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IMPEDANCE ANALYSIS OF LITHIUM SYSTEMS

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Summary

Complex lithium cell impedances have been measured over a wide frequency range. The frequency dispersion of loci obtained on a complex plane has been analysed in terms of an equivalent-circuit representation. The impedance locus has given a markedly depressed semicircle in Li–MnO_2 cells. A frequency-dependent element has been introduced to express the depressed semicircle in the equivalent circuit. This element could be a useful index for indicating the degree of circle depression.

Introduction

An impedance dispersion obtained by a non-destructive, complex impedance analysis provides useful information on electrochemical systems. The impedance dispersion, measured over a wide frequency range, is expressed by a complex plane plot and is analysed in terms of an equivalent circuit. The locus obtained in the plane is composed of several semicircles or arcs that can be respectively assigned to the electrolyte, the electrodes, and the electrode reactions taking place at the interfaces of the electrolyte and electrodes. Since a simple parallel resistor/capacitor (R–C) network is applicable to the ideal semicircle in the complex plane [1], the equivalent circuit of the total electrochemical system can be expressed by R–C networks in series/parallel connections.

The impedance locus observed experimentally, however, is affected by the large impedance component in the system. Hence, only one depressed, or distorted, arc over a wide frequency range is often observed. Sometimes, two or three arcs, which should be respectively assigned to different components, are synthesized to one arc. This difficulty in the analysis is caused by an overlap of the partial contributions of the different components in the same frequency range. Although numerous experimental results have been reported for lithium cells, a perfect, ideal semicircle has rarely been observed. An equivalent circuit composed of simple R–C couples thus appears to be inapplicable in these cases. There is scope, therefore, to develop a more precise circuit for impedance analysis. An advanced analysis method of this type for lithium cells is presented in this paper.

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Experimental

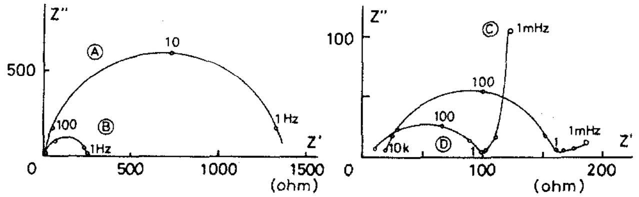
The complex impedance measurements were carried out using a frequency-response analyzer (Solartron 1172), a plotter interface (Solartron 1180) and an X–Y recorder (HP 7046A). A potentiostat was used to interface the test cell to the frequency-response analyzer. An electrometer with high input impedance and a differential amplifier were used for small signals. The precision of the total measuring system was maintained by making intermittent corrections using standard *R–C* networks. All test cells were commercially available products of Matsushita, Sanyo, Toshiba, and Catalyst Research. The sample cell, mounted on a purpose built holder, was protected from electrical noise by a shield case. The measurements were performed over a frequency range of 1 mHz to 10 kHz and in a current range of μA to mA at ambient temperature.

Results and discussion

The impedance dispersion of lithium cells was measured under several different conditions. Typical results are shown in Fig. 1. The impedance locus of $Li–I_2$ and $Li–(CF)_n$ cells is a semicircle with little distortion and can therefore be represented by a simple equivalent circuit (Fig. 1(a)). On the other hand, the impedance locus for an $Li–MnO_2$ cell shows a depressed arc (Fig. 1(b)) which barely coincides with the simple equivalent circuit.

Similar results have been obtained by other researchers. Miyazaki and Nishihama [2] reported that the depression of the arc in an $Li–MnO_2$ cell is mainly due to an impedance dispersion at the positive electrode, which consists of the active material (MnO_2), a conductive agent, and a viscous agent, *e.g.*, ethylene fluoride resin. Thevenin [3] studied the passivation of lithium metal in a non-aqueous electrolyte by means of complex impedance analysis and found that the impedance locus became larger with growth of the passivating film during storage.

The impedance locus of the $Li–MnO_2$ cell measured at room temperature after a storage of 6 months is shown in Fig. 2. Compared with the results for a fresh cell (Fig. 1), a small distortion of the arc is observed in the



(a) (b)

Fig. 1. Typical complex impedance plot for (a) $Li–CF_n$ and (b) $Li–MnO_2$ cells. (A), (C): fresh state; (B), (D): discharged state.

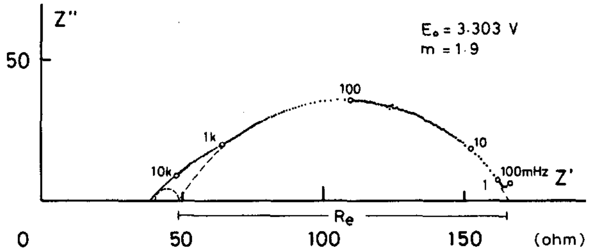


Fig. 2. Complex impedance locus of Li–MnO_2 cell measured at room temperature after storage of 6 months.

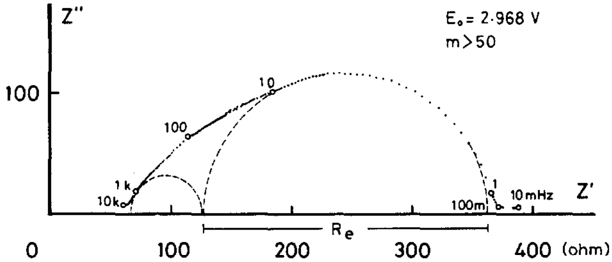


Fig. 3. Complex impedance locus of Li–MnO_2 cell measured at 0 °C after storage of 6 months.

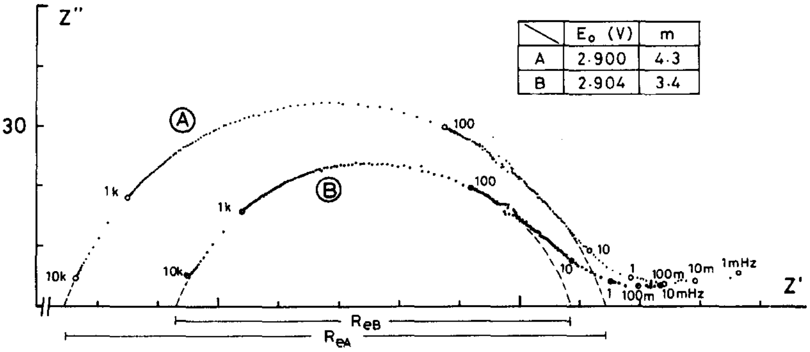


Fig. 4. Complex impedance loci of discharged cells through a constant resistance. (A): Discharged through 500 ohm resistor (18 mA h); (B): discharged through 2 kΩ resistor (17 mA h).

higher frequency range. Measurement at 0 °C resulted in a more noticeable distortion of the locus (Fig. 3). These distorted loci can be divided into two semicircles. The loci in Fig. 4, obtained after discharge of the fresh cell, are different from the above results as no distortion is observed in the higher frequency range, although there is a depression of the arc over the total frequency range. This is because passivation of lithium may be ignored when measurements are conducted immediately after the discharge of the cell. These results suggest that the distortion of locus in the higher frequency

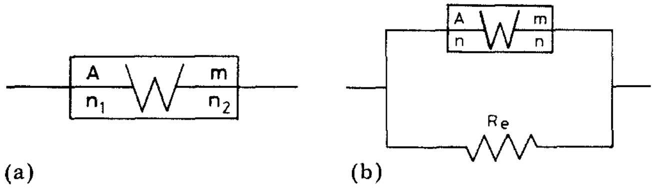


Fig. 5. (a) New symbol to represent the frequency-dependent element expressed by eqn. (1); (b) equivalent circuit to express the depressed-semicircle with the frequency-dependent element.

range may be due to the formation of a passivating film on the lithium electrode. The dispersion of a lithium passivating film in an $SOCl_2$–Li cell reported by Thevenin [3] may correspond to the distortion of the dispersion in the higher frequency range in the MnO_2–Li cell. Presumably, the difference in dispersion is related to the nature of the passivating film formed on Li. Consequently, the depression of the semicircle over the total frequency range in Fig. 4 can be attributed principally to an impedance in the positive electrode, as mentioned by Miyazaki [2].

Cole and Cole [4] have developed an equation to express the symmetrically depressed arc of the type shown in Fig. 4. However, the equation is not easily represented by R–C networks in parallel and series combinations. Recently, we proposed a new symbol [5] for these analyses; this is shown in Fig. 5(a). The symbol is expressed by

$$\dot{Z} = A\left(\frac{1}{\omega^{n_1}} - j\frac{m}{\omega^{n_2}}\right) \tag{1}$$

where: m is a weighting factor relating to the capacitive component, which dominates the shape of the arc; n_1 and n_2 are parameters indicating a frequency dependent broadness in the resistive and capacitive components; ω is angular frequency; and j is equal to $\sqrt{-1}$. The conditions of $n_1 = n_2 = n$ and $0.5 < n < 1$ are chosen as the best-fit value in this analysis. Under these conditions, the depressed arc in Fig. 4 can be expressed by the equivalent circuit given in Fig. 5(b). The values of R_e correspond to the length of the chord. The value m dominates the shape of the semicircular arc; a smaller m gives a more depressed arc. If m is larger than 20, eqn. (1) becomes nearly equal to the equation of a capacitor. In this case, a simple R–C network giving a non-depressed semicircle can be applied to the equivalent circuit in Fig. 5(b). Therefore, m is an index indicating the degree of circular depression. Experimentally derived values of m are also given in Figs. 2 - 4.

The MnO_2 electrode is a mixture of conductive and non-conductive materials. MnOOLi is formed as the discharge proceeds. The formation of MnOOLi, which has a higher resistance than MnO_2, affects the impedance dispersion in the electrode and the shape of the locus. The fresh MnO_2–Li cell (Fig. 1(b)) gives an m value of 5.5. The value of m decreases with discharge, as can be seen in Fig. 4. The value of m differs with the type of cells and their manufacturing origin. The parameter m given in eqn. (1) is considered to be a very useful index for the expression of the depressed semicircle and the study of the dispersion state.

Conclusion

Complex impedance analysis in lithium cells provides a useful method for the evaluation of electrodes, electrolyte, and interfacial phenomena. The determination of the predominant component in the system and the separation of the apparently synthesized arc into individual components are important problems in the analysis of the practical data. Furthermore, the equivalent-circuit representation of the locus including non-ideal semicircles poses another major difficulty. These problems can be solved by using a new symbol with a frequency-dependent element.

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