MLF Experimental Report	提出日 Date of Report 2015/2/23
課題番号 Project No. 2014A0251 実験課題名 Title of experiment Effects of charge and discharge process on crystal structure of oxygen-deficient Li(Mn,Co,Ni,Li)O_{2-d} cathodes by reduction methods 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 2014/6/6 - 2014/6/7 2014/6/21 - 2014/6/23 2014/11/7 - 2014/11/8

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.

$Li(Mn_{0.54}Co_{0.13}Ni_{0.13}Li_{0.2})O_{2-\delta}$, 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

$Li(Mn_{0.54}Co_{0.13}Ni_{0.13}Li_{0.2})O_{2-\delta}$ were synthesized by a conventional co-precipitation and solid-state reaction method using Mn-, Ni- and Co- nitrates and LiOH as starting materials. Reductive heat-treatments were performed with sucrose additives (0.03 g/mol, 0.05 g/mol). The lattice parameters of these samples were estimated by powder X-ray diffraction measurements, and the metal compositions were confirmed by inductively-coupled plasma (ICP) technique. The oxygen compositions were determined by titration technique. For these samples, cathode properties were investigated charge-discharge cycle tests.

In order to reveal crystal-structure changes of the samples after the reduction treatment, about 1 g powders were prepared. Neutron diffraction measurements of the powders were performed by iMATERIA installed at J-PARC. Each powder with a weight of 0.5 g 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. 20 min for each powder specimen. Crystal structures of the samples were refined by the Rietveld technique using the Z-Rietveld program.

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

Results

A Rietveld refinement patterns of $Li(Mn_{0.54}Co_{0.13}Ni_{0.13}Li_{0.2})O_{2-d}$ for pristine, adding 0.03 g/mol sucrose and 0.05 g/mol sucrose samples are presented in Fig. 1. In the analysis, we assumed a space group of the crystal structure as *C2/m* (the Li_2MnO_3-type structure), and refined atomic positions and displacement parameters of all the elements. Site occupancies of metals were also refined under constraints of analysis metal compositions. The oxygen occupancies in the two sites were fixed with equally divided values estimated by titration method. It was demonstrated that the samples after reduction had a single phase as well as pristine sample although the lattice parameter, *c* became shorter than pristine due to a decrease in the oxygen-oxygen repulsion.

The coulombic efficiency of the initial cycle was improved from 74% to 83% by addition of sucrose (0.03mol/g). From the results of Rietveld analysis, Mn-ordering increased after the reductive treatments while oxygen amounts and the cation-mixing decreased. Especially the sample with 0.03 mol/g addition of sucrose showed the lowest cation mixing of the present samples. It was found that the improvement for coulombic efficiency was attributed to the effect of suppression of the nickel mixing in Li layer.

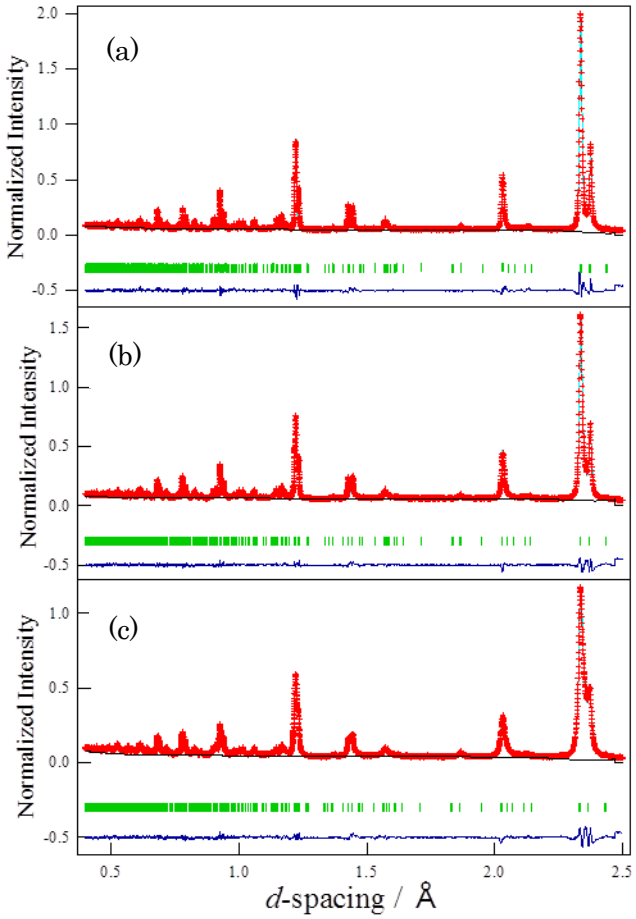

Fig. 1 Rietveld refinement patterns of $0.5Li_2MnO_3$-$0.5LiMn_{5/12}Ni_{5/12}Co_{1/6}O_2$ materials for (a)untreated, (b) heat-treatment with 0.03 mol/g sucrose, and (c) heat-treatment with 0.05 mol/g sucrose. Plus marks show observed neutron diffraction intensities [iMATERIA] and a solid line represents calculated intensities. The vertical marks indicate positions of allowed Bragg reflections. The curve at the bottom is a difference between the observed and calculated intensities in the same scale.