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Impedance parameters and the state-of-charge. III. Zinc-manganese dioxide and magnesium-manganese dioxide dry batteries

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The problem of non-destructive determination of the state-of-charge of zinc– and magnesium–manganese dioxide dry batteries is examined experimentally from the viewpoint of internal impedance and open-circuit voltage at equilibrium. It is shown that the impedance is mainly charge-transfer controlled at relatively high states-of-charge and progressively changes over to diffusion control as the state-of-charge decreases in the case of zinc–manganese dioxide dry batteries. On the other hand, the impedance is mainly diffusion controlled for undischarged batteries but becomes charge-transfer controlled as soon as there is some discharge in the case of magnesium–manganese dioxide batteries. It is concluded that the determination of state-of-charge is not possible for both types of batteries by the measurement of impedance parameters due to film-induced fluctuations of these parameters. The measurement of open-circuit voltage at equilibrium can be used as a state-of-charge indicator for Zn–MnO_2 batteries but not for Mg–MnO_2 batteries.

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1. Introduction

The state-of-charge of a battery refers to the ratio of residual capacity at a given instant to the maximum capacity available from the battery. A knowledge of this parameter helps in the case of primary batteries to predict the residual capacity and caution the user about the need for an impending battery replacement. Methods used in the literature to determine the state-of-charge of different battery systems have been summarized in part I of this series [1]. The applicability of the parameters of the internal impedance to the determination of the state-of-charge of nickel–cadmium and lead–acid batteries has been examined in parts I and II [1, 2].

In the present work the problem of non-destructive determination of the state-of-charge of zinc–manganese dioxide and magnesium–manganese dioxide dry batteries has been examined from the viewpoint of impedance parameters and open-circuit voltage at equilibrium.

2. Experimental

2.1. *Batteries*

Zinc–manganese dioxide dry batteries were of the conventional D-size (4 A h nominal capacity) flashlight dry cells manufactured by Toshiba Anand Batteries Ltd (India). Cells were selected at random from a single batch of manufacture. The tests began within three months of the date of manufacture. Four such cells were used for the experiments.

Magnesium–manganese dioxide batteries were of CL-size (2·5 A h nominal capacity) fabricated on a pilot plant scale by Bharat Electronics Ltd (India). Cells were selected at random from a single production batch, the production date being about two months before the tests began. Three cells were used for the experiments.

2.2. *Procedure*

As the absolute capacity of these primary cells

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could not be determined by charge–discharge cycling, the test cells were discharged at constant current until the anticipated state-of-charge was reached. After the termination of such a discharge, a ten-hour rest period was given for recovering from from polarization. Measurements were completed at this stage. The cells were then discharged again at a suitable constant current as above to attain the next state-of-charge and allowed a ten-hour rest period. After the completion of the tests at various states-of-charge, the absolute capacity C was calculated.

$$C = \sum_{m} I_m t_m \qquad (1)$$

where m is the total number of discharge steps involved during the complete discharge, I_m the discharge current for the mth discharge step, and t_m the duration of discharge at the mth step.

The actual state-of-charge for each cell at a given stage of measurements was then calculated from the above data.

2.3. *Set-up*

The open-circuit voltage at equilibrium was measured with a digital voltmeter of 10 MΩ input impedance. The voltage was measured correct to ± 1 mV.

The parameters of the internal impedance, namely, equivalent series/parallel resistance and capacitance, modulus of impedance and alternating current phase shift were calculated from measurements with an impedance bridge method as described earlier [1].

3. Results

The dependence of open-circuit voltage at equilibrium (i.e., the open-circuit voltage measured after 10 hours following any discharge) on the state-of-charge of zinc– and magnesium–manganese dioxide cells is shown in Figs. 1 and 2, respectively.

The e.m.f. of magnesium–manganese dioxide cells varies from about 1·85 V at $S = 0{\cdot}9$ to about 1·70 V at $S = 0{\cdot}1$ (S is the state-of-charge). The variation, however, is relatively small in the range $0{\cdot}6 > S > 0{\cdot}1$. The e.m.f. of zinc–manganese dioxide cells varies in a fairly monotonic manner from about 1·4 V at $S = 0{\cdot}9$ to about 0·9 V at $S = 0{\cdot}1$.

The monotonic decrease of e.m.f. with the state-of-charge of zinc–manganese dioxide cells by about 0·5 V between $S = 0{\cdot}9$ and $S = 0{\cdot}1$ fulfills the equilibrium open-circuit voltage criterion [1] to predict the state-of-charge from e.m.f. measurements. However, the criterion is not fulfilled in the case of magnesium–manganese dioxide cells and the state-of-charge is therefore not predictable in this case by the measurement of e.m.f.

It was possible to carry out the measurements of resistance and capacitance components up to about 1000 Hz in the case of Zn–MnO_2 and Mg–MnO_2 cells (unlike in the case of Ni–Cd [1] and Pb–acid [2] cells). The bridge could not be balanced due to an inductive reactance of the cells at higher frequencies. The correlation with state-of-charge was tried below 300 Hz as the impedance measurements below this frequency could be assumed to be devoid of any inductive reactance.

The results obtained are presented in Figs. 3 and 4. They show a substantial variation of the impedance parameters from cell to cell even in a given batch of apparently identical history. However, a fairly well-defined trend is still noticeable on the Argand diagrams and these are therefore discussed qualitatively below.

4. Discussion

The shape of the Argand plot at $S = 1{\cdot}0$, for magnesium–manganese dioxide batteries (Fig. 3) which is a straight line with a slope substantially exceeding unity, may be ascribed to the presence of a coherent protective film on the magnesium anode* in an undischarged cell. The electrode therefore behaves virtually as a capacitor and gives a straight line in the Argand plot with a slope substantially larger than unity. When the battery or cell is discharged, however, to any significant extent ($S < 1$). The protective film breaks down due to the anodic dissolution of magnesium. Thereafter, film repair is never complete as is well known from the continued corrosion of partially discharged magnesium dry cells. Thus, with par-

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* Magnesium anode cans are given a special chromate dip coating before being assembled into cells. The cell electrolyte also contains a reservoir of chromate ions to ensure the stability of the anode during prolonged storage.

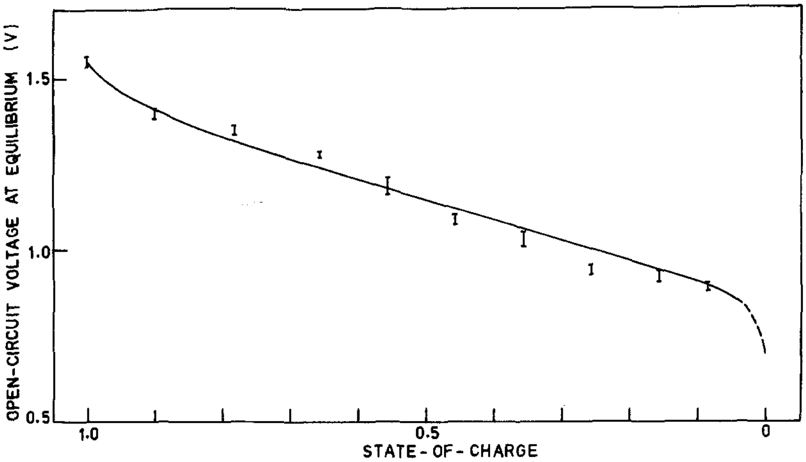

Fig. 1. Dependence of open-circuit voltage at equilibrium on state-of-charge for Zn–MnO_2 cells.

tially discharged cells, film repair (passivation) and breakdown (corrosion) occur even under open-circuit conditions leading to a random course of the impedance parameters as a function of state-of-charge reflected as cell to cell variations in Fig. 3.

The nearly semicircular shape of the Argand plot at $S \approx 1$ in Fig. 3 indicates that the impedance for the battery reaction is essentially charge-transfer controlled. The shrinkage of the area under the semicircle with a decrease in the state-of-charge indicates, in analogy with a Randles' type equivalent circuit for the electrodes, that both the double layer capacity and charge transfer polarization resistance are decreased with a progressive discharge of the cell. The decrease in the double layer capacity may be explained as due to a build-up of insoluble products such as $Mg(OH)_2$ (reducing the interfacial area at the anode). The decrease in polarization resistance as S decreases is more difficult to explain. Probably, at lower states-of-charge, there is a high degree of exposure of raw magnesium to the electrolyte solution due to the pitting of the metal. An increase in the electrochemically active area will then lead to a decrease in the charge-transfer resistance.

The Argand plot of zinc–manganese dioxide dry cells show (Fig. 4) that there is a progressive change from charge-transfer control of impedance at $S \approx 1$ to diffusion control at $S \approx 0$. In contrast to Mg–MnO_2 dry cells, there is no diffusion control at $S = 1$, apparently due to the absence of a

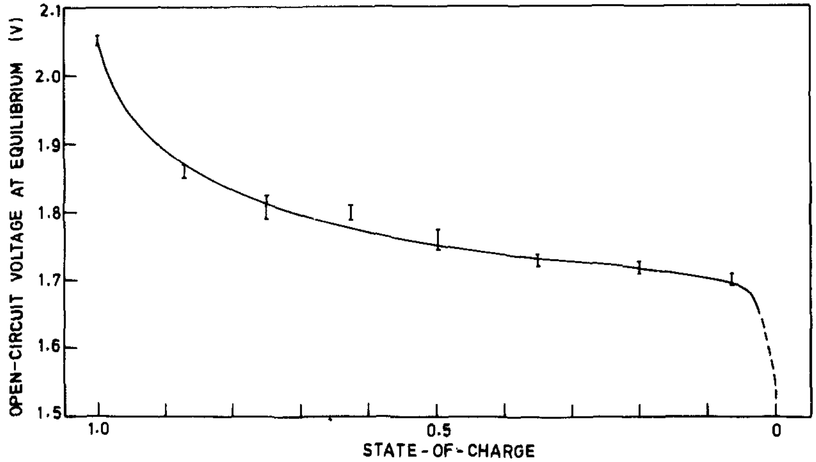

Fig. 2. Dependence of open-circuit voltage at equilibrium on state-of-charge for Mg–MnO_2 cells.

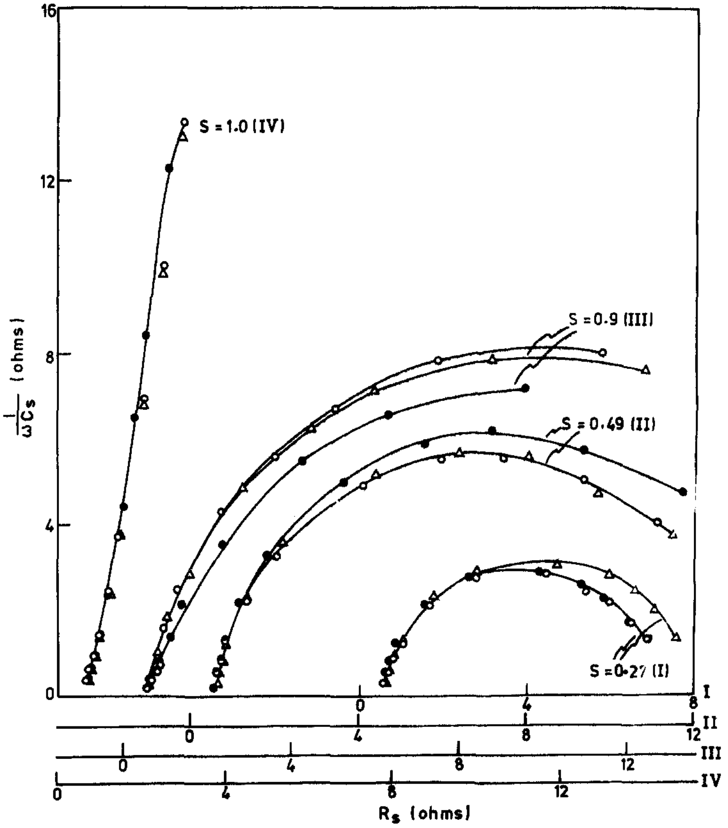

Fig. 3. Argand plot of Mg–MnO$_2$ cells at different states-of-charge. S = state-of-charge, the symbols ○, ●, △ represent three different cells used for each experiment at a given state-of-charge. a.c. frequencies (Hz) used are as follows (from left to right on each curve) 991, 492, 298, 198, 100, 60, 30, 20, 15, 10, 6.

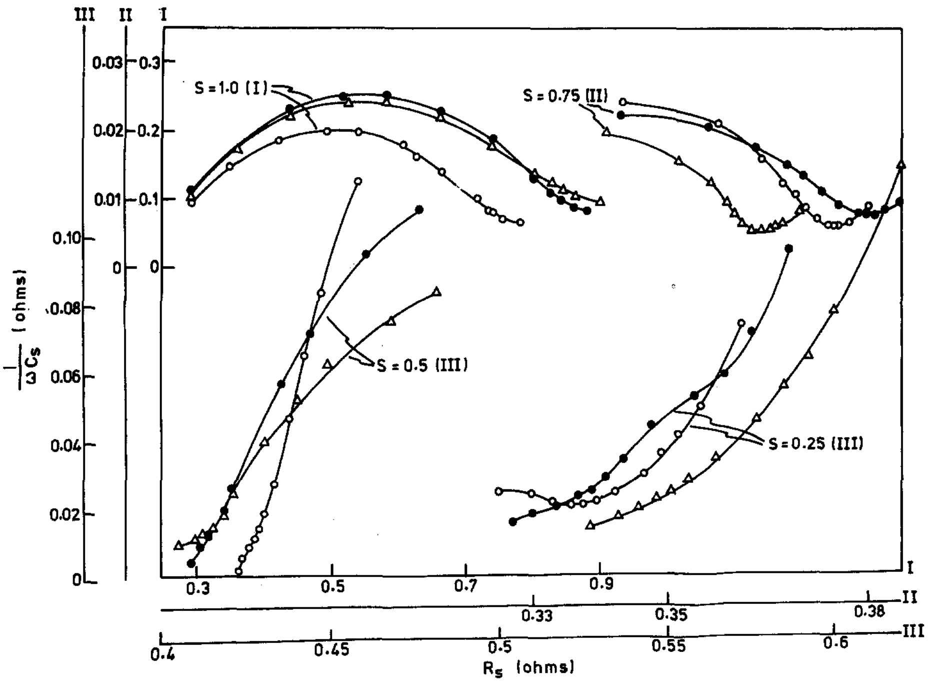

Fig. 4. Argand plot of Zn–MnO$_2$ cells at different states-of-charge. S = state-of-charge, the symbols ○, ●, △ represent three different cells used for each experiment at a given state-of-charge. a.c. frequencies (Hz) used are as follows (from left to right on each curve)' 991, 492, 298, 198, 100, 60, 30, 20, 15, 10, 6.

coherent protective film on the zinc surface even with a fresh/undischarged cell. The increase in diffusion impedance as the battery or cell is discharged is probably due to a passivation of the zinc anode by the reaction products such as $Zn(OH)_2$, which may also form other insoluble complexes with the electrolyte.

When the impedance parameters (equivalent series/parallel resistance and capacitance, modulus of impedance, alternating-current phase shift) are plotted against the state-of-charge (not shown in figures) it is observed for both $Zn–MnO_2$ and $Mg–MnO_2$ cell systems that there are large, apparently film-induced, fluctuations. The dependence of these impedance parameters on the state-of-charge is chaotic and none of the parameters is useful as a state-of-charge indicator for both of these cell systems.

5. Conclusions

It is shown that the impedance is mainly charge-transfer controlled at relatively high states-of-charge of $Zn–MnO_2$ cells, but there is a progressive change over to diffusion control as the state-of-charge decreases.

It is also shown that for $Mg–MnO_2$ cells the impedance is mainly diffusion controlled for undischarged cells but becomes charge-transfer controlled as soon as there is a slight discharge of the cell.

It is concluded that a determination of the state state-of-charge is not possible for $Mg–MnO_2$ and $Zn–MnO_2$ cell systems by the measurement of equivalent series/parallel resistance and capacitance, modulus of impedance, or a.c. phase shift apparently due to large fluctuations caused by film formation/breakdown processes.

The measurement of the open-circuit voltage at equilibrium can be used as a state-of-charge indicator in the case of $Zn–MnO_2$ dry cells but even this method fails with respect to $Mg–MnO_2$ dry cells.

References

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[2] M. L. Gopikanth and S. Sathyanarayana, *ibid* 9 (1979) 369.