The impedance of the alkaline zinc–manganese dioxide cell. III. The identification of a state-of-charge test

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The best available state-of-charge tests are identified for the case of 1800 mAh alkaline zinc manganese dioxide cells. These are not sufficiently good for the design of impedance based hardware.

1. Introduction

We have examined the impedance spectra of alkaline zinc-manganese dioxide cells in various states of charge and we have shown that the impedance changes significantly with the state-of-charge [1] and that the changes in the impedance spectra can be interpreted in terms of established electrochemical theory [2]. Our technological aim in this work is to identify a test suitable for state-of-charge indication. Neither the raw data [1] nor the computed kinetic and geometrical characteristics corresponding to our model [2] provided the variation required to establish a sensitive test. It was therefore decided to re-determine cell impedance as a function of state-of-charge using triple replication of sampling and impedance determination. Since our initial investigation [1] certain refinements have been incorporated in our circuitry which it was hoped would enable us to achieve a greater precision.

This paper records the results of these estimations and the attendant search for a state-of-charge test.

2. Experimental procedure

The experimental procedure was as described in the previous contribution [1] except that an electrochemical interface (Solatron 1186) was used to apply the current to drive the primary cell and provide the impedance responses for analysis by the frequency response analyser (FRA).

Three cells were chosen for investigation and these were progressively discharged and the impedance spectra estimated after specific amounts of charge had been removed. The variations in the impedance spectra due to possible time effects in the cells were followed by running control cells at the same time. One control cell was nominally 100% charged and another was nominally 95% charged. The impedance spectra of these two controls were estimated from time to time during the period in which the experiments were conducted.

3. Results and discussion

The time variation of the impedances of the control cells was of interest. In the case of the cell which was nominally fully-charged, at frequencies below 1000 Hz the impedance spectrum was unchanged over 2 months. However at high frequencies there was some variation over the same period. This was in the inductive part of the spectrum which occurred in the frequency range around 10 kHz. No reason could be advanced for this behaviour which was relatively small.

For the 95% charged cell the variation with time was found to be rather more significant. Figs. 1 and 2 show the change in the high frequency region which occurred over a 16 day period. The significant change was the increasingly inductive
nature of the high frequency region. This could be associated with geometrical effects inside the cell or the distribution of the chemical reactants through the porous MnO$_2$ electrode [3, 4]. However, neither of these possible causes seem to be appropriate since changes of this magnitude were absent in the 100% control.

The dihedral angle of the low frequency lines was $\sim 40^\circ$ with a tendency to curve towards the real axis in agreement with the porous nature of the electrodes as shown in our earlier work [1, 2].

The major part of the investigation was a simple computer search of the raw impedance data in order to find the best value of either the in-phase, out-of-phase or the complex impedance at any of the experimental frequency points. In order to facilitate the data handling procedure computer software was written to extract the real, imaginary and total impedance measurements at any frequency as functions of the available cell capacity and record the data in a suitable table. Hard copies of graphical data were also available.

The sensitivity of the impedance and respective components to the progressive removal of cell capacity was also extracted from the raw data and the correlation coefficients of the various cell characteristics for a linear relationship were calculated – for the 0–10% discharged region only.

![Fig. 1. High frequency region of impedance spectrum of (Duracell) MN1500 cell immediately after 5% of the available capacity has been removed at the 72 h rate.](image1)

![Fig. 2. As Fig. 1 but after 16 days open circuit period.](image2)

![Fig. 3. Plot of the in-phase component at 9.9 kHz as a function of the state-of-charge for cell No. 1.](image3)

![Fig. 4. Plot of the in-phase component at 2.479 Hz as a function of the state-of-charge for cell No. 3.](image4)