Investigation on Crystal and Electronic Structures of 0.5Li₂MnO₃−0.5LiMnxNi₅Co₁−2xO₂ (x = 1/3, 5/12) Samples Heat-Treated under Vacuum Reducing Conditions

Yasushi IDEMOTO,* Tetsuya KASHIMA, and Naoto KITAMURA

Faculty of Science & Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

* Corresponding author: idemoto@rs.noda.tus.ac.jp

ABSTRACT

We prepared two 0.5Li₂MnO₃−0.5LiMnxNi₅Co₁−2xO₂ (x = 1/3, 5/12) samples using the solution method, followed by heat treatment under vacuum reducing conditions. ICP and average-valence analyses clarified that the amounts of lithium and oxygen were decreased by reductive heat treatments. Results of a cycle performance test showed that the heat-treated samples exhibited a high discharge capacity, although the voltage regions contributing to the improvements depended on the metal composition, i.e., 3.3 and 3.8 V for x = 1/3 and x = 5/12, respectively. In order to discuss the crystal structure, a Rietveld analysis by neutron diffraction was carried out. A localized model in which Mn occupied the 4a site and Li occupied the 2b site in the Li₂MnO₃-type structure (S.G.; Cm̅m) resulted in good fitting.

Keywords: Li Ion Battery, Cathode, Crystal Structure, Pair Distribution Function

1. Introduction

Lithium-ion batteries used in cellphones and laptops have high energy densities and there has been a rapid growth in their demand. In recent years, their applications have extended to and are expected in hybrid electric vehicles (HEV), electric vehicles (EV), power storage, and emergency power supplies. Consequently, batteries with higher level energy densities are needed. Among the possible solutions, Li₂MnO₃-LiMO₂ (M = Mn, Ni, Co) materials possess a layered rock-salt structure and exhibit a high capacity of 200 mA g⁻¹ or more when charging at 4.6 V or higher as reported in publications. Consequently, they have gained prominence as cathode materials with high energy densities.

Li₂MnO₃-LiMO₂ (M = Mn, Ni, Co) is thought to exist in Mn⁴⁺, Ni⁴⁺, and Co³⁺ forms. It exhibits a higher capacity than the theoretical capacity predicted from valence changes. Consequently, the charge-discharge process has been the subject of considerable debate. M. M. Thackery et al. proposed that oxygen is generated at an initial charging of 4.4 V or higher, which caused electrochemically active domains to form, and observed the generation of oxygen by differential electrochemical mass spectrometry. There is also considerable debate has over structural complexity. Li₂MnO₃-LiMO₂ possesses a layered rock-salt structure, and all principal peaks observed in powder X-ray diffraction patterns can be attributed to space group R3̅m. At 2θ = 20 to 23°, however, a broad peak originating from space group C2/m of Li₂MnO₃ is present. Results of structural simulation studies, HR-TEM observations, and NMR spectra proposed an ordered arrangement of excess lithium within the transition metal layer in the form of LiMn₉ or LiMn₉₋ₓMₓ (M = Ni, Co), such that the broad peak occurs through the emergence of lamination defects.

Thus far, we have conducted neutron total scattering analysis and local structural analysis employing the pair distribution function (PDF) method for LiMn₁₋ₓNiₓCo₁ₓOₓ systems with respect to differences in local structures of samples prepared under different synthesis conditions. The aim of the present research is to improve battery characteristics by suppressing the change in electronic state and generation of oxygen accompanying the initial charging. Consequently, two types of compositions for the 0.5Li₂MnO₃-0.5LiMnxNi₅Co₁−2xO₂ (x = 1/3, 5/12) samples were synthesized, and oxygen-eliminated samples were subsequently synthesized by reductive heat treatment at the prescribed temperature, time, and oxygen partial pressure. Crystalline structure was studied by Rietveld analysis using powder neutron diffraction and PDF analysis by neutron total scattering. X-ray absorption spectroscopy was also used to study local and electronic structure changes by reductive heat treatment.

2. Experimental

2.1 Synthesis of samples

Two 0.5Li₂MnO₃-0.5LiMnxNi₅Co₁−2xO₂ (x = 1/3, 5/12) samples were synthesized by a solution method using citric acid, LiCH₃COO·2H₂O (99%, Wako Pure Chemical Industries, Ltd.), Li(CH₃COO)₂·4H₂O (99%, Wako Pure Chemical Industries, Ltd.), Mn(CH₃COO)₂·4H₂O (99%, Wako Pure Chemical Industries, Ltd.), Ni(CH₃COO)₂·4H₂O (99%, Wako Pure Chemical Industries, Ltd.), and Co(CH₃COO)₂·4H₂O (99%, Wako Pure Chemical Industries, Ltd.). The Li compound was weighed at 5 mol% excess of the normal amount, while the Ni, Co, and Mn compounds were weighed at the normal ratio. The same amount of citric acid as Li was added and they were dissolved in double-distilled water (300 ml). The mixture was dried at 130°C for 20 h in air and the obtained powder was pressed into a pellet (40 MPa). The obtained precipitate was calcined at 650°C for 15 h in air, heated at 950°C for 15 h in air and then quenched to room temperature. The obtained 0.5Li₂MnO₃-0.5LiMnxNi₅Co₁−2xO₂ (x = 1/3, 5/12) samples were heat-treated under respective vacuum reducing conditions at 800°C and 10⁻² Pa for 6 h, and at 800°C and 10⁻² Pa for 6 h.

2.2 Sample characterization

The phase of the obtained sample was identified by powder X-ray diffraction (Philips, X’PerPro; Cu Kα, 1°/min, 45 kV, 40 mA, 2θ = 10–70°). The lattice constants were determined from XRD data by the least squares method. The metal components in the sample were determined with an inductively coupled plasma (ICP) emission spectrometer (Shimadzu Corp., ICPS-7500, ICPE-9000).
The average valence of the transition metal (Mn, Ni, Co) were determined by potentiometric-titration measurements using potassium permanganate.

We also performed powder neutron scattering and X-ray absorption fine structure (XAFS) measurements to determine the effects of heat treatment on the average and local structures. The neutron powder diffraction patterns of \( x = 1/3 \) and \( x = 5/12 \) were measured by HERMES installed at JRR-3 and by SUPERHPD installed at J-PARC, respectively. The Rietveld analyses using the patterns were carried out using the RIETAN-FP program \(^{14} \) and Z-Code, \(^{15} \) respectively, and the effects of heat treatment on the average structures were then discussed. In addition, the neutron scattering patterns were measured by HIPPO installed at LANSCE in the USA. We investigated the local structures based on the PDF theory using PDFgetN \(^{16} \) and PDFFIT, \(^{17} \) as well as based on the XAFS spectra of \( x = 1/3 \) and \( x = 5/12 \) recorded at BL7C in KEK PF and BL14B2 in SPring-8 in Japan, respectively. The electronic and local structures were investigated using a REX2000 spectrometer (Rigaku Corp. Ltd., Japan). \(^{18} \)

2.3 Electrochemical measurement

We investigated the electrochemical characteristics of the samples by galvanostatic charge-discharge cycle measurements (Hokuto Denko Co., HJ1010mSM8) using a coin cell (HS cell, Hohsen). The cathode was a mixture of the sample (the active material), AB, KS-6, and PVdF at a weight ratio of 80:5:5:10. The cathode was hold at 50°C under vacuum, and pressed at about 40 MPa. The anode was a Li foil. A mixture of EC:DMC (a volume ratio of 1:2) with 1 mol/L LiPF\(_6\) (Kishida Chemical Ltd.) was used as the electrolyte, and a polypropylene film was used as the separator. A cell was assembled in a glove box under an argon atmosphere using the above materials.

The current density was 20 mA g\(^{-1}\) (0.1 C) for both the charge and discharge processes, and the respective cut-off voltages were 2.5 and 4.6 V vs. Li/Li\(^+\). The time between charging and discharging was 2 min.

3. Results and Discussion

3.1 Characterization of samples and electrode characteristics

Powder X-ray diffraction patterns of the 0.5Li\(_2\)MnO\(_3\)-0.5Li\(_2\)Mn\(_x\)Ni\(_{1-x}\)O\(_2\) samples prepared by the solution method are shown in Fig. 1. The principal peaks can be attributed to space group \( R3m \), but a peak arising from the ordered arrangement within the transition metal layer in the vicinity of 20 to 25° was observed. \(^{4} \) Differences in peak shapes caused by reductive heat treatment were mostly not observed, and retention of the original structure after heat treatment could be confirmed. The results of compositional and valence analyses are shown in Table 1. Composition ratios for untreated samples were calculated using a total of 2 for respective metal components, and by combining the total amounts of transition metals with the untreated samples for reductive heat-treated samples. Valences (theoretical valences) calculated using sample compositions derived by ICP emission spectroscopic analysis for Mn\(^{3+}\), Ni\(^{2+}\), and Co\(^{3+}\) are shown together. The ratios for Mn, Ni, and Co in the reductive heat-treated samples remained nearly constant, but Li elimination was confirmed. For the average valence, the untreated sample where \( x = 1/3 \) exhibited a value close to the theoretical valence, but the untreated sample where \( x = 5/12 \) exhibited a higher value compared to the theoretical valence. The presence of elements with a portion possessing high valence, such as Ni\(^{3+}\) or Co\(^{3+}\), is suggested in the latter untreated sample where \( x = 5/12 \). Valence decreased with reductive heat treatment and decreased slightly below the theoretical valence. The foregoing suggests that Li and oxygen relative to the decrease in transition metal valence are eliminated through reductive heat treatment.

![Figure 1. Powder X-ray diffraction patterns of 0.5Li\(_2\)MnO\(_3\)-0.5Li\(_2\)Mn\(_x\)Ni\(_{1-x}\)O\(_2\) materials for (a) \( x = 1/3 \), (b) \( x = 1/3 \) (800°C, 10\(^{-3}\) Pa, 6 h), (c) \( x = 5/12 \), (d) \( x = 5/12 \) (800°C, 10\(^{-2}\) Pa, 6 h).](image)

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<td>Co</td>
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<td>0.1350(1)</td>
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<td>[3.508]</td>
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<td>(c) 1.211(8)</td>
<td>0.562(3)</td>
<td>0.1616(3)</td>
<td>0.0642(4)</td>
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<td>[1.2] [0.5667] [0.1667] [0.0667]</td>
<td>[3.508]</td>
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<td>(d) 1.112(8)</td>
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The charge-discharge curves and the cycle characteristics of the samples are shown in Fig. 2 and Fig. 3, respectively. Every sample shows a long plateau at 4.4 V or higher during the initial charge process that is considered to be from oxygen elimination. \(^{4} \) Reductive heat-treated samples exhibited higher capacities than untreated samples. With respect to capacity retention, reductive heat-treated samples where \( x = 1/3 \) exhibited excellent cycle characteristics throughout the cycles without degradation. In contrast, reductive heat-treated samples where \( x = 5/12 \) experienced gradual capacity degradation as the number of cycles increased. In order to study the cause of capacity increase for reductive heat-treated samples, the capacities of respective discharge areas were examined.

In the discharging process, there are mainly 2 areas: approximately 4.6 to 3.6 V vs. Li/Li\(^+\) area (i) and approximately 3.6 to 2.5 V vs. Li/Li\(^+\) area (ii). Areas (i) and (ii) are respectively thought to correspond to the Ni and Co reduction processes and the Mn reduction process. For the sample where \( x = 1/3 \), area (ii) tended to increase through reductive heat treatment, and for the sample where \( x = 5/12 \), area (i) tended to increase. These observations suggest that reductive heat treatment caused Mn to be active in the samples where \( x = 1/3 \) and Ni or Co to be active in the samples where \( x = 5/12 \). The valence of the untreated sample is
believed to influence this phenomenon. As suggested by the valence analysis (Table 1), through reductive heat treatment Ni or Co redox involvement [area (ii)] is thought to increase for samples where $x = 1/3$ and high valence Ni or Co was not observed. For the irreversible capacity of the first cycle, samples where $x = 1/3$ decreased from 124 mAh g$^{-1}$ (untreated sample) to 111 mAh g$^{-1}$ (reductive heat-treated sample). This change corresponds to the capacity increase of the initial cycle according to reductive heat treatment (180 to 195 mAh g$^{-1}$). For $x = 5/12$, although an increase in capacity was observed (192 to 203 mAh g$^{-1}$), the observed change in irreversible capacity was small from 77 mAh g$^{-1}$ (untreated sample) to 80 mAh g$^{-1}$ (reductive heat-treated sample). From the above, control of irreversible capacity is thought to be possible through Mn activation.

3.2 Average structure analysis by powder neutron diffraction

In order to clarify the distribution of cations within the transition metal layer, Rietveld analysis was performed by employing powder neutron diffraction. Most peaks for the 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co$_{1-2x}$O$_2$ samples can be indexed by the layered rock-salt-type structure of $\alpha$-NaFeO$_2$ (space group R3m). Nonetheless, since some peaks caused by the ordered arrangement within the transition metal layer exist, analysis was performed for the monocristalline Li$_2$MnO$_3$-type structure (space group C2/m). For the present research, by conducting analysis where the occupancy of respective sites of the Li$_2$MnO$_3$-type structure (space group C2/m) was variable, the cation distribution in the transition metal layer (4g and 2b sites) and the change caused by reductive heat treatment were examined. As an example of analytical results, profiles of the 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co$_{1-2x}$O$_2$ ($x = 1/3$) sample analyzed using an angular-dispersion type powder neutron diffraction

**Figure 2.** Charge-discharge profiles for the 1st and 10th cycles of 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co$_{1-2x}$O$_2$ materials for (a) $x = 1/3$, (b) $x = 1/3$ (800°C, 10$^{-3}$ Pa, 6h), (c) $x = 5/12$, (d) $x = 5/12$ (800°C, 10$^{-3}$ Pa, 6h). (Temperature: 25°C, Current density: 20 mA g$^{-1}$, Cut off voltage: 2.5–4.6 V vs. Li/Li$^+$) →: 1st cycle, …: 10th cycle.

**Figure 3.** Cycle performances of 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co$_{1-2x}$O$_2$ materials. (Temperature: 25°C, Current density: 20 mA g$^{-1}$, Cut off voltage: 2.5–4.6 V vs. Li/Li$^+$) (i): (a) $x = 1/3$, (b) $x = 1/3$ (800°C, 10$^{-3}$ Pa, 6h), (ii): (c) $x = 5/12$, (iii): (d) $x = 5/12$ (800°C, 10$^{-3}$ Pa, 6h).

**Figure 4.** Differential-capacity plots of the 1st discharge profiles for 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co$_{1-2x}$O$_2$ [x = 1/3] materials. (Temperature: 25°C, Current density: 20 mA g$^{-1}$, Cut off voltage: 2.5–4.6 V vs. Li/Li$^+$)

**Figure 5.** Discharge capacity of (i) and (ii) areas in Fig. 4 for 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co$_{1-2x}$O$_2$ materials. (i): (a) $x = 1/3$, (b) $x = 1/3$ (800°C, 10$^{-3}$ Pa, 6h), (ii): (c) $x = 5/12$, (iii): (d) $x = 5/12$ (800°C, 10$^{-3}$ Pa, 6h).
apparatus (HERMES) and of x = 5/12 analyzed using a flight-time type powder neutron diffraction apparatus (SuperHRPD) are shown in Figs. 6 and 7, respectively, and obtained crystal structure parameters are shown in Tables 2 and 3, respectively. Crystal structure analysis was performed on the assumption that transition metals were present at 4g and 2b sites, Li at 2c and 4h sites, and O at 4i and 8j sites. In addition, cation mixing was considered, whereby Ni²⁺ whose ionic radius is close to Li⁺ could replace Li atoms at Li sites. Analysis was performed such that the total occupancy of metal components matched the analytical composition determined by ICP. As a result, each sample had a good match between the observed values and the calculated values. In the angular-dispersion type analysis, because occupancy of the respective elements at 4g and 2b sites could not be varied, analysis was performed by fixing some elements. Thus, to conduct detailed analysis, a flight-time type analysis must be employed. Nonetheless, because the occupancy for 2c and 4h sites in either analytical method could not be simultaneously varied with that for 4g and 2b sites, the analysis was performed by fixing the former sites. Table 4 provides the occupancy of the respective sites obtained from the analytical results of respective samples, and Fig. 8 depicts a model of the 4g and 2b sites in the Li₂MnO₃-type structure. Each sample exhibited a tendency for localized presence of Mn at the 4g site and Li at the 2b site. This tendency suggests the ordered arrangement of the 

Table 2. Final results of Rietveld refinements for 0.5Li₂MnO₃-0.5LiMnNi₃Co₁₋₂₉O₂ [x = 1/3] materials in space group C2/m at room temperature [HERMES]. B is an isotropic thermal parameter. Numbers in parentheses are estimated standard deviations of the last significant digits, and parameters without deviations are fixed. R-factor: Rwp = 7.35%, Refined = 5.41%, Rp = 5.80%, S = 1.27. Lattice parameter: a = 0.4943(1) nm, b = 0.8550(2) nm, c = 0.50236(7) nm, β = 109.24(2) degree.

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Table 3. Final results of Rietveld refinements for 0.5Li₂MnO₃-0.5LiMnNi₃Co₁₋₂₉O₂ [x = 5/12] materials in space group C2/m at room temperature [SuperHRPD]. B is an isotropic thermal parameter. Numbers in parentheses are estimated standard deviations of the last significant digits, and parameters without deviations are fixed. R-factor: Rwp = 8.76%, Refined = 6.80%, Rp = 5.39%, S = 1.63. Lattice parameter: a = 0.49495(5) nm, b = 0.85601(8) nm, c = 0.50301(5) nm, β = 109.287(2) degree.

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0.5Li₂MnO₃-0.5LiMnNi₃Co₁₋₂₉O₂ samples within the transition metal layer (Fig. 8). Ni and Co exhibited tendencies to occupy either the 4g or 2b site. Based on the composition analysis results, Li was
Table 4. Site occupancy of the 0.5Li₂MnO₂-0.5LiMn₁₋₃NiₓCo₁₋₃xO₂ materials for (a) x = 1/3, (b) x = 1/3 (800°C, 10⁻² Pa, 6 h), (c) x = 5/12, (d) x = 5/12 (800°C, 10⁻² Pa, 6 h).

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<thead>
<tr>
<th>Site</th>
<th>Atoms</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4g</td>
<td>Li</td>
<td>0.022</td>
<td>0.003</td>
<td>0.054(2)</td>
<td>0.0040(12)</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>0.726(1)</td>
<td>0.770(9)</td>
<td>0.774(5)</td>
<td>0.837(3)</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>0.105(7)</td>
<td>0.119(8)</td>
<td>0.1074(8)</td>
<td>0.092(4)</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>0.147</td>
<td>0.108</td>
<td>0.064(2)</td>
<td>0.065(1)</td>
</tr>
<tr>
<td>2b</td>
<td>Li</td>
<td>0.564</td>
<td>0.574</td>
<td>0.593(4)</td>
<td>0.671(2)</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>0.163(1)</td>
<td>0.081(9)</td>
<td>0.138(9)</td>
<td>0.0016(58)</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>0.163(7)</td>
<td>0.136(8)</td>
<td>0.204(2)</td>
<td>0.2171(9)</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>0.110</td>
<td>0.190</td>
<td>0.064(4)</td>
<td>0.062(2)</td>
</tr>
<tr>
<td>2c</td>
<td>Li</td>
<td>1.0</td>
<td>0.966</td>
<td>0.963</td>
<td>0.855</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>0.0</td>
<td>0.012</td>
<td>0.037</td>
<td>0.031</td>
</tr>
<tr>
<td>4h</td>
<td>Li</td>
<td>0.983</td>
<td>0.937</td>
<td>0.985</td>
<td>0.878</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>0.017</td>
<td>0.007</td>
<td>0.015</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Oxygen amounts: 1.95 [analysis value] 1.96 1.971 1.912

Figure 9. Relationship between r and observed G(r) for (i) LiMn₁₋₃NiₓCo₁₋₃xO₂ [x = 1/3], (ii) 0.5Li₂MnO₂-0.5LiMn₁₋₃NiₓCo₁₋₃xO₂ [x = 1/3, 5/12], (iii) 0.5Li₂MnO₂-0.5LiMn₁₋₃NiₓCo₁₋₃xO₂ [x = 5/12].

Therefore, the performance of the PDF analysis using neutron scattering data for the solid solution.

The observed Gₐb(r) values for the 0.5Li₂MnO₂-0.5LiMn₁₋₃NiₓCo₁₋₃xO₂ samples are shown in Fig. 9. The observed Gₐb(r) values were computed under the conditions of Rₘₐₓ = 18 Å and Qₘₐₓ = 22 Å⁻¹. The peak shapes of the observed Gₐb(r) values of the samples where x = 1/3 and x = 5/12 did not change, but LiMn₁₋₃NiₓCo₁₋₃xO₂ had peaks with different observed Gₐb(r) values whose different local structure could be anticipated. The difference in positive and negative peaks is thought to be caused by a composition of many Li (...)

3.3 Local structural analysis by neutron total scattering

PDF analysis employing neutron total scattering was conducted to study the detailed crystalline structure of the 0.5Li₂MnO₂-0.5LiMn₁₋₃NiₓCo₁₋₃xO₂ samples. In recent years, the PDF analysis has drawn much attention as one of the methods for a local structure analysis, and been applied for Li[Mn(Ni)O₂ and Li[Mn(Ni)O₂]-based samples. These works and some other works by means of first-principles calculation, electron and X-ray diffractions proposed some kinds of a transition-metal ordering, such as parallel, zigzag and \( \sqrt{3} \times \sqrt{3} \) R₃₀° type orderings. However, there were no systematic reports on a composition dependency of the ordering in the case of 0.5Li₂MnO₂-0.5LiMn₁₋₃NiₓCo₁₋₃xO₂. Therefore, we performed the PDF analysis using neutron scattering data for the solid solution.

Figure 8. (Color online) Transition metal layers of Li₂MnO₃-type structure.
model (III) were exchanged in model (VI). PDFFIT was employed for the PDF simulations. The results are shown in Fig. 10. From the PDF simulation results, different $G_{ab}(r)$ values based on each model are shown. With respect to the peak in the vicinity of 2 Å, peak splitting could be reproduced for only models (III) and (IV).

Differences in intensity are seen between these 2 models, and occupancy is thought to heavily influence the cause of this peak. Consequently, we attempt to study the cause of peak splitting in the vicinity of 2 Å using $G(r)$[Partial PDF] between the respective atoms. The observed $G_{ab}(r)$ values, calculated $G_{ab}(r)$ values of each simulation model, and Partial PDF are shown in Fig. 11. In order to study the most proximate distance for $G(r)$ between respective atoms, the metal-oxygen [Li-O, Mn-O, Ni-O, Co-O] lengths are shown. Partial PDF shows the presence of 2 local M-O environments at 1.9 Å [peak (1)] and 2.1 Å [peak (2)]. In addition, Li-O and Mn-O have negative scattering, Ni-O has positive scattering, and Co-O has hardly any scattering. Ni-O changed scattering depending on the occupancy, where Li exhibited negative scattering at 2.1 Å and Mn exhibited negative scattering at 1.9 Å. It is thought that the increase in Ni amount at the 2b site caused the Ni-O peak at 1.9 Å to approach 2.1 Å, to cancel the negative scattering of Li-O, and to have a peak shape closer to the observed value. Model (IV) whose 2b site was partially occupied with Co could reproduce the peak, but model (VI) whose 2b site was occupied with Mn could not reproduce the peak. From the above, PDF simulation results suggest that Li and Mn preferentially occupy 2b and 4g sites, respectively, while Ni and Co potentially occupy 2g and 4b sites. This matches the results of the Rietveld analysis described in section 3.2.

The change in peak shape according to the order was studied next. With model (III) as the reference standard since it gave the best reproduction under varying occupancy, the order was changed without varying occupancy. The models are shown in Fig. 12. Model (III) had a zigzag order with Ni and Co along axis b, while model (VII) had a random order. The PDF simulation results are shown in Fig. 13. Because peak shapes and intensities changed very little with the ordering, the distances are thought to have not changed despite the change in the order, since the initial model employed has an average structure and the parameters such as coordinates were constant. Thus, for PDF simulations based on average structures, only space groups and occupancy can be studied.

### Table 5. Number of atoms in 4g and 2b site for simulation model.

<table>
<thead>
<tr>
<th>Model</th>
<th>Li</th>
<th>Mn</th>
<th>Ni</th>
<th>Co</th>
<th>Li</th>
<th>Mn</th>
<th>Ni</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>12</td>
<td>32</td>
<td>8</td>
<td>8</td>
<td>6</td>
<td>16</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>(II)</td>
<td>6</td>
<td>36</td>
<td>9</td>
<td>9</td>
<td>12</td>
<td>12</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(III)</td>
<td>0</td>
<td>48</td>
<td>0</td>
<td>12</td>
<td>18</td>
<td>0</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>(IV)</td>
<td>0</td>
<td>48</td>
<td>6</td>
<td>8</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>(V)</td>
<td>0</td>
<td>42</td>
<td>6</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(VI)</td>
<td>0</td>
<td>42</td>
<td>3</td>
<td>12</td>
<td>18</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

Total of atoms is Li: 18, Mn: 48, Ni: 12, Co: 12.

### Table 6. Site occupancy in 4g and 2b site for simulation model.

<table>
<thead>
<tr>
<th>Model</th>
<th>4g</th>
<th>2b</th>
<th>4g</th>
<th>2b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li Mn Ni Co</td>
<td>Li Mn Ni Co</td>
<td>Li Mn Ni Co</td>
<td>Li Mn Ni Co</td>
</tr>
<tr>
<td>(I)</td>
<td>0.2 0.533 0.133 0.133</td>
<td>0.2 0.533 0.133 0.133</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(II)</td>
<td>0.1 0.6 0.15 0.15</td>
<td>0.4 0.4 0.1 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(III)</td>
<td>0 0.8 0 0.2</td>
<td>0.6 0 0.2 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(IV)</td>
<td>0 0.8 0.1 0.1</td>
<td>0.6 0 0.2 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(V)</td>
<td>0 0.8 0.2 0</td>
<td>0.6 0 0 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(VI)</td>
<td>0 0.7 0.1 0.2</td>
<td>0.6 0 0.2 0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 10.** PDF simulation of 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co$_{1-z}$O$_2$ [x = 1/3] materials with various site occupancies. ☐: $G_{ab}(r)$, □: Model (I), ▽: Model (II), ◻: Model (III), ●: Model (IV), ■: Model (V), ▲: Model (VI).

**Figure 11.** Partial PDF simulation of 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co$_{1-z}$O$_2$ [x = 1/3] materials with various site occupancies. Roman numbers in the figure corresponds to the model’s number (Table 5). ——: $G_{ab}(r)$, ⋯⋯: $G_{ab}(r)$, ☐: Li-O, □: Mn-O, ▽: Ni-O, ◻: Co-O.
Model fitting with variable coordinates and thermal vibrations is required to determine detailed ordering. Because Co-O scattering was mostly not observed, PDF analysis by only neutron total scattering presents difficulties in determining the structure. It is thought necessary to employ synchrotron X-ray spectroscopy together with neutron total scattering to study PDF analysis.

### 3.4 Electronic and local structure analysis (synchrotron X-ray spectroscopy)

Electronic and local structures were studied along with XAFS spectra by employing synchrotron X-rays. K-edge XANES spectra for Mn, Ni, and Co of the respective samples are shown in Fig. 14. According to the Mn XANES spectra, peak leading edges (1) for both $x = 1/3$ and $x = 5/12$ were shifted slightly toward low energy through reductive heat treatment, but peak crowns (2) were shifted toward high energy. Thus, the study of valence appears difficult. Nonetheless, the peak shapes of XANES changed with reductive heat treatment and suggested changes to the ordering environment.

For the Ni XANES, hardly any change was seen for $x = 1/3$, but a shift toward low energy suggesting a decrease in valence was seen for $x = 5/12$. Hardly any change was seen for the Co XANES.

From the above, Ni reduction is suggested for $x = 5/12$ by reductive heat treatment. This agreed with the valence analysis results.

EXAFS Fourier transform spectra of Mn, Ni, and Co are shown in Fig. 15 to Fig. 17. The figures show the EXAFS Fourier transform spectra of untreated samples after the initial charging and initial discharging together. In the Mn EXAFS (Fig. 15), the peak intensity originating from the first proximate distance of the Mn-O bond in the vicinity of 1.5 Å decreased after the initial charging and discharging for both $x = 1/3$ and 5/12. Since the intensities are nearly the same after charging and discharging, this is thought to be the influence of oxygen elimination during the initial charge process.

Similarly, since peak intensities of the Mn-O bond decreased by reductive heat treatment, elimination of oxygen by reductive heat treatment is suggested. In the Ni EXAFS (Fig. 16), although little change was seen for $x = 1/3$ by reductive heat treatment, the peak
intensity originating from the first proximate distance of the Ni-O bond in the vicinity of 1.5 Å increased for x = 5/12 by reductive heat treatment. As for the reason for the lower Ni-O peak intensities prior to heat treatment, it is thought that a portion of typical bivalent Ni became trivalent and the distortion of the Ni-O$_6$ octahedron increased due to the Jahn-Teller effect. This change supports the results of XANES and valence analysis. The Co EXAFS spectra, similar to the XANES spectra, showed very little change.

From the above, the XAFS spectra results suggested oxygen elimination by reductive heat treatment and Ni reduction for x = 5/12, and agreed with the results of valence analysis described in section 3.1. Consequently, Ni activation is thought to be a cause for the capacity increase of x = 5/12. Moreover, the influence of Mn, whose valence could not be studied, may be the cause for the decrease in valence compared to the theoretical valence seen in the valence analysis for x = 1/3.

4. Conclusion

Battery characteristics were evaluated. Rietveld, PDF and XAFS analyses were conducted to study the average, local, and electronic structures for the 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co(1-2x)O$_2$ materials for (i): (a) x = 1/3, (b) x = 1/3 (800°C, 10$^{-3}$ Pa, 6 h), and (ii): (c) x = 5/12, (d) x = 5/12 (800°C, 10$^{-2}$ Pa, 6 h). ⊂: untreated; pristine, □: untreated; 1st charge, △: untreated; 1st discharge, ◇: heat-treated; pristine.

![Figure 15](image1.png)

**Figure 15.** Fourier transform of EXAFS observed at Mn K-edge for 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co(1-2x)O$_2$ materials for (i): (a) x = 1/3, (b) x = 1/3 (800°C, 10$^{-3}$ Pa, 6 h), and (ii): (c) x = 5/12, (d) x = 5/12 (800°C, 10$^{-2}$ Pa, 6 h). ⊂: untreated; pristine, □: untreated; 1st charge, △: untreated; 1st discharge, ◇: heat-treated; pristine.

![Figure 16](image2.png)

**Figure 16.** Fourier transform of EXAFS observed at Ni K-edge for 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co(1-2x)O$_2$ materials for (i): (a) x = 1/3, (b) x = 1/3 (800°C, 10$^{-3}$ Pa, 6 h), and (ii): (c) x = 5/12, (d) x = 5/12 (800°C, 10$^{-2}$ Pa, 6 h). ⊂: untreated; pristine, □: untreated; 1st charge, △: untreated; 1st discharge, ◇: heat-treated; pristine.

![Figure 17](image3.png)

**Figure 17.** Fourier transform of EXAFS observed at Co K-edge for 0.5Li$_2$MnO$_3$-0.5LiMn$_x$Ni$_{1-x}$Co(1-2x)O$_2$ materials for (i): (a) x = 1/3, (b) x = 1/3 (800°C, 10$^{-3}$ Pa, 6 h), and (ii): (c) x = 5/12, (d) x = 5/12 (800°C, 10$^{-2}$ Pa, 6 h). ⊂: untreated; pristine, □: untreated; 1st charge, △: untreated; 1st discharge, ◇: heat-treated; pristine.
(x = 1/3, 5/12) samples showed that Li and Mn preferentially occupied 2b and 4g sites, respectively, and Ni and Co occupied either the 2b or 4g site of the Li2MnO3-type structure (space group C2/m). Thus, an ordered arrangement within the transition metal layer was suggested. An increasing order was seen for the reductive heat-treated samples.

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References