

## Synthesis of New Li-Mn Oxide ( $\text{Li}_3\text{Mn}_2\text{O}_5$ )

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A new type of Li-Mn oxide was synthesized from  $\gamma\text{-MnOOH}$  and LiOH aqueous solution by using wet method. The ICP analysis and the redox titration showed the compound had the composition of  $\text{Li}_3\text{Mn}_2\text{O}_5$ . From powder X-ray diffraction profile analysis the crystal structure of the compound was considered to be the MnO-type with a superlattice along [111]. The charge-discharge tests were carried out between 2.5 and 4.0V (vs.  $\text{Li}/\text{Li}^+$ ) using the obtained compound as a cathode material. Two kinds of redox steps corresponding to Li extraction/insertion were observed at the initial cycles. The potentials of the charge peaks were 2.9 and 3.4V. After repeating cycles, the two charge peaks changed gradually to the one peak around 2.7V.

Key words: Li-Mn oxide, Wet method, Li secondary battery

### 1. INTRODUCTION

Lithium manganese oxides are attractive cathode materials for lithium ion secondary batteries because of their low cost due to their abundance in nature and their friendly impact on environment. Much efforts have been devoted to synthesize and investigate the lithium manganese oxides, such as  $\text{LiMn}_2\text{O}_4$  or  $\text{LiMnO}_2$  with a tunnel or a layered structure, respectively.

For synthesizing lithium manganese oxides, wet methods have excellent advantages. One is their possibility to synthesize materials at a far lower reaction temperature than that of the conventional calcination method. Another expecting advantage of wet methods is to synthesize materials which are thermodynamically metastable and thus cannot be obtained by the calcination method. In our previous works, the spinel  $\text{LiMn}_2\text{O}_4$  could be synthesized using the hydrothermal method at lower temperatures than 200°C [1-2], while it is usually prepared using the calcination method at higher temperatures (>600°C) [3-5]. We also succeeded to synthesize  $\text{LiMnO}_2$  using the wet method at 50°C [6].

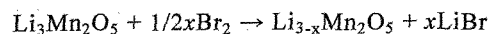
In the present paper, we research low temperature reaction of  $\gamma\text{-MnOOH}$  and LiOH aqueous solution using wet method, and report a new type of lithium manganese oxide,  $\text{Li}_3\text{Mn}_2\text{O}_5$ . The synthetic condition of this material was studied in detail, and the obtained compound was characterized by XRD, ICP, inverse oxidation-reduction titration, and SEM. Electrochemical properties of the compound as a cathode material in Li secondary batteries are also investigated.

### 2. EXPERIMENTAL

The preparation procedures were as follows.  $\gamma\text{-MnOOH}$  was dipped in a 1.0~4.6mol/l LiOH aqueous solution. The reaction vessel (OM LAB-TECH. co. Ltd., BF-2000) was kept at 60°C and stirred for 72h. The obtained precipitates were filtered, washed with distilled water and dried in air.

The phase states of the obtained samples were identified by using powder X-ray diffraction (XRD; JEOL, JDX-8030W). SEM (JEOL, JSM-890) was used for observing the morphology of the obtained particles. The molar ratio of Li to Mn was determined by using the inductively coupled plasma method (ICP; Nippon Jarrel Ash, ICAP575II). For ICP analysis, the lithium manganese oxides were treated in 0.1mol/l  $\text{HNO}_3$ , and then dissolved with  $\text{H}_2\text{O}_2$  additive. The average valence of Mn ions was determined by using Kozawa's method which is an inverse oxidation-reduction titration using ferrous sulfate as a reducing agent [7].

Delithiated samples were prepared by chemical oxidation of  $\text{Li}_3\text{Mn}_2\text{O}_5$  using  $\text{Br}_2$  as an oxidant.  $\text{Li}_3\text{Mn}_2\text{O}_5$  and  $\text{Br}_2$  were weighted at various molar ratios, and the mixtures were stirred and reacted in acetonitrile solvent at room temperature for 24h. The oxidation level was controlled by changing the amount of  $\text{Br}_2$ . The ideal reaction scheme is described as below.



After the reaction, the products were separated from the solvent by filtering and washed in pure acetonitrile several times.

Electrochemical properties of the obtained materials were investigated by using the cyclic

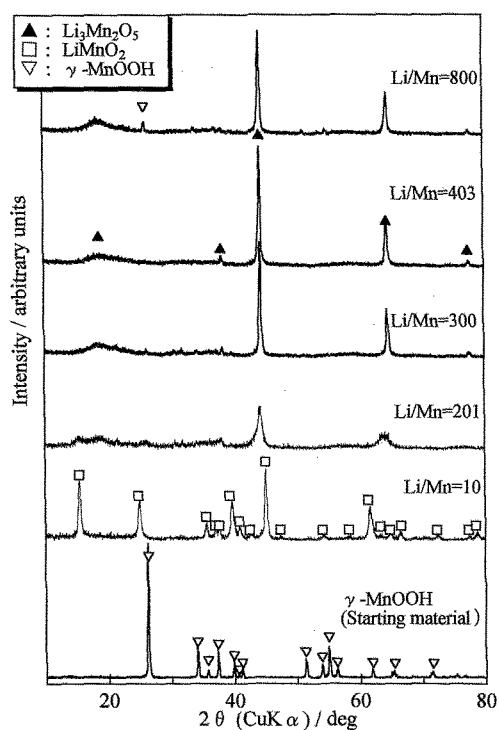


Fig. 1 : XRD patterns of  $\gamma$ -MnOOH (starting material) and the precipitates prepared by the wet method; 4.6mol/l LiOH solution, Li/Mn = 10~800, 60°C, 72h.

voltammetry. A cell was assembled in an argon-filled dry box. A working electrode was made of a composite of 60wt% obtained lithium manganese oxide, 30wt% acetylene black and 10wt% PTFE. The composite was pressed on a Ni mesh. The working electrode had an active area of 10mm in diameter. A 1mol/l  $\text{LiClO}_4$  in 1:1 mol% EC and DEC solution was used as an electrolyte, and a Li metal foil was used as a counter and a reference electrode. The cyclic voltammetry was carried out with a sweep rate of 0.1mV/s between 2.5 and 4.0V (vs.  $\text{Li/Li}^+$ ) at room temperature.

### 3. RESULTS AND DISCUSSION

#### 3.1 Formation of $\text{Li}_3\text{Mn}_2\text{O}_5$

The XRD patterns of the compounds precipitated in 4.6mol/l LiOH aqueous solutions at 60°C for 72h are given in Fig. 1. At this LiOH concentration, a new type of lithium manganese oxide was obtained as the single phase when the initial molar ratio of Li to Mn (Li/Mn) was 403. From the ICP analysis and the redox titration, the chemical composition of this material was estimated as  $\text{Li}_3\text{Mn}_2\text{O}_5$ . At lower initial Li/Mn (Li/Mn=10)  $\text{LiMnO}_2$  was obtained, whereas at higher initial Li/Mn (Li/Mn>500) the starting material  $\gamma$ -MnOOH remained as an impurity phase in the precipitates. Fig. 2 shows the formation diagram of the precipitates prepared by the wet method at 60°C for 72h when LiOH concentration and the initial Li/Mn were changed. Single phase of  $\text{Li}_3\text{Mn}_2\text{O}_5$

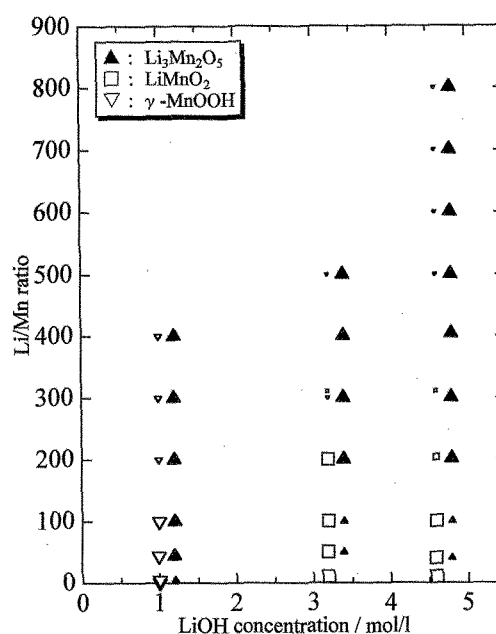


Fig.2 : Formation diagram of the precipitates prepared by the wet method; 1.0~4.6mol/l LiOH solution, Li/Mn=1~800, 60°C, 72h.

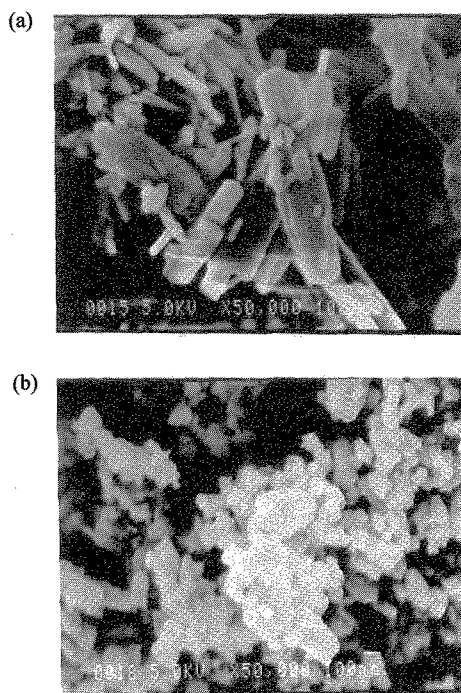


Fig. 3 : SEM images of (a)  $\gamma$ -MnOOH (starting material) and (b)  $\text{Li}_3\text{Mn}_2\text{O}_5$ .

could be obtained when the LiOH concentration and the initial Li/Mn were 3.2~4.6mol/l and 400, respectively.

Fig. 3 shows the SEM images of (a) starting material  $\gamma$ -MnOOH and (b)  $\text{Li}_3\text{Mn}_2\text{O}_5$  prepared by the wet method. The average size of the  $\text{Li}_3\text{Mn}_2\text{O}_5$  particles was around 100nm.

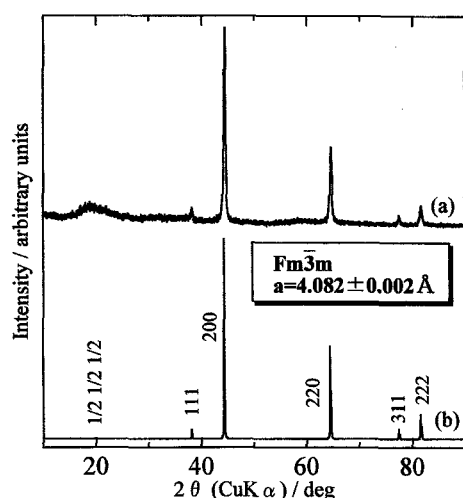


Fig. 4 : XRD patterns of  $\text{Li}_3\text{Mn}_2\text{O}_5$  (a) prepared by the wet method; 4.6mol/l LiOH solution, Li/Mn=403, 60°C, 96h, and (b) calculated based on the MnO-structure model.

### 3.2 Structure

Fig. 4 shows the XRD patterns of  $\text{Li}_3\text{Mn}_2\text{O}_5$  (a) prepared by wet method and (b) calculated based on the MnO-structure model by using RIETAN-2000 [8]. This simulation was performed under following assumptions:  $\text{Li}_3\text{Mn}_2\text{O}_5$  has the MnO-type rock-salt structure (space group  $Fm\bar{3}m$ ) and cations in the  $\text{Li}_3\text{Mn}_2\text{O}_5$  ( $\text{Li}^+$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ ) can be represented by one kind of imaginary cation which has an average valence calculated from chemical composition of  $\text{Li}_3\text{Mn}_2\text{O}_5$ . These assumptions mean cations are located randomly at the  $\text{Mn}^{2+}$  sites in the MnO structure. The calculated pattern was indexed based on the cubic symmetry and the lattice parameter  $a$  was calculated as  $4.082\pm 0.002\text{Å}$ . As seen in Fig. 4, the simulated pattern fitted well to the experimental one except for the broad peak around  $2\theta=20^\circ$ . This angle corresponds to the reflection from  $1/2\ 1/2\ 1/2$  when the MnO-structure is assumed. If the cations are distributed completely at random as the assumptions, this broad peak should not appear. Therefore, the existence of this broad peak indicates the configuration of cations in  $\text{Li}_3\text{Mn}_2\text{O}_5$  is not completely random, because each cation has its respective size and valence. Considering this, the crystal structure of  $\text{Li}_3\text{Mn}_2\text{O}_5$  is supposed as the MnO-type with a superlattice along [111].

### 3.3 Electrochemical properties

The chemical oxidation of  $\text{Li}_3\text{Mn}_2\text{O}_5$  by using  $\text{Br}_2$  as an oxidant was carried out in order to know whether  $\text{Li}^+$  could be extracted from the compound. Fig. 5 shows the molar ratios Li/Mn in oxidized precipitates as a function of the initial molar ratio of Br to Li (Br/Li). In all precipitates  $\text{Li}^+$  extraction was observed. As the amount of  $\text{Br}_2$  increased, the larger amount of  $\text{Li}^+$  was extracted. The molar ratio Li/Mn in the most oxidized precipitates in this study was 0.77.

Fig. 6 summarizes XRD patterns of the samples chemically delithiated. No impurities nor decomposition

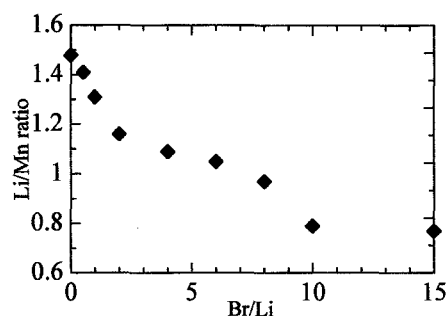


Fig. 5 : Li/Mn ratio in samples prepared through chemical oxidation by  $\text{Br}_2$  for 24h at room temperature. Br/Li represents the initial molar ratios of Br to Li in the oxidation reaction.

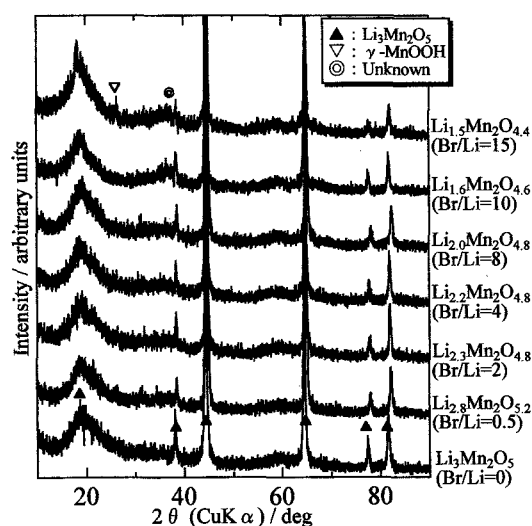


Fig. 6 : XRD patterns of  $\text{Li}_3\text{Mn}_2\text{O}_5$  and precipitates prepared after delithiating reaction by  $\text{Br}_2$  for 24h at room temperature.

phases were observed when Li/Mn in the delithiated samples were 1.5~1.0. In this Li/Mn range, the average valence of manganese ions were varied from 3.5 to 3.8. That is, charges of extracted  $\text{Li}^+$  were considered to be compensated by oxidizing  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$ . In addition, for the delithiated samples with Li/Mn of 1.5~1.0, only XRD peaks attributed to the original structure were observed, as seen in Fig. 6, indicating that the crystal structure was preserved even after  $\text{Li}^+$  extraction. These results suggested a potential of  $\text{Li}_3\text{Mn}_2\text{O}_5$  as a cathode material for Li secondary batteries having a high cycling performance. On the other hand, unknown phase was observed when Li/Mn were lower than 1.0. Appearance of such impurity phase is possibly caused by the material decomposition due to excess oxidation.

Fig. 7 shows the cyclic voltammograms of  $\text{Li}_3\text{Mn}_2\text{O}_5$ . At the initial cycles, two kinds of redox steps corresponding to extraction/insertion of  $\text{Li}^+$  ion were observed. The potentials of the charge peaks were 2.9 and 3.4V. This suggests the existence of two kinds of sites in which  $\text{Li}^+$

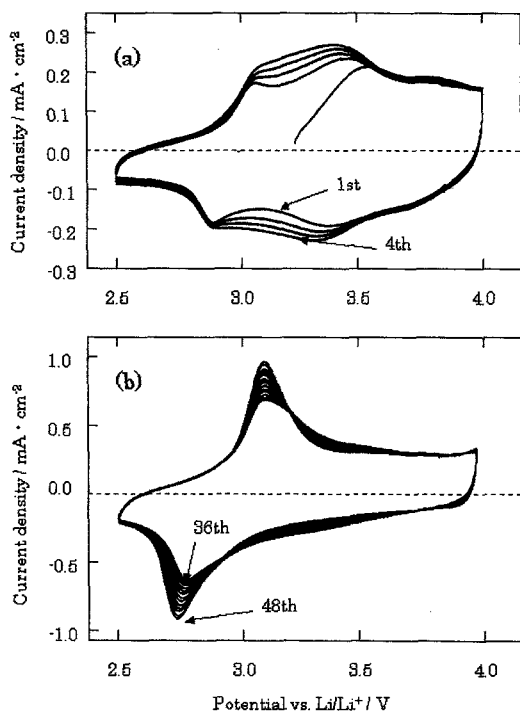


Fig. 7 : Cyclic voltammograms of  $\text{Li}_3\text{Mn}_2\text{O}_5$ . (a) 1st~4th cycles and (b) 36th~48th cycles ; Scan rate was  $0.1\text{mV}\cdot\text{s}^{-1}$ .

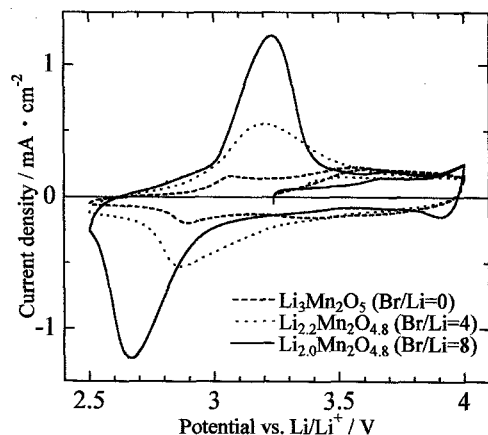


Fig. 8 : Cyclic voltammograms of  $\text{Li}_3\text{Mn}_2\text{O}_5$  and precipitates prepared through the chemical oxidation by  $\text{Br}_2$ . Each voltammogram represents 1st cycle. Scan rate was  $0.1\text{mV}\cdot\text{s}^{-1}$ .

ions can be inserted and extracted. From the results of chemical oxidation,  $\text{Li}_3\text{Mn}_2\text{O}_5$  was expected to retain the cathodic performance with repeating cycles. However, as shown in Fig. 7, the two charge peaks changed gradually to one peak around 2.7V after repeating cycles. This change of the cyclic voltammogram indicates the sites for  $\text{Li}^+$  extraction/insertion changed with repeating charge and discharge.

Cyclic voltammograms with the samples delithiated by  $\text{Br}_2$  were also taken. Fig. 8 shows the cyclic voltammograms at the first cycle with  $\text{Li}_3\text{Mn}_2\text{O}_5$  and the samples delithiated by  $\text{Br}_2$ . Cyclic voltammograms showed different behavior depending on the oxidation level of the samples. The change of the cyclic

voltammogram with the oxidation level, shown in Fig. 8, was similar to the change of cyclic voltammograms of  $\text{Li}_3\text{Mn}_2\text{O}_5$  with repeating cycles, shown in Fig. 7. Taking such a similarity into account, it can be considered that the  $\text{Li}^+$  extraction causes the change of the  $\text{Li}^+$  extraction/insertion sites, although the framework of the structure was preserved.

As regards cell capacity,  $\text{Li}_3\text{Mn}_2\text{O}_5$  became to exhibit larger value with repeating cycles as shown in Fig. 7. Moreover, cyclability also seemed to be enhanced with cycling. In Fig. 8, similar improvements of the cell performances were observed when the delithiated samples with higher oxidation level were used as cathode materials. At the present time the reason for such improvements is not clear, but will be discussed in future.

#### 4. CONCLUSION

A new type of lithium manganese oxide was synthesized by wet method using  $\gamma\text{-MnOOH}$  and  $\text{LiOH}$  solution as starting materials. The chemical composition was  $\text{Li}_3\text{Mn}_2\text{O}_5$  and the structure was thought to be the  $\text{MnO}$ -type with superstructure. The chemical oxidation by  $\text{Br}_2$  indicated that  $\text{Li}^+$  could be extracted from  $\text{Li}_3\text{Mn}_2\text{O}_5$ , while preserving its crystal structure. From the cyclic voltammetry, two kinds of redox steps corresponding to  $\text{Li}^+$  ion extraction/insertion were observed at the initial cycles. After repeating cycles, the two charge peaks changed gradually to the one peak. These suggested the  $\text{Li}^+$  extraction from  $\text{Li}_3\text{Mn}_2\text{O}_5$  might cause the change of  $\text{Li}^+$  extraction/insertion sites, although the framework of the structure was preserved.

#### References

- [1] T. Kanasaku, K. Amezawa and N. Yamamoto, *J. Jpn. Soc. Powder Metal.*, **45**, 758-762 (1998).
- [2] T. Kanasaku, K. Amezawa and N. Yamamoto, *Solid State Ionics*, **133**, 51-56 (2000).
- [3] M. M. Thackeray, W. I. F. David, P. G. Bruce and J. B. Goodenough, *Mat. Res. Bull.*, **18**, 461-472 (1983).
- [4] R. Kanno, M. Yonemura, T. Kohigashi, Y. Kawamoto, M. Tabuchi and T. Kamiyama, *J. Power Sources*, **97-98**, 423-426 (2001).
- [5] J. M. Tarascon, E. Wang and F. K. Shokooh, *J. Electrochem. Soc.*, **138**, 2859-2864 (2002).
- [6] M. Arakawa, T. Kanasaku, K. Amezawa and N. Yamamoto, *J. Jpn. Soc. Powder Metal.*, **48**, 1139-1144 (2001)
- [7] A. Kozawa, *Memoirs of Faculty of Engineering, Nagoya University*, **11**, 243-247 (1959).
- [8] F. Izumi and T. Ikeda, *Mater. Sci. Forum*, **198**, 321-324 (2000).

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