MLF Experimental Report	提出日 Date of Report 2013/1/13
課題番号 Project No. 2012A0015 実験課題名 Title of experiment Effect of reducing treatment on crystal-structure change of Li(Mn,Co,Ni,Li)$O_{2-\delta}$ cathode during electrochemical charge-discharge cycle 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 2012/6/8~9 2012/10/27~28

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: $Li_{1.167}Mn_{0.5}Ni_{0.167}Co_{0.167}O_2$, $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$, $Li_{1.2}Mn_{0.533}Ni_{0.133}Co_{0.133}O_2$
Physical form: Powder (pristine samples, vacuum-reduced samples)
: Film (samples after charge and discharge cycle tests)

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 Li-rich transition-metal cathode materials, Li(Mn,Ni,Co,Li)O_2, by means of a coprecipitation method. Precipitates were heat-treated in air at 650 ^{o}C for 15 h and then at 950 ^{o}C for 15 h. These products were also annealed under a vacuum reducing condition. Phases of these samples were identified by powder X-ray diffraction measurements, and their metal compositions were evaluated by an inductively-coupled plasma (ICP) technique. Electrochemical properties of the samples were studied by charge-discharge cycle tests using a coin cell. In order to clarify how the cycle processes affects their crystal structures, we prepared a sample after electrochemical charge and discharge for crystal-structure analyses.

Neutron diffraction patterns were measured at room temperature by iMATERIA with all the banks. In the measurements, powder or film of each sample was loaded in V or VNi alloy can. By using these data, the crystal structures were refined with Z-Rietveld program.

Results

Fig. 1 shows Rietveld refinement pattern of $Li_xMn_{0.533}Ni_{0.133}Co_{0.133}O_2$ film after 1st discharging process. In the analysis, a space group was assumed as *C*2/*m*, and the transition-metal occupancies of all the sites were refined so that the compositions were equal to the analytical values estimated by ICP. As shown in this figure, the Rietveld analysis could be successfully performed even though a weight of the cathode material in the film was about 10 mg. This result demonstrates that this experimental method is useful for investigations on crystal structures of cathodes in batteries.

Table 1 lists change in distortion parameters of metal-O_6 octahedra of $Li_xMn_{0.533}Ni_{0.133}Co_{0.133}O_2$ with charge/discharge cycle. It was found that the distortions around 4*g* and 4*h* sites tended to increase after the electrochemical tests, and such a tendency could be observed even after the initial cycle. Because the 4*g* and 4*h* sites were occupied mainly by Mn and Li, respectively, these elements may cause crystal-structure degradation during charge/discharge cycles.

As for the vacuum-reduced samples after charge and discharge processes, the analyses are in progress.

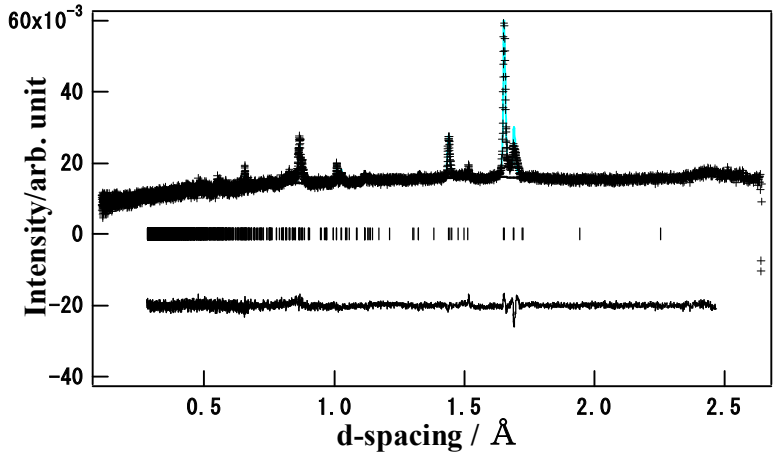

Fig. 1 Neutron diffraction pattern of $Li_xMn_{0.533}Ni_{0.133}Co_{0.133}O_2$ after the initial discharging process. Plus marks show observed neutron diffraction intensities, and a solid line represents calculated intensities. Vertical marks below them indicate positions of allowed Bragg refractions. A curve at the bottom is a difference between the observed and calculated intensities in the same scale.

Table 1 Quadratic elongations, λ, and bond angle variances, σ^2, of metal-O_6 octahedra in the transition-metal (TM) layer and the Li layer of $Li_xMn_{0.533}Ni_{0.133}Co_{0.133}O_2$.

Sample	4*g*-O_6 (TM layer)		2*b*-O_6 (TM layer)		4*h*-O_6 (Li layer)		2*c*-O_6 (Li layer)	
	Λ	σ^2(deg^2)	λ	σ^2(deg^2)	λ	σ^2(deg^2)	λ	σ^2(deg^2)
pristine	1.003	12.41	1.009	30.59	1.011	36.64	1.012	37.38
1st discharge	1.008	24.95	1.012	30.84	1.015	54.96	1.009	31.58
5th discharge	1.007	22.98	1.010	26.46	1.017	61.26	1.008	27.61