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Establishment of the relationship between capacity and impedance of trickle-charge nickel/cadmium cells by using electrolyte-deficient model cells

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Abstract

A relationship is established between the capacity and the impedance of trickle-charged nickel/cadmium cells by using electrolyte-deficient model cells. Loss of capacity is strongly related to cell weight and the logarithm of the impedance. Since the decrease in cell weight is thought to be caused by electrolyte loss, an electrolyte-deficient model cell has been prepared to simulate the deterioration conditions. The model cell and deteriorated cells exhibit linear relationships between cell capacity and the logarithm of impedance where its imaginary part is zero on a Cole–Cole plot. Furthermore, a linear relationship is obtained that follows closely the relationship obtained from measured data by modifying the relationship for the model cells by substituting for the capacity of the fresh (non-deteriorated) cell. This method provides an effective and time-saving way for obtaining the relationship because is not necessary to test many deteriorated cells or to carry out accelerated tests.

Keywords: Nickel/cadmium cells; Trickle-charged cells; Capacity; Impedance; Electrolyte-deficient cells

1. Introduction

Trickle-charged, nickel/cadmium (Ni/Cd) cells are used widely for stand-by power during failure of commercial a.c. supplies. Telecommunications systems will require many storage batteries in the near future [1]. This will increase the importance of battery monitoring to maintain reliability of these systems. A simple method of monitoring the state of a storage battery is to measure the capacity at a constant current. This method, however, has several disadvantages. For example, it is laborious and time-consuming. Obviously, the battery is not able to meet any emergency demand for power if a power failure occurs during the measurement. Therefore, faster monitoring procedures are required.

Impedance measurement and current-pulse techniques have been proposed for storage batteries, especially sealed lead/acid batteries [2–5]. These studies have demonstrated a good correlation between capacity and impedance, and between capacity and voltage change. Unfortunately, however, many samples and long-term testing are needed to obtain these relationships. Furthermore, such trials have to be repeated for each cell size and for each manufacturer because the relationship depends on both these factors.

The same approaches have been used for Ni/Cd cells. Hlavac et al. [6] have proposed on-line tests based on conductance measurements. Haak et al. [7] have reported good correlation between cell deterioration and impedance measurements. Andrieu et al. [8] have proposed pulse measurement of cell admittance instead of conductance or impedance [8]. All of these, however, have the same limitations as for sealed lead/acid cells. These limitations arise because there is no quantitative relationship between the measurement factors and the deterioration factors.

The authors have investigated characteristics of deteriorated trickle-charged Ni/Cd cells and have found that the amount of electrolyte is a major factor that controls deterioration. Model cells with a different amount of electrolyte have, therefore, been prepared to obtain the relationship between capacity and impedance. This work shows that it is possible to determine quickly this relationship by using model cells.

2. Experimental

2.1. Samples

C-size, sealed, trickle-charged Ni/Cd cells with 1800 and 1650 mAh nominal capacity were obtained from manufac-

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turer A and manufacturer B, respectively. Both types had been produced in the 1980s and used for over five years in emergency lighting equipment. These are termed 'used' cells. About twenty of each type of cell that showed different capacity were chosen for the measurements. Fresh cells were not available because they were no longer manufactured.

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. C-size cells were also obtained from manufacturer A. The nominal capacity of cells with standard amounts of electrolyte was 4000 and 2300 mAh for the D size and C size, respectively.

2.3. Cell performance measurements

The used and model cells were first discharged at 0.2 C to 1.0 V, and then charged repeatedly at 0.1 C for 15 h and discharged at 0.2 C to 1.0 V two or three times with 1 h intervals. The last discharge capacity was recorded and the cell was then fully charged and used for the impedance measurements. The charge/discharge measurements were carried out with a charge/discharge control unit (HJ-201B, Hokuto Denko Co.) at room temperature.

2.4. Impedance measurements

A Solartron 1250 FRA and a 1286 electrochemical interface were used for impedance measurements. Measurements were carried out from 10 kHz to 0.1 Hz using an a.c. signal of 0.2 A maximum for C-size and 0.5 A maximum for D-size cells. These values of current were chosen to minimize the scatter of the data on the Cole–Cole plot. The measurements were performed at room temperature.

2.5. Separator impedance

Separator impedance was measured using the cell shown in Fig. 1. The polypropylene separator was sandwiched between platinum electrodes and compressed with acrylic resin plates under a constant force. The amount of electrolyte in the separator was controlled as follows. First, the separator was fully wetted with electrolyte. Then, the separator was sandwiched between filter paper to remove the electrolyte until it contained the required amount of electrolyte. Measurement was made at 1 kHz a.c. and 5 mA maximum current at room temperature.

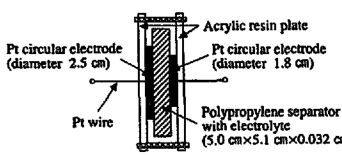

Fig. 1. Experimental setup for measuring the impedance of a separator.

3. Results and discussion

Plots of capacity versus weight for used cells made by manufacturers A and B are shown in Fig. 2. The cells that fall within the ellipses exhibited low voltage (below 0.3 V) while charging, and their open-circuit voltage after charging was nearly zero. This suggests that the cause of deterioration was a short circuit. For the other cells, the capacity tended to decrease with decrease in cell weight. In this case, electrolyte loss was the main cause of weight loss because no other factors could be found to account for such a large decrease in weight (about 7 g). Fresh electrolyte was injected into the cells and the capacities were found to recover. For example, 1.0 g of added electrolyte ion increased the capacity from 970 to 1995 mAh. This showed that electrolyte loss is a major deterioration factor for trickle-charged Ni/Cd cells.

The relationship between cell weight and impedance, Z_0, for used cells from manufacturers A and B is shown in Fig. 3. The data for the short-circuit cells are not included. Z_0 is the real part of the impedance when the imaginary part is zero (Fig. 4). It corresponds to the resistance of the electrodes and the separator with electrolyte. The value of Z_0 does not

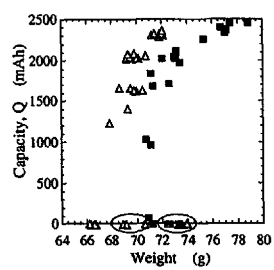

Fig. 2. Relationship between cell capacity and weight for used cells: (■) manufacturer A, and (△) manufacturer B.

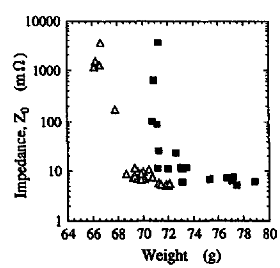

Fig. 3. Relationship between impedance Z_0 and weight for used cells: (■) manufacturer A, and (△) manufacturer B.

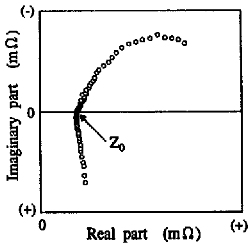

Fig. 4. Typical Cole–Cole plot for a Ni/Cd cell.

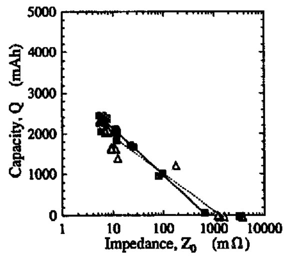

Fig. 5. Relationship between cell capacity and Z_0 for used cells: (■–■) manufacturer A, and (△...△) manufacturer B.

depend greatly on the measurement current. Fig. 3 shows a large increase in Z_0 in the region where capacity greatly decreases, cf., Fig. 2. Moreover, the used cell that recovered capacity on the injection of fresh electrolyte also showed a decrease in the value of Z_0, from 85.3 to 20.2 mΩ. These results suggest that the amount of electrolyte strongly affects both the capacity and the impedance.

The above finding warrants an investigation of the relationship between Z_0 and capacity. This is shown in Fig. 5 for the C-size used cells fabricated by manufacturers A and B. The relationship can be expressed by

$$Q = a \ln(Z_0) + b \tag{1}$$

where a and b are constants. The following equations were obtained by the method of least-squares

$$Q = -491 \ln(Z_0) + 3233 \tag{2}$$

for the cells from manufacturer A, and

$$Q = -386 \ln(Z_0) + 2809 \tag{3}$$

for the cells from manufacturer B. For the derivation of the equations, only the data for cells that showed minimum values of Z_0 were used among all the data that showed zero capacity. This was because it is possible that the impedance increased with time due to chemical degradation of cell components even after the capacity reached zero. Fig. 5 does not include the data for short-circuit deterioration. The results suggest that capacity evaluation by measuring impedance through Eq. (1) is an effective method for monitoring the state of trickle-charged Ni/Cd cells.

With respect to practical applications, a problem remains with evaluating capacity through impedance measurements, namely, deteriorated cells must be obtained quickly to allow the values of a and b in Eq. (1) to be determined rapidly. The usual method for accelerating deterioration is to charge and discharge cells at high temperatures, but even with this method, it takes more than six months to deteriorate Ni/Cd cells to a fraction of their nominal capacity. Moreover, the deterioration mode under these conditions is not always the same as that experienced in normal use.

To solve this difficulty, electrolyte loss was militated by making electrolyte-deficient model cells, which had less than the standard amount of electrolyte. These cells can be made easily and quickly. The characteristics of the model cells made by manufacturers A and B are given in Figs. 6–9. The same measurements as for used cells were performed on the model cells, and the same tendency for decrease in capacity was observed. In particular, linear relationships between capacity and Z_0, as expressed by Eq. (1), are clearly observed in Figs. 8 and 9. Therefore, if this relationship applies to deteriorated cells in practical use, an effective solution has been obtained to the above problem of finding a rapid method for evaluating cell performance.

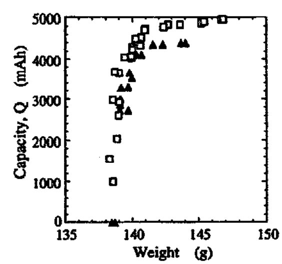

Fig. 6. Relationship between cell capacity and weight for D-size model cells: (□) manufacturer A, and (▲) manufacturer B.

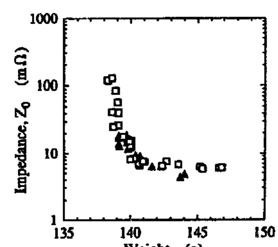

Fig. 7. Relationship between Z_0 and weight for D-size model cells: (□) manufacturer A, and (▲) manufacturer B.

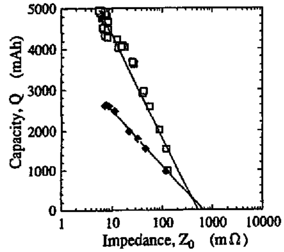

Fig. 8. Relationship between cell capacity and Z_0 for model cells made by manufacturer A: (□) D size, and (♦) C size.

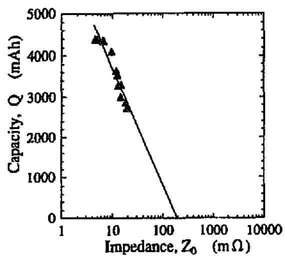

Fig. 9. Relationship between cell capacity and Z_0 for D-size model cells made by manufacturer B.

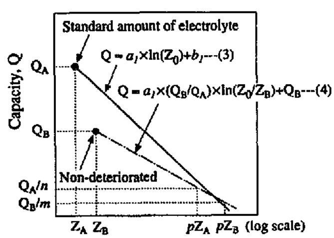

Fig. 10. Derivation of quantitative relationship between Z_0 and capacity: (———) model cells, and (– · –) used cells.

Equations for the relationship between capacity and Z_0 for used cells were derived from the relationship for electrolyte-deficient model cells, i.e.

$$Q=a_1\ \ln(Z_0)+b_1 \tag{4}$$

where a_1 and b_1 are constants. It is assume that: (i) the equation obtained is the same type as Eq. (4); (ii) the capacity of both used and model cells becomes nearly zero when the ratio (p) of Z_0 to its initial value is large (see Fig. 10).

If the capacity and Z_0 of the used cells that have to deteriorated are Q_b and Z_b, and the capacity of model cells that have the standard amount of electrolyte is Q_a, the following equation is obtained for the used cells (refer to the Appendix)

$$Q=a_1\ (Q_b/Q_a)\ \ln(Z_0/Z_b)+Q_b \tag{5}$$

Figs. 11 and 12 show plots of equations derived from the three types of model cells and from the data shown in Fig. 5. Since the values of Q_b and Z_b for used cells are not clear, the average values of the data within the circles shown in Figs. 11 and 12 were chosen.

Table 1 shows the equations obtained from the data for three types of model cells and for the used cells. The relative capacity error, E_c, is defined as

$$E_c=|Q_r-Q_e|/Q_r \tag{6}$$

where Q_r is the real capacity of a used cell and Q_e is the evaluated capacity that is obtained by substituting the value of Z_0 for used cells into the equation. For the evaluation of the error, the data of the cells that showed capacity less than a half of their nominal capacity were not included because, in practice, Ni/Cd cells are actually replaced with new ones before the capacity declines to such a level.

The equations obtained from model-cell data displayed good correlation with the equation obtained from used-cell data. The relative error was less than 15%, except for a standard deviation in the case where model cells from manufacturer B were compared with the used cells from the same

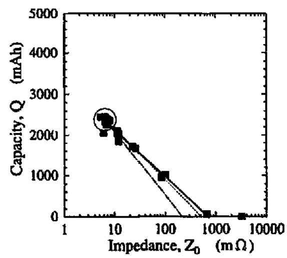

Fig. 11. Relationship obtained from used-cell data and relationships obtained from model cell data: (———) from used-cell data of manufacturer A; (· · ·) from model-cell data of manufacturer A: C and D size (overlapped); (– · –) from model-cell data of manufacturer B: D size.

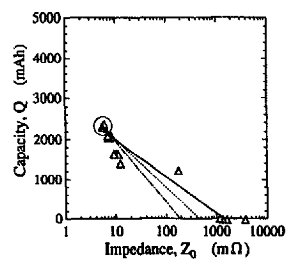

Fig. 12. Relationship obtained from used-cell data and relationships obtained from model-cell data: (———) from used-cell data of manufacturer B; (· · ·) from model-cell data of manufacturer A: C and D size (overlapped); (– · –) from model-cell data of manufacturer B: D size.

Table 1
Equations for used cells obtained from used-cell and model-cell data

		Model cell	Equation	Relative error (%)	
				Average	Standard deviation
Manufacturer A: used cells	Obtained from used-cell data		$Q=-491\times\ln(Z_0)+3233$	4.26	4.03
	Obtained model-cell data	A, D size	$Q=-546\times\ln(Z_0)+3413$	4.59	4.85
		A, C size	$Q=-547\times\ln(Z_0)+3415$	4.60	4.86
		B, D size	$Q=-681\times\ln(Z_0)+3669$	9.15	12.30
Manufacturer B: used cells	Obtained from used-cell data		$Q=-386\times\ln(Z_0)+2809$	10.35	9.56
	Obtained from model cell-data	A, D size	$Q=-533\times\ln(Z_0)+3251$	12.42	13.31
		A, C size	$Q=-534\times\ln(Z_0)+3253$	12.43	13.36
		B, D size	$Q=-666\times\ln(Z_0)+3480$	12.22	20.76

source. Therefore, it is concluded that the method of using electrolyte-deficient model cells is easy, time-saving and effective for monitoring the deterioration of trickle-charged Ni/Cd cells. The results showed that cells from manufacturer B tended to have a large error between the used and model cells. These cells did not show a consistent linear relationship between the capacity and the logarithm of impedance, as shown in Figs. 5 and 12. This inconsistency suggests that some other factors need to be considered in order to evaluate accurately cell deterioration although electrolyte loss is still the major factor. It has been demonstrated that the equation derived from the electrolyte-deficient model cells can be applied, with good correlation, to the relationship between the capacity and logarithm of impedance for the used cells. This is based on the assumption that electrolyte loss is the major cause of cell deterioration.

It is considered that loss of electrolyte emanates from non-optimum conditions of crimping and/or vent opening by oxygen-gas generation during overcharging. Improvement of electrode fabrication and assembly technology may reduce such electrolyte loss, so it is possible that the major factor may be changed to separator dry-up for currently produced cells. This does not result in electrolyte loss from the cells.

We therefore investigated the relationship between impedance and the amount of electrolyte in the separator, see Fig. 13. This relationship at 1 kHz was obtained by measuring the cell shown in Fig. 1. The separator became saturated with

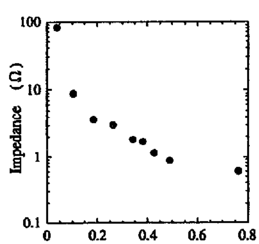

Fig. 13. Dependence of separator impedance at 1 kHz on amount of electrolyte.

0.75 g of electrolyte. The impedance increased rapidly as the electrolyte content fell below 0.5 g. The tendency for the impedance to decrease rapidly below a certain weight is similar to the effect in Figs. 3 and 7. This suggests that cell impedance is strongly affected by separator impedance in the case of separator dry-up.

It is difficult to fabricate model cells that simulate cells that have deteriorated through separator dry-up. Model cells would still be useful, however, to evaluate deterioration if the cell impedance mainly depends on the amount of electrolyte contained by the separator. This possibility in under consideration.

4. Conclusions

The results of this study are as follows.

1. Short circuiting is a major factor in the deterioration of trickle-charged Ni/Cd cells, and electrolyte loss is probably another major factor.
2. A linear relationship has been obtained between capacity and the logarithm of impedance for used cells and electrolyte-deficient model cells.
3. The equation obtained from the relationship for the model cells provides a good simulation of that for used cells. This provides an effective method for evaluating deterioration because it can be implemented both easily and quickly.

Appendix A (refer to Fig. 10)

The equation for electrolyte-deficient model cells is

$$Q=a_1 \ln(Z_0)+b_1 \quad \text{(A1)}$$

see Eq. (4) in Fig. 10.

Substitution of (Z_A, Q_A) and $(pZ_A/Q_A/m)$ into Eq. (1) yields

$$Q_A=a_1 \ln(Z_A)+b_1 \quad \text{(A2)}$$

$$Q_A/m=a_1 \ln(pZ_A)+b_1 \quad \text{(A3)}$$

Intergration of Eqs. (A2) and (A3) gives

$$(1-1/m)Q_A = a_1 \ln(1/p) \quad \text{(A4)}$$

The equation for used cells can be expressed as

$$Q = a_2 \ln(Z_0) + b_2 \quad \text{(A5)}$$

by assumption (i) in the discussion of this paper.

Substitution of (Z_B, Q_B) and $(pZ_B, Q_B/n)$ into Eq. (5) yields

$$Q_B = a_2 \ln(Z_B) + b_2 \quad \text{(A6)}$$

$$Q_B/n = a_2 \ln(pZ_B) + b_2 \quad \text{(A7)}$$

Intergration of Eqs. (A6) and (A7) gives

$$(1-1/n)Q_B = a_2 \ln(1/p) \quad \text{(A8)}$$

Intergration of Eqs. (4A) to (8A) gives

$$(1-1/m)/(1-1/n)(Q_A/Q_B) = a_1/a_2 \quad \text{(A9)}$$

Assumption (ii) in the discussion leads to the result that if $1/m$ approaches zero, $1/n$ also approaches zero. In this case, $(1-1/m)$ and $(1-1/n)$ are both close to unity. Thus, the following equation is obtained

$$Q_A/Q_B = a_1/a_2 \quad \text{(A10)}$$

By substituting Eqs. (6) and (9) into Eq. (5), the following equation is obtained for used cells

$$Q = a_1(Q_B/Q_A)\ln(Z_0/Z_B) + Q_B \quad \text{(A11)}$$

see Eq. (5) in Fig. 10.

References

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

[2] D.O. Feder, T.G. Croda, K.S. Champlin, S.J. McShane and M.J. Hlavac, *J. Power Sources, 40* (1992) 235–250.

[3] D.O. Feder, T.G. Croda, K.S. Champlin and M.J. Hlavac, *Proc. INTELEC'92, Washington, DC, USA, 1992*, pp. 218–233.

[4] T. Ogata and R. Tanaka, *Trans. Inst. Electr. Eng. Jpn., 107-D* (5) (1987) 606–611.

[5] Y. Konya, T. Takeda, T. Takano, M. Kohno, K. Yotsumoto and T. Ogata, *Proc. INTELEC'94, Vancouver, Canada, 1994*, pp. 256–262.

[6] M.J. Hlavac, D.O. Feder, T.G. Croda and K.S. Champlin, *Proc. INTELEC'93, Paris, France, 1993*, pp. 375–383.

[7] S. Haak, C. Ogden and D. Tench, *J. Power Sources, 12* (1984) 289–303.

[8] X. Andrieu and P. Poignant, in A. Attewell and T. Keily (eds.), *Power Sources 12*, Int. Power Sources Symp. Committee, Stratford-upon-Avon, UK, 1993, pp. 43–52.