

# *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.

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## **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

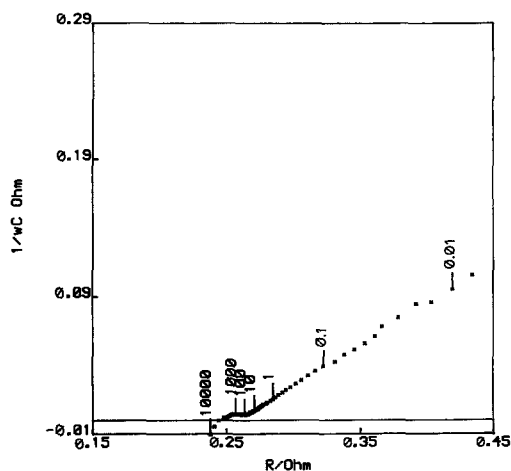


Fig. 1. High frequency region of impedance spectrum of (Duracell) MN1500 cell immediately after 5% of the available capacity has been removed at the 72 h rate.

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  $\text{MnO}_2$  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

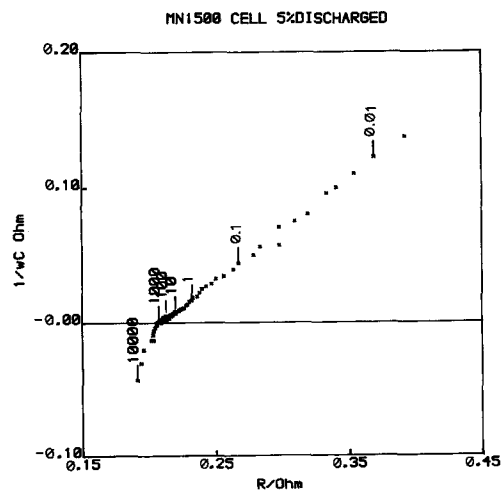


Fig. 2. As Fig. 1 but after 16 days open circuit period.

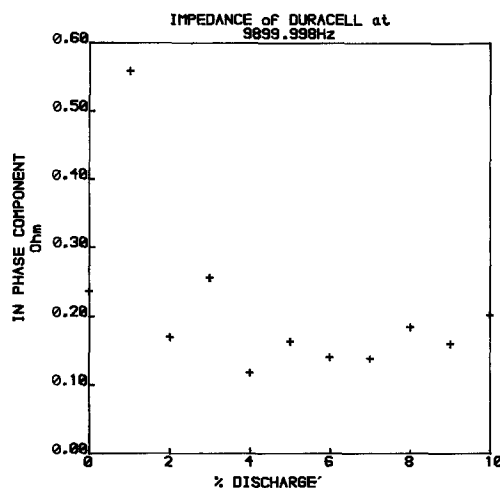


Fig. 3. Plot of the in-phase component at 9.9 kHz as a function of the state-of-charge for cell No. 1.

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.

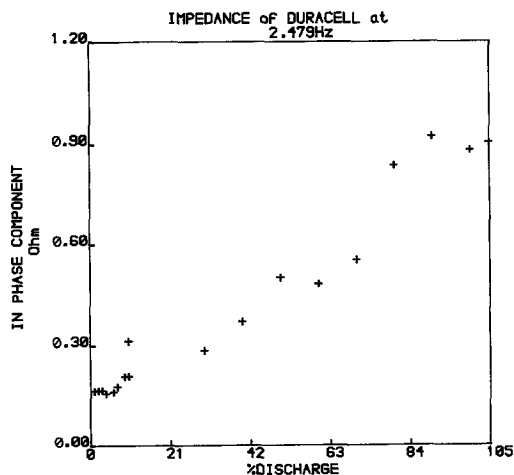


Fig. 4. Plot of the in-phase component at 2.479 Hz as a function of the state-of-charge for cell No. 3.

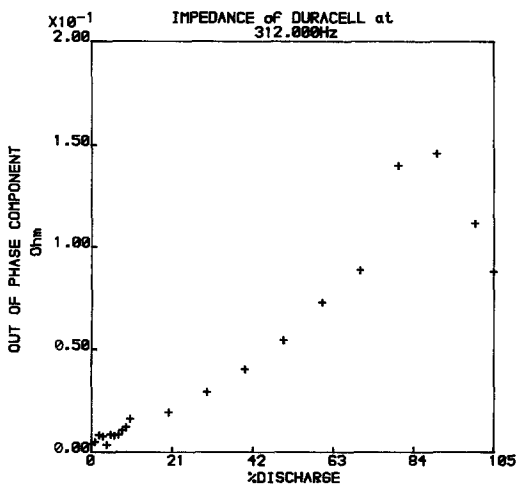


Fig. 5. Plot of the out-of-phase component at 312 Hz as a function of the state-of-charge for cell No. 3.

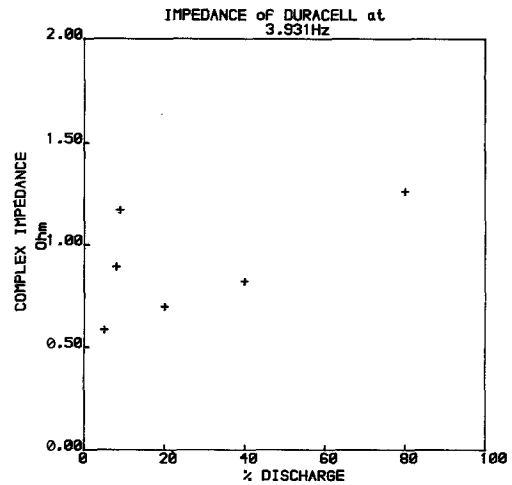


Fig. 7. Complex impedance plot at 3.931 Hz as a function of the state-of-charge for cell No. 2.

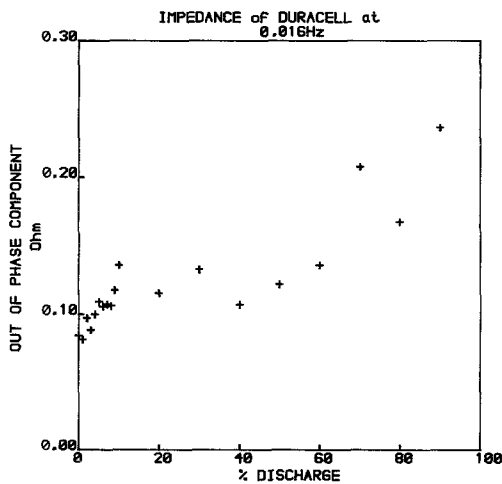


Fig. 6. Plot of the out-of-phase component at 0.016 Hz as a function of the state-of-charge for cell No. 1.

Typical results are shown in Figs. 3-7 and the frequencies at which the maximum correlation coefficients results are shown with the salient data in Table 1.

From Table 1 it can be seen that only a weak correlation exists between the characteristic cell impedance components and the state-of-charge throughout the experimental frequency range.

In the latter connection there is a considerable spread between the optimum (best available) frequency and the correlation coefficient as shown in Table 2. Thus the numerical correlation coefficients can be signed positive or negative depending on the measuring frequency. This is a complicating factor for if we attempt to optimise either the measuring frequency or maximise the correlation coefficient, then as we see from Table 1, the cells may have different 'properties'

Table 1. Maximum correlation coefficients obtained for the impedance, together with its real and imaginary components at the optimum frequency for the three Duracell batteries

	Battery 1		Battery 2		Battery 3	
	Correlation coefficient	Frequency	Correlation coefficient	Frequency	Correlation coefficient	Frequency
In phase	-0.477	9.9 kHz	0.913	3.931 Hz	-0.4815	2.479 Hz
Out of phase	0.914	15.63 mHz	-0.511	6.236 kHz	0.9562	3.931 Hz
Complex impedance	-0.566	3.12 Hz	-0.4343	2.479 Hz	0.3559	9.9 kHz

Table 2. The spread of the optimal measuring frequencies

	Frequency	Range (kHz)
In phase	2.479 Hz	to 9.9
Out of phase	15.63 mHz	to 6.236
Complex impedance	2.479 Hz	to 9.9

and behave differently between nominal replicates. Thus for cells 1, 2 and 3 not only does the optimal frequency appear to vary from 9.9 kHz to 2.75 Hz but the correlation coefficient reverses sign between 2.75 Hz and 3.9 Hz.

We are forced to conclude that the practical limitations of chasing an impedance based state-of-

charge test are likely to prove too great an obstacle in the case of the alkaline Zn-MnO<sub>2</sub> cell for the development of suitable hardware.

#### Acknowledgement

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#### References

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