MLF Experimental Report	提出日 Date of Report 2011/6/26
課題番号 Project No. 2010A0006 実験課題名 Title of experiment Effects of a synthetic process and a heat-treatment on crystal structures of lithium-rich layered cathode active materials for 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 2010/6/17 – 2010/6/18 2010/11/19-2010/11/20

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.

$Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$ ($0.5Li_2MnO_3$- $0.5LiMn_{0.417}Ni_{0.417}Co_{0.166}O_2$), powder
$Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_{2-\delta}$ (after a heat treatment under a vacuum), 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

Firstly, we prepared $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$ with a solution method in which a final sintering was carried out in air at 950 ^oC for 15 h. In order to investigate an effect of the oxygen content on the crystal structure, a part of the product was heat-treated in a vacuum at 800 ^oC for 6~12 h. Phases and metal compositions of these samples were confirmed by powder X-ray diffraction and ICP measurements, respectively. By redox titrations and XAS methods, valences of the transition metals were studied. We also investigated electrochemical properties with CV and charge-discharge cycle tests using a coin cell.

As for these samples, neutron diffraction patterns were measured at room temperature by SuperHRPD. In the measurements, the powder with a weight of 1 g was loaded in a vanadium can and then mounted in the apparatus. By using the data, the crystal structures were refined with Z-Rietveld program, based on the Rietveld technique.

Results

Figure 1 shows a Rietveld refinement pattern of $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_{2-\delta}$ after the heat treatment under the vacuum. As shown in this figure, the analysis was successfully performed by assuming a single phase of a layered rock-salt structure (S. G.; *R*-3*m*). The refined structure parameters are listed in Table 1. From the site occupancies of the metal sites, it was found that an amount of the cation mixing, i. e. Ni at 3a site in this case, was low in this sample. By comparing to results of the pristine $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$, it was also demonstrated that the lattice constants tended to expand by the heat-treatment in the vacuum and the oxygen-deficit amount in the heat-treated sample was larger than that of the pristine one. Because XAFS analyses suggested that the vacuum treatment made Mn valence lower, such an oxygen deficit was supposed to be compensated by the Mn-valence change. In addition, it was clarified that structure-distortion parameters (a quadratic elongation, λ, and a bond angle variance, σ^2) of the 3b-O_6 octahedron became larger by the heat-treatment.

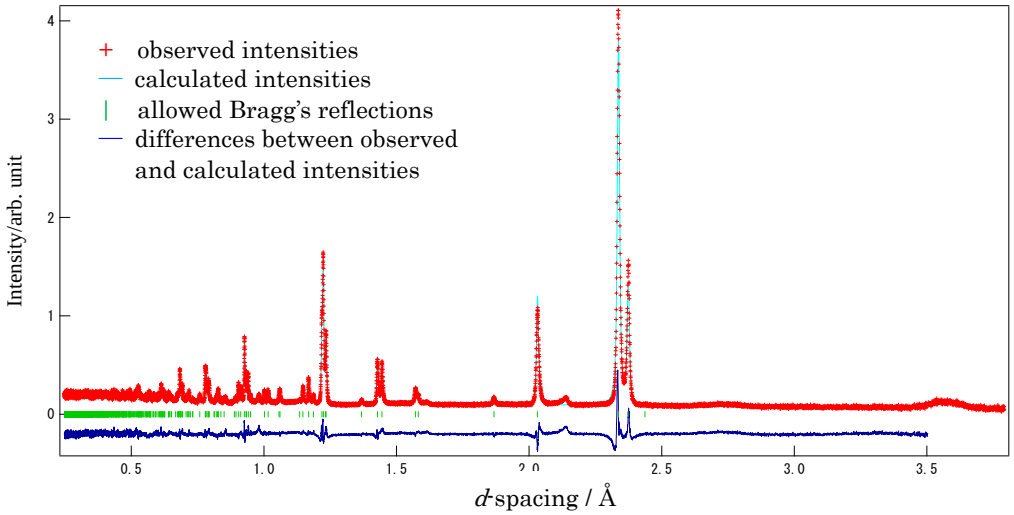

Fig. 1 Rietveld refinement pattern of $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_{2-\delta}$ heat-treated in the vacuum (S. G.; *R*-3*m*).

Table 1 Refined structure parameters of $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_{2-\delta}$ heat-treated in the vacuum. *R*-factors were R_{wp}=11.0 %, R_p=8.03 and R_e=4.76 %. Lattice constants were a=0.28568(2) nm and c=1.4245(2) nm.

Atoms	Site	x	y	z	$10^2 \times B$ (nm²)	Site occupancy
Li1	3a	0	0	0	1.41(8)	0.8772(7)
Ni1	3a	=Li1(x)	=Li1(y)	=Li1(z)	=Li1(B)	0.0223(7)
Ni2	3b	0	0	1/2	0.37(7)	0.1421(7)
Li2	3b	=Ni2(x)	=Ni2(y)	=Ni2(z)	=Ni2(B)	0.2345(7)
Mn	3b	=Ni2(x)	=Ni2(y)	=Ni2(z)	=Ni2(B)	0.5587
Co	3b	=Ni2(x)	=Ni2(y)	=Ni2(z)	=Ni2(B)	0.0647
O	6c	0	0	0.24130(2)	0.79(4)	0.948(8)