ELECTROCHEMICAL INSERTION OF LITHIUM IN MANGANESE DIOXIDE

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Summary

The insertion of lithium into compact electrolytic MnO_2 was studied by galvanostatic and admittance techniques. The diffusion coefficient, 3.4×10^{-14} m^2/s at 20 °C, and its activation energy of 30 kJ were determined. The rate of the process is controlled mainly by the high resistivity of MnO_2 and by the polarization of the electrode reaction itself. Similarly, the behaviour of MnO_2–C plastic bonded electrodes is controlled mainly by the high resistivity of MnO_2 if the content of carbon black is not sufficient to form a conductive network, and by polarization on the grains of MnO_2 at higher carbon black contents. The optimum concentration of carbon is 30 - 40% by volume.

Introduction

Many papers [1 - 3, 11] have been published on the insertion of lithium in MnO_2. This process has been studied on a plastic bonded powder of γ-MnO_2 and carbonaceous material. It occurs in the potential range 3.05 - 2.85 V *vs.* Li/Li^+ and it is partially reversible [2, 4]. The aim of this paper is to investigate this process on electrolytically manufactured compact MnO_2 and an attempt will be made to compare the results obtained with the properties of plastic-bonded MnO_2 cathodes.

Experimental

Compact electrolytic MnO_2 was cut into chips 0.5 - 3 mm thick. One side of each was coated with sputtered gold and then electroplated with copper, and a wire was soldered to the copper layer. The electrode was sealed in a glass tube using epoxy resin.

Battery-grade γ-MnO_2 (Knapsack GmbH, BDR) and carbon black CORAX 5 HS (Deutsche Gasrusswerke GmbH, Dortmund, BDR) were thoroughly mixed and the PTFE suspension Fluon (Imperial Chemical Industries, Ltd., U.K.) was added until the mixture attained the consistency of a dough;

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the blend was dried and deposited on a nickel screen, wrapped in aluminium foil and pressed. The screen of apparent area 1 cm^2 was then mounted by a platinum screw onto a PTFE holder.

A three-electrode cell and 1.0M $LiClO_4$ in propylene carbonate were used for all experiments. Potentials are referred to a lithium reference electrode.

Galvanostatic curves were measured in the usual way with prepolarization by means of a potentiostat or without it. A Solartron 1250 Signal Analyzer with a Solartron 1841 Electrochemical Interface was used for admittance measurements.

Electrical properties were measured on pellets pressed from blends of MnO_2 with carbon black; the resistivity was measured under constant pressure (approx. 70 kPA), and the thermoelectric power was measured in a device described earlier [5].

Results and discussion

(A) Compact MnO_2

Several galvanostatic curves can be successfully observed on a single electrode if the electrode is polarized, between successive experiments to 3.3 - 3.4 V. In Fig. 1, the potential is plotted against the product $i \times t^{1/2}$ for several current densities. From the results it follows:

(i) The transition time, τ, is inversely proportional to the square of the current density, i. Therefore, the insertion of lithium is limited by diffusion; on the assumption that $Li_{1.0}MnO_2$ is formed in a single-phase reaction [3],

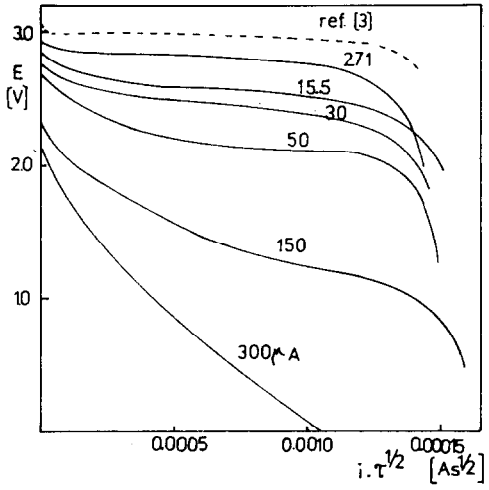

Fig. 1. Galvanostatic curves of lithium insertion into compact MnO_2 at various currents in 1M $LiClO_4$/PC electrolyte. - - - -, equilibrium according to ref. 3. Electrode area 5 mm^2.

the diffusion coefficient $D = 3.4 \times 10^{-14}$ m^2/s was evaluated from the average value of the product $i \times \tau^{1/2}$ (0.0290 ± 0.0032) using the Sand equation.

(ii) The beginning of all curves is shifted towards more negative potentials in proportion to the applied current. The resistance of the electrode, 48 ± 7 kΩ, was evaluated from this shift; the thickness of the electrode was about 2 mm and its surface area 0.05 cm^2.

(iii) The slope of the curves is higher for higher currents, indicating the occurrence of some polarization, which is increased by lithium enrichment of the electrode.

The admittance, plotted in a complex plane, is indicated in Fig. 2, in which the equivalent circuit is also shown. It consists of 7 components, which were found by means of extrapolation to infinite frequencies by a program on an H & P 9830 calculator in the interactive mode. The following conclusions can be drawn from the evaluated components:

(i) The resistance of the electrolyte, R_1, is approximately 100 Ω.

(ii) The capacity, C_1, is in the range 30 - 80 nF for an electrode surface of 0.08 cm^2; most probably, it is the capacity of some barrier layer of a semiconductive nature.

(iii) The resistance R_2 is the volume resistance of the electrode; its value at 20 °C (1.9 kΩ) and the dimensions of the sample (0.08 cm^2 × 0.5 cm) yield a specific resistivity of 30.4 Ω m. The activation energy, 2.69 kJ (0.027 eV), was obtained from its dependence on temperature.

(iv) The admittance, W_1, has a phase shift of 45° and is proportional to $(\omega \times C_1/R_2)^{1/2}$; therefore it is the admittance of fissures in the electrode seal or of pores in the electrode, which should behave as an infinite R–C line.

(v) The interfacial capacity C_2 is approximately 100 - 200 μF/cm^2.

(vi) The resistance R_3 is the true polarization resistance of the intercalation process; at 20 °C, 3.0 V, and 0.08 cm^2 electrode surface, its value is 260 Ω and its activation enthalpy is 20.6 kJ. Its value increases slightly with decrease of potential.

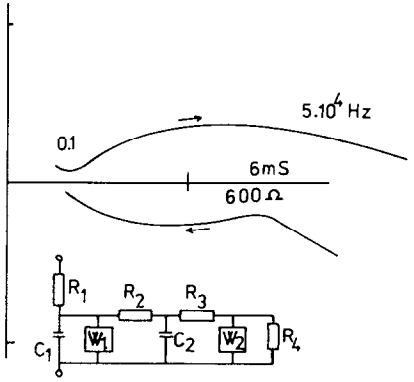

Fig. 2. Admittance (upper curve) and impedance (lower curve) of compact MnO_2 electrode in the frequency range between 0.1 and 50 000 Hz. Electrode area 8.05 mm^2.

(vii) The diffusion admittance, W_2, passes through a maximum 18.3 mS $Hz^{-1/2}$ at 2.95 - 2.85 V. At 3.0 V it falls to 1.205 mS $Hz^{-1/2}$. Using these data in the classical formula [6, 7] a diffusion coefficient, $D = 1.2 \times 10^{-16}$ m^2/s has been evaluated. However, the agreement with galvanostatic measurements would be better if the proper value of $\partial E/\partial C_{Li}$, the activity coefficient γ_{Li} of lithium in MnO_2 and related quantities were available [8].

(viii) The activation energy of diffusion is quite high (30.3 kJ). Therefore, the lithium insertion diffusion control is a true, solid-state diffusion rather than the diffusion of lithium ions, Li^+, in the electrolyte contained in pores present, or perhaps created, in the electrode material [13 - 15]. Moreover, the admittance attached to the diffusion in the electrolyte in a porous electrode should be proportional to $\omega^{1/4}$ and its phase angle should be 22.5° rather than 45°.

(B) Electrical properties of MnO_2–C mixtures

The apparent specific conductivity, κ, and the thermoelectric power, α, are shown in Fig. 3. Essentially, the mixtures can be divided into two subgroups according to their properties and the carbon concentration.

(i) In range I (up to 30% C by volume), the conductivity is low and the properties gradually differ from those of compact MnO_2. It is considered that the grains of MnO_2 are in contact with each other. The carbonaceous material fills the free space between the grains of MnO_2 and forms continuous short-circuits and bridges.

(ii) In range II (over 30% C by volume), the carbon bridges fill the free space completely and form a continuous conductive network which provides contact with all the grains of MnO_2; the electrical properties are quite close to those of pure carbon.

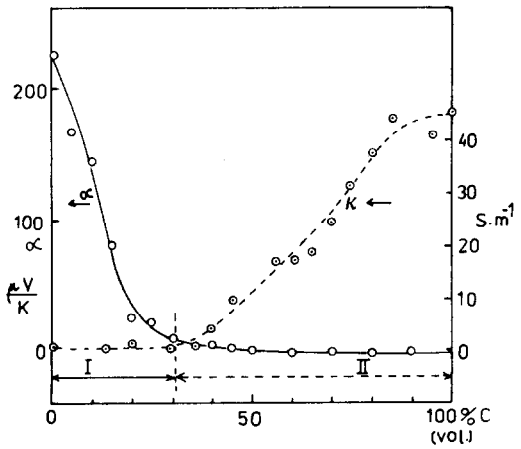

Fig. 3. The influence of carbon black content (in vol.%) on the thermoelectric power, α, and the electrical conductivity, κ, of MnO_2–C mixtures.

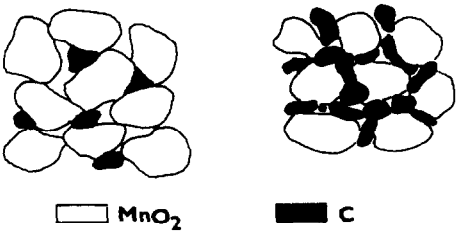

Fig. 4. Idealized view of MnO_2 blends. Left: concentration of carbon lower than 25%, right: concentration higher than 25% (by volume).

Figure 4 shows an idealized view of blends of MnO_2 and C of both concentration ranges.

(C) Electrochemical properties of MnO_2–C mixtures

Usually two waves appear on the cathodic galvanostatic curves of MnO_2–C mixtures (see Fig. 5). The wave of lithium insertion is in the expected potential range (3.1 - 2.2 V according to current density) and it is followed by a second wave starting at 1.6 V, at which lithium is inserted in carbon black and propylene carbonate is reduced [9, 10]. This wave is less pronounced on blends of low C content.

The coefficient of MnO_2 utilization, K, depends both on applied current and composition, as Fig. 6 shows. For mixtures from range I it is approximately proportional to the conductivity of the blend (*cf.* Fig. 3), while it passes through a maximum at the lower end of range II, *i.e.*, for

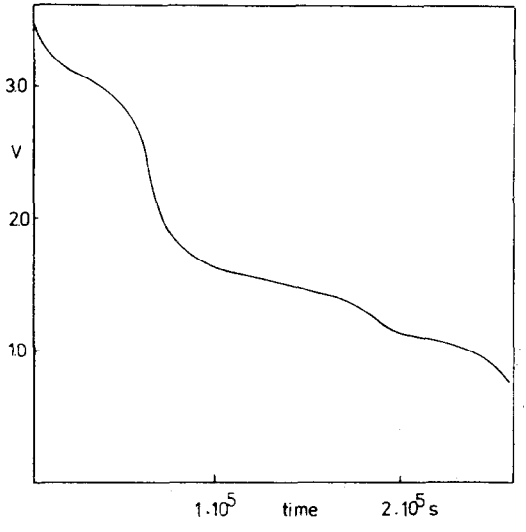

Fig. 5. Example of an electrode discharge containing 50% C by volume, 0.03 g by weight, at a current of 0.1 mA.

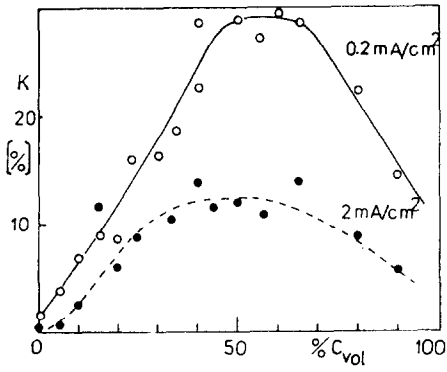

Fig. 6. The coefficient of MnO_2 utilization, K, at 0.2 and 2.0 mA/cm^2.

carbon contents of 40 - 50% by volume. At the highest carbon content, K decreases markedly; this can be explained by the increase in the true current density on the MnO_2 grains in blends with a low MnO_2 content, resulting in a higher influence of electrochemical overvoltage.

Conclusions

The diffusion coefficient of lithium in MnO_2 is fairly high ($D = 10^{-14}$ m^2/s), apparently due to the tunnel structure of MnO_2, and connected with a higher coordination saturation of oxygen ions in such structures than in layered structures [12]. However, the influence of high electrical resistivity and, under certain circumstances, also of polarization effects, predominates and diffusion control can be observed only under certain conditions, both on compact and powdered electrodes. Hence, the diffusion of lithium in MnO_2 is sufficiently rapid and does not strongly influence the behaviour of Li–MnO_2 cells.

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