Toward Positive Electrode Materials with High-Energy Density: Electrochemical and Structural Studies on LiCo$_{x}$Mn$_{2-x}$O$_{4}$ with 0 $\leq x \leq$ 1

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Supporting Information

ABSTRACT: To obtain positive electrode materials with higher energy densities (Ws), we performed systematic structural and electrochemical analyses for LiCo$_{x}$Mn$_{2-x}$O$_{4}$ (LCMO) with 0 $\leq x \leq$ 1. X-ray diffraction measurements and Raman spectroscopy clarified that the samples with $x \leq 0.5$ are in the single-phase of a spinel structure with the $Fd\bar{3}m$ space group, whereas the samples with $x \geq 0.75$ are in a mixture of the spinel-phase and Li$_2$MnO$_3$ phase with the $C2/m$ space group. The $x$-dependence of the discharge capacity ($Q_{dis}$) indicated a broad maximum at $x = 0.5$, although the average operating voltage ($E_{ave}$) monotonically increased with $x$. Thus, the W value obtained by $Q_{dis} \times E_{ave}$ reached the maximum (=627 mW h g$^{-1}$) at $x = 0.5$, which is greater than that for Li[Li$_{1/2}$Mn$_{3/2}$]O$_4$. Furthermore, the change in the lattice volume ($AV$) during charge and discharge reactions approached 0%, that is, zero-strain, at $x = 1$. Because $AV$ for $x = 0.5$ was smaller than that for Li[Li$_{1/2}$Mn$_{3/2}$]O$_4$, the $x = 0.5$ sample is found to be an alternative positive electrode material for Li[Li$_{1/2}$Mn$_{3/2}$]O$_4$ with a high W.

1. INTRODUCTION

The bottom line of batteries in baseball is the harmonizing of a pitcher and a catcher. In the same way, the balancing of the electrochemical performances between a positive electrode and a negative electrode is crucial for secondary batteries. As previously reviewed for lithium-ion batteries (LIBs), the energy densities (Ws) for positive electrode materials are significantly lower than those for negative electrode materials. This imbalanced situation still restricts the widespread applications of LIBs, such as in electric vehicles (EVs) and stationary energy storage systems (ESSs). In other words, positive electrode materials with higher Ws are urgently required to realize more practical EVs and ESSs.

The W value for a positive electrode material is determined as follows

$$ W = \int Q_{recha} dQ \times E_{ave} $$(1)

where $Q_{recha}$ is the rechargeable capacity and $E_{ave}$ is the average operation voltage. Therefore, a positive electrode material with a high $Q_{recha}$ or a high $E_{ave}$ or both provides a high W. Over the past decade, lithium–nickel–manganese spinel Li[Li$_{1/2}$Mn$_{3/2}$]O$_4$ has attracted much attention because it offers ~135 mA h g$^{-1}$ of $Q_{recha}$ and 4.5 V versus Li$^+/Li$ of $E_{ave}$, resulting in more than 600 mW h g$^{-1}$ of W. Lithium–cobalt–manganese spinel LiCo$_{0.5}$Mn$_{1.5}$O$_4$ (LCMO) with 0 $\leq x \leq$ 1 is also promising from the viewpoint of $E_{ave}$, namely, the redox reaction of Co$^{3+}$ $\leftrightarrow$ Co$^{4+}$ in LCMO is ~0.3 V higher than that of Ni$^{3+}$ $\leftrightarrow$ Ni$^{4+}$ in Li[Li$_{1/2}$Mn$_{3/2}$]O$_4$.

Previous X-ray absorption near-edge structure (XANES) analyses and magnetic measurements of electron paramagnetic resonance (EPR) and susceptibility indicated that Co ions in LCMO are in the trivalent state with a low-spin $t_{2g}^0$ ($S = 0$) configuration. The ideal electrochemical reaction of LCMO is thus represented as

$$ \text{LiCo$_{3/4}$Mn$_{1/4}$O}_4 \rightarrow \text{Li}^+ + e^- + \text{Co$_{3/4}$Mn$_{1/4}$O}_4 $$(2)

where the theoretical capacity ($Q_{theo}$) is calculated to be (148.23 – 32.1x) mA h g$^{-1}$. The current $Q_{recha}$ for $x = 1$ is, however, significantly lower than $Q_{theo}$ and is usually limited to ~100 or 116 mA h g$^{-1}$ at the maximum. This comes from the presence of Li$_2$MnO$_3$ impurities in $x = 1$, which are electrochemically inactive. By contrast, the $E_{ave}$ for LCMO almost linearly increases on increasing the amount of the Co$^{3+}$ $\leftrightarrow$ Co$^{4+}$ redox reaction. Because W is the product obtained by the multiplication of $Q_{recha}$ and $E_{ave}$ as shown by eq 1, the opposite trend between $Q_{recha}$ and $E_{ave}$ in LCMO is expected to indicate a maximum W value at a certain $x$ composition. Despite the intensive studies on LCMO thus far, a
systematic study to explore the optimum $x$ composition for the highest $W$ has not been undertaken.

In this contribution, we report the results of $Q_{\text{char}}$, $E_{\text{ave}}$, and $W$ as a function of $x$ in LCMO and compare them with Li[Ni$_{1/3}$Mn$_{3/2}$]O$_4$. Structural analyses using synchrotron radiation X-ray diffraction (XRD) measurements and Raman spectroscopy were also performed to clarify the relation between the electrochemical properties and crystal structures of LCMO. Consequently, we revealed that the $x = 0.5$ composition provides the maximum $W$ value of 627 mW h g$^{-1}$, with a change in the lattice volume of $\sim 4\%$. These performances were found to be superior to those of Li[Ni$_{1/3}$Mn$_{3/2}$]O$_4$.

2. RESULTS AND DISCUSSION

2.1. Particle Morphology. For positive electrode materials with high $E_{\text{ave}}$ values, the particle size and morphology significantly affect their electrochemical properties, probably due to the decomposition of electrolytes. To clarify changes in the particle size and morphology with $x$, Figure 1 shows the scanning electron microscopy (SEM) images for the LCMO samples with (a) $x = 0$, (b) $x = 0.5$, and (c) $x = 1$. One of the particles in the $x = 1$ sample (surrounded by the red dotted line) shows a truncated octahedron with a facet growth velocity ratio ($\alpha$) of 2.25 $< \alpha < 2.5$.

![Figure 1. SEM images on the 5 $\mu$m scale for the LiCo$_{0.5}$Mn$_{2.5}$O$_4$ samples with (a) $x = 0$, (b) $x = 0.5$, and (c) $x = 1$. One of the particles in the $x = 1$ sample (surrounded by the red dotted line) shows a truncated octahedron with a facet growth velocity ratio ($\alpha$) of 2.25 $< \alpha < 2.5$.](image)

2.2. Electrochemistry. Figure 2 shows the charge and discharge curves of the LCMO/Li cells with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1$. The cells were operated at a current of 0.6 mA (0.3 mA cm$^{-2}$) in the voltage range between 3.0 and 5.4 V at 25 $^\circ$C.

![Figure 2. Charge and discharge curves of the LiCo$_{0.5}$Mn$_{2.5}$O$_4$/Li cells with (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, and (e) $x = 1$.](image)
dependence of $Q_{\text{dis}}$ indicates a broad maximum at around $x = 0.5$, whereas $E_{\text{ave}}$ almost monotonically increases from 4.166 V at $x = 0$ to 4.996 V at $x = 1$. The observed $Q_{\text{dis}}$ is lower than the calculated $Q_{\text{theo}}$ over the whole $x$ range. Consequently, $W$ gradually increases from 480 mW h g$^{-1}$ at $x = 0$, then reaches the maximum ($=627$ mW h g$^{-1}$) at $x = 0.5$, and finally decreases to $516$ mW h g$^{-1}$ at $x = 1$. The maximum $W$ value for $x = 0.5$ is slightly greater than that for Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ ($=607$ mW h g$^{-1}$), and as far as we are concerned, the $x$-dependence of $W$ in LCMO has been clarified for the first time because previous studies on LCMO were focused on the $Q_{\text{dis}}$ values.$^{20-21}$

2.3. Crystal Structure. In this section, we examined the crystal structures before and after the charge reaction to understand the electrochemical reaction scheme of LCMO.

Figure 4 shows the results for the Rietveld analyses for the pristine Li$_{1-x}$Mn$_2$O$_4$ samples with (a) $x = 0$, (b) $x = 0.5$, and (c) $x = 1$. Enlarged XRD patterns are also shown in the insets to clarify the presence of the Li$_2$MnO$_3$ phase (indicated by *). The 220 diffraction in $x = 1$ indicates the presence of Co ions at the tetrahedral 8a site.

Before describing the result for $x = 0.5$, we wish to mention the result for $x = 1$. The majority of the $x = 1$ sample is in the $Fd\bar{3}m$ space group, as in the case for $x = 0$. However, as seen in the inset of Figure 4c, the diffraction lines indicated by * are clearly observed in the vicinity of the diffraction line around $2\theta = 10^\circ$ (the 111 diffraction line of the spinel structure). These diffraction lines originate from the Li$_2$MnO$_3$ phase with the monoclinic structure, whose weight fraction is determined to be

![Figure 3. Results of the electrochemical measurements for the LiCo$_{1-x}$Mn$_{2+x}$O$_4$ samples with $0 \leq x \leq 1$. (a) discharge capacity at the initial cycle ($Q_{\text{dis}}$), (b) average voltage ($E_{\text{ave}}$) of the initial discharge curve, and (c) energy density ($W$) obtained by $Q_{\text{dis}} \times E_{\text{ave}}$. The solid line indicates the $Q_{\text{theo}}$ for LCMO calculated by (148.23 $-$ 3.21$L_x$) mA h g$^{-1}$. The results for Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ with the P4$_3$2 space group are taken from ref 5.](image-url)
6.23%. Coexistence of the Li$_2$MnO$_3$ phase is also reported in previous structural analyses on $x = 1$. Moreover, the intensity of the 220 diffraction line at around 2$\theta$ = 17° is slightly larger than that for $x = 0$ [compare Figure 4a,c], indicating that a small amount of metal (Co) ions exists in the tetrahedral 8a site. As a result, the crystal structure for the $x = 1$ sample is assigned as a mixture of the spinel phase with the Fd$\bar{3}$m space group and the Li$_2$MnO$_3$ impurity with the C2/m space group. Because the amount of Co ions at the 8a site is determined to be 0.113(1), the actual formula for $x = 1$ can be represented as Li$_{0.887}$Co$_{0.113}$[CoMn]O$_4$. Note that the mixture of 93.77 wt % Li$_{0.887}$Co$_{0.113}$[CoMn]O$_4$ and 6.23 wt % Li$_2$MnO$_3$ is consistent with the Li/Co/Mn (=1/1/1) composition of the starting material: mol % of Li$_{0.887}$Co$_{0.113}$[CoMn]O$_4$ and Li$_2$MnO$_3$ are calculated to be 89.3 and 10.7, respectively, providing the composition of Li/Co/Mn = 0.887/1/1.00.

The Li$_2$MnO$_3$ impurity is not observed in the $x = 0$ sample [see Figure 4b]. The crystal structure for $x = 0.5$ is thus assigned as the single-phase of the spinel structure with the Fd$\bar{3}$m space group. Figure S3 shows the results for the Rietveld analyses for the pristine (a) $x = 0.25$ and (b) $x = 0.75$ samples. The situation for $x = 0.25$ is similar to that for $x = 0.5$; the sample crystallized into a single-phase of the spinel structure. By contrast, the Li$_2$MnO$_3$ impurity was observed in the XRD pattern for the $x = 0.75$ sample [see diffraction lines indicated by * in Figure S3b]. The weight fraction of the Li$_2$MnO$_3$ phase in $x = 0.75$ is determined to be 1.67%, and the actual formula for $x = 0.75$ can be represented as Li$_{0.970}$Co$_{0.030}$[CoMn]O$_4$. As seen from Figure S4, the amount of the Li$_2$MnO$_3$ phase in LCMO rapidly increases at $x \geq 0.75$.

We next examined the distributions of the Li$_2$MnO$_3$ phase in the $x = 1$ sample by Raman spectroscopy. Figure S5 shows the Raman spectra for the LCMO samples with 0 $\leq x \leq 1$. According to a factor group analysis, five Raman active modes of A$_{1g}$ + E$_g$ + 3F$_{2g}$ are predicted for the spinel structure with the Fd$\bar{3}$m space group. The Raman spectrum for $x = 0$ shows a major Raman band at around 623 cm$^{-1}$ and three minor Raman bands at 572, 477, and 365 cm$^{-1}$. The major Raman band is assigned as the A$_{1g}$ mode, which corresponds to a symmetric vibration between Mn$^{3+}$/Mn$^{4+}$ and O$^{2-}$ ions.16,23 The major Raman band at around 623 cm$^{-1}$ splits into two or three Raman bands with $x$, probably due to the change in the proportion of Mn$^{3+}$/Mn$^{4+}$ ions.16,23 As seen in Figure 5a, the $x = 1$ sample indicates three major Raman bands at around 652, 575, and 538 cm$^{-1}$ and three minor Raman bands at around 475, 382, and 179 cm$^{-1}$. Although these Raman bands are still unassigned, the Raman spectrum for $x = 1$ significantly differs from that for the single-phase of Li$_2$MnO$_3$ [Figure Sb]. This enables the LiCoMnO$_4$ sample to be distinguished into Li$_{0.887}$Co$_{0.113}$[CoMn]O$_4$ and Li$_2$MnO$_3$ phases. As provided in Figure Sc, the Li$_2$MnO$_3$ phase segregates from the Li$_{0.887}$Co$_{0.113}$[CoMn]O$_4$ phase, not coexisting in the Li$_{0.887}$Co$_{0.113}$[CoMn]O$_4$ phase.

Table 1. Structural Parameters for the Pristine LiCo$_{0.25}$Mn$_{0.75}$O$_4$ Samples with $x = 0, 0.25, 0.5, 0.75, 1$ Determined by the Rietveld Analyses

| $x$ in LiCo$_{0.25}$Mn$_{0.75}$O$_4$ | atom | Wyckoff position | occupancy | $x$ | $y$ | $z$ | $B_{	ext{ave}}$ (Å$^2$) |
|---|---|---|---|---|---|---|---|
| $x = 0$ | Li | 8a | 1.00 | 0.125 | 0.125 | 0.125 | 0.86(1) |
| | Mn | 16d | 1.00 | 0.5 | 0.5 | 0.5 | 0.61(1) |
| | O | 32e | 1.00 | 0.264(1) | 0.264(1) | 0.264(1) | 0.87(1) |
| $x = 0.25$ | Li | 8a | 1.00 | 0.125 | 0.125 | 0.125 | 0.67(1) |
| | Co | 16d | 0.125 | 0.5 | 0.5 | 0.5 | 0.45(1) |
| | Mn | 16d | 0.875 | 0.5 | 0.5 | 0.5 | 0.45(1) |
| | O | 32e | 1.00 | 0.264(1) | 0.264(1) | 0.264(1) | 0.52(1) |
| $x = 0.5$ | Li | 8a | 1.00 | 0.125 | 0.125 | 0.125 | 1.2(1) |
| | Co | 16d | 0.25 | 0.5 | 0.5 | 0.5 | 0.37(1) |
| | Mn | 16d | 0.75 | 0.5 | 0.5 | 0.5 | 0.37(1) |
| | O | 32e | 1.00 | 0.264(1) | 0.264(1) | 0.264(1) | 0.50(1) |
| $x = 0.75$ | Li | 8a | 0.970(1) | 0.125 | 0.125 | 0.125 | 0.76(1) |
| | Co | 16d | 0.030(1) | 0.125 | 0.125 | 0.125 | 0.76(1) |
| | Co2 | 16d | 0.371(1) | 0.5 | 0.5 | 0.5 | 0.26(1) |
| | Mn | 16d | 0.629(1) | 0.5 | 0.5 | 0.5 | 0.26(1) |
| | O | 32e | 1.00 | 0.264(1) | 0.264(1) | 0.264(1) | 0.37(1) |
| $x = 1$ | Li | 8a | 0.887(1) | 0.125 | 0.125 | 0.125 | 0.43(1) |
| | Co | 16d | 0.113(1) | 0.125 | 0.125 | 0.125 | 0.43(1) |
| | Co2 | 16d | 0.5(1) | 0.5 | 0.5 | 0.5 | 0.22(1) |
| | Mn | 16d | 0.5(1) | 0.5 | 0.5 | 0.5 | 0.22(1) |
| | O | 32e | 1.00 | 0.264(1) | 0.264(1) | 0.264(1) | 0.52(1) |
consumed for electrolyte decompositions. As seen from Figures 6 and S6, all LCMO samples maintain a spinel structure with the Fd3m space group, as in the cases for the initial (pristine) state. Structural parameters, such as $a_i$ and $u$, are summarized in Table 2.

2.4. $\Delta a_i$ and $\Delta V$ for LCMO. Figure 7a shows the $a_i$ values before and after the fully charged reaction as a function of $x$ in LiCo$_{\delta}$Mn$_{1-\delta}$O$_4$. The $a_i$ value before the charge reaction (pristine sample) monotonically decreases from 8.2225(1) Å at $x = 0$ to 8.0589(1) Å at $x = 1$. This linear decrease in $a_i$ agrees with the change in the ionic radius ($r$) from Mn$^{3+}$ ions with $CN = 6$ ($r_{Mn^{3+}} = 0.58$ Å) to Co$^{3+}$ ions ($r_{Co^{3+}} = 0.55$ Å) with $CN = 6$, where $CN$ is the coordination number. The $a_i$ value after the fully charged reaction also indicates a linear decrease in $a_i$ with $x$, however, its slope ($a_i/x$) is much smaller than that for the LCMO samples before the charge reaction. That is, the $a_i$ value slightly decreases from 8.0581(1) Å at $x = 0$ to 8.0083(1) Å at $x = 1$.

Using these $a_i$ values for LCMO, the change in $a_i$ ($\Delta a_i$) and the change in the lattice volume ($\Delta V$) are determined. As seen in Figure 7b, both $\Delta a_i$ and $\Delta V$ values decrease with increasing $x$; for instance, $\Delta a_i = -1.99$% and $\Delta V = -5.88$% for $x = 0$, $\Delta a_i = -1.36$% and $\Delta V = -4.01$% for $x = 0.5$, and $\Delta a_i = -0.63$% and $\Delta V = -1.87$% for $x = 1$. Here, the $\Delta a_i$ and $\Delta V$ values for Li$_{[Ni_{1/2}Mn_{3/2}]}$O$_4$ are calculated to be $-1.98$% and $-5.83$%, respectively, using the reported $a_i$ values before ($8.167$ Å) and after ($8.005$ Å) the fully charged reaction. Therefore, the $\Delta a_i$ and $\Delta V$ values for $x = 0.5$ are smaller than those for Li$_{[Ni_{1/2}Mn_{3/2}]}$O$_4$, although the $V$ value for $x = 0.5$ is greater than that for Li$_{[Ni_{1/2}Mn_{3/2}]}$O$_4$.

It should be noted that the $\Delta a_i$ and $\Delta V$ values for $x = 1$ are significantly smaller compared with those for other positive electrode materials, such as LiCoO$_2$ ($\Delta V \approx 2.5$% at the half-charged state) and LiFePO$_4$ ($\Delta V \approx 6$%$\text{−}6.9$%). The $\Delta V$ value of $-1.87$% for $x = 1$ can be regarded as a “zero-strain” lithium insertion material because one of the zero-strain lithium insertion materials, Li$_{[CrTi]}$O$_4$, indicates a $\Delta V$ of $+0.7$%. Thus far, this statement has not been explicitly expressed, although Alcántara et al. reported the change in $a_i$ for Li$_{CoMnO_4}$.

Zero-strain lithium insertion materials such as Li$_{[CrTi]}$O$_4$ and Li$_{[Li_{1/2}Ti_{1/2}]}$O$_4$ (LTO) are used as negative electrode materials, whereas the $x = 1$ sample is used as a positive electrode material. XRD and Raman spectroscopy clarified that the zero-strain reaction scheme of LTO is achieved by a change in $u$ on proceeding with the discharge reaction, that is, local structural changes in the Li$_{O_4}$ and Ti$_{O_4}$ environments. To compare with such a zero-strain reaction scheme, $u$ values during various charge states were determined by the Rietveld analyses for $x = 1$. As shown in Figure 8a, $u$ for Li$_{CoMnO_4}$ maintains a constant value ($\approx 0.263$) up to the fully charged state, suggesting that the zero-strain reaction scheme for $x = 1$ is different from that for LTO. Considering the $a_i$ value ($\approx 8.00$ Å) at the fully charged state, one can understand the zero-strain reaction scheme for $x = 1$. That is, the minimum $a_i$ value for face-centered cubic (FCC) consisting of only O$^{2-}$ ions is calculated to be $\approx 7.8$ Å, using the relations $a_i = 4\sqrt{2}r_{O^{2-}}$ and $r_{O^{2-}} = 1.38$ Å (CN = 4) [see Figure 8b]. Hence, the zero-strain character for $x = 1$ is achieved by a rigid framework structure of O$^{2-}$ with FCC packing. In other words, negative electrode materials with zero-strain are due to reversible changes in the local structures, whereas positive electrode materials with zero-strain are due to invariance in the local structures.

Finally, we wish to describe the strategy for positive electrode materials with more high-energy density. Although the $x = 0.5$ sample indicates the maximum $W$ value among the various spinel oxides, its $W$ value is still lower than layered oxides; for instance, layered oxides comprising Li/Ni/Mn/O$^{2-}$ exhibit more than 300 mA h g$^{-1}$ of $Q_{dis}$ and $\sim 3.5$ V of $E_{out}$ resulting in more than 1000 mW h g$^{-1}$ of $W$. The present findings confirm that the redox reaction of Co$^{3+}$ $\leftrightarrow$ Co$^{4+}$ is effective to increase...
Thus, layered oxides comprising Li/Co/Mn/O would exhibit greater $W$ values, although the combination of Co and Mn ions in the layered structure is reported to be thermodynamically unstable. Trials for preparing layered Li/Co/Mn/O oxides are underway in our laboratory.

### 3. CONCLUSIONS

To pair harmoniously with the high $W$ value negative electrode materials, explorations for positive electrode materials with high $W$ values have been performed in a series of LCMO spinels with $0 \leq x \leq 1$. The maximum $Q_{\text{dis}}$ value for LCMO was exhibited at $x = 0.5$, whereas $E_{\text{ave}}$ increased monotonically with

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**Table 2. Structural Parameters for the Fully Charged Li$_y$Co$_x$Mn$_{2-x}$O$_4$ Samples with $x = 0$, 0.25, 0.5, 0.75, and 1 Determined by the Rietveld Analyses**

| $x$ in Li$_y$Co$_x$Mn$_{2-x}$O$_4$ | atom | Wyckoff position | occupancy | $x$ | $y$ | $z$ | $B_{\text{iso}}$ ($\text{Å}^2$) |
|----------------------------------|------|-----------------|-----------|----|----|----|------------------|
| $x = 0$                          | Li   | 8a              | 0.15      | 0.125 | 0.125 | 0.125 | 0.86(1)         |
|                                 | Mn   | 16d             | 1.00      | 0.5   | 0.5   | 0.5   | 0.61(1)         |
|                                 | O    | 32e             | 1.00      | 0.262(1) | 0.262(1) | 0.262(1) | 0.87(1)         |
| **SG: Fd$ar{3}$m, $a_0 = 8.0585(1)$ Å, $R_{wp} = 5.46\%$, and $S = 0.489$** | | | | |
| $x = 0.25$                       | Co   | 16d             | 0.125     | 0.5   | 0.5   | 0.5   | 0.45(1)         |
|                                 | Mn   | 16d             | 0.875     | 0.5   | 0.5   | 0.5   | 0.45(1)         |
|                                 | O    | 32e             | 1.00      | 0.263(1) | 0.263(1) | 0.263(1) | 0.52(1)         |
| **SG: Fd$ar{3}$m, $a_0 = 8.0525(1)$ Å, $R_{wp} = 5.90\%$, and $S = 0.539$** | | | | |
| $x = 0.5$                        | Co   | 16d             | 0.25      | 0.5   | 0.5   | 0.5   | 0.37(1)         |
|                                 | Mn   | 16d             | 0.75      | 0.5   | 0.5   | 0.5   | 0.37(1)         |
|                                 | O    | 32e             | 1.00      | 0.263(1) | 0.263(1) | 0.263(1) | 0.50(1)         |
| **SG: Fd$ar{3}$m, $a_0 = 8.0196(1)$ Å, $R_{wp} = 7.70\%$, and $S = 0.692$** | | | | |
| $x = 0.75$                       | Li   | 8a              | 0.008     | 0.125 | 0.125 | 0.125 | 0.76(1)         |
|                                 | Co1  | 8a              | 0.030     | 0.125 | 0.125 | 0.125 | 0.76(1)         |
|                                 | Co2  | 16d             | 0.371     | 0.5   | 0.5   | 0.5   | 0.26(1)         |
|                                 | Mn   | 16d             | 0.629     | 0.5   | 0.5   | 0.5   | 0.26(1)         |
|                                 | O    | 32e             | 1.00      | 0.263(1) | 0.263(1) | 0.263(1) | 0.37(1)         |
| **SG: Fd$ar{3}$m, $a_0 = 8.0081(1)$ Å, $R_{wp} = 6.02\%$, and $S = 0.535$** | | | | |
| $x = 1$                          | Li   | 8a              | 0.228     | 0.125 | 0.125 | 0.125 | 0.43(1)         |
|                                 | Co1  | 8a              | 0.113     | 0.125 | 0.125 | 0.125 | 0.43(1)         |
|                                 | Co2  | 16d             | 0.22(1)   | 0.5   | 0.5   | 0.5   | 0.22(1)         |
|                                 | Mn   | 16d             | 0.5       | 0.5   | 0.5   | 0.5   | 0.22(1)         |
|                                 | O    | 32e             | 1.00      | 0.263(1) | 0.263(1) | 0.263(1) | 0.52(1)         |
| **SG: Fd$ar{3}$m, $a_0 = 8.0052(1)$ Å, $R_{wp} = 11.49\%$, and $S = 1.04$** | | | | |

**Figure 7.** (a) Cubic lattice parameters ($a_0$) for the pristine LiCo$_x$Mn$_{2-x}$O$_4$ samples and fully charged Li$_y$Co$_x$Mn$_{2-x}$O$_4$ samples. The solid line in (a) indicates the calculated $a_0$ value from $4\sqrt{2}r_{\text{O}^{2-}}$. (b) Change in $\Delta a_0$ and change in the lattice volume ($\Delta V$) during charge and discharge reactions as a function of $x$ in LiCo$_x$Mn$_{2-x}$O$_4$. The $\Delta V$ value for Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ was calculated from the data in ref 4.

**Figure 8.** (a) Change in the oxygen positional parameter ($u$) as a function of $y$ in Li$_y$CoMnO$_4$. (b) Schematics of zero-strain reaction scheme for Li$_y$CoMnO$_4$. The $a_0$ value ($\approx 8.0$ Å) for Li$_y$CoMnO$_4$ is close to the minimum lattice parameter ($4\sqrt{2}r_{\text{O}^{2-}} \approx 7.8$ Å) for the FCC consisting of O$^{2-}$ ions.
x. Therefore, the maximum W value (=627 mW h g\(^{-1}\)) was obtained at the x = 0.5 composition. The W value for x = 0.5 was slightly greater than that for Li\([Ni_{1/2}Mn_{3/2}]O_4\) which has attracted much attention because of its high W value. XRD measurements using synchrotron radiation clarified another advantage for the x = 0.5 sample; that is, the ΔV value for x = 0.5 was about 2% smaller than that for Li\([Ni_{1/2}Mn_{3/2}]O_4\). Thus, the x = 0.5 sample is regarded as a next-generation positive electrode material with a high W value and a long cycle-life. Concerning the ΔV values, the x = 1 sample showed the minimum ΔV value (=2%) among the various positive electrode materials and can be thought of as a zero-strain lithium insertion material, similar to LTO and Li\([CrTi]O_4\). The zero-strain character for x = 1 is due to the invariance in the local structures, which is different from those for LTO and Li\([CrTi]O_4\).

4. EXPERIMENTAL SECTION

4.1. Synthesis and Characterization. Powder samples of LCMO with x = 0, 0.25, 0.375, 0.5, 0.75, and 1 were prepared using a two-step solid-state reaction technique, as reported previously\(^{4,5,19}\) to obtain highly crystallized LCMO samples. Regent grade LiOH·H\(_2\)O (Wako Pure Chemical Industries, Ltd.), Co\(_3\)O\(_4\) (Kojundo Chemical Laboratory Co., Ltd.), and Mn\(_2\)O\(_3\) (Kojundo Chemical Laboratory Co., Ltd.) were mixed with a pestle and mortar and then pressed into a pellet of 16 mm (ϕ) size. A stainless steel plate (ϕ 19 mm) was pressed onto the lithium metal and used as the counter electrode. The electrolyte was 1 M LiPF\(_6\) dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (EC/DMC = 3/7 by volume) solution (KISHIDA Chemical Co. Ltd.). After fabricating the lithium cells in an argon-filled glovebox, the cells were operated at a current of 0.6 mA (≈0.3 mA cm\(^{-2}\)) in the voltage range between 3.0 and 5.4 V. This applied current corresponds to ∼2 C rate. The temperature for the electrochemical measurements was 25 °C.

4.2. Electrochemical Measurements. Electrochemical properties for the LCMO samples were examined in a nonaqueous lithium cell. The mixed electrode consisted of 88 wt % LCMO, 6 wt % conducting carbon, and 6 wt % polyvinylidene binder, as reported previously\(^{5,19}\). The surface area of the electrode was ∼2.00 cm\(^2\) (ϕ 16 mm). A stainless steel plate (ϕ 19 mm) was pressed onto the lithium metal and used as the counter electrode. The electrolyte was 1 M LiPF\(_6\) dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (EC/DMC = 3/7 by volume) solution (KISHIDA Chemical Co. Ltd.). After fabricating the lithium cells in an argon-filled glovebox, the cells were operated at a current of 0.6 mA (≈0.3 mA cm\(^{-2}\)) in the voltage range between 3.0 and 5.4 V. This applied current corresponds to ∼2 C rate. The temperature for the electrochemical measurements was 25 °C.

4.3. Synchrotron Radiation Study. To clarify changes in the crystal structures in the charged states, XRD measurements were also performed at the synchrotron radiation facility, Aichi Synchrotron Radiation Center. All of the charged LCMO samples were prepared using electrochemical reactions and packed into borosilicate capillary tubes with a diameter of 0.3 mm (W. Müller Glas Technik) in the argon-filled glovebox. The XRD patterns were recorded in the 2θ range between 5 and 95° using the two-dimensional detector (PILLATUS 100 K, DECTRIS Ltd.) of the BL52 beamline. The wavelength of X-ray was determined to be 0.779547(3) Å from the XRD measurement of a silicon standard (NIST 640d). Rietveld analyses were carried out using the RIETAN-FP software,\(^{34}\) and the schematics of the crystal structures were drawn by the VESTA software.\(^{35}\) The weight fraction, that is, the mol fraction of the LCMO and Li\(_2\)Mn\(_2\)O\(_3\) phases were determined by the multiphase mode in the RIETAN-FP program.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00948.

SEM images for the LCMO samples with x = 0.25 and 0.75, charge and discharge curves for the x = 1 samples prepared at the maximum temperatures at 1000 and 1100 °C, results of the Rietveld analyses for the pristine LCMO samples with x = 0.25 and 0.75, weight fraction of the Li\(_2\)Mn\(_2\)O\(_3\) phase in the LCMO samples, Raman spectra for the LCMO samples with x = 0, 0.25, 0.5, 0.75, and 1, and results of the Rietveld analyses for the fully charged LCMO samples with x = 0.25 and 0.75 (PDF)

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REFERENCES

(1) Tarascon, J.-M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. Nature 2001, 414, 359–367.
(2) Ohzuku, T.; Brodd, R. J. An Overview of Positive-Electrode Materials for Advanced Lithium-Ion Batteries. J. Power Sources 2007, 174, 449–456.

(3) Zhong, Q.; Bonakdarpour, A.; Zhang, M.; Gao, Y.; Dahn, J. R. Synthesis and Electrochemistry of LiNiMn2−xO4. J. Electrochem. Soc. 1997, 144, 205–213.

(4) Ariyoshi, K.; Iwakoshi, Y.; Nakayama, H.; Ohzuku, T. Topotactic Two-Phase Reactions of Li[Ni0.5Mn0.5]O2 (P43m) in Nonaqueous Lithium Cells. J. Electrochem. Soc. 2004, 151, A296–A303.

(5) Mukai, K.; Sugiyama, J. An Indicator to Identify the Li[Ni0.5Mn0.5]O2 (P43m): DC-Suscceptibility Measurements. J. Electrochem. Soc. 2010, 157, A672–A676.

(6) Hu, M.; Pang, X.; Zhou, Z. Recent progress in high-voltage lithium-ion batteries. J. Power Sources 2013, 237, 229–242.

(7) Kawai, H.; Nagata, M.; Tukamoto, H.; West, A. R. A New Lithium Cathode LiCoMoO4: Toward Practical 5 V Lithium Batteries. Electrochem. Solid-State Lett. 1998, 1, 212–214.

(8) Kawai, H.; Nagata, M.; Kageyama, H.; Tukamoto, H.; West, A. R. 5 V Lithium Cathodes Based on Spinel Solid Solutions LiCo1−xMn1−yO4 with 0.07 ≤ x ≤ 1 and 1 ≤ y ≤ 1. Electrochem. Acta 1999, 45, 315–327.

(9) Mandal, S.; Rojas, R. M.; Amariia, J. M.; Calle, P.; Kosova, N. V.; Antipin, V. F.; Rojo, J. M. High Temperature Co-Doped LiMn2O4 Based Spinel. Structural, Electrical, and Electrochemical Characterization. Chem. Mater. 2002, 14, 1598–1605.

(10) Alcañiza, R.; Jaraba, M.; Lavela, P.; Tirado, J. L. Electrochemical, (Li,Na)MnO4 NMR, and X-ray and Neutron Diffraction Study of LiCoO2/MnO2 Intercalation Compounds Synthesized from Wet-Chemical Route. J. Power Sources 2005, 147, 3592–3597.

(11) Hu, M.; Tian, Y.; Su, L.; Wei, J.; Zhou, Z. Preparation and Ni-Doping Effect of Nanosized Truncated Octahedral LiCoMoO4 as Cathode Materials for 5 V Li-Ion Batteries. ACS Appl. Mater. Interfaces 2013, 5, 1215–1216.

(12) Julien, C. M.; Mauger, A. Review of 5-V Electrodes for Li-Ion Batteries: Status and Trends. Ionics 2013, 19, 951–988.

(13) Hu, M.; Tian, Y.; Wei, J.; Wang, D.; Zhou, Z. Porous Hollow LiCoO2/MnO2 Microspheres As Cathode Materials for 5 V Lithium Batteries. J. Power Sources 2014, 247, 794–798.

(14) Zhecheva, E.; Stoyanova, R.; Alcañiza, R.; Lavela, P.; Tirado, J. L. EPR Studies of Li Deintercalation from LiCoMoO4 Spinel-Type Electrode Active Material. J. Power Sources 2006, 159, 1389–1394.

(15) Stoyanova, R. K.; Zhecheva, E. N.; Gorova, M. Y. EPR Evidence on Short-Range Co/Mn Order in LiCoMoO4 Spinel. J. Mater. Chem. 2000, 10, 1377–1381.

(16) Amouri, N.; Gendron, K.; Mauger, A.; Zarrouk, H.; Julien, C. M. LiMn2−xCo1−yO4 (0 ≤ y ≤ 1) Intercalation Compounds Synthesized from Wet-Chemical Route. Mater. Sci. Eng., B 2006, 129, 64–75.

(17) Ariyoshi, K.; Maeda, Y.; Kawai, T.; Ohzuku, T. Effect of Primary Particle Size upon Polarization and Cycling Stability of 5 V Lithium Insertion Material of Li[Ni1/3Mn2/3]O2. J. Electrochem. Soc. 2011, 158, A281–A284.

(18) Smereka, P.; Li, W.; Russo, G.; Srolovitz, D. J. Simulation of Faceted Film Growth in Three Dimensions: Microstructure, Morphology and Texture. Acta Mater. 2005, 53, 1191–1204.

(19) Mukai, K.; Sugiyama, J.; Ikedo, Y.; Nozaki, H.; Kamazawa, K.; Andreica, D.; Amato, A.; Månsén, M.; Brewer, J. H.; Ansoldo, E. J.; Chow, K. H. Microscopic Magnetic Study on the Nominal Composition Li[Li1/3Mn2/3]O4 by Muon-Spin Rotation/Relaxation Measurements. J. Phys. Chem. C 2010, 114, 11320–11327.

(20) Iwata, E.; Takeda, S.; Iwamasa, M.; Ohzuku, T. XRD Observation on Fully-Charged Li[Li1/3Mn2/3]O4 in Nonaqueous Lithium Cells. Electrochemistry 2003, 71, 1187–1191.

(21) Mukai, K.; Sugiyama, J.; Kamazawa, K.; Ikedo, Y.; Andreica, A.; Amato, A. Magnetic Properties of the Chemically Delithiated LiMnO2 with 0.07 ≤ x ≤ 1. J. Solid State Chem. 2011, 184, 1096–1104.

(22) Bhagavantam, S.; Venkataramudu, T. Theory of Groups and Its Application to Physical Problems; Academic Press: New York, 1969; pp 140–158.

(23) Julien, C. M.; Massot, M. Lattice Vibrations of Materials for Lithium Rechargeable Batteries I. Lithium Manganese Oxide Spinel. Mater. Sci. Eng., B 2003, 97, 217–230.

(24) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. 1976, 32, 751–767.

(25) Ohzuku, T.; Ueda, A. Solid-State Redox Reactions of LiCoO2 (RSm) for 4 Volt Secondary Lithium Cells. J. Electrochem. Soc. 1994, 141, 2972–2977.

(26) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. Phospho-Olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. J. Electrochem. Soc. 1997, 144, 1188–1194.

(27) Ohzuku, T.; Tatumi, K.; Matoba, N.; Sawai, K. Electrochemistry and Structural Chemistry of LiCrO4 (FeSm) in Nonaqueous Lithium Cells. J. Electrochem. Soc. 2000, 147, 3592–3597.

(28) Mukai, K.; Ariyoshi, K.; Ohzuku, T. Comparative Study of Li[CrTi]O4, Li[Li1/3Ti2/3]O4 and Li[Li1/2Fe1/2]Li1/3Ti2/3O4 in Nonaqueous Lithium Cathodes. J. Power Sources 2005, 146, 213–216.

(29) Ohzuku, T.; Ueda, A.; Yamamoto, N. Zero-Strain Insertion Material of Li[Li1/3Ti2/3]O4 for Rechargeable Lithium Cells. J. Electrochem. Soc. 1995, 142, 1431–1435.

(30) Ariyoshi, K.; Yamato, R.; Ohzuku, T. Zero-Strain Insertion Mechanism of Li[Li1/3Ti2/3]O4 for Advanced Lithium-Ion (Shuttlecock) Batteries. Electrochem. Acta 2005, 51, 1125–1129.

(31) Mukai, K.; Kato, Y.; Nakano, H. Understanding the Zero-Strain Lithium Insertion Scheme of Li[Li1/3Ti2/3]O4: Structural Changes at Atomic Scale Clarified by Raman Spectroscopy. J. Phys. Chem. C 2014, 118, 2992–2999.

(32) Ohzuku, T.; Nagayama, H.; Tsuji, K.; Ariyoshi, K. High-Capacity Lithium Insertion Materials of Lithium Nickel Manganese Oxides for Advanced Lithium-Ion Batteries: Toward Rechargeable Capacity More Than 300 mA h g−1. J. Mater. Chem. 2011, 21, 10179–10188.

(33) Li, W.; Song, B.; Manthiram, A. High-Voltage Positive Electrode Materials for Lithium-Ion Batteries. Chem. Soc. Rev. 2017, 46, 3006–3059.

(34) Izumi, F.; Momma, K. Three-Dimensional Visualization in Powder Diffraction. Solid State Phenom. 2007, 130, 15–20.

(35) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. J. Appl. Crystallogr. 2011, 44, 1272–1276.