

LITHIUM MANGANESE DIOXIDE CELLS—AN IMPEDANCE STUDY

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Chemical manganese dioxide heat treated at 623K was used as cathode material in a lithium cell. One molar solution of LiClO_4 in propylene carbonate and 1, 3 - dioxolane was used as electrolyte. The cells were subjected to impedance measurements at 303K, 293K and 278K. The kinetic parameters have been calculated.

Key words: Lithium cell, chemical manganese dioxide, (CMD), impedance measurement

INTRODUCTION

In a battery, the system is far removed from the precise conditions of usual laboratory electrochemical systems where the behaviour of each electrode could be studied. In a battery, the porosity of the electrode, limited availability of electrolyte solution, presence of separator materials, roughness of the electrodes and the changing area of the electrodes make much difference. The cell can be taken to be nearer to a complex series circuit. It is quite likely that one electrode may dominate the impedance behaviour of the cell. In the study of the impedance behaviour of a battery, two electrode system unlike conventional experiments, has to be studied. The possible inclusion of a third electrode will alter the system. Any test of impedance on a battery would be credible and reliable only if kinetic data could also be obtained from these studies. Interpretation of impedance data on battery systems done so far have utilized the already established cell reactions. Some of the advantages of the ac impedance are: the use of only very small signals which do not disturb the electrode properties to be measured, the possibility of studying electrode reactions in low conductivity media where traditional dc methods as well as double layer capacitance data can be obtained in the same measurement. Extensive investigations have been carried out on the impedance characteristics of Leclanche [1], Zn - alkaline MnO_2 [2], Zn-HgO [3], Li- SO_2 [4], Li-CuO [5], Li- SOCl_2 [6] and Li- $\text{S}(\text{CF}_3)_n$ [7] cells. For Li- MnO_2 cells, Ikeda et al have established the reaction mechanism to be the intercalation of Li^+ ions at the MnO_2 lattice [8]. Battery impedance may be represented by an equivalent circuit [7]. In Li- MnO_2 cell, it is a one step one electron transfer reaction. Butler-Volmer equation can be used to derive kinetic parameters. The exchange current density i_0 can be obtained by the relation

$$\left(\frac{\partial \eta}{\partial i}\right)_{C_{\text{Li}^+}, T} = \frac{RT}{Fi_0} = R_{\text{act}} \quad (1)$$

Values of C_{dl} could be obtained from the relationship

$$2\pi f_{\text{max}} R_{\text{act}} C_{\text{dl}} = 1 \quad (2)$$

and a plot of $\ln R_{\text{act}}$ vs $1/T$ is linear and the slope gives the value of the activation energy. By measuring the double layer capacitance of lithium half cells and batteries separately, it has been proved [7] that the complex plot could be divided so that the R_{sol} , R_{act} and low frequency regions of the complex diagram represent the solution, the anode and the cathode respectively. Thus the impedance spectrum of a battery could be used to study the electrodes and the electrolyte in a single experiment. Impedance studies on Li/ MnO_2 cells with electrolytic MnO_2 have been carried out earlier in a 1 M solution of LiClO_4 in propylene carbonate (PC) [9] and mixed solvent of propylene carbonate and 1,2 - dimethoxy ethane. In this study, chemical MnO_2 in a coin cell of 25 mm dia and 5 mm

thickness has been investigated using 1 M solution of LiClO_4 in a mixed solvent of PC and 1, 3 - dioxolane (DIOX).

EXPERIMENTAL

Manganese dioxide: Sedema (Belgium) chemical MnO_2 (CMD) was heated to 623K and used.

Lithium: Lithium ingots (Foote) were flattened and cut to size and used.

Propylene carbonate: (PC) [Merck Schuchart, Munich] was stored over calcium oxide for 24 h. Then it was distilled with calcium oxide under reduced pressure. The first and last 10% portions of the distillate were rejected to avoid steam and low boiling impurities. Afterwards, the solvent was stored over 4A Linde molecular sieves for 48 hours. The water content was less than 50 ppm.

1,3 - dioxolane: This was stored over lithium metal for 24 h and distilled under reduced pressure. Then it was stored over 4A molecular sieves.

Lithium perchlorate: LiClO_4 (Fluka, AG) was fused in vacuum at 423K for more than 48 h. This dried sample was used for preparing electrolyte solution. The calculated weights of LiClO_4 for the various concentrations of solutions were fused separately and the fusion was repeated several times till there was no reduction in weight.

Cathode: The cathode material was a 90:10 mixture of CMD and acetylene black which was thoroughly mixed with colloidal teflon binder (ml/10g) and dried. Cathode pellets of dimension 20 mm dia and 2 mm thickness were made at a pressure of 2000 kg.cm^{-2} .

Separator: Porous nonwoven polypropylene sheet was used as separator.

Electrolyte solution: PC and LiClO_4 were mixed inside a dry box in inert atmosphere. DIOX and LiClO_4 were also similarly mixed. Equal amounts of the solution of LiClO_4 in PC and DIOX were mixed and used as the electrolyte. The specific conductivity of this solution was 12.344×10^{-3} mho at 303K.

Cell fabrication: Cells were assembled in a dry box. The cell case was stainless steel. Cells were crimp sealed after assembly to give coin cells of 25 mm dia and 5 mm thick.

Impedance measurements: Impedance measurements of these cells at frequencies ranging from 100 mHz to 15 kHz were made with a solartron 1250 FRA at different temperatures. The cell was immersed in a nonaqueous solvent and this vessel was kept in a thermostat. AC signal of 5 mV was applied. Cells were stored for 10 days after fabrication and then experiments were commenced.

RESULTS AND DISCUSSION

The complex plane plots are shown in Figs. 1-3. It can be seen that all the plots are more or less similar. The general shape is a slightly distorted, semicircle ending in a Warburg line. The semicircle is elongated owing to the change in the area of the electrodes and the surface roughness. The process is controlled mainly by faradaic phenomena. The high frequency part of the diagram is generally representative of the anode of the cell [10]. It has also been suggested that the lithium anode can suffer film formation upon reaction with atmospheric components and the solvent. It is also likely that the anode in the battery formed a film, most probably during manufacturing process. In such cases the solid electrolyte interphase (SEI) controls the electrode-electrolyte properties including kinetic parameters and the double layer capacitance. Electrodes with double layer capacitances of less than $5 \mu\text{F}\cdot\text{cm}^{-2}$ are considered suitable candidates

TABLE—I: Variation of impedance parameters of Li/MnO₂ cell with temperature

Temperature (K)	R _{sol} (ohms)	R _{act} (ohms)	f _{max} (Hz)	C _{dl} (μ F. cm ⁻²)	i ₀ (mA.cm ⁻²)
303	85	100	751.8	2.1	0.083
293	110	110	751.8	1.9	0.073
278	160	400	75.18	5.2	0.019

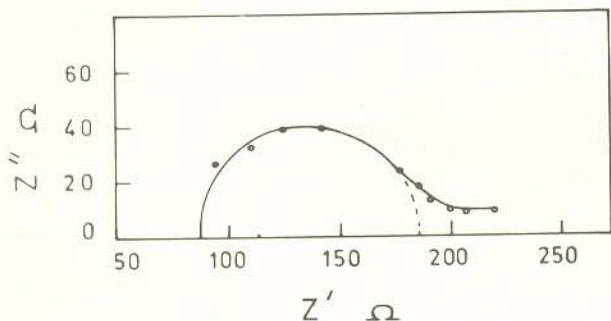


Fig. 1: Complex plane plots of Li/MnO₂ cell at 303K

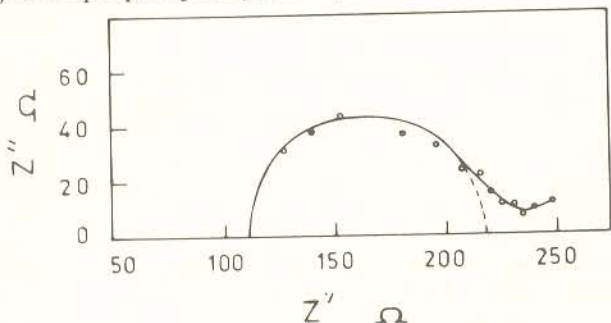


Fig. 2: Complex plane plot of Li/MnO₂ cell at 293K

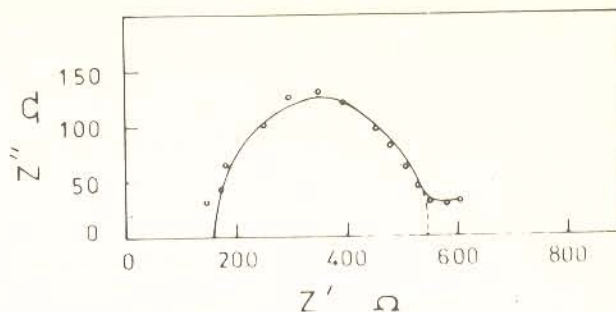


Fig. 3: Complex plane plot of Li/MnO₂ cell at 278K

for SEI. A double layer capacitance of 2.4 to $5.2 \mu\text{F}\cdot\text{cm}^{-2}$ has been measured for PC/LiClO₄ system [12]. Table I shows that the measured C_{dl} values are 2.1 to $5.2 \mu\text{F}\cdot\text{cm}^{-2}$ and i₀ values are in the range 0.083 to $0.019 \text{ mA}\cdot\text{cm}^{-2}$. It has been reported that i₀ values decrease from 0.59 to $0.055 \text{ mA}\cdot\text{cm}^{-2}$ after one week of intermittent exposure to air in lithium tetrafluoroborate/γ-butyrolactone (BL) half cell [7]. This suggests that surface film formation is possible in the tested cells because, close agreement exists between i₀ and C_{dl} values obtained in the present study and those reported [7, 11].

It is known that higher temperature is conducive to better performance of batteries as viscosity becomes less, facilitating the diffusion process. In this study also, i₀ values increase upon changing the temperature from 278K to 303K while R_{act} values decrease. Solution resistance also decreases. There is a fourfold increase in i₀ for a 25° increase in the temperature from 278K to 303K. With PC-DME mixed solvent system also, a fourfold increase in i₀ was observed for a rise in temperature from 283K to 303K[10]; at lower temperatures, diffusion will be impeded. Thus mixed solvents have been found to be beneficial when compared to single solvents like PC. The results indicate that PC-DIOX mixtures can prove to be a good solvent system for lithium cells.

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