	Capacity (Ah) 1.0 V	Mid-DV	Capacity (Ah) 1.0 V	Mid-DV	Capacity (Ah) 1.0 V	Mid-DV	Capacity (Ah) 1.0 V	Mid-DV
Initial	22.9	26.3	23.0	26.1	21.9	25.4	23.0	26.2	22.8	26.2
Storage Test after	22.5	27.1	22.7	27.5	21.3	26.0	22.8	27.5	22.0	27.3
Storage Test after	22.8	26.5	23.0	26.9	22.4	26.2	22.9	27.4	22.8	27.5
Storage Test after	22.8	27.9	23.1	28.2	21.8	27.0	22.5	28.2	22.5	27.8

TABLE 5. CAPACITY OF CELLS STORED AT 28°C

ITEM	VALUE			
			CELL 68	CELL 24
INITIAL				
CAPACITY (TO 1V),Ah				
	AT 0°C		61.9	62.1
	AT 10°C		61.1	61.3
	AT 20°C		59.3	59.3
MID-DISCHARGE VOLTAGE,V				
	AT 0°C		1.216	1.216
	AT 10°C		1.233	1.234
	AT 20°C		1.234	1.235
AFTER FIRST 30 DAY STORAGE				
CAPACITY (TO 1V), Ah				
	AT 0°C		57.7	58.2
	AT 10°C		56.8	57
	AT 20°C		56.8	56.7
MID-DISCHARGE VOLTAGE,V				
	AT 0°C		1.235	1.236
	AT 10°C		1.238	1.238
	AT 20°C		1.235	1.235
AFTER SECOND 30 DAY STORAGE				
CAPACITY (TO 1V),Ah				
	AT 0°C		62.1	62.3
	AT 10°C		61.2	60.5
	AT 20°C		55.9	55.9
MID-DISCHARGE VOLTAGE,V				
	AT 0°C		1.233	1.233
	AT 10°C		1.236	1.237
	AT 20°C		1.237	1.237

TABLE 6. CAPACITY AND VOLTAGE OF THE CYCLED CELLS

ITEM	Value	CELL 10	CELL 38	CELL 75	CEL 68	CELL 24
	CELL 1	CEL 10	CELL 38	CELL 75	CEL 68	CELL 24
	0°C stored cells	cells	10°C stored cells	cells	28°C stored cells	CELL 24
Initial Capacity (to 1V), at 20°C at 10°C at 0°C	59.8	59.2	58.9	58.9	59.3	59.3
	61.7	61.3	60.8	61	61.1	61.3
	62.6	62.1	61.6	61.9	61.9	62.1
End of Discharge voltage at cycle 2379 (V)	1.21	1.211	1.21	1.21	1.213	1.21
	54.3	54.9	54.2	53.8	54.2	52.4
Final Capacity (to 1V) at 20°C at 10°C at 0°C	56.4	57	56.1	55.7	55.8	52.4
	57.4	58	56.8	55.6	56.8	53.9

FIGURE 1. COMPARISON OF END OF DISCHARGE VOLTAGES DURING CYCLING

