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Electrochemical Characteristics of Layered Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ (C2/m) as a Lithium-Battery Cathode

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In the past two decades, considerable efforts have been devoted to the development of rechargeable energy-storage devices that can be used in diversified technical applications, expanding over to portable electronics, electric cars, and large-scale industrial equipments. Lithium-ion batteries, which can realize a high energy density, are a promising candidate for such devices. The performance of lithium-ion batteries shows considerable fluctuation depending on that of the cathode materials, as a result of which much attention has focused on the various kinds of lithiated transition-metal oxides for their possible use as a promising cathode material. Layered compounds, such as LiCoO$_2$ and LiNiO$_2$, have been significantly studied as a high-voltage cathode material. However, their high cost and safety hazard have inhibited their use in a wide range of applications. In contrast, olivine-type LiFePO$_4$ does not carry these problems, but the available capacities are reaching their theoretical limit.

Manganese-based layered oxides, such as LiMnO$_2$ (C2/m or Pmmn),1−3 Li$_2$MnO$_3$ (C2/m),4 and solid solutions of Li$_5$Mn$_3$O$_4$−LiMnO$_2$ (M = Ni, Co, and Mn: R3m),5,6 are attractive materials because they are safer, cheaper, and less toxic than LiCoO$_2$ or LiNiO$_2$ and exhibit a higher operating voltage (>3.5 V vs. Li/Li$^+$ in average). Especially, much attention has been increasingly placed on the solid solutions of Li$_5$Mn$_3$O$_4$−LiMnO$_2$ due to their high capacities. Recently, Yabuchi et al.7 reported that the high capacities of the Li$_5$Mn$_3$O$_4$−LiMnO$_2$ systems result from the activated manganese redox reaction (Mn$^{3+}$/Mn$^{4+}$) and the oxygen reduction reaction at the electrode surface. However, the need for improvement in their capacity retention is also recognized when they are used in practical applications.

The charge-discharge behaviors of Li$_5$Mn$_3$O$_4$−LiMnO$_2$ systems are characterized by an irreversible high charge capacity (>300 mAh g$^{-1}$) for the first charge process. This is because of the extraction of oxygen molecules from the electrode materials. While such an extraction leads to the activated manganese redox reaction, it is a major cause of a poor cycle life of the systems. The rapid generation of oxygen vacancies causes the structural destruction of active materials, and a poor cycle life is thus induced. To suppress structural destruction, several surface modifications of the electrode materials, such as acid treatment with an aqueous H$_2$SO$_4$ solution$^{10}$ and surface coating with AlPO$_4$ or TiO$_2$,$^{11,12}$ have been reported.

Recently, we have synthesized a manganese-based solid solution having the composition of Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ due to the space group symmetry of C2/m. It was found that the material shows unique and favorable electrochemical characteristics as a lithium-battery cathode, i.e., an increasing capacity during the first ten-odd cycles and improved capacity retention after around the 23rd cycle in the charge-discharge potential range of 2.0−4.8 V. In this paper, we describe the synthesis and structure of the material and then discuss its electrochemical properties.

Experimental

Synthesis of the material.—Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ was synthesized from a mixed manganese-cobalt carbonate precursor which was obtained by the coprecipitation technique based on a modification of previously reported methods.$^{6,7}$ Manganese sulfate (MnSO$_4$·5H$_2$O) and cobalt sulfate (CoSO$_4$·7H$_2$O) were weighed to achieve a molar ratio of Co/Mn = 0.15/0.9 and dissolved in distilled water to obtain a 0.2 M aqueous solution of manganese and cobalt sulfates. The solution was added to an aqueous solution of sodium carbonate (Na$_2$CO$_3$) containing an equimolar amount of Na$_2$CO$_3$ with manganese and cobalt sulfates and stirred for about 20 h. The produced green precipitate in the solution was then filtered with suction through a 0.2-μm pore size polytetrafluoroethylene (PTFE) membrane, thoroughly washed with distilled water, and dried at 110 °C to yield the manganese-cobalt carbonate coprecipitate. The resulting coprecipitate was heated at 500 °C in air for 5 h, thoroughly mixed with lithium hydroxide (LiOH·H$_2$O), and finally heated at 900 °C for 12 h under flowing oxygen to obtain the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ material.

Characterization.—Neutron-diffraction data were collected by monochromized neutron radiation at a wavelength of 1.8244 Å at room temperature using a high-resolution powder diffractometer (HRPD) at the research reactor (JRR-3M) of the Japan Atomic Energy Agency. The synthesized powder (about 5 g) was contained in a cylindrical vanadium cell (5-mm radius, 55-mm height). Based on the neutron-diffraction data, the structural parameters of Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ were refined using the Rietveld refinement program RIETAN-FP.$^{11,12}$

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Powder X-ray diffraction (XRD) measurements were also performed for the as-prepared material and cycled cathode samples using an X-ray diffractometer (Rigaku RINT-TTR III). In addition, an X-ray photoelectron spectroscopy (XPS) measurement was carried out on the as-prepared material and cathode samples after charge-discharge cycles using the PHI Quantera SXM spectrometer (ULVAC-PHI).

**Electrochemical test.**—Electrochemical charge-discharge measurements were carried out using a 2032-type coin cell. The electrolyte was a 1 M solution of LiPF6 in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed at a volume ratio of 1:1 (Ube Industries, Ltd., Japan). The anode was a lithium metal foil disk (11-mm diameter, 0.5-mm thickness). A polypropylene filter was used as the separator. The cathodes were comprised of an aluminum grid on which the finely ground powder of the samples, mixed with 15 wt% carbon black and 10 wt% PTFE powders, was pressed; these cathodes were dried at 140 °C for 4 h under a vacuum immediately before the measurements. The charge-discharge measurements were carried out in the potential ranges of 2.0–4.8 and 2.0–4.6 V at current densities of ±30 mAg−1 or ±10 mAg−1 and 23 C. Every charge-discharge cycling in this study began from the charge process. Cyclic voltammogram (CV) measurements were also conducted in the potential ranges of 2.0–4.8 and 2.0–4.6 V at the scan rate of 0.2 mVs−1 using potentiostat equipment (Bio-Logic VSP Modular).

### Results and Discussion

The results of the Rietveld refinement for Li1.95Mn0.9Co0.15O3 with the neutron-diffraction data are summarized in Fig. 1 and Table I. The best fit was realized by setting the atomic distributions to those due to an Li2MnO3-type structure model corresponding to a monoclinic symmetry with the space group of C2/m (z = 4). All the Bragg reflections can be indexed on such a monoclinic cell, and both low R factors (Table I) and good fitting between the observed and calculated patterns (Fig. I) are acquired. It is noted that the substitution of Mn for Li characteristically occurs on the (101) plane with z = 0 in the Li1.95Mn0.9Co0.15O3. It should be also pointed out that refinements employing structure models other than the Li2MnO3-type structure, such as a model based on the R3m symmetry, did not converge or led to poorer convergence. The results of the Rietveld refinement ensure the validity of the Li2MnO3-type structure model.

Figure 2 shows the charge and discharge curves at the 1st, 2nd, 3rd, 22nd, and 58th cycles measured with the Li/Li+ cell in the potential range of 2.0–4.8 V at current densities of ±30 mAg−1. Small irreversibility is observed at the 1st, 2nd, and 3rd cycles, in which the charge capacity is slightly larger than the discharge one. At the 22nd and 58th cycles, symmetrical charge and discharge curves with an enhanced capacity of ~180 mAh−1 are observed, suggesting the occurrence of a reversible electrochemical reaction at those cycles. It is important to note that these charge and discharge curves are markedly different from those reported for conventional Li1.2MnO3-LiMO2 (M = Ni, Co, and Mn) systems, in which

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**Table I. Rietveld refinement results for Li1.95Mn0.9Co0.15O3 with neutron-diffraction data measured at room temperature.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>(g^a)</th>
<th>(B^b(\AA^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>2b</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>0.9</td>
<td>1.0(3)</td>
</tr>
<tr>
<td>Mn1</td>
<td>2b</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>0.1</td>
<td>0.7(3)</td>
</tr>
<tr>
<td>Li2</td>
<td>2c</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>1.0</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>Li3</td>
<td>4h</td>
<td>0</td>
<td>0.662(2)</td>
<td>1/2</td>
<td>1.0</td>
<td>1.6(2)</td>
</tr>
<tr>
<td>Mn2</td>
<td>4g</td>
<td>0</td>
<td>0.1674(10)</td>
<td>0</td>
<td>0.85</td>
<td>0.1(1)</td>
</tr>
<tr>
<td>Co</td>
<td>4g</td>
<td>0</td>
<td>=YMe2</td>
<td>0</td>
<td>0.15</td>
<td>=BMe2</td>
</tr>
<tr>
<td>O1</td>
<td>4i</td>
<td>0.2249(8)</td>
<td>0</td>
<td>0.2262(9)</td>
<td>1.0</td>
<td>0.74(8)</td>
</tr>
<tr>
<td>O2</td>
<td>8j</td>
<td>0.2500(6)</td>
<td>0.3250(3)</td>
<td>0.2219(5)</td>
<td>1.0</td>
<td>0.83(4)</td>
</tr>
</tbody>
</table>

Lattice parameters: \(a = 4.9289(3)\ \AA, \ b = 8.5321(3)\ \AA, \ c = 5.0248(2)\ \AA, \ \beta = 109.2700(3)^\circ\)

Reliability factors: \(R_p = 9.92\% , \ R_o = 7.08\% , \ R_B = 15.05\% , \ R_B^3 = 3.24\% , \ R_B^4 = 4.38\% , \ R_B^5 = 10.45\%\)

*Occupancy factor

Isotropic atomic displacement parameter

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**Figure 1.** Rietveld refinement pattern of the neutron-diffraction data measured for Li1.95Mn0.9Co0.15O3. The plus marks (+) are the raw diffraction data, and the overlapped continuous line is the calculated pattern. The short vertical lines below the pattern indicate the positions of the allowed Bragg reflections. The difference between the observed and calculated intensities is shown at the bottom on the same scale. An ac plane projection of the structure is also shown.

**Figure 2.** Charge and discharge curves of the 1st, 2nd, 3rd, 22nd, and 58th cycles measured with the Li/Li+ cell in the potential range of 2.0–4.8 V at current densities of ±30 mAg−1.
an irreversible long plateau with a high capacity (>250 mAhg\(^{-1}\)) develops at 4.5–4.6 V for the first charge process.\(^7\) As discussed below, the difference in the charge-discharge behaviors between the systems is associated with their activation behaviors of the manganese redox reaction (Mn\(^{3+}/\text{Mn}^{4+}\)) during the cycling.

Figure 3 shows the cycling data measured with the Li/Li\(^{+}/\text{Li}_{1.95}\text{Mn}_{0.9}\text{Co}_{0.15}\text{O}_{3}\) cell in the potential ranges of 2.0–4.8 and 2.0–4.6 V, in which the discharge capacities are plotted as a function of the number of cycles. For the potential range of 2.0–4.8 V, the capacity characteristically increases from 46.3 to 196.5 mAhg\(^{-1}\) as the cycle increases from 1 to 11 and then slightly decreases to 179.8 mAhg\(^{-1}\) until the 23rd cycle. Subsequently, capacities of >175.5 mAhg\(^{-1}\) are obtained up to the 58th cycle with only a slight decrease. In fact, capacity fading between the 23rd and 58th cycles is 2.41%. Here, it may be noted that the capacities of >175.5 mAhg\(^{-1}\) and capacity retention observed between the 23rd and 58th cycles seem to be superior to those reported for the conventional solid solution of 0.6Li\(_2\)MnO\(_3\)-0.1LiCoO\(_2\) (R\(_3\)m\(_3\)), which has the same composition of Li\(_{1.95}\text{Mn}_{0.9}\text{Co}_{0.15}\text{O}_{3}.\)\(^5\) For the potential range of 2.0–4.6 V, although the capacity increased to ~110 mAhg\(^{-1}\) during the first ten-odd cycles, the subsequent capacities do not exceed 113 mAhg\(^{-1}\).

In order to investigate the redox reactions of the Li\(_{1.95}\text{Mn}_{0.9}\text{Co}_{0.15}\text{O}_{3}\) system during the cycling, we conducted CV measurements in two types of potential ranges: 2.0–4.8 and 2.0–4.6 V. Figure 4 shows the resulting CVs measured with the Li/Li\(^{+}/\text{Li}_{1.95}\text{Mn}_{0.9}\text{Co}_{0.15}\text{O}_{3}\) cell at the scan rate of 0.2 mVs\(^{-1}\) over 15 or 16 cycles. Compared with the CVs shown in Fig. 4a and 4b, there are significant differences in the CV variation for the respective potential ranges. For the potential range of 2.0–4.8 V (Fig. 4a), the CV loop becomes increasingly larger as the number of cycles increases. Especially, a remarkable enlargement in size is observed for the peak at around 3.0 V in the reduction process during the first ten-odd cycles. In contrast, the peak at around 4.0 V in the reduction process rarely changes in size during the cycling. The former and latter peaks can be assumed to result from the manganese redox reaction (Mn\(^{3+}/\text{Mn}^{4+}\)) and the cobalt redox reaction (Co\(^{3+}/\text{Co}^{4+}\)), respectively.\(^5\) For the potential range of 2.0–4.6 V (Fig. 4b), an enlarging trend of the CV loop is also observed, but the variation is considerably smaller than that seen in Fig. 4a. These observations show that the manganese redox reaction of the Li\(_{1.95}\text{Mn}_{0.9}\text{Co}_{0.15}\text{O}_{3}\) system is progressively activated upon cycling and the stage of activation is also associated with the maximum voltage for the charge process, in a similar manner to the variation of the capacities.

We carried out another CV measurement to further investigate the relationship between the manganese redox reaction and the charge-discharge conditions. Figure 5 shows CVs measured with the Li/Li\(^{+}/\text{Li}_{1.95}\text{Mn}_{0.9}\text{Co}_{0.15}\text{O}_{3}\) cell in the potential range of 2.0–4.6 V over 10 cycles at the scan rate of 0.2 mVs\(^{-1}\). The cell was previously charge-discharged in the potential range of 2.0–4.8 V at current densities of 30 mAg\(^{-1}\) over 15 cycles before the measurement.
respectively. Thus, it was suggested that oxygen molecules in the LiCoO$_2$, suggesting the binding energies of O 1s are 530.5 and 531.5 eV, respectively (Fig. 6a). It has been reported that the binding energy of O 1s varies according to the chemical species and the values for oxygen ion (O$^{2-}$) in the crystal lattice and free oxygen ions based on Li$_2$O or Li$_2$CO$_3$ are 529 and 532 eV, respectively. Thus, it was suggested that oxygen molecules in the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ system are extracted from the active material during the cycling and the extracted oxygen exists at the electrode surface. In addition, since the position of the 10-cycled sample is higher than those of the as-prepared material and 5-cycled sample, it was also suggested that continual extraction of oxygen molecules occurs, at least during the first ten cycles. The binding energies of Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ for the as-prepared material are estimated to be 653.9 and 642.2 eV, respectively (Fig. 6c). These values are almost constant with those reported in MnO$_2$, indicating that the charge state of Mn is $4+$. In the as-prepared material, it can also be observed in Fig. 6c that the spectrum positions of both Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ slightly shift to lower binding energies as the number of cycles increases. Additionally, as shown in the inset of the figure, the spectra become more asymmetrical due to swelling toward lower binding energies. These observations indicate that the quantity of Mn$^{4+}$ in the active material increases as the number of cycles increases, which is in agreement with the CV results.

Figure 7 shows the XRD profiles of the as-prepared Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ and the electrochemical Li$^{+}$ extraction and insertion accompanying the redox reaction of cobalt (Co$^{3+}$/Co$^{4+}$). On the other hand, for the cycled samples, profiles are substantially changed to that for the LiMnO$_2$ ($R3m$). Especially, the profile of the 10-cycled sample is shown to be almost a single phase of the LiMnO$_2$. It could be assumed that the structural change from $C2m$ to $R3m$ during the cycling is responsible for the reduction of crystal distortion due to the irreversible extraction of Li$^{+}$ ions at the 2b site.

For manganese-based cathode materials, it is commonly accepted that electrochemical Li$^{+}$ extraction occurs in conjunction with the oxidation of Mn up to a maximum oxidation state of 4+. Since the charge state of Mn is already 4+ in Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$, the small charge and discharge capacities observed at the first cycle in the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ system can be understood in terms of this concept. In other words, the capacities at the first cycle are mostly caused by the Li$^{+}$ extraction and insertion accompanying the redox reaction of cobalt (Co$^{3+}$/Co$^{4+}$). On the other hand, the CV and XPS results suggest that the high capacities obtained after ten-odd cycles in the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ system refer to the enhanced Li$^{+}$ extraction and insertion based on the activated manganese redox reaction (Mn$^{4+}$/Mn$^{3+}$) following the extraction of oxygen molecules from the active material, as reported for Li$_2$MnO$_3$-LiMnO$_2$ systems. Furthermore, taking into account the structural variation shown in Fig. 7, the small charge and discharge capacities observed at the first cycle in the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ system can be understood in terms of this concept. In other words, the capacities at the first cycle are mostly caused by the Li$^{+}$ extraction and insertion accompanying the redox reaction of cobalt (Co$^{3+}$/Co$^{4+}$). On the other hand, the CV and XPS results suggest that the high capacities obtained after ten-odd cycles in the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ system refer to the enhanced Li$^{+}$ extraction and insertion based on the activated manganese redox reaction (Mn$^{4+}$/Mn$^{3+}$) following the extraction of oxygen molecules from the active material, as reported for Li$_2$MnO$_3$-LiMnO$_2$ systems. Furthermore, taking into account the structural variation shown in Fig. 7, the small charge and discharge capacities observed at the first cycle in the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ system can be understood in terms of this concept.
Contribute to the improved capacity retention. However, a full discussion of these aspects must await a detailed comparison of the microstructures at various electrochemical stages for both systems.

Conclusions

In this paper, we have described the synthesis of a manganese-based solid solution of Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ and discussed its structural and electrochemical characteristics. The material is assigned to a Li$_2$MnO$_3$-type structure model characterized by a monoclinic cell due to the space group symmetry of C$2/m$. Unlike the conventional solid solutions of Li$_2$MnO$_3$-LiMO$_2$ (M = Ni, Co, and Mn: R$3m$), the material shows more favorable electrochemical properties as a lithium-battery cathode, namely, higher capacities and improved capacity retention after around the 23rd cycle. Such electrochemical properties may probably be associated with the extraction behavior of oxygen molecules from the active material during the cycling in the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ system. The electrochemical characteristics observed in the Li$_{1.95}$Mn$_{0.9}$Co$_{0.15}$O$_3$ system may be useful for designing manganese-based cathode materials for practical applications.

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References