

## ALTERNATING-CURRENT IMPEDANCE OF MAGNESIUM/ MANGANESE DIOXIDE DRY CELLS IN ABSENCE OF ANODE-FILM BREAKDOWN

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### Summary

Alternating current impedance of magnesium/manganese dioxide dry cells has been measured under conditions that do not harm the protective passive film on the magnesium electrode. Several electrical equivalent-circuits for the cell have been theoretically analysed, and a comparison of theoretically derived criteria with experimental results has led to the choice of the most suitable model. In principle, the methodology of measurement and analysis can be applied to other battery systems that involve reactive metals covered by protective films, in order to obtain information on the electrochemical properties of the film-covered metal/solution interface under non-destructive conditions.

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### Introduction

High-energy primary batteries based on either lithium or magnesium are becoming increasingly important. Such batteries have a long shelf-life due to the presence of a protective passive film on the anode [1, 2]. These passive films are either formed by reaction with the electrolyte, as in the case of lithium [3], or applied at the time of manufacture, as in the case of magnesium [2]. Inadequate passivation leads to premature failure of the cells through corrosion of the anode. Excessive passivation, on the other hand, results in a long delay in the attainment of the operating voltage following initiation of discharge. The protective action and voltage delay are governed by the physical and electrochemical properties of the film-covered metal/solution interface. These properties are the major factors determining performance of high-energy primary batteries.

The magnesium/manganese dioxide (Mg/MnO<sub>2</sub>) dry cell is a typical representative of the above class of primary batteries that have high energy

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density and long shelf-life. The advantages of this cell over conventional types (e.g., Leclanché Zn/MnO<sub>2</sub>) have been discussed elsewhere [2, 4, 5]. The magnesium electrode is covered by a passive film of inhibitors.

In the present investigation, the frequency dependence of the alternating current (a.c.) impedance of Mg/MnO<sub>2</sub> dry cells has been measured under conditions that cause no damage to the passive film. The results have been interpreted using plausible equivalent circuits that are consistent with a physical model proposed for the film-covered anode/solution interface. The experimental conditions identified for the non-destructive evaluation of the a.c. impedance of Mg/MnO<sub>2</sub> dry cells may, in principle, be extended to the study of analogous battery systems employing electrodes such as lithium, aluminium, etc. The technique may be used to verify the stability of the protective passive film in assembled cells, to detect electronic shorts, and to optimize design for improved performance.

### *Previous studies*

The impedance method has been widely used in the study of electrochemical processes in both primary and secondary batteries (see, for example, refs. 6 - 9, 14). Impedance studies on high-energy primary cells with reactive metal anodes have been limited to lithium- and magnesium-based cells [7, 8, 10]. Several studies have also been conducted on the impedance of the lithium/solution interface in battery electrolytes [11 - 13, 15].

While the results of the above studies have been interpreted in terms of the properties of the passive film-covered electrode/solution interface, no special precautions seem to have been taken to preclude damage to the film during experimental investigation, especially given the fact that these films break down easily on anodic polarisation [1, 5]. Further, interpretation of the frequency response of impedance has not considered, in a systematic manner, all possible equivalent-circuit models consistent with the facts known about the physical system.

In the light of these observations, it has been considered desirable to identify experimental conditions under which impedance measurements can be made on such high-energy primary cells such that no damage is caused to the protective passive film during testing. The experimental data so obtained may then be compared with the theoretically predicted response of several plausible equivalent circuits in order to identify the circuit model that is the most consistent with the phenomenological description of the Mg/MnO<sub>2</sub> cell, and to evaluate the equivalent-circuit parameters.

It is also known that the voltage delay in Mg/MnO<sub>2</sub> dry cells is affected by temperature [28]. Under practical conditions of discharge, the delay time at 0 °C is four times greater than that at 23 °C [26]. Since the voltage delay is associated with the electrochemical properties of the film-covered electrode/solution interface, it is appropriate to investigate the cell impedance at 0 °C and at 23 °C.

## Experimental

The impedance parameters, namely, the series-equivalent resistance ( $R_s$ ) and the series-equivalent capacitance ( $C_s$ ), were measured in the frequency range 1 Hz - 30 kHz at 23 °C and at 0 °C by the bridge method detailed below.

### Bridge configuration

Earlier studies [5] on the galvanostatic discharge of Mg/MnO<sub>2</sub> dry cells at ultra-low rates have shown that discharge currents exceeding  $10^{-9}$  A for a CD-size cell (anode area 100 cm<sup>2</sup>), passed for about 5 min, are sufficiently large to cause damage to the protective passive film. Thus, if the a.c. impedance measurements are to be non-destructive, then the steady-state direct-current (d.c.) density flowing under the test conditions must be maintained below  $10^{-11}$  A cm<sup>-2</sup>.

In the conventional bridge configuration employing resistive ratio arms shown in Fig. 1 [14], values of  $R_1$  and  $R_2$  in the range 100 - 1000 M $\Omega$  would be required to limit the steady-state d.c. to the above value. The use of such large values of resistance would severely limit the sensitivity of measurement [16] and would require strict control of humidity and extensive shielding from noise pick-up. For these reasons, an alternative bridge configuration employing capacitive ratio arms (Fig. 2) was developed and was successfully used in the present study. The values of the low-loss capacitors  $C_1$  and  $C_2$  were 1  $\mu$ F and 0.1  $\mu$ F, respectively, in order to minimise the charge

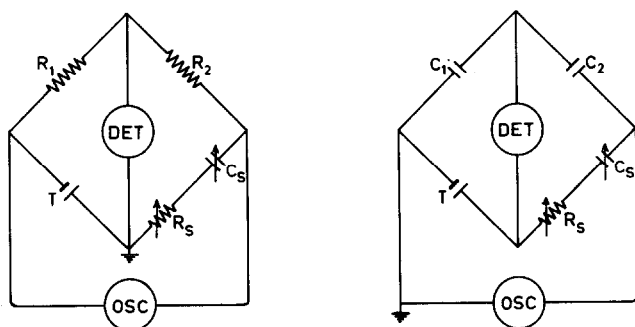


Fig. 1. Conventional a.c. bridge configuration for measurement of impedance parameters.  $R_1$  and  $R_2$ , resistive ratio-arms;  $T$ , test cell;  $R_s$ , series-equivalent balancing resistance;  $C_s$ , series-equivalent balancing capacitance;  $DET$ , phase-sensitive null detector;  $OSC$ , sinusoidal oscillator. Implication: anode-film breakdown in test cell  $T$  occurs due to d.c. current through  $R_1$ - $DET$ - $T$  and  $R_1$ - $R_2$ - $OSC$  loops.

Fig. 2. Schematic of a.c. bridge configuration used in present work employing capacitive ratio-arms for measurement of impedance.  $C_1 = 1.0 \mu$ F and  $C_2 = 0.1 \mu$ F low-loss polystyrene capacitors (values known to  $\pm 0.05\%$ );  $T$ , test cell;  $R_s$ , GR 1433-N,  $0.1 \Omega - 20 \text{ k}\Omega$ , 5 decades;  $C_s$ , GR 1423-A  $10^{-3} \mu$ F -  $1.11 \mu$ F, 5 decades;  $DET$ , two-phase vector lock-in amplifier (PAR 5204), both inputs floating with built-in sinusoidal oscillator,  $OSC$ , with one-end grounded output; a.c. voltage across  $T \leq 0.3 \text{ mV}$  (rms).

withdrawn from the test cell. The steady-state a.c. through the cell was minimized by restricting the a.c. excitation voltage to 0.3 mV r.m.s. across the cell. The Mg/MnO<sub>2</sub> cell formed the test arm, and the balancing arm comprised  $R_s$  and  $C_s$  adjustable standard resistances and capacitances, respectively. The bridge balance was located by a phase-sensitive null detector. Under these experimental conditions, an accuracy of  $\pm 1\%$  was attainable even when the steady-state d.c. current through the cell was limited to the extremely low leakage current (about  $10^{-11}$  A) through  $C_1$  and  $C_2$ .

In order to demonstrate further the non-destructive character of the measurements, the galvanostatic discharge experiments described earlier [5] were carried out before, and after, the impedance measurements. It was thus found that the cell voltage transients and high values of internal resistance, that were typical of the Mg/MnO<sub>2</sub> cell with an intact passive film, could be reproduced at the end of the impedance measurements. The latter would not have been possible if the anode had suffered a film breakdown during the impedance measurements.

### *Test cells*

The CD-size Mg/MnO<sub>2</sub> dry cells were supplied by Messrs. Bharat Electronics Ltd., Pune, India. The cells had a cylindrical construction and an effective magnesium electrode area of about 100 cm<sup>2</sup>. The latter was passivated by a coating of fatty acid esters and chromates to inhibit corrosion. The cells had a nominal capacity of 2.5 A h at 25 °C when discharged at 500 mA to 1.25 V.

### *Temperature*

The test temperature was controlled either to  $23 \pm 0.5$  °C or to 0 °C. The latter temperature was achieved by immersing the cells in a cryostatic bath of water/glycerol mixture; special care was taken to exclude condensation of moisture on the cells.

## **Experimental results**

The dependence of the series-equivalent reactance ( $1/\omega C_s$ ) on the series-equivalent resistance ( $R_s$ ) in the frequency range 1 Hz - 30 kHz is shown in Figs. 3 and 4 (23 °C) and Figs. 5 and 6 (0 °C) for five Mg/MnO<sub>2</sub> cells. The plots tend to intersect the  $R_s$  axis at frequencies around 30 kHz, and show a sharp rise in the values of  $1/\omega C_s$  at low frequencies. For a given frequency, the values of  $R_s$  and  $1/\omega C_s$  at 0 °C are greater than those at 23 °C.

These experimental results have been analysed theoretically to obtain information on the physicochemical processes at the film-covered electrode/solution interface.

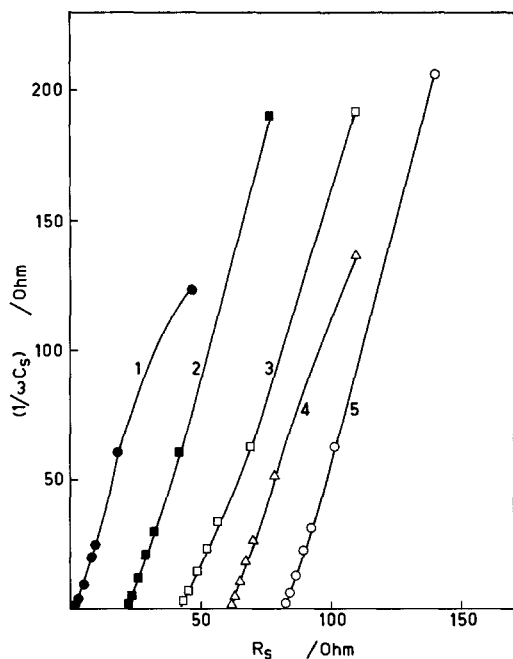


Fig. 3. Dependence of series-equivalent reactance ( $1/\omega C_s$ ) on series-equivalent resistance ( $R_s$ ) for five Mg/MnO<sub>2</sub> dry cells at 23 °C at a.c. frequencies (increasing from right to left): 2, 10, 23, 36, 72, 220, 755 Hz. Curves identified by cell number. For clarity, curves for cells 2 - 5 shifted along  $R_s$  axis by +20, +40, +60 and +80  $\Omega$ , respectively.

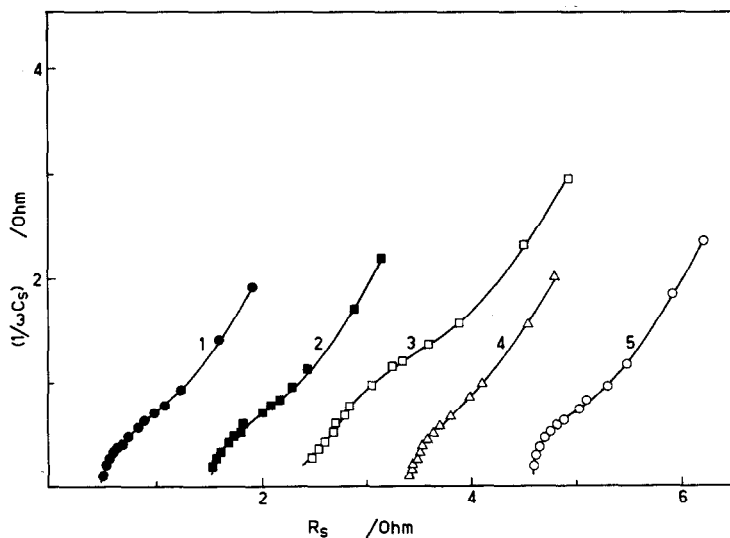


Fig. 4. As Fig. 3, but for a.c. frequencies (increasing from right to left): 0.76, 1.1, 2.5, 3.6, 4.8, 5.8, 7.0, 10.5, 11.7, 13.5, 16.0, 22.0, 24.0, 30.0 kHz. For clarity, curves for cells 2 - 5 shifted along  $R_s$  axis by +1, +2, +3, and +4  $\Omega$ , respectively.

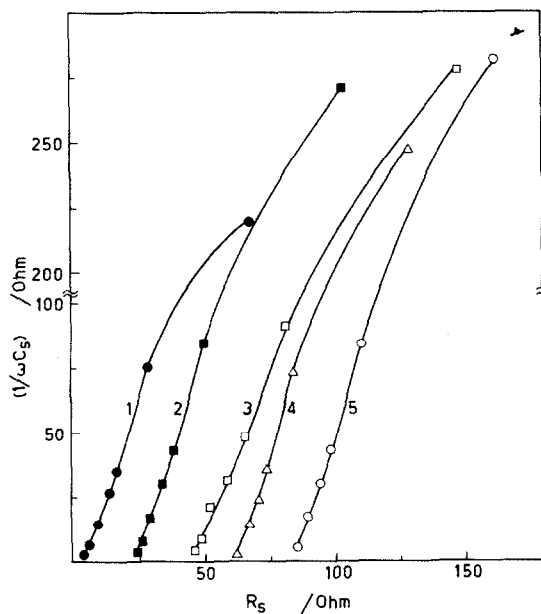


Fig. 5. As Fig. 3, but determined at 0 °C.

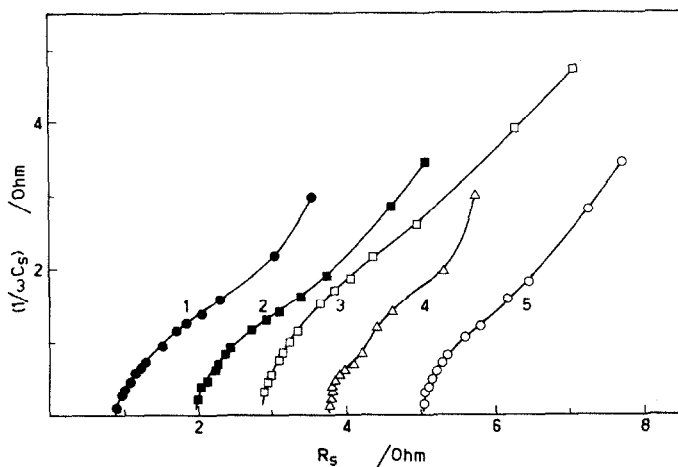
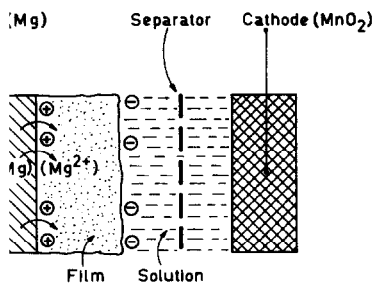


Fig. 6. As Fig. 4, but determined at 0 °C.

## Theoretical analysis

### *Physical model for film-covered Mg/solution interface*

Under the test conditions, the anode-film is intact and the electrochemical response is governed by the physical model [5] shown in Fig. 7. The magnesium electrode is covered by a thin, dielectric passive film of



Physical model of Mg/MnO<sub>2</sub> dry cell without breakdown of the passive film on the magnesium anode.

magnesium hydroxide<sup>13\*</sup>. The physicochemical processes that occur at this electrode are: magnesium dissolution; hydrogen evolution; diffusion of reactants and products at both the metal/film interface and across the film; and ion transport across the film to the MnO<sub>2</sub> electrode. The latter is a large-porous electrode and exhibits low polarisability; its impedance is, therefore, negligible under the test conditions.

#### Electrical equivalent circuits

Four plausible electrical equivalent-circuit models consistent with the above phenomenological description are shown in Fig. 8. In general, the best

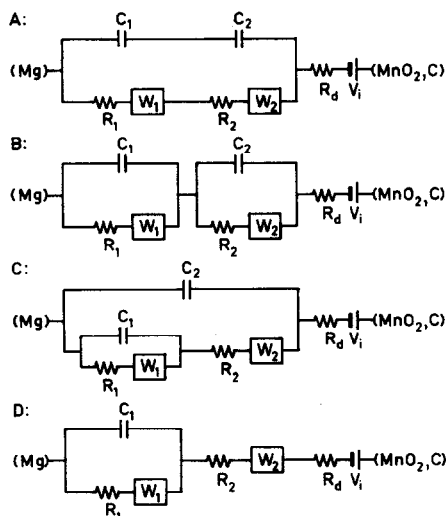


Fig. 8. Models of electrical equivalent circuits for Mg/MnO<sub>2</sub> dry cell with anode-film model.  $R_1$ , charge-transfer resistance;  $R_2$ , film resistance;  $R_d$ , ohmic resistance of solution, separator, and cathode;  $C_1$ , double-layer capacitance;  $C_2$ , film capacitance;  $W_1$  and  $W_2$ , Warburg impedances;  $V_i$ , open-circuit cell voltage.

\*The actual composition of the passive film could be quite complex, e.g., MgO·H<sub>2</sub>·MgCrO<sub>4</sub>, etc. This possibility is, however, not crucial to the discussion.

choice of model must employ a minimum of electrical elements but still be sufficient to include all facts known about the system [17]. Thus, the equivalent circuits include: charge-transfer resistance ( $R_1$ ) for magnesium dissolution in parallel with a double-layer capacitance ( $C_1$ ); impedance to diffusion of reactants and products across the metal/film interface ( $W_1$ ); capacitance of the dielectric film ( $C_2$ ); resistance to charge transport across the film ( $R_2$ ); impedance to mass transport across the film ( $W_2$ ); and resistance of solution, separator and  $\text{MnO}_2$  ( $R_d$ ). The impedance of the  $\text{MnO}_2$  electrode is neglected for the reason given above.

Several equivalent-circuit configurations have been reported in the literature to describe the impedance response of the film-covered metal/solution interface [18 - 23]. Configurations that are consistent with the properties of the magnesium/solution interface are shown in Fig. 8. Model A is based on the well-known Randles circuit [18]. Model B invokes the presence of an equi-potential surface at the metal/film interface and is widely used to explain the impedance characteristics of anodic films on aluminium and lithium [19, 20], as well as in studies on iron oxide dissolution [21]. Model C has been used to interpret the impedance of paint films [22, 23]. Model D ignores the capacitance of the dielectric film and has been employed to explain the delayed action of Mg/ $\text{MnO}_2$  dry cells [4].

#### *Absence of diffusion control*

Although diffusion is a physical process that occurs at film-covered metal/solution interfaces, the relatively low importance of diffusion in determining the electrochemical impedance in the present study may be deduced from the following considerations.

(i) Faradaic currents in the bridge measurements have been minimised to  $10^{-11}$  A  $\text{cm}^{-2}$ , and thus the concentration gradients caused by the test perturbations are small during the measurement interval ( $\sim 5$  min) required to obtain  $R_s$  and  $C_s$  data at any chosen frequency. Indeed, the perturbation is well below the quiescent corrosion current ( $\sim 0.1$   $\mu\text{A cm}^{-2}$ ) that is commonly associated with such passive systems. Therefore, depletion or accumulation effects can be ignored and any concentration gradient arising from the test measurements will be small.

(ii) The characteristic time during which the concentration differences are equalized by diffusion can be estimated from the Einstein relationship:  $L^2 = 2Dt$  (where  $L$  is the distance over which diffusion occurs,  $D$  is the diffusion coefficient of the species under consideration, and  $t$  the characteristic time for the process). The concentration gradients in the present situation must develop across the thickness of the film. For thin, passive films with thicknesses of the order of  $10^{-6}$  cm or less [25], and a diffusion coefficient of  $10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ , the characteristic time is about  $10^{-7}$  s or less. Thus, such a calculation suggests that the concentration gradients, even if set up, would vanish within about  $5 \times 10^{-7}$  s. In the present study, the impedance response has been investigated at frequencies lower than 30 kHz (characteristic time  $3 \times 10^{-5}$  s). As shown above, diffusion processes are at least a hundred times



aster and, therefore, are not likely to be reflected in the experimental responses.

(iii) For an electrochemical system represented by a Randles-type equivalent circuit (Fig. 9), the series-equivalent resistance and capacitance as  $\omega \rightarrow 0$  can be given as:

$$Z_s = R + R_{ct} + \sigma\omega^{-1/2} \tag{1}$$

$$1/\omega C_s = \sigma\omega^{-1/2} + 2\sigma C_d \tag{2}$$

where  $\sigma$  is the Warburg coefficient and  $\omega$  the angular frequency [24]. Figures 10 and 11 show  $R_s$  and  $1/\omega C_s$  versus  $\omega^{-1/2}$  in the region of the lowest frequencies studied. The plots are non-linear and therefore suggest that

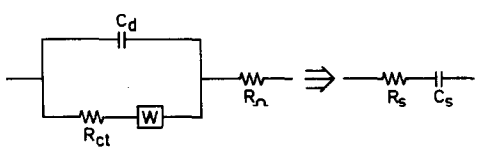


Fig. 9. Randles equivalent circuit for electrode/solution interface and its series-equivalent resistance and capacitance.  $R_{ct}$ , charge-transfer resistance at electrode/solution interface;  $C_d$ , double-layer capacitance;  $W$ , Warburg impedance;  $R$ , ohmic resistance;  $R_s$ , series-equivalent resistance;  $C_s$ , series-equivalent capacitance.

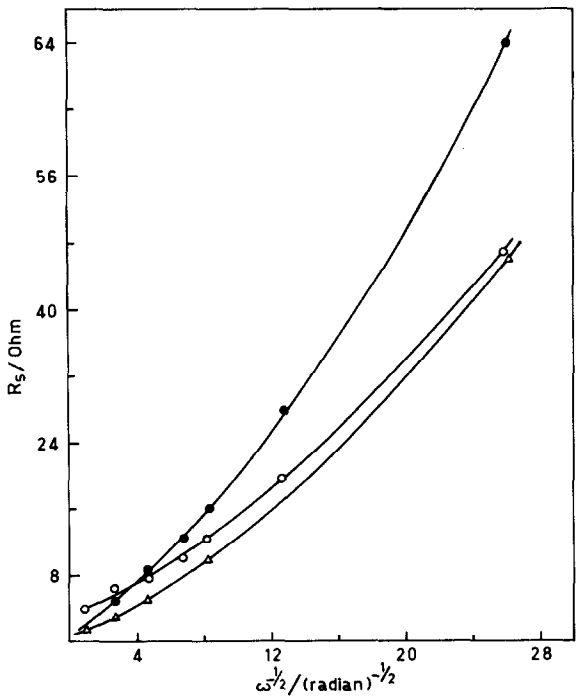


Fig. 10. Plot of  $R_s$  vs.  $\omega^{-1/2}$  for three Mg/MnO<sub>2</sub> dry cells in the frequency range 2 Hz - 1 kHz at 23 °C.