MLF Experimental Report	提出日 Date of Report 2011/6/25
課題番号 Project No. 2010B0058 実験課題名 Title of experiment Changes of crystal structures during charge-discharge processes in Li(Mn, Co, Ni, Li)O_2 as a cathode active material for a lithium ion battery 実験責任者名 Name of principal investigator Yasushi Idemoto 所属 Affiliation Tokyo University of Science	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/（BL No.） SuperHRPD/BL08 実施日 Date of Experiment 2010/12/16 - 2010/12/17 2011/2/14 - 2011/2/15

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.

Pristine sample: $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$ ($0.6Li_2MnO_3$- $0.4LiMn_{0.417}Ni_{0.417}Co_{0.166}O_2$), powder
Charged sample: $Li_{0.3}Mn_{0.567}Ni_{0.167}Co_{0.067}O_{2-\delta}$, powder

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.

Experimental method

$Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$ was synthesized by a solution method using a citric acid as a dispersing agent. The precursor obtained from the solution was heat-treated in air at 650 ^oC for 15 h and then at 950 ^oC for 15 h. Preliminary phase identification was carried out by powder X-ray diffraction technique, and the metal composition was determined by ICP. The cathode property was evaluated by charge-discharge cycle tests using a coin cell. We also prepared a sample after electrochemical charge, $Li_{0.3}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$, in order to clarify an effect of the charging process on the crystal structure.

Crystal-structure analyses were performed based on the Rietveld method. In this experiment, neutron diffractions were collected by SuperHRPD. Each sample was applied to Al foil, and then the sheet was loaded in a vanadium can. Diffraction patterns of the sheets were measured under vacuum at room temperature. By using the data, the crystal structures were refined with Z-Rietveld program.

Results

Table 1 shows structure parameters of pristine $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$ refined by assuming the space group as *R*-3*m*. As shown in this table, the Rietveld analysis could be successfully carried out even though the measured specimen was a film with a weight of ca. 0.7 g. From these parameters, it was found that a cation mixing amount — *i.e.*, an amount of Ni^{2+} occupying Li^+ site in this case — was low and an oxygen deficit amount was negligible in this material.

In order to reveal a crystal-structure change of the cathode material during charge-discharge cycle, we also measured neutron diffraction patterns of the electrochemically-charged sample, which was a film with a weight of **ca. 0.01 g.** The diffraction pattern is given in Fig. 1. As a reference, this figure also shows the diffraction pattern of the pristine sample discussed above. From this figure, it was clarified that the crystal structure was varied and some impurity phases were formed by the charging process. Such a change in the cathode may be related with a deterioration process of the battery.

Table 1 Refined structure parameters of $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$ ($0.6Li_2MnO_3$- $0.4LiMn_{0.417}Ni_{0.417}Co_{0.166}O_2$) in the space group of *R*-3*m*. *R*-factors were R_{wp}=12.0 %, R_p=8.81 % and R_e=5.80 %. Lattice constants were *a*=0.28579(5) nm and *c*=1.4243(3) nm.

Atom	Site	*x*	*y*	*z*	$10^2 \times B(nm^2)$	Site occupancy
Li1	3a	0	0	0	1.98(10)	0.980(2)
Ni1	3a	=*x*(Li1)	=*y*(Li1)	=*z*(Li1)	=*B*(Li1)	0.020(2)
Ni2	3b	0	0	1/2	0.37(10)	0.131(2)
Li2	3b	=*x*(Ni2)	=*y*(Ni2)	=*z*(Ni2)	=*B*(Ni2)	0.214(2)
Mn	3b	=*x*(Ni2)	=*y*(Ni2)	=*z*(Ni2)	=*B*(Ni2)	0.554
Co	3b	=*x*(Ni2)	=*y*(Ni2)	=*z*(Ni2)	=*B*(Ni2)	0.0931
O	6c	0	0	0.24104(5)	0.85(2)	0.990(3)

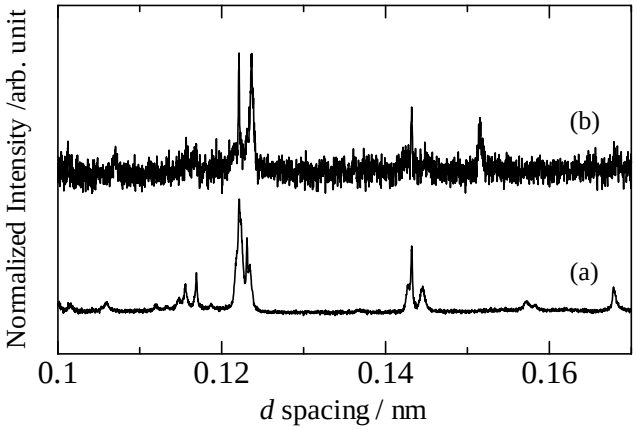

Fig. 1 Neutron diffraction patterns of (a) the pristine $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$ and (b) the electrochemically-charged sample.