Charge–Discharge Properties of Polypyrrole Films Containing Manganese Dioxide Particles

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Electrochemical preparation of β-MnO_2-incorporated polypyrrole films resulted in high energy capacity cathode-active materials for rechargeable lithium batteries.

Recently, intensive studies have been carried out on the use of conducting polymers as cathode-active materials of rechargeable lithium batteries.[1–5] The charge–discharge capacity of the polymer films is limited by the maximum amount of electrolyte anions incorporated into oxidized films, which have been reported to be *ca.* 0.3 and 0.5 moles per mole of monomer unit of polypyrrole[1] and polyaniline,[5] respectively; these values are not large enough to construct high energy density Li batteries. In the construction of high energy density Li batteries, the energy capacity per unit volume rather than the energy capacity per unit weight is important because of the limitation of the cell volume. This is another serious problem in the use of conducting polymers as the active materials for the Li batteries. Here we report the preparation of polypyrrole (PPy) films containing β-MnO_2 particles which allow the redox reactions of both PPy and the incorporated MnO_2 particles and improve the low energy capacity per unit volume of PPy.

Electrolysis at 0.1 mA cm^{-2} of a propylene carbonate solution containing pyrrole (0.1 mol dm^{-3}), tetraethylammonium chloride (0.5 mmol dm^{-3}) and various amounts of suspended β-MnO_2 yielded β-MnO_2-incorporated polypyrrole films (PPy–MnO_2) on a glassy carbon anode. The β-MnO_2 particles used had a specific surface area of 23.3 $m^2\,g^{-1}$. X-Ray microanalysis revealed that the MnO_2 particles were distributed uniformly in the films. In our previous study on the incorporation of TiO_2 into PPy films in aqueous solutions containing small amounts of Na_2SO_4 or NaI,[6] Cl^- anion-adsorbed MnO_2 must be incorporated into the PPy film as a charge compensator for oxidized PPy produced by the electrochemical oxidation of pyrrole. The amount of the incorporated MnO_2 was determined by first firing the PPy films at 1000 °C, then dissolving the resulting MnO_2 in a boiling acid mixture consisting of 10% H_2SO_4, 12% H_3PO_4, 17% HNO_3 and 5% KIO_4, and finally by applying absorption spectrometry to the resulting solution at 525 nm. PPy–MnO_2 prepared with the deposition charge (Q_d) of 900 mC cm^{-2} from deposition baths containing 5, 10, 20 and 40 g dm^{-3} of MnO_2 contained 40.7, 50.4, 49.7 and 50.2 wt% of MnO_2 particles, respectively, suggesting that the amount of the incorporated MnO_2 in the PPy film became constant for suspended MnO_2 greater than 10 g dm^{-3}. If Q_d of PPy–MnO_2 was varied, the amount of MnO_2 incorporation seemed to change, depending on Q_d, as judged from rough proportionality between Q_d and the charge–discharge capacity of the resulting PPy–MnO_2, which will be described in a later section.

The charge–discharge test of the prepared PPy films was carried out in a mixed solution of propylene carbonate and dimethoxyethane (1:1) containing $LiClO_4$ (1 mol dm^{-3}). Figure 1 shows the charge–discharge profiles of the PPy–MnO_2 and MnO_2-free PPy films taken at 0.1 mA cm^{-2} in a potential range between 2.5 and 3.8 V *vs.* Li/Li^+. The charge–discharge capacity of MnO_2-free PPy film was 26.6 mC cm^{-2}, while that of the PPy–MnO_2 was 54 mC cm^{-2}. X-Ray diffraction analyses were carried out for oxidized and reduced forms of the PPy–MnO_2 films prepared by polarizing the film at 3.8 and 2.5 V *vs.* Li/Li^+, respectively, for 30 min in the

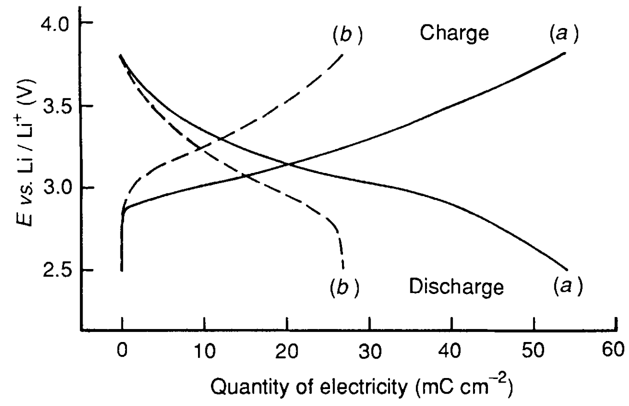

Fig. 1 Charge–discharge curves of polypyrrole film containing 50.2 wt% β-MnO_2 particles (*a*) and MnO_2-free PPy film (*b*) taken at 0.2 mA cm^{-2} in a mixed solution of propylene carbonate and dimethoxyethane (1 : 1) containing $LiClO_4$ (1 mol dm^{-3}). β-MnO_2-incorporated polypyrrole film was prepared using a coating bath containing 40 g dm^{-3} MnO_2. The quantity of electricity used for the polypyrrole preparation was 200 mC cm^{-2} for both PPy–MnO_2 and MnO_2-free PPy films.

above-mentioned electrolyte solution, followed by vacuum drying for 5 h. Sharp diffraction peaks due to (100), (101) and (211) phases of the β-MnO_2 crystals were observed for both films, but these diffraction peaks were shifted as much as *ca.* 0.7° to lower diffraction angles when the oxidized film was reduced, suggesting that the β-MnO_2 lattice was expanded with reduction of the film due to intercalation of electrolyte cations into the MnO_2 lattice. Since the shift in the diffraction angle was reversible in the charge–discharge cycles, the redox reaction detailed in eqn. (1)[7] seemed to be valid in the MnO_2-incorporated PPy films.

$$MnO_2 + nLi^+ + ne^- \rightleftharpoons Li_nMnO_2 \qquad (1)$$

Considering that two electrons are involved in the oxidation of a pyrrole ring to be polymerized and the resulting polymers contain fractional charges *m* per unit pyrrole ring, the theoretical capacity (Q_c) is correlated to the deposition charge (Q_d) as given by $Q_c = Q_d \times m/(2 + m)$. By inserting $Q_d = 200$ mC cm^{-2} and $m = 0.31$, which was obtained by elemental analysis of the as-grown MnO_2-free films, into this equation, 26.8 mC cm^{-2} was obtained for Q_c. In the case of MnO_2-free PPy films,there was fair agreement between the theoretical Q_c and the experimentally obtained one (26.6 mC cm^{-2}). If it is assumed that the capacity due to the redox reaction of polypyrrole of the PPy–MnO_2 films is the same as that of MnO_2-free PPy films, then the excess capacity evaluated from the difference in the experimentally determined Q_c and the theoretical one is attributable to the charges involved in the redox reaction of the incorporated MnO_2 particles. It was found that the amount of N and MnO_2 in the PPy–MnO_2 film was 7.55 and 50.2 wt%, respectively, which gave 1.07 of the molar ratio of MnO_2 to the pyrrole ring. Since the molar ratio of Cl^- ions incorporated in the PPy–MnO_2 film to the pyrrole ring was found to be 0.31, the number of moles of pyrrole rings (M_{Py}) in the film was evaluated from the equation given by $M_{Py} = Q_d/F \times 1/(2 + 0.31)$, where *F* is Faraday constant. By inserting $Q_d = 200$ mC cm^{-2} into the equation, M_{Py} of 8.97×10^{-7} mol cm^{-2} was obtained, from which 9.6×10^{-7} mol cm^{-2} was obtained for the amount of MnO_2 incorporated in the film. Accordingly, the utilization of the incorporated MnO_2 was 0.30.

Table 1 gives the results of charge–discharge tests of the PPy and the PPy–MnO_2 films, the film thickness determined by observation of the cross-section of the films using a scanning electron microscope (SEM) and the energy capacity per unit volume of the film, which was evaluated from the charge–discharge capacity and the film thickness. The surface of the PPy–MnO_2 was found to be fairly smooth with unevenness of ±0.1 μm. As shown in Table 1, the film thickness was increased by only 20% by incorporating *ca.* 50 wt% MnO_2 particles into the polypyrrole film, while the increase in the capacity of the PPy–MnO_2 film was almost double that of the MnO_2-free polypyrrole film, as described above. Therefore, the energy capacity per unit volume of the PPy–MnO_2 film was 1.70 times that of the MnO_2-free PPy film, indicating that the incorporation of MnO_2 particles into the film is effective for improving the energy capacity per unit volume of the PPy film. The weight of the PPy–MnO_2 and MnO_2-free PPy films prepared with $Q_d = 200$ mC cm^{-2} was estimated to be 151.6 and 68.2 μg, respectively, from the above-mentioned molar ratio of Cl^- to pyrrole rings, the number of moles of pyrrole rings and MnO_2 in the film. Then, the energy capacity per unit weight of the PPy–MnO_2 and the MnO_2-free PPy films was estimated to be 350 and 390 C g^{-1}, respectively, indicating that the incorporation of β-MnO_2 particles caused a small decrease in the energy capacity per unit weight of polypyrrole.

Table 1 Charge–discharge test of polypyrrole films containing β-MnO_2 particles[a]

Film	Q_d[b]/ mC cm^{-2}	Charge–discharge capacity/ mC cm^{-2}	Utilization of MnO_2	Film thickness/ μm	Energy capacity per unit volume/ C cm^{-3}
PPy	200	26.6	—	1.0	266
PPy–MnO_2	100	26.5	0.29	0.6	441
	200	54.0	0.30	1.2	450
	500	140.5	0.31	3.1	453

[a] The films were prepared from propylene carbonate solution containing pyrrole (0.1 mol dm^{-3}), tetraethylammonium chloride (0.5 mmol dm^{-3}) and 40 g dm^{-3} of β-MnO_2 particles with stirring of the solution. [b] The quantity of electricity used for preparation of the film.

Table 1 shows that the film thickness and the charge–discharge capacity of the PPy–MnO_2 film were roughly proportional to Q_d, indicating that the PPy matrix worked well as conducting networks for charge-transfer between the electrode substrate and MnO_2 particles in the film. In the use of MnO_2 as an active material for batteries, carbon powders like acetylene black are mixed with MnO_2 to make the conducting networks for MnO_2; the carbon in this case does not work as the active material. In contrast polypyrrole in PPy–MnO_2 works not only as the conducting networks but also as active materials, as already shown above. From this viewpoint too, the PPy–MnO_2 is superior to conventional MnO_2-cathodes as the active materials in batteries.

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