



Layered Li-Co-Mn Oxide as a High-Voltage Positive Electrode Material for Lithium Batteries

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A layered Li-Co-Mn oxide was synthesized from a host layered Na-Co-Mn oxide by ion-exchange technique. Its electrode performance showed anomalous high redox potential of *ca.* 4.5 V vs. Li/Li⁺ for the intercalation and deintercalation of lithium, although the end members of solid solution LiCoO₂ and LiMnO₂ did only 4.0 V. The oxidation state of the cobalt was measured by X-ray photoelectron spectroscopy and was trivalent.

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At present, secondary lithium batteries are widely used for portable equipment. Such batteries, so-called lithium-ion batteries, have LiCoO₂ as a positive electrode material.¹⁻⁶ Many efforts have been made to find out alternatives to improve performance or reduce materials cost. Some groups focused their attention on substituting the expensive Co with cheaper elements to reduce the cost of the battery⁷⁻¹² and others on searching for high voltage positive electrodes.

In order to reduce the cost of LiCoO₂, many trials have been made to substitute Co with cheaper Fe and Mn. Layered LiMnO₂ had a tendency to change to its spinel-type derivative during charge-discharge cycles.¹³⁻¹⁵ Armstrong *et al.* succeeded in stabilizing the layer structure of LiMnO₂ by partial substitution of Mn for Co, which resulted in excellent cycle characteristics.¹⁶ The potential profiles of LiCo_xMn_{1-x}O₂ with 0.1 ≤ *x* ≤ 0.3¹⁷ consisted of two potential plateaus, one of which was centered at *ca.* 4.5 V, and the incremental capacity plots indicated an increase near 4.5 V with an increasing content of cobalt. Their result suggests that the substitution may be effective not only for cycle performance but also for generation of higher redox potential.

High-voltage positive electrodes can result in high energy density, which meets increasing demands on the battery as well as opens up wider application fields, *e.g.*, power sources for electric vehicles. Another advantage of high-voltage positive electrodes is that they make it possible to use a variety of anode materials. Commercial lithium-ion batteries have carbon materials (C₆-Li_x) as the anode. Many substitute candidates have been proposed, *e.g.*, lithium alloys, oxides, and nitrides. However they show a more noble potential than C₆-Li_x. Positive electrodes, which generate higher voltage, should allow the use of such alternatives without decreasing operation voltage of the battery.

Recently, some high-voltage positive electrode materials with operating voltage over 4.5 V vs. Li/Li⁺ have been investigated.¹⁸⁻²⁴ Most of the positive electrodes have a spinel structure in which manganese ions are partially replaced with other transition metal ions in the spinel LiMn₂O₄. As far as we know, high-voltage positive electrode materials, having a layered structure, have not been reported.

In this study, we focused on the high redox potential of the layered LiCo_xMn_{1-x}O₂ and found that lithium could be intercalated to and deintercalated from the interlayer in one stage centered at 4.5 V. Here we give the description on the synthesis and electrode properties of layered Li-Co-Mn oxide.

Experimental

Preparation of Li-Co-Mn oxide.—Layered Li_xCo_{0.5}Mn_{0.5}O₂ was prepared by ion-exchanging Na_xCo_{0.5}Mn_{0.5}O₂ in a 2-(2-

ethoxyethoxy)ethanol solution of LiBr. The starting layered oxide, Na_xCo_{0.5}Mn_{0.5}O₂, was synthesized from an aqueous solution containing the component elements. Sodium nitrate (NaNO₃), cobalt acetate tetrahydrate [Co(CH₃COO)₂·4H₂O], and manganese acetate tetrahydrate [Mn(CH₃COO)₂·4H₂O] were dissolved at an appropriate ratio in distilled water. The solution was boiled while mechanically stirred, and then the water was evaporated under atmospheric pressure. The residual solid was calcined at 300°C to remove gases. Obtained powder was ground in an agate mortar, pressed in pellet form, and then heated at 800°C for 20 h, and the product, Na_xCo_{0.5}Mn_{0.5}O₂, was obtained by quenching to room temperature.

Ion exchange was performed in a 2-(2-ethoxyethoxy)ethanol solution of lithium bromide (LiBr). 1.5 g of Na_xCo_{0.5}Mn_{0.5}O₂ powder was dispersed in 50 mL of the solution (4 M) and then heated at 150°C for 6 h to exchange sodium with lithium. After the ion exchanging, the suspension was filtered and the filter cake was washed with ethanol to remove residual lithium bromide and with methanol to remove the by-product, sodium bromide.

Lithium and sodium contents of the final product were determined by inductively coupled plasma (ICP) analysis.

X-ray diffraction and Rietveld refinement.—Products were identified by the powder X-ray diffraction (XRD) method using RINT2100S (Rigaku) system with Cu Kα. Diffraction data were collected by step scanning over an angular range of 10° < 2θ < 120° with a step width of 0.02°. The sample was kept at room temperature during measurement. The structural refinement was performed by using the Rietveld analysis computer program RIETAN-94.²⁵

X-ray photoelectron spectroscopy experiments.—The charge state of Mn and Co in the products were examined by X-ray photoelectron spectroscopy (XPS) Micro spot Sigma Probe (VG Scientific) with monochromatized Al Kα radiation at 1486.6 eV. Data were collected in a resolution of 0.1 eV and calibrated on the basis of the C 1s line as 284.0 eV.

Electrochemical measurement.—Electrode properties of the synthesized oxide were investigated in a coin-type cell (20 mm diam and 1.6 mm thick). The sample powder was mixed with an electronic conductor of acetylene black and a binder of polytetrafluoroethylene at a weight ratio of 6:3:1. The mixture was rolled into a sheet, cut in disk form, and then dried under vacuum at 120°C. This disk and a foil of lithium metal were used as the positive electrode and a counter electrode, respectively. 1 M propylene carbonate solution of LiPF₆ was used as an electrolyte. The cell was charged and discharged at a constant current of 0.1 mA at room temperature. The applied voltage was varied between 3.5 and 5.2 V.

Results and Discussion

Figure 1a shows an XRD pattern of the Na_xCo_{0.5}Mn_{0.5}O₂. The best result of the Rietveld refinement was given on the basis of the

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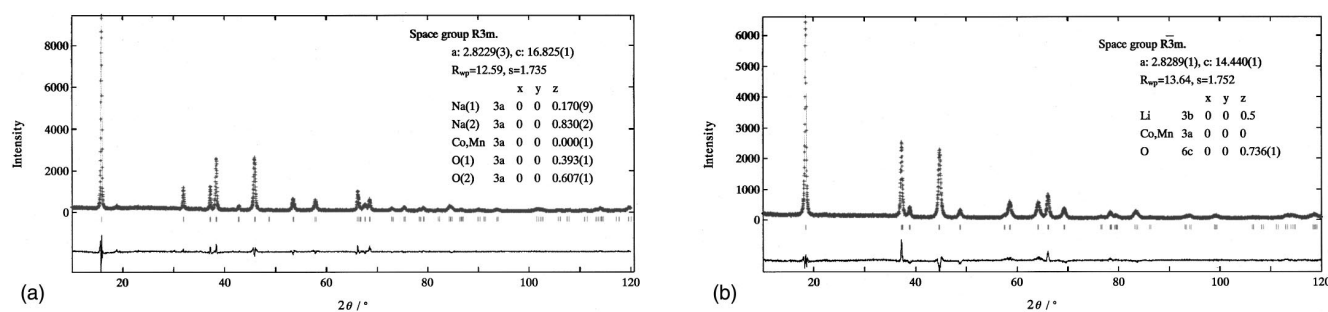


Figure 1. (a) Powder X-ray diffraction pattern of (a, left) $\text{Na}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (before ion exchanging) and (b, right) $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (after ion exchanging): (+) experimental, (—) calculated, and difference (below) patterns resulting from the Rietveld refinement of XRD data are also given.

hexagonal unit cell with $a: 2.8229(3)$ Å, $c: 16.825(1)$ Å, and the $R\bar{3}m$ space group. This crystal structure was consistent with the Paulsen's $P3$ structure.²⁶ In the structure, Co and Mn are coordinated by six oxide ions and these MO_6 octahedra form MO_2 layers. The unit cell is constructed with three layers stacked parallel to each other, and the sodium ions are placed in interlayer spaces and in a triangle prismatic environment of oxide ions belonging to the layers. Therefore, it could be said that the structure of the compound was not spinel but layered, whereas the actual amount of Na was close to that of spinel.

The XRD pattern in Fig. 1b was obtained for the layered oxide ion-exchanged with lithium. Initial sodium compound was unobservable. ICP analysis revealed that the obtained layered oxide has a chemical composition of $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and a negligible amount of residual sodium. The pattern was well fitted on the ground of a rhombohedral lattice ($R\bar{3}m$, $O3$ structure) with $a: 2.8289(1)$ Å, $c: 14.440(1)$ Å. In the crystal structure of $R\bar{3}m$, lithium ions are located in octahedral interstices. Delmas *et al.* have shown that the structural change between $P3$ NaCoO_2 and $O3$ LiCoO_2 can be explained in a simple way with no structural modification occurring within the sheets, with the sheets gliding with respect to each other.²⁷⁻³⁰ In this case, the same process had occurred, every two layers glided in an opposite direction along the a axis and the initial $P3$ $\text{Na}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ structure was changed to the $O3$ $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ during ion exchange. Therefore, it seems that this material is quite similar to LiCoO_2 in structural characteristics.

In spite of the same structure type as LiCoO_2 , the present lithium compound showed an interesting electrode performance. The charge-discharge curves of the test cell ($\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2/\text{LiPF}_6\text{-PC/Li}$) are shown in Fig. 2, which were measured during the intercalation-deintercalation cycles of lithium ion. Only one plateau

appeared at *ca.* 4.5 V vs. Li/Li^+ , although end members of the solid solution $\text{LiCo}_x\text{Mn}_{1-x}\text{O}_2$, *i.e.*, LiCoO_2 and LiMnO_2 with layered structure, have a potential plateau at around only 4.0 V.

In general, layered LiMnO_2 was likely to change to the spinel type during intercalation and deintercalation of the lithium ion and it lead to the capacity fading. However Armstrong *et al.* reported that such fading was suppressed with an increase of cobalt content.¹⁷ The present result on lithium compound was also consistent with theirs. The capacity fade was significantly improved in comparison with that of LiMnO_2 .⁷ In addition, its electrode potential was maintained during the repetitive intercalation and deintercalation of lithium. Kawai *et al.* found a 5.0 V plateau for LiCoMnO_4 with spinel structure,²⁴ but it indicated a small plateau at 4.0 V, probably arising from an impurity of LiMn_2O_4 , and a large plateau from 4.7 to 5.3 V. The present lithium cobalt manganese oxide showed a single plateau from 4.0 to 5.0, which is quite different from the spinel phase.

An irreversible capacity of 75 mAh/g between the first charge and discharge was observed, whereas the capacity was relatively stable after the subsequent charge and discharge cycles. According to the report about such an irreversible capacity by Mueller-Neuhaus *et al.*,³¹ when lithium is inserted into layered $\text{Li}_{1-y}\text{Fe}_x\text{Ni}_{1-x}\text{O}_2$ at a comparatively high rate, a lithium excessive phase is formed on the surface of active material, and the phase causes the inhibition of lithium intercalation to induce an irreversible capacity. As a result, the capacity fade of that layered material tended to decrease as decreasing a lithium insertion rate. On the other hand, the present irreversible capacity did not change with a lowering insertion rate. Its origin, therefore, would be attributed to the inhibition of lithium insertion by a partial structural change induced at the first lithium deintercalation rather than by the formation of lithium excess phase on the surface of active materials at the first intercalation. In addition, the absence of 4.0 and 5.0 V plateaus in charge/discharge cycles suggests a negligible amount of a spinel type such as LiMn_2O_4 or LiCoMnO_4 , converted from the original $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. The reason for the present capacity fade is now under investigation.

LiCoO_2 and LiMnO_2 contain trivalent transition metals and indicate only about 4.0 V for $\text{M}^{3+}/\text{M}^{4+}$ redox couple. It seems strange for their solid solution to show a plateau at 4.5 V. Therefore their electronic structures were investigated to understand the origin of the 4.5 V plateau. Previously, Armstrong *et al.* suggested from the M-O bond length in their structural analysis that cobalt was trivalent in $\text{LiCo}_x\text{Mn}_{1-x}\text{O}_2$.¹⁷ We examined the electronic structure of cobalt more directly by using X-ray photoelectron spectroscopy (XPS).

Figure 3 shows Co XPS core lines for $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$, LiCoO_2 , and LiCoPO_4 . Binding energy of Co $2\text{P}_{3/2}$ for $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was *ca.* 780 eV, which is quite similar to Co^{3+} peak in LiCoO_2 rather than Co^{2+} in LiCoPO_4 . The cobalt is trivalent, which is consistent with the result from the structural study. It could be concluded, therefore, that the $\text{Co}^{3+}/\text{Co}^{4+}$ redox results in the 4.5 V plateau structure by partial replacement of cobalt with manganese

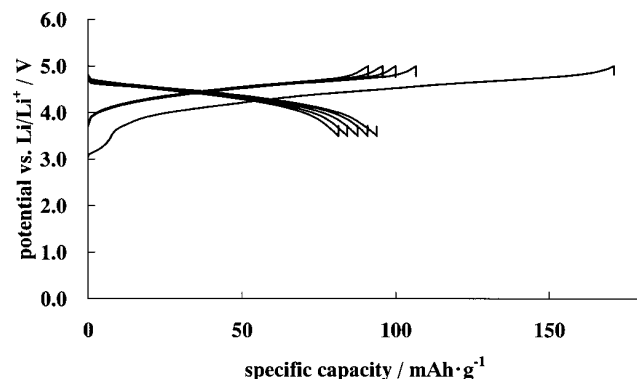


Figure 2. Potential profile of layered $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ during the charge and discharge.

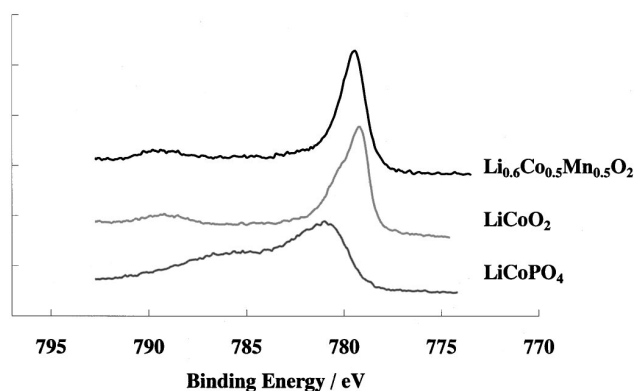


Figure 3. Comparison of XPS, Co $2P_{3/2}$ emission spectra.

in the layered LiCoO_2 . The capacity during the first charge amounted to 170 mAh/g, which corresponded to an extraction of 0.6 electrons from $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. These extracted electrons exceeded cobalt composition. This means both $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ redox couples play a part in this 4.5 V plateau.

It is very interesting that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ redox couples showed a high electrode potential of 4.5 V in the LiCoO_2 structure. It was reported that Co^{3+} partially substituted in the structure changed its redox potential.^{32,33} Cation mixing in the octahedral sites may be expected to modify the electronic structure of the initial cation and result in a high electrode potential such as in the present study. Further analysis based on computational chemistry is on the way.

Conclusion

Layered $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was prepared by heating a solution consisting raw materials, followed by ion exchanging with Li^+ ion in organic solvent. The redox potential of the material was ca. 4.5 V, although it resulted from a trivalent/tetravalent redox couple of the transition metal elements in the layer structure the same as that of LiCoO_2 . The high potential was promising for a new positive electrode material in lithium-ion batteries.

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