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Journal of Power Sources 69 (1997) 89–96

JOURNAL OF POWER SOURCES

Using a pulse-current technique and measured resistance to evaluate the capacity of trickle-charged nickel/cadmium cells

Naoki Kato [a,*], Tsutomu Ogata [a], Toshiro Hirai [a], Harumi Hirota [b]

[a] *NTT Integrated Information and Energy Systems Laboratories, 3-9-11 Midori-cho, Musashino-shi, Tokyo 180, Japan*

[b] *NTT Advanced Technology Corporation, 3-9-11 Midori-cho, Musashino-shi, Tokyo 180, Japan*

Received 18 November 1996; accepted 31 January 1997

Abstract

The use of a pulse-current technique to evaluate the capacity of trickle-charged nickel/cadmium (Ni/Cd) cells is investigated. A current pulse is applied to the cells in the charging mode and the resistance is estimated from the change in voltage. A linear relationship between the capacity and the logarithm of the resistance is observed. The combination of a pulse current of 0.1–1.0 C and a pulse width of 10 ms or less displays a high correlation coefficient for deteriorated cells. The error between the evaluated and the measured capacity is less than 10%, on average, under these conditions in the capacity range of greater than 50% nominal capacity. © 1997 Elsevier Science S.A.

Keywords: Nickel/cadmium cells; Trickle-charge; Deterioration; Electrolyte loss; Pulse-charging; Resistance

1. Introduction

Trickle-charged nickel/cadmium (Ni/Cd) cells are widely used to provide power to telecommunications equipment when commercial a.c. power supplies fail. Future telecommunication systems running on optical networks will require many storage cells [1], and it will be important to maintain the reliability of these systems. The aim of the research reported here is to develop a simple, less time-consuming, method for monitoring the condition of trickle-charged Ni/Cd cells.

Many studies [2–6] have investigated the effectiveness of impedance and pulse-current methods for determining the state-of-charge of Ni/Cd cells. These methods were shown to be effective and non-destructive; good correlation was found between the state-of-charge and the impedance, and between the state-of-charge and the admittance.

We previously proposed [7] using electrolyte-deficient model cells instead of high-temperature accelerated testing for the determination methods that use the impedance technique [7]. For both model and practical cells, a linear relationship was found between the capacity and the logarithm of the impedance at the point of the imaginary part of zero in the Cole–Cole plot. Using this relationship, the capacity can be determined quickly. This method, however, requires expensive equipment to measure the impedance. A simpler and easier method is thus needed.

In this paper, a simpler determination method is presented in which the resistance is first determined by measuring the voltage change created by the charge current pulse. A linear relationship can then be obtained between capacity and resistance under certain pulse conditions. The effectiveness of this method is determined by tests on used cells.

2. Experimental

2.1. Samples

Measurements were performed on C-size, trickle-charged Ni/Cd cells that had been used for emergency lighting. The cells had nominal capacities of 1800 and 1650 mAh and were produced by Manufacturers A or B in either the 1980s or the early 1990s. These cells are termed 'used' cells. Unfortunately, equivalent fresh cells could not be obtained because current Ni/Cd cells have been greatly improved, both in component materials and in production processes.

* Corresponding author. Tel.: +81 (422) 59 30 15; Fax: +81 (422) 59 43 50.

PII S0378-7753(97)02577-9

2.2. Electrolyte-deficient model cells

New D-size Ni/Cd cells with different amounts of electrolyte for trickle-charging were obtained from Manufacturers A and B. The nominal capacity of cells with a standard amount of electrolyte was 4000 mAh for both manufacturers

2.3. Cell performance measurements

The used and model cells were first discharged at 0.2 C to 1.0 V. Next, the cells were charged at 0.1 C for 15 h and then discharged at 0.2 C to 1.0 V. This cycle was repeated two or three times with 1 h intervals. After the last discharge capacity was recorded, the cells were fully charged and used for impedance measurement. The 'fully charged' state was taken when the cell-charging voltage either became constant or lower after having a voltage peak. The charge/discharge measurements were performed with a charge/discharge control unit (Hokuto Denko, HJ-201B) at room temperature.

2.4. Resistance measurements

A current pulse was applied to the used and model cells in the charging-current direction by using a current pulse generator (ADVANTEST R6246). The cell-voltage change was monitored using a digital oscilloscope (Yokogawa DL-1300); the applied pulse current was monitored using a current-probe amplifier (Tektronix AM502A) and a high-frequency active probe (Universal Probe ASP500). The resistance, R, was defined as

$$R = \Delta V / I \quad (1)$$

where ΔV is the difference between the cell voltage before the pulse current is applied and that immediately before it is switched off (see Fig. 1); I is the pulse current. The value of R depends on both I and the pulse width, t. The tests were conducted at room temperature under the 15 conditions defined by a matrix of three currents (0.1, 0.5, and 1.0 C) and five pulse widths (0.0001, 0.001, 0.01, 0.1, and 1 s).

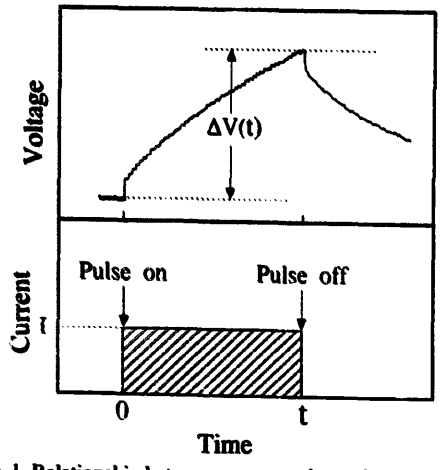

Fig. 1. Relationship between current pulse and cell voltage.

2.5. Impedance measurements

The cell impedance was measured in order to determine the effect on cell resistance when a pulse current is applied. A frequency-response analyser (Solartron 1250) and an electrochemical interface (Solartron 1286) were used for the measurements, which were taken at room temperature from 10 kHz to 0.05 Hz using a.c. signals with a maximum current of 0.2 and 0.5 A for the used and model cells, respectively. These current values were chosen to minimize the scatter of the data on the Cole–Cole plot.

3. Results and discussion

Fig. 2(a)–(e) shows the time dependencies of the cell voltage when a current pulse of 0.1 C was applied for the five pulse widths to electrolyte-deficient model cells, whose amount of electrolyte was half the standard amount, and to electrolyte-normal model cells; both types were from Manufacturer A. Table 1 shows the relationship between pulse width and voltage change, ΔV, at 0.1 C for both types of cells. The value of ΔV increased significantly above 0.01 s.

The time-dependence of cell voltage can be expressed in terms of equivalent circuits. Ilangovan [8] advocated the use of the equivalent circuit shown in Fig. 3 for short-duration, galvanostatic, non-destructive testing at a low current. This equivalent circuit was adopted in the present study. When using this circuit, the time dependence of the change in cell voltage can be written as

$$\Delta V(t) = IR_0 + IR_1[1 - \exp(-t/R_1C_1)] + IR_2[1 - \exp(-t/R_2C_2)] \quad (2)$$

Since the Cole–Cole plot for the Ni/Cd cells examined here has only one clear semicircle (the other semicircle was negligible), as shown in Fig. 12 later, Eq. (2) can be simplified to

$$\Delta V(t) = IR_0 + IR_1[1 - \exp(-t/R_1C_1)] \quad (3)$$

and then to

Table 1
Relationship between pulse width and voltage change at 0.1 C for a model cell with standard amount of electrolyte and that with 50% of the standard amount, both types from Manufacturer A

Pulse width (s)	Voltage change, ΔV (mV)	
	Standard amount	50% of standard amount
0.0001	3.5	22.1
0.001	3.5	24.0
0.01	4.0	25.1
0.1	7.4	33.6
1	27.9	73.4

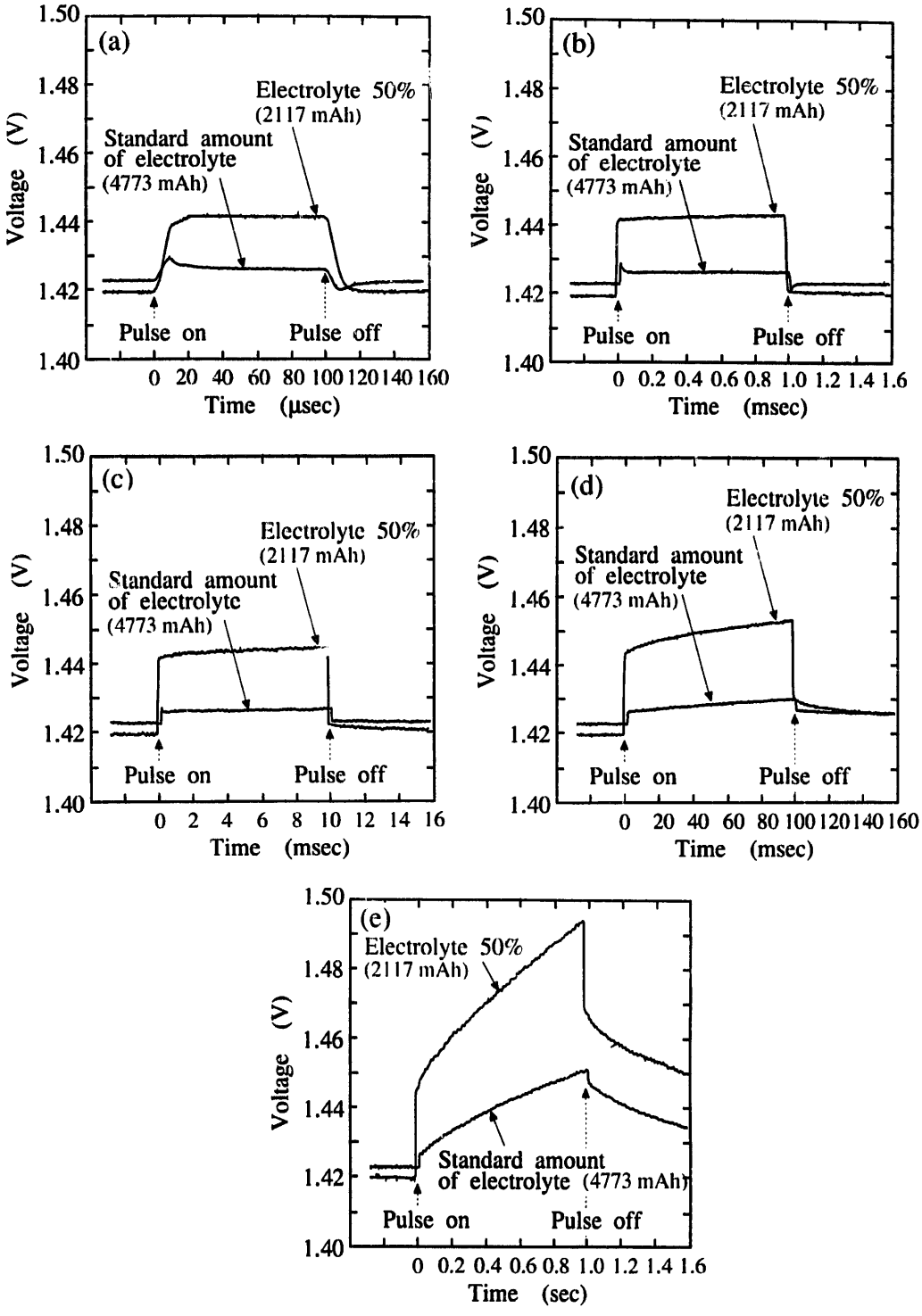

Fig. 2. Time vs. cell voltage at 0.1 C for electrolyte-deficient model cells of Manufacturer A with a pulse width of: (a) 0.1 ms, (b) 1 ms, (c) 10 ms, (d) 0.1 s, and (e) 1 s.

$$\Delta V(t) = \Delta V_0 + \Delta V_1[1 - \exp(-t/\tau)] \quad (4)$$

where V_0, V_1, and τ are constants.

Applying Eq. (4) to the voltage change in Fig. 2 produces

$$\Delta V(t) = 3.5 + 27.8[1 - \exp(-t/1.2)] \quad (0 \le t \le 1) \quad (5)$$

for model cells with a standard amount of electrolyte, and

$$\Delta V(t) = 25.0 + 82.9[1 - \exp(-t/1.1)] \quad (0 \le t \le 1) \quad (6)$$

for cells with 50% of the standard amount of electrolyte; the respective values of V_0 were 3.5 and 25.0 mV. The data given in Table 1 suggest that a linear relationship can be obtained between the capacity and the logarithm of resistance based on Eq. (1) from the voltage change for current pulses of 0.01 s or less. The following investigations were performed to confirm this relationship.

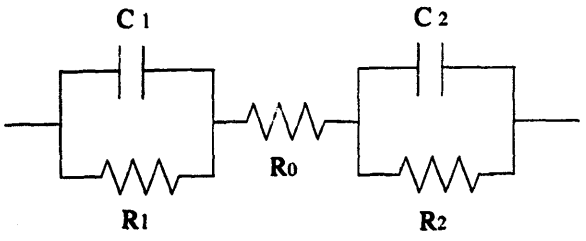

Fig. 3. Equivalent circuit.

Figs. 4 and 5 show the relationship at a pulse current of 0.1 C and pulse widths of 1 ms, 0.1 s and 1 s for electrolyte-deficient model cells from Manufacturers A and B. All of the results approximately fit a linear relationship between the logarithm of the resistance and the capacity, as was shown for the relationship between the logarithm of the impedance and the capacity [7]. As an approximation, the linear relationships are obtained by the method of least squares. The data for zero capacity for Manufacturer A (Fig. 4) are deleted because the resistance of zero-capacity cells increases as the amount of electrolyte decreases; the data for zero capacity is thus not necessarily the minimum resistance values. The data for capacities below 2000 mAh for Manufacturer B (Fig. 5) cannot be observed because the capacity suddenly falls to zero when the amount of electrolyte falls below 70% of the standard amount. Furthermore, the resistance of cells with zero capacity cannot be measured because when a pulse is applied, the cell voltage exceeds the limit of the voltmeter.

Figs. 6 and 7 show the relationship between the pulse width and the correlation coefficient for the three pulse currents and five pulse widths for the electrolyte-deficient model cells. All have a high correlation coefficient (above 0.9). These results indicate that when Ni/Cd cells deteriorate only, or at least mainly, due to electrolyte loss, their capacity can be evaluated with only a small error by measuring the resistance with the

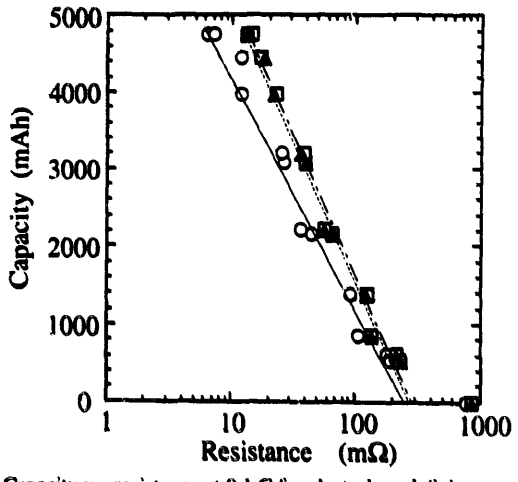

Fig. 4. Capacity vs. resistance at 0.1 C for electrolyte-deficient model cells from Manufacturer A: (○) 1 ms, (▲) 0.1 s, and (□) 1 s.

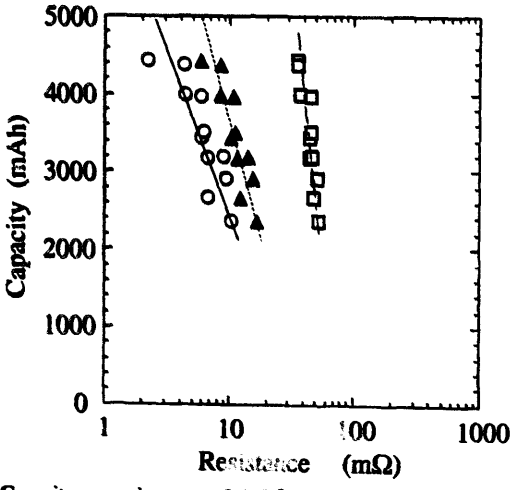

Fig. 5. Capacity vs. resistance at 0.1 C for electrolyte-deficient model cells from Manufacturer B: (○) 1 ms, (▲) 0.1 s, and (□) 1 s.

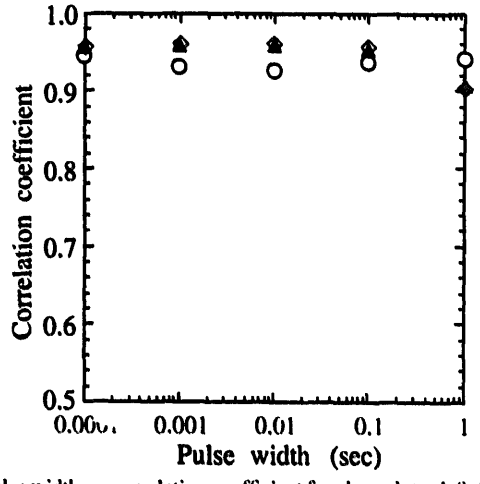

Fig. 6. Pulse width vs. correlation coefficient for electrolyte-deficient model cells from Manufacturer A: (○) 0.1 C, (▲) 0.5 C, and (◇) 1.0 C.

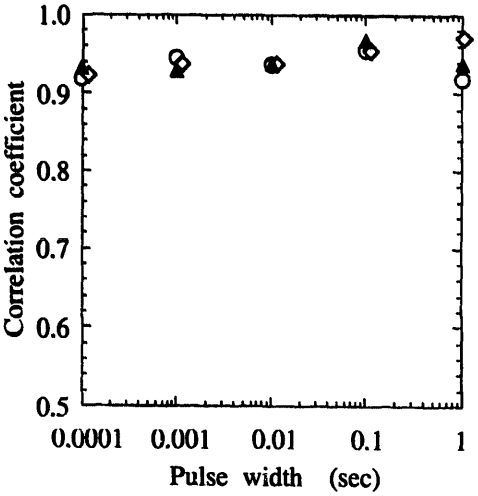

Fig. 7. Pulse width vs. correlation coefficient for electrolyte-deficient model cells from Manufacturer B: (○) 0.1 C, (▲) 0.5 C, and (◇) 1.0 C.

combination of a pulse current of 0.1–1.0 C and a pulse width of 1 s or less, then substituting the measured resistance into

$$Q = a \ln R + b \quad (7)$$

where Q is evaluated capacity, R the resistance based on Eq. (1); a and b are constants.

The relationship between capacity and resistance was examined for the used cells. The results are shown in Figs. 8 and 9; the relationship between the pulse width and correlation coefficient for the same cells is shown in Figs. 10 and 11. The data for the used cells of Manufacturer A, (Fig. 8) tend to deviate from a linear relationship for capacities larger than 1700 mAh, especially, in the regions above 2000 mAh at a pulse width of 0.1 s, and above 1700 mAh at a pulse width of 1 s, where the capacities change independently of the resistance. The data in Fig. 10 show that the correlation coefficients were above 0.9 at a pulse width of 10 ms or less for each current. The coefficients are below 0.9 at a pulse width of 0.1 s or more. The coefficient is below 0.7 when the pulse width is 1 s. Correlation coefficients less than 0.9 at pulse widths of 0.1 and 1 s are related to the large deviation shown in Fig. 8. This may be because the voltage change caused by the current pulse is based not only on the ohmic resistance but also on other factors, such as a delay in reactantion transfer in the electrolyte.

Analysis of the corresponding data for Manufacturer B (Figs. 9 and 11) shows that the relationship between capacity and resistance is clearly less linear and the correlation coefficients are smaller. The cells made by Manufacturer B tended to have a smaller internal resistance than that of cells made by Manufacturer A. This may be the reason for the lower tendency for a linear relationship between capacity and resistance.

The correlation coefficient for used cells from Manufacturer A is high when the pulse width is 10 ms or less, regardless of the pulse current. By contrast, the coefficient for used

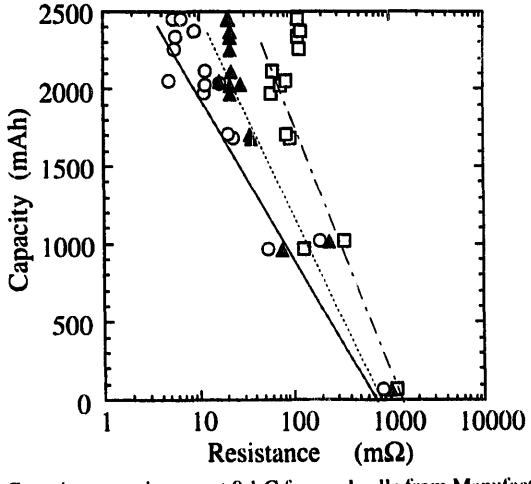

Fig. 8. Capacity vs. resistance at 0.1 C for used cells from Manufacturer A: (○) 1 ms, (▲) 0.1 s, and (□) 1 s.

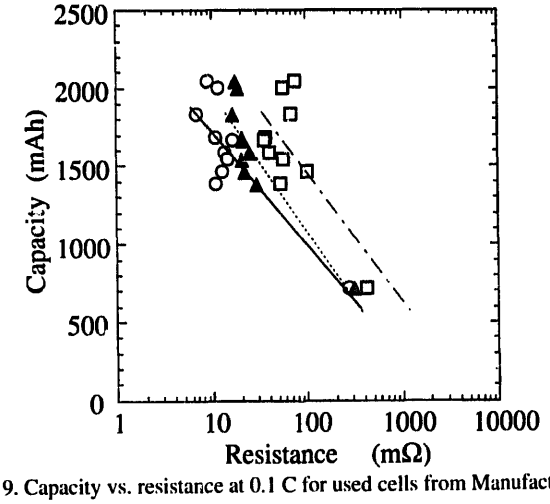

Fig. 9. Capacity vs. resistance at 0.1 C for used cells from Manufacturer B: (○) 1 ms, (▲) 0.1 s, and (□) 1 s.

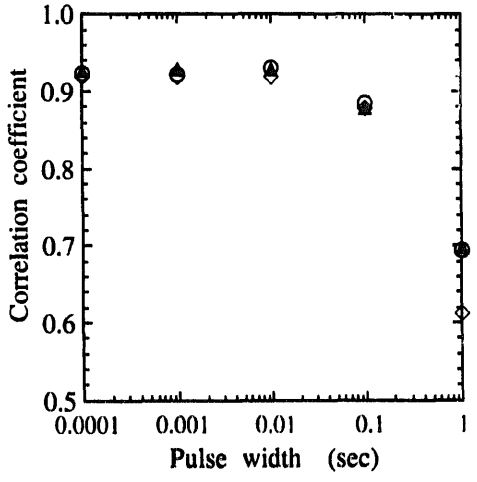

Fig. 10. Pulse width vs. correlation coefficient for used cells from Manufacturer A: (○) 0.1 C, (▲) 0.5 C, and (◇) 1.0 C.

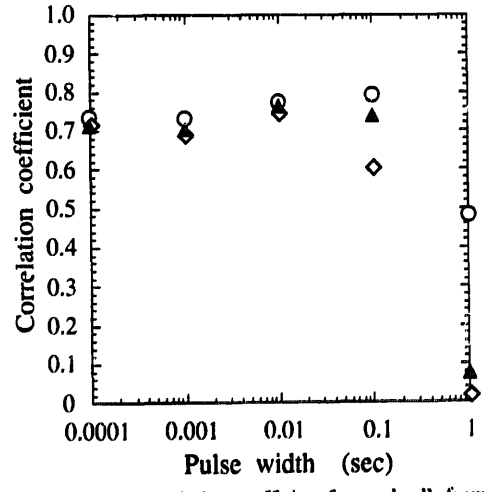

Fig. 11. Pulse width vs. correlation coefficient for used cells from Manufacturer B: (○) 0.1 C, (▲) 0.5 C, and (◇) 1.0 C.

cells from Manufacturer B is relatively high under the same measuring conditions. Tables 2 and 3 show the error between the measured capacity and that estimated from the resistance at 0.1 C for used cells from Manufacturers A and B, respectively. The capacity error, E_c, is defined as

$$E_c = |Q_m - Q_e| / Q_m \quad (8)$$

where Q_m is the measured capacity, and Q_e is the evaluated capacity. The errors are obtained in the capacity range of more than half the nominal capacity. The capacity can thus be evaluated within an average error of 10% when the pulse width is 10 ms or less for used cells from both manufacturers. Figs. 12 and 13 show the relationship between impedance Z_0 at the imaginary part of zero in the Cole–Cole plot and the ratio of resistance R to Z_0 for used cells from Manufacturers A and B, respectively. Since the ratio of R/Z_0 is almost constant for both types of cell when the pulse width is 10 ms or less, the measured resistance R at a pulse width of 10 ms or less is nearly equivalent to the measured impedance Z_0.

As described above, the characteristics of the used cells are different from those of the electrolyte-deficient model cells: their correlation coefficients are smaller at pulse widths of 0.1 s or more. This suggests that the degradation of the used cells is not exclusively due to loss of electrolyte. Even when a current pulse of 0.01 s or less is applied, the voltage change $\Delta V(t)$ equates to the second term on the right-hand side of Eq. (4). The effect on $\Delta V(t)$ can be relatively small for the model cells because the electrode conditions are the same among the model cells except for the electrolyte wet condition. For the used cells, the electrode conditions may have differed considerably depending on the deterioration. Thus, the voltage change is $\Delta V(t)$ affected more strongly by the second term on the right-hand side of Eq. (4) for the used cells than for the model cells. Fig. 14 shows the relationship between pulse width, t, and the ratio of resistance $R(t)$ to $R(0.0001)$ for the electrolyte-deficient model cells and the used cells from Manufacturer A. The capacity of both cells was 54% of the nominal value. The ratio $R(t)/R(0.0001)$ for the used cells was larger than that of the model cells over the entire pulse-width range.

The second term on the right-hand side of Eq. (4) is related to the electrochemical reaction of the electrodes. Therefore, an investigation was conducted of the relationship between the reaction resistance and the capacity. The reaction resis-

Table 2
Relative error between measured capacity and one evaluated from resistance at 0.1 C for used cells from Manufacturer A

Pulse width (s)	Relative error (%)	
	Average	Standard deviation
0.0001	9.1	11.1
0.001	9.1	10.5
0.01	9.0	10.6
0.1	11.7	11.6
1	19.8	18.9

Table 3
Relative error between measured capacity and one evaluated from resistance at 0.1 C for used cells from Manfacturer B

Pulse width (s)	Relative error (%)	
	Average	Standard deviation
0.0001	9.0	6.6
0.001	9.0	7.3
0.01	8.4	6.9
0.1	8.0	5.5
1	12.7	6.8

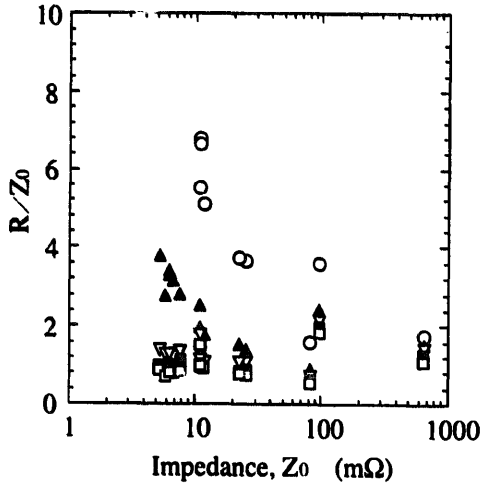

Fig. 12. Impedance Z_0 at the imaginary part of zero in the Cole–Cole plot vs. resistance ratio R/Z_0 for used cells from Manufacturer A: (□) 0.1 ms, (■) 1 ms, (▽) 10 ms, (▲) 0.1 s, and (○) 1 s.

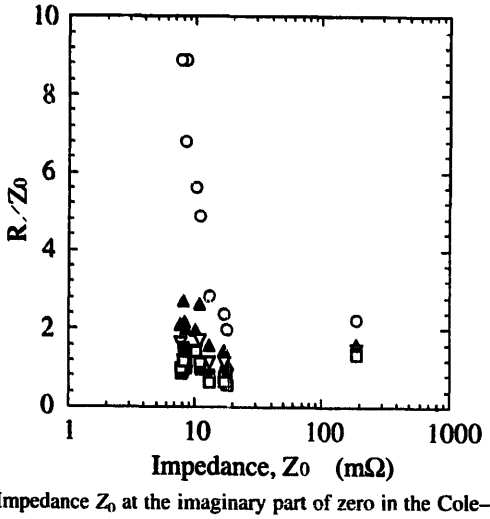

Fig. 13. Impedance Z_0 at the imaginary part of zero in the Cole–Cole plot vs. resistance ratio R/Z_0 for used cells from Manufacturer B: (□) 0.1 ms, (■) 1 ms, (▽) 10 ms, (▲) 0.1 s, and (○) 1 s.

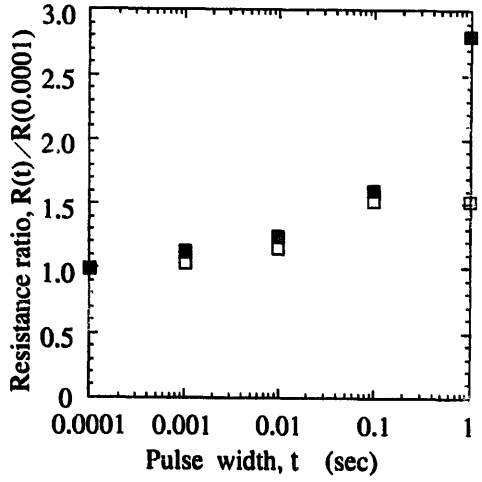

Fig. 14. Pulse width vs. resistance ratio $R(t)/R(0.0001)$ for Manufacture A: (□) electrolyte-deficient model cells, and (■) used cells.

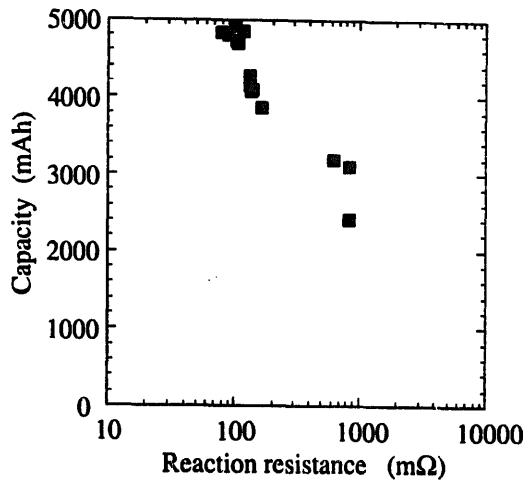

Fig. 16. Capacity vs. reaction resistance for electrolyte-deficient model cells from Manufacturer A.

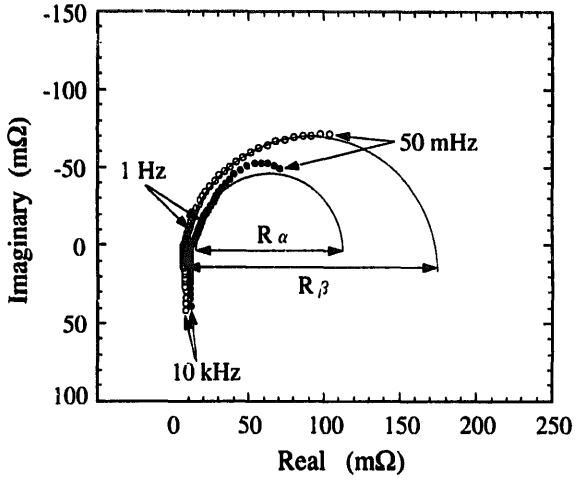

Fig. 15. Cole–Cole plot for used cells from Manufacturer A: (○) 1983 mAh, and (●) 2260 mAh.

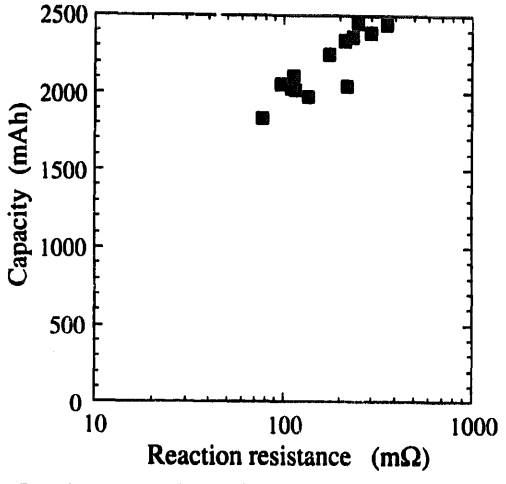

Fig. 17. Capacity vs. reaction resistance for used cells from Manufacturer A.

tance was obtained by approximating the imaginary part of the Cole–Cole plot to a semicircle, as shown in Fig. 15. The reaction resistance corresponds to the diameter of the semicircle. Figs. 16 and 17 show the relationship between the reaction resistance and the capacity for the electrolyte-deficient model cells and the used cells from Manufacturer A. The reaction resistance below 1800 mAh capacity cannot be obtained for the used cells because the Cole–Cole plot is sufficiently distorted not to approximate a semicircle. The reaction resistance of the electrolyte-deficient model cells increased with a decrease in capacity, while that of the used cells decreased with a decrease in capacity in the region above 1800 mAh. This corresponds to the difference in relationship between resistance and capacity at a pulse width of 1 s for electrolyte-deficient model cells and for used cells (Figs. 4 and 8). Consequently, the decrease in the correlation coefficient at a pulse width of 0.1 s or more for used cells is caused by the reaction resistance. Further research is being undertaken to determine the factors that affect reaction resistance for used cells.

4. Conclusions

A linear relationship between capacity and the logarithm of resistance is observed for both used and electrolyte-deficient model cells.

To estimate the capacity with a small error for used cells, it is necessary to measure the resistance at a pulse current of 0.1–1.0 C and a pulse width of 10 ms or less, where the reaction resistance is small.

References

[1] N. Dalarsson, *Ext. Abstr., Proc. INTELEC'94, Vancouver, Canada, 1994*, pp. 108–114.

[2] M.A. Reid, *Electrochim. Acta, 38* (1993) 2037–2041.
[3] R. Haak, C. Ogden and D. Tench, *J. Power Sources, 12* (1984) 289–303.
[4] X. Andrieu and P. Poignant, *Power Sources 14*, Stratford upon Avon, UK, 1993, pp. 43–52.
[5] X. Andrieu and P. Poignant, *Power Sources, 15* (1995) 49–64.
[6] S. Sathyanarayana, S. Venugopalan and M.L. Gopikanth, *J. Appl. Electrochem., 9* (1979) 125–139.
[7] N. Kato, K. Yamamoto, T. Ogata, T. Hirai and H. Hirota, *J. Power Sources, 62* (1996) 187–192.
[8] S.A. Ilangovan, *J. Power Sources, 50* (1994) 33–45.