High-pressure synthesis and electrochemical properties of tetragonal LiMnO$_2$†

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Tetragonal structured LiMnO$_2$ (t-LiMnO$_2$) samples were synthesized under pressures above 8 GPa and investigated as a positive electrode material for lithium-ion batteries. Rietveld analyses based on X-ray diffraction measurements indicated that t-LiMnO$_2$ belongs to a γ-LiFeO$_2$-type crystal structure with the $I4_1/amd$ space group. The charge capacity during the initial cycle was 37 mA h g$^{-1}$ at 25 °C, but improved to 185 mA h g$^{-1}$ at 40 °C with an average voltage of 4.56 V vs. Li$^+$/Li. This demonstrated the superiority of t-LiMnO$_2$ over other lithium manganese oxides in terms of energy density. The X-ray diffraction measurements and Raman spectroscopy of cycled t-LiMnO$_2$ indicated an irreversible transformation from the γ-LiFeO$_2$-type structure into a Li$_2$Mn$_2$O$_4$ spinel structure by the displacement of 25% of the Mn ions to vacant octahedral sites through adjacent octahedral sites.

Introduction

Lithium manganese oxides (LMOs) have been extensively studied as a potential positive electrode material for lithium-ion batteries (LIBs), due to their low cost and environmental friendliness. Since such properties are crucial for large-scale applications for LIBs such as electric vehicles and grid energy storage systems, research efforts have been devoted to the development of LMOs with high energy densities ($W_a$). Table 1 summarizes the structure types, synthesis methods, and electrochemical properties of previously reported LMOs, and their crystal structures are shown in Fig. 1a-g. Of these LMOs, a cubic spinel-structured LiMn$_2$O$_4$ (Fig. 1a) is widely accepted as the most practical positive electrode material.\textsuperscript{1,2,8} LiMn$_2$O$_4$ exhibits a rechargeable capacity ($Q_{\text{recha}}$) of approximately 120 mA h g$^{-1}$ with an average voltage ($E_{\text{ave}}$) of 4.1 V vs. Li$^+$/Li, and its $W_a$ approaches the theoretical limit value due to the moderate theoretical capacity ($Q_{\text{theo}}$) of 148 mA h g$^{-1}$.

In terms of the $Q_{\text{theo}}$, LiMnO$_2$ and its derivatives are appealing, and their structural and electrochemical properties vary depending on their composition and method of synthesis. A monoclinic layered Li$_2$MnO$_3$, also written as Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ (Fig. 1b), has a large $Q_{\text{theo}}$ of 458 mA h g$^{-1}$. However, Li$_2$MnO$_3$ is essentially electrochemically inactive because of the difficulty in further oxidizing the Mn$^{3+}$ species,\textsuperscript{a} unless a proton exchange and/or an oxygen loss\textsuperscript{a} in its lattice proceed during the initial charge reaction. An orthorhombic LiMnO$_2$ (o-LiMnO$_2$)\textsuperscript{3,5} and a monoclinic LiMnO$_2$ (m-LiMnO$_2$)\textsuperscript{4,6,7} have a formal oxidation state of Mn$^{4+}$ (Fig. 1c and d) and their charge capacities ($Q_{\text{recha}}$) reach a maximum of 230 mA h g$^{-1}$ for o-LiMnO$_2$ and 270 mA h g$^{-1}$ for m-LiMnO$_2$. However, delithiated o- and m-LiMnO$_2$ can be irreversibly and spontaneously transformed into a Li$_2$Mn$_2$O$_4$ spinel; thus, the $Q_{\text{recha}}$ values for both of these compounds decrease in a manner similar to that seen in LiMn$_2$O$_4$ as the changes in the charge and discharge curves echo those of Li$_2$Mn$_2$O$_4$.\textsuperscript{1,2,6,7} In contrast, O$_2$-type layered Li$_{2/3}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$ (ref. 20) and Li$_{1/4}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$ with $p$ = 1 (ref. 21) (Fig. 1e and f) were reported to display good cycleability without transformation into the Li$_2$Mn$_2$O$_4$ spinel. The oxygen stacking, which is ABACAB for Li$_{2/3}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$ and Li$_{1/4}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$ ( unlike the ABCABC stacking seen in m-LiMnO$_2$), plays an important role in this. As a result, the $Q_{\text{recha}}$ is 150 mA h g$^{-1}$ for Li$_{2/3}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$ and 200 mA h g$^{-1}$ for Li$_{1/4}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$. In the initial cycle, the $Q_{\text{cha}}$ ranges between 20 and 50 mA h g$^{-1}$, and is smaller than the $Q_{\text{recha}}$ due to lithium deficiency in these compounds. This triggers a decrease in the $Q_{\text{recha}}$ whenever these compounds are used in full cells with negative electrode materials that do not contain residual lithium, e.g. graphite and silicon.

Sugiyama et al. synthesized a tetragonal LiMnO$_2$ (t-LiMnO$_2$) from o-LiMnO$_2$ by a high-pressure and high-temperature method, with pressures between 4 and 6 GPa and temperatures between 900 and 1200 °C.\textsuperscript{22} Rietveld analyses based on X-ray diffraction (XRD) measurements showed that t-LiMnO$_2$ has a γ-LiFeO$_2$-type structure with $I4_1/amd$ space group (Fig. 1g). In this structure, Mn$_{6}$ octahedra form a three-dimensional...
| Compounds                  | Structure types (space group) | Synthesis methods | Electrochemical properties | Remarks                                      |
|---------------------------|------------------------------|-------------------|---------------------------|---------------------------------------------|
| LiMnO₄                    | Cubic spinel (Pm₃m)          | Solid-state reaction | Q_{cha} ~ 120 mA h g⁻¹ , E_{ave} ~ 3.8 V | Electrochemically inactive 9 and 10          |
| o-LiMnO₂                  | Monoclinic layer (C2/n)      | Solid-state reaction | Q_{cha} = 180–230 mA h g⁻¹ , E_{ave} ~ 3.6 V | Transformation into spinel phase on the charge reaction phase in a full cell because of the Q_{cha} in a full cell |
| m-LiMnO₂                  | Monoclinic layer (C2/n)      | Ion exchange method | Q_{cha} = 270 mA h g⁻¹ , E_{ave} ~ 3.5 V | Decrease of the Q_{cha} on the charge reaction |
| Li₂[Li₁/₃Mn₂/₃]O₂         | O₂-type layer (R₃m)         | Ion exchange method | Q_{cha} = 190 mA h g⁻¹ , E_{ave} ~ 3.2 V | Transformation into spinel phase on the charge reaction |
| Li₁/₃Li₄/₃MnO₂           | γ-LiFeO₂ (Pm₃n)             | High-pressure and high-temperature method | Q_{cha} = 200 mA h g⁻¹ , E_{ave} ~ 3.0 V | Decrease of the Q_{cha} in a full cell |
| Li₄/₃Li₁/₃MnO₂           |                             |                   |                           |                                             |
| t-LiMnO₂                  |                             |                   |                           | This work                                    |

Table 1 Crystal structures, synthesis methods, and electrochemical properties of various lithium manganese oxides

Despite its unique crystallographic character, the electrochemical properties of t-LiMnO₂ remain unclear. This is likely due to the difficulty in conducting large-scale synthesis via the high-pressure method because a tiny sample container is generally used to generate high pressure (>10 GPa). However, recent technological developments, including the use of belt-, ring-, and multi-anvil-type equipment, enabled us to evaluate a variety of functional materials. In the current study, we synthesized t-LiMnO₂ under high pressures up to 12 GPa and reported its electrochemical performance as a positive electrode material for LIBs for the first time, in order to clarify the relationship between the structural and electrochemical properties of t-LiMnO₂. The Q_{cha} of t-LiMnO₂ reached 185 mA h g⁻¹ with an E_{ave} of 4.56 V upon increasing the operating temperature to 40 °C, which is superior to other LMOs. This information will be helpful in designing advanced LMOs with high W in terms of their structure and composition.

**Experimental**

**Sample preparations**

t-LiMnO₂ was synthesized from o-LiMnO₂ by the high-pressure and high-temperature method using a Walker-type apparatus. o-LiMnO₂ was first synthesized via solid-state reactions. Stoichiometric amounts of LiOH·H₂O (Wako Pure Chemical Industries Ltd.) and Mn₃O₄ (Wako Pure Chemical Industries Ltd.) were mixed in ethanol and the mixture was dried and pressed into a 5 mm-thick pellet with a diameter of 15 mm. The pellet was heated at 1000 °C for 12 h under argon gas flow at a heating rate of 200 °C h⁻¹ and a cooling rate of 1 °C min⁻¹. The obtained o-LiMnO₂ was crushed and re-pressed into a 5 mm-thick pellet with a diameter of 2.8 mm before being packed into a platinum capsule. The capsule was then placed in a BN insulation sleeve, which was placed in a cylindrical graphite heater. The assembled sample was placed in a (Mg, Co)O octahedral pressure medium with side lengths of 14 mm. The (Mg, Co)O octahedra were slowly compressed to 5, 8, or 12 GPa by eight tungsten carbide truncated 8 mm edges. The compressed samples were then heated at 1000 °C for 30 min and subsequently quenched to room temperature, and the pressure was slowly released until an ambient pressure was achieved. Hereafter, the o-LiMnO₂ samples treated at 5, 8, and 12 GPa are represented as LMO (5 GPa), LMO (8 GPa), and LMO (12 GPa), respectively, to avoid a misunderstanding of the actual phase purity. A powder sample of LiMn₂O₄ was also synthesized by heating a mixture of LiOH·H₂O and MnO₂ (Kojundo Chemical Laboratory Co., Ltd.) at 1000 °C for 12 h under oxygen gas flow.
Characterization of the samples

The powder samples of o-LiMnO₂, LMO (5 GPa), LMO (8 GPa), and LMO (12 GPa) were characterized by scanning electron microscopy (SEM), synchrotron XRD measurements, and Raman spectroscopy. The SEM images were recorded using an S-3600N (Hitachi High-Technologies, Company Ltd.) at an accelerating voltage of 15 kV. The XRD measurements were conducted at a BL5S2 beamline available at the Aichi Synchrotron Radiation Center. The samples were packed into borosilicate glass capillary tubes with a diameter of 0.3 mm (WJM-Glas Müller GmbH). The XRD patterns were collected using a two-dimensional detector, PILATUS 100K (Dectris Ltd., Baden-Daettwil), over a 2θ range between 5° and 95°. The incident X-ray wavelength (λ) was determined to be 0.799323(2) or 0.799670(2) Å from the XRD patterns of silicon powders (NIST 640d). Rietveld analyses and drawings of crystal structures were carried out using the Rietan-FP²⁹ and VESTA softwares,³⁰ respectively. The Raman spectra were collected on an NRS-3300 (Jasco Co. Ltd.) using an excitation laser wavelength of 532 nm and a laser power of 0.1 mW. The duration of exposure was 600 s.

Electrochemical properties

The electrochemical reactivities of the o-LiMnO₂, LMO (5 GPa), LMO (8 GPa), and LMO (12 GPa) samples were examined with sandwich-type two-electrode cells. The powdered sample, acetylene black (AB, Denka Co., Ltd.), and polytetrafluoroethylene (PTFE, Daikin Industries Ltd.) were combined in a ratio of 70 : 20 : 10 to give a viscoelastic mixture, which was then pressed onto an aluminum mesh current collector with a diameter of 16 mm. The mixture functioned as a working electrode. Lithium metal pressed onto 19 mm-wide stainless steel was used as a counter electrode. The electrolyte was made from a solution of 1 M LiPF₆ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) at an EC : DMC ratio of 3 : 7 v/v (Kishida Chemical Company Ltd.) and the separator was constructed from two sheets of porous polyethylene membrane (Tonen-General Sekiyu K. K.). The cells were assembled in an argon-filled glove box and operated at a current density of 0.025 mA cm⁻². The voltage ranged from 1.8 to 4.8 V and the operating temperature was set at 25 or 40 °C.

After cycling test at 25 °C, crystal structures of the samples were investigated using synchrotron XRD and Raman measurements to clarify both macroscopic and microscopic structural changes during the cycling. The cells were charged and discharged twenty times at 25 °C. The cycled samples were then taken from the working electrodes, which had been thoroughly rinsed with a diethyl carbonate solution. Each of the samples was packed into a capillary tube with a diameter of 0.7 mm and put into a quartz glass cell (GL Sciences Inc.) for the XRD measurements and for the Raman spectroscopy, respectively. All the procedures were conducted in the argon-filled glove box, so as not to contact with the atmosphere. The laser power of the Raman spectroscopy was set at 1.0 mW in consideration of absorbance of the quartz cell. The Raman spectra of the charged LMO (12 GPa) sample, LiMn₂O₄, PTFE, and AB were also measured.

Results and discussion

Morphological and structural characterization

Fig. 2a–d show SEM images for the o-LiMnO₂, LMO (5 GPa), LMO (8 GPa), and LMO (12 GPa) samples, respectively. Particles of o-LiMnO₂ exhibit flake-like shapes with widths between 2–10 μm and thicknesses less than 2 μm. The particle shapes appear to round out and become uniform in size with increasing applied pressure, i.e., rough shapes with a dispersive size of 1–10 μm at 5 GPa and smooth morphologies with a dominant size of ~8 μm at 8 GPa and 12 GPa were observed. This morphological change is likely due to a phase transformation, as will be discussed below.

Fig. 3 shows the results of Rietveld analyses for the (a) o-LiMnO₂, (b) LMO (5 GPa), (c) LMO (8 GPa), and (d) LMO (12 GPa) samples. The crystal structure of the o-LiMnO₂ sample was
assigned as an orthorhombic $\beta$-NaMnO$_2$-type structure with $Pmmn$ space group; that is, a zigzag layered structure in which Li and Mn atoms occupy each of the octahedral $2b$ sites (Fig. 1c). However, the $\alpha$-LiMnO$_2$ sample is not in a single phase but contained some impurity phases as shown by asterisk marks at around $2\theta = 10^\circ$ and $16^\circ$, and these were found to be hausmannite (Mn$_3$O$_4$ with $I4_1/amd$ space group) and spinel LiMn$_2$O$_4$ by examining the possible crystal structures of LMOs and manganese oxides. Thus, we performed Rietveld analyses with three coexisting phases, in which a Mn under-stoichiometric Li$_{1+\delta}$Mn$_{1-\delta}$O$_2$ is adopted to refine the crystal structure of $\alpha$-LiMnO$_2$. Here, $\delta$ represents the Mn deficiency due to impurities. Moreover, we considered Li and Mn atoms to randomly occupy each of the $2b$ sites, as a cation mixing of Li and transition metal ions occasionally occurs in lithium insertion materials.$^{34}$ The structure parameters of the $\alpha$-LiMnO$_2$ sample are listed in Table 2. The lattice parameters of $\alpha$-LiMnO$_2$ were calculated to be $a_0 = 2.80700(2)$ Å, $b_0 = 4.57721(2)$ Å, and $c_0 = 5.75210(3)$ Å. The actual composition was determined to be Li$_{1.005}$Mn$_{0.995}$O$_2$ ($\delta = 0.005$), where 1.5% of the Mn ions occupied Li ($2b$) sites. The weight fractions were 98.9 wt% for Li$_{1.005}$Mn$_{0.995}$O$_2$, 0.7 wt% for Mn$_3$O$_4$, and 0.4 wt% for LiMn$_2$O$_4$, giving a Li/Mn ratio of 0.999/1.000, which was consistent with the Li/Mn ratio of the starting material.

For the LMO (5 GPa) sample, the diffraction line at $2\theta = 12.8^\circ$ decreases, but the diffraction line at $2\theta = 12.3^\circ$ clearly generates, due to the formation of the $t$-LiMnO$_2$ phase (see the inset of Fig. 3b). As listed in Table S1,† the mass fractions of $\alpha$-LiMnO$_2$ and $t$-LiMnO$_2$ were found to be 86.6 and 8.6 wt%, respectively. For the LMO (8 GPa) and LMO (12 GPa) samples,
the diffraction line at 2θ = 12.8° disappears, and almost all diffraction lines can be assigned as the tetragonal γ-\text{LiFeO}_2-type structure with \text{I}4_1/\text{amd} space group (Fig. 3c and d). The hausmannite impurity also transformed into a CaMnO_2-type structure (\textit{Pbcm}) with an applied pressure up to 8 GPa.\textsuperscript{22} Table 3 shows the structure parameters of the LMO (12 GPa) sample as determined by Rietveld analyses under identical assumptions as the o-LiMnO_2 sample. The tetragonal lattice parameters, \(a_t\) and \(c_t\), were determined to be 4.18278(2) and 8.22922(6) Å, respectively. Note that the actual composition of t-LiMnO_2, Li_{1.012}Mn_{0.988}O_2 (\(\delta = 0.012\)), was almost identical to that of o-LiMnO_2. From the occupancy factor, \(g\), it was shown that Mn ions occupy 0.8% of the Li (\(4a\)) sites. As shown in Table S3,\textsuperscript{4} there were no significant differences in the structural parameters, including the \(a_t\), \(c_t\), composition, atomic coordination, and \(g\) between the LMO (8 GPa) and LMO (12 GPa) samples.

The change in the XRD patterns indicated that o-LiMnO_2 gradually transformed into t-LiMnO_2 at 5 GPa, with the phase transformation occurring as the pressure reached 8 GPa. Conversely, Sugiyama \textit{et al.} reported that this phase transformation was completed at a pressure of 5 GPa in Mn overstoichiometric \text{Li}_{0.93}\text{Mn}_{1.07}O_2.\textsuperscript{23} Therefore, the transformation from o-LiMnO_2 to t-LiMnO_2 is very sensitive to the Li/Mn ratio of o-LiMnO_2: Mn under-stoichiometric \text{Li}_{1.1}\text{Mn}_{0.9}O_2 (\(\delta = 0.1\)) actually transformed into a rock-salt structure rather than into t-LiMnO_2 at 5 GPa and 1000 °C.\textsuperscript{22}

Fig. 4a–d show Raman spectra of the o-LiMnO_2, LMO (5 GPa), LMO (8 GPa), and LMO (12 GPa) samples, respectively. Factor group analyses\textsuperscript{31} predicted twelve Raman bands of 4\(A_g\) + 4\(B_{2g}\) + 4\(B_{3g}\) for o-LiMnO_2 structure and eight Raman bands of 4\(A_{1g}\) + 3\(B_{1g}\) + 4\(E_g\) for t-LiMnO_2 structure. The Raman spectrum for the o-LiMnO_2 sample shows three major Raman bands at 411, 556, and 657 cm\(^{-1}\) and three minor Raman bands at 191, 363, and 488 cm\(^{-1}\). Although all of the Raman bands are not fully assigned, according to the previous reports,\textsuperscript{34–36} the major Raman bands are attributed to vibrations in the \text{MnO}_6 octahedra, that is, the O–Mn–O stretching modes at 657 cm\(^{-1}\), the O–Mn–O bending modes at 556 cm\(^{-1}\), and the Mn–O–Mn deformation modes at 441 cm\(^{-1}\). The Raman spectrum of the LMO (5 GPa) sample is similar with that of the o-LiMnO_2 sample, however, the intensities of the Raman bands at ~411, 556, and 657 cm\(^{-1}\) become weak compared with its original Raman spectrum. Furthermore, new and weak Raman bands are observed at 406, 510, and 617 cm\(^{-1}\), and these Raman bands are clearly observed in the Raman spectra of the LMO (8 GPa) and LMO (12 GPa) samples. There are at least ten Raman bands in the Raman spectrum of the LMO (12 GPa) sample, although the theoretical calculation predicted eight Raman bands. This difference is probably due to the nonstoichiometry and/or impurity phases in the LMO (12 GPa) sample. Anyway Raman spectroscopy clarified that the transformation from o-LiMnO_2 to t-LiMnO_2 is achieved under pressures above 8 GPa, which is consistent with the results of the XRD measurements.

\textbf{Electrochemical properties}

Fig. 5a shows charge and discharge curves of the Li cell with the LiMnO_2 sample, operated at temperature of 25 °C. The cell voltage (\(\mathcal{E}\)) increases rapidly from an open circuit voltage (~3.1

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**Table 2** Structure parameters of the o-LiMnO_2 sample determined by Rietveld analyses

| Phase    | Space group | Atom | Wyckoff position | \(g^a\)  | x   | y   | z   | \(B^d/Å^2\) |
|----------|-------------|------|------------------|--------|-----|-----|-----|-------------|
| o-LiMnO_2 | \textit{Pmmn} | Li1  | 2b               | 0.985(1) | 1/4 | 3/4 | 0.1188(9) | 1.32(8)     |
|          |             | Mn1  | 2b               | 0.015(1) | 1/4 | 3/4 | 0.6347(1) | 0.55(1)     |
|          |             | Mn2  | 2b               | 0.980(1) | 1/4 | 3/4 | 0.6347(1) | 0.55(1)     |
|          |             | Li2  | 2b               | 0.020(1) | 1   | 1   | 0.1432(3) | 0.58(2)     |
|          |             | O1   | 2a               | 1       | 1   | 1   | 0.6004(3) | 0.58(2)     |
|          |             | O2   | 2a               | 1       | 1   | 1   | 0.6004(3) | 0.58(2)     |

\textbf{Table 3} Structure parameters of the LMO (12 GPa) sample determined by Rietveld analyses

| Phase    | Space group | Atom | Wyckoff position | \(g^a\)  | x   | y   | z   | \(B^d/Å^2\) |
|----------|-------------|------|------------------|--------|-----|-----|-----|-------------|
| t-LiMnO_2 | \textit{I}4_1/\text{amd} | Li1  | 4a               | 0.992(1) | 0   | 3/4 | 1/8 | 1.31(9)     |
|          |             | Mn1  | 4a               | 0.008(1) | 0   | 3/4 | 1/8 | 1.31(9)     |
|          |             | Mn2  | 4b               | 0.980(1) | 0   | 1   | 3/8 | 0.51(1)     |
|          |             | Li2  | 4b               | 0.020(1) | 0   | 1   | 3/8 | 0.51(1)     |
|          |             | O1   | 8e               | 1       | 0   | 1/4 | 1.213(1) | 1.2(2)      |

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\textbf{Composition: }\text{Li}_{1.000}\text{Mn}_{0.995}O_2 (\(\delta = 0.005\)), \(a_t = 2.87007(2) Å, \ b_t = 4.57721(2) Å, \) and \(c_t = 5.75210(3) Å\)

Reliable factors: \(R_{wp} = 5.685\%, \ R_p = 4.184\%, \) and \(S = 0.4501\)

Mass fractions: 98.9 wt% for o-LiMnO_2, 0.7 wt% for Mn_{3}O_{4}, and 0.4 wt% for LiMn_2O_4

\(\delta \) Constraints: \(g(Mn1) = 1 - g(Li1), g(Mn2) = g(Li1) - \delta, g(Li2) = 1 + \delta - g(Li1), g(Mn1) = z(Li1), g(Mn2) = z(Mn2), g(B(Mn1)) = g(B(Li1)), g(B(Li2)) = g(B(Mn2)), \) and \(g(B(O2)) = g(B(O1))\).
V) before plateauing at $\sim 3.5$ V when the $Q_{\text{cha}}$ reaches 120 mA h g$^{-1}$. Then, the $E$ climbs to 4.8 V with a gentle gradient during the initial charge. In the discharge curve, however, the $E$ drops sharply to 3.5 V, and gradually decreases to $\sim 3.0$ V without any clear voltage plateaus. The $Q_{\text{cha}}$ is 160 mA h g$^{-1}$, whereas discharge capacity ($Q_{\text{dis}}$) is only 70 mA h g$^{-1}$. New voltage plateaus appeared at 3.0 and 4.0 V in subsequent charge and discharge curves. The differences in charge and discharge curves between 1st and subsequent cycles is caused by an irreversible structural transformation to the Li$_{x}$Mn$_2$O$_4$ spinel during the initial cycle, as previously reported.\(^{12,18,37}\)

Fig. 5b-d display the charge and discharge curves of the lithium cells with the LMO (5 GPa), LMO (8 GPa), and LMO (12 GPa) samples, respectively. The charge and discharge curves of these three samples are clearly different from those of o-LiMnO$_2$; i.e., the $E$ monotonically increases from 3.2 V to 4.8 V without any apparent voltage plateaus. The $Q_{\text{cha}}$ of LMO (5 GPa) is 154 mA h g$^{-1}$, while the $Q_{\text{cha}}$ values of LMO (8 GPa) and LMO (12 GPa) are 41 and 37 mA h g$^{-1}$, respectively, which are approximately 13% of the $Q_{\text{theo}}$. The initial discharge curves have a similar $E$ profile with a broad center at $\sim 3.0$ V. The $Q_{\text{dis}}$ values of the LMO (5 GPa), LMO (8 GPa), and LMO (12 GPa) samples are 52, 21, and 22 mA h g$^{-1}$, respectively. Besides the decline in the $E$, as similarly noted for o-LiMnO$_2$, both the charge and discharge curves display multiple voltage plateaus with an increasing cycle number. This implied that t-LiMnO$_2$ irreversibly transformed into the Li$_{x}$Mn$_2$O$_4$ spinel with the electrochemical cycling. The cycle performances of these four samples are given in Fig. S1.\(^{1}\) The $Q_{\text{cha}}$ and $Q_{\text{dis}}$ values of o-LiMnO$_2$ [LMO (5 GPa)] increase with the cycle numbers until tenth cycles, and then maintain at $\sim 150$ (100) mA h g$^{-1}$. On the other hand, the $Q_{\text{cha}}$ and $Q_{\text{dis}}$ values of LMO (8 GPa) and LMO (12 GPa) increase with the cycle numbers up to twenty cycles. The $Q_{\text{cha}}$ and $Q_{\text{dis}}$ values of LMO (12 GPa) are similar with those of o-LiMnO$_2$.

Fig. 6a and b show charge and discharge curves of the lithium cells with the o-LiMnO$_2$ and LMO (12 GPa) samples, respectively, operated at temperature of 40 °C. The initial $Q_{\text{cha}}$ of o-LiMnO$_2$ is approximately 200 mA h g$^{-1}$, which is larger than the value ($\sim 160$ mA h g$^{-1}$) obtained at 25 °C. This originates from the appearance of a moderate voltage plateau over 4.0 V with a $Q_{\text{cha}}$ of $\sim 50$ mA h g$^{-1}$, as reported for an o-LiMnO$_2$/Li cell at 55 °C by Cho.\(^{38}\) Subsequent charge and discharge curves reveal the increases in $Q_{\text{cha}}$ from 200 mA h g$^{-1}$ to 225 mA h g$^{-1}$ and in $Q_{\text{dis}}$ from 155 mA h g$^{-1}$ to 220 mA h g$^{-1}$. The irreversible transformation into the Li$_{x}$Mn$_2$O$_4$ spinel is thought to be accelerated, compared to the measurements at 25 °C.
could be kinetically removed from the lattice during the initial charge. A high $E_{\text{ave}}$ is favorable for the potential application of t-LiMnO$_2$ in this field.

The initial discharge curve, by contrast, could not maintain this $E_{\text{ave}}$ and exhibited a $Q_{\text{dis}}$ of 87 mA h g$^{-1}$, resulting in a $W$ value of 273 mW h g$^{-1}$. This was due to the type of polarization, which was similar to that seen in the results obtained at 25 °C. With an increasing cycle number, the $Q_{\text{cha}}$ and $Q_{\text{dis}}$ improved to approximately 210 mA h g$^{-1}$. Nevertheless, the $E_{\text{ave}}$ was about 2.9 V at discharge and 4.0 V at charge over the course of more than two cycles. The $W$ in the charge and discharge curves during the fifth cycle was 815 mW h g$^{-1}$ and 618 mW h g$^{-1}$, respectively.

### Crystal structure change upon electrochemical cycling

**Ex situ** XRD measurements and Raman spectroscopy were conducted on the cycled electrodes to understand the phase transformation of t-LiMnO$_2$ during cycling. The XRD patterns of the cycled o-LiMnO$_2$ and LMO (12 GPa) samples are shown in Fig. 7a and b, respectively. The XRD pattern of o-LiMnO$_2$ is assigned as a mixture of the Li$_x$Mn$_{2-x}$O$_4$ spinel and LiMn$_2$O$_4$ with a spinel-type structure. The lattice parameters, which were calculated using the least squares method with more than five non-overlapping diffraction lines, are found to be $a_c = 8.224(9)$ Å for Li$_x$Mn$_{2-x}$O$_4$ and $a_t = 5.666(6)$ Å for LiMn$_2$O$_4$. Since these lattice parameters correspond to those for Li$_{0.92}$Mn$_{0.08}$O$_4$ ($a_c = 8.230$ Å) and Li$_{1.82}$Mn$_2$O$_4$ ($a_t = 5.654$ Å and $c_t = 9.202$ Å), the $x$ and $y$ values are estimated to be 0.98 and 1.82, respectively.

As seen in Fig. S3,† the Raman spectrum of the charged LMO (12 GPa) sample is similar with that of the pristine LMO (12 GPa) sample, except for the Raman band at 650 cm$^{-1}$, resulting in a $W$ value of 263 mW h g$^{-1}$. This indicates that the local structure of LMO (12 GPa) is maintained during the initial charge reaction. However, Fig. 8 clarifies that the extended twenty cycle test converts the t-LiMnO$_2$ structure into the spinel structure. That is, there are only three broad Raman bands at 650, 620, and 490 cm$^{-1}$ in the cycled LMO (12 GPa) sample, except for the Raman band at 654 cm$^{-1}$.
in Fig. S5,† the Raman spectrum of PTFE shows three major Raman bands at 733, 385, and 290 cm\(^{-1}\), while that of AB is featureless. The contributions of PTFE and AB are, hence, negligibly small to the Raman spectra of the cycled (or charged) LMO samples.

Fig. 9 shows possible mechanisms of the transformation into the spinel structure from the delithiated (a) o-LiMnO\(_2\) and (b) t-LiMnO\(_2\). Oxide ions in o-LiMnO\(_2\), t-LiMnO\(_2\), and Li\(_x\)Mn\(_2\)O\(_4\) spinel are arranged in the same ABCABC stacking manner along the [012] direction for o-LiMnO\(_2\), [112] for t-LiMnO\(_2\), and [111] for Li\(_x\)Mn\(_2\)O\(_4\), although the orderings between Mn and vacancy (or Li) octahedral sites are different each other. According to Thackeray et al.,\(^{15}\) Li\(_x\)Mn\(_2\)O\(_4\) is formed from two repeating types of MnO\(_2\) sheets, as shown in the left and right sides of Fig. 9. Thus, there are two ways for the transformation into the spinel from o-LiMnO\(_2\) or t-LiMnO\(_2\). In the case of o-LiMnO\(_2\), the transformation is caused by the displacement of half of the Mn ions to adjacent vacant octahedral sites.\(^{15-17}\) By contrast, the transformation of t-LiMnO\(_2\) is achieved by the displacement of a quarter of the Mn ions in the 4\(b\) sites into the vacant octahedral sites (4\(a\) via adjacent octahedral sites without a rearrangement of the ABCABC oxygen packing (Fig. 9b). In this transformation, t-LiMnO\(_2\) has 50% lower amounts of migrated Mn ions, resulting in approximately twice longer in routes of Mn ions, compared to the case for o-LiMnO\(_2\).

The transformation mechanism of t-LiMnO\(_2\) shows that a suppression of the Mn displacement at the charged state is essential for realizing electrochemical properties such as the \(Q_{\text{rch}}, E_{\text{avr}},\) and \(W\) in the initial charge state over several cycles. Although the blocking effect of the movement of Mn ions in o-LiMnO\(_2\) has not been reported for the substitution of different cations with Li ions, a small amount of doping could be suitable for t-LiMnO\(_2\) due to the small amount of migrated Mn ions and their long displacement distance. Recently, electrochemical properties of tetragonal structured Li\(_{0.35}\)MnO\(_2\) (ref. 45) and Li\(_{0.59}\)MnO\(_2\) (ref. 46) nanoparticles were reported; i.e., the initial \(Q_{\text{rch}}\) and \(Q_{\text{dis}}\) values of the nanosized Li\(_{0.35}\)MnO\(_2\) are 72.9 and

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**Fig. 7** Ex situ XRD patterns of the cycled (a) o-LiMnO\(_2\) and (b) LMO (12 GPa) samples. The measurements were performed at the discharged states, as indicated by the red arrows in Fig. 5a and d. Diffraction lines represented by red triangles, green squares, blue circles, and magenta diamonds, originate from those from Li\(_x\)Mn\(_2\)O\(_4\) with the spinel structure, Li\(_y\)Mn\(_2\)O\(_4\) with tetragonal structure, t-Li\(_x\)MnO\(_2\), and PTFE, respectively. The Bragg positions for each of these phases are also shown in the bottom using identically colored vertical lines.

**Fig. 8** Ex situ Raman spectra of the cycled (a) o-LiMnO\(_2\) and (b) LMO (12 GPa) samples together with the Raman spectrum of the pristine (c) LiMn\(_2\)O\(_4\). Raman spectra of (a) and (b) were taken at the discharged state, as indicated by the red arrows in Fig. 5a and d.

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during the initial charge, even though it was only 37 mA h g\(^{-1}\) at 25 °C. Furthermore, the initial charge curve showed that the \(E_{\text{ave}}\) (4.56 V) with Mn\(^{3+}/\text{Mn}^{4+}\) redox was the highest among LMOs such as \(\alpha\)-LiMnO\(_2\) and LiMn\(_2\)O\(_4\). However, the initial discharge curve did not maintain the \(E_{\text{ave}}\) and exhibited a \(Q_{\text{dis}}\) of 87 mA h g\(^{-1}\) due to an irreversible phase transformation into the Li\(_2\)Mn\(_2\)O\(_4\) spinel during the initial charge. Substitution of different cations and optimization of Li content and particle size will be necessary to maintain the electrochemical properties of t-LiMnO\(_2\) throughout long cycles.

**Conflicts of interest**

There are no conflicts to declare.

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