FULL PAPER

Improved cathode performance and relaxation properties of LiMn_2O_4 prepared by optimized ball-milling with single-step sintering

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LiMn_2O_4 has been prepared by means of high-energy ball-milling of Li_2CO_3 and MnCO_3 followed by one-pot sintering. Milling at 800 rpm for 4 h with sintering at 700 °C for 12 h leads the enhanced cathode performance as 123.5 mAh g^{-1} of initial discharge capacity under 1 C charge–discharge rate, retaining 95.1 and 91.6 % of capacity after 100 and 200 cycles, respectively. Mechanochemical reaction facilitates the sintering reaction to form the favorable microstructure homogeneously without second phase. Relaxation analysis showed that, at the charging around $x = 0.2$ for $\text{Li}_x\text{Mn}_2\text{O}_4$, the sample prepared by optimal milling time varies mainly lithium concentration in Li-rich phase, while excessively milled sample alter the molar ratio of Li-rich and Li-lean phases. This indicates that optimal milling time allows the sample to undergo the less structural change at the charging, which enables the improved cycle performance.

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1. Introduction

Spinel-type structured LiMn_2O_4 has been one of the major cathode materials for lithium-ion batteries.^{1),2)} The advantage of this compound is low-cost for fabrication without expensive elements as well as environmentally friendly characteristics, although the theoretical capacity in 4 V region is smaller than that of LiCoO_2 or LiNiO_2 .^{3)–6)} The more severe drawback of LiMn_2O_4 is capacity fading at the charge–discharge process especially at high-temperature operation.^{7),8)} Wide variety of investigations have been performed on LiMn_2O_4 focusing on the capacity decay during charge–discharge cycles so far,^{9)–11)} and it has been believed that degeneration of cathode performance is mainly due to the dissolution of manganese ions into electrolyte,^{12)–15)} effect of Jahn–Teller distortion^{16),17)} or structural failure caused by oxygen deficiency.^{18),19)} In addition to cation doping,^{20)–23)} coating with other oxides^{24)–26)} or formation of composites,^{27)–29)} modification of morphologies has been reported to effectively improve the cathode performance,^{30)–33)} which would be associated with the preparation technique. The bulk form of LiMn_2O_4 has been prepared by conventional solid-state reaction,³⁴⁾ sol–gel,^{35)–37)} co-precipitation,^{38),39)} hydrothermal reac-

tion,⁴⁰⁾ combustion methods^{41)–43)} or other miscellaneous routes,^{44),45)} and recent review is also available.⁴⁶⁾ As for the typical solid-state reaction method, commonly adopted sintering temperature is as high as 800 °C to accomplish the reaction without formation of LiMnO_2 or Mn_2O_3 .^{47),48)} Along with the soft chemical route as mentioned above, mechanochemical process often yields the favorable microstructure by homogeneous mixing with reducing sintering temperature,^{49)–54)} whereas only few reports have focused upon the precise synthesis condition to address the improvement of cycle performance. In the present study, we investigate the contribution of milling and post-sintering conditions for the preparation of LiMn_2O_4 cathode material emphasizing on the microstructure and electrochemical performance.

Concerning that the capacity fading is related to the structural deterioration during charging and discharging, which might be caused by manganese dissolution or Jahn–Teller distortion, difference in structure between the charge–discharge and the equilibrium states should be significant, since the larger structural deviation would be derived from the difficulty in variation toward the equilibrium structure, and introduction of potential structural distortion. We have analyzed the structural transient or relaxation toward the equilibrium state after the termination of Li-extraction or insertion for various cathodes^{55)–61)} or anodes^{62)–64)} including LiMn_2O_4 .⁶⁵⁾ In the present study,

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we apply this technique, named as relaxation analysis,⁶⁶⁾ to the LiMn_2O_4 prepared by high-energy ball-milling with post-sintering in the optimal condition to study on the enhanced electrochemical performance of mechanocemically treated LiMn_2O_4 .

2. Experimental procedure

About 0.5 g of stoichiometric mixture of MnCO_3 (Kishida Chem, 92.7%) and Li_2CO_3 (Hayashi Pure Chem.) reagents were put into a silicon nitride milling vessel (20 ml in volume) accompanied by 10 silicon nitride balls ($\phi 10$ mm in diameter), which corresponds to 40:1 of ball-to-powder weight ratio. A planetary ball-milling machine (Premium Line P-7, Fritch) was employed with 800 rpm taking an interval every 30 min of operation. After a given time of milling, the products were subjected to single-step sintering at various temperatures and periods. The crystalline phases of the obtained samples were investigated by means of X-ray diffraction (XRD, Ultima IV, Rigaku) using $\text{Cu K}\alpha$ radiation (40 kV and 40 mA). The surface morphologies of the samples were observed by using a Field-Emission Scanning Electron Microscope (FE-SEM, SU6600, HITACHI).

The obtained LiMn_2O_4 was mixed with acetylene black (Denka) and polyvinylidene difluoride with the weight ratio of 80:10:10 using N-methyl 2-pyrrolidone solvent, which were spread on an aluminum foil, and then dried in vacuum to fabricate the working electrodes. The two-electrodes test cells (Hosen) were assembled employing lithium metal as a counter electrode and 1 M LiPF_6 in EC/DMC solution (2:1 v/v, Kishida Chem.) as electrolyte in an Ar gas-filled glove box. Charge-discharge characteristics were tested using a galvanostat (HJ-SM8, Hokuto Denko) at 25 °C with the current density of 1 C-rate (148 mA g^{-1}). Cut-off potentials were selected as 3.2 to 4.5 V vs. Li^+/Li , and 20 min of rest time was inserted for every step.

Relaxation analysis has been carried out to compare the structural relaxation properties between the optimized and longer-time milled samples. After the electrochemical lithium extraction to $x = 0.20$ of $\text{Li}_x\text{Mn}_2\text{O}_4$ with 1 C-rate, the electrode with current collector was immediately detached out of the cell to prevent unfavorable local cell reaction,⁶⁷⁾ which was then washed with EC and EC/DMC solvents and dried in the glove box. The electrode was placed in a sealed holder (2391A201, Rigaku) equipped with beryllium window to mount on an X-ray diffractometer as mentioned above. The diffraction data were collected in the 2θ range from 15 to 90° with the scan speed of 2°min^{-1} and recorded every 0.04° steps. The diffraction experiments were carried out every 25 h of relaxation up to 100 h. The Rietveld refinements were carried out using RIEVEC code^{68),69)} under the coexistence of Li-rich and Li-lean phases, both of which belong to the spinel-type structure with the space group $Fd\bar{3}m$. The mole fraction M is evaluated from the following equation,

$$M_r = \frac{S_r \cdot Z_r \cdot V_r}{S_r \cdot Z_r \cdot V_r + S_l \cdot Z_l \cdot V_l}, \quad (1)$$

where S , Z and V denote scale factor, number of formulae in unit cell and cell volume, respectively.⁷⁰⁾ Subscripts r and l denote the parameters of Li-rich and Li-lean phases, respectively.

3. Results and discussion

On the preparation of LiMn_2O_4 by milling of Li_2CO_3 and MnCO_3 followed by one-pot sintering, we have optimized milling time, sintering temperature, and sintering time in terms of the cycle performance. The optimization of each parameter is described in the following subsections 3.1–3.3, while we have examined other various conditions. In the subsection 3.4, we show the results of the relaxation analysis on the optimized LiMn_2O_4 .

3.1 Optimization of milling time

We at first optimize the milling time before the sintering process. **Figure 1** shows XRD patterns of the milled products of Li_2CO_3 and MnCO_3 without sintering. Mixing the starting powders with mortar and paste, the obtained diffraction pattern indicates the simple mixture of Li_2CO_3 and MnCO_3 as labeled by 0 h. After 1 h of milling, the diffraction peaks of Li_2CO_3 diminish with remaining the peaks of MnCO_3 , which continues for prolonged milling time up to 6 h. It should be noted that 112 diffraction peak of MnCO_3 around $2\theta = 60.1^\circ$ shifts toward higher 2θ with milling as the enlarged plot, suggesting that a part of Li_2CO_3 incorporates into the rhombohedral MnCO_3 lattice forming a solid solution. Moreover, small amount of LiMn_2O_4 appears even after 1 h of milling, which develops with milling as indicated by asterisks. Therefore, present ball-milling process is not a simple mixing but the mechanochemical reaction and the enhancement of catalytic property is also expected.⁷¹⁾ While Soiron et al. reported the formation of LiMn_2O_4 only by means of milling,⁷²⁾ present sample require the post-sintering to obtain single phase of LiMn_2O_4 . These precursors have been sintered at 700 °C for 12 h, which is inductively deduced from the results of subsequent sections. XRD patterns of the sintered materials are shown in **Fig. 2**. Without ball-milling, small amount of Mn_2O_3 can be detected in addition to the main peaks of LiMn_2O_4 . It has been also reported in the previous literature that unreacted Mn_2O_3 is likely to occur for relatively lower sintering temperature as 700 °C.^{73),74)} However, milled samples in the present study does not show such an impurity phase even for sintering at 700 °C. The crystallite size has been estimated from 111 diffraction peak around 18.6° using Sherrer's equation, which is plotted versus milling time in Fig. S1. The crystallite size initially decreases within 2 h of milling, and thereafter remains almost constant until 6 h of milling. SEM photographs of the sintered products are displayed in **Fig. 3**. While un-milled sample shows an inhomogeneous microstructure with particle size ranging between 0.1–1 μm as Fig. 3(a), 1 or 2 h of milling improves the homogeneity in particle size and anomalously aggregated particles have been disappeared in Figs. 3(b) or 3(c). For 4 h of milling, the morphology becomes more homogeneous consisting of

Fig. 1. Powder XRD patterns for the milled products of Li_2CO_3 and MnCO_3 . Ball-milling has been carried out at 800 rpm for 0, 1, 2, 4 and 6 h. Card data of Li_2CO_3 , MnCO_3 and LiMn_2O_4 are also represented. 122 diffraction peak of MnCO_3 around 60.1° is enlarged to plot at right figure, in which dashed lines are drawn as a guide of peak position. The diffraction peaks of LiMn_2O_4 are indicated by asterisks on the pattern of 6 h-milled sample.

Fig. 2. Powder XRD patterns of LiMn_2O_4 obtained by single-step sintering at 700°C for 12 h after ball-milling for 0, 1, 2, 4 and 6 h. Diffraction peaks of Mn_2O_3 are indicated by asterisks for 0 h of milling.

fine particles with $0.1\mu\text{m}$ in size, indicating that ball-milling process attributes to restrict anomalous grain growth. For the sample milled for 6 h, the edge of the grain particles seems to be weld with neighboring particles, although the particle size is unchanged or a little smaller than that of 4 h-milled sample. Consequently,

milling time seems to attribute to the sample morphology, although the crystallite size is not altered after 2 h of milling.

Charge–discharge experiments have been carried out using above LiMn_2O_4 as a cathode material with 1 C of current density. The charge–discharge curves at the selected cycles are represented in Fig. S2, in which all samples exhibit typical profiles of two-step plateaus even at 200th cycle. The discharge capacity and its retention rate are plotted versus cycle number in **Fig. 4**. Since the 1st discharge capacity appears to be attributed by an irreversible reaction and the measured capacity in early cycles sometimes shows a slight increase, we take the initial discharge capacity as the maximum between 2nd and 5th cycles, based on which the retention rate has been deduced. LiMn_2O_4 prepared without milling exhibits relatively lower initial capacity as 118.4mAh g^{-1} , and with the charge–discharge cycles, the capacity gradually decreases to show the retention rate as 88.5 and 82.7 % after 100 and 200 cycles, respectively. On the other hand, for 1 h- and 2 h-milled samples, the initial capacities increase up to 123.4 and 132.5mAh g^{-1} , respectively, whereas the capacity retention curves exhibit the similar behavior with the non-milled sample. For 4 h-milled sample, the initial capacity slightly decreases to 123.5mAh g^{-1} , while the capacity retention improves as 95.1 and 91.6 % after 100 and 200 cycles, respectively, showing higher capacities at the later cycles compared to 1 h- or 2 h-milled samples. Such a high retention rate is one of the highest among the bulk form of pure LiMn_2O_4 cathode materials^{40),41),75)} under the similar charge–discharge conditions, except for doped, coated or nanostructure-designed ones.^{76),77)} Extending the milling

Fig. 3. SEM micrographs of LiMn_2O_4 prepared by high-energy ball-milling followed by one-pot sintering at 700°C for 12 h. Ball-milling has been subjected for (a) 0 h, (b) 1 h, (c) 2 h, (d) 4 h and (e) 6 h.

Fig. 4. Cycle performance of LiMn_2O_4 prepared by ball-milling with single-step sintering at 700°C for 12 h. (a) Discharge capacity and (b) capacity retention rate are plotted versus number of cycles. Milling time is varied as $\square$: 0 h, $\diamond$: 1 h, $\triangle$: 2 h, $\circ$: 4 h, and ∇ : 6 h.

time up to 6 h, the discharge curve exhibits the similar characteristics as 1 h- or 2 h-milled samples, showing relatively higher initial capacity with a little faster decay in comparison with 4 h-milled sample. In terms of the retention rate, the optimal milling time is determined as 4 h under the present condition, which would be largely related to the microstructure consisting of homogeneous particle size without welded edges.

3.2 Temperature dependence at post-sintering

Effect of sintering temperature is then investigated fixing the milling and sintering periods as 4 and 12 h, respectively. Note that the optimal data of 700°C -sintered sample are the same as the above section. XRD patterns of milled LiMn_2O_4 obtained after sintering at various temperatures are shown in **Fig. 5**. Due to the mechanochemical reaction, single phase of LiMn_2O_4 is achieved without any apparent impurity even for lower sintering temperature as 650°C . With increasing the sintering temperature, the profiles of XRD peaks become sharper, resulting in the obvious increase in crystallite size in Fig. S3. The more apparent is the change in morphology as shown in **Fig. 6**. While relatively smaller sphere-like particles are observed for sintering at 650°C , the particle develops in size with increasing the sintering temperature, and finally it changes into a distinct octahedral shaped morphology as 800°C -sintered sample.

The charge–discharge curves for LiMn_2O_4 sintered at various temperatures after milling are represented in Fig. S4. All the samples exhibit the typical two-step curves over 200 charge–discharge cycles. The cycle performances of discharge capacities and their retention rates are shown in Fig. 7. The sample sintered at 650°C delivers 125.2 mAh g^{-1} of the initial discharge capacity with the retention rate as 89.7% after 100 cycles, which is a little inferior to the best condition of 700°C -sintering. Increasing the sintering temperature to 750°C , although the initial capacity becomes higher as 128.0 mAh g^{-1} , the capacity declines rather rapidly with cycles. As for the sample sintered at 800°C , the initial discharge capacity lowers and the capac-

ity drops within early 50 cycles followed by gradual decreasing, the feature of which is qualitatively different from the lower-temperature sintered samples. Concerning the decay curve of retention, 750°C -sintered sample appears as the intermediate decay profile between the samples sintered at 800°C and those at lower-temperatures. The change in retention profile is thought to be associated with the morphology as observed in Fig. 6. One of the strategies to improve the cycle performance is making the crystal facet

Fig. 5. XRD patterns of LiMn_2O_4 prepared by mechanochemical treatment followed by sintering at various temperatures. Milling and sintering times are fixed as 4 and 12 h, respectively.

Fig. 7. Cycle performance of LiMn_2O_4 prepared by ball-milling with single-step sintering. (a) Cycle number dependences of discharge capacity and (b) capacity retention rate. Ball-milling has been performed for 4 h and sintering was made at various temperatures for 12 h. $\square$: 650°C , $\triangle$: 700°C , ∇ : 750°C and $\diamond$: 800°C .

Fig. 6. SEM images of LiMn_2O_4 prepared by 4 h of ball-milling followed by 12 h of single-step sintering at various temperatures. Sintering has been performed at (a) 650°C , (b) 700°C , (c) 750°C and (d) 800°C .

as {111} plane to prevent the manganese dissolution, which would lead to the truncated octahedral-shaped morphology with relatively larger crystallite size.^{78),79)} Although the present sample sintered at 800 °C exhibits the similar morphology, cycle performance is poorer than the lower-temperature sintered ones. Notwithstanding, the capacity decay at later cycles seems to be restricted, which might be caused by such a contribution.

3.3 Contribution of sintering time

For the last parameter of synthesis, sintering time is optimized with keeping other conditions as 4 h of milling with 700 °C of sintering. **Figure 8** represents the XRD patterns of LiMn_2O_4 obtained by 6, 12 and 18 h of sintering after milling. All the samples possess the spinel-type structured single phase and any apparent deviation in

Fig. 8. XRD patterns of LiMn_2O_4 obtained by single-step sintering at 700 °C after 4 h of ball-milling. Sintering was carried out for 6, 12 and 18 h.

peak profile is not observed. However, the crystallite size is gradually enhanced with sintering time as shown in Fig. S5, the tendency of which is much milder than the sintering temperature dependence. SEM micrographs in **Fig. 9** also show little difference in morphology depending on the sintering time, while 12 h-sintered sample shows slightly larger particles.

The charge–discharge curves and cycle performances are represented in Figs. S6 and **10**, respectively. The 6 h-sintered sample possesses a little smaller initial discharge

Fig. 10. (a) Discharge capacities and (b) capacity retention rates of LiMn_2O_4 prepared by ball milling for 4 h followed by sintering at 700 °C. □: 6 h, ○: 12 h and △: 18 h of sintering time.

Fig. 9. SEM photographs of LiMn_2O_4 prepared by 4 h of ball-milling followed by single-step sintering at 700 °C for various time. The sintering periods are (a) 6 h, (b) 12 h and (c) 18 h.

capacity, which declines rapidly with cycles. In addition, it has a little higher charging potential even at the initial cycle compared to the longer sintered samples, which would be due to the larger overpotential for the charge transfer. Then, it is suggested that sintering time is inadequate to establish the intimate contacts between particles to endure the charge–discharge process, despite of similar XRD patterns and morphology with the sample of longer time sintering. On the other hand, 12 h- or 18 h-sintered samples exhibit good cathode performances, while the latter shows a little inferior in cycle performance.

3.4 Relaxation analysis

According to the above experiments, the optimal cathode performance is attained for the sample prepared by 4 h of milling followed by sintering at 700 °C for 12 h. At the sintering process, the sample morphology would develop as follows: small sphere particles of LiMn_2O_4 occur at first, which grow larger with temperature or time, and they finally turn into the octahedral-shaped crystals. For the sample with homogeneous microstructure but just before getting into octahedral shape, the highest retention is achieved with the charge–discharge cycles. However, it is rather ambiguous that the 4 h-milled sample exhibits the optimum rather than and excess milling as 6 h. We thus compare the structural relaxation properties on the samples of 4 h and 6 h-milling followed by sintering to clarify the effect of milling time. In the present study, lithium ions are electrochemically extracted to $x = 0.20$ of $\text{Li}_x\text{Mn}_2\text{O}_4$, in which the Li-rich and Li-lean phases with the ideal compositions of $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ and MnO_2 , respectively are coexisting.

Figure S7 exemplifies the measured and refined diffraction patterns of $\text{Li}_{0.2}\text{Mn}_2\text{O}_4$ after the 50 h of relaxation, using the sample prepared by 4 h of milling with 12 h of sintering at 700 °C. By the successful refinement with small R_{wp} , the relaxation-time variation of lattice parameters of Li-rich and Li-lean phases as well as their mole fractions are obtained.

Figure 11 represents the lattice parameter variations of Li-rich and Li-lean phases plotted as a function of relaxation time. 6 h-milled sample possesses the larger difference in lattice parameters between these two phases. As for the relaxation time dependence, the lattice parameter of both phase remains almost constant, although Li-rich phase shows slight increases at the initial stage. On the other hand, 4 h-milled sample gradually increases the lattice parameter of Li-rich phase. Assuming that lattice parameter is associated with lithium content in a unit cell, 6 h-milled sample should have the wider lithium-concentration difference between Li-rich and Li-lean phases. In addition, 4 h-milled sample would be able to alter the lithium concentration to some content. **Figure 12** plots the mole fraction of Li-rich phase, the rest of which corresponds to that of Li-lean phase. While the mole fraction of 4 h-milled sample keeps the value almost constant with a slight increase at the initial relaxation stage, that of 6 h-milled sample gradually increases over the relaxation time. There-

Fig. 11. Variation of lattice parameters of $\text{Li}_{0.2}\text{Mn}_2\text{O}_4$ after lithium extraction plotted as a function of relaxation time. Open and filled symbols indicate the Li-rich and Li-lean phases, respectively.

Fig. 12. Mole fraction of Li-rich phase plotted versus relaxation time for electrochemically delithiated $\text{Li}_{0.2}\text{Mn}_2\text{O}_4$. Samples are prepared by milling for 4 and 6 h followed by sintering.

fore, at the lithium extraction, 4 h-milled sample mainly reduces the lithium concentration of Li-rich phase, while 6 h-milled one allows the excessive transformation from Li-rich into Li-lean phases. Then, at the relaxation, they should return into equilibrium by varying lithium concentration in Li-rich phase for 4 h-milled sample and mole fractions for 6 h-milled one. Compositional dependence of lattice parameter of Li-lean phase is thought to be small, since the difference in lattice parameter of Li-lean phase between 4 h and 6 h-milled samples is much smaller than that of Li-rich phase. Accordingly, 6 h-milled sample undergoes the excess amounts of transformations between the two phases accompanied by larger structural distortion as Fig. 11, which would result in the inferior cycle performance in comparison with 4 h-milled one. The extended

milling does not simply attribute to the homogeneous mixing but slightly changes the condition of precursor which would shift the optimal sintering condition to alter the lithium extraction process. Within the present sintering condition, 4 h of milling achieves the smooth structural change toward the equilibrium due to the less structural distortion, which would enable the better cycle performance.

In summary, employing the mechanochemical treatment followed by one-pot sintering for the preparation of LiMn_2O_4 , the optimal condition is deduced as 4 h of milling with sintering at 700 °C for 12 h from the cycle performance. This feature is discussed with morphology and relaxation property. While the analyses have been carried out on the first discharge process in the present study, additional experiments should be made on the cycled samples to clarify the cycle performance improvement mechanism. Moreover, electrochemical measurements as Cyclic Voltammogram or Electrochemical Impedance Spectroscopy are also planned for better understanding the contribution of mechanochemical process.

4. Conclusions

On the synthesis of LiMn_2O_4 cathode material through the mechanochemical reaction accompanied by the one-pot sintering, we have optimized the synthesis conditions as milling time, sintering temperature and sintering time in terms of the discharge capacity and its retention rate under 1 C-rate charging-discharging. The optimal sample obtained by 4 h of milling at 800 rpm with post-sintering at 700 °C for 12 h delivers 123.5 mAh g^{-1} of initial discharge capacity with the retention rate 95.1 and 91.6 % after 100 and 200 cycles, respectively.

As for the post-sintering process, small sphere particles of LiMn_2O_4 are initially created, and increasing the sintering temperature or time, the particles grow larger, and finally change the morphology into octahedral shape. Just before turning the crystal shape into the octahedral morphology, the optimum sample is available.

The relaxation analysis after the lithium extraction revealed that the sample prepared by the best milling time as 4 h deviate the lithium concentration of Li-rich phase from the equilibrium structure, while excessively milled sample as 6 h is likely to alter the molar ratio of Li-rich and lean phases. Excessive phase transformation in the latter sample would degrade the cathode performance during the cycles, which allows the 4 h-milled sample as the optimal condition.

Supplementary file Figs. S1–S7

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