# Synthesis of Orthorhombic $LiMnO_2$ as a High Capacity Cathode for Li-Ion Battery by Emulsion Drying Method

Seung-Taek Myung, Shinichi Komaba,* and Naoaki Kumagai
*Department of Chemical Engineering, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551*

(Received March 30, 2001; CL-010291)

Orthorhombic $LiMnO_2$ was readily synthesized by calcination of an emulsion-dried powder precursor. The optimum synthesis condition to crystallize into zigzag layered $\beta$-$NaMnO_2$ system was to calcine at 925 °C for 12 h in an Ar atmosphere. According to TEM observation, the prepared material from the emulsion-dried precursor consisted of highly ordered single crystalline particle. Li/$LiMnO_2$ cell showed the capacity of about 173 mAh (g-oxide)$^{-1}$ and excellent capacity retention upon cycling with help of cycle-induced spinel like phase, more than 155 mAh g$^{-1}$ over 300 cycles at 25 °C.

---

Intercalation compounds of the layered rock salt structure such as $LiCoO_2$ and $LiNiO_2$, and spinel such as $LiMn_2O_4$, are widely studied and used as electrodes in advanced lithium batteries. In particular, $LiMnO_2$ is a promising cathode material because manganese is cheaper and more abundant than cobalt or nickel.

Orthorhombic layered $LiMnO_2$ (space group of *Pmnm*, hereafter referred as to *o*-$LiMnO_2$) which has a zigzag layered $\beta$-$NaMnO_2$ structure is expected to work as 3-V class cathode material for Li-ion secondary battery. Most of the synthesis routes in previous studies concerning *o*-$LiMnO_2$ powders have been developed by solid-state reaction, that is, prolonged calcination with intermittent grinding, caused relatively larger particle size. It was reported that electrochemical behavior of *o*-$LiMnO_2$ is highly dependent on its crystallite size.[1] So, wet-process has advantages to synthesize homogeneous oxide powders. Low-temperature solution technique seemed to be necessary to obtain high capacity upon cycling, but obvious capacity fading is usually observed during cycling, though the capacity fading is more moderate than $LiMn_2O_4$.[2,3]

Recently, the capacity fading was improved by using an well-ordered *o*-$LiMnO_2$ oxide. Jang et al.[4] reported that highly ordered *o*-$LiMnO_2$ prepared by calcination of freeze-dried precursor at 950 °C showed a high capacity retention upon extensive cycling. Though the *o*-$LiMnO_2$ exhibited good electrochemical properties, its powder preparation process is too difficult, that is, only sensitively controlled oxygen atmosphere ($p_{O_2} = 10^{-6}$ atm).

To overcome the difficulty of *o*-$LiMnO_2$ synthesis and enhance electrochemical properties, we previously reported hydrothermal synthesis of *o*-$LiMnO_2$.[5] To develop powder and electrochemical properties more and more, we employed the emulsion drying method which can intermix cations homogeneously in atomic scale.[6–9] In the present work, we investigated the preparation condition and electrochemical properties of *o*-$LiMnO_2$ synthesized by an emulsion drying method.

Reagent-grade $LiNO_3$ and $Mn(NO_3)_2{\cdot}6H_2O$ (Kanto) with a ratio of Li/Mn = 1 were used as starting materials. Precursor powder was prepared by an emulsion drying method, as reported previously.[6–9] The obtained powder precursor was firstly treated at 400 °C in air for 3 h, and then it was calcined at various temperatures in an Ar atmosphere, and cooled to room temperature in a tube furnace. X-ray diffractometry (XRD; Rigaku Rint 2200) was employed to identify crystal structure of the prepared powder. The powder morphology was observed using transmission electron microscopy (TEM; H-800, Hitachi) with an acceleration voltage of 200 kV.

For electrochemical testing, cathode was fabricated by blending the prepared powder, acetylene black and polyvinylidene fluoride (75:20:5) in *N*-methylpyrolidinon. The slurry was pasted on nickel ex-met (1 cm$^2$). The cell consisted of the oxide cathode as a working electrode and lithium ribbon as a counter electrode was assembled in an Ar-filled glove box. The cells were charged and discharged between 2.0 and 4.3 $V_{Li/Li^+}$ at current density of 0.1 mA cm$^{-2}$ at 25 °C.

Figure 1 shows phase evolution step of *o*-$LiMnO_2$ as a function of calcination temperature. As-received powder was firstly calcined at 400 °C in air to oxidize from $Mn^{2+}$ to $Mn^{3+}$ and/or $Mn^{4+}$. The resultant (hereafter called precursor) was confirmed as amorphous manganese and $Li_2MnO_3$ compounds. It is likely that the average oxidation state of Mn is in more than 3+ in the compounds. When the precursor calcined at 600 °C in Ar atmosphere, it began to convert to spinel $LiMn_2O_4$ which consists of $Mn^{3+}$ and $Mn^{4+}$, indicating that partial reduction of $Li_2MnO_3$ phase in the precursor is in progress. From 700 °C, the *o*-$LiMnO_2$ appeared as a minor phase, meaning that $Li_2MnO_3$ phase is partially reduced in each particle. After calcination at 925 °C, *o*-$LiMnO_2$ phase was formed as a major phase, deducing that the oxidation state of manganese reached nearly 3. In the case of calcination in the range of 700 to 950 °C in air, we would obtain mixture phase of $Li_2MnO_3$ and $LiMn_2O_4$ where the average oxidation state of Mn is between 3.5

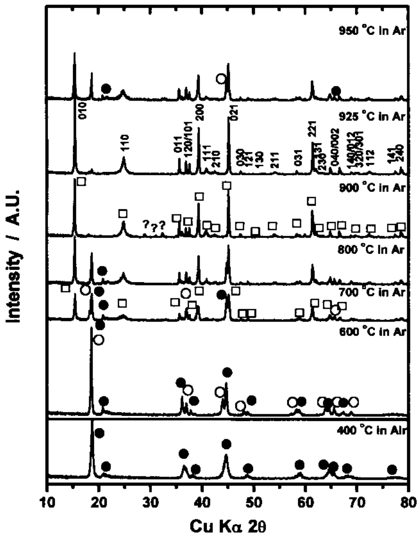

**Figure 1**. XRD patterns of *o*-$LiMnO_2$ calcined at various temperatures for 12 h in Ar or Air atmosphere. (●:$Li_2MnO_3$, ○:$LiMn_2O_4$ and □:*o*-$LiMnO_2$.)

and 4, while the calcination in Ar atmosphere gave us a well-crystallized *o*-$LiMnO_2$, of which the average oxidation state of Mn is nearly 3. Crystallographic parameters of the synthesized powder is in a good agreement with literatures.[5,10,11] As can be seen in the XRD pattern at 950 °C of Figure 1, there are two secondary phases, $LiMn_2O_4$ and $Li_2MnO_3$. In our previous report,[6] we confirmed that Li could be evaporated as an oxide form of $Li_2O$ at around 940 °C. At higher temperature about 950 °C in Figure 1, lithium can evaporates from particles. On that way, the formation of $Li_2MnO_3$ and $LiMn_2O_4$ is due to after lithium evaporation.[12] And, the amount of $Li_2MnO_3$ ($Mn^{4+}$) is relatively small, comparing to *o*-$LiMnO_2$.

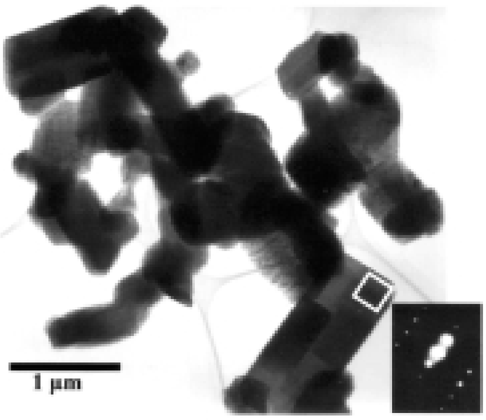

**Figure 2**. Bright-field image and selected-area electron diffraction (SAD) pattern obtained from the *o*-$LiMnO_2$ calcined at 925 °C for 12 h in Ar atmosphere. The SAD was taken from the squared part.

Figure 2 shows TEM bright-field image and selected-area electron diffraction (SAD) pattern obtained from *o*-$LiMnO_2$ calcined at 925 °C for 12 h in an Ar atmosphere. As can be seen in SAD pattern of Figure 2, the product consists of single crystalline particle oxide. Most of particles have smoothly developed edges and corners. The particle size distribution was 0.5–1.5 μm in diameter from TEM observation. It is interesting to note that the colors of calcined powder changed from a tone of brown to olive green with increasing calcination temperature from 700 to 925 °C. During the heat-treatment, there must happen changes in band gap between conduction and valence bands. From XRD and TEM experiments, the emulsion drying method is how effective to intermix the cations homogeneously in atomic scale, leading to highly fine single crystal particle oxide.

Figure 3 shows charge–discharge curves and their corresponding cyclability of the *o*-$LiMnO_2$ calcined at 925 °C for 12 h in Ar atmosphere. The cell showed two potential plateaus (3.7 and 4.1 V) in the initial charge process. It was thought that phase transformation to spinel might occur during electrochemical lithium deintercalation, leading to much faster phase transformation to reach highest capacity upon cycling. As cycle goes by, 4-V subplateaus and 3-V plateau are getting longer, meaning that activation of the oxide derived from the phase transformation is in progress to show high capacity, as reported previously.[4,13] During the activation to produce high capacity derived from phase transition from orthorhombic to cycled-induced spinel like phase, the charge–discharge curves confirm that structural reordering from orthorhombic to spinel $LiMn_2O_4$ occurs to result in higher capacity. Indeed, ex-situ XRD experiment showed close result to refs 4 and 13 that the original *o*-$LiMnO_2$ structure was gradually changed to cycle-induced spinel like phase during cycling. After activation from about the 40th cycle, the material begins to show a capacity of more than 160 mAh $g^{-1}$ reversibly. The higher capacity was maintained upon 300 cycles. The excellent cyclability is due probably to the fine single crystalline particle oxide.

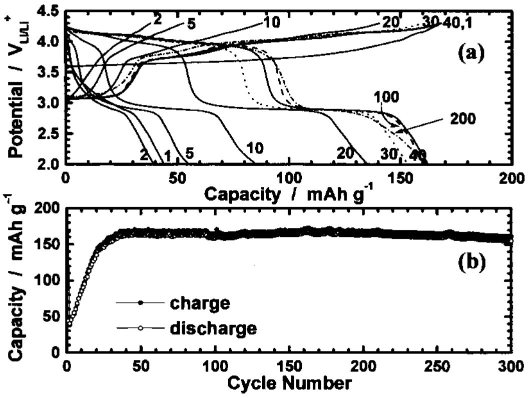

**Figure 3.** (a) charge and discharge curves and (b) cyclability of *o*-$LiMnO_2$ synthesized by the emulsion drying method at 925 °C in Ar atmosphere.

From these results, it was found that *o*-$LiMnO_2$ was easily formed from reduction of $Li_2MnO_3$ prepared by the emulsion drying method. This method is quite effective to synthesize fine single crystalline oxide electrode material. The product calcined from emulsion dried powder precursor would show enhanced battery performance than other powders prepared by other synthetic routes.[1,2] We are going to develop the physical and electrochemical properties of the *o*-$LiMnO_2$, and report elsewhere in near future.

The authors would like to thank Ms. Nobuko Kumagai for her helpful assistance in the experimental work. This study was supported by Industrial Technology Research Grant Program in '00 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan, the Iwatani Naoji Foundation's Research Grant, and Yazaki Memorial Foundation for Science and Technology.

## References and Notes

1 L. Croguennec, P. Deniard, and R. Brec, *J. Electrochem. Soc.*, **144**, 3323 (1997).
2 G. Pistoia, A. Antonini, and D. Zane, *Solid State Ionics*, **78**, 115 (1995).
3 J. N. Reimers, E. W. Fuller, E. Rossen, and J. R. Dahn, *J. Electrochem. Soc.*, **140**, 3396 (1993).
4 Y.-I. Jang, B. Huang, H. Wang, D. R. Sadoway, and Y.-M. Chiang, *J. Electrochem. Soc.*, **146**, 3217 (1999).
5 S.-T. Myung, S. Komaba, and N. Kumagai, *Chem. Lett.*, **2001**, 80.
6 S.-T. Myung and H.-T. Chung, *J. Power Sources*, **84**, 32 (1999).
7 S.-T. Myung, H.-T. Chung, N. Kumagai, S. Komaba, and H.-B. Gu, *J. Power Sources*, **90**, 103 (2000).
8 S.-T. Myung, N. Kumagai, S. Komaba, and H.-T. Chung, *Solid State Ionics*, **139**, 47 (2001).
9 S.-T. Myung, S. Komaba, and N. Kumagai, *J. Electrochem. Soc.*, **148**, A482 (2001).
10 *Joint Committee on Powder Diffraction Standards*, File no. 24-0734.
11 V. R. Hoppe, G. Brachtel, and M. Jansen, *Z. Anorg. Allg. Chem.*, **417**, 1 (1975).
12 M. M. Thackeray, M. F. Mansuetto, and J. G. Bates, *J. Power Sources*, **68**, 153 (1997).
13 I. M. Kötschau and J. R. Dahn, *J. Electrochem. Soc.*, **145**, 2672 (1998).