

LITHIUM-CONTAINING MANGANESE DIOXIDE (COMPOSITE DIMENSIONAL MANGANESE OXIDE: CDMO) AS POSITIVE MATERIAL FOR A LITHIUM SECONDARY BATTERY

T. NOHMA*, Y. YAMAMOTO, K. NISHIO, I. NAKANE and N. FURUKAWA

Functional Materials Research Center, Sanyo Electric Co. Ltd., 1-18-13 Hashiridani, Hirakata-shi, Osaka 573 (Japan)

(Received May 5, 1990)

Summary

Lithium-containing manganese dioxide (CDMO) has been developed as the positive material for lithium secondary batteries. CDMO is prepared from lithium salt and manganese dioxide by heat treatment. It is a composite oxide of γ/β - MnO_2 and Li_2MnO_3 .

The influence on rechargeability of lithium salts, heat-treatment temperature, and manganese dioxide type has been investigated by conducting cycle tests with flat cells. Lithium hydroxide is more reactive with MnO_2 in the production of Li_2MnO_3 than either Li_2O or Li_2CO_3 . The optimum condition for preparing CDMO is to heat treat LiOH and MnO_2 at about 375°C . CDMO prepared from EMD (electrolytic manganese dioxide) yields a larger and more stable capacity than CDMO prepared from CMD (chemical manganese dioxide). Sodium-free EMD exhibits the largest discharge capacity.

Introduction

The demand for a secondary battery with high energy density increases with the advancement of electronic devices. As a result, research and development of secondary lithium batteries has intensified. In the work reported here, a high-voltage, inexpensive lithium secondary battery has been investigated using MnO_2 as the positive material. We have previously studied the applicability of MnO_2 [1, 2] as the positive material for a primary lithium battery. The latter is now used worldwide as a stable positive material. It has been reported, however, that MnO_2 has poor rechargeability [3, 4].

In order to improve the rechargeability of MnO_2 , a lithium-containing manganese dioxide has been prepared from lithium salt and MnO_2 . It is a composite oxide of γ/β - MnO_2 and Li_2MnO_3 (Composite Dimensional Mangan-

* Author to whom correspondence should be addressed.

nese Oxide:CDMO). We have documented the crystal structure and cycling performance of CDMO previously [5]. CDMO exhibited superior performance to γ/β - MnO_2 and spinel LiMn_2O_4 ; the latter is known as a lithium-containing manganese oxide. In this report, a study is made of the influence on rechargeability of lithium salts, heat-treatment temperature, and manganese dioxide materials.

Experimental

CDMO was prepared by heat treating the following mixture: LiOH , Li_2O , Li_2CO_3 and MnO_2 : CMD (I.C. No. 12), EMD (IBA No. 16, 17 or 18). The crystal structure was confirmed by XRD ($\text{Cu K}\alpha$ radiation with a graphite monochromator, type XD-3, Shimazu Corp., Japan). The x value of MnO_x was obtained by chemical analysis of the available amount of MnO_2 and the total amount of Mn.

Cycle performance was examined with flat cells (dia. 24 mm; thickness: 3 mm). Both discharge and charge current densities were 1.1 mA cm^{-2} . A mixture of CDMO, conductive agent (carbon black), and Teflon binder was used as the positive electrode, while a lithium-aluminum alloy served as the negative electrode. The electrolyte was a 1:1 mixture of 1 M LiClO_4 -PC:DME.

Results and discussion

A model of the crystal structure of CDMO is shown in Fig. 1. CDMO is composed of γ/β - MnO_2 and Li_2MnO_3 [5]. γ/β - MnO_2 has a one-dimensional channel while Li_2MnO_3 has a structure in which lithium atoms reside as layers (composite dimension) [6]. It has been reported [5] that the optimum atomic ratio of lithium in CDMO ($\text{Li}/\text{Li} + \text{Mn}$) lies between 0.3 and 0.5 [5].

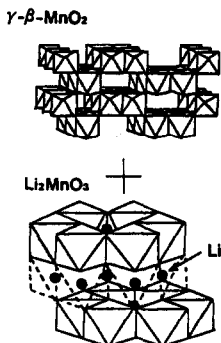


Fig. 1. Proposed structure of CDMO.

Reactivity of lithium salts with MnO_2

Figure 2 shows the XRD patterns of CDMO prepared from LiOH, Li_2O , or Li_2CO_3 and MnO_2 (CMD, I.C. No. 12).

The atomic ratio of lithium in CDMO was 0.3 and the heat-treatment temperature was 375 °C. Peaks for γ/β - MnO_2 and Li_2MnO_3 are observed in all the XRD patterns. The peaks for Li_2MnO_3 were most pronounced in CDMO prepared from LiOH and MnO_2 . Thus, LiOH exhibits the greatest reactivity with MnO_2 to produce Li_2MnO_3 .

Figure 3 presents the charge/discharge cycling performance of the above CDMO electrodes for depth of discharge of 0.26 e/Mn. In the first cycle, there is no difference between the discharge curves. After 80 cycles, however, a deterioration in rechargeability is observed for CDMO prepared either from Li_2CO_3 and MnO_2 , or from Li_2O and MnO_2 . Differences in the cycle performance of the three lithium salts were virtually indiscernible at a shallower depth of discharge of 0.14 e/Mn.

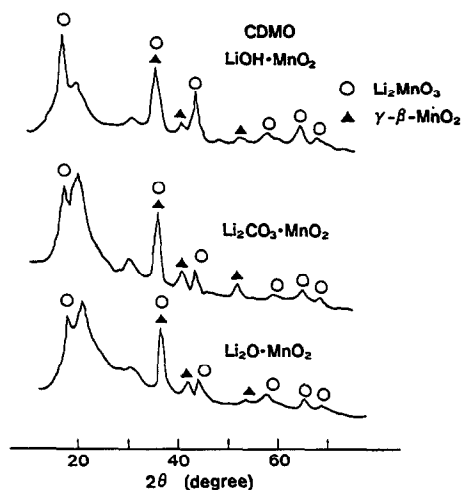


Fig. 2. X-ray diffraction patterns of CDMO prepared from given lithium salts and MnO_2 .

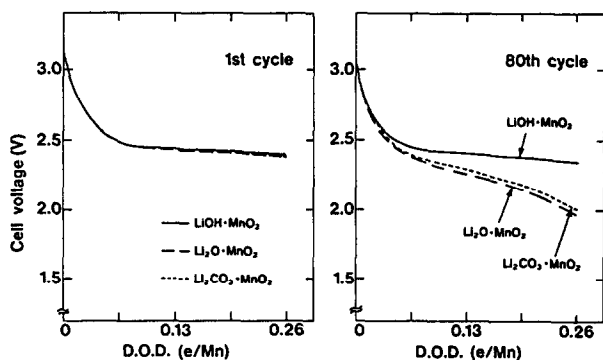


Fig. 3. Discharge characteristics of CDMO electrode prepared from given lithium salts and MnO_2 . (I.C. No. 12). Depth of discharge = 0.26 e/Mn; current density 1.1 mA cm^{-2} .

From the results of XRD and cycle tests, it is considered that the transformation of the crystal structure of $\text{Li}_2\text{O}\cdot\text{MnO}_2$ or $\text{Li}_2\text{CO}_3\cdot\text{MnO}_2$ was smaller compared with that of $\text{LiOH}\cdot\text{MnO}_2$ because of the lower reactivity of the lithium salt with MnO_2 .

Effect of heat-treatment temperature on CDMO preparation

Figure 4 shows XRD patterns of heat-treated $\text{LiOH}\cdot\text{MnO}_2$ prepared at different temperatures ($\text{Li}/\text{Li} + \text{Mn} = 0.3$). Mn_2O_3 peaks appeared for $\text{LiOH}\cdot\text{MnO}_2$ prepared at 500 °C and 650 °C, and the peaks for $\gamma/\beta\text{-MnO}_2$ and Li_2MnO_3 shifted to lower angles. This indicates a change in crystal structure from $\gamma/\beta\text{-MnO}_2$ and Li_2MnO_3 to spinel LiMn_2O_4 .

The x value for MnO_x in heat-treated CDMO prepared at 375 °C was 1.90. This indicates that the valence of Mn is nearly 4. The x value of heat-treated CDMO prepared at 500 °C or 650 °C is 1.65. Because the x value is 1.75 and 1.50 in spinel LiMn_2O_4 and Mn_2O_3 , respectively, it is concluded that these materials are composed of spinel LiMn_2O_4 and Mn_2O_3 .

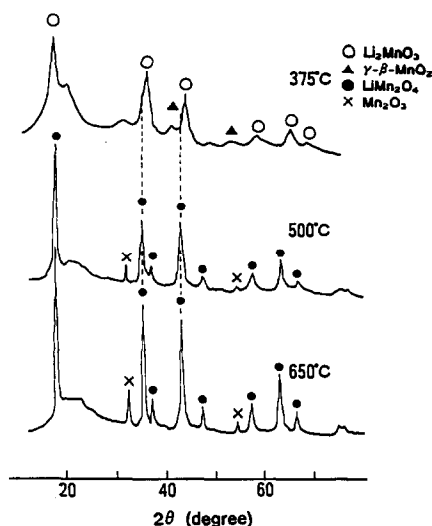


Fig. 4. X-ray diffraction patterns of heat-treated $\text{LiOH}\cdot\text{MnO}_2$ prepared at different temperatures.

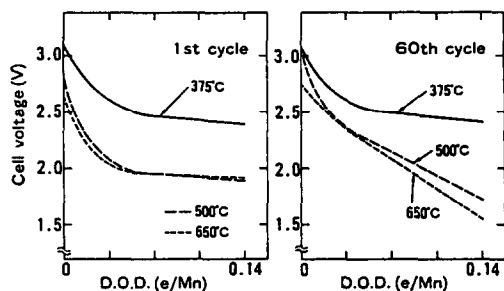


Fig. 5. Discharge characteristics of heat-treated $\text{LiOH}\cdot\text{MnO}_2$ (I.C. No. 12) prepared at different temperatures. Depth of discharge = 0.14 e/Mn; current density = 1.1 mA cm^{-2} .

The results of cycle tests on flat cells at a depth of discharge of 0.14 e/Mn are given in Fig. 5. It is found that CDMO prepared at 375 °C has the highest discharge voltage on the first cycle and its rechargeability is better than that of the others. It is considered that heat-treated LiOH·MnO₂ prepared above 500 °C has a poor discharge performance and an inferior rechargeability because there is an increase in trivalent manganese.

Influence of manganese dioxide type

Table 1 shows specific surface areas and the Na content of CDMO prepared from LiOH and EMD type IBA Nos. 16, 17 and 18. Each EMD is neutralized with Na₂CO₃, NH₄OH, and NaOH. CDMO prepared from LiOH and EMD has a much smaller specific surface area than that prepared from LiOH and CMD. The Na content of LiOH-IBA No. 17 is much smaller than that of the others.

Figure 6 shows the deep-discharge cycling characteristics of CDMO electrodes prepared from LiOH and EMD. Discharge was terminated at 2 V. CDMO prepared from IBA No. 17 yields the highest capacity. It is not clear why IBA No. 17 exhibits a larger capacity than either IBA No. 16 or No. 18. It is thought, however, that Na ion exerts an adverse effect during heat treatment because IBA Nos. 16, 17 and 18, which are heat-treated not with LiOH but singly, display similar discharge characteristics.

The deep-discharge cycling performance of LiOH-IBA No. 17 (EMD) is compared with that of LiOH-I.C. No. 12 (CMD) in Fig. 7. The discharge was terminated at 2 V. The former material gives a higher initial capacity and exhibits less deterioration in capacity with cycling. Indeed, the capacity of LiOH-IBA No. 17 remains virtually constant over the first 50 cycles.

Figure 8 presents the dependence of specific surface area on Li atomic ratio. Whereas the value for LiOH-I.C. No. 12 declines gradually, that for LiOH-IBA No. 17 falls sharply beyond an Li atomic ratio of 0.3. This indicates that a radical change in the surface state occurs at this Li atomic ratio. Thus, it appears that for LiOH-IBA No. 17, improvement of rechargeability

TABLE 1

Properties of CDMO prepared from LiOH and different manganese dioxides

(Li:0.3 atomic ratio 375 °C in air)	Specific surface area (m ² g ⁻¹)		Neutralization	Na content (ppm) ^b
	before heat treatment ^a	after heat treatment		
LiOH-IBA No. 16 (EMD)	36.7	13.7	Na ₂ CO ₃	5210
LiOH-IBA No. 17 (EMD)	30.2	16.3	NH ₄ OH	50
LiOH-IBA No. 18 (EMD)	37.8	13.1	NaOH	4800
LiOH-I.C. No. 12 (CMD)	103.6	58.2		550

^aRef. 7.

^bRef. 8.

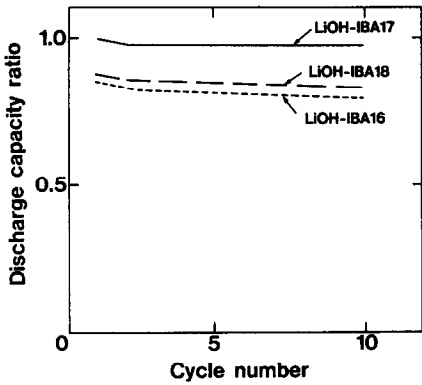


Fig. 6. Cycle performance of LiOH-IBA No. 16, 17 and 18.

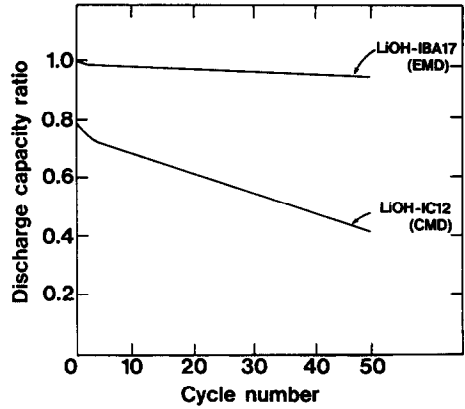


Fig. 7. Cycle performance of LiOH-I.C. No. 12 and LiOH-IBA No. 17.

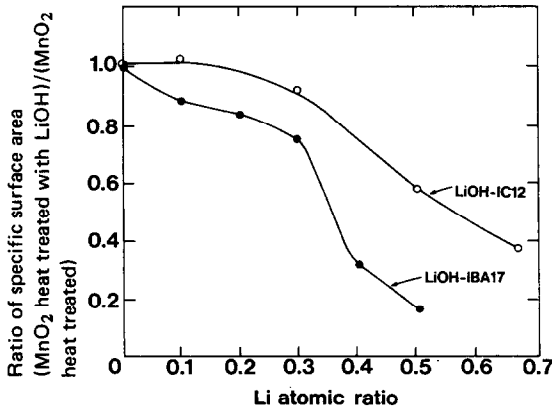


Fig. 8. Dependence of specific surface area on lithium atomic ratio.

extends over much of the surface at 0.3 Li atomic ratio. In LiOH-I.C. No. 12, however, improvement is not sufficient because of the large surface area.

Conclusions

Conditions for preparing CDMO have been investigated. Optimum performance is achieved by heat-treating LiOH and MnO_2 at about 375°C . CDMO prepared from EMD shows a larger and more stable capacity than CDMO prepared from CMD. Na-free EMD exhibits the largest capacity. Lithium secondary batteries using CDMO prepared from LiOH and Na-free EMD are expected to have both a large capacity and good cycle performance.

References

- 1 H. Ikeda, T. Saito and H. Tamura, in A. Kozawa and R. J. Brodd (eds.), *Manganese Dioxide Symposium*, Vol. 1, Cleveland, 1975, p. 384.
- 2 N. Furukawa, K. Moriwaki, S. Narukawa and M. Hara, in J. Thompson (ed.), *Power Sources 10: Research and Development in Non-mechanical Electrical Power Sources*, Paul Press, London, 1985, p. 183.
- 3 F. W. Dampier, *J. Electrochem. Soc.*, **121** (1974) 656.
- 4 G. Pistoia, *J. Electrochem. Soc.*, **129** (1982) 1861.
- 5 T. Nohma, T. Saito, N. Furukawa and H. Ikeda, *J. Power Sources*, **26** (1989) 389.
- 6 M. Jansen and R. Hoppe, *Z. Anorg. Allg. Chem.*, **397** (1973) 279.
- 7 M. Yamasita, H. Takemura, M. Ide and A. Kozawa, *3rd Battery Material Symp.*, Vol. 3, Honolulu, 1987, p. 33.
- 8 D. Glover, B. Schumm, Jr. and A. Kozawa (eds.), *Measurements on Battery Materials*, Atlanta, 1988, p. 22.