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Evaluation of composite-MnO₂ as cathode material for rechargeable Li/MnO₂ batteries

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Abstract

Composite manganese dioxide is developed from electrochemical manganese dioxide (EMD) and LiOH·H₂O in the temperature range 350–450 °C. To evaluate its performance as a cathode material, several experiments were carried out. In AA-size cells, it works for about 100 cycles at 62.5 mAh/g DOD, while about 300 cycles are achieved at 58.3 mAh/g DOD in prototype cells. During discharge, the *d* values of Li₂MnO₃ become larger and shift to the low angle area with the insertion of lithium. The characteristics of the crystal lattice structure of the material in the charge process are also given and analyzed with the help of X-ray diffraction patterns.

Keywords: Rechargeable lithium batteries; Manganese oxide; Cathodes

1. Introduction

Recently, much attention has been paid to secondary Li/MnO₂ batteries for their excellent performances, low cost and their contribution to the environment protection. In research and development activities, many types of manganese dioxide cathode materials are concerned: α-MnO₂, spinel-MnO₂, defect-spinel-MnO₂ and composite-MnO₂, etc. [1–4]. Composite-MnO₂ synthesized at relative low temperatures can cycle steadily at low depth-of-discharge (DOD) (≤20%) in flat cells [5]; it is supposed to be composed of Li₂MnO₃ and γ-β-MnO₂. To evaluate composite-MnO₂ cathode materials, the experiments are carried out at different DOD in prototype and AA-size cells. The characteristic changes of its crystal lattice during cycling are obtained by X-ray diffraction (XRD) analysis.

2. Experimental

2.1. Charge/discharge

Cells used in the experiments were constructed in a glove box, in which dry air was constantly circulating. The humidity inside the glove box was less than 5%. The cathode consisted of composite-MnO₂ mixed with

acetylene black and a Teflon binder. It was prepared by pressing two sheets of the mixture on to a nickel grid, and sintered in an argon atmosphere at 150 °C for 12 h. The electrolyte was 1 M LiClO₄/propylene carbonate–dimethoxycarbonate (1:1)-Celgard® 2400 was used as separator.

2.2. X-ray diffraction

Samples used for XRD analysis were disassembled from the prototype cells after being discharged to different DOD, and soaked and rinsed in 1,2-dimethoxyethane (DME) for three times, and then dried under vacuum for 24 h. The proportion composite-MnO₂ to acetylene black and polytetrafluoroethylene (95:2.5:2.5) XRD experiments were carried out by using a Y-4Q-type diffractometer with Cu Kα.

3. Results and discussion

Fig. 1 shows the comparison of XRD patterns of composite-MnO₂, electrochemical manganese dioxide (EMD) and heat-treated EMD. In the area of low angles, there are obvious changes in diffraction peaks. With the increase in temperature, the peak of γ-MnO₂ appears at *d*=3.95 instead of the peak of β-MnO₂ at *d*=3.11. With the reaction with Li₂O (decomposed from LiOH·H₂O), a peak of Li₂MnO₃ occurs at *d*=4.71.

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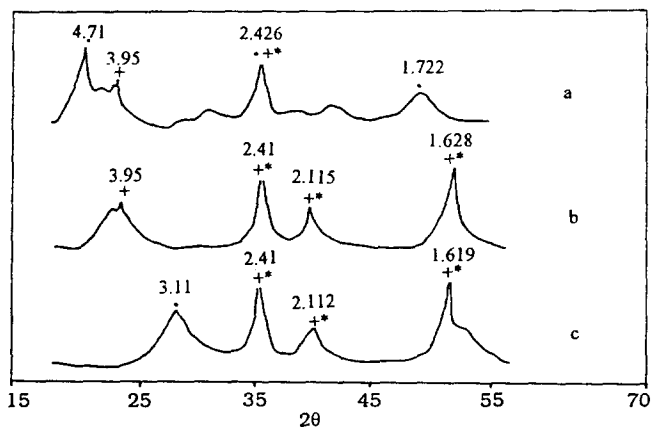


Fig. 1. XRD patterns of three types of materials: (a) composite-MnO₂; (b) heat-treated EMD, and (c) EMD. (·) Li₂MnO₃; (+) γ -MnO₂, and (*) β -MnO₂.

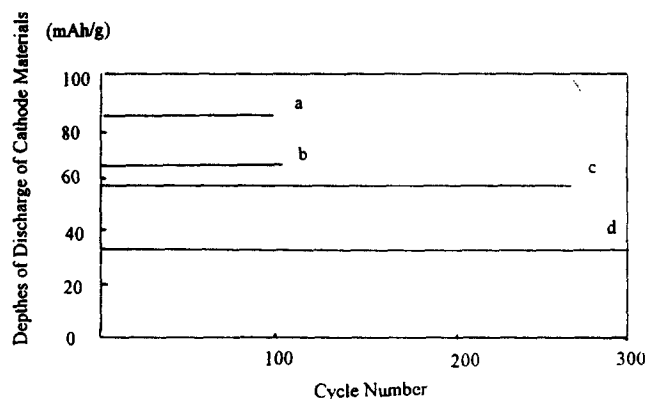


Fig. 2. Cycling performance of composite-MnO₂ at different depths-of-discharge in prototype and AA-size cells: (a), (c), (d) in prototype cells, and (b) AA-size cells.

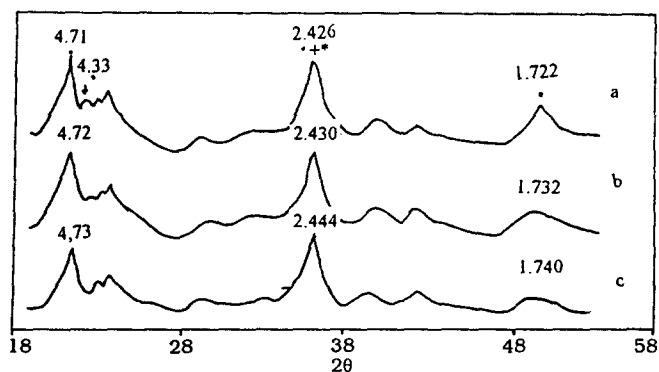


Fig. 3. XRD patterns of composite-MnO₂ discharged to different depths-of-discharge: (a) $X=0$; (b) $X=0.1$, and (c) $X=0.55$. (·) Li₂MnO₃; (+) γ -MnO₂, and (*) β -MnO₂. X =amount of lithium inserting into composite-MnO₂ (gram equivalent).

Composite-MnO₂ can deliver 120 to 130 mAh/g as initial discharge and 150 mAh/g after modification. In the prototype cells, it can cycle steadily and achieve about 300 cycles at low DOD, but its cycling performance deteriorates at deeper DOD (Fig. 2). The characteristic changes of the lattice parameters are shown in Fig. 3.

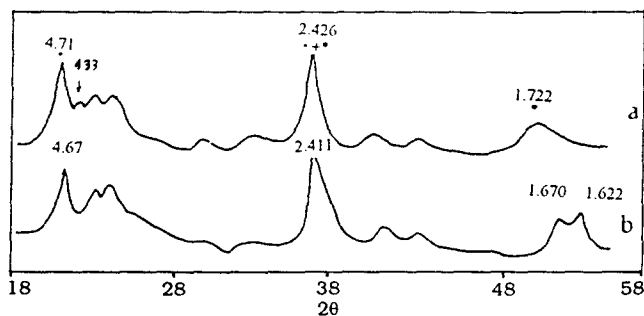


Fig. 4. XRD patterns of composite MnO₂: (a) was not charged, and (b) was charged to 4.2 V. (·) Li₂MnO₃; (+) γ -MnO₂, and (*) β -MnO₂.

With the insertion of lithium ions into the crystal lattice of composite-MnO₂, the diffraction peaks shift in the direction of low angle and d values become larger. This indicates that there is an expansion of its crystal lattice. The peak of Li₂MnO₃ at $d=1.722$ becomes smaller and the one at 4.33 diminishes gradually and disappears finally. From these changes, it is concluded that Li₂MnO₃ takes part in the intercalation reaction more actively than γ - β -MnO₂. It seems that considerable changes of the d values in the large angle area will lead to a deterioration of its cycling performance at deeper DOD.

In order to get more information on the cell reaction, we try to charge the cell just after being assembled, and let its voltage rise from 3.42 to 4.2 open-circuit voltage. After preparation and measurement of cathodes, XRD patterns are obtained and given in Fig. 4. While charging, a few peaks of composite-MnO₂ shift in the direction of large angle area. Two of them are the peaks of Li₂MnO₃, and another represents the peak of both Li₂MnO₃ and γ - β -MnO₂. In the large angle area, the peak of Li₂MnO₃, $d=1.72$, breaks up and turns into two peaks, at $d=4.33$, the peak of Li₂MnO₃ disappears. Although it is hard to determine and to illustrate precisely the mechanism of lithium ion's intercalation getting into and out of crystal lattice of composite MnO₂. It is obvious that Li₂MnO₃ plays an important role in the cell reaction. This, is not only consistent with the conclusion drawn from Fig. 3, but can also be a supplementary evidence.

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