

Synthesis of Rhombohedral $\text{LiCo}_{0.64}\text{Mn}_{0.36}\text{O}_2$ Using a High-Pressure Method

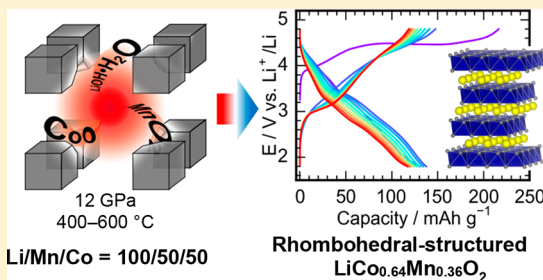
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Supporting Information

ABSTRACT: Lithium transition metal (M) oxides with a rhombohedral structure, $r\text{-LiMO}_2$, have attracted a great deal of attention as a positive electrode material for lithium-ion batteries. Despite intensive studies thus far, Mn-rich $r\text{-LiMO}_2$ compounds have remained unattainable, due to a cooperative Jahn–Teller distortion of Mn^{3+} ions in the MnO_6 octahedra. We employed a high-pressure method for synthesizing $r\text{-LiCo}_x\text{Mn}_{1-x}\text{O}_2$ ($r\text{-LCMO}$) with $x = 0.5$ and examined its electrochemical properties in a nonaqueous lithium cell. The high-pressure method successfully suppressed the Jahn–Teller distortion of Mn^{3+} ions, and the $r\text{-LCMO}$ phase was observed in a wide temperature–pressure region when using a $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor. The rechargeable capacity of the sample synthesized at 600 °C and 12 GPa reached 126 mAh g^{-1} , although the $r\text{-LCMO}$ phase was contaminated with electrochemically inactive rock-salt LCMO and hexagonal LCMO phases. Compositional and structural analyses clarified that the actual Co/Mn ratio of the $r\text{-LCMO}$ phase was 64/36, which deviated slightly from the initial composition (50/50). The high-pressure method was found to be effective for synthesizing Mn-rich $r\text{-LiMO}_2$ compounds, although their electrochemical properties should be improved.



1. INTRODUCTION

Secondary batteries with a high energy density (W) and a long cycle life are currently indispensable for issues such as energy conservation and sustainable development. Lithium-ion batteries (LIBs), which consist of two insertion electrodes and a nonaqueous electrolyte, could be a candidate battery; however, W is still insufficient for these goals.¹ The W value of LIBs strongly depends on that of a positive electrode material,^{2,3} where the rechargeable capacity (Q_{recha}) multiplied by the average redox potential ($E_{\text{redox}}^{\text{ave}}$) equals W . A review article⁴ on positive electrode materials with various crystal structures clarified that the highest W is reached when using a layered LiMO_2 (M represents a 3d transition metal) with the $R\bar{3}m$ space group ($r\text{-LiMO}_2$), in which Li^+ , M^{3+} , and O^{2-} ions occupy the $3b$, $3a$, and $6c$ sites, respectively (Figure 1a). Although many other materials have been developed over the past 30 years, $r\text{-LiMO}_2$ compounds, such as LiCoO_2 , LiNiO_2 , and their derivatives, remain attractive positive electrode materials for high- W LIBs.^{5–7}

Figure 1b shows the ternary phase diagram consisting of LiCoO_2 , LiNiO_2 , and LiMnO_2 . As described above, LiCoO_2 ^{8,9} and LiNiO_2 ^{10,11} crystallize into a layered structure with the $R\bar{3}m$ space group, whereas LiMnO_2 crystallizes into an orthorhombic (zigzag) structure with the $Pmmn$ space group ($o\text{-LiMnO}_2$)¹² or a monoclinic structure with the $C2/m$ space group ($m\text{-LiMnO}_2$).¹³ This is probably a consequence of cooperative Jahn–Teller (JT) distortion in the MnO_6

octahedra, in which Mn^{3+} ions are in a high-spin state with $t_{2g}^3e_g^1$ ($S = 2$).¹⁴ Note that LiNiO_2 exhibits noncooperative JT distortion, although Ni^{3+} ions have a JT-active configuration, i.e., a low-spin state with $t_{2g}^6e_g^1$ ($S = 1/2$).¹⁵ Such intrinsic behavior of Mn^{3+} ions has limited the production of Mn-rich $r\text{-LiMO}_2$. Actually, $r\text{-LiMO}_2$ compounds, as reported in the International Centre for Diffraction Data (ICDD) accessed with PDF-4+ 2018 software,¹⁶ are extremely localized on the right side of the $\text{LiCoO}_2\text{–LiMnO}_2\text{–LiNiO}_2$ phase diagram. Seventeen exceptions^{17–33} appear in the left region; among these, nine compounds^{17–25} were prepared by an ion-exchange reaction originating from $\text{NaCo}_x\text{Mn}_{1-x}\text{O}_2$ compounds, while one compound, $\text{Li}_{0.89}\text{Co}_{0.67}\text{Mn}_{0.33}\text{O}_2$,²⁶ contained a significant amount of hydrated water ($\sim 0.72\text{H}_2\text{O}$). Note that the Li composition of materials synthesized by the ion-exchange method is less than 1, resulting in a decrease in Q_{recha} .^{17–25} Thus, the upper limit of the Mn substitution for Co, namely, x in $r\text{-LiCo}_{1-x}\text{Mn}_x\text{O}_2$ ($r\text{-LCMO}$), is located at $x \leq 0.2$ when using a conventional solid-state reaction technique.^{26–33}

Assuming one electron transfer per molecule, the theoretical capacity (Q_{theo}), i.e., the maximum Q_{recha} is similar among the LiCoO_2 , LiMnO_2 , and LiNiO_2 phases ($\approx 280 \text{ mAh g}^{-1}$), suggesting that the W value is determined from $E_{\text{redox}}^{\text{ave}}$. Table 1 summarizes $E_{\text{redox}}^{\text{ave}}$ values and redox species for various $r\text{-LiMO}_2$

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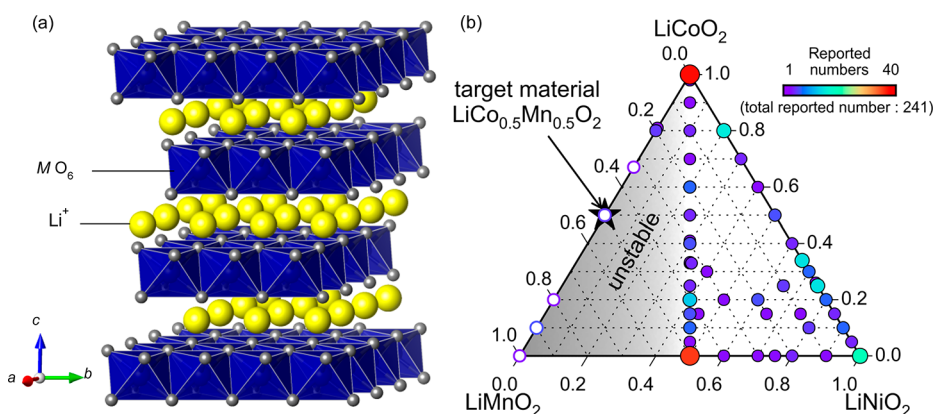


Figure 1. (a) Crystal structure of LiMO_2 in the $R\bar{3}m$ space group ($r\text{-LiMO}_2$), where M represents a 3d transition metal. (b) Ternary phase diagram composed of LiCoO_2 , LiNiO_2 , and LiMnO_2 . The $r\text{-LiMO}_2$ compounds, reported in the ICDD database accessed with PDF-4+ 2018 software and in the database of Web of Science, are denoted by circles. The Mn-rich $r\text{-LiMO}_2$ compounds are limited to 17, although the total number of $r\text{-LiMO}_2$ compounds is 241. The target material in this experiment, $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$, is shown by the black star.

Table 1. Electrochemical Properties and Synthesis Methods for Various $r\text{-LiMO}_2$ Compounds

compound	$E_{\text{redox}}^{\text{ave}}$ (V vs Li^+/Li)	redox species	synthesis method	refs
LiCoO_2	4.21	$\text{Co}^{3+} \leftrightarrow \text{Co}^{4+}$	solid-state reaction	9
LiNiO_2	3.90	$\text{Ni}^{3+} \leftrightarrow \text{Ni}^{4+}$	solid-state reaction	11
$\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$	4.08	$\text{Ni}^{3+}/\text{Co}^{3+} \leftrightarrow \text{Ni}^{4+}/\text{Co}^{4+}$	solid-state reaction	34
$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$	4.10	$\text{Ni}^{2+} \leftrightarrow \text{Ni}^{4+}$	solid-state reaction	35
$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$	4.12	$\text{Ni}^{2+}/\text{Co}^{3+} \leftrightarrow \text{Ni}^{4+}/\text{Co}^{4+}$	solid-state reaction	36
$\text{Li}_9\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2^a$	~ 4.5	$\text{Co}^{3+}/\text{Mn}^{3+} \leftrightarrow \text{Co}^{4+}/\text{Mn}^{4+}$	ion exchange	23, 24
$\text{LiCo}_{0.64}\text{Mn}_{0.36}\text{O}_2^b$	2.97	$\text{Co}^{3+}/\text{Mn}^{3+} \leftrightarrow \text{Co}^{4+}/\text{Mn}^{4+}\text{O}^{2-} \leftrightarrow \text{O}^-$	HP	this work

^aThe Li composition (δ) for the redox reaction is limited to 0.2–0.7. ^bThe chemical composition is specifically represented as $\text{Li}_{1.09}(\text{Co}_{0.64}\text{Mn}_{0.36})_{0.91}\text{O}_2$.

compounds to clarify which $\text{LiCoO}_2\text{--LiMnO}_2\text{--LiNiO}_2$ region provides the higher W . Obviously, $E_{\text{redox}}^{\text{ave}}$ of LiCoO_2 (4.21 V)⁹ is greater than those of LiNiO_2 (3.90 V)¹¹ and $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ (4.08 V),³⁴ while on the basis of the results of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ³⁵ or $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$,³⁶ the substitution of Mn ions for Ni or Co/Ni ions increases $E_{\text{redox}}^{\text{ave}}$. Moreover, the ion-exchanged synthesized $r\text{-LCMO}$ compound ($r\text{-Li}_9\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$) exhibits the highest $E_{\text{redox}}^{\text{ave}}$ value (~ 4.5 V),^{23,24} although the Li composition (δ) for the redox reaction was limited to 0.2–0.7. These experimental results indicate that Mn-rich $r\text{-LiMO}_2$, namely, $r\text{-LCMO}$, exhibits higher W values among the ternary LiCoO_2 , LiMnO_2 , and LiNiO_2 compounds. However, returning to the reason why $r\text{-LCMO}$ is unavailable, we find the JT distortion in the MnO_6 octahedra destabilizes the rhombohedral structure. The distortion index in the MnO_6 octahedra $[\text{DI}(\text{MnO}_6)]$ is defined as³⁷

$$\text{DI}(\text{MnO}_6) = \frac{1}{6} \sum_{i=1}^6 \frac{|d_i - d_{\text{ave}}|}{d_{\text{ave}}} \quad (1)$$

where d_i and d_{ave} are the i th and average bond lengths between Mn and O atoms in the MnO_6 octahedra, respectively. For instance, the $\text{DI}(\text{MnO}_6)$ of $o\text{-LiMnO}_2$ is calculated to be 0.0811(2),³⁸ while that of $o\text{-LiCo}_{0.1}\text{Mn}_{0.9}\text{O}_2$ is calculated to be ~ 0.076 .^{39,40} Therefore, decreasing $\text{DI}(\text{MnO}_6)$ would be an effective way to attain $r\text{-LCMO}$ compounds.

In this contribution, we employed a high-pressure (HP) method for synthesizing $r\text{-LCMO}$, because our previous HP studies successfully decreased $\text{DI}(\text{MnO}_6)$ in LiMnO_2 .³⁸ Specifically, a decrease in $\text{DI}(\text{MnO}_6)$ to 0.0378(1) from 0.0811(2) was associated with a structural transformation to a

tetragonal structure ($I4_1/amd$, $t\text{-LiMnO}_2$) from the orthorhombic structure ($Pmmn$).³⁸ Furthermore, the HP environment could facilitate a decrease in the difference between the ionic radii (r) of Mn^{3+} ($r = 0.58$ Å) and Co^{3+} ($r = 0.55$ Å) ions,⁴¹ leading to the homogeneous mixing of these ions on an atomic scale.⁴² The HP method has been employed for synthesizing LiCoO_2 -based⁴³ and LiNiO_2 -based compounds^{44–47} but not for synthesizing $r\text{-LCMO}$ compounds. In this report, we focused on the $x = 0.5$ composition of $r\text{-LCMO}$. Consequently, $r\text{-LCMO}$ samples, i.e., phases for which $\text{DI}(\text{MnO}_6) = 0$, were obtained at 400–600 °C and 5–12 GPa. The crystal structures and electrochemical properties of the LCMO samples are presented in detail.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Three types of Li precursors were employed to synthesize $r\text{-LCMO}$, i.e., Li_2O (Wako Pure Chemical Industries, Ltd.), LiOH (Sigma-Aldrich Co. LLC), and $\text{LiOH}\cdot\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd.), to maintain the stoichiometric composition or to improve the compatibility of the starting materials. As described below, the three types of Li precursors have both advantages and disadvantages. The Co and Mn precursors were CoO and MnO_2 (Kojundo Chemical Industries, Ltd.), respectively.

The HP syntheses were performed with Walker-type equipment located at Osaka Prefecture University.^{48–50} Panels a and b of Figure 2 show photos of all of the parts and schematics of the part assembly, respectively. Approximately 100 mg of the reaction mixture was pressed into a pellet with a height of 5 mm and a diameter of 2.8 mm. Then, the pellet was sealed in a Pt capsule (Tanaka Kikinzoku Kogyo Co.) and packed into an octahedral (Mg,Co)O pressure medium with one side length of 14 mm (Mino Ceramics Co., Ltd.), together with a BN sleeve (Denka Company Ltd.), a graphite heater (Mechanical

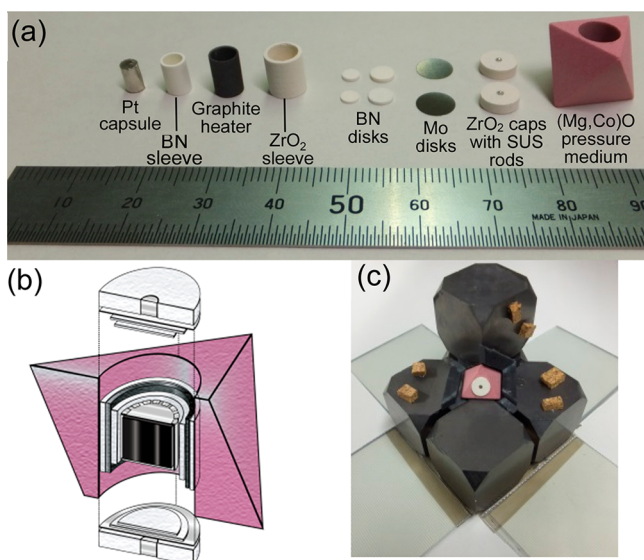


Figure 2. Setup of the HP synthesis. (a) All of the parts for the HP synthesis, consisting of a Pt capsule, a BN sleeve, a graphite heater, a ZrO₂ sleeve, BN disks, Mo disks, ZrO₂ caps with SUS rods, and octahedral (Mg,Co)O pressure medium. Schematic assemblies of (b) the (Mg,Co)O pressure medium and (c) the (Mg,Co)O pressure medium located at the corner of eight WC anvils, the edges of which were truncated by a length of 8 mm.

Carbon Industry Co., Ltd.), a ZrO₂ sleeve (Mino Ceramics Co., Ltd.), BN disks, Mo disks, and ZrO₂ caps with stainless steel (SUS) rods. SUS rods and Mo disks were used to conduct electricity during the heating. Note that only for the Li₂O precursor was the (Mg,Co)O octahedron assembled in an Ar-filled glovebox to avoid a reaction with moist air. The (Mg,Co)O octahedron was placed at the corner of eight WC anvils (TF06, Fuji Die Co., Ltd.), the edges of which were truncated by a length of 8 mm, as shown in Figure 2c. The WC anvil was finally compressed at 5, 9, or 12 GPa at room temperature and then heated at 200, 400, 500, 600, 800, 1000, or 1200 °C for 30 min. The time to reach each desired temperature was 15 min, and the WC anvil was quenched to room temperature after the heating. The obtained samples were finally retrieved after a slow decompression to ambient pressure. A total of 28 samples were synthesized, and their synthesis conditions, such as the starting materials and applied pressures, are summarized in Table 2. Hereafter, each sample in Table 2 is labeled as sample #XX.

2.2. Characterization. Particle morphologies and particle sizes were investigated by scanning electron microscopy (SEM) (S-3600N, Hitachi High-Technologies, Co. Ltd.) with an accelerating voltage of 15 kV. The crystal structures of the samples were studied by X-ray diffraction (XRD) measurements using conventional Fe K α radiation (D8 ADVANCE, Bruker AXS, Inc.).

2.3. Electrochemical Measurements. The electrochemical properties of the samples were examined in nonaqueous lithium cells. The active material, acetylene black (Denka Co., Ltd.), and polytetrafluoroethylene (Daikin Industries Ltd.) were mixed at a weight ratio of 70:20:10, and then, the black elastic mixture was pressed on an aluminum mesh current collector with a diameter of 16 mm. This mixed electrode was used as the electrode. The electrolyte

Table 2. Synthesis Conditions Such as Temperature and Pressure, Obtained Phases, and Rechargeable Capacities (Q_{recha}) of the LCMO Samples

sample	starting materials	temperature (°C)	pressure (GPa)	phases ^a	Q_{recha} ^b (mAh g ⁻¹)
1	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	400	5	<i>r</i> -LCMO + <i>c</i> -LCMO§ + Li ₆ CoO ₄ + Li ₂ CO ₃	45
2	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	600	5	<i>m</i> -LCMO + <i>c</i> -LCMO§ + Li ₂ CO ₃	8
3	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	800	5	<i>c</i> -LCMO§ + Li ₂ CO ₃	4
4	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	400	9	<i>r</i> -LCMO + <i>c</i> -LCMO§ + Li ₆ CoO ₄ + Li ₂ CO ₃	51
5	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	600	9	<i>m</i> -LCMO + <i>c</i> -LCMO§ + Li ₂ CO ₃	13
6	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	800	9	<i>c</i> -LCMO§ + Li ₂ CO ₃	5
7	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	400	12	<i>c</i> -LCMO§ + Li ₂ O + Li ₂ CO ₃	19
8	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	600	12	<i>m</i> -LCMO + <i>c</i> -LCMO§ + Li ₂ CO ₃	23
9	0.5Li ₂ O + 0.5CoO + 0.5MnO ₂	800	12	<i>c</i> -LCMO§ + Li ₂ CO ₃	7
10	LiOH + 0.5CoO + 0.5MnO ₂	600	5	<i>m</i> -LCMO + <i>c</i> -LCMO§ + MnCo ₂ O ₄ + Li ₂ CO ₃	7
11	LiOH + 0.5CoO + 0.5MnO ₂	400	9	<i>r</i> -LCMO§ + <i>c</i> -LCMO + MnOOH + <i>h</i> -LCMO + Li ₂ CO ₃	89
12	LiOH + 0.5CoO + 0.5MnO ₂	600	9	<i>m</i> -LCMO + <i>c</i> -LCMO§ + Li ₂ CO ₃	7
13	LiOH + 0.5CoO + 0.5MnO ₂	800	9	<i>c</i> -LCMO§ + Li ₂ CO ₃	5
14	LiOH + 0.5CoO + 0.5MnO ₂	400	12	<i>r</i> -LCMO + <i>c</i> -LCMO§ + MnOOH + Li ₂ CO ₃	64
15	LiOH + 0.5CoO + 0.5MnO ₂	600	12	<i>r</i> -LCMO + <i>c</i> -LCMO§ + Li ₂ CO ₃	23
16	LiOH + 0.5CoO + 0.5MnO ₂	800	12	<i>c</i> -LCMO§ + Li ₂ CO ₃	8
17	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	400	5	<i>m</i> -LCMO§ + <i>c</i> -LCMO + MnCo ₂ O ₄ + Li ₂ CO ₃	27
18	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	800	5	<i>m</i> -LCMO§ + MnCo ₂ O ₄ + Li ₂ CO ₃	10
19	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	400	9	<i>r</i> -LCMO§ + <i>c</i> -LCMO + MnOOH + <i>h</i> -LCMO + Li ₂ CO ₃	118
20	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	600	9	<i>m</i> -LCMO§ + <i>c</i> -LCMO + MnOOH + <i>h</i> -LCMO + Li ₂ CO ₃	16
21	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	800	9	<i>m</i> -LCMO§ + <i>c</i> -LCMO + <i>h</i> -LCMO + Li ₂ CO ₃	5
22	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	200	12	<i>sp</i> -LCMO§ + <i>c</i> -LCMO + Li ₂ CO ₃	—
23	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	300	12	<i>r</i> -LCMO + MnOOH + <i>c</i> -LCMO + <i>h</i> -LCMO§ + Li ₂ CO ₃	92
24	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	400	12	<i>r</i> -LCMO + MnOOH + <i>c</i> -LCMO + <i>h</i> -LCMO§ + Li ₂ CO ₃	138
25	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	500	12	<i>r</i> -LCMO + MnOOH + <i>c</i> -LCMO + <i>h</i> -LCMO§ + Li ₂ CO ₃	106
26	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	600	12	<i>r</i> -LCMO + <i>c</i> -LCMO + <i>h</i> -LCMO§ + Li ₂ CO ₃	126
27	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	800	12	<i>c</i> -LCMO§ + Li ₂ CO ₃	8
28	LiOH·H ₂ O + 0.5CoO + 0.5MnO ₂	1200	12	<i>c</i> -LCMO + CoO§ + Co + MnO + LiOH·H ₂ O + Li ₂ CO ₃	—

^aPrefixes *c*-, *r*-, *m*-, *h*-, and *sp*- indicate cubic rock-salt, rhombohedral, monoclinic, hexagonal, and cubic spinel structures, respectively. The major phase in each sample is represented as §. ^bThe Q_{recha} values of samples #22 and #28 were not examined.

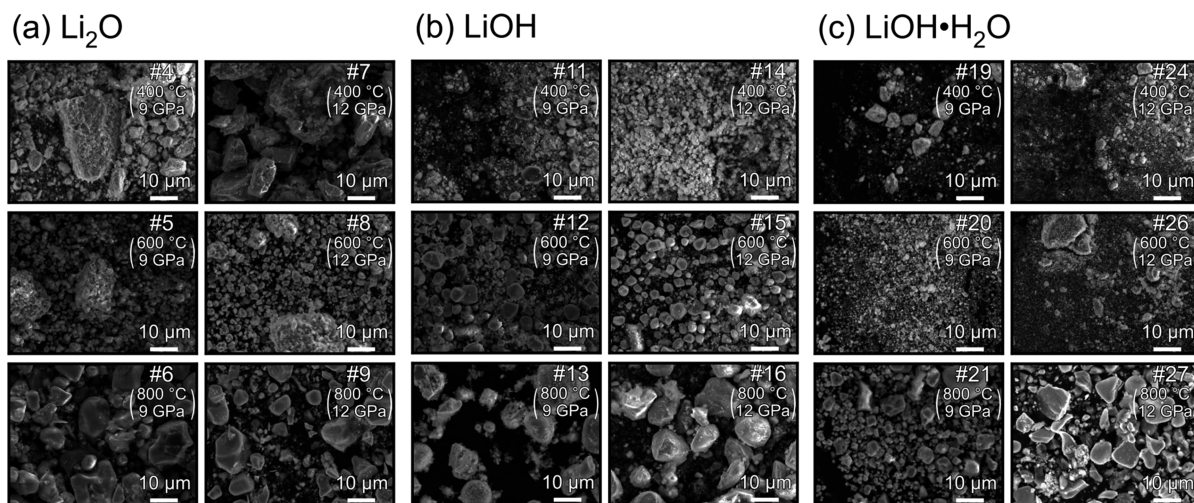


Figure 3. SEM images of the LCMO samples synthesized from the (a) Li_2O , (b) LiOH , and (c) $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors.

was 1 M LiPF_6 dissolved in ethylene carbonate and dimethyl carbonate [3:7 (v/v); Kishida Chemical Co. Ltd.], and the separator was composed of two sheets of a porous polyethylene membrane (Tonen-General Sekiyu K. K.). The lithium cells were fabricated in the Ar-filled glovebox. They were then operated outside the glovebox in the voltage range of 1.8–4.8 V at a current density of 0.025 mA cm^{-2} . The environmental temperature of the cells was 25 °C.

2.4. Further Characterization of Sample #26. As described below, sample #26 exhibited a large Q_{recha} of 126 mAh g^{-1} with a high-crystallinity *r*-LCMO phase. We, hence, performed an extended cycle test for only sample #26 over 30 cycles at a current density of 0.05 mA cm^{-2} at 25 °C. Furthermore, the distribution of Co and Mn elements in the particles was examined by an electron probe microanalyzer (EPMA) (JXA-8500F, JEOL Ltd.) with an accelerating voltage of 15 kV. The sample was embedded in an epoxy resin and then cut into a rectangle form using a cross-sectional polisher (SM-09010, JEOL Ltd.) equipped with Ar^+ ions. The polishing time was 5 h. The synchrotron XRD measurement was also performed at beamline BL5S2 at the Aichi Synchrotron Radiation Center. The sample was packed into a glass capillary tube with a diameter of 0.3 mm (WHM-Glas Müller BmbH) and then exposed to synchrotron X-ray radiation for 10 min. The X-ray wavelength was determined to be 0.799436(2) Å using a silicon standard (NIST 640d). The XRD pattern was recorded in the 2θ range between 5° and 90° using Pilatus 100K detectors (Dectris Ltd.). Rietveld analyses were conducted using RIETAN-FP software⁵¹ or PDXL software (Rigaku Co. Ltd.), and the crystal structures were drawn using VESTA software.⁵² The Pawley method⁵³ using PDXL software was also employed to analyze the structure of sample #26.

3. RESULTS AND DISCUSSION

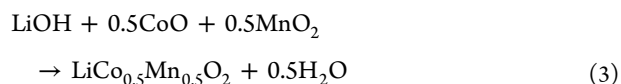
3.1. Particle Morphology. Figure 3a shows SEM images of samples #4–#9 (400–800 °C and 9–12 GPa), which were synthesized from the Li_2O precursor. In contrast to syntheses under ambient pressure, the chemical composition of starting materials should be adjusted to that of a product if possible, because the environment in HP syntheses is close to a closed system. In this sense, the utilization of the Li_2O precursor is ideal because of the synthetic reaction expressed by



A precursor of Li_2O_2 was employed for the HP synthesis of monoclinic structured $\text{Li}[\text{Li}_{1/3}\text{Ni}_{2/3}]\text{O}_2$.^{44–47} With a heating temperature of 400 °C, particle sizes are scattered in the range between 2 and 100 μm , regardless of the applied pressure (9 or 12 GPa). As shown in Figure S1a–c, the Li_2O precursor

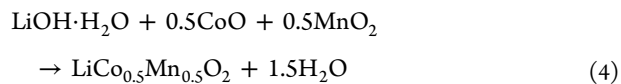
indicates large primary particles with diameters of 10–50 μm , whereas the CoO and MnO_2 precursors exhibit small particles with diameters of <5 μm . Hence, the solid-state reaction did not proceed due to the high melting temperature (T_m) of the Li_2O precursor (1570 °C). The large particles in samples #4 and #7 are thought to originate from the Li_2CO_3 or Li_2O phase on the basis of their aforementioned XRD patterns. With an increase in the heating temperature, particles exhibit a smoother surface and a nonuniform particle shape, with an average size of 10 μm at a heating temperature of 800 °C.

Figure 3b shows SEM images of samples #11–#16 (400–800 °C and 9–12 GPa), which were synthesized from the LiOH precursor. The synthetic reaction for the LiOH precursor is expressed by



Although the H_2O phase is co-produced by the reaction, the lower T_m (462 °C) of LiOH would be an advantage in the compatibility of the starting materials. Indeed, particle sizes in samples #11 and #14 are <5 μm , which was significantly smaller than those in samples #4 and #7. Note that the particle size of the LiOH precursor is >10 μm , as shown in Figure S1d. As the heating temperature increases, particles grow and then have a spherical morphology with an average size of 10 μm , independent of the applied pressure.

Figure 3c shows SEM images of samples #19–#21 (400–800 °C and 9 GPa) and #24, #26, and #27 (400–800 °C and 12 GPa), which were synthesized from the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor. The synthetic reaction for the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor is given by



where the T_m of $\text{LiOH}\cdot\text{H}_2\text{O}$ (450 °C) is slightly lower than that of LiOH . Figure S1e shows the SEM images of the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor, where its particle size is approximately 50 μm . Particles synthesized from the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor are similar to those synthesized from the LiOH precursor, when the heating temperature is 400 °C. However, differences appear when the heating temperature reaches 800 °C; i.e., particles

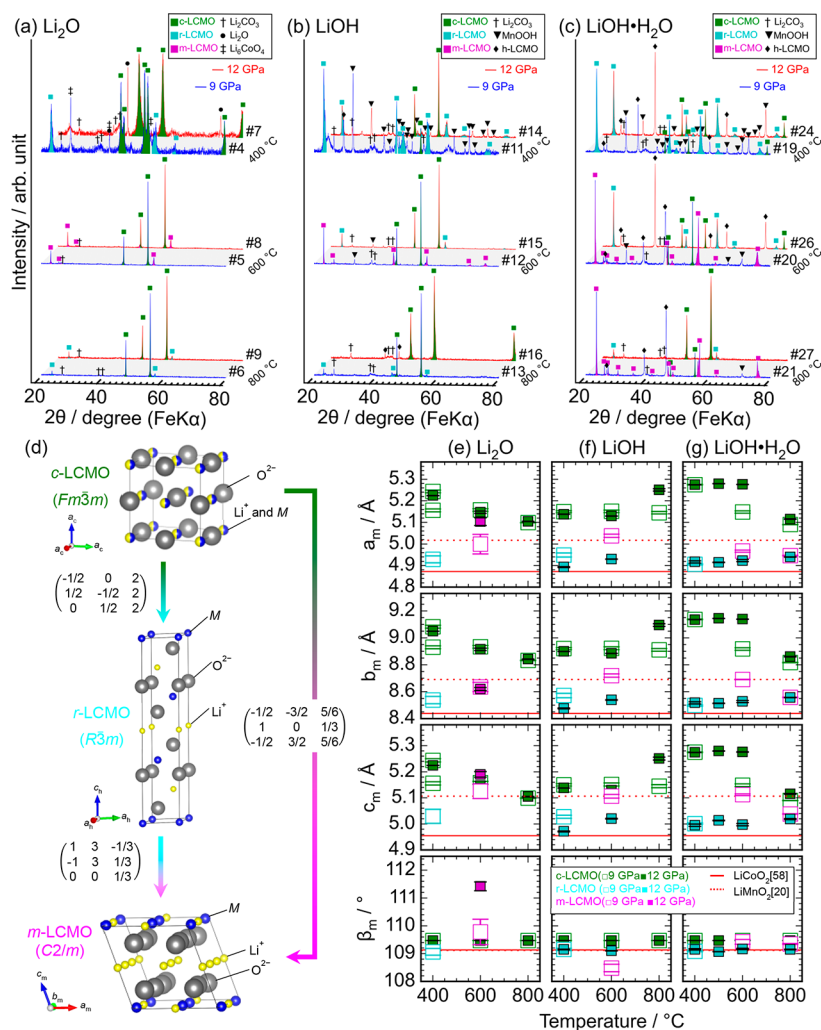


Figure 4. XRD patterns of the LCMO samples synthesized from the (a) Li_2O , (b) LiOH , and (c) $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors. (d) Structural relationship among the c -LCMO ($Fm\bar{3}m$), r -LCMO ($R\bar{3}m$), and m -LCMO ($C2/m$) phases. Changes in lattice parameters a_m , b_m , c_m , and β_m of the LCMO samples synthesized from the (e) Li_2O , (f) LiOH , and (g) $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors. Empty and filled circles in panels e–g indicate the lattice parameters of samples synthesized at 9 and 12 GPa, respectively. The lattice parameters of LiCoO_2 and LiMnO_2 with the $R\bar{3}(-)m$ space group are shown by solid and dashed lines, respectively.

show a flat, smooth morphology only at 12 GPa. The average size of these particles is approximately $5\ \mu\text{m}$, which is slightly suppressed in grain growth, compared with the case for the LiOH precursor.

3.2. Crystal Structure. To investigate the crystal structure, XRD patterns were recorded. The phases obtained for all of the samples are listed in Table 2, and the major phase in each sample is indicated by §. Figure 4a shows the XRD patterns of samples #4–#9 (400–800 $^\circ\text{C}$ and 9–12 GPa), and those of samples #1–#3 (400–800 $^\circ\text{C}$ and 5 GPa) are shown in Figure S2a, all of which were synthesized from the Li_2O precursor. Sample #4 (400 $^\circ\text{C}$ and 9 GPa) contains the r -LCMO phase but consists of a mixture of at least five different phases, i.e., r -LCMO, rock-salt cubic (c -) LCMO ($Fm\bar{3}m$), Li_2CO_3 , Li_2O , and Li_6CoO_4 . The presence of Li_2CO_3 indicates that the Li_2O precursor was not completely consumed during the HP synthesis, which is consistent with the SEM observations in Figure 3a. The XRD pattern of sample #5 (600 $^\circ\text{C}$ and 9 GPa) is similar to that of sample #4. When the heating temperature reaches 600 $^\circ\text{C}$, the r -LCMO phase almost disappears, and in turn, the c -LCMO phase becomes the major phase. Besides the c -LCMO phase, a monoclinic (m -) LCMO phase ($C2/m$) is

observed in both samples #6 (800 $^\circ\text{C}$ and 9 GPa) and #7 (400 $^\circ\text{C}$ and 12 GPa). Samples #6 and #9 (12 GPa), which were both synthesized at 800 $^\circ\text{C}$, present almost a single c -LCMO phase. When the applied pressure decreases from 9 to 5 GPa, the Li_2CO_3 phase is still observed, even at 800 $^\circ\text{C}$ (Figure S2a). This result suggests that high temperatures above 400 $^\circ\text{C}$ and high pressures above 5 GPa are required for the Li_2O precursor to completely react.

Figure 4b shows the XRD patterns of samples #11–#16 (400–800 $^\circ\text{C}$ and 9–12 GPa), and that of sample #10 (600 $^\circ\text{C}$ and 5 GPa) is shown in Figure S2b, all of which were synthesized from the LiOH precursor. The r -LCMO phase was observed in samples #11, #14, and #15, demonstrating that the ranges of temperature and pressure in which the r -LCMO phase is stable are broader than those constructed for Li_2O . However, these samples also contain Li_2CO_3 and MnOOH phases; the latter is thought to be a product of the hydroxyl group of the LiOH precursor. The m -LCMO phase is observed in samples #10 (Figure S2b) and #12 (600 $^\circ\text{C}$ and 9 GPa), which were both heated at 600 $^\circ\text{C}$ and pressures of <12 GPa. The c -LCMO phase was stabilized at 800 $^\circ\text{C}$, which is similar to the case for Li_2O .

As for the samples synthesized from the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor, Figure 4c shows the XRD patterns of samples #19–#21 (400–800 °C and 9 GPa) and #24, #26, and #27 (400–800 °C and 12 GPa); those of samples #17 and #18 (400–800 °C and 5 GPa) are shown in Figure S2c, and those of samples #22, #23, #25, and #28 (200–1200 °C and 12 GPa) are shown in Figure S3. The *r*-LCMO phase was observed in samples #21 and #25–#28, the temperature of which was 400 °C at 9 GPa and 300–600 °C at 12 GPa. This suggests that the hydroxyl group and hydrated water of $\text{LiOH}\cdot\text{H}_2\text{O}$ act as a flux medium when producing the *r*-LCMO phase. A similar catalytic effect of water was also reported for the formation of cubic BN from hexagonal BN.⁵⁴ As shown in the XRD patterns in Figure 4c and Figure S3, unidentified diffraction lines indicated by ♦ appear at 2θ values of 25.9°, 37.0°, 55.1°, 60.3°, and 72.9°. We confirmed that these diffraction lines do not originate from any oxides, hydroxides, or oxyhydroxides composed of Li, Co, and/or Mn ions. This phase possesses a hexagonal or orthorhombic system, as described in section 3.5; thus, it is hereafter represented as *h*-LCMO. The *m*-LCMO phase was observed in samples #20 and #21 (600–800 °C and 9 GPa), while the *c*-LCMO phase was observed in samples #22, #27, and #28 (200–1200 °C and 12 GPa). Note that a cubic spinel LCMO (*sp*-LCMO) phase partially appeared at 200 °C [sample #22 (see Figure S3)].

The general trend of the structural changes with an increasing temperature was *r*-LCMO → *m*-LCMO → *c*-LCMO for all of the Li precursors. Figure 4d schematically shows the structural relationships among these three structures, derived from group theory.⁵⁵ The transformation from the *c*-LCMO phase to the *r*-LCMO phase is represented using the hexagonal (h) and cubic (c) settings:

$$(abc)_h = (abc)_c P = (abc)_c \begin{pmatrix} -1/2 & 0 & 2 \\ 1/2 & -1/2 & 2 \\ 0 & 1/2 & 2 \end{pmatrix} \quad (5)$$

where *P* is the matrix for the transformation. Meanwhile, the transformation from *r*-LCMO to *m*-LCMO is represented by

$$(abc)_m = (abc)_h Q = (abc)_h \begin{pmatrix} 1 & 3 & -1/3 \\ -1 & 3 & 1/3 \\ 0 & 0 & 1/3 \end{pmatrix} \quad (6)$$

where *m* stands for the monoclinic setting for the *m*-LCMO phase and *Q* is the matrix for the transformation. Hence, the transformation from the *c*-LCMO phase to the *m*-LCMO phase is expressed by

$$(abc)_m = (abc)_c PQ = (abc)_c \begin{pmatrix} -1/2 & -3/2 & -5/6 \\ 1 & 0 & 1/3 \\ -1/2 & 3/2 & 5/6 \end{pmatrix} \quad (7)$$

As a result, the cubic lattice parameter (a_c) of *c*-LCMO is converted into the lattice parameters of *m*-LCMO, namely, a_m , b_m , c_m , and β_m :

$$\begin{cases} a_m = \frac{\sqrt{6}}{2} a_c \\ b_m = \frac{3\sqrt{2}}{2} a_c \\ c_m = \frac{\sqrt{6}}{2} a_c \\ \cos \beta_m = -\frac{1}{3} \end{cases} \quad (8)$$

Moreover, the lattice parameters of the *r*-LCMO phase in the hexagonal setting are given by

$$\begin{cases} a_m = \sqrt{3} a_h \\ b_m = 3a_h \\ c_m = \frac{\sqrt{3a_h^2 + c_h^2}}{3} \\ \cos \beta_m = -\sqrt{\frac{3a_h^2}{3a_h^2 + c_h^2}} \end{cases} \quad (9)$$

Using the relations described in eqs 8 and 9, the lattice parameters of *c*-LCMO and *r*-LCMO are converted into the monoclinic setting and compared with those of *m*-LCMO. Figure 4e shows the changes in lattice parameters a_m , b_m , c_m , and β_m of samples #4–#6 (400–800 °C and 9 GPa) and #7–#9 (400–800 °C and 12 GPa), which were synthesized from the Li_2O precursor, as a function of heating temperature. Empty and filled squares represent the lattice parameters of the samples synthesized at 9 and 12 GPa, respectively. For *c*-LCMO, the lattice parameters a_m , b_m , and c_m decrease almost linearly with the increasing temperature, while β_m remains constant at $\sim 109.5^\circ$. Because the a_c values of CoO and MnO have been reported to be 4.260 Å ($a_m = 5.217$ Å)⁵⁶ and 4.440 Å ($a_m = 5.438$ Å),⁵⁷ respectively, changes in a_m , b_m , and c_m imply changes in the Co:Mn ratio in the samples. The lattice parameters of the *m*-LCMO phase are slightly different from those of the *c*-LCMO phase, particularly the β_m value at 12 GPa [111.4(2)°].

Figure 4f shows the lattice parameters of samples #11–#16 (400–800 °C and 9–12 GPa), which were synthesized from the LiOH precursor. Figure 4g shows the lattice parameters of samples #19–#21 (400–800 °C and 9 GPa) and #24–#27 (400–800 °C and 12 GPa), which were synthesized from the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor. The lattice parameters of the *c*-LCMO phase demonstrate opposite trends for the LiOH and $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors. That is, the lattice parameters a_m , b_m , and c_m increase slightly with an increase in temperature for the LiOH precursors, whereas these parameters decrease with an increase in temperature for the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor. Such changes could be attributed to differences in the Co:Mn ratio in the samples. The lattice parameters of *r*-LCMO are comparable for the LiOH and $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors. Their lattice parameters of a_m , b_m , and c_m increase almost linearly with the increasing temperature, while β_m remains constant at $\sim 109^\circ$. For instance, the lattice parameters of the *r*-LCMO phase in sample #26 (600 °C, 12 GPa, and $\text{LiOH}\cdot\text{H}_2\text{O}$) are determined to be $a_m = 4.923(5)$ Å, $b_m = 8.528(8)$ Å, $c_m = 4.998(5)$ Å, and $\beta_m = 109.17(2)^\circ$ by a least-squares method. These a_m , b_m , and c_m values are approximately halfway between those for

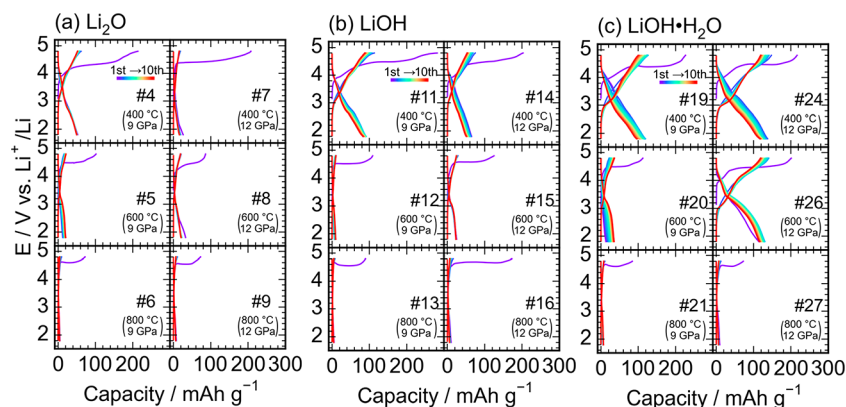


Figure 5. Charge and discharge curves of the Li/LCMO cells operated at a current density of 0.025 mA cm^{-2} . The LCMO samples were synthesized from the (a) Li_2O , (b) LiOH , and (c) $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors.

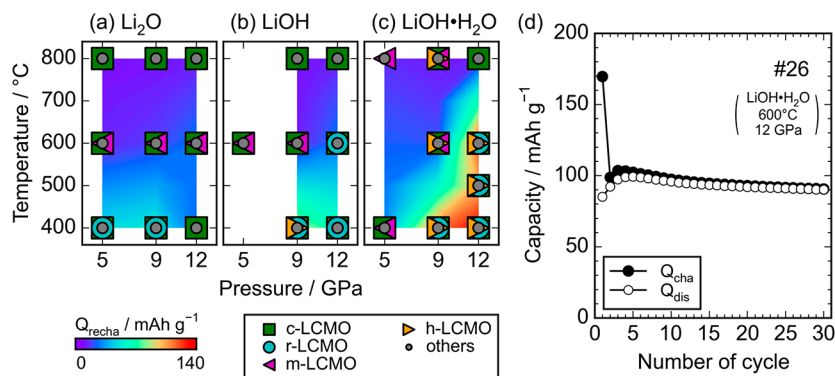


Figure 6. Relationship between the crystal structure and electrochemical properties of LCMO samples synthesized from the (a) Li_2O , (b) LiOH , and (c) $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors. (d) Cycle performance of sample #26. The lithium cell was operated at a current density of 0.05 mA cm^{-2} .

rhombohedral-structured LiCoO_2 ^{9,58} and LiMnO_2 ^{17–20} which are distinguished by the solid and dotted red lines, respectively, in Figure 4e–g. The transformed lattice parameters were calculated to be $a_m = 4.872(1) \text{ \AA}$, $b_m = 8.439(1) \text{ \AA}$, $c_m = 4.955(1) \text{ \AA}$, and $\beta_m = 109.13(1)^\circ$ for LiCoO_2 and $a_m = 5.018(1) \text{ \AA}$, $b_m = 8.691(1) \text{ \AA}$, $c_m = 5.107(1) \text{ \AA}$, and $\beta_m = 109.12(1)^\circ$ for LiMnO_2 . Note that the rhombohedral-structured LiMnO_2 , which was synthesized using the ion-exchange method, contains a spinel LiMn_2O_4 secondary phase.¹⁸

3.3. Electrochemical Properties. Figure 5a shows the charge and discharge curves for samples #4–#9 (400–800 °C and 9–12 GPa), and those for samples #1–#3 (400–800 °C and 5 GPa) are shown in Figure S4a, all of which were synthesized from the Li_2O precursor. The Q_{recha} values except for those of samples #22 and #28 are listed in Table 2. The voltage of sample #4 rapidly increases from $\sim 3.0 \text{ V}$ at the beginning of the charge reaction and then remains almost constant at $\sim 4.4 \text{ V}$. The charge capacity (Q_{cha}) is 214 mAh g^{-1} , which corresponds to 77% of Q_{theo} based on a one-electron transfer reaction (279.5 mAh g^{-1}). However, the subsequent discharge voltage drops to 1.8 V with a discharge capacity (Q_{dis}) of 52 mAh g^{-1} . Q_{recha} is limited to 51 mAh g^{-1} , although the capacity hardly fades for all 10 cycles. As the heating temperature increases or as the applied pressure increases to 12 GPa, the electrochemical performance significantly degrades. For instance, the Q_{recha} values of samples #6 and #9 are $< 7 \text{ mAh g}^{-1}$. Because the *m*- and *c*-LCMO phases are essentially

electrochemically inactive, their presence in samples #5–#9 decreases Q_{recha} .

As for samples synthesized from the LiOH precursor, Figure 5b shows the charge and discharge curves for samples #11–#16 (400–800 °C and 9–12 GPa), while those for sample #10 (600 °C and 5 GPa) are shown in Figure S4b. The electrochemical performance for the LiOH precursor is better than that of the Li_2O case. For example, Q_{recha} of sample #11 reaches 89 mAh g^{-1} , after exhibiting a large Q_{cha} during the initial cycle (282 mAh g^{-1}). The high-temperature and/or HP treatments degrade the electrochemical performance, but sample #14 still exhibits a Q_{recha} of $> 60 \text{ mAh g}^{-1}$. As shown in Figure 5c and Figures S4c and S5, utilizing the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor further improves the electrochemical performance. For example, sample #24 (400 °C and 12 GPa) attains the highest Q_{recha} of 138 mAh g^{-1} , whereas sample #26 (600 °C and 12 GPa) attains a Q_{recha} of $\sim 126 \text{ mAh g}^{-1}$ with an average voltage (E_{ave}) of 2.97 V , yielding an energy density (W) of 374 mWh g^{-1} . This W value is approximately 60% of the actual W values for LiCoO_2 ,⁹ LiNiO_2 ,¹¹ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$.³⁶ In the dQ_{cha}/dV and dQ_{dis}/dV curves from the second cycle, oxidation reaction peaks are observed at 3.45, 3.95, and 4.46 V , whereas reduction reaction peaks are observed at 2.74, 3.40, and 3.97 V (Figure S6).

Via comparison of Q_{recha} values among the synthesized samples, there is a general trend between Q_{recha} and heating temperature; the Q_{recha} value decreases with an increase in the heating temperature. This is because the amount of the electrochemically inactive phase, *c*-LCMO, increases with an

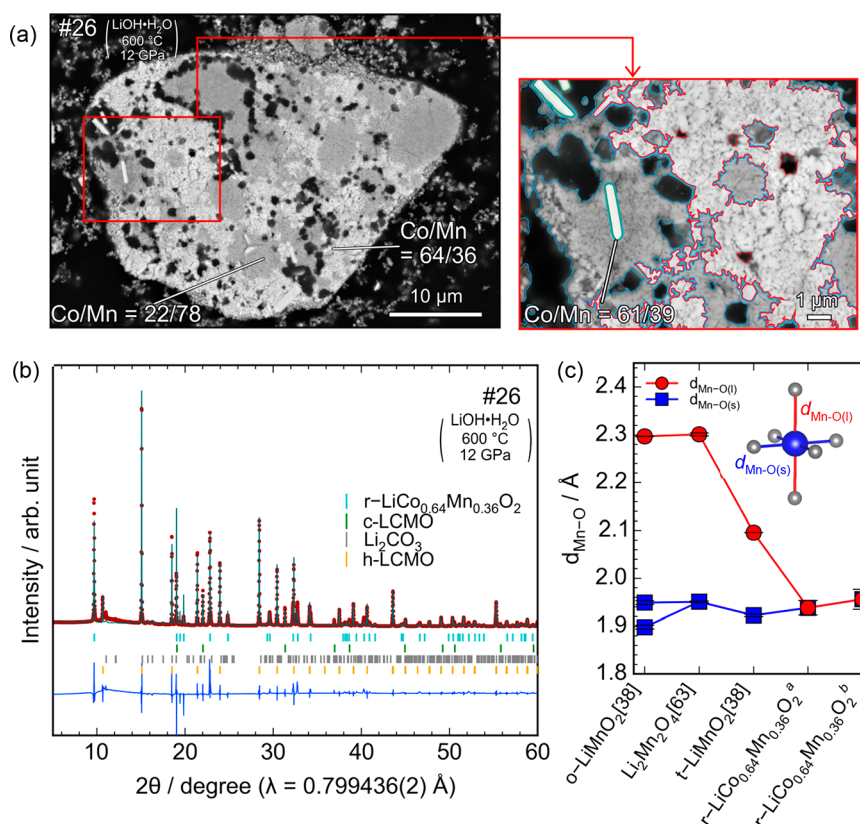


Figure 7. (a) Cross-sectional views of sample #26 on scales of 10 and 1 μm . The Co:Mn ratios are 64:36 for the light-gray region, 22:78 for the dark-gray region, and 61:39 for the white columnar region. The black region corresponds to the epoxy resin. (b) Results of the structural analysis of sample #26 using both Rietveld and Pawley methods. (c) Bond lengths between the Mn^{3+} ion and O^{2-} ion ($d_{\text{Mn-O}}$) in $o\text{-LiMnO}_2$,³⁸ electrochemically prepared tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$,⁶³ $t\text{-LiMnO}_2$,³⁸ and the present $r\text{-LiCo}_{0.64}\text{Mn}_{0.36}\text{O}_2$ phase. The two $d_{\text{Mn-O}}$ values of the $r\text{-LiCo}_{0.64}\text{Mn}_{0.36}\text{O}_2$ phase come from different methods. Footnote a indicates the test employs both Rietveld and Pawley methods, while footnote b indicates the test employs only the Rietveld method.

increase in the heating temperature. However, exceptions are observed in samples synthesized at 12 GPa when using the Li_2O and $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors (samples #7–#9 and #23–#26). In the case of $\text{LiOH}\cdot\text{H}_2\text{O}$, the Q_{recha} value increases as the temperature increases to 400 $^{\circ}\text{C}$ (138 mAh g^{-1}), then slightly drops at 500 $^{\circ}\text{C}$ (106 mAh g^{-1}), and finally increases again at 600 $^{\circ}\text{C}$ (126 mAh g^{-1}). This is an indication of the presence of other factors affecting the Q_{recha} value of the samples. Considering the XRD patterns shown in Figure 4c and the obtained phases listed in Table 2, the increasing heating temperature provided the formation of the high-crystallinity $r\text{-LCMO}$ phase and suppression of the electrochemically inactive MnOOH phase. Therefore, under a pressure of 12 GPa, at least two opposite factors are involved in the electrochemical properties of the samples. The contribution of the $h\text{-LCMO}$ phase will be discussed in section 3.4.

Note that the initial charge curves for all of the samples exhibit a similar plateau at ~ 4.5 V. Moreover, the Q_{cha} value that originated from this plateau almost decreases with an increase in the heating temperature, i.e., decreasing the amount of the electrochemically active phase. The plateau at 4.5 V was also observed in lithium-excess manganese oxides $z\text{Li}_2\text{MnO}_3\cdot(1-z)\text{LiMO}_2$, which release oxygen from the lattice during the initial charge reaction and exhibit an oxygen redox reaction at the electrode surface.^{5559–61}

3.4. Relationship between Crystal Structure and Electrochemical Properties. To clarify the relationship

between the crystal structures and electrochemical properties, the obtained phases and Q_{recha} values are summarized as a phase diagram, together with a contour plot. Panels a–c of Figure 6 show the results for compounds synthesized from the Li_2O , LiOH , and $\text{LiOH}\cdot\text{H}_2\text{O}$ precursors, respectively. In the case of the Li_2O precursor, the $r\text{-LCMO}$ phase was observed only in samples #1 (400 $^{\circ}\text{C}$ and 5 GPa) and #4 (400 $^{\circ}\text{C}$ and 9 GPa), and $m\text{-LCMO}$ and $c\text{-LCMO}$ are stabilized in the high-temperature region above 600 $^{\circ}\text{C}$. Note that “others” in the figure legend includes MnOOH , Li_6CoO_4 , MnCo_2O_4 , and Li_2CO_3 phases. For samples #1 and #4, even their Q_{recha} values were limited to less than ~ 50 mAh g^{-1} . In the case of the LiOH precursor, the $r\text{-LCMO}$ phase was observed over a wider temperature–pressure region, and consequently, the Q_{recha} value increased to ~ 90 mAh g^{-1} . Utilizing the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor further increased the Q_{recha} value to >126 mAh g^{-1} , although the temperature–pressure region for the $r\text{-LCMO}$ phase is similar to that of the LiOH precursor. These results indicate an increase in the amount of the $r\text{-LCMO}$ phase for these samples. Because the $h\text{-LCMO}$ phase coexists in the $r\text{-LCMO}$ phase, the question of which phase has a Q_{recha} naturally arises. Considering the fact that Q_{recha} values of samples #20 (600 $^{\circ}\text{C}$ and 9 GPa) and #21 (800 $^{\circ}\text{C}$ and 9 GPa) were <16 mAh g^{-1} , only the $r\text{-LCMO}$ phase is likely to be electrochemically active.

These phase diagrams reveal the optimal conditions for obtaining the $r\text{-LCMO}$ phase with a large Q_{recha} , namely, the $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor, a heating temperature of 400–600 $^{\circ}\text{C}$,

Table 3. Comparison of the Structural Parameters of Lithium Manganese Oxides Containing Mn³⁺ Ions

compound	crystal system (space group)	structure type	Mn–O bond length (Å)		DI(MnO ₆)	ref
			$d_{\text{Mn–O}(s)}$	$d_{\text{Mn–O}(l)}$		
LiMnO ₂	orthorhombic (<i>Pmmn</i>)	zigzag layer	1.898(1) and 1.949(1)	2.297(1)	0.0811(2)	38
Li ₂ Mn ₂ O ₄	tetragonal (<i>I4₁/amd</i>)	spinel	1.951(1)	2.301(1)	0.0753(1)	63
LiMnO ₂	tetragonal (<i>I4₁/amd</i>)	ordered rock-salt (γ -LiFeO ₂)	1.922(1)	2.096(1)	0.0378(1)	38
LiCo _{0.64} Mn _{0.34} O ₂ ^a	rhombohedral (<i>R3m</i>)	layer	1.938(5)	1.938(5)	0	this work
LiCo _{0.64} Mn _{0.34} O ₂ ^b	rhombohedral (<i>R3m</i>)	layer	1.956(7)	1.956(7)	0	this work

^aEmploying combined Rietveld and Pawley methods. ^bEmploying only the Rietveld method.

and an applied pressure of 9–12 GPa. These conditions suggest that it is not the stoichiometry of the starting materials as represented by eq 4 but the compatibility of the starting materials that plays the most important role in synthesizing *r*-LCMO. To clarify the cyclability of the *r*-LCMO phase, a charge and discharge cycle test was performed on sample #26, because the crystallinity of sample #26 is higher than that of sample #24 (see Figure 4c). Figure 6d shows this sample's Q_{cha} and Q_{dis} values as a function of the number of cycles. Except for the Q_{cha} value from the first cycle, the Q_{cha} and Q_{dis} values remain at approximately 100 mAh g^{−1}. The capacity hardly fades over 30 cycles. Note that these Q_{cha} and Q_{dis} values are slightly lower than those in Figure 6d, which is due to the higher current density; namely, the cycle test was performed at a current density of 0.05 mA cm^{−2}, which was twice as high as that in Figure 6d.

3.5. Compositional and Structural Analyses of the *r*-LCMO Phase. LCMO samples containing the *r*-LCMO phase were successfully synthesized using the HP method; however, the maximum Q_{recha} was <140 mAh g^{−1}, which is approximately half of Q_{theo} (279.5 mAh g^{−1}). Q_{recha} is lower because the *r*-LCMO phase was contaminated with electrochemically inactive *c*-LCMO and/or *h*-LCMO. To determine the synthetic conditions that can further improve the electrochemical properties of LCMO, compositional and structural analyses of sample #26 were undertaken. Figure 7a shows the cross-sectional view of a particle of sample #26 obtained with the EPMA. An enlarged cross-sectional view on a 1 μm scale is also shown on the right side of Figure 7a. Various regions appear in the particle in three distinct colors: light-gray phases with a Co:Mn ratio of 64:36, dark-gray phases with a Co:Mn ratio of 22:78, and white columnar phases with a Co:Mn ratio of 61:39, in descending order of Co content. Note that the black region surrounding the particle is the epoxy resin for the EPMA. Because the Co:Mn ratio of the starting material was 50:50, the overall Co:Mn ratio of the particle must also be 50:50.

Figure 7b shows the results of the structural analysis of sample #26. Detailed structural parameters are listed in Table S1. Four phases exist in the sample, *r*-LCMO, *h*-LCMO, *c*-LCMO, and Li₂CO₃, in descending order of the intensity of their diffraction lines. Therefore, the Co:Mn ratios of the *r*-LCMO, *h*-LCMO, and *c*-LCMO phases are found to be 64:36, 22:78, and 61:39, respectively; in other words, the *r*-LCMO phase can be represented as LiCo_{0.64}Mn_{0.36}O₂. The lattice parameters of *r*-LCMO are calculated to be $a_{\text{h}} = 2.834(1)$ Å and $c_{\text{h}} = 14.217(1)$ Å. Note that the structure in Figure 7b was analyzed using a combination of the Rietveld and Pawley methods, among which the latter is usually employed to decompose XRD patterns and refine lattice parameters.⁵³ Results of the structural analysis using only the Rietveld method are summarized in Figure S7 and Table S1. With this

method, the lattice parameters were found to be $a_{\text{h}} = 2.836(2)$ Å and $c_{\text{h}} = 14.206(1)$ Å, which are comparable to the values obtained by combining the Rietveld and Pawley methods.

Figure S8 shows the comparison of the lattice parameters of a_{h} and c_{h} axes between the present *r*-LCMO phase and previously reported *r*-LCMO compounds with $x \leq 0.2$.^{20,23–29,31–33} Both lattice parameters increase almost monotonically with an increase in the Mn content (x). The lattice parameters of the *r*-LCMO phase are slightly larger than the expected values using the linear relation, indicating that a small amount of Li ions occupy the 3a (transition metal) site, as in the case for Li-excess manganese oxides $z\text{Li}_2\text{MnO}_3 \cdot (1-z)\text{LiMO}_2$.^{5559–61} According to a bond valence sum analysis on *r*-LCMO, its effective oxidation state was calculated to be 3.2. The chemical composition of the *r*-LCMO phase is specifically represented as Li_{1.09}(Co_{0.64}Mn_{0.36})_{0.91}O₂ by ignoring the case for the Li-deficient phase. The estimation of the chemical composition is consistent with the results of electrochemical measurements, such as the plateau at ~4.5 V at the initial charge curve and relatively lower $E_{\text{redox}}^{\text{ave}}$ value (2.97 V).

The details of the *h*-LCMO phase are currently unclear, and six space groups are possible (*P6₃*, *P3₂*, *P3₂1*, *P6₃mc*, *Cmc2₁*, and *Ccm*) according to an automatic program for finding the unit cell,⁶² as listed in Table S2. The first four space groups have a hexagonal crystal system with lattice parameters $a_{\text{h}} = 4.98$ Å and $c_{\text{h}} = 4.31$ Å, while the last two space groups have an orthorhombic crystal system with lattice parameters $a_{\text{o}} = 8.62$ Å, $b_{\text{o}} = 4.98$ Å, and $c_{\text{o}} = 4.31$ Å. Because the figures of merit for the hexagonal system are lower than those for the orthorhombic system (see Table S2), the *h*-LCMO phase is likely to exhibit the hexagonal system. If we ignore the contribution of the *h*-LCMO phase, the weight fractions of the *r*-LCMO, *c*-LCMO, and Li₂CO₃ phases were determined to be 62%, 10%, and 28%, respectively, by the combination of the Rietveld and Pawley methods (Table S1). These weight fractions are almost the same as those determined only by the Rietveld method (Table S1).

Because the *r*-LCMO phase has rhombohedral symmetry, the bond lengths between the Mn³⁺ and O^{2−} ions ($d_{\text{Mn–O}}$) should be equal to each other, yielding a DI(MnO₆) of 0 (see eq 1). Figure 7c compares these $d_{\text{Mn–O}}$ values with those of other lithium manganese oxides consisting of Mn³⁺ ions. The $d_{\text{Mn–O}}$ values of *o*-LiMnO₂³⁸ and tetragonal-structured Li₂Mn₂O₄⁶³ separate into two different lengths, namely, ~2.30 and ~1.95 Å, due to the JT distortion in the MnO₆ octahedron. The *t*-LiMnO₂ compound, which was synthesized from *o*-LiMnO₂ using the HP method, also exhibits two $d_{\text{Mn–O}}$ values, but the longer $d_{\text{Mn–O}}$ value decreases from ~2.30 to ~2.10 Å.³⁸ Notably, all of the $d_{\text{Mn–O}}$ values of *r*-LCMO are approximately 1.94 (or 1.96) Å; thus, the HP environment is found to shrink the longer $d_{\text{Mn–O}}$ in the MnO₆ octahedron.

The substitution of Co ions for Mn ions also contributes to the stabilization of the *r*-LCMO phase (Table 3).

Keeping in mind that at least 38 wt % impurity exists in sample #26, we found its Q_{recha} of 126 mAh g⁻¹ and W of 374 mWh g⁻¹ are not so small compared to those for previously reported *r*-LiMO₂ compounds, such as LiCoO₂⁹ and LiNiO₂.¹¹ Although we expected a high $E_{\text{redox}}^{\text{ave}}$ value (~4.5 V) for *r*-LCMO, the actual $E_{\text{redox}}^{\text{ave}}$ of sample #26 was approximately 2.97 V, probably due to a redox reaction of O²⁻/O⁻ ions together with a redox reaction of Co³⁺, Mn³⁺, Co⁴⁺, or Mn⁴⁺ ions (Table 1). Therefore, a possible way to further improve the electrochemical properties is to synthesize single-phase LiCo_{0.64}Mn_{0.36}O₂ because the Co:Mn ratio of the electrochemically active *r*-LCMO phase decreased to 64:36 from the initial composition (50:50). In addition, the co-substitution of Ni ions would facilitate the rhombohedral structure, although we focused on synthesizing LiCo_{0.5}Mn_{0.5}O₂ in this study. Evidently, the temperature–pressure region of *r*-LCMO was stabilized by using the LiOH·H₂O precursor, indicating the importance of compatibility in starting materials. Utilizing other Mn and Co precursors that improve the reactivity during the synthesis would be effective for obtaining high-purity *r*-LCMO samples.

4. CONCLUSION

We have successfully synthesized *r*-LCMO samples using a HP method, and we examined their electrochemical properties in nonaqueous lithium cells. When using the Li₂O precursor, the *r*-LCMO phase was observed in a limited temperature–pressure region, whereas it transformed into the cubic rock-salt LCMO (*c*-LCMO) phase above 600 °C. When using the LiOH or LiOH·H₂O precursor, however, *r*-LCMO was stable over a wider temperature–pressure region. The Q_{recha} in the voltage range between 1.8 and 4.8 V reached 138 mAh g⁻¹ with sample #24 and 126 mAh g⁻¹ with sample #26, which were synthesized at 400 °C and 12 GPa and at 600 °C and 12 GPa, respectively. The $E_{\text{redox}}^{\text{ave}}$ value of sample #26 was approximately 2.97 V, yielding a W of 374 mWh g⁻¹. These Q_{recha} and W values were not so small compared to those for LiCoO₂ and LiNiO₂, because at least 38 wt % of electrochemically inactive phases such as *c*-LCMO and *h*-LCMO coexisted in the sample. Moreover, the compositional analyses of sample #26 clarified that the Co:Mn ratio of the *r*-LCMO phase is not exactly the same as the initial composition (50:50) but slightly changed to 64:36. In addition, the comparison of the lattice parameters and the bond valence sum analysis indicated that the chemical composition of *r*-LCMO can be written as Li_{1.09}(Co_{0.64}Mn_{0.36})_{0.91}O₂, which is consistent with the observed electrochemical properties. Future work includes further HP syntheses using an initial composition ratio of 64:36, which could improve the electrochemical properties of *r*-LCMO.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00066.

SEM images of the precursors employed, XRD patterns of the samples synthesized at 5 and 12 GPa, charge and discharge curves of the samples synthesized at 5 and 12 GPa, dQ_{cha}/dV and dQ_{dis}/dV curves of sample #26,

results of the Rietveld refinement of sample #26, structural parameters of sample #26, changes in the lattice parameters of *r*-LCMO, and possible structural parameters for the *h*-LCMO phase (PDF)

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