

## LITHIUM MANGANESE DIOXIDE CELLS – STATE OF CHARGE STUDY BY IMPEDANCE

R JANAKIRAMAN, P N N NAMBOODIRI and R GANGADHARAN

Central Electrochemical Research Institute, Karaikudi-623 006

Lithium-manganese dioxide button cells were fabricated with propylene carbonate as solvent and lithium perchlorate as electrolyte salt. The cells were discharged and impedance measurements were made at different stages of discharge. The kinetic parameters were calculated, and correlated with the state of charge.

**Key words:** Lithium cells, state-of-charge, impedance study

## INTRODUCTION

The problem of state-of-charge monitoring is an important aspect of all electrochemical storage devices. Open circuit voltage, specific gravity etc. have been used to determine the residual capacity of the battery. In the case of lead acid cell where the electrolyte is taking part actively in the cell reaction, there will be a change in the electrolyte concentration. This can be measured in terms of the changes in the specific gravity. This electrolyte concentration influences the cell potential and the open circuit potential. But in the case of Li/MnO<sub>2</sub> button cells, the electrolyte is not directly participating in the reaction. Moreover, in a button cell the measurement of specific gravity is not possible. The open circuit potential is a qualitative test only, whereas state-of-charge requires the determination of available active material and the coulombs they can produce.

Impedance was chosen as a technique for measuring the state-of-charge since this is a non-destructive test and a signal of only a few millivolts are applied. The system will not be disturbed significantly. The test when perfected will be a quick one.

Several attempts have been made to study the state-of-charge of a battery by impedance technique [1-13]. Li-SO<sub>2</sub> [10], Li-SOCl<sub>2</sub> [11], Li-CuO [12] and Li-(CF)<sub>n</sub> [13] cells have been subjected to state-of-charge investigations by impedance technique.

## EXPERIMENTAL

Cells were fabricated with Indian EMD [14] heated to 300°C as cathode material, one molar solution of lithium perchlorate in propylene carbonate as electrolyte and cellulose material as separator. Propylene carbonate was distilled under reduced pressure and then stored over molecular sieves. LiClO<sub>4</sub> was fused in vacuum for 48 hours. The preparation of solution and cell assembly were done inside a dry box. Solartron 1174 frequency response analyser was used for impedance measurements. The cell was connected galvanostatically across 100 K-resistance, and 100 mV a.c. signal was applied.

Cells were assembled with the above selected materials and impedance measurements were made as a fresh cell, and after discharging at 50 μA to 33.3%, 66.6%, 83% and full capacity based on the performance of cells with these compositions. From the impedance values, kinetic parameters were calculated [13] and these are given in Table I. Figs. 1-3 show the Sluyster's plots for the Li/MnO<sub>2</sub> cell with the above selected composition as a fresh cell and at 33.3%, 66.6%, 83% and 100% discharged conditions respectively.

Fig. 4 shows the variation of open circuit potential with discharge.

TABLE I: Kinetic parameters of Li-MnO<sub>2</sub> cell at various states of discharge

State of discharge %	R <sub>sol</sub> ohms	R <sub>act</sub> ohms	C <sub>dl</sub> μF	i <sub>0</sub> mA/cm <sup>2</sup>
0	215	280	0.57	0.06
33.3	180	400	0.50	0.04
66.6	270	330	0.60	0.05
83	400	570	0.70	0.03
100	400	900	0.22	0.02

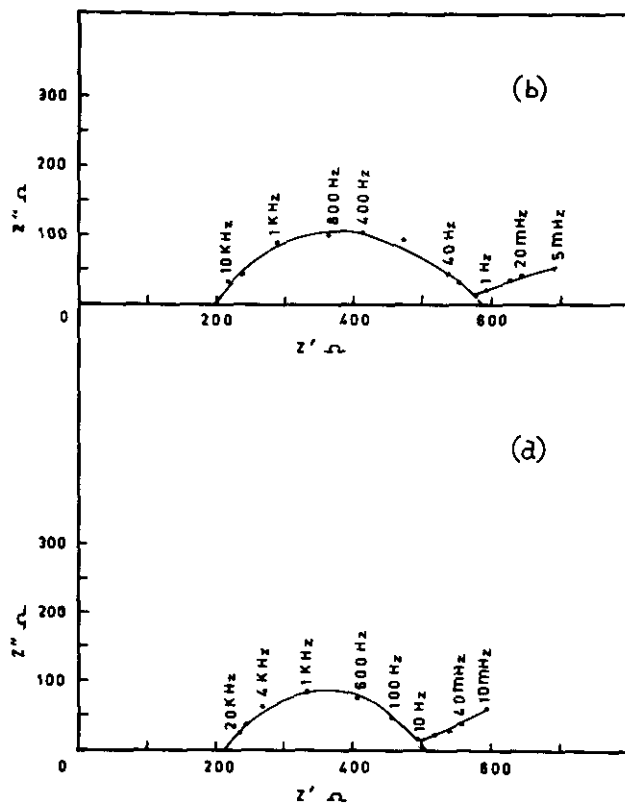


Fig. 1

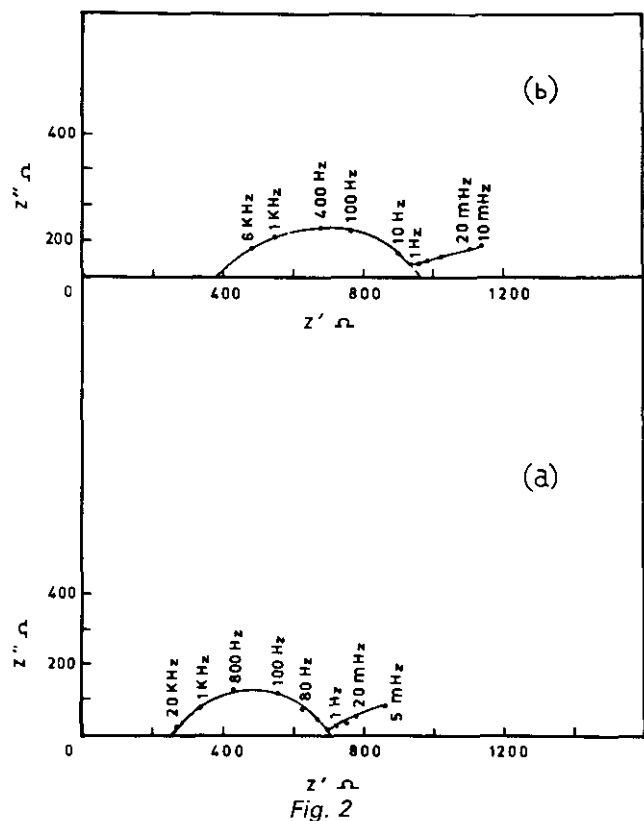


Fig. 2

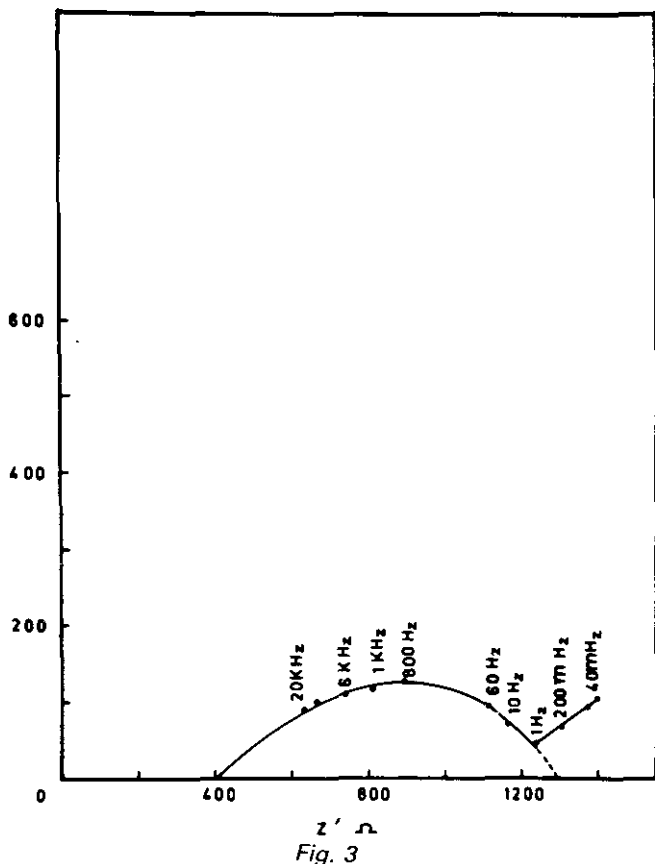


Fig. 3

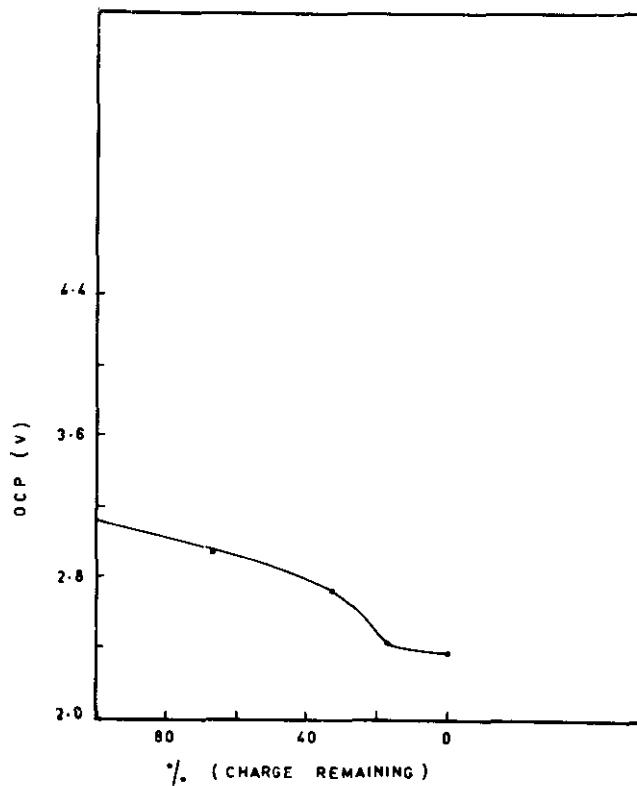


Fig. 4

**DISCUSSION**

The undischarged fresh cell shows a fairly well defined semicircle at high frequencies and a straightline with a slope of around 40° and 50° at low frequencies. As discharge proceeded, the diameter of the high frequency semicircle,  $R_{act}$ , increased. We can see that the  $R_{act}$  value for the fresh cell is 280 ohm and it increases to 400 ohm at 33.3% discharge. It finally reaches 900 ohms at the completely discharged state. The  $i_0$  value decreases from 0.06 mA/cm<sup>2</sup> for the fresh cell to 0.03 mA/cm<sup>2</sup> at 83% discharge and 0.02 mA/cm<sup>2</sup> at 100% discharge.  $R_{sol}$  value increases. The Li<sup>+</sup> ion intercalated into the MnO<sub>2</sub> lattice is the cause of increase in solution resistance as the solution would be depleted of Li<sup>+</sup> ions which are responsible for conduction.

The frequency at the maximum of the semicircle shifts towards lower values. For example, for the fresh cell the  $f_{max}$  is 1 kHz. For the 33.3% discharged cell it is 400 Hz and for the 66.6% discharged state it is 100Hz. At 83% and 100% discharged conditions the  $f_{max}$  values are 400 Hz and 800 Hz respectively. The reduction in frequency maximum values may be due to the lithium surface film break down on discharge and passage of current. The values increase again probably due to the reformation of the film.

The manner in which the  $R_{act}$  value varies with the coulombs removed precludes the use of this data to measure the state of charge of the battery.

The double layer capacitance remains more or less the same but decreases at complete discharge. At the maximum frequency, the real component value increases with discharge.

These parameters, when investigated with various types of batteries, could help in designing a state of charge indicator. If the  $R_{act}$  values with states of charge are plotted into a graph, then it would be easy to find out the state of charge of the battery from this graph. The real component of impedance, the minimum or maximum frequency and such factors can give an idea of the state of charge in a few minutes.

By studying the impedance behaviour at various states of charge and correlating these data, an attempt is being made to develop a state-of-charge monitor. From the above discussion, it can be seen that the  $R_{sol}$ ,  $R_{act}$  and  $i_0$  values vary with the state of charge of a cell. So it should be possible to fix a particular frequency and measure the impedance at that frequency. Then one may give a minimum and maximum value of impedance at the frequency for a particular state of charge.

(This paper forms a part of the doctoral thesis submitted to the Banaras Hindu University by one of the authors)

#### REFERENCES

1. M L Gopikanth and S Sathyanarayana, *J Appl Electrochem*,

9 (1979) 369

2. M Hughes, R T Barton, S A G R Karunathilaka and N A Hampson, *ibid* 16 (1986) 555

3. M L Gopikanth and S Sathyanarayana, *ibid* 9 (1979) 581

4. S A G R Karunathilaka, N A Hampson, R Leek and T J Sinclair, *ibid*, 10 (1980) 799

5. *Idem*, *ibid*, 11 (1981) 715

6. A K Jonscher and M A Bari, *Electrochem Soc Extd, Abstract*, 23, 87-1 (1987) Philadelphia

7. S A G R Karunathilaka, N A Hampson, R Leek, and T J Sinclair, *J Appl Electrochem*, 11 (1981) 573

8. M Hughes, R T Burton, S A G R Karunathilaka, N A Hampson and R Leek, *ibid*, 15 (1985) 129

9. M F Bell, *Electrochem Soc Extd Abstr*, 55, 86-2 (1986) Cal

10. M Hughes, S A G R Karunathilaka, N A Hampson and T J Sinclair, *J Appl Electrochem*, 12 (1982) 537

11. *Idem*, *ibid*, 13 (1983) 669

12. N A Hampson, S A G R Karunathilaka, R Leek and T J Sinclair, *Surface Technology*, 15 (1982) 101

13. J R Sandifer and M R Suchansti, *J Appl Electrochem*, 14 (1984) 329

14. V Aravamuthan, R Srinivasan, S C Chockalingam, S Kulandaisamy, C C Gopalakrishnan, J P R Raja, S Visvanathan and H V K Udupa, *Proc 2nd Int Symp Industrial and Oriented Basic Electrochemistry, Madras* (1980) 2.5.1 - 2.5.17