MLF Experimental Report	提出日 Date of Report 2013/4/4
課題番号 Project No. 2012B0029 実験課題名 Title of experiment Composition dependence of crystal structure of vacuum-reduced Li_2MnO_3-Li(Mn,Co,Ni)O_2 system in electrochemical charge/discharge process 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 Toru Ishigaki 装置名 Name of Instrument/（BL No.） iMATERIA/BL20 実施日 Date of Experiment 2012/11/28~30 2013/01/16~18

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.

Compositions: zLi_2MnO_3-$(1-z)Li(Mn_{1/3}Co_{1/3}Ni_{1/3})O_2$ (reduced; charged, discharged)
zLi_2MnO_3-$(1-z)Li(Mn_{5/12}Co_{1/6}Ni_{5/12})O_2$ (reduced; charged, discharged)
Physical form: Powder or film

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

Lithium-rich layered cathode active materials were synthesized by a coprecipitation method. In this process, the final heating was carried out at 950 ^{o}C in air regardless of the metal composition. As for the synthesized samples, a heat-treatment under vacuum condition (P=10^{-4} Pa) at 800 ^{o}C was carried out. Phases of the obtained samples were identified by powder X-ray diffraction measurements, and their metal compositions and the metal valences were evaluated by the inductively coupled plasma emission and redox titration analyses. In order to clarify the composition dependence of the vacuum-reducing effects on the crystal structures at electrochemically charged and discharged states, cathodes after charge-discharge cycling were prepared.

As for these cathodes, neutron diffraction patterns were measured by iMATERIA installed at J-PARC. Each cathode(10mg) was loaded in a vanadium can, and then mounted in a sample holder. The measurements were carried out at room temperature with a SF mode. Crystal structures of the samples were refined by the Rietveld technique using a Z-Rietveld program.

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

Results

Fig. 1 shows Rietveld refinement pattern of vacuum-reduced $0.5Li_2MnO_3$-$0.5LiMn_{5/12}Co_{1/6}Ni_{5/12}O_2$ after an initial charging process (BS bank). In these analyses, the transition-metal occupancies were refined so that the compositions were equal to the analytical values estimated by ICP. The result given in Fig. 1 indicated that the sample kept a Li_2MnO_3-type structure (S. G.: *C*2/*m*) even after electrochemical tests. In addition, it was found that a *c*-axis length became longer and the others became shorter by the charging process in the reduced samples. Such a tendency was also observed in the samples without the reducing treatment.

Table 1 lists distortion parameters of metal-O_6 octahedra and the bond valence sums (B. V. S.) of vacuum-reduced $0.5Li_2MnO_3$-$0.5LiMn_{5/12}Co_{1/6}Ni_{5/12}O_2$ after the initial charging. This table also presents the distortion values of the pristine sample, i. e., the sample without the reducing treatment. In the reduced sample, the distortions were smaller than the pristine specimen. Since a cycle performance of $0.5Li_2MnO_3$-$0.5LiMn_{5/12}Co_{1/6}Ni_{5/12}O_2$ cathode was improved by the vacuum-reducing heat-treatment, the lower distortions at the charged state can be considered as an important factor to enhance the cathode performance.

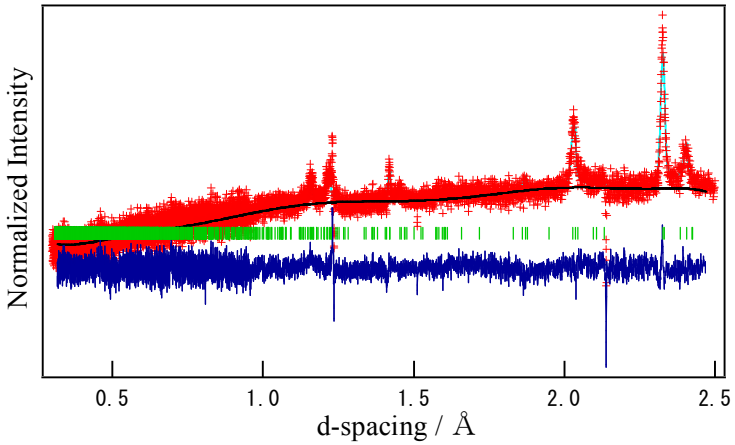

Fig. 1 Neutron diffraction pattern of vacuum-reduced $0.5Li_2MnO_3$-$0.5LiMn_{5/12}Co_{1/6}Ni_{5/12}O_2$(cathode:10mg) after an initial charging process. Plus marks show observed neutron diffraction intensities, and a solid blue line represents calculated intensities. Vertical marks below them indicate positions of allowed Bragg refractions. A curve at the bottom is a difference between the observed and calculated intensities in the same scale.

Table 1 Quadratic elongations, λ, bond angle variances, σ^2, of metal-O_6 octahedra and B. V. S. in the transition-metal layer of $0.5Li_2MnO_3$-$0.5LiMn_{5/12}Co_{1/6}Ni_{5/12}O_2$ after an initial charging.

Sample	4*g*-O_6			2*b*-O_6		
	λ	σ^2(deg.^{2})	B. V. S.	λ	σ^2(deg.^{2})	B. V. S.
Pristine	1.012	37.68	3.764	1.019	59.93	2.142
Vacuum reduction	1.011	34.19	4.051	1.019	57.86	1.772