Short Communication

Effects of charged open-stand in nickel/hydrogen cells

M.S. Suresh and A. Subrahmanyan
Battery Division, ISRO Satellite Centre, Airport Road, Vimanapura, Bangalore - 560017 (India)

Abstract

Nickel/hydrogen cells used in spacecraft have to undergo planned and unplanned open-stand during spacecraft testing and launching. The effects of different durations of such a stand on cell performance have been evaluated through tests conducted on a 36-Ah cell. Results indicate that: (i) the pressure loss is not an accurate indicator of the decline in capacity, and (ii) open-stand results in electrode passivation. The reactions responsible for pressure loss are not of the simple first-order type, but are more complicated. The passivation and history-dependent pressure loss are due to the presence of hydrogen and two phases of the nickel oxide (i.e., β, γ). These findings emphasize that considerable care is necessary in handling nickel/hydrogen cells if passivation of the electrodes is to be avoided.

Introduction

It is well known that nickel/hydrogen cells on charged open-stand lose their capacity with decrease in both hydrogen pressure and cell voltage. A knowledge of such capacity loss is essential as batteries may undergo planned and unplanned open-stands during the testing and launch phases of spacecraft. Apart from the loss of capacity, open-stand may result in other effects that could modify the cell performance either temporarily or permanently. A change in the pressure versus capacity relation, for example, could cause problems in the management of batteries on board a spacecraft.

It has been reported that the dependence of capacity on cell pressure is not a simple log–linear relationship (i.e., a first-order reaction), but depends on the open-circuit duration and charge input [1]. Several other aspects of electrode passivation have also been discussed [2]. In order to characterize the effects of open-stand on the cell performance, a 36-Ah nickel/hydrogen cell was subjected to stands that varied from 10 min to 100 h. All other conditions were kept the same in order to avoid ambiguities in the interpretation of the results.

Experimental

A 36-Ah (nominal) nickel/hydrogen cell (type HRN 36, manufactured by SAFT, France) was fitted with sensors to measure pressure, temperature and voltage.

The cell was housed in a hot/cold chamber with the temperature maintained at 15 ± 0.5 °C. The cell was charged at a rate of 3.6 A until the pressure reached about 70 bar; this took about 18.5 h. After charging, the cell was held at open-circuit for a specified period. The cell was then discharged at the 18-A rate to 1.0 V, and then at the 7.2-A rate to 0.2 V. Subsequent to the discharge to 0.2 V, a resistor of 0.5 Ω was connected across the cell for 16 h. The procedure was repeated with open-stand durations of 100, 75, 20 h and 10 min. The resistive discharge period was always kept constant (16 h) and, when required, the cell was kept at open-circuit between the end of resistive discharge and the start of charge for the next cycle. During charged open-stand, the cell pressure, voltage and temperature were monitored at suitable intervals.

Results and discussions

The decay of cell pressure with time is shown in Fig. 1 for different open-periods. The pressure fall in each of these cases followed the same trend; the values were within about 0.6 bar. The input pressure/charge ratio $(\Delta p/\Delta Ah)$ varied between 1.03 to 1.04 bar/Ah. It has been reported earlier [1] that a plot of log pressure versus open-stand time is a combination of two linear regions, with a larger slope for the first 10 h followed by a smaller slope for the subsequent period. It was hypothesized that the larger slope was due to the reduction of higher oxide states (γ-NiOOH) and the lower slope was due to the reduction of β-NiOOH by hydrogen at the nickel catalytic interface. In view of this, the curve of Fig. 1 was replotted as log pressure
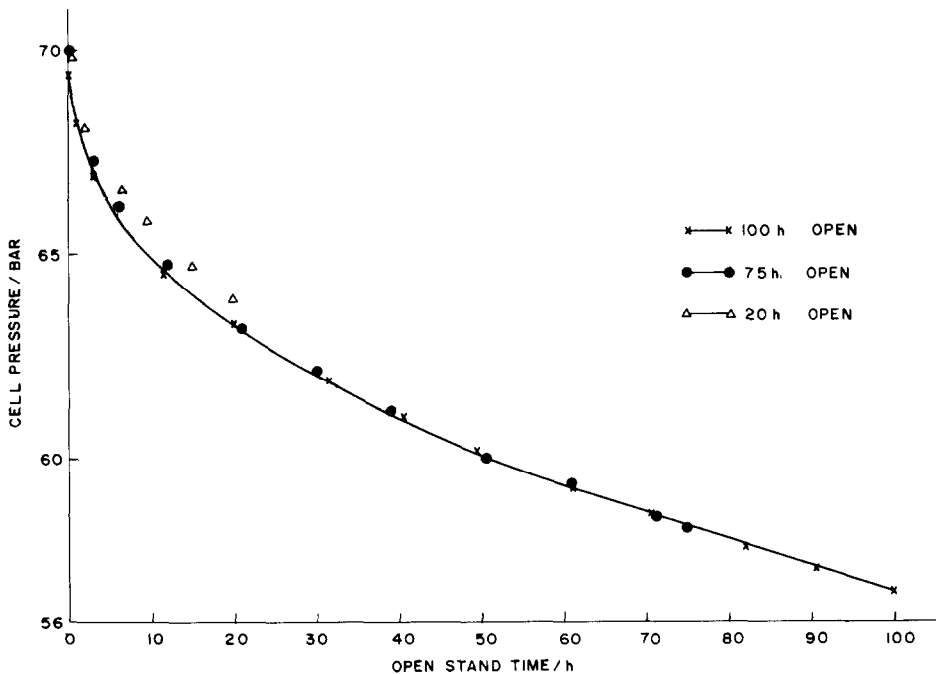

Fig. 1. Variation of cell pressure vs. time for a nickel/hydrogen cell on open-stand.

versus time in Fig. 2. Surprisingly, this plot is more complex than a combination of two straight lines. Beyond 60 h, however, the curve tends towards a straight line.

During the initial period of charged open-stand, the cell voltage is above the oxygen-evolution potential. Hence, oxygen continues to evolve. This, together with the oxygen produced during overcharge, recombines with hydrogen at the negative electrode during the open-stand. Higher oxides of nickel (γ-NiOOH) produced during overcharge and the adsorbed oxygen are reduced at the nickel catalytic interface. Thus, three reactions are occurring simultaneously in the cell and these consume hydrogen and decrease the cell pressure. Thus, it is too simplistic to assume that the reactions follow a first-order reaction. This is clearly shown by the non-linear region of the log pressure versus time plot for the first 60 h. As time elapses, the cell voltage decays and, consequently, evolution of oxygen decreases markedly. The reduction of adsorbed oxygen and γ-NiOOH is fairly fast. Thus, the reduction of β-NiOOH is the only reaction that occurs after a long open-stand. Accordingly, the log pressure versus time curve tends towards a straight line after about 60 h.

The cell pressure at different points in the charge/discharge cycle is given in Table 1 for each of the open-stand experiments. From this, the change in cell pressure per Ah discharged ($\Delta p / \Delta Ah$ discharged) to 1.0 V was calculated. This varied from 0.999 to 1.059 bar/Ah; it increased as the open-period was decreased. The factor $\Delta p / \Delta Ah$, when discharged to 0.2 V, also increased from 1.002 to 1.059 bar/Ah with decrease in the stand period. This variation in $\Delta p / \Delta Ah$ can be explained easily by the fact that at the end of charge, particularly with overcharge, hydrogen and oxygen evolution are responsible for the cell pressure. As the cell is open-circuited, oxygen and hydrogen
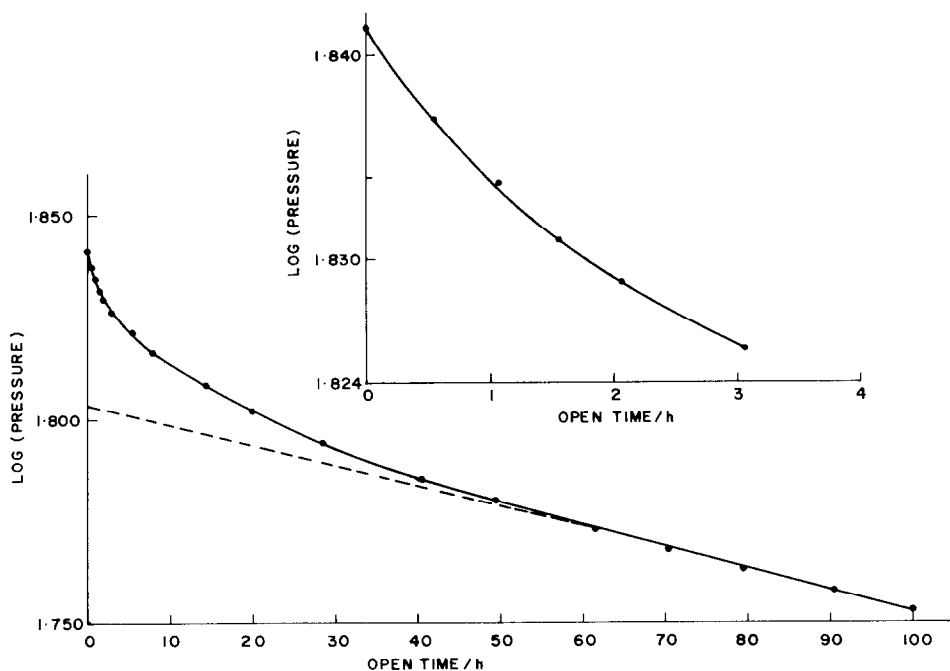

Fig. 2. Replot of data shown in Fig. 1 as log pressure vs. time. In the inset, the variation during the first 3 h is expanded.

TABLE 1

Cell pressure at different points in the charge/discharge cycle[a]

Period of open-stand (h)	Start-of-charge pressure (bar)	End-of-charge pressure (bar)	Start-of-discharge pressure (bar)	End of discharge pressure (bar)		
				to 1 V	to 0.2 V	RLD[b]
100	4.83	69.47	56.67	18.02	15.96	10.65
75	8.05	70.08	58.27	19.21	15.83	10.47
20	5.35	70.00	63.92	19.45	11.55	6.76
0.17	5.66	69.39	69.14	19.57	8.93	4.82

[a]Base line $\Delta p/\Delta Ah = (69.14-19.57)/46.8 = 1.059$ bar/Ah.
[b]RLD is resistive letdown across 0.5 Ω.

TABLE 2

Available capacity from the cell for discharges after different open-stands[a]

Period of open-stand (h)	Capacity to 1 V		$\Delta p/\Delta Ah$ measured (bar/Ah)	Total capacity to 0.2 V (Ah)	Capacity below 1 V (Ah)	$\Delta p/\Delta Ah$ measured (bar/Ah)
	Measured (Ah)	Estimated[b] (Ah)				
100	38.7	34.7	0.999	40.62	1.92	1.002
75	39.0	35.65	1.002	42.24	3.24	1.005
20	43.5	41.06	1.022	50.94	7.44	1.028
0.17	46.8		1.059	56.88	10.08	1.059

[a]Capacities are measured based on the $\Delta p/\Delta Ah$ value for 0.17-h open-stand and discharged to 1.0 V.
[b]Estimated capacity = (46.8 − (end-of-charge pressure − start-of-discharge pressure)/1.059).

recombine during the initial period to cause a lowering of the pressure. It may also be seen that the oxygen produced during overcharge does not result in a capacity loss to 1 V. Hence, if the loss of capacity is calculated in terms of the total pressure, the measured capacity will be more than the calculated value. This discrepancy will become larger as the open-stand period is extended.

The capacity available from the cell for discharges to 1.0 V (18-A rate) and to 0.2 V (7.6-A rate) after different open-stands has been tabulated in Table 2. For each of the open-stands, the estimated capacity based on the cell pressure and $\Delta p/\Delta Ah$ out has also been given. As expected, the measured capacity is more than the estimated capacity and the discrepancy increases at longer open periods. From Table 2, it can be observed that the loss of capacity below 1 V is (82%), much more than the loss of capacity to 1 V (17%). The available capacity up to 1 and 0.2 V, for different open-stands, has been plotted in Fig. 3.

In earlier work [3], it was shown that the γ-NiOOH produced on overcharge discharges at low voltages contributing to the capacity below 1 V. This higher nickel oxide, however, reduces at a faster rate at the nickel catalytic interface in the presence of hydrogen. The capacity up to 1 V is largely contributed by β-NiOOH which is
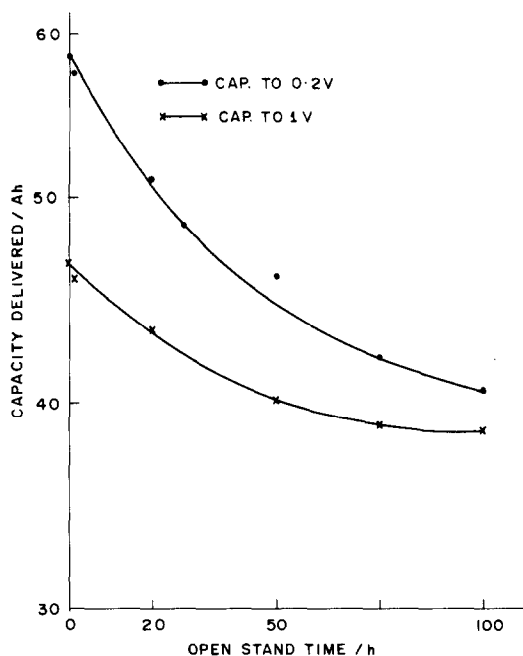
Fig. 3. Variation of cell capacity to 1 V at C/2 rate and to 0.2 V at C/5 rate, with different periods of open-stand.

more easily discharged. Thus, on open-circuit, more capacity is lost below 1 V compared with the capacity loss up to 1 V.

After discharge to 0.2 V, the cell was put on a resistive discharge with 0.5 Ω for 16 h. The cell pressure at the end of discharge (RLD) is given in Table 1. The variation in the end of RLD pressure with open-stand duration has been plotted in Fig. 4. It is interesting to note that the end of RLD pressure increases with open-stand duration. This means that even by a resistive letdown after discharge to 0.2 V, the cell could not be returned to the same low state-of-charge, when the open-period was large. Does this inability to discharge mean that the electrode interface has been passivated due to the long open-period?

In an earlier work [2] it was suggested that, in the presence of β-NiOOH and γ-NiOOH, hydrogen passivates the electrode by forming a layer of high-resistivity active material that limits the dischargeability of the electrode even at very low discharge rates. In this test, the cell was sufficiently overcharged to produce γ-NiOOH before open-stand. Thus, increase in cell pressure after resistive discharge is caused by passivation of the positive electrode. Further, the tests were done in decreasing order of open-stand period. The fact that the cell pressure after resistive discharge is not affected by the previous test shows that the passivated electrode can be reactivated by charging the cell.

If a cell is overcharged such that the β- and the γ-phases of NiOOH are present and is subsequently kept at open-circuit for a period of over 24 h, then, on discharge, due to passivation, the cell state-of-charge will be high. If such a cell is stored at open-circuit for a long period (e.g. 6 months or more), the presence of the β- and γ-phases could lead to a higher level of passivity. This passivity may not be removed
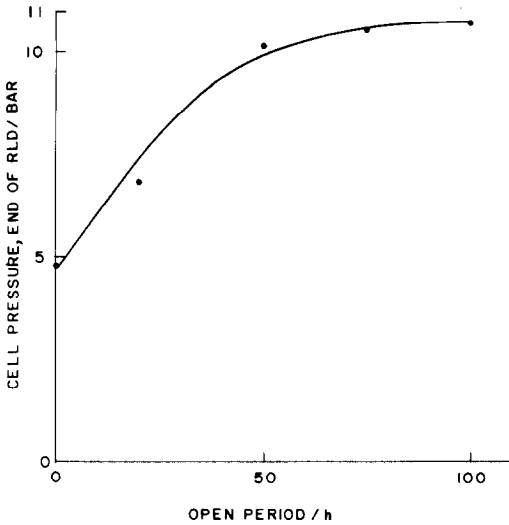
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Fig. 4. Variation of cell pressure at the end of 16 h of letdown across 0.5 Ω (following discharge to 1 V at *C*/2 rate and to 0.2 V at *C*/5 rate) with open-stand period.

within one charge cycle and this will lead to a lower capacity. Further, since the cells are generally stored in an open condition, a higher state-of-charge, even after a resistive letdown, may pose operational problems in handling batteries, especially if they are mounted in a spacecraft. This is particularly true as the state-of-charge after RLD is history dependent. It is concluded, therefore, that a specific planned charge/discharge cycle without overcharge must always preceed a possible storage of the cell/batteries. A consequence of the variable dischargeability of the nickel oxide electrode is that the start and end of charge/discharge pressures are not absolute indicators in terms of available capacity and considerable care must be taken to account for the effects of previous use.

Conclusions

In this work, it has been shown that the decay of pressure in a nickel/hydrogen cell is more complex than hitherto accepted. Charged open-stand of a nickel/hydrogen cell leads to electrode passivation and loss of capacity. The loss of capacity, however, is less than that indicated by the loss of cell pressure. The results of this study suggest that it is beneficial to apply a standard charge/discharge cycle without overcharge prior to any long storage period.

Acknowledgements

References

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