

Three V or 4 V Li–Mn composite as cathode in Li batteries prepared by LiNO_3 method as Li source

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Abstract

Four types of lithium-containing manganese oxide obtained by the LiNO_3 method, namely (i) $\text{Li}_{0.3}\text{MnO}_2$ obtained from 1/3 mixture of Li/Mn molar ratio heated at 320–350 °C; (ii) $\text{Li}_x\text{Mn}_2\text{O}_4$ obtained from the mixture with 1.2–1.8 molar ratio of $\text{LiNO}_3/\text{MnO}_2$ heated at 300 °C; (iii) the spinel LiMn_2O_4 by 1/2 mixture of $\text{LiNO}_3/\text{MnOOH}$ and (iv) non-stoichiometric spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, will be reported and their electrochemical behaviour in lithium cells will be described.

Keywords: Cathodes; Lithium batteries; Manganese; Lithium

1. Introduction

Several Li-containing manganese oxides obtained by the LiNO_3 method using it as a Li source were reported as cathode materials in Li batteries [1,2]. In this method, melted LiNO_3 is adsorbed into manganese compounds at 260 °C. The obtained homogeneous mixture is utilized in a wide variety of synthesis processes, such as heating temperatures above 300 °C and various initial mixing ratios of Li/Mn.

In this process, the mixture is further heated at 300 to 350 °C for 3 V cathodes or 600 to 800 °C for 4 V cathodes. In general, these products have a high surface area and do not need to be ground because of the lower final heating temperature.

LiOH instead of LiNO_3 can be used from the same principle as mentioned before, because the melting point of LiOH is 450 °C. However, the LiNO_3 method has the advantage in the processing of heating at a lower temperature.

2. Experimental

Li–Mn composite oxides were obtained by heating MnO_2 or $\gamma\text{-MnOOH}$ with LiNO_3 . A typical three-step heating was adopted, that is at 260, 300 °C for removing NO_x and at the final temperature. The used MnO_2 's were as follows:

(i) chemical manganese oxide (CMD); IC (International common MnO_2 sample) 12 (Sedema, 100 $\text{m}^2 \text{g}^{-1}$), Cellmax, CMD-1 (Chuoh Denki Kogyo, 42 and 34 $\text{m}^2 \text{g}^{-1}$, respectively), IC 22 (Toho Zinc, 54 $\text{m}^2 \text{g}^{-1}$);

(ii) Electrochemically prepared MnO_2 (EMD); IC 17 (Mitsui Mining, 30 $\text{m}^2 \text{g}^{-1}$),

(iii) and high surface area (HSA) EMD (100 $\text{m}^2 \text{g}^{-1}$) [3,4] prepared by anodic deposition from $\text{MnSO}_4/\text{H}_2\text{SO}_4$ electrolyte at high current densities. $\gamma\text{-MnOOH}$ was supplied by Tosoh Co.

Electrolytes for 3 or 4 V cells are 1 M LiPF_6 in ethylene carbonate (EC):propylene carbonate (PC):diethylcarbonate (DEC):benzene = 4:4:1:1 or PC:DEC = 1:4, respectively.

The electrochemical test method is reported in Ref. [5].

3. Results and discussion

3.1. Electrochemical behaviour of $\text{Li}_{0.3}\text{MnO}_2$ as a 3 V cathode

Discharge and charge curves of various $\text{Li}_{0.3}\text{MnO}_2$'s obtained from different MnO_2 's are shown in Fig. 1 under different heating conditions. In the heating process of a 3:1 mixture at 260 °C, a heating time of 5 h was used for the adsorption of LiNO_3 . The final heating temperature was 320 or 350 °C for 5 or 10 h, depending on the nature of MnO_2 . Longer heating times at 320 or 350 °C causes a formation of a disordered spinel.

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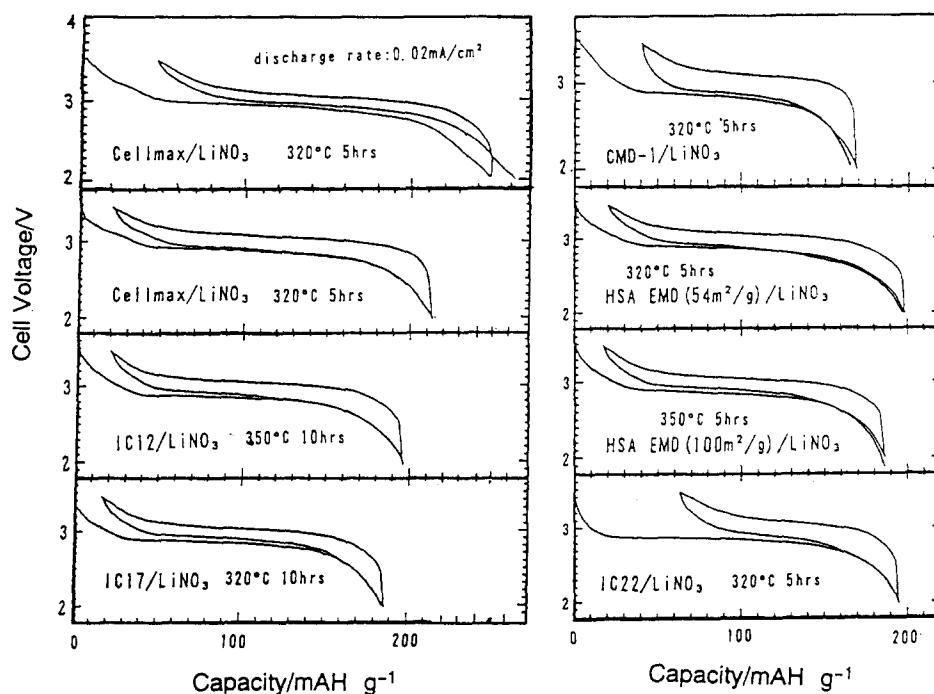


Fig. 1. Discharge/charge curves of $\text{Li}_{0.3}\text{MnO}_2$'s made from various MnO_2 's under different heating conditions. Discharge rate is 0.4 mA cm^{-2} .

The first discharge capacity of $\text{Li}_{0.3}\text{MnO}_2$ made from Cellmax at a discharge rate of 0.4 mA cm^{-2} was 213 mAh g^{-1} , this value corresponds to the content of Mn(IV) in the products. The rechargeable capacity was 193 mAh g^{-1} (corresponding to $\text{Li}_{0.36}\text{MnO}_2\text{--Li}_{1.0}\text{MnO}_2$). This supports that the chemical composition of our product is $\text{Li}_{0.3}\text{MnO}_2$ determined by Job's method [5].

The content of the residual NO_x is around 1–2 wt.%, this content can be reduced to <0.3% by washing with water.

The Li cells containing $\text{Li}_{0.3}\text{MnO}_2$ made from Cellmax show excellent stable cycleability with a reversible capacity of $160\text{--}180 \text{ mAh g}^{-1}$ at 0.4 mA cm^{-2} . The discharge capacity at 0.02 mA cm^{-2} is 250 mAh g^{-1} , which is a too large capacity with regard to the value corresponding to Mn(IV) content. Studies are in progress to clarify this phenomenon.

Fig. 2 shows plots by DCC (differential capacity curve) [6] for the rechargeable region obtained by the first charge and second discharge curves. The DCC of the $\text{Li}_{0.3}\text{MnO}_2$ cathode shows one peak in both the reduction and oxidation directions. This indicates that discharge and charge reactions proceed as a homogeneous solid-state reaction.

3.2. New 3–4 V $\text{Li}_x\text{Mn}_2\text{O}_4$ prepared from $\gamma\text{-MnOOH}$ by the LiNO_3 method

We have discovered a new Li–Mn composite prepared from $\gamma\text{-MnOOH}$ and LiNO_3 , which was obtained by heating the mixture of $\gamma\text{-MnOOH}$ and LiNO_3 with a molar ratio of $\text{Mn/Li}=1.2\text{--}1.8$ at 300°C . Typical X-

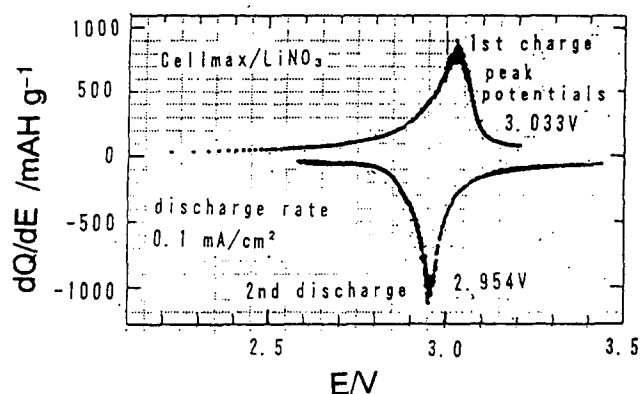


Fig. 2. Differential capacity curves of $\text{Li}_{0.3}\text{MnO}_2$ based on the first charge and second discharge at 0.1 mA cm^{-2} .

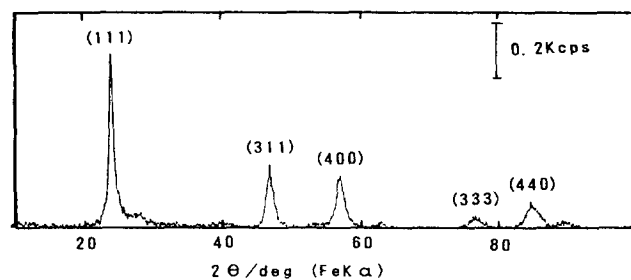


Fig. 3. X-ray diffraction pattern of $\text{Li}_x\text{Mn}_2\text{O}_4$ made from $\gamma\text{-MnOOH}$ and LiNO_3 ($\text{Mn/Li}=1.4$) by heating at 300°C . (Miller index is based on spinel phase.)

ray diffraction (XRD) patterns of the products show the disordered spinel structure as shown in Fig. 3. All the broad XRD peaks can be assigned to the spinel LiMn_2O_4 -phase, whose structure is different from those

of low-temperature LiMnO_2 prepared by Dahn and co-workers [7]. This indicates that oxides obtained from MnOOH have a tendency to transform to a spinel structure at very low temperatures. One of the typical chemical analyses of the heated sample after removing the unreacted LiNO_3 with water shows its low-temperature formula as $\text{Li}_{1.09}\text{Mn(III)}_{0.35}\text{Mn(IV)}_{1.47}\text{O}_4$.

In many cases, we got the higher x value than unity as $\text{Li}_x\text{Mn}_2\text{O}_4$, by chemical analyses. The excess Li greater than the value corresponding to LiMn_2O_4 (spinel composition) can be incorporated into our compounds even at low-temperature heating. Its discharge curves of the product Li_xMnO_2 is similar to those of the disordered spinel (Fig. 4).

3.3. Spinel (LiMn_2O_4) prepared from $\gamma\text{-MnOOH}$ as a 4 V cathode

High purity (SiO_2 , CaO and Na contents were 0.007, 0.009 and 0.003%, respectively) $\gamma\text{-MnOOH}$ was used and its mean particle size is $0.91\ \mu\text{m}$. Scanning electron microscopy (SEM) photographs of original $\gamma\text{-MnOOH}$ and spinel LiMn_2O_4 made from $\gamma\text{-MnOOH}$ heated at $650\ ^\circ\text{C}$ are shown in Fig. 5. It is of a fibrous shape with particles of about $0.2\text{--}0.4\ \mu\text{m}$ in diameter and $1\text{--}2\ \mu\text{m}$ in length. The formation of such unique compounds made from $\gamma\text{-MnOOH}$ would be due to their particle size and its 3-valent oxidation state in addition to the LiNO_3 method.

Excellent cycleability of LiMn_2O_4 made from $\gamma\text{-MnOOH}$ at a discharge rate of $1\ \text{mA cm}^{-2}$ (0.34C rate) is shown with a rechargeable capacity of $120\ \text{mAh g}^{-1}$ in Fig. 6.

3.4. New spinels, $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ ($x \geq 0$) prepared under nitrogen atmosphere as 4 V Li-ion cells

Although the preparation of $\text{Li}_{1+x}\text{MnO}_2$ was reported by Tarascon and Guyomard [8], we prepared this compound by the LiNO_3 method and have found the following characteristic features: (i) its discharge and charge process in a Li cell proceeds in the homogeneous phase reaction, and (ii) the crystallographic lattice

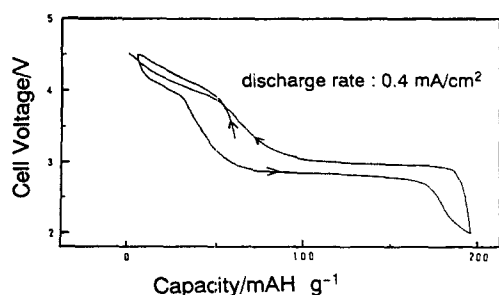


Fig. 4. Initial charge/discharge curves of Li_xMnO_2 made from $\gamma\text{-MnOOH}$ and LiNO_3 at $300\ ^\circ\text{C}$.

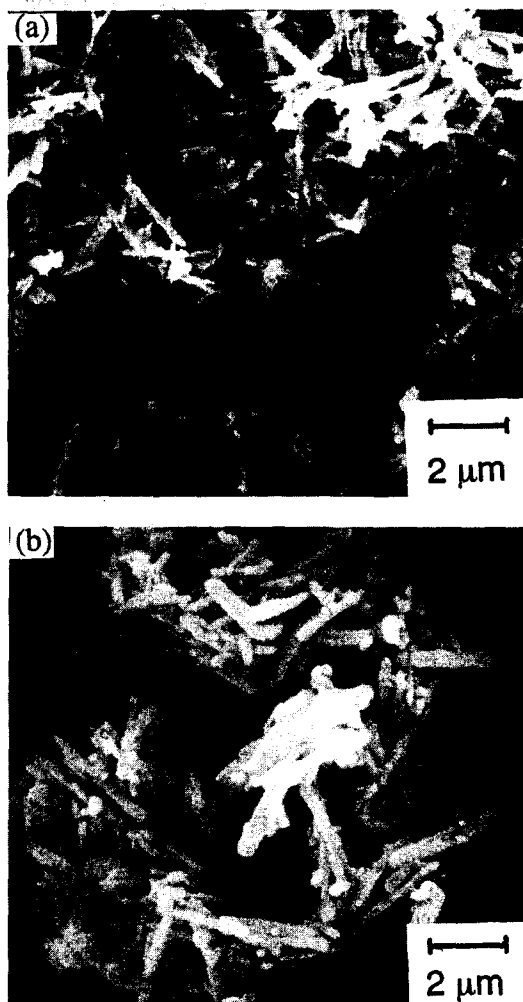


Fig. 5. Scanning electron micrographs of (a) $\gamma\text{-MnOOH}$ and (b) spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ made from $\gamma\text{-MnOOH}$ and LiNO_3 .

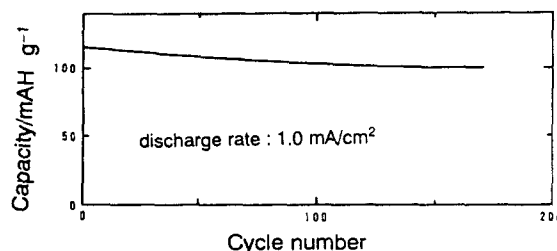


Fig. 6. Discharge capacity of spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ made from $\gamma\text{-MnOOH}$ and LiNO_3 ($600\ ^\circ\text{C}$) vs. cycle number.

parameter of a_0 ($8.21\text{--}8.23\ \text{\AA}$) is smaller than conventional one ($8.24\ \text{\AA}$).

Fig. 7 shows the initial charge/discharge curves of $\text{Li}_x\text{Mn}_2\text{O}_4$ obtained by heating the mixture of IC 17 and LiNO_3 at $0.26\ \text{C}$ in lithium cell. Though the spinel LiMn_2O_4 (Fig. 7(a)) shows two voltage plateaus at about $4.2\text{--}4.1\ \text{V}$ and $4.0\text{--}3.9\ \text{V}$, the voltage of the new spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ is increasing continuously with the de-intercalation of lithium.

XRD patterns during the de-intercalation process of the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ is shown in Fig. 8. We could not

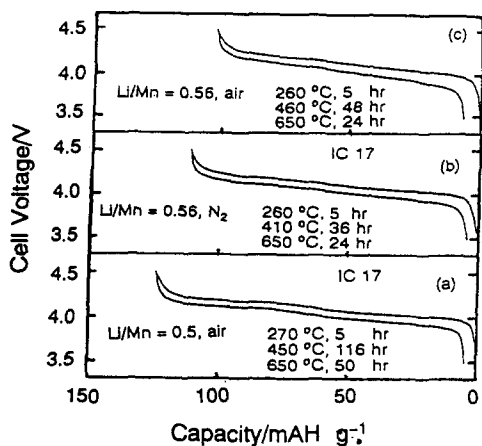


Fig. 7. Initial charge/discharge curves of (a) LiMn_2O_4 , (b) $\text{Li}_{1.12}\text{Mn}_2\text{O}_4$, obtained in N_2 , and (c) in air at a discharge rate of 0.4 mA cm^{-2} .

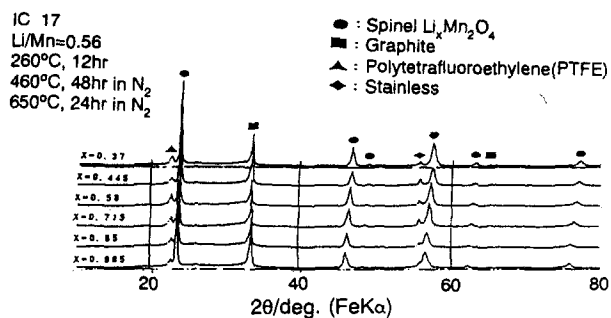


Fig. 8. X-ray diffraction patterns of $\text{Li}_{1.12}\text{Mn}_2\text{O}_4$ during delithiation as a function of x in $\text{Li}_x\text{Mn}_2\text{O}_4$.

observe any splitting of (311) and (400) peaks during de-intercalation of the Li ions. Two peaks shift continuously to higher angles during the delithiation. We

concluded the reaction proceeds in a homogeneous single-phase reaction. On the contrast, electrochemical delithiation from stoichiometric LiMn_2O_4 in the range of $\text{Li}_{0.27}\text{Mn}_2\text{O}_4$ – $\text{Li}_{0.6}\text{Mn}_2\text{O}_4$ proceed in a two-phase reaction; their XRD patterns show a splitting of the two peaks [9].

4. Conclusions

The advantages of the use of LiNO_3 for the unique preparation of lithiated manganese oxides for the cathode in Li cells are described. The preparation and the electrochemical behaviour of four types of new lithiated manganese oxide obtained from MnOOH and MnO_2 are reported.

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