The structural variation of \( \text{Li}_2\text{MnO}_3 \) during charge–discharge cycling as a lithium-battery cathode was investigated. The Rietveld refinement of neutron diffraction data revealed that the \( \text{Li}_2\text{MnO}_3 \) synthesized at 900°C was assigned to the monoclinic symmetry corresponding to the \( C2/m \) space group \((\beta = 4)\). The transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were carried out using the samples after cycling in the potential ranges of 2.0–4.6, 2.0–4.8, and 2.0–5.0 V. As a result, it was observed that structures based on the cubic (\( Fd\bar{3}m \)) and rhombohedral (\( R3m \)) symmetries, having the compositions of \( \text{LiMn}_2\text{O}_4 \) and \( \text{LiMnO}_2 \), respectively, are locally generated on the surface of the particles, depending on the upper voltage for the charge process. It was also found that the voltage at which the \( R3m \) rhombohedral structure is generated tended to be higher than the voltage at which the \( Fd\bar{3}m \) cubic structure is formed. Such a structural variation of \( \text{Li}_2\text{MnO}_3 \) is anticipated to be related to the extraction of oxygen molecules which is induced during the charge processes. Furthermore, the generation of the \( R3m \) \( \text{LiMnO}_2 \) could be understood by the introduction of oxygen vacancies into the material.

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Key-words : \( \text{Li}_2\text{MnO}_3 \), Structural variation, Lithium-ion battery cathode

1. Introduction

Many efforts have been devoted to the development of rechargeable energy storage devices that can be used in diversified technical applications, expanding over portable electronics, electric cars, and large-scale industrial equipment. Lithium-ion batteries, which can realize a high energy density, are a promising candidate for these devices. The characteristics of the cathode materials have a significant influence on the performance of the lithium-ion batteries, and as a result, much attention has focused on the various kinds of lithiated transition-metal oxides for their possible use as cathode materials. Manganese-based layered oxides, such as solid solutions of \( \text{LiMnO}_2 – \text{Li}_2\text{MnO}_3 \) (\( M = \text{Ni}, \text{Co}, \) or \( \text{Ti} \)), are attractive materials, because they are safer, cheaper, and less toxic than \( \text{LiCoO}_2 \) or \( \text{LiNiO}_2 \) and exhibit a higher operating voltage \((>3.5\) V vs \( \text{Li}/\text{Li}^+ \) on average\)). However, the need of an improvement in capacity retention is also recognized when they are put into practical use.

\( \text{Li}_2\text{MnO}_3 \) also shows an electrochemical activity as a lithium-battery cathode. The electrochemical activities of \( \text{Li}_2\text{MnO}_3 \) and solid solutions of \( \text{LiMnO}_2 – \text{Li}_2\text{MnO}_3 \) are attributed to the enhanced \( \text{Li}^+ \) desorption and insertion accompanying the activated manganese redox reaction \((\text{Mn}^{3+}/\text{Mn}^{4+})\) following the extraction of oxygen molecules induced during the charge processes. It is noted that the proton exchange with \( \text{Li}^+ \) between the electrolyte and active material was proposed in order to account for the electrochemical activity of \( \text{Li}_2\text{MnO}_3 \).

Nanoparticles with a large surface area typically promote the extraction of oxygen molecules and thus achieve enhanced electrochemical activities for the manganese-based cathode materials. However, the rapid extraction of oxygen molecules sometimes leads to structural destruction causing a poor capacity retention of the systems. Such a structural destruction would be associated with the intergranular fracture of the crystallite caused by the structural variations during cycling. To suppress structural destruction, several surface modifications of the electrode materials, such as acid treatment with an aqueous \( \text{H}_2\text{SO}_4 \) solution and surface coating with \( \text{AlPO}_4 \) or \( \text{TiO}_2 \) have been reported. However, there are only a few reports in which the structural variation of manganese-based cathode materials is discussed related to the charge–discharge conditions.

We have studied the structural variation of \( \text{Li}_2\text{MnO}_3 \) during cycling and found that it undergoes a fluctuation depending on the charge–discharge potential range. In this paper, we briefly describe the charge–discharge characteristics of \( \text{Li}_2\text{MnO}_3 \) as a lithium-battery cathode and then report the structure of the as-synthesized \( \text{Li}_2\text{MnO}_3 \) and its structural variation during cycling.

2. Experimental

\( \text{Li}_2\text{MnO}_3 \) powder was synthesized based on a modification of a previously reported method. Manganese sulfate \((\text{MnSO}_4 \cdot 5\text{H}_2\text{O})\) was dissolved in distilled water, added to an aqueous solution of sodium carbonate \((\text{Na}_2\text{CO}_3)\) containing an equimolar amount of \( \text{Na}_2\text{CO}_3\), and stirred for 24 h. The produced precipitate in the solution was filtered with suction through a 0.2-μm pore size polytetrafluoroethylene (PTFE) membrane, washed by distilled water, and dried at 110°C. The resulting precipitate was mixed with lithium hydroxide \((\text{LiOH} \cdot \text{H}_2\text{O})\) after calcination at 500°C in air and then heated at 900°C for 12 h under flowing oxygen to obtain the crystalline \( \text{Li}_2\text{MnO}_3 \) powder.

The cycling properties of \( \text{Li}_2\text{MnO}_3 \) as a lithium-battery cathode were measured in the potential ranges of 2.0–4.6, 2.0–4.8, and 2.0–5.0 V. The measurements were carried out using a 2032-type coin cell. The electrolyte was a 1 M solution of \( \text{LiPF}_6 \) in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed at the volume ratio of 1:1.
ratio of 1:1 (Ube Industries, Ltd., Japan). The anode was a lithium metal foil disk (11-mm diameter, 0.5-mm thickness). A porous polypropylene film was used as the separator. The cathode consisted of an aluminum grid on which the ground Li$_2$MnO$_3$ powder, mixed with 15 wt% carbon black and 10 wt% PTFE powder, was pressed; these cathodes were dried at 140°C for 4 h under vacuum before placing them in the cells. The charge–discharge data were collected at the current densities of ±20 mAg$^{-1}$ and 23°C. Every cycling began from the charge process and was repeated 99 times.

In order to determine the structure of the as-synthesized powder, neutron diffraction data were collected by monochromized neutron radiation at the wavelength of 1.8244 Å at room temperature using a high-resolution powder diffractometer (HRPD) at the research reactor (JRR-3M) of the Japan Atomic Energy Agency. The as-synthesized Li$_2$MnO$_3$ powder (about 5 g) was contained in a cylindrical vanadium cell (5-mm radius, 55-mm height). Based on the neutron diffraction data, the structural parameters of the Li$_2$MnO$_3$ were refined using the Rietveld refinement program RIETAN-FP.15) To investigate the morphologies and structures of the as-synthesized and cycled samples, transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements were carried out by a JEOL JEM-ARM 200F electron microscope. For these measurements, the particles were dispersed in CCl$_4$ and transferred onto carbon-coated copper grids. Simulated plane images for the various structures were drawn using a CaRine software program.

3. Results and discussion

Figure 1 shows the cycling data measured for the Li/Li$^+$/Li$_2$MnO$_3$ cell in the potential ranges of 2.0–4.6, 2.0–4.8, and 2.0–5.0 V, in which the charge and discharge capacities are plotted as a function of the number of cycles. The load curves for the 1st, 50th, and 99th cycles in the potential range of 2.0 V are also shown in Fig. 1. Noted is the fact that the electrochemical capacities continuously increase over all the cycles in all the charge–discharge potential ranges. It was also found that the increased capacities depend on the charge–discharge potential ranges. For example, compared to the discharge capacities for the potential ranges of 2.0–4.6 and 2.0–5.0 V, the former increased from 12.5 to 22.5 mAhg$^{-1}$ between the 1st and 99th cycles, whereas the latter increased from 20.0 to 110.2 mAhg$^{-1}$ during the same cycling regime. On the other hand, the plateaus, observed at around 3.0 V in the charge curves in the inset, correspond to the redox reaction of Mn$^{4+}$/Mn$^{3+}$.

During the cycling of Li$_2$MnO$_3$ or solid solutions of LiMO$_2$–Li$_2$MnO$_3$ (M = Ni or Co), the extraction of oxygen molecules is induced in a high voltage region for the charge processes.20) On the other hand, the electrochemical Li$^{+}$ desinsertion during the charge processes for manganese-based cathode materials generally arises in conjunction with the oxidation of Mn to a maximum oxidation state of 4+. However, since the charge state of Mn in Li$_2$MnO$_3$ or solid solutions of LiMO$_2$–Li$_2$MnO$_3$ (M = Ni or Co) is already 4+, the extraction of oxygen molecules plays a major part in the Li$^{+}$ desinsertion in the systems.21,22) The results of cycling measurements and load curves in this study suggest that the extraction of oxygen molecules in Li$_2$MnO$_3$ continuously occurs during all the cycles and is accelerated as the voltage for the charge process increased.

The results of the Rietveld refinement of the neutron diffraction data for the as-synthesized Li$_2$MnO$_3$ are summarized in Table 1. Almost all the Bragg reflections can be indexed to a monoclinic cell, and both the low R factors and good fitting between the observed and calculated patterns were acquired. The as-synthesized Li$_2$MnO$_3$ is assigned to the monoclinic space group P2$_1$/c,18) in which the structure is characterized by a mutual substitution between the Li$^+$ and manganese ions on the $ab$ plane with $z = 0$ (the LiMn$_2$O$_3$ layer). With respect to the structure of the Li$_2$MnO$_3$, the trigonal (P3$_1$21$^\text{I}$) or monoclinic (C2/c19$^\text{I}$) structures was reported as well as the C2/m monoclinic. On the other hand, Lei et al.20) reported that a well-annealed Li$_2$MnO$_3$ powder predominately contains the C2/m monoclinic polymorph. The results of the Rietveld refinement ensured the validity of a structure model due to the C2/m monoclinic for the as-synthesized Li$_2$MnO$_3$.

Figure 3 shows typical bright-field TEM images of a particle in the as-synthesized Li$_2$MnO$_3$. As shown in Fig. 3(a), the particle exhibits a rod-like morphology with an ~0.2 μm diameter and ~0.5 μm length; note that such particle characteristics are substantially maintained during the subsequent charge–discharge processes, as will be mentioned later. In Fig. 3(b), stripe structures, lying perpendicular to the c axis, are observed inside the crystallite. The electron diffraction (ED) pattern is indexed on the basis of a monoclinic cell with additional streaks parallel to the c axis at (02n0) (n = integer), suggesting the existence of planar defects in the crystallite.

The HAADF-STEM image of a crystallite in the as-synthesized Li$_2$MnO$_3$ is shown in Fig. 4. The crystallite is comprised of a two-dimensional array of dumbbell-like dots, in which the dots are arranged at intervals of 0.43 nm along the horizontal axis and simultaneously stacked in the vertical direction with three types of sequences. As indicated by the red line in Fig. 4, the stacking sequences are classified into the straight (S) and oblique (O and O' ) types, corresponding to the planes projecting the C2/m monoclinic [100], [110], and [110] zone axes, respectively. Schematic drawings of the (Li, Mn) planes in the Li$_2$MnO$_3$ viewed along these zone axes are also shown in Fig. 4. We also understand that the dumbbell-like dot is equivalent to the sequence of –Li–Mn–Mn–Li– as seen in the drawings. The stacking sequences are regarded as the origin of the stripe structures and streak diffractions, observed in Figs. 3(a) and 3(b), respectively.21,22) On the other hand, we previously reported that a unit cell sequence of the trigonal P3$_1$21 platelets exists between the
LiMn2O4 and LiMnO2, respectively. Moreover, it is noted that C2/m stacking sequences in Li2MnO3,23) but such a sequence was not detected in these measurements. This is probably because the trigonal P3112 sequence is energetically less favorable than the C2/m stacking sequence.

Figure 5 shows the bright-field TEM images of particles in the samples after cycling in the potential ranges of 2.0–4.8 and 2.0–5.0 V, together with the selected-area ED patterns taken for various separated regions in the respective particles. The individual particles in each sample have a rod-like morphology with an ~0.22 μm diameter and ~0.52 μm length. Referring to Fig. 3, these characteristics are almost the same as those observed for the as-synthesized sample, which suggests that a drastic change, such as intergranular fracture, does not occur during cycling. In the ED patterns, there are patterns due to structures other than the C2/m monoclinic. For the sample after cycling in the potential range of 2.0–4.8 V [Fig. 5(a)], patterns due to the C2/m monoclinic and cubic spinel (Fd3m) were detected. For the sample after cycling in the potential range of 2.0–5.0 V [Fig. 5(b)], besides these patterns, a pattern based on a rhombohedral structure with the space group of R3m was observed. The stoichiometric compositions for the Fd3m cubic and R3m rhombohedral structures are represented to be LiMnO2 and Li2MnO3, respectively. Moreover, it is noted that both the Fd3m cubic and R3m rhombohedral structures tend to be generated in the surface neighborhood of the crystallites. We also carried out TEM measurements for the cycled sample in the potential range of 2.0–4.6 V, but ED patterns due to structures other than the C2/m monoclinic were not detected.

The results of the TEM measurements suggested that the structural variation of Li2MnO3 is associated with the upper voltage for the charge process as well as the electrochemical characteristics; the voltage at which the R3m rhombohedral structure is generated tends to be higher than the voltage at which the Fd3m cubic structure is formed. As a matter of course, it may be that the number of cycles also affects the structural variation. These details will be reported in the future.

We also carried out a fast Fourier transform (FFT) analysis to understand the distribution of crystallites due to the C2/m, Fd3m, and R3m structures in the particle. Figure 6 shows the FFT patterns based on the various regions in the TEM image of a crystallite in the sample after cycling in the potential range of 2.0–5.0 V. The FFT pattern varies according to the region. The pattern

![Fig. 2. Rietveld refinement pattern of the neutron diffraction data measured for the as-synthesized Li2MnO3. The red plus marks (+) are the raw data, and the overlapped continuous line is the calculated pattern. The short vertical lines below the pattern indicate the positions of the allowed Bragg reflections. The difference between the observed and calculated intensities is shown at the bottom on the same scale.](image)

![Fig. 3. Bright-field TEM images of a particle in the as-synthesized Li2MnO3 and the associated selected-area electron-diffraction pattern.](image)
representing the internal region in the particle is indexed on the basis of a $C_2/m$ monoclinic cell [Fig. 6(a)], whereas the patterns assigned to the $Fd\bar{3}m$ cubic and $R\bar{3}m$ rhombohedral structures are obtained in the regions around the surface of the particle [Figs. 6(b) and 6(c)]. These results are consistent with those in Fig. 5 and suggest that the structural variation in Li$_2$MnO$_3$ predominately arises at the particle surface.

**Figure 7** shows the HAADF-STEM image of a crystallite in the sample after cycling in the potential range of 2.0–5.0 V and the associated FFT image and pattern. Boxed images A and B, indicated in Fig. 7, show representative images of the interior and the surface region of the crystallite, respectively. The structure observed in image A is equivalent to that of type S (Fig. 4). In contrast, image B shows a structure unlike that of image A. In fact, the FFT image based on the boxed image B is comprised of a two-dimensional array of single dots, in which the dots are arranged to form horizontal and vertical arrays. The distance between the dots in the vertical direction was 0.25 nm. The corresponding FFT pattern can be indexed on the basis of a rhombohedral $R\bar{3}m$ cell viewed along the [1\bar{1}0] zone axis. Furthermore, it is noteworthy that a periodicity with respect to the brightness of arrays is observed in the FFT image in which a horizontal array, consisting of brighter single dots, appears alternately along the vertical axis. The observations in the FFT image and the FFT pattern suggest the existence of a disordered $R\bar{3}m$ structure.
Figure 8 shows a schematic drawing of the (Li, Mn) plane in LiMnO$_2$ with a rhombohedral $R3m$ structure viewed along the [110] zone axis. Assuming that Mn atoms are disordered at the 3a and 3b sites in the structure, the interatomic distance between Mn atoms along the c axes are estimated to be 0.25 nm. This value is in good agreement with the observed values in the FFT pattern (Fig. 7). In addition, it can be assumed that the occupancy of the Mn atom at the 3a site is larger than that at the 3b site. Such a difference in the occupancy is regarded as the cause of the periodicity about the brightness of the array observed in the FFT image (Fig. 7).

It is known that manganese-based cathode materials, including Li$_2$MnO$_3$, generally convert to the $Fdar{3}m$ spinel during cycling.$^{24-26}$ On the other hand, it was reported that the $R3m$ LiMnO$_2$ does not exist at room temperature due to a cooperative monoclinic distortion related to the Jahn–Teller activity of Mn$^{3+}$. However, we consider that the $R3m$ LiMnO$_2$ can exist by assuming the introduction of oxygen vacancies into the material. For LiMnO$_2$ in which oxygen vacancies are introduced, the average crystal field, formed by oxygen molecules around Mn$^{3+}$, must show a lower symmetry than that in the stoichiometric LiMnO$_2$. The crystal field of the lower symmetry causes an energy splitting of two degenerated 3$d$ orbitals, and the energy of the spin system is thus lowered. In the non-degenerated state, the energy increase caused by lattice distortion cannot be compensated. Consequently, the Jahn–Teller distortion is impossible or suppressed in the material.

The generation of the $R3m$ LiMnO$_2$ due to the suppression of the Jahn–Teller distortion was reported for the Co- or Cr-substituted LiMnO$_2$. On the other hand, there are only a few reports in which the structural stability in materials is discussed related to the suppression of the Jahn–Teller distortion based on
the introduction of oxygen vacancies.31) However, a full understanding of the generation of the $R3m$ LiMnO$_2$ must await further investigations. However, we believe that the results of this study are useful in improving the electrochemical performance of manganese-based cathode materials.

4. Conclusions

We have synthesized the $C2/m$ Li$_2$MnO$_3$ and described its structural variation as a cathode material for lithium-ion batteries. In a sample after cycling, crystallites due to both $R3m$ rhombohedral and $Fd\overline{3}m$ cubic structures are generated in the vicinity of the particle surface depending on the voltage for the charge process. The generation of these structures is related to the upper voltage for the charge process; the voltage at which the $R3m$ rhombohedral structure is generated tends to be higher than the voltage at which the $Fd\overline{3}m$ cubic structure is formed. The structural variation of Li$_2$MnO$_3$ is associated with the introduction of oxygen molecules which is accelerated as the voltage for the charge process increases. Furthermore, the generation of the $R3m$ rhombohedral structure could be interpreted by the suppression of the Jahn–Teller distortion due to the introduction of oxygen vacancies during cycling.

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