

Open-circuit voltage recovery of nickel/cadmium cells

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Abstract

Destructive study of nickel/cadmium cells is generally a preferred method of measuring cell degradation. The voltage recovery of these cells at a low state-of-charge has been in use as an acceptance test, even though efforts to correlate the cell voltage to degradation mechanisms have not been successful. In this study, the shape of the cell voltage recovery curve is correlated with the capacity-limiting electrode. It is shown that voltage recovery can give useful information of soft shorts in nickel/cadmium cells.

Keywords: Nickel; Cadmium; Cells

1. Introduction

Nickel/cadmium cells have been in use for over fifty years in both commercial and aerospace applications. Despite the fact that advanced batteries such as nickel/hydrogen and nickel/metal hydride cells are replacing nickel/cadmium cells, the latter still find a wide variety of applications. Since the positive nickel oxide electrode in all these cells is the same, studies of the performance of this electrode are essential.

One of the common features of interest in all cells is their degradation with use. There are many degradation mechanisms and modes and, depending on the application, one mechanism may overtake the other. Several destructive chemical and physical analysis techniques and methods have been developed to this end. While they have been successful in providing information about degradation, destructive methods suffer from the disadvantage that they alter some of the cell conditions. Thus, such approaches are unsuitable for measuring the progress of cell degradation. Non-destructive methods have been developed to measure the extent of cell degradation without destroying or vitiating the condition of the cells.

Open-circuit voltage recovery of nickel/cadmium cells has been employed as a screening test for cell acceptance. In this test, a cell is discharged to a very low state-of-charge and then the voltage is allowed to recover over 24 h. If the cell voltage recovers to greater than 1.15 V, the cell is considered to be in a good condition. Such tests are suitable for accep-

tance testing, but they do not throw light on the degradation of the cells.

NASA investigated [1] the voltage recovery of cells as a means of measuring/detecting cell degradation. The work did not, however, provide a sound basis for cell degradation studies. The NASA study concluded that the voltage to which a cell recovers, at low states-of-charge, cannot be correlated to degradation as the cell component variables are too complex. It is to be noted that in the studies conducted to date, efforts have been made to correlate the final cell voltage with the cell mechanisms. No effort has been made to study the nature of the voltage recovery or the shape of the voltage recovery curve (increase of voltage with time) with a view to assessing cell degradation.

In the present work, a study of the shape of the voltage recovery of a nickel/cadmium cell at low states-of-charge has been made. The work is restricted mainly to vented aircraft-grade cells in order to understand the recovery mechanism and develop an appropriate theoretical basis. The voltage recovery of sealed cells has also been measured for the purpose of comparison. Three vented 25 Ah cells and two hermetically sealed cells have been discharged to different, low states-of-charge, and the open-circuit voltage recovery has been monitored until an equilibrium is reached. The positive electrode and negative electrode potentials and the total cell voltages are measured using a Hg/HgO reference electrode. Different, low states-of-charge are achieved by shorting the cells for 1, 2, 4, 8 and 16 days, after a resistive discharge to 10 mV. This study has led to the possibility of

measuring and identifying degradation mechanisms in nickel/cadmium cells.

2. Experimental

2.1. Setup

The cell voltage is sensitive to temperature. Further, the dischargeability of the cells is also highly dependent on the temperature. Hence, the temperature of the cells during the whole experiment was kept within $\pm 0.5^\circ\text{C}$ by placing them in a hot and cold chamber. A temperature of 15°C was selected for the test as this is the most probable temperature of operation for nickel/cadmium cells. Suitable wires were taken out from the chamber for conditioning and measurement. The cell temperature was measured by a 10K YSI precision thermistor mounted on one of the cells and was recorded at regular intervals.

This study required the measurement of total cell voltages and the potentials of individual electrodes in the vented cells. The electrode potentials were measured with reference to a Hg/HgO reference electrode in the same electrolyte as the cell (31% KOH). The electrode potentials were measured by introducing the luggin bridge through a vent tube that was in contact with the bulk of the electrolyte. Since it was not possible to introduce the luggin very close to one of the electrodes without interfering with the cell arrangement, the luggin was introduced by removing the vent cap in the vented cells. This introduces an unknown voltage drop in the potential measurements during charging/discharging of the cells. During open-circuit measurements, however, this does not introduce any error as the current through the electrolyte is zero and the bulk of the electrolyte is equipotential.

In order to ensure that the reference electrodes do not introduce measurement errors, about eight Hg/HgO reference electrodes were made and the difference between their potentials were monitored in a 31% KOH solution for 72 h. Only those reference electrodes whose potentials did not differ by more than 1 mV over the entire period were selected for this study.

The cell voltages, the electrode potentials and the cell temperatures were measured by a data logger with a very high input impedance ($> 10\text{ G}\Omega$). The latter is essential to avoid loading of the cell. The voltages were monitored approximately once every hour and the voltmeter of $10\text{ G}\Omega$ impedance was connected to the cell for less than 20 ms. This ensured a very insignificant loading of the cell/electrode and a low cumulative discharge. A schematic diagram of the experimental setup is given in Fig. 1. The cell voltages were logged regularly and the cell data were printed with time tag for future analysis.

Cells were specifically selected to include all designs, so that maximum information could be collected in one run. Test were performed on: (i) three 23 Ah vented cells; and (ii) two fresh 18 Ah sealed cells. Out of the three vented cells

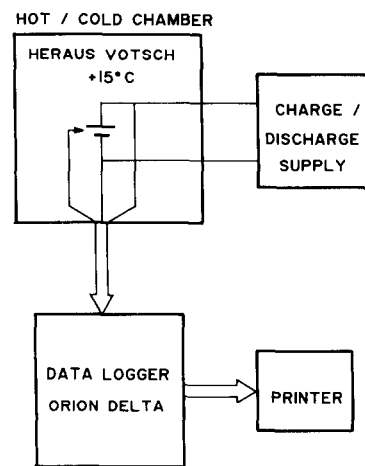


Fig. 1. Experimental setup.

of aircraft grade, one cell was positive limited, one was negative limited, and one was a marginal cell.

2.2. Procedure

The cells were first conditioned by a standard procedure to remove any effects due to previous storage. The cells were discharged to 1 V at the $C/2$ rate and then to 10 mV across $0.14\ \Omega$, $0.2\ \Omega$ and $0.3\ \Omega$ for 25 Ah vented cells, 18 Ah GAB cells and 12 Ah APPLE cells, respectively. The resistor values were selected in such a way that the relative discharges of all cells were same (i.e., higher the capacity, lower the resistance). Following resistive discharge, the cells were dead-shortened for 24 h using 16 AWG copper wires soldered to the terminals.

After 24 h of shorting, the cells were open circuited and the voltages were allowed to relax until the change in cell voltage was less than 1 mV in 2 h. This ensured that the cells had relaxed to their final voltage.

At the conclusion of one such test, the cells were dead-shortened for another 24 h to give a cumulative short period of 48 h. The cells were open circuited again and allowed to relax to their final value. The experiments were repeated to achieve cumulative short periods of up to 32 days. During this complete period, the cells were maintained at $15 \pm 0.5^\circ\text{C}$ inside a chamber.

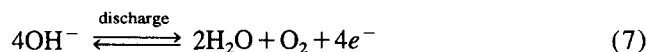
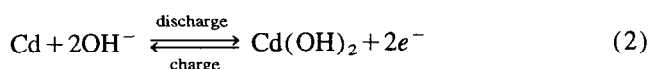
3. Results and discussion

The potential of a nickel/cadmium cell (E^r) is equal to the difference between the potentials of the positive electrode (E_+) and the negative electrode (E_-)

$$E^r = E_+ - E_- \quad (1)$$

3.1. Potential of negative electrode (cadmium electrode)

The equilibrium potential of the negative electrode can be determined from the corresponding half-cell reaction, i.e.:



Cadmium is a pure metal and, by definition, its activity is unity. Cadmium hydroxide is sparingly soluble in a 30–31% KOH solution and, hence, its activity is constant irrespective of the concentration of $\text{Cd}(\text{OH})_2$. Accordingly, the cadmium electrode potential depends only on the activity of the common anion $[\text{OH}^-]$. Hence:

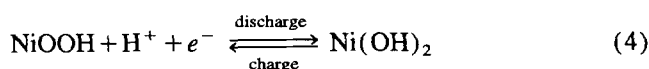
$$\begin{aligned} E_- &= E'_- + \frac{RT}{2F} \ln \frac{1}{a^2[\text{OH}^-]} \\ &= E'_- - \frac{RT}{F} \ln a[\text{OH}^-] \end{aligned} \quad (3)$$

where $E'_- = E_-^0 + RT/2F \ln a[\text{Cd}(\text{OH})_2]$, E_-^0 is the standard potential of the cadmium electrode; $a[i]$ is the activity of the species $[i]$; the other parameters have the standard meanings.

KOH is a strong electrolyte and its dissociation into K^+ and OH^- is complete. Water is added or removed during charge/discharge reaction, however, and thus slightly modifies the activity of OH^- between full charge and full discharge. Nevertheless, over small changes in the state-of-charge, the activity of OH^- can be treated as constant and, consequently, the electrode potential remains constant. The negative electrode potentials is fairly constant over a wide range of its state-of-charge and has a value of -0.91 V at 25°C versus Hg/HgO in a 31% KOH solution.

3.2. Potential of positive electrode (nickel oxide electrode)

The reaction at the positive electrode is:



From this equation, the electrode potential can be written as:

$$E_+ = E_+^0 + \frac{RT}{F} \ln \frac{a[\text{NiOOH}]a[\text{H}^+]}{a[\text{Ni}(\text{OH})_2]} \quad (5)$$

$$E_+ = E_+^0 + \frac{RT}{F} \ln \frac{a[\text{Ni}_3]a[\text{H}^+]}{a[\text{Ni}_2]} \quad (6)$$

where Ni_3 is NiOOH and Ni_2 is $\text{Ni}(\text{OH})_2$.

From Eq. (6), it can be seen that the positive electrode potential is dependent on the activities of Ni_3 , Ni_2 and H^+ . Both Ni_3 and Ni_2 are in solid solution; the diffusion of H^+ ions causes the change in the oxidation state. Hence, the potential changes as the cell is charged or discharged and depends on the state-of-charge. The change in the latter is due to diffusion of H^+ ions from the electrolyte into the bulk of the (electrode) active material.

The positive electrode potential can become more complicated as the oxygen-evolution potential on the nickel oxide electrode is fairly close to the Ni_3/Ni_2 reaction potential. The standard potential of the oxygen evolution reaction is:

where $E_0 = +0.401$ V versus standard hydrogen electrode (SHE) which is close to the E_+^0 value of 0.49 V versus SHE. Hence, the potential of the positive electrode is a mixed potential and will depend on the relative kinetics of the two reactions. A further complication occurs because of the presence of several crystalline states of the nickel oxide (i.e., α , β , Γ), which have different standard potentials. Hence, the open-circuit potential of a nickel oxide electrode is not equal to the equilibrium potential of the $\text{Ni}(2)/\text{Ni}(3)$ couple, but is a mixed potential. Accordingly, the open-circuit potential of the nickel oxide electrode displays a hysteresis that depends on the state-of-charge and the direction of approaching the state-of-charge [2].

3.3. Electrode potential when a cell is shorted and recovery on open circuit

When a nickel/cadmium cell is shorted across its terminals, after discharging to a very low state-of-charge, the electrode potentials depend on their respective charge states, namely, positive limited, negative limited or balanced.

3.4. Positive-limited cell; electrode potentials when shorted

In a positive-limited cell, the cell capacity is determined by the positive electrode and the capacity of negative is in excess. When the positive electrode is discharged completely, the negative electrode still has cadmium and its hydroxide in sufficient quantity. As the potential of the negative electrode is independent of its state-of-charge, its potential is constant at -0.91 V versus SHE. If the cell terminals are shorted then:

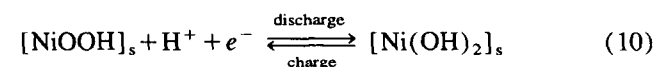
$$E = E_+ - E_- = 0 \quad (8)$$

$$E_+ = E_- \quad (9)$$

Thus, the positive electrode potential reaches -0.91 V versus SHE. During the shorted period, the positive electrode continues to discharge at very low rates ($C/1000$ or less). The discharge rate is limited by the solid-state diffusion of H^+ ions within the positive electrode (Eq. (4)). (Since the density of H^+ ions at low states-of-charge can be small and the diffusion constant low ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$), the discharge rate is small).

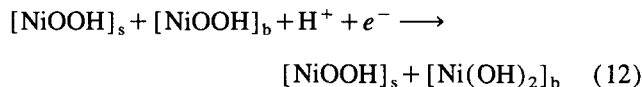
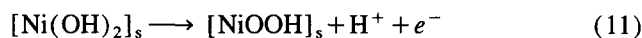
The diffusing species within the electrode have been studied by several workers [3,4]. The suggested sequence of reactions is as follows:

(i) At the active-material/electrolyte interface the reaction taking place is:

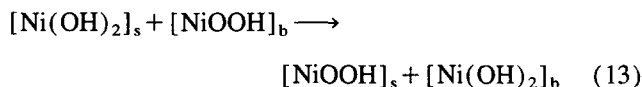


(ii) Later, H^+ ions diffuse from the $\text{Ni}/\text{Ni}(\text{OH})_2/\text{KOH}$ interface into the bulk of the electrode. This is driven by a

gradient in the electrochemical potential between the interface and the bulk. Thus:



and the net reaction is:



It follows that when a positive-limited cell is shorted, H^+ ions diffuse from the surface to the bulk and the discharge current is limited by the H^+ ion diffusion rate. Further, a gradient of the concentration of Ni_3 and Ni_2 is set up between the surface and the bulk of the positive electrode. It may be emphasized here that the electrode potential is determined by the surface activity (concentration) rather than by the bulk activity of the reacting species.

When a positive-limited cell is shorted, the positive electrode potential is close to that of the hydrogen-evolution reaction (HER). Thermodynamic calculations show [5] that the partial pressure of hydrogen under these circumstances is 0.07 atm at 25 °C. The kinetics of the HER have been studied [6] and confirm that the HER does occur at these potentials.

3.5. Recovery of cell voltage on open circuit of a previously shorted, positive-limited cell

When a shorted cell is open circuited, the cell voltage recovers. In a positive-limited cell, the potential of the negative electrode is constant, irrespective of the short or open condition of the cell. By contrast, the potential of the positive electrode recovers from about -0.91 V to about $+0.1$ to 0.3 V, as determined by the short duration. Fig. 2 shows the relaxation in potential of a vented cell (No. 4) which is marginally positive-limited. The potential of the positive electrode during shorting decreases from 0.0 V for a 1-day short to -0.88 V for a 8-day short.

When shorted, the concentration of $\text{NiOOH}(\text{Ni}_3)$ is zero at the electrolyte surface and the current is equal to the diffusion-limited current (i_{dl}). Soon after open-circuiting of the cell, the external current is zero and the current due to the Faradaic reaction charges the double-layer capacitor of the positive electrode. There will be no change in the potential of the negative electrode as its activities are constant. As the double-layer capacitor charges and the electrode potential increases from -0.91 V to less negative potentials, the concentration of NiOOH increases at the surface by diffusion of H^+ ions. As the concentration of NiOOH at the surface increases, the electrode potential increases and the diffusion rate of H^+ decreases. This results in a decrease in double-layer capacitor charge current. Hence, the rate of rise of positive electrode potential decreases asymptotically and reaches

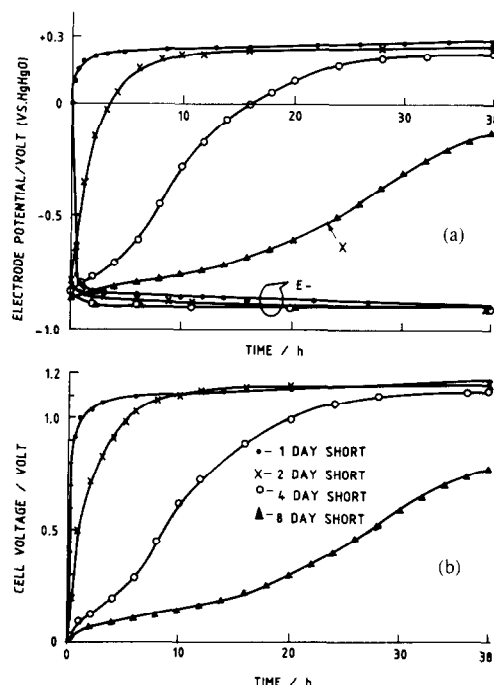


Fig. 2. Recovery of (a) cell voltage and (b) electrode potentials in a positive-limited nickel/cadmium vented cell following different periods of shorting.

an equilibrium value, that is decided by the bulk concentrations of Ni_3 and Ni_2 .

If a Nernstian reaction is assumed for the Ni_3/Ni_2 reaction, then:

$$\begin{aligned} E_+(t \longrightarrow \infty) &= E'_+ + \frac{RT}{F} \ln \frac{a[\text{NiOOH}]_b}{a[\text{Ni}(\text{OH})_2]_b} \\ &= E'_+ + \frac{RT}{F} \ln \frac{a[\text{Ni}_3]_b}{a[\text{Ni}_2]_b} \end{aligned} \quad (13)$$

where E'_+ is the formal potential.

$$E_+(t) = E'_+ + \frac{RT}{F} \ln \frac{[\text{Ni}_3]_s}{1 - [\text{Ni}_3]_s} \quad (14)$$

and $E_+(t)$ will depend on the surface concentration.

The time dependence of the voltage recovery will depend on the diffusion of H^+ ions to the surface. This, in turn, is dependent on the following factor: (i) the amount of NiOOH remaining, which depends on the electrode resistance and the duration of the short, and (ii) the distance of diffusion or the size of the crystallites in the pores of the positive electrode. These two factors are not independent of each other and also vary from cell to cell. Hence, it is not easy to model the cell voltage recovery with time in a closed mathematical form. It is very likely that two cells of the same capacity and type, when subjected to the same preconditioning, may give rise to different voltage recovery patterns.

Despite variations between cell to cell, certain general patterns can be observed in the voltage recovery of positive-limited cells (Fig. 2). Namely:

(i) region between 0 and 0.2 V where two faradaic reactions occur, namely, HER and Ni_3/Ni_2 , with a smaller rate of voltage rise (Ni_3/Ni_2 current feeding the HER and capacitor charging);

(ii) region between 0.3 and 0.7 V, where the rate of voltage rise is maximum and the current produced by the Ni_3/Ni_2 reaction goes only to charging of the double-layer capacitor, and

(iii) region between 0.9 and 1.1 V where the cell positive is fairly close to its equilibrium potential.

It has been shown that in the last region, the cell voltage/time can be modelled by first-order differential equations with diffusion as the limiting factor [7].

In the region between 0.3 and 0.7 V, the potential of the positive is well removed from the HER and Ni_2/Ni_3 reactions. Hence, this region can be modelled as a diffusion-limited Faradaic reaction that charges the double-layer capacitor. The diffusion current is dependent on the aspects discussed above. The double-layer capacitance is not constant in this potential range, but exhibits a minimum value around 0.45 V. Hence, even if the diffusion-limited current is constant in this voltage region, the capacitor charging curve will be non-linear.

In the voltage range between 0.0 and 0.3 V, it has been shown that the HER occurs. Hence, the current produced by discharge of the Ni_3/Ni_2 reaction goes to ionization of hydrogen and charging of the positive double layer.

The above discussion shows that the recovery of the cell voltage in a positive-limited cell cannot be easily modelled. The parameters that affect the voltage recovery depend on cell history, and the cell internal construction. Even though the parameters affecting the voltage recovery are known qualitatively, they cannot be quantified easily.

3.6. Comparison of voltage recovery of two identical cells

Two, 18 Ah sealed aerospace cells were included in the study. These two cells were from the same batch of manufacture and had undergone exactly same tests and use. They were relatively fresh cells and were selected to examine differences in the voltage recovery profiles. The two cells (027 and 032) underwent identical preparation and tests. The results are plotted in Figs. 3 and 4 for shorting periods of 1, 2, 4 and 8 days prior to open circuiting at 15 °C. The following observations can be made from these data:

(i) The final voltage to which the cell recovers is about the same (within ± 0.1 V) for shorting periods up to 4 days. For 8 days shorting, the final voltage is highly variable between cells of the same pedigree.

(ii) The time taken by the cell to reach 10% of the final voltage is not same for the two cells; this is also true for the time taken to reach 90% of final voltage. Though larger shorting periods lead to longer times to reach 10 and 90% values, the spread between cells is large.

These observations indicate that the final cell voltage and time to reach 10 and 90% of the final voltage are subject to large variations. Hence, they cannot be used to compare the

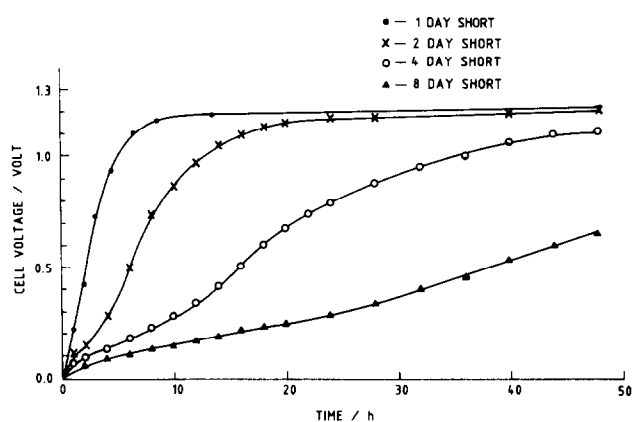


Fig. 3. Recovery of cell voltage in a sealed nickel/cadmium following different periods of shorting.

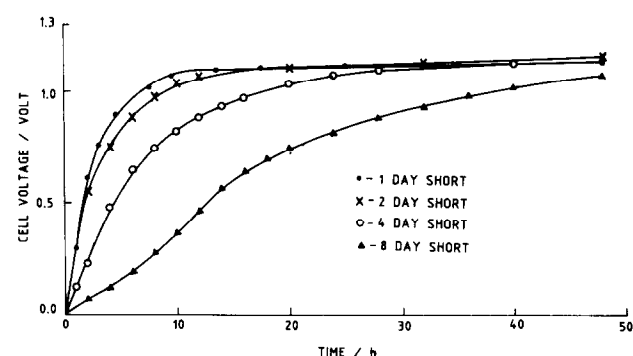


Fig. 4. Recovery of cell voltage in a sealed nickel/cadmium following different periods of shorting.

states of cells or their degradation in a general sense. These parameters may, however, be used for looking at the progression of degradation within a cell.

3.7. Negative-limited cells

3.7.1. Electrode potentials when shorted

Cells with capacity that is limited by that of the negative electrode are termed 'negative-limited' cells. Generally, negative-limited cells are not produced, but due to degradation in the capacity of the cadmium electrode, a previously positive-limited cell can become negative limited. In vented cells, the capacities of positive and negative electrodes are nearly the same, but after use for a short while they can become negative-limited.

When a negative-limited cell is discharged and shorted, the negative electrode approaches a zero state-of-charge but the positive electrode still has some capacity. Thus, the potential of the negative electrode increases from -0.91 V (versus Hg/HgO) to that of the positive electrode. The latter could be at a potential anywhere between $+0.31$ and 0.0 V, as determined by the state-of-charge. Thus, the nickel oxide electrode can be discharged only up to 0.0 V (maximum).

3.7.2. Recovery of cell voltage

When a negative-limited nickel/cadmium cell is open circuited from a shorted condition, the potential of the positive electrode increases from about 0.1 to about 0.2–0.3 V (versus Hg/HgO). The potential of the negative electrode, however, decreases from about +0.1 to -0.91 V (versus Hg/HgO). On open-circuit cell, Eq. (2) produces electrons that charge the double-layer capacitor of the cadmium electrode. The negative electrode can relax only if sufficient cadmium remains in the electrode for Eq. (2) to occur from left to right. This is generally possible as $\text{Cd}(\text{OH})_2$ is an insulator and, hence, the total discharge of cadmium will take a very long time (i.e., several days). Also, since cadmium is an electrode of the second kind, only a very small quantity of cadmium (sufficient to form a monolayer) is required to stabilize the potential of the electrode. It is seen from Eq. (3) that the potential of the negative electrode is dependent on the activity of cadmium at the interface; as soon as a monolayer of cadmium is formed, the potential stabilizes at -0.91 V. The negative electrode as it tries to relax, after open circuit, has to charge the double-layer capacitor. As this reaction is a dissolution/precipitation reaction and does not involve diffusion, the fall of potential will be very fast compared with the positive electrode, the potential of which is determined by the diffusion in solid solution.

In a negative-limited cell, the increase in the cell voltage is dominated by the negative electrode. Hence, the shape of the voltage relaxation curve must be markedly different from that for a positive-limited cell. Fig. 5 shows the cell voltage (cell No. 6) relaxation curve for a nearly negative-limited

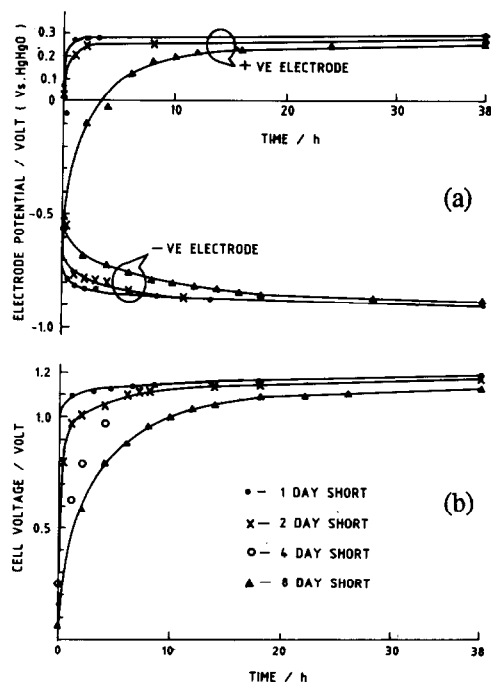


Fig. 5. Recovery of (a) cell voltage and (b) electrode potentials in a negative-limited nickel/cadmium vented cell following different periods of shorting.

vented nickel/cadmium cell. The relaxation of the potentials of the individual electrodes is also given with respect to a Hg/HgO reference electrode. It can be seen that the potential of the negative electrode rises to about 0.0 to +0.1 V during shorting. Soon after open circuit of the cell, the potential of the negative electrode decreases rather sharply to about -0.6 to -0.7 V and then to its final value of -0.88 to -0.89 V slowly. The potential of the positive electrode also increases rather rapidly as sufficient capacity is still left in the electrode. The capacity of negative electrode is marginally more than the positive and, hence, when the short duration increases, the positive electrode discharges sufficiently for its voltage to reach to -0.5 V (for 8 days short).

The cell voltage relaxation curve for a 1-day short resembles that of a negative-limited cell, while for shorts of 4 days and 8 days the cell voltage relaxation curve resembles that of a diffusion-limited relaxation as in a positive-limited cell.

3.8. Comparison between cell voltage relaxation curves of positive-limited and negative-limited cells

The voltage relaxation of both positive and negative electrodes involve charging of the double-layer capacitor, but with differing limiting currents. Thus, if sufficient positive active material is left in the positive electrode (i.e., when short duration is small), the relaxation pattern of the total cell voltage in a positive- or negative-limited cell may be indistinguishable. Under these circumstances, it is essential to study the voltage-relaxation characteristics for different short durations to differentiate between limiting electrodes.

In Table 1, the time taken by the cell to reach 10 and 90% of the final voltage is given. It may be observed that the time taken to reach 10% of the final value is practically zero (< 10 min) in a negative-limited cell. In a positive-limited cell, this time increases from about 0.4 to about 3 h, depending on the short duration.

Fig. 6 compares the voltage relaxation of a vented negative-limited cell, a vented positive-limited cell and a sealed positive-limited cell following a short period of 4 days. Comparing the voltage relaxations, the following conclusions can be drawn:

(i) An exact, quantitative description of the cell voltage relaxation cannot be made in a closed mathematical form. It is also not interesting to attempt such a modelling, as the parameters to be introduced in such a model vary from cell to cell and from manufacturer to manufacturer. This renders the model restricted/non-versatile for cell degradation studies.

(ii) There is a marked difference in the nature of the cell voltage relaxation between positive-limited and negative-limited cells. Even though the general description of the relaxation curve is qualitative, the time required to attain 10 and 90% of the final voltage can be treated as indicators of the capacity-limiting electrode in a cell on semi-quantitative basis. A very short time (< 0.1 h) taken to reach 10% value

Table 1
Time required to reach 10 and 90% of final voltage for different cells

Short period (days)	Final voltage (V)	Time to reach 10% of final voltage (h)	Time to reach 90% of final voltage (h)
<i>Cell No. 6 vented (negative limited)</i>			
1	1.19	0	0
2	1.18	0	4
3	1.17	0	6
4	1.16	0	13
<i>Cell No. 4 vented (positive limited)</i>			
1	1.17	0.0	2
2	1.16	0.1	5
4	1.15	1.5	21
8	1.13	6.0	53
<i>Cell No. 27 sealed (fresh cell)</i>			
1	1.16	0.4	8
2	1.16	0.4	11
4	1.15	1.0	20
8	1.15	2.0	41
<i>Cell No. 32 sealed (fresh cell)</i>			
1	1.21	0.46	6.4
2	1.19	1.0	15.5
4	1.16	3.2	39
8	1.11	2.6	83

indicates that the negative electrode is the capacity-limiting electrode.

(iii) A positive-limited cell tends to have an 'S' shaped relaxation curve, which is characteristic of diffusion-dominated process.

(iv) It is necessary to observe voltage-relaxation curves for different durations of shorting before the above observations can be conclusively made.

3.9. Electronic short between positive and negative electrodes

An electronic short between the cell electrodes in a previously good cell is possible by migration of cadmium from the negative to the positive electrode and deposition of cadmium on the separator. The cell shorting can be accentuated by swelling of the positive electrode and compressing of the electrode stack.

A very low resistance short ($\sim 0.1 \Omega$) can be easily recognized by the inability of the cell to deliver capacity. But shorts with resistances of the order 200Ω cannot be detected by capacity measurement or charge-retention tests. Consider a cell of 20 Ah capacity, with a loss of charge that is due to purely electrochemical reasons, such a cell could lose about 2 to 3% charge per day at 15 to 25 °C. Thus, in a 8-day charge-retention test, the charge lost could amount to 16 to 24%. Hence, in a standard charge-retention test, loss of up to 20% of measured capacity is considered normal. If such a cell has a 100Ω electronic short, the charge lost in this path is about

6%: charge lost = $8 \times 24 \times (1.3/200) = 2.5$ Ah, or 6% for 20 Ah cell.

A 6% change is within the acceptable limits of a standard charge-retention test and a soft short cannot be detected.

Electronic shorts of the order of 100 to 10 000 Ω can be detected by a potentiostatic test from a stable power supply or a potentiostat. This technique has been developed previously [7]. Another method of detecting electronic shorts of the order of 100 Ω is by voltage recovery. The standard voltage spring-back test, performed generally as part of acceptance test procedure, is expected to detect such shorts. The failure criterion of the voltage spring-back test is the maximum voltage to which the cell recovers in 24 h after a 24-h short; this voltage has to be greater than 1.16 V. It has been observed that the ultimate cell voltage varies by about ± 0.2 V, as dictated by the cell temperature and previous history. Further, the 24-h short period selected is rather arbitrary.

The voltage-recovery characteristic depends on the dischargeability of the cell and the resistance of the electronic short between the electrodes. Since, the cell dischargeability varies from cell to cell, it is necessary that voltage recovery characteristics are studied for different periods of shorting. When a cell with an electronic short is allowed to relax, the residual charge flows in two paths, namely, (i) to charge the electrode double-layer capacitors, and (ii) across the electronic short that is discharging the cell. Depending on which of the two processes is faster, the voltage characteristic will change. If there is sufficient active material still left in the charged state, the diffusion currents are larger than the dis-

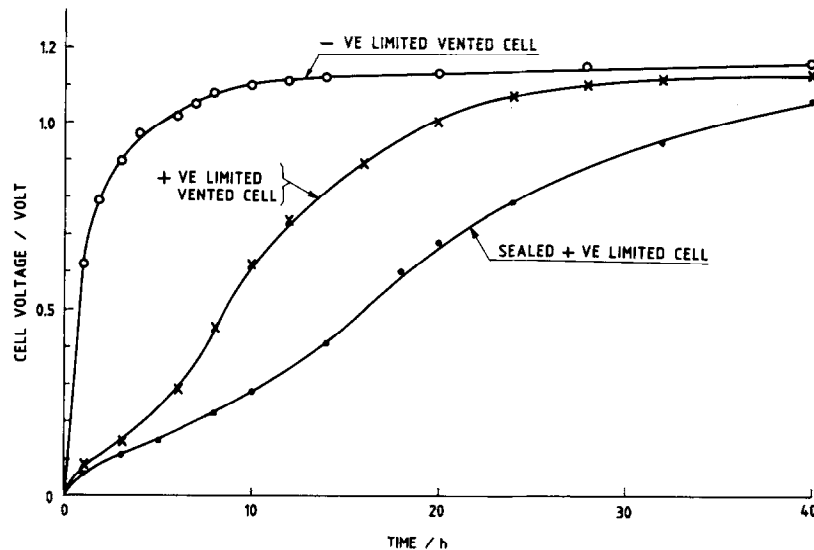


Fig. 6. Comparison of cell voltage recovery of (×) a positive-limited vented, (○) a negative-limited vented, and (●) a sealed nickel/cadmium cell, following 4 days of shorting.

charge through the electronic resistance path. In such a situation, the cell voltage will increase to a peak value of about 1.15 to 1.2 V and then start decreasing. The rate of the voltage drop will depend on the resistance of the short. If, on the other hand, the cell has undergone shorting for a long duration, the discharge current through the electronic short at that voltage will be more than the diffusion current and the voltage will be determined by the diffusion current. Under such conditions, the cell voltage will increase to a value is determined by the electronic resistance between plates.

The voltage recovery of a sealed nickel/cadmium cell with a resistor of 100 Ω connected between the positive and negative plates is shown in Fig. 7. The resistor simulates an internal electronic short. Depending on the period of shorting, the cell voltage recovers to a maximum voltage and then decreases.

Thus, it may be possible to detect the presence of an electronic resistive path between the cell electrodes from a study of the voltage recovery of cells. A quantitative estimate of the value, however, may require a potentiostatic test.

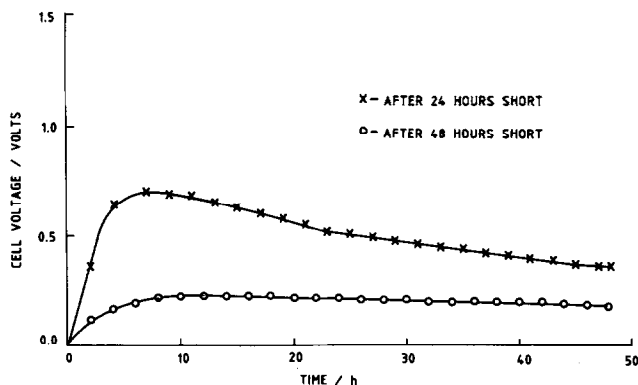


Fig. 7. Recovery of cell voltage with an external resistor of 100 Ω connected across a sealed nickel/cadmium cell.

4. Conclusions

This study has shown that the open-circuit recovery method can be used to examine cell degradation non-destructively. In particular, electronic shorting and negative-limited cell conditions can be easily identified with this method. A more thorough study with several types of cells may be necessary to extend the scope of prediction.

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