A New Polymorph of Layered $LiCoO_2$

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A new polymorph of layered $LiCoO_2$ was prepared from OP4-$Li_xNa_yCoO_2$ by ion exchange. Structural analysis by synchrotron X-ray diffraction revealed that the new polymorph of $LiCoO_2$ is O4-type $LiCoO_2$ whose structure corresponds to intergrowth of O2- and O3-type $LiCoO_2$. It was also confirmed that the O4-type $LiCoO_2$ shows electrochemical activity and different reversible voltage in aprotic lithium cells in comparison to those of O2- and O3-type $LiCoO_2$, which are well-known electrode materials as polymorphs of $LiCoO_2$.

$LiCoO_2$ compounds are among the most important materials for rechargeable batteries since layered $LiCoO_2$ has been applied in practical lithium-ion batteries. According to the stacking classification as proposed by Delmas, commercialized $LiCoO_2$ possesses O3 stacking. The high capacity performance around 4 V vs. Li was first reported by Mizushima et al. in 1980.[1] Two years later, O2-$LiCoO_2$, the first metastable lithiated oxide synthesized by ion-exchange reaction, was found in Delmas' group.[2] The variety of chemical composition, stacking type, and local structure of the layered oxides, such as $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, $LiNi_{0.5}Mn_{0.5}O_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, and their lithium-deintercalated phases, attracts a lot of interest in the field of electrochemistry and solid-state chemistry.[3] The unique stacking of OP4-$Li_xNa_yCoO_2$ ($x \approx 0.43$, $y \approx 0.35$) was prepared and its crystal structure was analyzed by Balsys et al. in 1994 (Figure 1).[4] By lithium ion exchange in OP4-$Li_xNa_yCoO_2$, we first reported a new polymorph of layered lithium cobalt oxide, O4-Li_zCoO_2.[5] In this paper, synthesis, crystal structure, and electrochemical lithium intercalation of O4-Li_zCoO_2 are described.

OP4-$Li_xNa_yCoO_2$ was prepared by heating a mixture of lithium and sodium carbonates and Co_3O_4 in air at 850 °C for 72 h. The prepared OP4-$Li_xNa_yCoO_2$ powder was hydrothermally treated with an aqueous solution of LiOH (2.5 mol dm^{-3}) and LiCl (2.5 mol dm^{-3}) for 24 h in an autoclave to exchange sodium ions with lithium ions. Electrochemical investigation was carried out at ca. 25 °C in coin type cells, in which excess lithium foil was used as a negative electrode. The working electrode consisted of the oxide mixed with 10 wt % acetylene black and 10 wt % PVdF binder. The electrolyte solution was 1 mol dm^{-3} $LiPF_6$ ethylene carbonate:dimethyl carbonate (1:1 by volume). For comparison, O2- and O3-$LiCoO_2$ were prepared. O2-$LiCoO_2$ was prepared by ion exchange of P2-$Na_{0.7}CoO_2$, which was prepared by solid-state method from Na_2CO_3 and Co_3O_4 heated at 800 °C for 48 h in oxygen. O3-$LiCoO_2$ was also prepared from Li_2CO_3 and Co_3O_4 at 850 °C for 12 h in air. Chemical composition of Li, Na, and Co was determined by ICP analysis after dissolving the product in HCl solutions.

The starting atomic ratio of Li:Na:Co and heating conditions were investigated to prepare single phase OP4-$Li_xNa_yCoO_2$ product without any contamination, such as O3-$LiCoO_2$, P2-$Na_{0.7}CoO_2$, and Co_3O_4 phases. When the starting mixture was heated at a rate of 15 °C min^{-1} and quenched in air, we obtained a single phase of OP4-$Li_xNa_yCoO_2$ ($x = 0.37$, $y = 0.31$) product as confirmed by XRD (Figure 2) and ICP. Rietveld refinement of the XRD data supported that the OP4-structure has alternating Li and Na layers intercalated between CoO_2 slabs, that is, the intergrowth of O3 and P2 phase along the *c* axis, and revealed that the OP4-$Li_xNa_yCoO_2$ consists of well-ordered Na and Li layers with a space group symmetry of $P6_3mc$, and lattice parameters are calculated to be $a = 2.819$ and $c = 20.269$ Å.

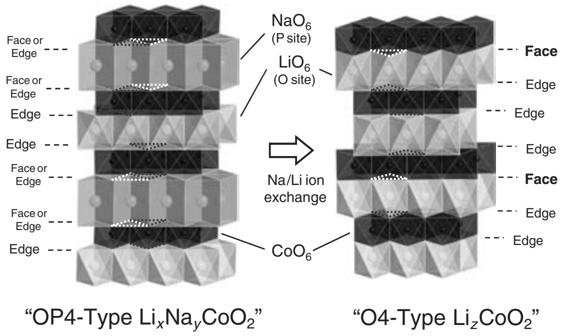

Figure 1. Schematic illustrations of crystal structures of OP4-$Li_xNa_yCoO_2$ and O4-type Li_zCoO_2 polymorphs. The O4 can be transformed by the Na/Li exchange and CoO_2 slab gliding.

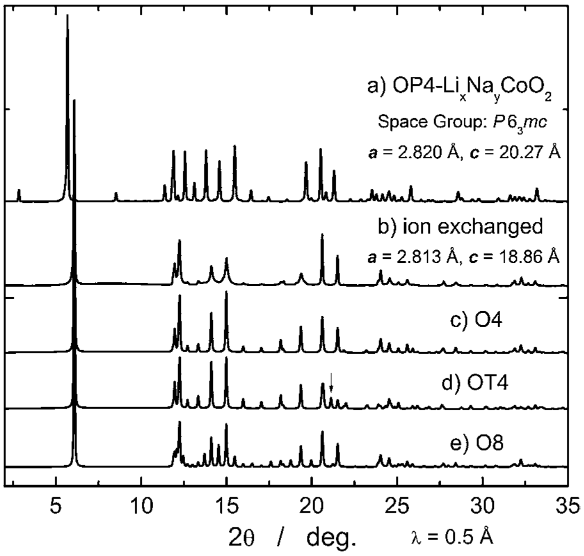

Figure 2. Synchrotron X-ray diffraction patterns of a) OP4-type $Li_{0.37}Na_{0.31}CoO_2$ and b) its ion-exchanged product. Simulated XRD patterns with different stacking models of c) O4, d) OT4, and e) O8 are shown for comparison.

We investigated the Li/Na ion-exchange conditions, that is, $LiNO_3$–LiCl molten salt, aqueous solution, and organic solution media. The ion exchange of the OP4-$Li_xNa_yCoO_2$ was accomplished under hydrothermal conditions in a solution containing LiCl and LiOH at 120 °C as the chemical composition analyses showed $z = 0.85$ in Li_zCoO_2 with trace of sodium in the hydrothermally treated product. As a result, there appeared to be a new diffraction pattern without any residual diffraction peaks of OP4-$Li_xNa_yCoO_2$ as shown in Figure 2. The diffraction pattern totally differs from those of the O2, O3, O6, and $T^{\#}2$ structures as previously described.[6] When we assume that the opposite CoO_2 slabs, sandwiching the prismatic Na layers for the OP4 framework,[4] glided toward the direction of (1/3, 2/3, 0) without breaking Co–O bonds, the O4-Li_zCoO_2 should be formed as illustrated in Figure 1. One can notice that the difference between O2-, O3-, and O4-structures is the sharing sequence between LiO_6 and CoO_6 octahedra and also the oxygen packing sequences. The O4-type stacking is considered to be the intergrowth of O3- and O2-$LiCoO_2$ phases along the *c* axis. In Figure 2, the observed pattern of the synthesized Li_zCoO_2 was compared with three simulated diffraction patterns of O4-, OT4- ($OT^{\#}4$-), and O8-type stacking manners by assuming the different gliding manners, that is, (0, 1/2, 0) for OT4, and (1/3, 2/3, 0) and (2/3, 1/3, 0) alternately for O8-$LiCoO_2$. Figure 2 confirms that the observed pattern agrees with the calculated pattern of the O4 structure ($P6_3mc$), and we can eliminate the possibilities of O8 and OT4 structures because of unmatched diffraction lines. The experimental diffraction peaks are broadened because of the extent of stacking fault along the *c* axis, which was also supported by scanning and transmission electron microscopy observation. Consequently, the O4 structure took place by the combination of OP4 precursor with the hydrothermal treatment. The composition of lithium of O4-Li_zCoO_2 was below the stoichiometric value, which is probably due to vacancy or incorporation of protons.

In aprotic Li cells at 25 °C, the O4-Li_zCoO_2 electrode demonstrated excellent cycle performance comparable to that of commercially successful O3-$LiCoO_2$ as shown in Figure 3. Since the potential plateau appeared during successive cycles between 3.5 and 4.5 V, the reversible phase transition would occur under these conditions. For O4-Li_zCoO_2, the irreversibility was observed only at the initial cycle, and the stable reversible capacity of ca. $170\,\mathrm{mA\,h\,g^{-1}}$ was maintained during successive cycles similar to O3-$LiCoO_2$. To clarify the difference of potential plateau for O2, O3, and O4 electrodes, the differential curves are obtained from the initial galvanostatic curve and compared in Figure 4. Clearly, the O4 electrode exhibited at least two redox couples around 3.8 and 4.5 V, and the differential curves are completely different from those of the O2- and O3-$LiCoO_2$ electrodes. When we compare the main plateau between 3.6–4.0 V, the plateaux at 3.84 and 3.80 V are located between those of O2 and O3. It is interesting to note that this electrochemical feature seemed to correspond to the structural feature of the intergrowth of O3- and O2-$LiCoO_2$ phases as already mentioned. Figure 4 proves that the O4 undergoes different phase transition by electrochemical lithium intercalation since the O4 is a new polymorph of layered Li_zCoO_2. It is believed that Li_zCoO_2 is the third polymorph of the layered $LiCoO_2$.

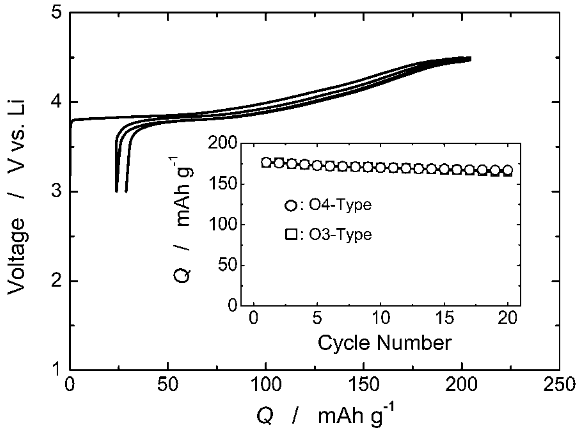

Figure 3. Galvanostatic charge and discharge curves of O4-type Li_zCoO_2 at a rate of $20\,\mathrm{mA\,g^{-1}}$ at room temperature. Discharge capacity of the O3 and O4 as a function of the cycle number is shown in the inset.

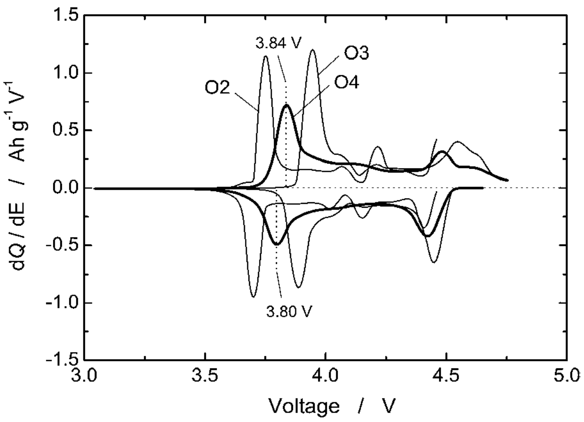

Figure 4. Differential capacity (dQ/dE) plots obtained from the chronopotentiograms for Li/$LiCoO_2$ cells with different $LiCoO_2$ polymorphs.

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