

Synthesis and electrochemical properties of $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$

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Abstract

$\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$, single phase, which is the starting material of layered $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$, was obtained by optimized synthesis conditions. The layered $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with $\alpha\text{-NaFeO}_2$ structure obtained from $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ by ion exchanging showed an electrode potential of 4.5 V vs. Li/Li^+ , higher than 4.0 V for those end members, LiCoO_2 and LiMnO_2 , and lower than 5.0 V of spinel-type LiCoMnO_4 . The specific capacity of the layered $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was increased with an increase in a Li^+ content of the products and showed a maximum with a composition of $\text{Li}_{0.8}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Layered compounds, which show intercalation and deintercalation of lithium ions in its interlayer, have been studied as an electrode material of lithium secondary batteries. The so-called “lithium ion battery” is widely used nowadays, and LiCoO_2 with layered $\alpha\text{-NaFeO}_2$ structure is used as a cathode material in it. Cobalt is an expensive element and, hence, there have been many trials to substitute cobalt with cheaper elements, e.g., manganese or iron. However, substitution of cobalt with manganese has not resulted in the layered compound with $\alpha\text{-NaFeO}_2$ -

type structure by conventional solid-state reactions. Cation alignment in double oxides with rock salt structure was reported to depend on a ratio of ionic radii of the cations. When one of the cations has larger radius than cobalt, another cation needs to have a larger ionic radius than lithium to form a layered structure [1]. Therefore, layered LiMnO_2 is hardly obtained, while NaMnO_2 has a layered structure. Possible route to obtain layered LiMnO_2 is a soft chemical synthesis, i.e., ion exchange of the interlayer sodium in layered NaMnO_2 with lithium [2–6]. Armstrong and Bruce [7] reported that lithium ion in the layered LiMnO_2 synthesized by that route could be inserted and extracted electrochemically. However, the layered LiMnO_2 tends to be transformed to spinel structure by repetitive intercalation and deintercalation of lithium. They improved its crystal stability during the intercalation and deintercalation by partial

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substitution of manganese with cobalt [8]. That potential profiles of $\text{LiCo}_x\text{Mn}_{1-x}\text{O}_2$ with $0.1 \leq x \leq 0.3$ 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 stabilization of the layer structure, but also for generation of higher redox potential. We had focused on that high redox potential of the layered $\text{LiCo}_x\text{Mn}_{1-x}\text{O}_2$ and found that lithium could be inserted to and extracted from the material in a potential plateau centered at 4.5 V [9]. In that study, inductively coupled plasma (ICP) analysis showed that the layered material had a composition of $\text{Li}_{0.6}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. The smaller composition of lithium compared to a stoichiometric one seems to be the result of its lower specific capacity. In this study, we tried to optimize the synthesis condition to improve the capacity. $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was synthesized with various sodium compositions at various calcination temperatures. After the sodium was ion-exchanged with lithium, the electrode properties of obtained layered $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was examined.

2. Experimental

2.1. Sample preparation

Layered $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was prepared by ion-exchanging $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in a 2-(2-Ethoxyethoxy)-ethanol solution of lithium bromide (LiBr). The starting layered oxide $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was synthesized from an aqueous solution of sodium nitrate (NaNO_3), cobalt acetate tetra hydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), and manganese acetate tetra hydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$). These salts were dissolved at predetermined amounts of atomic ratio ($\text{Na}/(\text{Co} + \text{Mn}) = 0.6, 0.7, 0.8, 0.9$ and 1.0) in distilled water. The solution was heated while mechanically stirred, and then the water was evaporated under atmospheric pressure. The residual solid was calcined at 320 °C to remove gases. Obtained powder was ground in an agate motor, pressed into a pellet, heated at a temperature range 700–900 °C for 20 h, and then quenched to room temperature.

Ion exchange was performed in a 2-(2-Ethoxyethoxy)ethanol solution of LiBr. An amount of 1.5 g of

$\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ powder was dispersed in a 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 excess lithium bromide and with methanol to remove the byproduct, sodium bromide.

2.2. Characterization

Contents of lithium and sodium in the final product were determined by inductively coupled plasma (ICP) analysis. Crystal structures of the products were identified by powder X-ray diffraction (XRD), using RINT2100S (Rigaku) system with $\text{CuK}\alpha$. Diffraction data were collected by step scanning over an angular range of $10^\circ < 2\theta < 120^\circ$ with a step width of 0.02° . The structure was refined by the Rietveld analysis computer program, RIETAN-2000 [10].

Electrode properties of the synthesized oxide were investigated in a coin-type cell (20 mm in diameter and 1.6 mm thick). The sample powder was mixed with acetylene black as an electronic conductor and polytetrafluoroethylene as a binder at a weight ratio of 6:3:1. The mixture was rolled into a sheet, cut into a disk, and then dried under vacuum at 120 °C. This disk and a foil of lithium metal were used as a working and a counter electrode, respectively. Propylene carbonate solution of LiPF_6 (1 M) was used as an electrolyte. The cell was charged and discharged at a constant current of 0.1 mA at room temperature in a voltage range between 3.5 and 5.2 V.

3. Results and discussion

Two kinds of $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ phases were obtained in the synthesis conditions. Typical XRD patterns of them are shown in Fig. 1. Both phases have layered structures consisting of alternating layers of Na sheet and MO_2 sheets, where Na^+ ions occupy trigonal prismatic sites formed by oxygen atoms. The phases are distinguished by the stacking of the oxygen atoms. P2 structure, one of the single phases, has two sheets of MO_2 layers per unit cell, while P3 phase has three sheets. Both sodium contents and calcination temperatures were influenced to the obtained phase. The relationship between obtained phases and syn-

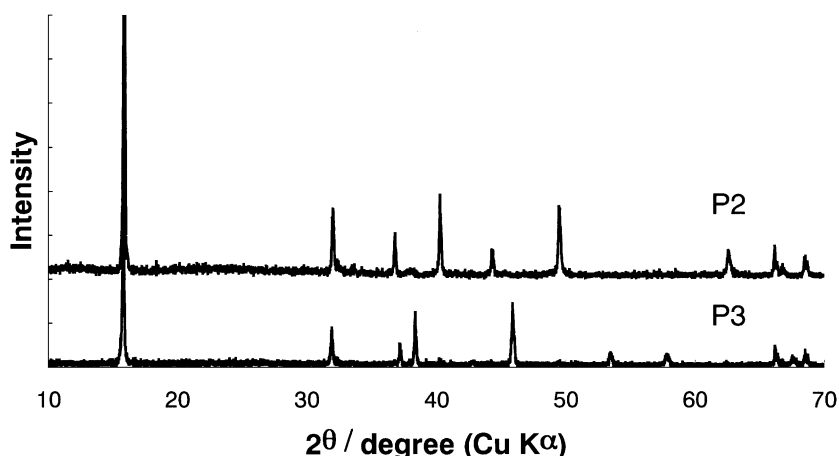


Fig. 1. The XRD patterns of $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with P2 and P3 phase.

thesis condition is shown in Fig. 2. Single phase of P2 structure was obtained at relatively higher contents of sodium and high calcination temperatures, while that of P3 phase whose periodic structure is longer than that of P2-type was obtained alone at lower sodium contents and lower calcination temperatures. When the heating temperature was much lower than that, Co_3O_4 was observed, besides P3 phase, as an impurity, which seems to be attributable to the incompleteness of the reaction.

The lattice parameter of the c -axis of P3 phase obtained at a heating temperature of 700°C increased with a decrease in the sodium content as shown in Fig. 3. The expansion of the c -axis was caused by the increasing electrostatic repulsion force, served between oxide anions in adjacent MO_2 layers oppos-

ing each other, with decreasing interlayer sodium cations.

Sodium ions in P3-type $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$, which was calcined at 700°C , were exchanged with lithium ions in 2-(2-Ethoxyethoxy)ethanol. ICP analysis revealed that sodium ions were almost completely exchanged with lithium ions. High boiling temperature of 2-(2-Ethoxyethoxy)ethanol enabled the reaction at high temperature, resulting to a complete ion exchange. SEM observation of $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$

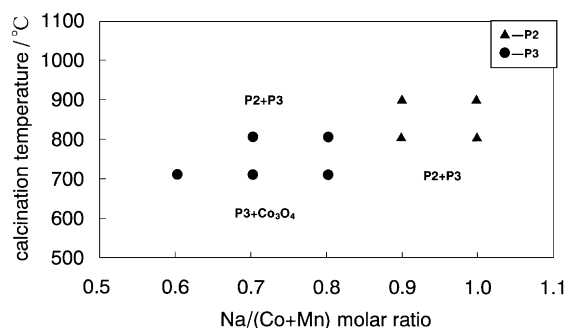


Fig. 2. Phase diagram of $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$.

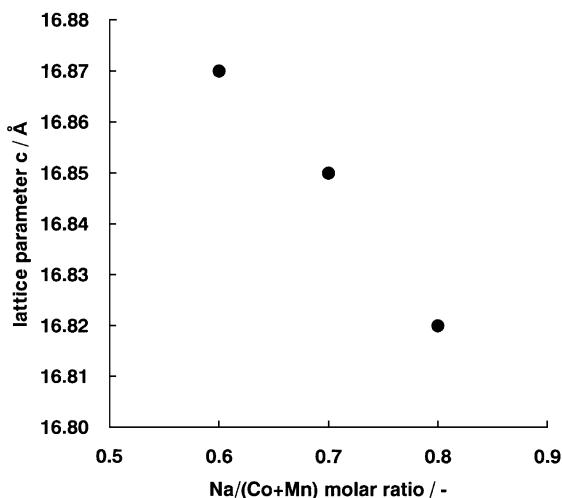


Fig. 3. Variation of c -axis of the $\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with sodium content.

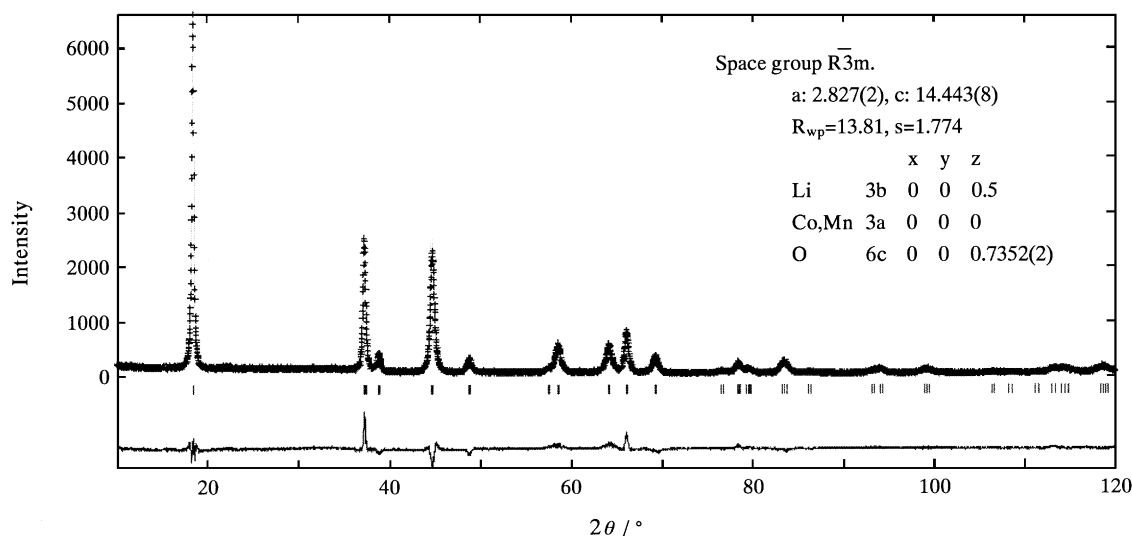


Fig. 4. XRD pattern of the lithium compound which was obtained by ion exchanging.

showed its average grain size as 0.1 μm or lower than that. The small particle size was also helpful for the complete ion exchange since it resulted to a large area of solid/liquid interface during the ion exchange. Fig. 4 shows a XRD pattern of the lithium compound obtained by ion exchanging of $\text{Na}_{0.7}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. All diffraction peaks were fitted by hexagonal unit cell with space group $R\bar{3}m$. This crystal structure has oxygen ions with cubic close packing same as that of spinel structure with space group of $Fd\bar{3}m$; thus, the XRD patterns are similar. However, the difference could be obviously seen in a region of high scattering angle as shown in Fig. 5. The $R\bar{3}m$ structure is called as O3 phase, resulting from a glide of the MO_2 sheet in P3 structure. The sheet gliding induces a change in polyhedron shape, in which the interlayer ions are occupied from trigonal prismatic to octahedral one. This sheet gliding process is similar to that of LiCoO_2 ; it is obtained by ion exchange from P3 NaCoO_2 [11]. Hence, it appeared that the layered compound of the present study has quite similar structural characteristic to LiCoO_2 .

$\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($x=0.6, 0.7$, and 0.8) were obtained from their sodium counterparts with P3 structure, which have various $\text{Na}/(\text{Co}+\text{Mn})$ molar ratios, and their electrode properties were investigated. Fig. 6 shows the charge–discharge curve of the cells, $\text{Li}/\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. Charge and discharge

capacity were increased with an increasing in $\text{Na}/(\text{Co}+\text{Mn})$ ratio, and the maximum charge and discharge capacities (221 and 125 mA h g^{-1} , respectively) were achieved at a composition of $\text{Li}_{0.8}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. On the other hand, ion exchanging of P2 structure has not allowed a completed ion exchanging. The research of other ion exchanging method to obtain a stoichiometric compound $\text{Li}_{1.0}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$, which seems to show much higher capacity, is now in progress.

Fig. 6 indicates large irreversible capacities between the first lithium extraction (charge) and the following reinsertion (discharge). One possible

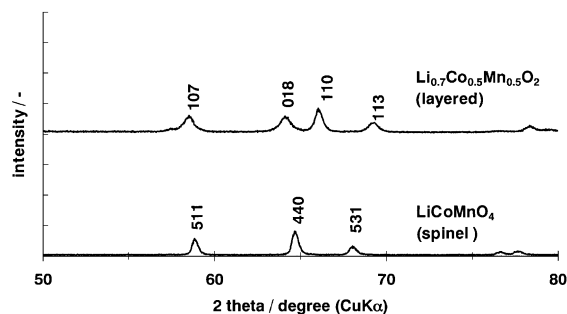


Fig. 5. Comparison of XRD peaks between spinel LiCoMnO_4 and layered $\text{Li}_{0.7}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. The diffraction peaks were indexed with space group $R\bar{3}m$ (upper) and $Fd\bar{3}m$ (lower).

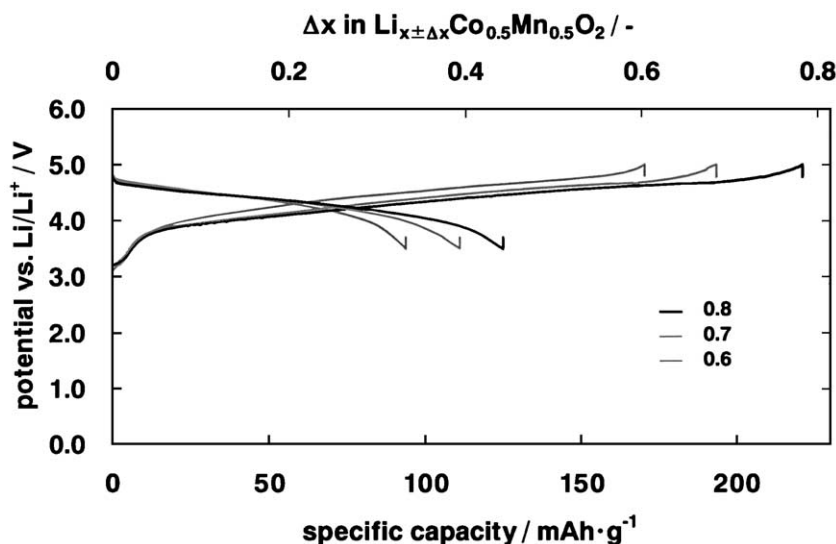


Fig. 6. Charge–discharge curves of the cell; $\text{Li}/\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$. $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was obtained from the sodium counterparts with $\text{Na}/(\text{Co} + \text{Mn})$ molar ratios of 0.8 (a), 0.7 (b) and 0.6 (c).

explanation is that lithium ions were not completely reinserted because of the high insertion, or discharging speed. However, the irreversible capacity did not depend on the insertion rate, i.e., the discharge curves at lower discharge rates were almost the same as that at higher rates. This independency of the irreversible capacity in the discharging rate suggested that it was not caused by kinetic reasons.

Another possible explanation for the irreversible capacity was a decomposition of the electrolyte. High-voltage positive electrode sometimes showed a large irreversible capacity, which were attributed to a decomposition of the electrolytes due to its high voltage (e.g., in Refs. [12–15]). If the irreversible capacity was caused by a decomposition of the electrolyte, it will be smaller with shallower charge depth because of its lower cutoff voltage. Fig. 7 shows the first charge and discharge curves at various charge depths. Irreversible capacity was large even at a quite shallow charge depth. Fig. 8 indicates a relationship between the capacities at the first charge and discharge. It shows a linear relationship, i.e., coulombic efficiency did not depend on the charge depth since the capacity fading certainly existed even after the second cycle, but became quite smaller than that after second cycle, as described on a previous report [9].

Therefore, it should be concluded that decomposition of the electrolyte was not the dominant reason for the irreversible capacity.

An alternative explanation is that the extraction of lithium caused structural change, resulting to a change of lithium site. Fig. 6 indicated that almost all of the lithium ions in the compound were extracted when the cell was charged and, hence, its apparent chemical composition at the end of the first discharge was considered the same in every case. If they had the identical crystal structure there, they would show the same discharge capacity. However, the observed discharging capacity was also increased with an increase in the atomic ratio of $\text{Na}/(\text{Co} + \text{Mn})$. Charge and discharge capacities of $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$, shown in Fig. 6, are also plotted in Fig. 8. They showed the same relationship as those at various charge depths. These results show directly that the ratio of amount of inserted Li^+ ions to that of extracted Li^+ ions was constant regardless of both the Li content of the products and charge depth. Hagenmuller [16] suggested that the extraction of interlayer ions from some layered compound causes the transfer of the transition metal ions to the absent interlayer site. Their study anticipates that such displacement of the transition metal ions has occurred at a certain probability in the

present study. The displaced transition ions seem to locate in the site where Li^+ ions had originally occupied to prevent the reinsertion of Li^+ ions, and resulted in the irreversible capacity. Hence, the irreversible capacity was considered proportional to the extracted amount of lithium.

Packing of oxygen in the layered structure is equivalent to that in spinel structure. Therefore, the layered LiMnO_2 was reported to transform to spinel structure by repetitive charge–discharge cycles [17]. The layered oxide in the present study did not show potential plateaus at 4 nor 5 V during cycling [9]. Considering these facts, the displacement of transition metal is expected to cause the local structure change nearby the lithium-extracted sites to that equivalent to

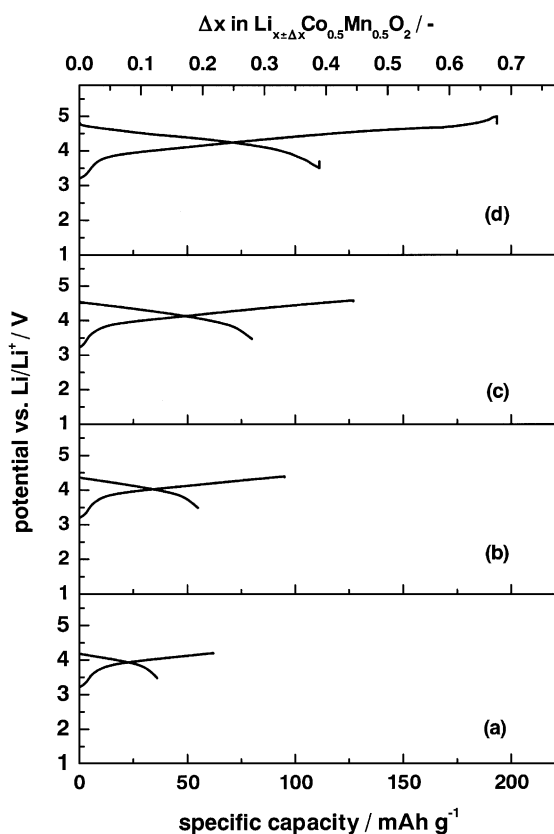


Fig. 7. Charge–discharge curves of the cell; $\text{Li}/\text{Li}_{0.7}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ during the first cycle with various charge depths. Charge depths correspond to changes in lithium composition of 0.22 (a), 0.33 (b), 0.44 (c) and 0.66 (d).

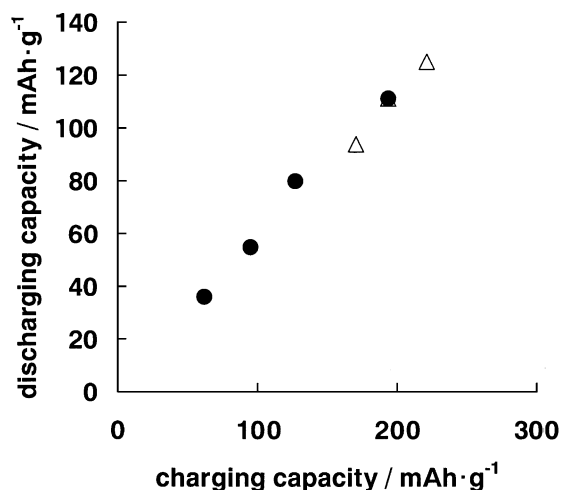


Fig. 8. Relationship between charging and discharging capacity at the first cycle. Data indicated in Figs. 6 and 7 are plotted by open triangles and close circles, respectively.

spinel, i.e., macroscopically, to intermediate structure between the layered type and spinel one. This intermediate structure is considered the reason of its redox potential located between 5.0 V for spinel-type LiCoMnO_4 and 4.0 V for layered LiCoO_2 .

4. Conclusion

$\text{Na}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was synthesized under various conditions. The maximum sodium composition of one with P3 structure was 0.8. $\text{Li}_{0.8}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with layered structure synthesized by ion exchanging from it showed the largest specific capacity due to the largest lithium composition. The irreversible capacity between the first charge and discharge cycle was proportional both to its original lithium composition and to the charge depth, i.e., to the extracted amount of lithium. It is considered that the extraction of lithium caused a local structural change, resulting in a decrease in lithium site, to which lithium ions were reinserted. The structural change was also supposed to be the cause of the higher electrode potential of $\text{Li}_x\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_2$ as compared to its isostructural end members, LiCoO_2 and LiMnO_2 , whose electrode potentials are 4.0 V.

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