

# Studies on the storage of electrochemically impregnated nickel/cadmium cells

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## Abstract

The storage procedure commonly used for space-quality nickel cadmium cells is to keep the fully discharged cells in the shorted condition. These cells use chemically impregnated positive and negative electrodes and maintain good capacity during such storage. By contrast, space-quality nickel/cadmium cells developed in-house with electrochemically impregnated electrodes exhibit a fall in capacity. It is suggested that segregation of cobalt is the cause of capacity reduction after shorted-mode storage.

## Introduction

The storage procedure that is normally used for space-quality nickel/cadmium (Ni/Cd) cells is to keep the fully discharged cells in a shorted condition. This practice has arisen partly out of safety considerations and partly out of folklore. The cells use chemically impregnated (CI) positive and negative electrodes and such designs do not show any decline in capacity in the shorted mode of storage.

Loss of capacity during the storage of nickel/hydrogen (Ni/H<sub>2</sub>) cells is a problem in spacecraft applications. Lim and Standnick [1] propose the use of positive precharged Ni/H<sub>2</sub> cells to alleviate the problem. The storage procedures for Ni/H<sub>2</sub> cells are different to those for Ni/Cd cells because of the interaction of hydrogen with the nickel electrodes [2]. Pickett *et al.* [3] have observed a fall in capacity in the case of electrochemically impregnated (EI) positive electrodes. This behaviour did not occur, however, with CI electrodes. From studies on Ni/H<sub>2</sub> cells, Manzo [4] showed that nickel electrodes from Hughes exhibited a fall in capacity due to the presence of alcohol in the impregnation bath.

The Battery Division of the Materials and Metallurgy Group at the Vikram Sarabhai Space Centre has designed and developed hermetically sealed 12-Ah Ni/Cd cells for satellite applications. Details of the cell design, the qualification test, and the results of real-time life-cycle tests have been published elsewhere [5]. EI positive and negative electrodes were used in these cells. A fall in capacity was noticed when the cells were stored in a shorted condition. This paper describes experiments that have been conducted on cells and electrodes. Based on the results, a plausible mechanism is suggested for the capacity reduction that follows shorted-mode storage.

## Experimental

Nickel plaques (78 mm × 70 mm × 0.8 mm), obtained by dry powder sintering, were employed throughout. The cell design details are itemized in Table 1.

TABLE 1  
Cell design

Characteristic	Positive	Negative
Plaque dimensions (mm)	78×70×0.8	78×70×0.8
Substrate	Nickel expanded mesh	Nickel expanded mesh
Number of electrodes	10	11
Loading levels (g cm <sup>-3</sup> )	1.70	2.60
Additives	nil	proprietary
Separator	Non-woven nylon	Non-woven nylon
Cell case material	Stainless-steel 304 L	Stainless-steel 304 L
Seals	Ceramic-to-metal seal	Ceramic-to-metal seal
Negative to positive ratio	1.5	1.5
Negative precharge	40% of excess negative capacity	40% of excess negative capacity

An electrochemical impregnation method was used to load the active material into the pores. The impregnation solution contained 10% (v/v) alcohol. In the case of the positive electrodes, Co(OH)<sub>2</sub> and Cd(OH)<sub>2</sub> were coprecipitated along with Ni(OH)<sub>2</sub>.

The EI method was also applied to a batch of plaques without alcohol in the impregnation bath in order to determine the effect of shorted storage on such electrodes. All other compositions (e.g., concentration of bath, amounts of cobalt and cadmium) were maintained at the same levels.

Studies were performed on positive electrodes in a flooded-electrolyte condition. Higher capacity cadmium electrodes were used as counter electrodes so that the capacity was limited by the test electrode. The discharge was taken to 0.3 V. For test on cells, however, the discharge was terminated at 1.00 V. Between cycles, a 1-Ω resistor was used to bring the voltage down to 10 mV.

All chemicals were of AnalaR grade quality. MilliQ+ water with a resistivity better than 5 MΩ was employed in the experiments. For cell studies, an HP 9000 series Data Acquisition System provided automatic charge/discharge cycles in conjunction with a calibrated Aplab power supply (model No. 7261). The cells were 12-Ah hermetically sealed units. The capacity measurements were made at 15 °C in a hot and cold chamber (Heraeus Votsch model VMT 02-04/140). By contrast, experiments on electrodes were undertaken at ambient temperature.

Isolation of the nickel electrode active material was achieved by powdering the electrode and removing the grid. The nickel metal powder was then separated from the active material powder in an aqueous slurry using a Teflon-coated magnetic stirrer. After filtering and drying, the active material was digested with 10% acetic acid at 70 °C for 24 h. The undissolved portion was filtered from the solution, washed and dried. This sample was then subjected to X-ray diffraction phase analysis.

## Results and discussion

### Cell studies

Table 2 gives the capacity details of two cells (QC1 and QC2) before and after storage. The cells were charged at the *C*/3 rate for 4.5 h (where *C* is the nominal capacity, i.e., 12 Ah). The discharge was performed at the *C*/2 rate to a cut-off voltage

TABLE 2

Capacity of cells before/after storage

Cell	Capacity before storage (Ah)	Capacity after storage (Ah)			
		Cycle 1	Cycle 2	Cycle 3	Cycle 6
QC1	13.74	12.30	12.24	12.32	12.38
QC2	13.67	12.63	12.59	12.54	12.53

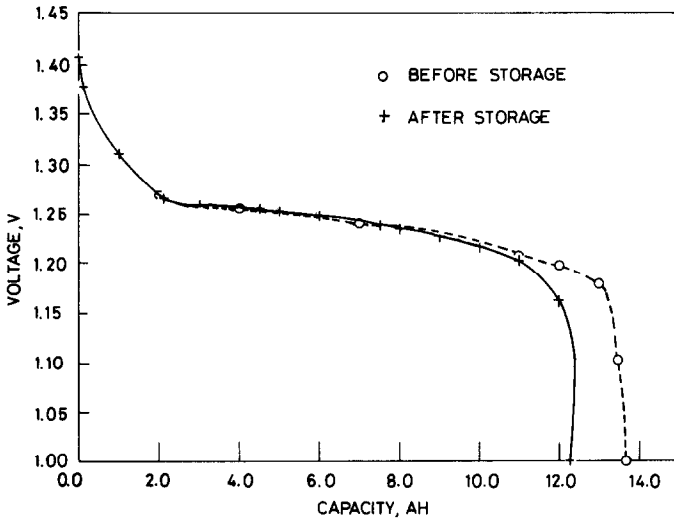


Fig. 1. Discharge characteristics of cell QC1 before and after storage.

of 1.00 V. As mentioned earlier, a  $1 \Omega$  resistive load was applied to bring the cell voltage to 10 mV. The listed capacities (before storage) are stabilized values with a variation of  $\pm 0.05$  Ah between cycles.

The cells were stored at  $15^\circ\text{C}$  in a shorted condition. After a period of 42 days, the short was removed and the capacity was evaluated. The capacity exhibits a considerable fall after storage (Table 2). It is known [6] that 10 to 12 cycles are required under most conditions to bring the electrodes back to the initial impedance after short-term storage. Further cycling did not restore the capacity to its original value.

Capacity fall was noticed for all the cells when stored in shorted mode under ambient conditions. The discharge curve for a typical cell before and after storage is shown in Fig. 1. It is evident that the voltage before and after storage matches very well up to 80% state-of-discharge. The fall in capacity after shorted-mode storage occurs suddenly near the 'knee' region. This may be due to an increase in the internal impedance of the cell.

### Electrode level studies

Table 3 gives the capacity of the positive electrode before and after 30 days of shorted-mode storage under ambient conditions. There is a perceptible change in capacity after shorted-mode storage, even in the flooded condition. On average, there is a fall of 0.13 Ah per electrode. At the cell level, 10 positive electrodes will account for 1.3 Ah fall in capacity without taking into account the starved loss and stack loss. Indeed, when cells were kept in the shorted mode, a fall in capacity of 1.5 Ah was observed.

Experiments were also carried out at the electrode level under open-circuit conditions. Table 4 lists the capacity of electrodes before and after storage in open mode at ambient. Clearly, there is no decline in capacity when electrodes are stored in the open mode.

As mentioned above, storage studies were performed on electrodes that were impregnated in an aqueous bath without the presence of alcohol. The stabilized capacity of electrodes together with the capacity after shorted- or open-mode storage for 30 days at ambient are presented in Tables 5 and 6, respectively. The data show (Table 5) that there is a reduction in capacity even for electrodes impregnated from an EI bath that does not contain alcohol. Thus, it can be concluded that the presence of alcohol in the impregnation bath is not responsible for the decrease in capacity

TABLE 3

Capacity of positive electrodes before and after shorted-mode storage

Electrode no.	Stabilized capacity before storage (Ah)	Capacity after storage (Ah)		
		Cycle 1	Cycle 5	Cycle 8
546	1.73	1.45	1.50	1.54
552	1.73	1.48	1.55	1.59
560	1.69	1.49	1.52	1.56
927	1.70	1.50	1.57	1.59
939	1.76	1.52	1.64	1.66
953	1.71	1.42	1.54	1.54
957	1.75	1.42	1.61	1.63
973	1.70	1.53	1.59	1.60

TABLE 4

Capacity of positive electrodes before and after open-mode storage

Electrode no.	Stabilized capacity before storage (Ah)	Capacity after 30 days open-mode storage (Ah)	
		Cycle 1	Cycle 20
463	1.69	1.69	1.69
465	1.72	1.69	1.72
469	1.73	1.69	1.70
432	1.76	1.73	1.76

TABLE 5

Capacity of positive electrodes before and after shorted-mode storage at ambient

Electrode no.	Stabilized capacity before storage (Ah)	Capacity after storage (Ah)	
		Cycle 1	Cycle 8
289	1.67	1.37	1.48
374	1.70	1.37	1.53
402	1.71	1.43	1.56
404	1.66	1.39	1.47
414	1.72	1.44	1.59

TABLE 6

Capacity of positive electrodes before and after open-mode storage at ambient

Electrode no.	Stabilized capacity before storage (Ah)	Capacity after storage (Ah)	
		Cycle 1	Cycle 8
415	1.70	1.73	1.70
424	1.71	1.74	1.69
482	1.72	1.76	1.72
771	1.74	1.77	1.74

TABLE 7

X-ray diffraction data for material isolated from an electrode

Observed $d$ values	Theoretical $d$ values ( $\text{Co}_3\text{O}_4$ )
4.65	4.67
2.87	2.86
2.46	2.44
2.34	2.33
1.90	2.02
1.66	1.65
1.43	1.43

after shorted-mode storage. By contrast, there is no fall in capacity after open-mode storage (Table 6) similar to that found above for electrodes processed from an alcoholic bath.

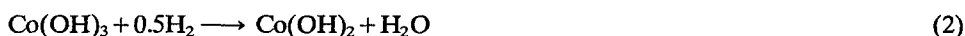
One of the cells that had exhibited a reduction in capacity was cut open for destructive physical and chemical analysis. It was evident that the decline in performance was due solely to the positive electrodes. X-ray diffraction data for a sample of active material is given in Table 7, together with the  $d$  values for  $\text{Co}_3\text{O}_4$ . A 1:1 matching is found between the experimental and the theoretical  $d$  values. This confirms the presence of  $\text{Co}_3\text{O}_4$  in positive electrodes after shorted-mode storage. By contrast, electrodes stored in the open mode did not indicate the presence of  $\text{Co}_3\text{O}_4$  when analysed.

From the above studies, it is clear that cobalt segregation in the positive electrode is the cause for the fall in capacity under shorted-mode storage. Such behaviour is not uncommon in Ni/H<sub>2</sub> cells [1].

Is there any source of H<sub>2</sub> in hermetically sealed Ni/Cd cells? The reversible potential for the hydrogen-evolution reaction (HER) is  $-0.02$  V versus Cd/Cd(OH)<sub>2</sub> (or  $-0.93$  V versus Hg/HgO) at 1 atm and 30% KOH [7, 8]. The potential of the nickel electrode is  $0.0$  V versus Cd/Cd(OH)<sub>2</sub> (or  $-0.91$  V versus Hg/HgO at 25 °C) when a sealed discharged Ni/Cd cell is maintained at  $0.0$  V. Since the potential of the nickel electrode is close to that of the HER, it is reasonable to assume that the HER will be sustained at a cell voltage of  $0.0$  V. Indeed, the impedance studies have confirmed [9] the existence of hydrogen in sealed Ni/Cd cells. The hydrogen can interact with cobalt, present as either Co(OH)<sub>3</sub> or CoOOH, in a way similar to that proposed for Ni/H<sub>2</sub> cells [1].



or



Overall:



or



Although the suggested mechanism explains the experimental observation, the study is not conclusive. For example, cobalt is present in chemically impregnated electrodes, but why is there no fall in capacity when these cells are stored in the shorted condition? Further fundamental studies have to be carried out in order to unravel the full details of the mechanism.

## Conclusions

The following conclusions are drawn from the experimental programme undertaken in this study.

1. Hermetically sealed Ni/Cd cells with EI positive and negative electrodes display a loss in capacity when stored in the shorted-mode condition at ambient.
2. The capacity lost is not recoverable during subsequent charge/discharge cycling.
3. Cells stored at open circuit do not exhibit a fall in capacity.
4. For cells prepared with EI positive and negative electrodes, an open-mode storage is recommended.

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