

Unique Grinding Effect of Orthorhombic LiMnO_2 Material

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Well-defined orthorhombic LiMnO_2 was synthesized using LiOH and $\gamma\text{-MnOOH}$ as starting materials at 1000°C in an argon atmosphere by quenching method. It showed a very small initial discharge capacity of about 34 mAh/g at room temperature. However, after a 24 h grinding, the LiMnO_2 delivered not only a large initial discharge capacity of 210 mAh/g, but also a high cycling retention rate of 96% in the (3 + 4) V region after 50 cycles. We found that the grinding treatment was very effective to activate lithium insertion/extraction into the LiMnO_2 layers in the 3 V region.

The battery industries have aimed to supply safe power sources with high energy density and good cycle performance. Lithium secondary batteries are the most promising candidate among the many possibilities to satisfy this demand.^{1,2}

Layered lithium metal oxide with the general formula LiMO_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}$) has a rock salt structure where lithium and transition metal cation occupy alternate layers of octahedral sites in a distorted close-packed oxygen ion lattice.³ It was well-known that LiMnO_2 structure with an almost ideal layered arrangement of the Li and Mn ions could be prepared by a Li^+ ion-exchange from $\alpha\text{-NaMnO}_2$. According to the synthetic condition and mechanism, LiMnO_2 forms an orthorhombic structure with space group $Pnmm$ ($a = 2.805 \text{ \AA}$, $b = 5.757 \text{ \AA}$, and $c = 4.527 \text{ \AA}$) and a monoclinic unit cell with a space group $C2/m$ ($a = 5.439 \text{ \AA}$, $b = 2.809 \text{ \AA}$, and $c = 5.388 \text{ \AA}$). Furthermore, a second polymorph of LiMnO_2 has been prepared by chemical lithiation of the spinel $\text{Li}_2\text{Mn}_2\text{O}_4$. A tetragonal cell was indicated with $a = 5.662 \text{ \AA}$ and $c = 9.274 \text{ \AA}$ ($I41/amd$, $Z = 8$).⁴⁻⁶

Since Orthorhombic LiMnO_2 (herein referred to as $o\text{-LiMnO}_2$) with the ordered rock salt structure synthesized at 150°C by Ohzuku et al., many research groups reported lots of new synthetic processes to obtain a well-defined $o\text{-LiMnO}_2$ with an excellent cycling performance. Some groups have reported many interesting characteristics of $o\text{-LiMnO}_2$; such as the relation between grain size and discharge capacity, some impurities by which the electronic conductivity of $o\text{-LiMnO}_2$ structure may be enhanced, and the phase transformation from orthorhombic to spinel structure, which could a main reason of capacity decline of Li/LiMnO_2 cell.⁷⁻¹⁰

Recently, we have reported a new synthetic method using quenching process, which could synthesize a well-developed $o\text{-LiMnO}_2$ material at 1000°C by one-step method. This work showed that $o\text{-LiMnO}_2$ material with an excellent cycling performance could be obtained easily without the exchange reaction of Li^+/Na^+ or maintaining the sensitive synthetic condition. It also revealed that the marvelous relation between particle size (or surface area) and initial discharge capacity of $o\text{-LiMnO}_2$ compound by adopting the grinding process. However, there was no clear explanation of the role and mechanism of grinding treatment for the $o\text{-LiMnO}_2$ powder in our previous

report.¹¹ Most recently, we found that the grinding process could result in the various electrochemical characterization of Li/LiMnO_2 cell, depending on the tested voltage region. We present here the unique effect and role of grinding for the $o\text{-LiMnO}_2$ in the 3 V and 4 V region, respectively.

The orthorhombic LiMnO_2 material was synthesized using $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\gamma\text{-MnOOH}$. The mixture of LiOH and $\gamma\text{-MnOOH}$ (molar ratio of $\text{Li/Mn} = 1.02$) was thoroughly ground in an agate mortar. The mixture was calcined at 1000°C for 10 h under an argon atmosphere by quenching.

The powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) using $\text{Cu K}\alpha$ radiation was employed to identify the crystalline phase of the synthesized materials. A three-electrode glass cell was used for cyclic voltammetry (CV) measurement. The working electrode was consisted of 3 mg of the active material and 2.2 mg of conducting binder (TAB), which was pressed onto stainless steel mesh. The counter and reference electrodes were prepared by pressing lithium foil onto stainless steel gauze. The CV measurement was performed with an Arbin Instruments Model MSTAT4 test system at 0.2 mV/s scan rate between the voltage limits of 2.0–4.5 V. The cycling test was performed using CR2032 coin-type cell. The cell was assembled as detailed elsewhere.¹¹ The charge/discharge process were performed at a current density of 0.4 mA/cm^2 with a cutoff voltage of 2.0–4.3 V for (3 + 4) V test, 3.0–4.3 V for 4 V test, and 2.2–3.6 V for 3 V test, respectively.

Figure 1 exhibits the XRD pattern of the $o\text{-LiMnO}_2$ materials before and after grinding at various grinding times (0–24 h). The (010) peak at $2\theta = 15.3^\circ$ in the XRD diagram was slightly moved to the higher angle after 6 h grinding. As the grinding time increases, as the full width at half maximum (FWHM) of major peaks, (011), (002), (102), and (122), remarkably decrease. Specially, the two small concrete peaks at $2\theta = 41\text{--}43^\circ$, which were (111) and (012) peaks, after 24 h grinding totally changed and could not be detected any more in the same scan position.

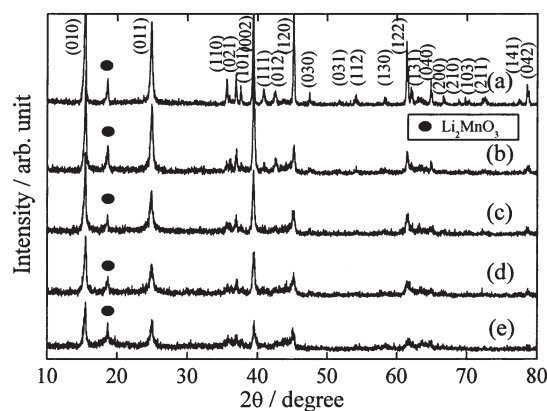


Figure 1. XRD patterns of LiMnO_2 before and after grinding (a) 0 h (b) 6 h (c) 12 h (d) 18 h (e) 24 h.

Figure 2 shows the morphology of the *o*-LiMnO₂ compound before and after grinding using TEM analysis. It clearly reveals that the particle size after 24 h grinding surprisingly decreased and exhibited a nano-crystalline size of about 50–500 nm. The similar indication was already reported that the amorphous manganese oxide with nano-crystalline could be obtained the higher discharge capacity due to the increase in the electrical conductivity by ball milling and it exhibited higher lithium intercalation than high crystalline oxide material.^{12,13} Therefore, we assumed that the structure of LiMnO₂ in this study changed into the partially amorphous phase with nano-crystalline after grinding and enlarged surface area improved the initial discharge capacity by extending the contact area between the electrolyte and *o*-LiMnO₂ powders.

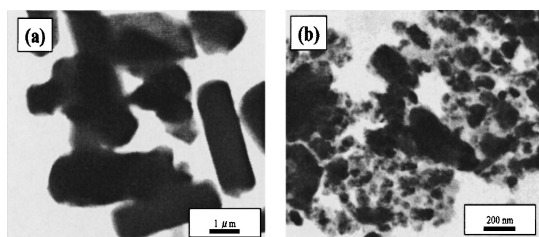


Figure 2. TEM images of LiMnO₂ (a) before grinding, (b) after 24 h grinding.

Figure 3(a) shows the discharge capacity as a function of cycle number for Li/LiMnO₂ cell before and after 24 h grinding in the different voltage regions. The two Li/LiMnO₂ cells before grinding commonly showed very small discharge capacity about 5–15 mAh/g in the 3 V and the 4 V region, respectively. The discharge capacity of *o*-LiMnO₂ before grinding in the 4 V region was larger than that in the 3 V region, although the difference of capacity was very small. On the other hand, the results of cycling test for the Li/LiMnO₂ cells after grinding showed the opposite cycling performance compared to that of *o*-LiMnO₂ before grinding, which the capacity in the 4 V region was smaller than that in the 3 V region.

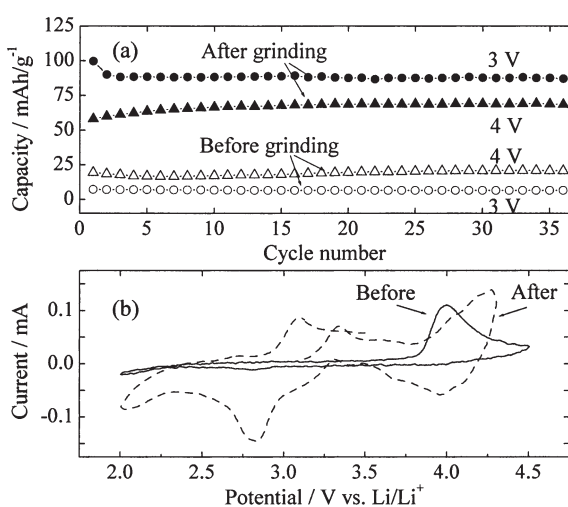


Figure 3. (a) Specific discharge capacity (b) Cyclic voltammogram of Li/LiMnO₂ before and after grinding.

Furthermore, we found one more interesting fact that the *o*-LiMnO₂ in the 3 V region initially delivers a small discharge capacity of 7.2 mAh/g before grinding and 99.8 mAh/g after 24 h grinding, respectively. The increased capacity of *o*-LiMnO₂ in the 3 V region was 14 times as large as that before grinding. While the discharge capacity of *o*-LiMnO₂ after grinding in the 4 V region was increased to only 3 times of that before grinding. This indication is very interesting to note the grinding treatment may induce the different electrochemical reaction of *o*-LiMnO₂ material depending on the tested voltage regions.

To investigate the effect of grinding, we measured the cyclic voltammograms of *o*-LiMnO₂ before and after grinding. The potential was scanned at a scan rate of 0.2 mV/s between 2.0 and 4.5 V. Figure 3(b) shows the typical electrochemical reaction of LiMnO₂ before and after grinding. The cyclic voltammogram of before grinding exhibited an oxidation peak at 3.9 V and a very small reduction peak at 2.8 V. It seems there is hardly an electrochemical reaction in the 3 V region. However, for the LiMnO₂ after 24 h grinding, it exhibits two concrete reaction peaks of the oxidation/reduction process, respectively. Specially, the reduction peak at 2.85 V is remarkably increased after grinding and differentiated clearly from that of the original LiMnO₂ compound. This cyclic voltammogram explained clearly why Li/LiMnO₂ cell after grinding showed a high discharge capacity in the 3 V region, as mentioned in Figure 3(a).

As expected, the Li/LiMnO₂ cell in the (3 + 4) V showed a very high initial discharge capacity of 211 mAh/g and still delivered 202 mAh/g after 50 cycles at room temperature. The difference in the initial capacity between before and after grinding at room temperature is about 177 mAh/g. Although the cycle retention rate of LiMnO₂ after grinding decreased to 87% in the high temperature test, it still exhibited a pretty good cycle performance up to 50 cycles. From the result, we concluded that the grinding treatment resulted in activating the lithium insertion/extraction reaction into the LiMnO₂ structure in the 3 V region, which is a main reason to exhibit a high initial discharge capacity of Li/LiMnO₂ cell in the (3 + 4) V region at room temperature.

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