MLF Experimental Report	提出日 Date of Report 2010/8/6
課題番号 Project No. 2009B0016 実験課題名 Title of experiment Structural analyses of new $LiCoO_2$ for lithium-ion batteries 実験責任者名 Name of principal investigator 駒場慎一 所属 Affiliation 東京理科大学	装置責任者 Name of responsible person 石垣 徹 装置名 Name of Instrument/（BL No.） iMATERIA/BL20 実施日 Date of Experiment 2010/5/14～2010/5/15

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

$Li_{0.9}CoO_2$

$Li_{0.5}CoO_2$

$Li_{0.37}Na_{0.31}CoO_2$

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Layered $LiCoO_2$ is used as positive electrode materials for commercial lithium-ion batteries. Two different polymorphs of $LiCoO_2$, thermodynamically stable O3-type and meta-stable O2-type $LiCoO_2$, are known so far. Very recently we have found that possible new polymorph of $LiCoO_2$, which has been prepared from OP4-type $Li_xNa_yCoO_2$ ($x < 0.5$, $y < 0.5$). For OP4-type $Li_xNa_yCoO_2$, sodium and lithium ions occupy prismatic sites and octahedral sites, respectively, which are stacked alternately along *c*-axis. In this research proposal, we have examined the ion-exchanged product of OP4-type $Li_xNa_yCoO_2$, and its reaction mechanism has been studied by ToF neutron diffraction method. When the sodium ions are exchange by the lithium ions, we found that CoO_2-Li-CoO_2 slabs glide by (2/3, 1/3, 0) because of the difference in the ionic radii and / or distance in the inter-slabs (Figure 1). Detailed structural analysis reveals that this phase can be classified as O4-type $LiCoO_2$, which is new polymorph of $LiCoO_2$. It is noted that profiles of all diffraction lines are broadened, except $(00l)_{hex.}$ and $(110)_{hex.}$ lines, suggesting that stacking fault exists for O4-type $LiCoO_2$. To examine the reaction mechanism of O4-type $LiCoO_2$, $Li_{0.5}CoO_2$ has been prepared by the electrochemical extraction of the lithium ions and examined by the neutron diffraction.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Figure 2 compares neutron diffraction patters of O4-$LiCoO_2$ and $Li_{0.5}CoO_2$. Lithium ions were extracted in the electrochemical cells, in which the composite electrodes consisting of $LiCoO_2$, acetylene black, and PVdF as binder were utilized. Lithium metal was used as a negative electrode, and 1 mol dm^{-3} $LiPF_6$ dissolved in EC : DMC = 1 : 1 was used as electrolyte solution. After the lithium extraction process, two new diffraction lines appear beside the $(110)_{hex.}$ diffraction line. In order to explain the experimental observation, possible models, which have different stacking sequences, were tested. Figure 3 shows simulated neutron diffraction patterns of O4 and OT$^{\#}$4-type models. For the OT$^{\#}$4-type model, half of lithium ions are located at distorted tetrahedral sites. This is achieved by the gliding of the plane with (1/3, 1/6, 0) as shown in Figure 4 if no stacking fault is assumed.

Since the OT$^{\#}$4 model generates the additional diffraction lines, which are consistent with the observed diffraction patterns, we conclude that O4-type $LiCoO_2$ changes to the OT#4-type by the lithium extraction. In addition, this phase transition reversibly occurs. O4-type $LiCoO_2$ was confirmed after the discharging process (lithium insertion to the lattice).

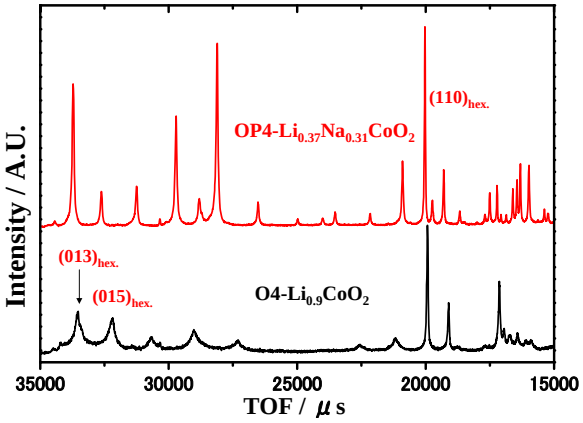

Figure 1. ToF Neutron diffraction patterns of OP4-$Li_{0.37}Na_{0.31}CoO_2$ and O4-$Li_{0.9}CoO_2$.

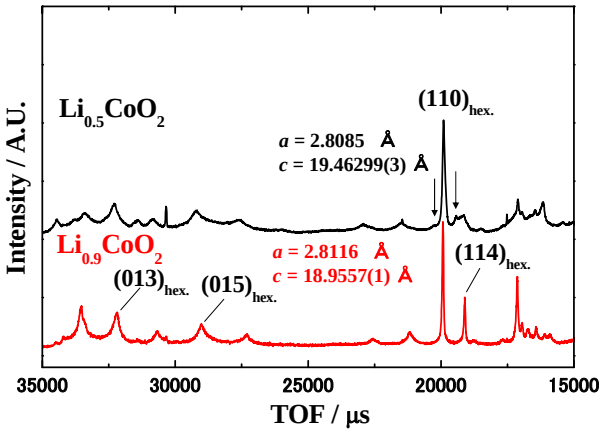

Figure 2. ToF Neutron diffraction patterns of O4-$Li_{0.9}CoO_2$and $Li_{0.5}CoO_2$.

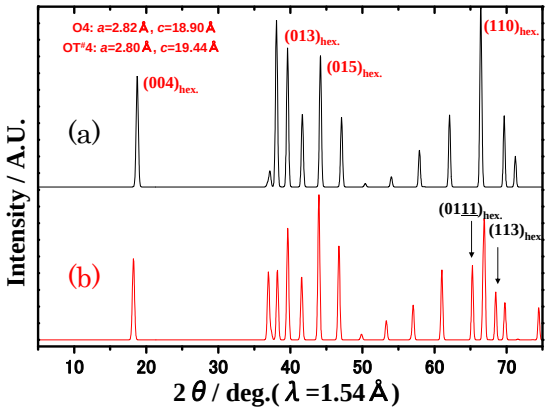

Figure 3. Simulated neutron diffraction patterns of (a) O4-$LiCoO_2$ and (b) OT$^{\#}$4-$LiCoO_2$.

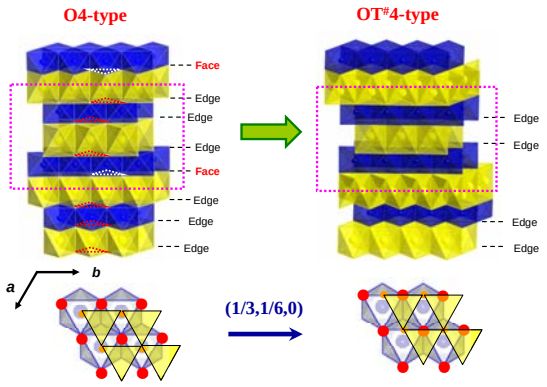

Figure 4. Proposed model of the phase transition from O4-$LiCoO_2$ to OT$^{\#}$4-Li_zCoO_2.