

New lithium–manganese composite oxide for the cathode of rechargeable lithium batteries*

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Abstract

An $\text{LiNO}_3\text{-MnO}_2$ mixture, heat treated in the presence of H_2O_2 or HNO_3 , has shown excellent rechargeability as an electrode material for rechargeable lithium batteries. XRD patterns of this compound are completely different from known Li–Mn composite oxides such as LiMn_2O_4 or Li_2MnO_3 . The presence of H_2O_2 or HNO_3 preferentially reduces the LiMn_2O_4 content. The physicochemical properties of this new compound have been compared with those of other types of Li–Mn composite oxides.

Introduction

Of the various cathode materials for use in rechargeable lithium batteries, manganese compounds would be excellent candidates because of their high voltage, reduced pollution, and low cost. When EMD, heat treated at 300–400 °C, is used in Li/MnO_2 cells that are subjected to repeated charge and discharge, an expansion of the tetragonal cell unit of the β -like structure is observed during the first discharge. Indeed, we have reported [1, 2] a change in the structure from tetragonal to orthorhombic after two or three charge/discharge cycles. Details of this structural change have been confirmed recently by Ohzuku *et al.* [3].

The first discharge capacity of heat treated EMD is considerably higher than subsequent values after charging, and it appears that about 40% of the lithium ion intercalated into the MnO_2 from the lithium anode cannot be used as active cathode material. In order to overcome this disadvantage, the Sanyo group has developed a heat treated $\text{MnO}_2\text{-LiOH}$ mixture [4, 5]. It was reported that this compound was made from a mixture of $\gamma\text{-}\beta\text{-MnO}_2$ and Li_2MnO_3 .

We have produced a new Li–Mn composite oxide by heating CMD with LiNO_3 in the presence of additives. This new composite oxide has a rechargeable structure with a capacity of 160–170 mA h g^{-1} . The synthesis and charge/discharge behaviour of this new compound is reported in this paper.

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Experimental

CMD (Sedema, Faradiser M) was mixed with LiNO_3 or LiOH at 300–400 °C in air. The amounts of the lithium salts were varied between 10 and 50 mol.%. The cathode was prepared by pressing a disc (18 mm dia.) consisting of a mixture of 64% Mn compounds, 10% acetylene black, 10% graphite, and 16% PTFE. The anode was a lithium disc (0.2 mm thick). A porous polypropylene separator and a glass-fibre mat for the electrolyte absorber were placed in the cell. The electrolyte was 1 M LiPF_6 in a mixed solvent of PC (40%), EC (40%), DME (10%), and benzene (10%). The addition of benzene increases the lithium cycling efficiency [6].

The molar ratio of Mn(III)/Mn(IV) in the heat-treated products was calculated following determination of the total manganese- and Mn(IV) ions according to Kozawa's method [7]. Determination of Mn(II) ion [8] indicated that the Mn(II) content could be ignored. The unreacted LiOH or LiNO_3 in the heat-treated products was ascertained by atomic absorption spectrophotometry following several extractions of lithium ion from the samples into the aqueous solution.

Results and discussion

Figure 1 shows typical XRD patterns of CMD and lithium nitrate compounds (molar ratio of $\text{LiNO}_3/\text{MnO}_2 = 3/7$) heat treated at various temperatures for 20 h. The composite oxide obtained by heat treatment of MnO_2 with LiNO_3 at 500 °C shows an XRD pattern that is typical of spinel LiMn_2O_4 ($2\theta = 23.8, 46.1, 56.0, 75.6,$ and 83.6°). Chemical analysis shows the Mn(III)/Mn(IV) value to be essentially unity; this agrees well with the formula LiMn_2O_4 , as shown in Fig. 2. The Mn(III) content decreases to an Mn(III)/Mn(IV) value of about 0.4 to 0.5 with decrease in temperature.

XRD patterns for the product formed at low temperature (e.g., 300 and 350 °C for 20 h) displayed markedly different peaks from those of spinel

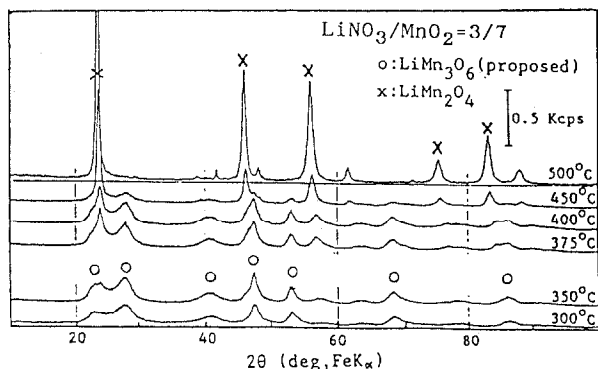


Fig. 1. Typical XRD patterns of LiNO_3 -CMD mixture heat treated at various temperatures.

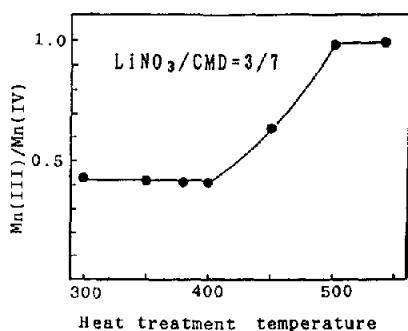


Fig. 2. Molar ratio of LiNO_3 - MnO_2 mixture heat treated at various temperatures.

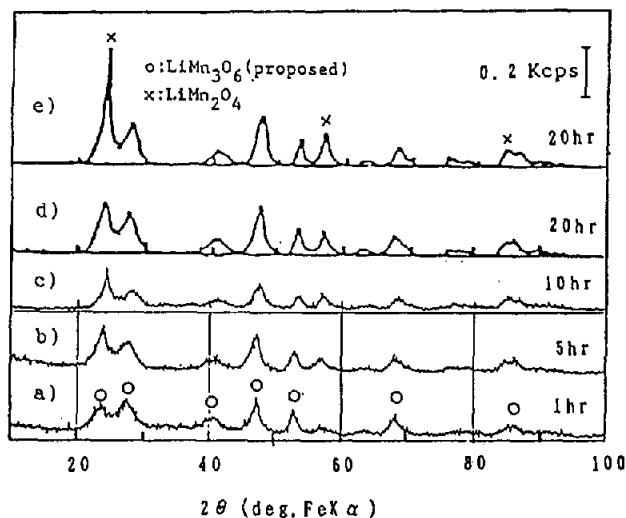


Fig. 3. XRD patterns of LiNO_3 - MnO_2 mixture (molar ratio, 3:7) heat treated at 400°C . (a) - (c) MnO_2 heat treated at 150°C for 1 h before mixing with LiNO_3 . Mixture heated in presence (d), and absence (e), of H_2O_2 .

LiMn_2O_4 (see Fig. 1). This compound has relatively wide peaks at $2\theta = 22.8, 27.6, 40.1, 47.2, 52.8, 68.1,$ and 86.3° . We have found that the low-temperature product is selectively formed when: (i) a mixture of CMD with LiNO_3 is heated with H_2O_2 or HNO_3 first at 100 – 150°C for 1 h and then at 350 – 400°C for 10 h, or (ii) CMD is heat treated at around 100 to 150°C for 1 h with H_2O_2 or HNO_3 before mixing with LiNO_3 .

Figure 3 shows the time dependency of the XRD patterns of a heat-treated mixture of CMD (after heating with H_2O_2) and LiNO_3 at 400°C . The lower-temperature product was formed after 1 h; the presence of spinel-type LiMn_2O_4 was confirmed after 5 h. Therefore, 3–5 h of heating at 400°C is sufficient to avoid the formation of LiMn_2O_4 when MnO_2 is treated with H_2O_2

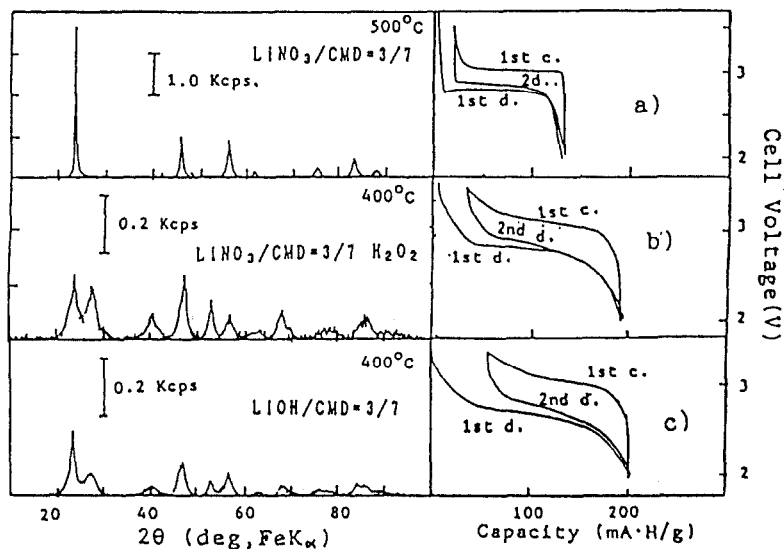


Fig. 4. Typical discharge/charge curves of Li-Mn composite oxides. (a) LiMn_2O_4 obtained by heating mixture of LiNO_3 -CMD at 500°C ; (b) proposed composite oxide of LiMn_3O_6 ; (c) heat-treated mixture of LiOH -CMD at 400°C .

or HNO_3 . The amount of by-product (such as spinel LiMn_2O_4) can, however, be reduced, even with 20 h of heating at 400°C , when an MnO_2 - LiNO_3 - H_2O_2 mixture is treated using a two-step heating method (110°C then 400°C). The sharp and intense (111) peak for LiMn_2O_4 is decreased in the presence of H_2O_2 or HNO_3 during the heating process, as shown in Fig. 3 (d), (e).

The charge/discharge behaviour of spinel LiMn_2O_4 prepared by heat treatment of MnO_2 - LiNO_3 at 500°C takes the form of typical L-shape curves (Fig. 4). By contrast, rechargeable S-shape curves are obtained for the lower-temperature product. This finding, together with the results of XRD studies discussed above, suggests that the compound is a new lithium-manganese composite oxide.

Chemical analysis of the LiNO_3 - MnO_2 mixture heat treated at 375 – 400°C in the presence of HNO_3 or H_2O_2 showed that the molar ratios of Mn/Li and Mn(III)/Mn(IV) were 2.95 and 0.42, respectively. The initial capacity was 160 – 180 mA h g^{-1} . Therefore, we propose that the chemical formula of this new composite oxide is LiMn_3O_6 , despite the fact that the values of the molar ratios and the initial capacity are somewhat different from those of pure LiMn_3O_6 . For example, the molar ratio of Mn(III)/Mn(IV) should be 0.50 and the discharge capacity of pure LiMn_3O_6 should be 200 mA h g^{-1} . These differences could, however, be explained by the fact that heat treated Li-Mn oxides contain some by-products and materials such as LiMn_2O_4 , MnO_2 , etc.

The Mn(III)/Mn(IV) molar ratio of products heat treated at 400°C versus the initial mixing molar ratio of $\text{LiNO}_3/\text{MnO}_2$ or LiOH/MnO_2 are plotted in

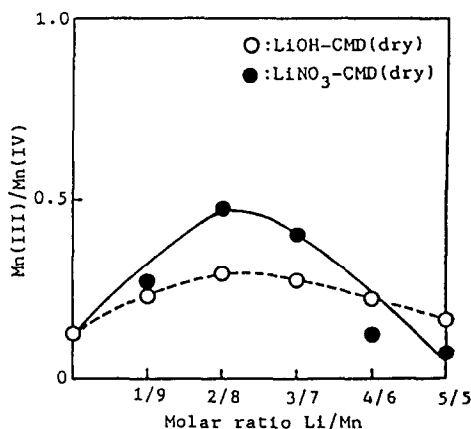


Fig. 5. Relation between Li/Mn molar ratio before heating and Mn(III)/Mn(IV) ratio of samples heat treated at 400 °C for 20 h.

Fig. 5. The content of Mn(III) increases at first with increase in the mixing ratio of Li/Mn. This is due to the formation of the new composite oxide, LiMn_3O_6 . The content of Mn(IV) then increases. This results from the formation of a rock-salt-type of Li_2MnO_3 . XRD analysis shows the formation of Li_2MnO_3 , even at temperatures as low as 400 °C.

In the case of LiOH, the content of Mn(IV) is always higher than that of the heat treated LiNO_3 -CMD mixture. An aqueous solution containing a dispersed, heat treated, LiOH -CMD mixture produces a strong alkaline solution. This suggests the existence of LiOH in the heat treated products. Indeed, chemical analysis showed that the content of unreacted LiOH reached 25%. The higher melting point of LiOH (445 °C) versus LiNO_3 (261 °C) would prevent complete reaction with MnO_2 . In the presence of a small amount of water, however, the reaction between LiOH and MnO_2 proceeds rapidly. The content of LiOH in the heat treated product at 400 °C is reduced to about 15% of its initial value. This is because lithium ion is strongly adsorbed onto the MnO_2 particles from the LiOH solution. The products contain a rather high content of spinel LiMn_2O_4 . The discharge behaviour of the heat treated LiOH -CMD mixture indicates a large capacity loss during the second discharge. Such behaviour also suggests the existence of unreacted MnO_2 , as shown in Fig. 4.

Figure 6 presents the results of cycle testing at deep depths of discharge between 3.5 and 2.0 V at a current density of 0.4 mA cm^{-2} . After 200 cycles, the capacity was 60% of the initial value.

Conclusions

A new Mn-Li composite oxide has been synthesized by heating an MnO_2 - LiNO_3 mixture in the presence of H_2O_2 or HNO_3 . This material can

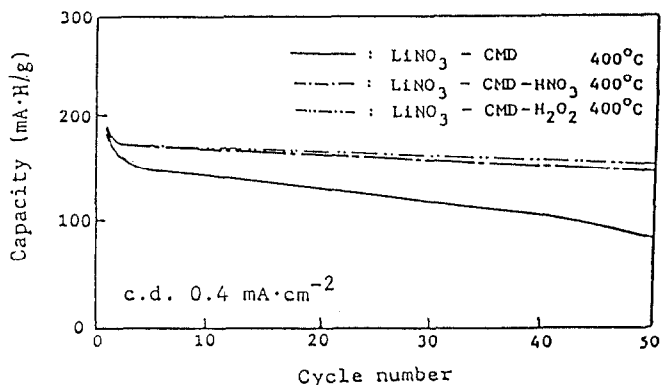


Fig. 6. Capacity performance of various Li-Mn composite oxides in a lithium secondary battery.

be successfully used as a 3 V cathode material for rechargeable lithium batteries.

The proposed heating process is as follows: a mixture of CMD-LiNO₃ (molar ratio, 3:7) with H₂O₂ (molar ratio Mn/H₂O₂, 1:10) or with HNO₃ (molar ratio Mn/HNO₃, 2:15) is heated at a temperature between 70 and 150 °C and then the temperature is raised to between 350 and 400 °C for 5–20 h.

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