Synthesis of Orthorhombic $LiMnO_2$ Material and Its Optimization

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Orthorhombic $LiMnO_2$ was synthesized using LiOH and γ-MnOOH at 1000 °C in the argon flow by quenching method. X-ray diffraction revealed that the $LiMnO_2$ showed a well-defined orthorhombic phase of a space group with *Pmnm*. The lattice constants were $a = 2.806$ Å, $b = 5.750$ Å, and $c = 4.593$ Å. The $LiMnO_2$ after grinding delivered 212 mAh/g in the 9th cycle and still delivered 200 mAh/g after 50 cycles at room temperature. The well-defined orthorhombic $LiMnO_2$ by the quenching method exhibited an excellent cycle performance.

The layered oxide materials, $LiMO_2$ (M=Co, Ni, Mn…) and the $LiMn_2O_4$ spinel are the most widely studied from the viewpoint of their application to 4 V cathode materials for lithium secondary batteries.[1,2] The Mn-based materials have attracted wide attention as intercalation cathode materials because of their low cost and nontoxicity.

Orthorhombic $LiMnO_2$ (herein referred to as o-$LiMnO_2$) of the ordered rock salt structure described by Johnston et al.[3] and Hoppe et al.[4] has been studied by many research groups.[5–10] The low temperature synthesis (170–450 °C) first reported by Ohzuku et al. showed a large rechargeable capacity above 190 mAh/g using lithium hydroxide and manganite at 450 °C.[5] Reimers et al. also reported a new ion exchange method and revealed an irreversible structural change to the spinel phase using in situ XRD.[6]

Davidson et al. and Jang et al. have also reported the synthesis of o-$LiMnO_2$ material by a high temperature synthetic method (> 800 °C).[8–10] Jang et al. successfully synthesized o-$LiMnO_2$ using LiOH and Mn_3O_4 under a reduced oxygen atmosphere by a high temperature synthetic method, which exhibited an excellent cycleability at room temperature between 4.4 and 2.0 V. Although they also first reported the high temperature performance at 55 °C, the capacity loss of o-$LiMnO_2$ at high temperature was much larger than that during the room temperature test.[10]

From a review of previous studies, we found the following problems: First, the complexity of the synthetic process. For the low temperature synthesis, most cases used an excess amount of lithium salt or lithium/sodium exchange reaction to form the homogeneous $LiMnO_2$ phase, which requires a long reaction time and other reaction steps. Even for the high temperature synthesis, very sensitive synthetic conditions and some treatments to improve the reaction between the starting materials are necessary. Second, there is no report showing a good cycle performance of o-$LiMnO_2$ at high temperature. And last, o-$LiMnO_2$, which was synthesized at high temperature, needed enough time to reach the maximum discharge capacity at room temperature. Although it critically depends on current density and the cycle testing conditions, this indication is not desirable for the use of this cathode material for lithium secondary batteries.

Recently, we reported that the $LiAl_{0.1}Mn_{1.9}O_4$ material using LiOH and γ-MnOOH showed a quite good cycleability in both the 3 and 4 V regions.[11,12] Furthermore, tetragonal $Li_2Mn_2O_4$ material, which was synthesized using LiI as a reducing agent, showed not only a high discharge capacity over 200 mAh/g, but also good cycle performance in the (3+4) V region.[13] Based on our previous research, we successfully synthesized a new type of o-$LiMnO_2$ material using LiOH and γ-MnOOH by a quenching method. In this paper, we report a new synthetic method and cycle characterization of o-$LiMnO_2$, which can satisfy the above problems at the same time.

The o-$LiMnO_2$ material was synthesized using $LiOH{\cdot}H_2O$ and γ-MnOOH. The mixture of LiOH and γ-MnOOH (molar ratio of Li/Mn = 1.02) was thoroughly ground in an agate. A small amount of lithium was added to compensate for lithium evaporation during the calcination process. It was pressed at a 300 kg/cm^2 pressure into a 25-mm diameter pellet. It calcined at 950–1100 °C for 10 h in the box furnace under argon at a flow rate of 500 cm^3/min. The powder X-ray diffraction (XRD) using Cu Kα radiation was employed to identify the crystalline phase of the synthesized materials. The electrochemical tests were performed using CR2032 coin-type cells. The cells were assembled as detailed elsewhere.[11,12] The charge and discharge cycling was performed at a current density of 0.4 mA/cm^2 (40 mA/g) with a cut-off voltage of 2.0–4.5 V at room and high temperatures.

The chemical analysis showed that the powder real composition obtained at 1000 °C was $Li_{0.99}MnO_{2.01}$. Well-defined o-$LiMnO_2$ was obtained from the calcination at 1000–1050 °C for 10 h under argon flow by quenching. The pellet was removed from the furnace at 1000 °C and directly quenched in air. We would like to emphasize that $LiMnO_2$ in this study was synthesized by a one-step method without intermediate regrinding or some other treatments. From the thermal analysis, it revealed another reaction at about 950 °C that may be the conversion from the $LiMn_2O_4$ spinel phase, which occurred at about 800 °C, to the o-$LiMnO_2$ compound. Figure 1(a) shows the XRD pattern of the o-$LiMnO_2$ materials obtained at 1000 °C. For calcination temperature $T < 950$ °C, it showed mixed structure patterns with cubic and tetragonal phase in the XRD diagram. However, when the calcination temperature is above 950 °C, the (010) peak at $2\theta = 15.4°$ was rapidly increased and other peaks also indicated a major phase of the o-$LiMnO_2$ material. The lattice constants are $a = 2.806$ Å, $b = 5.750$ Å, and $c = 4.593$ Å, which showed a slightly large *c*-value compared with other reports.[4,5] This material consisted of particles of about 5–15 μm diameter with a bar-shape and small spherical ones of about 2–3 μm, which is the typical crystallite pattern of the compound using the γ-MnOOH.[14] Figure 1(b) shows the discharge capacity of the $LiMnO_2$ electrode as a function of the cycle number at room and high temperatures (50 °C). The $LiMnO_2$ electrode, which was cycled at room temperature,

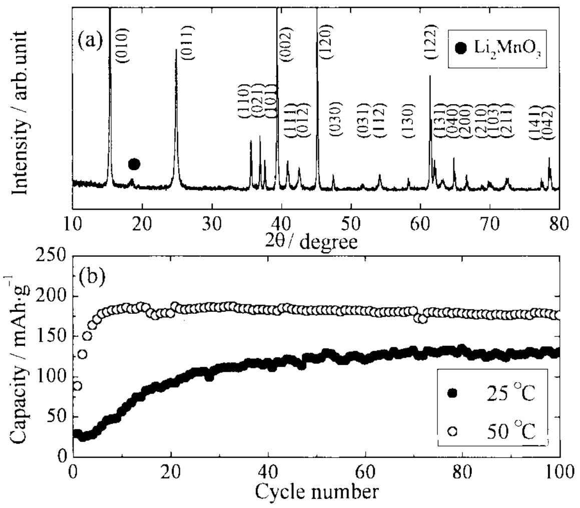

Figure 1. (a) XRD pattern (b) discharge capacity with the number of cycles for the Li/1M $LiPF_6$-EC/DMC/$LiMnO_2$ cell.

showed a very small initial discharge capacity of about 34 mAh/g and a slowly increasing capacity on cycling. However, for the high temperature test cell, even if it also showed a small initial discharge capacity during the first cycle, the capacity increasing was very fast and reached a maximum point during the early stage. This is characteristic of the o-$LiMnO_2$ using the high temperature synthetic method. Although Jang et al. have already reported a similar result for o-$LiMnO_2$, which exhibited a rather good cycleability under almost the same test conditions, the discharge capacity continuously decreased and reached about 80 mAh/g after the 100th cycle.[10] However, the $LiMnO_2$ in this study delivered 186 mAh/g during the 10th cycle and still delivered 176 mAh/g after 100 cycles at high temperature. The cycle retention rate is 95% in the 3 and 4 V regions.

Although o-$LiMnO_2$ in this study showed excellent cycling performance in the high temperature test, it is not desirable to use a cathode material for lithium secondary batteries as described above. Croguennec et al. reported the effect of the crystal and grain sizes of o-$LiMnO_2$ on the various discharge capacities.[15,16] Therefore, we assume that the grinding treatment is a very useful way to change the characteristic of o-$LiMnO_2$, because it showed a relatively large particle size of about 5–15 μm, which affected the contact between the electrolyte and particle surface. In order to increase the initial discharge capacity of o-$LiMnO_2$, it was thoroughly ground in an agate mortar by a milling machine (ANM 1000, Nito. Co., Japan). The average particle size and shape of $LiMnO_2$ after grinding was surprisingly decreased and changed compared to that of the original o-$LiMnO_2$. The average particle size for the compound after 6 h grinding was 0.5–3 μm. Furthermore, BET analysis strongly supported our assumption about the grinding effect for o-$LiMnO_2$ material. The surface areas of the two compounds were 0.55 m^2/g before grinding and 9.25 m^2/g after 6 h grinding. It is noticeable that the specific surface area after 6 h grinding was as much as 17 times larger than that before grinding. This unique characteristic was due to the large particle size of o-$LiMnO_2$ material which was obtained by quenching method.

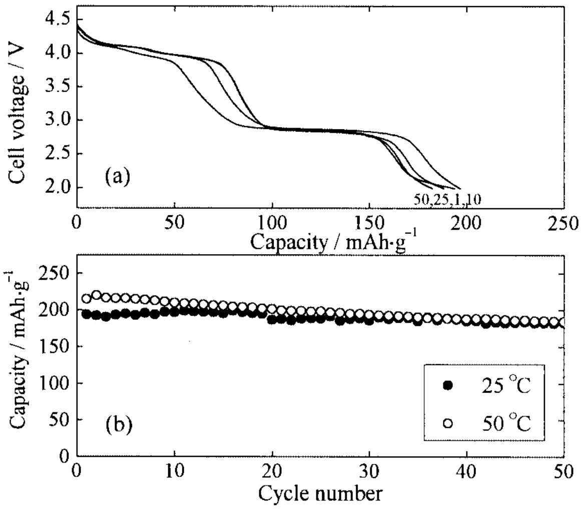

Figure 2. (a) Discharge curves at 25 °C (b) discharge capacity of $LiMnO_2$ after grinding.

Figure 2 shows the cycle characterization of $LiMnO_2$ cells after 6 h grinding. As expected, it showed a very high initial discharge capacity of 193 mAh/g as well as a good cycleability at room temperature. The difference in the initial discharge capacity between before and after grinding at room temperature was about 160 mAh/g. Although the cycle retention rate of $LiMnO_2$ after grinding decreased to 87% in the high temperature test, it still exhibited a fairly good cycle performance up to 50 cycles. From these results, o-$LiMnO_2$ in this study has a high possibility to be commercialized as a cathode material for lithium secondary batteries by optimizing the condition of pulverization.

The o-$LiMnO_2$ in this study could be obtained at 1000 °C by quenching and it showed a high initial discharge capacity (≥ 190 mAh/g), which accelerated the rapid reaction between the particles and electrolyte at room temperature by grinding. A more detailed discussion about electrochemical properties and capacity loss mechanism will be reported elsewhere.

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