

EFFECT OF PRECHARGE ON NICKEL—HYDROGEN CELL STORAGE CAPACITY

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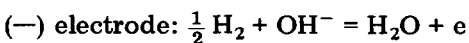
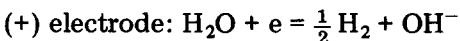
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Summary

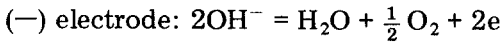
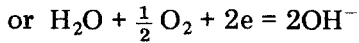
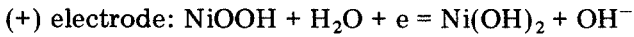
Loss of capacity for Ni/H₂ cells on storage has been a problem for spacecraft applications. A relief from this problem is demonstrated by the use of nickel electrode precharge (deficit amount of hydrogen) rather than the customarily used hydrogen precharge (excess amount of hydrogen). The use of this precharge does not appear to have any short or long term harmful effects on the cell performance. Nickel electrode precharge not only is harmless but also may be beneficial by relieving a long term pressure build-up which might be a problem for a long life application.

Introduction

There are two alternate methods of precharge of a Ni/H₂ cell. One is hydrogen precharge which means an excess amount of hydrogen in the cell when the cell is fully discharged such that cell capacity is not limited by lack of hydrogen. The other is nickel electrode precharge (nickel precharge) which means an excess capacity of nickel electrode (or a deficit amount of hydrogen) in the cell when the cell is fully discharged such that cell capacity is limited by the amount of hydrogen. Almost all Ni/H₂ cells manufactured in early years of development had hydrogen precharge rather than the alternate nickel precharge. The electrode reactions for charge, overcharge, and discharge are indistinguishable between the two different precharges. However, electrode reactions for overdischarge (reversal) are quite different from each other for these two different types of precharges. In a hydrogen precharged cell, reversal reactions are



Hydrogen will evolve from nickel electrodes during reversal. There will be no net composition change of the cell due to reversal. In a nickel precharged cell, reversal reactions are



In this cell oxygen will evolve from the hydrogen electrode. Although both hydrogen evolution at the nickel electrode and oxygen evolution at the hydrogen electrode are not desired, the latter reaction is generally of more concern due to its damaging effects on the electrode. The reason why early Ni/H₂ cells had hydrogen precharge instead of the nickel precharge was mainly due to this difference in the reversal reaction and also partially for the maximum utilization of capacity of the nickel electrode which is a heavier component of the two electrodes.

One of the most puzzling characteristics of the early Ni/H₂ cells which were fabricated by Hughes Aircraft Company using the hydrogen precharge (typically 50 psig) has been the loss of capacity during storage. Some cells which had passed acceptance testing would lose between 20 and 40 percent of their capacity after a period of storage longer than two to three weeks. This capacity loss was not permanent, and most of the capacity loss was found to be recoverable by either cycling the cells at high rate in low earth orbit (LEO) with an 80% depth of discharge (DOD) or by subjecting the cells to an extended period of trickle charge or periodic recharge. However, full initial capacity of the cell could not be demonstrated as required for a state-of-health check prior to launch, although long term life testing demonstrated that the full initial capacity could be recovered after a long period of cycling. For example, several cells were built for a long term life test with a design capacity of 22 A h. During initial testing, the capacity of these cells dropped to a value between 16 and 18 A h. After six years of life testing in a geosynchronous earth orbit (GEO), the capacity was increased to 21.3 to 21.7 A h.

To ensure that the battery will deliver sufficient power throughout the given mission, it is required to have, preferably, a method of preventing the capacity loss or, at least, a method of ensuring that the initial capacity is sufficient to support the mission requirement even after worst capacity fading. Recently, the storage behavior of Hughes-built Ni/H₂ cells having hydrogen and nickel precharge was reported in an article showing the merits of nickel precharge over hydrogen precharge [1]. The present report also shows that capacity loss is easily preventable by the use of nickel precharging, without any adverse effects on the cell performance, and describes a possible mechanism of the capacity loss phenomenon.

Possible recovery method of lost capacity

Initial efforts for recovery of the lost capacity by LEO cycling and periodic top-off or trickle charge were partially successful. Although the capacity was eventually but slowly recovered to a near initial value, the time

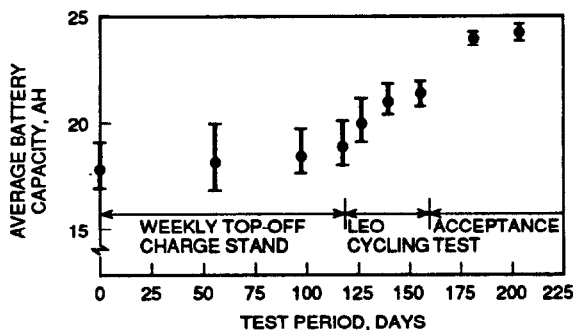


Fig. 1. Effect of weekly top-off charge stand and LEO cycling on the recovery of the lost capacity changes of 25 A h nine-cell Ni/H₂ battery pack. The cells were charged for 10 h at C/10 rate for the weekly top-off. The LEO cycling was carried out at 80% depth-of-discharge.

and equipment required for this recovery technique were considered to be severe disadvantages of these methods. For example, the capacity recovery of a 25 A h cell is shown in Fig. 1 as a function of both periodic top-off and LEO cycling. However, the capacity of these cells did not return to the full initial capacity of 28 A h even after 200 days of testing. An impractically longer period of testing, in the order of a year, is required to restore the capacity to the full initial level.

Voltage/pressure characteristics change with capacity loss

Capacity loss on storage was accompanied by change in voltage and pressure characteristics. Typical discharge voltage curves of Ni/H₂ cells without and with capacity loss are shown in Fig. 2. The enhanced mid-discharge voltage and the reduction of capacity below 1.20 V (sharp voltage 'knee') were characteristics of the capacity loss. The pressure characteristics of cells without and with capacity loss were as follows. The capacity loss always resulted in increased end-of-discharge pressures (EODP) without changing end-of-charge pressures (EOCP) as shown in Table 1. This pressure behavior of capacity loss cells appeared to indicate that the state of charge of active material at end of charge remained unaffected by capacity loss, while the active material did not discharge as deep as one without capacity loss. The increased EODP by capacity loss appeared to return to the initial value as lost capacity is gradually recovered by LEO cycling, trickle charge, or periodic top-off, indicating that capacity loss and its recovery are somewhat reversible.

Effects of the two different types of precharge

The effects of conventional hydrogen precharge and nickel precharge on capacity loss were studied using flight type Ni/H₂ cells. Nickel precharge

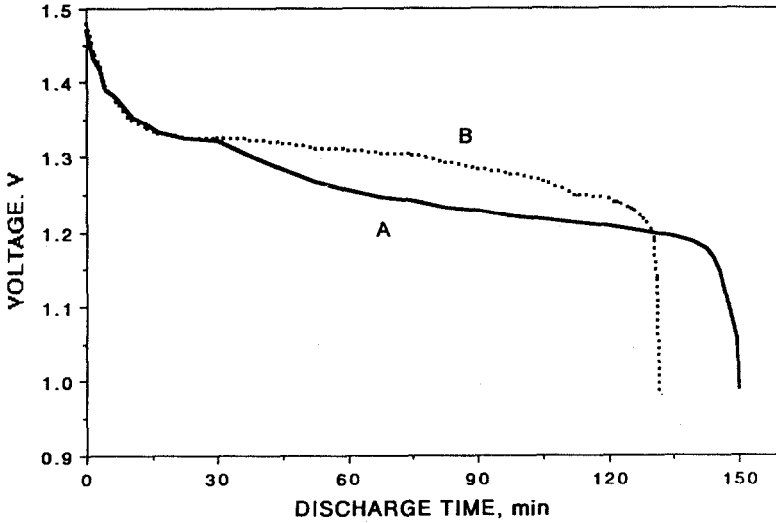


Fig. 2. Comparison of discharge voltage curves of Ni/H₂ cells without (A) and with (B) the capacity loss on storage. (C/2 rate discharge.)

TABLE 1

End-of-charge (EOCP) and end-of-discharge (EODP) pressures of 48 A h Ni/H₂ cells with capacity loss vs. those without capacity loss. Capacity of 16-cell packs (I-6) was measured by charging packs at C/10 (4.8 A) for 18 h followed by discharge at C/2 rate to 0.7 V of the first cell or pack voltage of 17.3 V, whichever occurred first

| Pack no. | Capacity (A h) | EOCP (psig) | EODP (psig) |
|----------|----------------|-------------|-------------|
| Q3 | 50.62 | 766 - 742 | 221 - 256 |
| Q4 | 52.42 | 742 - 736 | 190 - 202 |
| F001 | 44.83 | 774 - 782 | 273 - 301 |
| F002 | 44.94 | 749 - 771 | 280 - 303 |
| F003 | 45.82 | 746 - 780 | 267 - 308 |
| F004 | 45.01 | 714 - 760 | 237 - 299 |

was set by charging the cells to a specified level (typically five to seven percent of the total capacity) and then removing hydrogen that was generated during the charge. Thus, during discharge, all hydrogen would be consumed before the positive electrode was fully discharged. Therefore, discharge of these cells would be limited by negative electrode capacity (amount of hydrogen).

Capacity changes of cells with different precharges on storage are shown in Figs. 3 and 4 for two different series of flight cells. Each series included cells with a nickel precharge of 6.6% of the rated capacity and H₂ precharges of 2.8% (0 psig) and 12.3% (50 psig). The capacity of the latter two hydrogen precharged cells decreased steadily with storage without an indication of being stable even after 120 days. The rate of capacity loss was

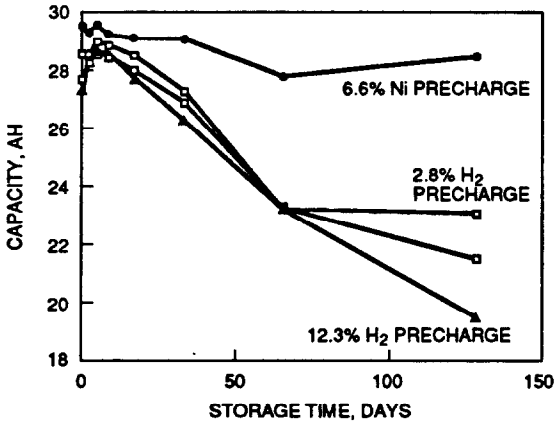


Fig. 3. Effect of precharge on capacity changes with open circuit storage time at 20 °C of 25 A h Ni/H₂ cells. Capacities were measured by discharge to 1.0 V after charging for 18 h at C/10 rate.

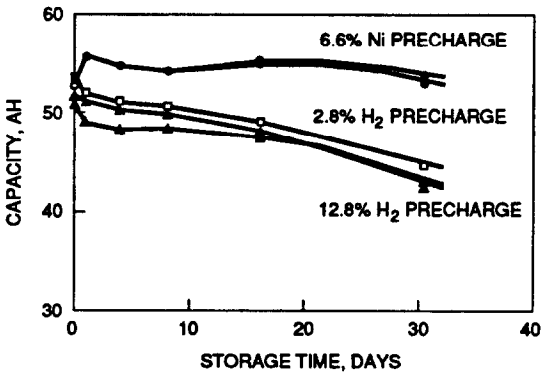


Fig. 4. Effect of precharge on capacity changes with open circuit storage time at 20 °C of 50 A h Ni/H₂ cells. Capacities were measured by discharge to 1.0 V after charging for 18 h at C/10 rate.

neither quantitatively correlated to the amount of H₂ precharge, nor reproducible with different cell fabrication lots as indicated by comparison of data in Figs. 3 and 4. However, there was no significant capacity loss with cells which had nickel precharge.

Effects of precharge types on the capacity of sixteen-cell flight battery packs for Intelsat VI (I-6) are summarized in Fig. 5. One of these packs (F1) was activated with normal hydrogen precharge (50 psig), and the other two were activated with nickel precharge (about 6%, -50 psig of H₂). Capacities of nickel precharge packs were apparently not changed significantly in about three years of overall storage period which included discharged open circuit stand, top-off charge storage, and capacity testing as shown in Fig. 5. F2 pack was first put into discharged open circuit storage for about 1.5 years and then a weekly top-off charged (8 to 9 h of C/10 rate) storage for about

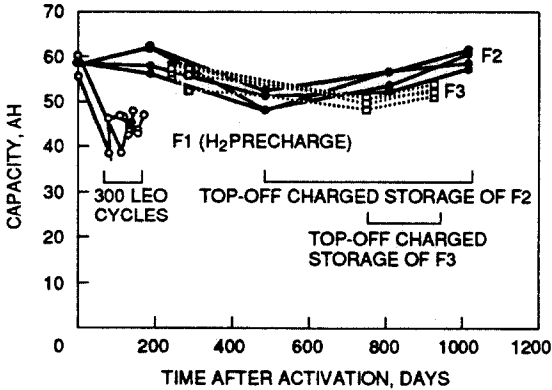


Fig. 5. Capacity changes of I-6 sixteen-cell battery packs having hydrogen (F1 pack) and nickel (F2 and F3 packs) precharges with lapse of time periods of storage and testing. Storage mode was discharged open circuit stand unless otherwise described.

5 months followed by a biweekly top-off charged storage thereafter. F3 packs was stored in a discharged open circuit condition for about two years before it was put into a biweekly top-off charged storage. In contrast to these nickel precharged packs, F1 pack which had H₂ precharge suffered a severe capacity loss almost from the beginning as shown in Fig. 5. The lost capacity was not recovered significantly even after 300 LEO cycles. These results appear to indicate that the presence of hydrogen during storage might be the cause of the capacity loss.

Additional results of other flight type cells with various amounts of nickel precharge up to 18% also showed no problems of capacity fading on storage. Results of another independent study on the capacity loss of cells with nickel electrodes of various designs also showed that capacity loss occurs only when H₂ is present during open circuit or shorted storage [2].

Long term effects of the precharge type on cycling in a geosynchronous earth orbit (GEO) were studied on I-6 flight battery cells [3]. End-of-discharge voltages (EODV) of battery cells are shown in Fig. 6 for both types of precharge (with and without reconditioning). The difference in voltage performance between the two different precharge types was not significant throughout long cycling periods of 30 eclipse seasons at a maximum depth-of-discharge of 69.2%.

Cell reversal

A logical concern for a Ni/H₂ cell with nickel precharge is possible damage of the cell during reversal. There is no such concern for a hydrogen precharge cell because a short term hydrogen evolution at nickel electrode is relatively harmless. During reversal of a nickel precharge cell, oxygen is generated at the negative electrode instead of hydrogen, and the cell could

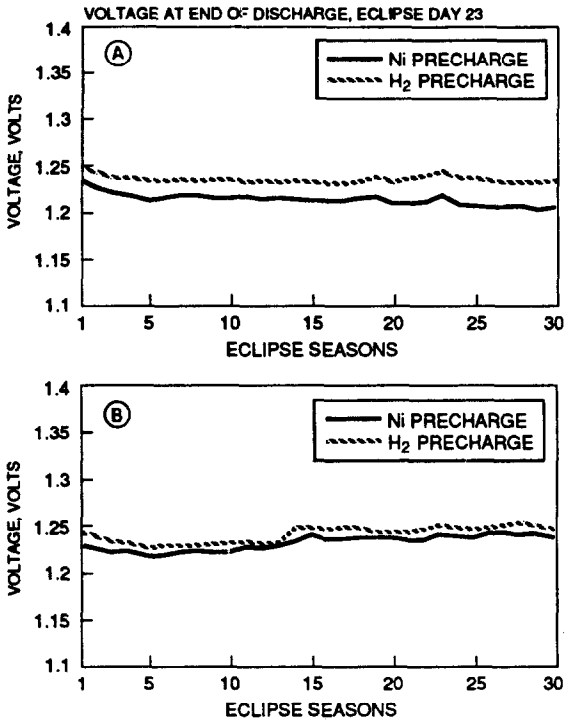


Fig. 6. End-of-discharge voltage (EODV) performance comparison of I-6 batteries having hydrogen and nickel precharges in GEO regime at maximum depth-of-discharge of 69.2%. (A) Cycled without reconditioning the battery. (B) Cycled with reconditioning the battery after each eclipse season by shorting across a 20Ω resistor to 5.00 V of sixteen-cell pack voltage.

be operating as an oxygen cell. Therefore, it is generally not recommended that cells be reversed, especially at high rate.

In order to evaluate the effects of reversal, several boilerplate cells with nickel precharge were cycled in a reversal mode. The performance data and the cell disassembly results have shown that the cells did not suffer any measurable degradation. For example, a six-electrode boilerplate cell (6.5 A h) was deliberately reversed twice at 0.8 to 1 C rate in nickel precharged condition as indicated in voltage curves in Fig. 7. This cell showed neither a sign of degradation in performance after the test nor of physical damage of cell stack components on subsequent teardown analysis, indicating that a short term reversal of the nickel precharged cell would not have any detrimental effects. In addition, the chance of having this type of reversal with actual flight battery cells will be reduced rapidly as the cells are used, because a nickel precharged cell will be quickly converted to hydrogen precharged cell with cycling. Since a Ni/H₂ cell normally increases in internal hydrogen pressure with cycling [4, 5], probably due to the normal corrosion of nickel electrode sinter, the cells will not be subjected to

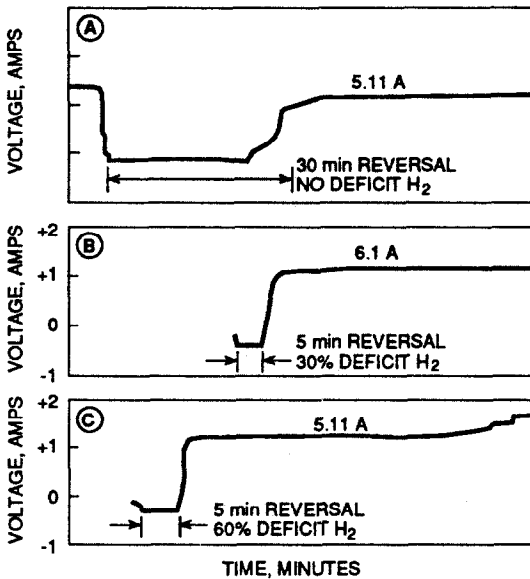


Fig. 7. Voltage curves of a 6.5 A h boiler plate Ni/H₂ cell during discharge which includes reversals. (A) In the presence of excess H₂ (a H₂ precharged condition). (B) In 30% deficit (nickel precharged) condition. (C) In 60% deficit (nickel precharged) condition.

the 'oxygen cell' type of reversal even with in-orbit reconditioning, should it be necessary. During normal in-orbit operation, of course, the cells are never subjected to reversal of any kind, and there should be no performance difference between cells regardless of precharge. Instead of a disadvantage, we believe that there will be an advantage with a nickel precharged cell over a hydrogen precharged cell. Pressure of a Ni/H₂ cell builds up gradually as it is cycled as discussed above. This H₂ pressure build-up will increase the self-discharge rate of the cell. For a long life application, it will also create a concern on possible pressure vessel safety. In addition, a low pressure cell using nickel precharge will eventually last longer than a high pressure hydrogen precharged cell.

Possible mechanisms

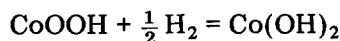
Cell pressure data discussed above indicated that the capacity loss is due to an incomplete discharge of the charged active material rather than due to an inefficient charging process. This pressure behavior associated with the capacity loss is consistent with an isolation mechanism of the charged active material [6, 7]. Active material near the current collecting nickel sinter discharges before those located further away from the current collector. Since fully discharged active material (Ni(OH)₂) can be an insulator, especially without cobalt additive, a layer of the early-discharged active material at the surface of the nickel sinter might shut off further

discharge of remaining undischarged active material located away from the surface. Occurrence of such an isolation mechanism might be facilitated if the cobalt additive is deactivated. The cobalt additive is known to enhance utilization and electrochemical reversibility of nickel active material [8 - 10]. We speculate that cobalt additive might reduce contribution of the isolation mechanism by improving conductivity of the active material in its reduced state. The active material of nickel electrodes used in this study had a nominal value of Ni to Co molar ratio of 9.

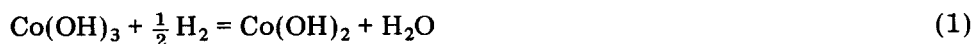
Both present results as well as other results [2] on storage effects indicate that the presence of hydrogen causes the capacity loss. It appears that something in the active material is slowly reacting with hydrogen causing the incomplete discharge of the charged active material. It appears that cobalt additive used in the nickel electrode is closely related to this capacity loss phenomena.

We assume that depletion of electrochemically active cobalt additive in the active material causes the capacity loss phenomena which means reduction of electrochemical utilization of active material. The depletion occurs through conversion of active cobalt into an inactive form. We further assume that the active form of the cobalt is either CoOOH or Co(OH)_3 which can be reduced slowly by H_2 . Electrochemical data [11, 12] appear to indicate that cobalt should stay in the Co(III) state in a fully or partially charged nickel electrode, but Co(III) can be reduced by Co(II) only when the nickel active material is fully discharged.

We further assume that the capacity loss is caused by the following reactions which take place during the storage period



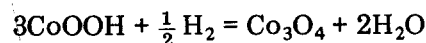
or



or



Overall



or



The overall reaction (3) is thermodynamically favorable. Co_3O_4 is insoluble in most acids including dilute nitric acid. We expect that this compound is an inactive form of cobalt which does not contribute in improving electrochemical utilization of the active material. Therefore, when

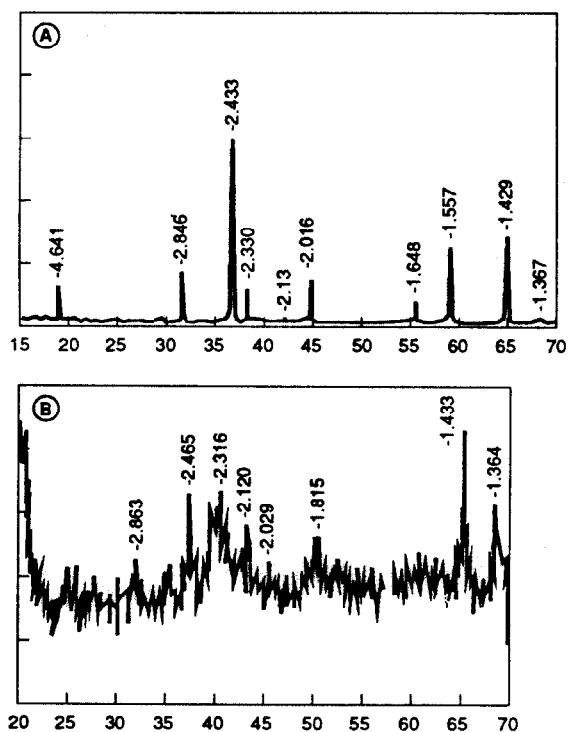


Fig. 8. X-ray diffraction pattern of an authentic sample of Co_3O_4 (A) and a brown acid-insoluble residue (B) from a nickel electrode having capacity loss.

the concentration of CoOOH (or $\text{Co}(\text{OH})_3$) is depleted in the active material through reactions (1) and (2), the cell capacity will decrease. We were able to isolate a brown solid residue from an electrode showing capacity loss. A chemical analysis result of this solid showed cobalt content of about 48% by weight with no indication of nickel by a dimethylglyoxime solution. The main component of this residue was identified as Co_3O_4 by comparing its X-ray diffraction pattern with that of Co_3O_4 as shown in Fig. 8. However, we could not detect such brown residue in a new electrode supporting our suggested capacity loss mechanism. Although the suggested mechanism appears to explain the observation as discussed above, these results are not conclusive, yet. An additional study is in progress in order to understand the mechanism better.

Concluding remarks

- When a sufficient amount of nickel precharge was used, capacity did not fade on open circuit or shorted storage of a Ni/H_2 cell containing 31% KOH electrolyte.
- A short term reversal of a nickel precharged cell did not damage the cell.

- A nickel precharge setting of up to 18% of the cell capacity did not affect short or long term voltage performance of Ni/H₂ cells. The nickel precharge has the advantage of low operation pressure, therefore possible long life because the cell pressure is known to increase gradually with cycling.

- Reaction of cobalt with H₂ might be the cause of the capacity loss. Therefore, according to our suggested mechanism, the amount of the nickel precharge has to be sufficient to use up all H₂ when the cell is fully discharged before storage.

- All cells made to date at Hughes having nickel precharge show stable capacity. No difference in orbit performance is expected between the nickel and hydrogen precharge methods.

Acknowledgement

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