

MANGANESE OXIDES FOR A LITHIUM SECONDARY BATTERY — COMPOSITE DIMENSIONAL MANGANESE OXIDE (CDMO)

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Summary

Manganese dioxide was adopted as a positive material for a lithium secondary battery that is both inexpensive and has a high discharge voltage. In this report, the rechargeability of several manganese oxides that contain lithium in their structures was investigated by cycle tests on flat cells and by X-ray diffractometry (XRD). The results were compared with the rechargeability of γ/β - MnO_2 .

In a cycle test at a depth of 0.14 e/Mn, spinel LiMn_2O_4 and CDMO (heat treated $\text{LiOH}\cdot\text{MnO}_2$) showed much better rechargeability than γ/β - MnO_2 . At a depth of 0.26 e/Mn, the rechargeability of CDMO was better than that of spinel LiMn_2O_4 . The crystal structure of CDMO consists of Li_2MnO_3 and γ/β - MnO_2 (composite dimension). We also investigated the optimum lithium molar ratio from which CDMO could be prepared. We consider that the optimum molar ratio of lithium is between 30 and 50 mole percent.

Introduction

Recently, lithium rechargeable batteries have been actively investigated around the world. Various layer compounds have been examined with regard to the electrochemical characteristics, crystal structures, physical properties, and methods of synthesis [1 - 3], since they were suggested as positive materials for lithium secondary batteries. Transition-metal chalcogenides such as TiS_2 , TiSe_2 , MoS_2 , NbS_3 , NbSe_3 are found to have good rechargeability. However, cells with these compounds have voltages of 1.5 - 2.0 V, which are lower than ordinary nonaqueous cells. Based on that information, we adopted MnO_2 as a positive material for a lithium secondary battery

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that is both inexpensive and has a high discharge voltage. In addition, MnO_2 has been developed by us [4, 5] as the positive material for a lithium primary battery; it is now practically used worldwide as a stable positive material.

We have already reported on the cycle performance of CMD, NMD and EMD [6]. It was suggested in the report that CMD had better rechargeability than the others. But the rechargeability of CMD, whose crystal structure is a γ/β type, was insufficient. In $\gamma/\beta\text{-MnO}_2$, an expansion of the crystal lattice occurs when lithium ions are inserted into its crystal structure. However, the degree of expansion does not increase much after a large initial change at a quite low depth of discharge. We considered that, if manganese dioxide contained small amounts of lithium in its crystal structure beforehand, the reversibility of its crystal structure would be improved. In this report, we investigated the rechargeability of several manganese oxides that contain lithium in their structures. Furthermore, the optimum conditions for preparing them were examined.

Experimental

The preparation methods and physical properties of various manganese oxides employed in this study have been reported earlier [7]. Their crystal structures were confirmed by XRD (Cu $K\alpha$ radiation with graphite monochromator, type XD-3, Shimazu Corp., Japan).

The weight decrease of a sample was measured by thermogravimetric analysis (type DT-30, Shimazu Corp., Japan). The water content in a sample was measured by the Karl Fischer method (type CA-02, Mitsubishi Chemical Ind. Ltd., Japan). The cycle tests and discharge tests were carried out with flat cells. A mixture of various manganese oxides, a conductive agent (carbon black), and a Teflon binder was used as the positive electrode. Lithium-aluminium alloy was used as the negative electrode. The electrolyte was 1 M $\text{LiClO}_4\text{-PC/DME}$.

Results and discussion

In order to improve the rechargeability of $\gamma/\beta\text{-MnO}_2$, we prepared two types of lithium-containing manganese oxides, spinel LiMn_2O_4 and heat-treated $\text{LiOH}\cdot\text{MnO}_2$, which we named composite-dimensional manganese oxide (CDMO). First, the discharge and charge curves of $\gamma/\beta\text{-MnO}_2$, spinel LiMn_2O_4 , and CDMO were measured. The results are shown in Fig. 1. Spinel LiMn_2O_4 and CDMO were discharged to 2 V. Both showed stable curves. In respect of capacity, CDMO showed a 0.2 e/Mn larger capacity than spinel LiMn_2O_4 . On the other hand, $\gamma/\beta\text{-MnO}_2$ could not be fully charged to the 0.4 e/Mn depth; in the second discharge, the discharge voltage of $\gamma/\beta\text{-MnO}_2$ was lower than that in the first discharge.

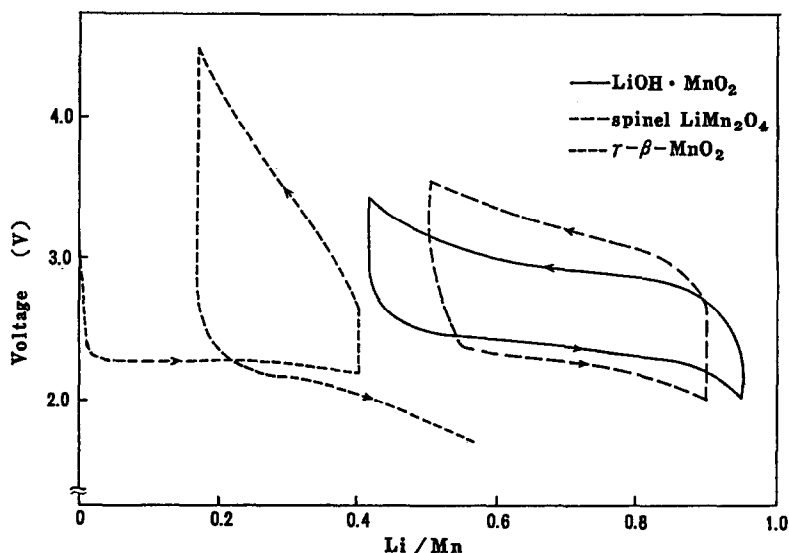


Fig. 1. Discharge and charge curves of γ/β - MnO_2 , spinel LiMn_2O_4 , and heat treated $\text{LiOH}\cdot\text{MnO}_2$ electrodes.

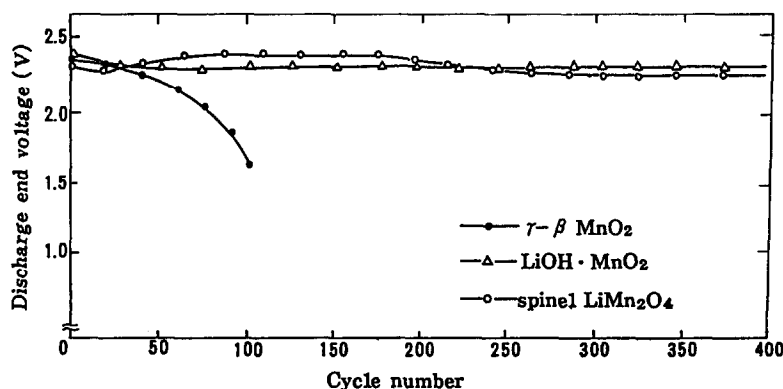


Fig. 2. Cycle performances of various manganese oxide electrodes.

Figure 2 shows the results of cycle tests of flat cells at a depth of 0.14 e/Mn. It was found that spinel LiMn_2O_4 and CDMO had better rechargeability than γ/β - MnO_2 . No deterioration was observed in spinel LiMn_2O_4 and CDMO, even at the 400th cycle. The XRD patterns of γ/β - MnO_2 , spinel LiMn_2O_4 , and CDMO after charging at several cycle numbers are shown in Fig. 3. The crystal structure of γ/β - MnO_2 was changed at the end of the tests; that is, the peak shifted to a lower angle and a weakening of crystallinity was observed. In spinel LiMn_2O_4 and CDMO, the crystal structures recovered to the initial states after charging. From these results, it is considered that the

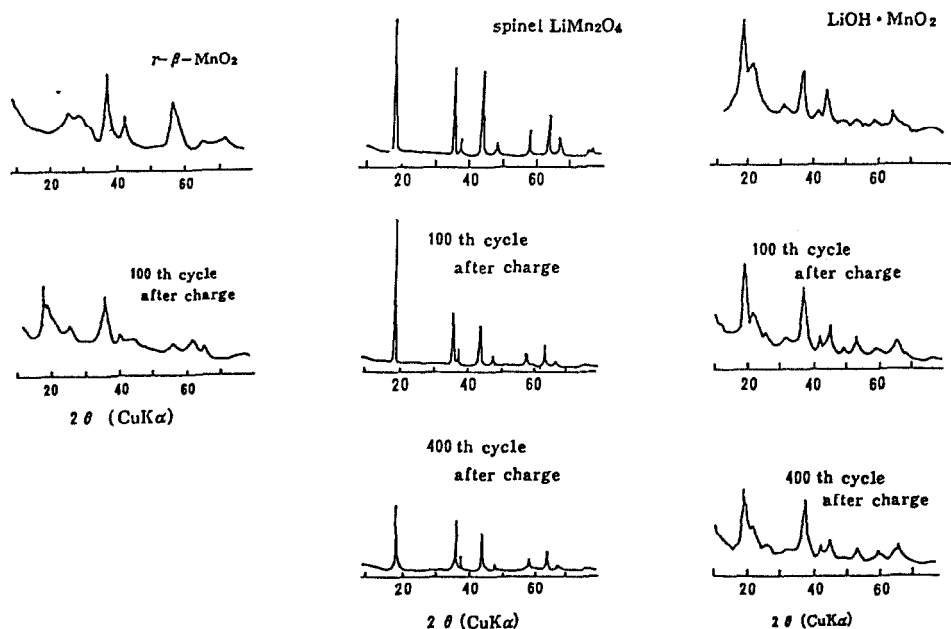


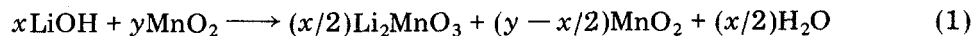
Fig. 3. X-ray diffractograms of γ/β - MnO_2 , spinel LiMn_2O_4 , and heat treated $\text{LiOH}\cdot\text{MnO}_2$ after charge following extended cycling.

excellent cell performance of spinel LiMn_2O_4 and CDMO must be attributed to the good reversibilities of their crystal structures at the insertion and removal of lithium ion.

We also compared the rechargeabilities of spinel LiMn_2O_4 and CDMO at a deeper depth of discharge. Figure 4 shows the results of cycle tests at a depth of 0.26 e/Mn. It was found from this Figure that CDMO had better rechargeability than spinel LiMn_2O_4 . Over 200 cycles have been obtained up to the present time with CDMO at a depth of 0.26 e/Mn.

It was thought that CDMO showed better rechargeability than spinel LiMn_2O_4 because CDMO had a larger discharge capacity and its polarization during charge was smaller.

From the above results, we chose CDMO as a positive material for the lithium secondary battery and investigated the optimum conditions for its preparation. Figure 5 shows the discharge performance of CDMO prepared at various molar ratios of lithium and manganese. The discharge capacity of CDMO decreased as the lithium molar ratio increased. The XRD patterns of CDMO measured at various molar ratios of lithium and manganese are shown in Fig. 6. The peaks of Li_2MnO_3 and γ/β - MnO_2 were observed. The peaks of Li_2MnO_3 increased with increase in the molar ratio of lithium. We considered the reaction of LiOH and MnO_2 to be as follows:



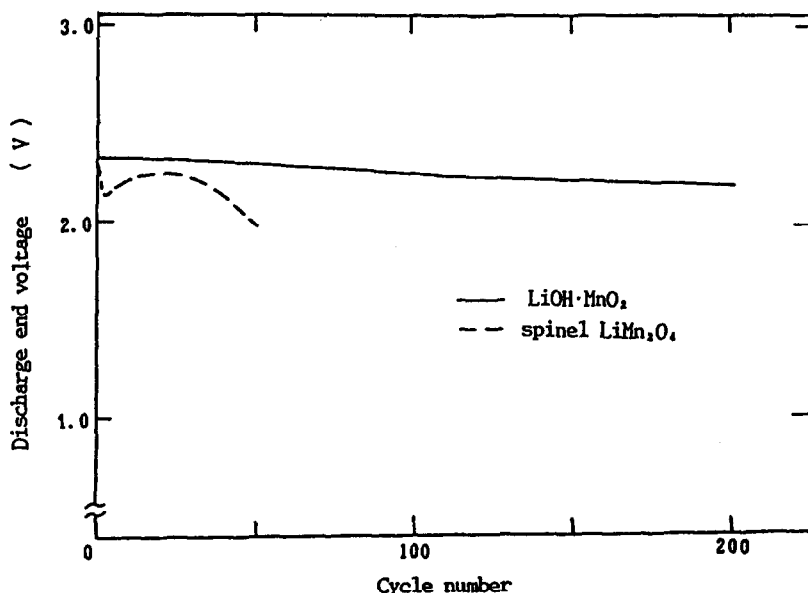


Fig. 4. Cycle performances of heat treated $\text{LiOH}\cdot\text{MnO}_2$ and spinel LiMn_2O_4 electrodes.

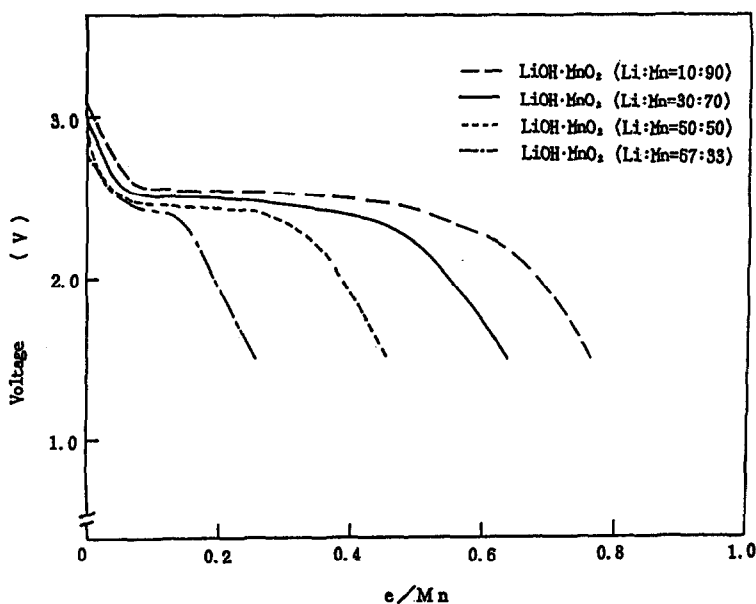


Fig. 5. Discharge curves of heat treated $\text{LiOH}\cdot\text{MnO}_2$ electrodes of different Li to Mn molar ratios.

The weight decrease of the mixture of LiOH and MnO_2 during heat treatment was measured by thermogravimetric analysis. The theoretical amount of water calculated from eqn. (1) agreed with the experimental

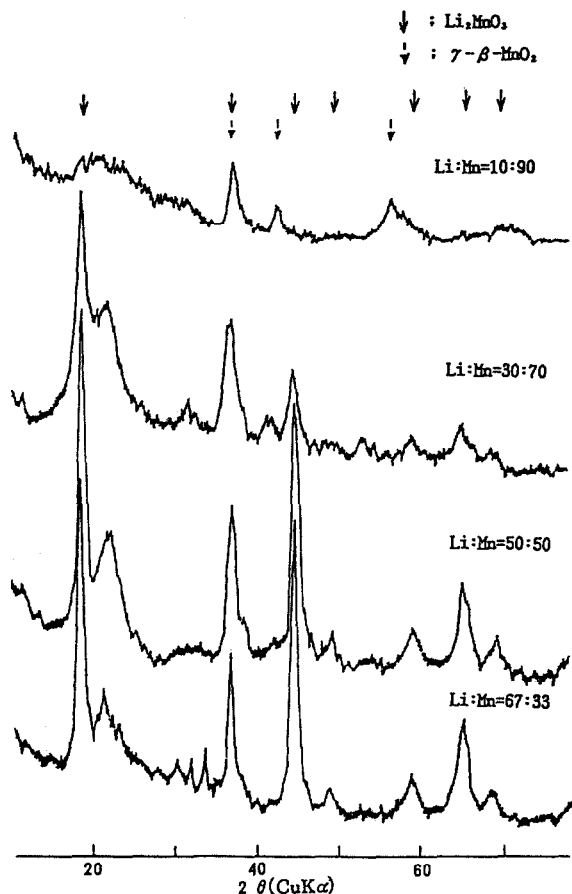


Fig. 6. X-ray diffractograms of heat treated $\text{LiOH}\cdot\text{MnO}_2$ of different Li to Mn molar ratios.

value. The weight decrease was confirmed, by the Karl Fischer method, as corresponding to the production of water. From Fig. 5 and eqn. (1), it is considered that Li_2MnO_3 has poor dischargeability. Li_2MnO_3 has a layer structure and $\gamma/\beta\text{-MnO}_2$ has a crystal structure with one dimensional channels [8].

Finally, we measured the variation of the discharge capacity of CDMO electrodes prepared at various molar ratios of lithium and manganese by the cycle number. The electrodes were discharged to 2 V. Figure 7 compares the discharge capacity on the 1st cycle and the 10th cycle.

The discharge capacity of the lithium-free $\gamma/\beta\text{-MnO}_2$ decreased to 40% of the 1st cycle on the 10th cycle, although it showed the highest capacity on the 1st cycle. Its discharge capacity decreased rapidly after that. On the other hand, the discharge capacity of CDMO containing 30 mole percent. lithium decreased by only 10% of the 1st cycle. It showed a discharge capacity of 78% of $\gamma/\beta\text{-MnO}_2$ at the 1st cycle.

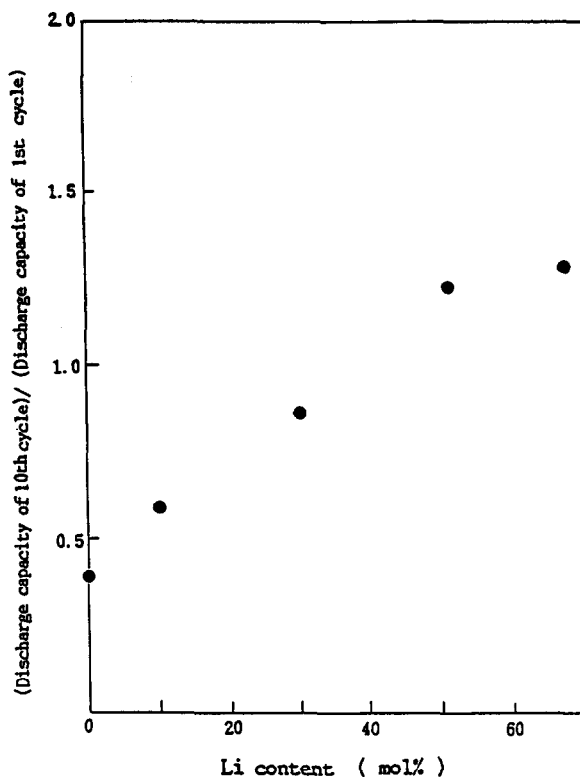


Fig. 7. A comparison of discharge capacities at the 1st and 10th cycles.

Furthermore, the discharge capacities of CDMO containing 50 or 67 mole percent. Li increased at the 10th cycle, although their discharge capacities were low on the 1st cycle.

From these results, it was considered that the good rechargeability of CDMO depended on its crystal structure, that is, lithium initially contained in CDMO supported the diffusion of inserted lithium ions. The optimum molar ratio of lithium lies between 30 and 50 mole percent. from the standpoint of discharge capacity and rechargeability.

Conclusion

It was found that spinel LiMn_2O_4 and CDMO (heat treated $\text{LiOH}\cdot\text{MnO}_2$) showed much better rechargeability than $\gamma/\beta\text{-MnO}_2$. Their excellent cell performances were thought to be attributed to the good reversibilities of their crystal structures. At a deeper depth of discharge, the rechargeability of CDMO was better than that of spinel LiMn_2O_4 .

The crystal structure of CDMO consists of Li_2MnO_3 , which has a layer structure, and $\gamma/\beta\text{-MnO}_2$, which has one-dimensional channels. From discharge-capacity variation measurements, it is considered that the optimum molar ratio of lithium in CDMO lies between 30 and 50 mole percent.

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