MLF Experimental Report	提出日 Date of Report 2011/6/30
課題番号 Project No. 2010B0065 実験課題名 Title of experiment Crystal structure analysis of lithium-excess layered material $Li_{1+x}MO_2$ (M=Ni, Co, Mn) - New cathode material for lithium batteries 実験責任者名 Name of principal investigator Ryoji Kanno 所属 Affiliation Tokyo Institute of Technology	装置責任者 Name of responsible person Touru Ishigaki 装置名 Name of Instrument/（BL No.） iMateria (BL No.20) 実施日 Date of Experiment 2011/3/9 - 3/10

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.

Powdered $Li_{1.6}Ni_{0.3}Co_{0.2}Mn_{0.3}O_2$ and $Li_{1.7}Ni_{0.3}Co_{0.2}Mn_{0.3}O_2$ in the lithium excess $Li_xM_{0.8}O_2$ (M=Ni, Co, Mn) system were synthesized by a high-pressure synthesis method. We confirmed a continuous lattice expansion with increasing lithium compositions from 1.4 to 1.7 using X-ray diffraction measurements, but lithium positions have not been clarified. These compounds show an excellent charge/discharge characteristic as a cathode material for lithium batteries.

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.

Neutron diffraction data of $Li_{1.6}Ni_{0.3}Co_{0.2}Mn_{0.3}O_2$ and $Li_{1.7}Ni_{0.3}Co_{0.2}Mn_{0.3}O_2$ were taken at room temperature on a time-of-flight (TOF) neutron powder diffractometer at iMATERIA (BL20) using the BS (Back Scattering) bank. The specimen of ca. 1.5 cc is contained in a cylindrical vanadium cell of dimensious 10 mm inradius, 20 mm in height. The data were analyzed by the Rietveld method using the Z-Rietveld program.

Figure 1 shows a preliminary Rietveld analysis result using neutron diffraction data of $Li_{1.7}Ni_{0.3}Co_{0.2}Mn_{0.3}O_2$. Structural parameters are summarized in Table 1. The structure was refined based on the structure model with a layered rocksalt structure investigated by the X-ray Rietveld analysis. The present refined structure cannot explain positions of the excess lithium in the layered structure. The detailed structure is under analyzing to clarify (i) extent of disordering

at the lithium layer, (ii) stacking disorder perpendicular to the two-dimensional lithium layer, (iii) distribution of transition metals, Mn, Ni, and Co. These parameters that are variable and controllable by changing synthesis conditions affect significantly for its lithium storage capacity, and it is necessary to clarify the charge-discharge mechanism, which provides extremely high capacity for our new material.

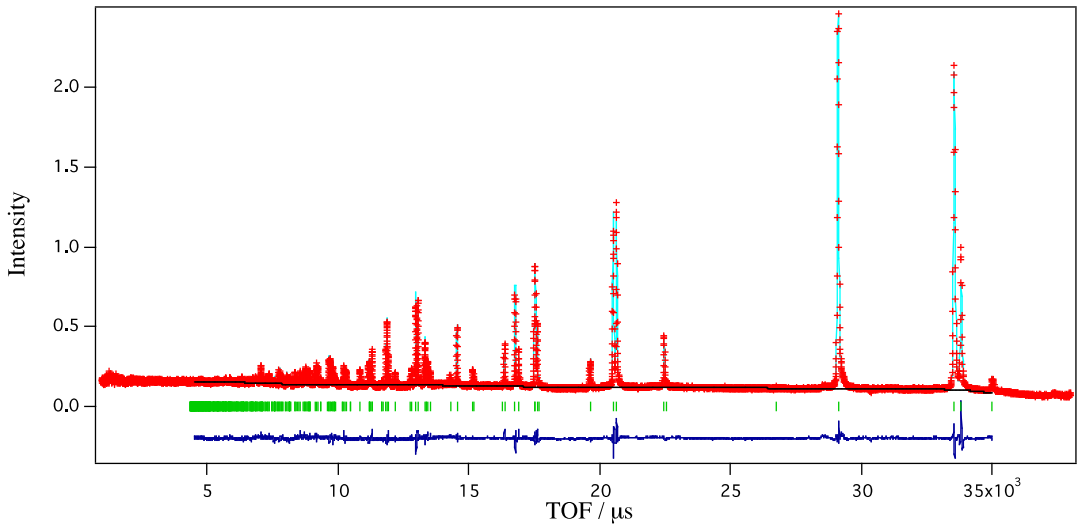

Fig. 1 Observed (plus marks), calculated (solid line), and difference (bottom) patterns for the Rietveld refinement from neutron diffraction data of $Li_{1.7}Mn_{0.3}Co_{0.2}Ni_{0.3}O_2$. The short vertical lines below the profiles mark the peak positions of all the possible Bragg reflections.

Table 1 Rietveld refinement results for $Li_{1.7}Mn_{0.3}Co_{0.2}Ni_{0.3}O_2$.

Atom	Site	*g*	*x*	*y*	*z*	*B* / Å^2
Li1	3*a*	0.8393(7)	0	0	0	1
Li2	3*b*	0.1992(6)	0	0	0.5	0.5
Ni1	3*b*	0.3002(1)	0	0	0.5	0.5
Mn1	3*b*	0.2996(3)	0	0	0.5	0.5
Co1	3*b*	0.2007(5)	0	0	0.5	0.5
O1	6*c*	1	0	0	0.24286(2)	0.8
Ni2	3*a*	0.1607(7)	0	0	0	1
Li3	6c	0.022(1)	0	0	0.125	1

a = 2.895711(4) Å, *c* = 14.31221(5) Å, R_{wp} = 5.18%, R_p = 3.95%, R_e = 2.16%, S^2 = 5.731, R_B= 7.15%, R_F = 2.17%