MLF Experimental Report	提出日 Date of Report 2014/06/09
課題番号 Project No. 2013B0027 実験課題名 Title of experiment Effects of charge and discharge cycles on crystal structure of vacuum-reduced Li(Mn,Co,Ni,Li)$O_{2-\delta}$ cathode 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 2013/03/24-25 2014/04/04-07

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: $z$$Li_2MnO_3$-(1-$z$)$Li(Mn_{1/3}Co_{1/3}Ni_{1/3})O_2$
(pristine and reduced samples after several charge and discharge cycles)

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

We synthesized lithium-rich layered cathode materials by a coprecipitation, and then heated them under vacuum condition at 800 ^{o}C for 6 h. Phases identification was carried out 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. For these samples, cathode properties were investigated by charge/discharge cycle tests.

In order to clarify crystal-structure changes of the samples during the cycle tests, cathodes after the several cyclings were prepared. Neutron diffraction measurements of the cathodes were performed by iMATERIA installed at J-PARC. Each cathode with a weight of about 10 mg was loaded in a vanadium can, and then mounted in a sample holder. The measurements were conducted at room temperature with a SF mode, and the measurement time was ca. 6 h for each specimen. Crystal structures of the samples were refined by the Rietveld technique using the Z-Rietveld program.

Results

Fig. 1 shows Rietveld refinement pattern of $0.6Li_2MnO_3$-$0.4LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ after a fifth discharging process, assuming the crystal structure as the Li_2MnO_3-type structure (S. G.: *C*2/*m*). From this figure, it is found that the crystal structure was kept even after the charge and discharge cycles. The refined site occupancies reveals that lithium ions could be extracted during charging processes from both the transition-metal layers and the lithium-ion layers. These tendencies were also observed in the vacuum-reduced sample.

Table 1 shows the distortions of M-O_6 octahedra, i. e. the quadratic elongation λ and bond the angle variances σ^2, in $0.6Li_2MnO_3$-$0.4LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$. The distortion of M-$O_6$ octahedra in the transition-metal layer tended to increase after a first discharging process, but such a change was not observed in the following cycles. This means that the structure distortion was induced significantly especially at the first cycle. Similar analysis is in progress for the vacuum-reduced samples.

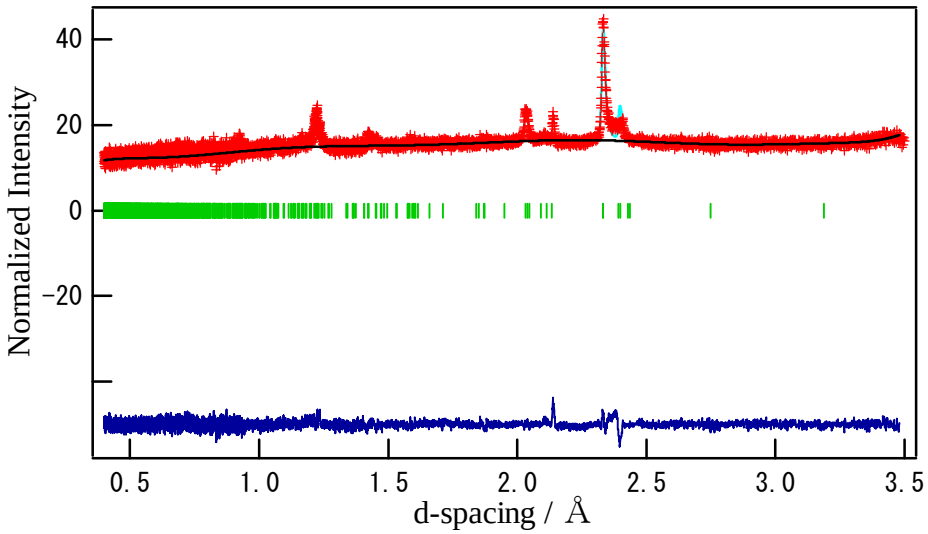

Fig. 1 Rietveld refinement pattern of the fifth-discharged $0.6Li_2MnO_3$-$0.4LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ in the space group *C*2/*m*. Plus marks show observed neutron diffraction intensities and a solid line represents calculated intensities. Vertical marks indicate positions of allowed Bragg reflections. A curve at the bottom is a difference between the observed and calculated intensities in the same scale.

Table 1 Changes of quadratic elongations, λ, bond angle variances, σ^2, of M-O_6 octahedra in the transition-metal layer of $0.6Li_2MnO_3$-$0.4LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ in the cycle tests.

Sample	4*g*-8*j* , 4*g*-4*i*		2*b*-8*j* , 2*b*-4*i*	
	λ	σ^2(deg^2)	λ	σ^2(deg^2)
Pristine	1.004	12.41	1.009	30.59
First discharge	1.008	24.95	1.012	30.84
Fifth discharge	1.007	22.98	1.010	26.46