ELECTRODE KINETICS OF A NICKEL/CADMIUM CELL AND FAILURE-MODE PREDICTION. ESTIMATION OF EQUIVALENT RESISTANCE OF AN INTERNAL SHORT

M DURGA PRASAD and S SATHYANARAYANA*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore - 560 012 (India)

(Received December 23, 1985, in revised form August 4, 1986)

Summary

A quantitative expression has been obtained for the equivalent resistance of an internal short in rechargeable cells under constant voltage charging. The expression has been experimentally verified with both positive-limited and negative-limited nickel–cadmium cells, using simulated internal electronic shorts. Findings show that the absolute values of the resistance of such internal shorts can be predicted in an accelerated and non-destructive manner.

Introduction

One of the common failure modes of rechargeable batteries, such as the nickel/cadmium system, is extensive self-discharge resulting from the spontaneous development of internal shorts. Both the detection and the quantitative determination of the resistance due to such internal shorts is therefore essential if reliability of operation is to be achieved.

An internal short may be defined as a conducting path in parallel with the normal electrolytic path between the positive and negative electrodes of a cell. Depending on the resistance of this conducting path, the internal short can be classified into two types, *viz*, "hard short" and "soft short". The hard short occurs when the internal-shorting resistance is small enough to cause the cell to self-discharge rapidly after charging. It can easily be detected since the cell voltage does not rise significantly from zero volts on charge. However, the soft short, whereby the resistance of the conducting path causes self-discharge to be substantially higher than that for a hard short, cannot easily be detected. An internal short may form as a result of: (i) shedding of electrode material during cycling; (ii) penetration and deposi-

*Author to whom correspondence should be addressed

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tion of electrode material in the separator during cycling, (iii) deformation of electrodes causing contact between electrodes of opposite polarity

Techniques [1, 2] used to detect internal shorts in nickel/cadmium cells include (i) measurement of decay in open-circuit voltage (OCV) and subsequent discharge capacity after a given standing period, (ii) recovery of OCV after a full discharge, (iii) decay of OCV after a partial charge following a full discharge All these methods have been critically reviewed [3] It has been pointed out in ref 3 that the criteria adopted to screen "good" cells from "bad" cells in methods (ii) and (iii) are inadequate and often lead to erroneous conclusions It has also been emphasized that the results obtained by these methods are influenced by the capacity of the cells and the type of separator used Further, even the qualitative screening tests (ii) and (iii) require 72 - 96 h, and test (i) takes about 240 h To-date no method has been reported to determine the ohmic resistance of an internal short and, hence, to quantitatively characterise the extent of capacity degradation*. In the present work, we present details of a simple, non-destructive technique to achieve this aim and show that the procedure can be applied to nickel/cadmium cells of either a positive-limited or a negative-limited design.

Theory

The technique basically involves the measurement of steady-state current or voltage of a cell when subjected to constant-voltage charging. The procedure may be understood with reference to the test circuit schematically shown in Fig. 1. On application of Kirchoff's law, the following relation is obtained·

$$V^0 - JR_x - V = 0 \tag{1}$$

where

$$V = E_c - E_a + J_i R_i \tag{2}$$

Since R_e is a parallel resistance across the cell electrodes, V is again given by

$$V = J_e R_e \tag{3}$$

Also,

$$J = J_e + J_i \tag{4}$$

*The typical rate of self-discharge of a good (i e., without any internal short) vented, sintered-plate, nickel/cadmium cell is about 10% of its nominal capacity after 30 days of charged stand [4] For a cell of capacity Q, A h, this self-discharge rate current is therefore 0 1 $Q/(30 \times 24)$, $\approx 1\ 4 \times 10^{-4}\ Q$, A Assuming a cell voltage of 1 26 V, the equivalent resistance of the normal self-discharge process is therefore $\sim 9000/Q$, Ω In a nickel/cadmium cell, an internal soft short may be considered to exist when its equivalent resistance is comparable with or less than the normal value

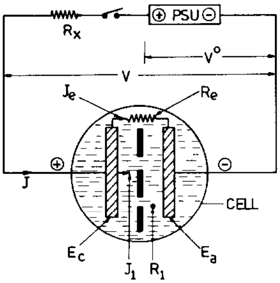

Fig 1 Schematic for constant-voltage charging of a cell from an initial zero state-of-charge to a final voltage V^0 corresponding to a pre-determined state-of-charge (~ 0 01) PSU Power Supply Unit, other features given in list of symbols

Equations (1) - (4) may be combined to give:

$$E_c - E_a = \frac{R^2}{R_e R_x} V - \frac{R_1}{R_x} V^0 \tag{5}$$

where

$$R^2 = R_e R_1 + R_1 R_x + R_x R_e \tag{6}$$

Eventually, charging at a constant voltage V^0 results in the electrodes becoming fully charged and thus attaining their open-circuit potentials (which are equal to the respective reversible potentials when there are no side-reactions at the electrodes). At the same time, the cell current due to the normal cell reaction reduces to zero. In other words:

$$E_c \longrightarrow E_c^r; E_a \longrightarrow E_a^r; J_1 \longrightarrow 0, \text{as } t \longrightarrow \infty \tag{7}$$

Under these conditions, the voltage of the cell, which may be represented as V_∞, is obtained from eqn. (2) as:

$$V_\infty = V^r = E_c^r - E_a^r \tag{8}$$

From eqns. (5), (7) and (8), it follows that:

$$V_\infty = \frac{R_e}{(R_e + R_x)} V^0 \tag{9}$$

and

$$R_e = \frac{V_\infty}{(V^0 - V_\infty)} R_x \tag{10}$$

Equation (10) is of great practical importance in that it provides a means of quantitatively obtaining the value of the internal shorting resistance, R_e, by recording the cell-response curve (*i e.*, *V versus t*, Fig. 2) during constant-voltage charging until a steady-state is attained, and measuring V_∞ and V^0. (Note, in eqn (10), the value of R_x is always known experimentally, being the resistance of the circuit external to the cell.)

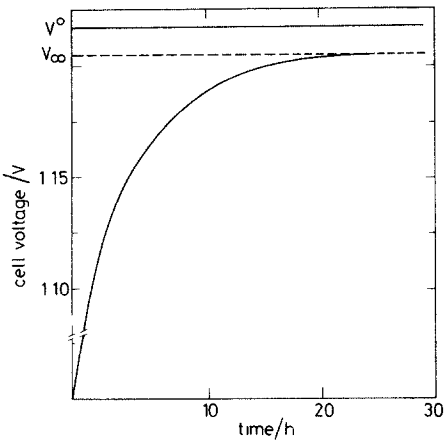

Fig 2 Schematic dependence of cell voltage (V) on charging time

It is to be noted that eqns. (1) - (10) are valid for any rechargeable cell subjected to a constant-voltage charge provided reactions other than the normal cell reaction do not occur at that voltage Hence, the selection of voltage range assumes importance in this method.

For a nickel/cadmium cell, the region around state-of-charge (SOC) = 1 is unsuitable due to the occurrence of overcharge reactions. The plateau region (SOC $\approx$ 0.5) is unsuitable due to· (a) the small slope of the curves, which leads to a poor sensitivity since a relatively large change in SOC corresponds to a small change in cell voltage, (b) the presence of oxygen evolution as a side reaction on the positive electrode in this region The portion of the curves corresponding to an SOC $\approx$ 0 01 is appropriate, since a small change in SOC corresponds to a large change in cell voltage and the extent of side reactions is likely to be insignificant in the steady state

Experimental

The nickel/cadmium cells under test were fabricated and supplied by the Vikram Sarabhai Space Centre, Trivandrum, India. The cells were pressure-vented and used a sintered-plate construction with electrochemically impregnated positive and negative electrodes. Both positive-limited and negative-limited designs were tested. In all cases the nominal capacity ($C/2$ rate) was 3 A h

After a conditioning cycle (charging at $C/10$ rate for 16 h, discharging at $C/2$ rate to zero volts), the cells were individually dead-shorted for 24 h. This shorting ensured that the initial SOC of the cell was close to zero.

The test circuit is shown schematically in Fig 3. An internal 'soft' short as explained above was experimentally simulated by connecting a resistance (R_2) of suitable value across the terminals of the cell

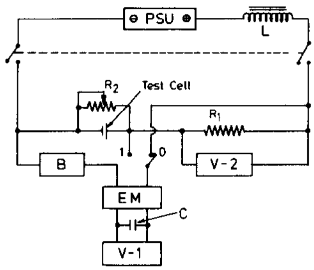

Fig 3 Schematic set up employed for the detection and determination of internal short PSU, Wenking scanning potentiometer SMP-72, R_1, 1 Ω precision resistor, R_2, resistance box (1 - 10^4 Ω) for simulating internal short, B, off-set voltage source ('Knick' precision voltage source S-16), L, inductance (1 Ω, 100 mH), C, low-loss metallized polystyrene capacitor (2 5 μF, 100 V), EM, Keithley Electrometer, input impedance 10^{12} Ω, V-1, $4\frac{1}{2}$ digit panel meter in 200 mV range with a resolution of ±0 01 mV, V-2, As V-1, for measuring potential drop across R_1

The set voltage was held constant to within ±10 μV. Alternating voltage noise pick-up by the sensitive meter V-1 was eliminated by a low-loss capacitor connected across its terminals

It was frequently found that sudden line-voltage fluctuations (voltage spikes) caused the constant-voltage power supply unit (PSU) to malfunction and exhibit a reverse voltage at its output. This was overcome by the inductance (L) in the test circuit.

Results and discussion

The time dependence of the deviation of the cell voltage from the constant charging voltage for different values of the latter, and for various values of external shorting resistances is shown in Figs. 4 and 5 for positive-limited and negative-limited cells, respectively. As expected, the cell voltage approaches a limiting value that is closer to the charging voltage for the higher value used for the resistance of the simulated internal short. Further, the time taken to attain a steady-state voltage increases with an increase in the applied voltage.

The above facts may be readily understood as follows. The cell is initially close to zero SOC. Thus, for any applied constant voltage, the cell will sustain both an ionic current required for the electrodes to reach a new SOC, as well as an electronic current through the simulated short. Since the applied voltage is chosen so that the equilibrium SOC of the cell will still be small compared with unity, no side reactions such as oxygen evolution or hydrogen evolution are likely to occur to any significant extent. In other words, the ionic current will decay to zero with time. Any quiescent current observed in the steady state is therefore totally governed by the (simulated) shorting resistance between the cathode and anode As the voltage chosen

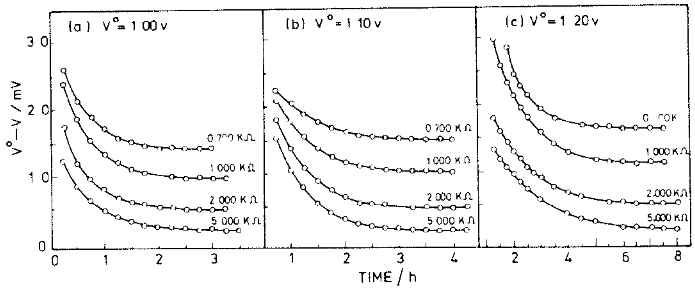

Fig 4 Deviation of cell voltage from charging voltage ($V^0 - V$) *vs* time for a 3 A h *positive-limited* nickel/cadmium cell with different simulated internal shorts of resistance as shown, and for different charging voltages, V^0

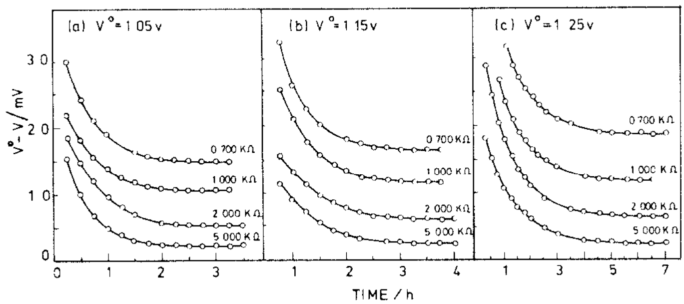

Fig 5 Deviation of cell voltage from charging voltage ($V^0 - V$) *vs* time for a 3 A h *negative-limited* nickel/cadmium cell with different simulated internal shorts of resistance as shown, and for different charging voltages, V^0

(V^0) increases, a higher A h input (and, hence, a longer time) is required for the cell to attain a steady state

The resistance of the simulated internal short, R_e can be determined by applying eqn (10) to the data obtained from Figs. 4 and 5. Table 1 presents a comparison of the actual and calculated values of the resistance due to simulated internal shorts in positive-limited and negative-limited cells The results show that, for both cell designs, the resistance causing a cell short is quantitatively predictable to within about 4% for charging voltage $V^0 \leqslant$ 1.150 V, but that the accuracy decreases as the values chosen for V^0 are increased. The latter is mainly due to the inadequate attainment of a steady state in an experiment of a given duration and therefore may not be a basic limitation of the method.

Although the above problem does not arise at low values of V^0, the well-known phenomenon [1, 2, 5] of the spontaneous recovery of the open-circuit voltage of a discharged nickel/cadmium cell to a value of about 1 10 V will vitiate measurements if V^0 is much less than this value Hence, a value of about 1.150 V for V^0 is appropriate for the test.

Inspection of Figs. 4 and 5 shows that the duration of the test is $\leqslant$ 8 h for a 3 A h cell if the external circuit resistance (R_1) is 1 Ω The test duration could be decreased by decreasing the external-circuit resistance, since this,

TABLE 1

Comparıson of expected (R_e) and observed (R_e') values of resıstance due to sımulated ınternal short ın posıtıve-lımıted and negatıve-lımıted nıckel–cadmıum cells

Set voltage, V^0 (V)	R_e (kΩ)	Steady state voltage, V_∞ (mV)	R_e' (kΩ)	Error (%)
Posıtıve-lımıted cells				
1 0000	5 0000	999 79	4 761	4 78
	2 0000	999 49	1 960	2 00
	1 0000	999 00	0 999	0 10
	0 7000	998 56	0 693	1 00
1 100	5 0000	1099 77	4 781	4 38
	2 0000	1099 43	1 923	3 85
	1 0000	1098 89	0 990	1 00
	0 7000	1098 42	0 695	0 71
1 200	5 0000	1199 74	4 614	7 72
	2 0000	1199 36	1 874	6 30
	1 0000	1198 74	0 951	4 90
	0 7000	1198 23	0 677	3 29
Negatıve-lımıted cells				
1 050	5 0000	1049 78	4 772	4 56
	2.0000	1049 46	1 943	2 85
	1 0000	1048 94	0 989	1 10
	0 7000	1048 50	0 699	0 14
1 150	5 0000	1149 75	4 599	8 02
	2 0000	1149 39	1 884	5 80
	1 0000	1148 81	0 965	3 50
	0 7000	1148 34	0 962	1 14
1 250	5 0000	1249 72	4 463	10 74
	2 0000	1249 32	1 837	8 15
	1 0000	1248 78	1 023	−2.30
	0 7000	1248 10	0 657	6 14

together wıth the charging voltage, controls the charging current of a nıckel/cadmıum cell. Such an approach could be particularly useful for hıgh capacıty cells.

Conclusions

A new method has been evolved to detect, and to quantıtatıvely determıne ın an accelerated and non-destructıve manner, the presence of an ınternal electronıc short ın rechargeable cells. The method ınvolves measurement of the steady-state voltage of the cell when subjected to a constant-voltage charge. An experimental verification of the proposed method has been carried out successfully with vented nickel/cadmium cells of both positive-limited and negative-limited designs

Acknowledgement

Financial support by Indian Space Research Organisation through a RESPOND grant is gratefully acknowledged.

List of symbols

E_a	Potential of anode
E_a^r	Reversible potential of anode
E_c	Potential of cathode
E_c^r	Reversible potential of cathode
J	Total circuit current
J_e	Current through internal short
J_i	Current through the cell due to double-layer charging and charge-transfer reactions
R_e	Equivalent resistance of internal short
R_e'	Experimental value of resistance of internal short.
R_i	Internal resistance of cell
R_x	Resistance of ammeter
SOC	State-of-charge
V^0	Charging voltage
V	Cell voltage
V^r	Reversible cell voltage
V_∞	Steady-state cell voltage (= V_r).

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