| MLF Experimental Report | 提出日 Date of Report<br>2015/5/5 |
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| 課題番号 Project No.<br>2014B0139<br>実験課題名 Title of experiment<br>Effects of reducing heat treatments on local structures of $zLi_2MnO_3$-(1-z)$LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ as a cathode for the lithium ion battery<br>実験責任者名 Name of principal investigator<br>Yasushi Idemoto<br>所属 Affiliation<br>Tokyo University of Science | 装置責任者 Name of responsible person<br>Toshiya Otomo<br>装置名 Name of Instrument/（BL No.）<br>NOVA/BL21<br>実施日 Date of Experiment<br>2015/3/23 - 2015/3/24<br>2015/4/16 - 2015/4/17 |

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: $0.4Li_2MnO_3$-$0.6LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$
Physical form: 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**

We prepared $0.4Li_2MnO_3$-$0.6LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ by means of a co-precipitation method, and heat treated a part of the sample under a reducing condition. Phases of the samples were identified by powder X-ray diffraction measurements and then the lattice parameters were estimated from the diffraction patterns. Their metal compositions were evaluated by the inductively-coupled plasma analysis.

In order to investigate local structure, i.e. cation distribution in a transition-metal layer and a distortion around each metal, neutron total scattering patterns of the samples were measured by NOVA installed at J-PARC. Each powder with a weight of 0.5~1.0 g was loaded in a sample container, and then mounted to a sample holder. The measurements were performed at room temperature for 3~4 hours. Normalized structure factors, $S(Q)$, were obtained and then were converted to reduced pair distribution functions, $G(r)$. The $G(r)$ were analyzed by fittings using the PDFgui (PDFFIT) program.

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

**Results**

As for $0.4Li_2MnO_3$-$0.6LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$, we measured neutron $G(r)$ and synchrotron X-ray $G(r)$ with BL04B2 at SPring-8, and then performed fittings of these data simultaneously. In the analysis, an intimal atomic configuration was constructed by the density functional theory (DFT) calculation with a crystal structure refined by the Rietveld analysis. Figure 1 and 2 show the fitting patterns and the refined atomic configuration for the pristine sample, respectively. The analytical strategy enabled us to achieve good fittings (Fig. 1: $R_w$=6.10 %), and thus we could obtain a reasonable atomic configuration successfully (Fig. 2). From the refined structure, bond lengths of Mn-O, Ni-O and Co-O were estimated as 0.1945, 0.1993 and 0.1957 nm, respectively. Taking ionic radii into account, it was suggested that Mn and Co were tetravalent and trivalent, respectively, and a valence of Ni was between +2 and +3 in the sample. Such a result was consistent well with electronic density of states calculated on the basis of DFT.

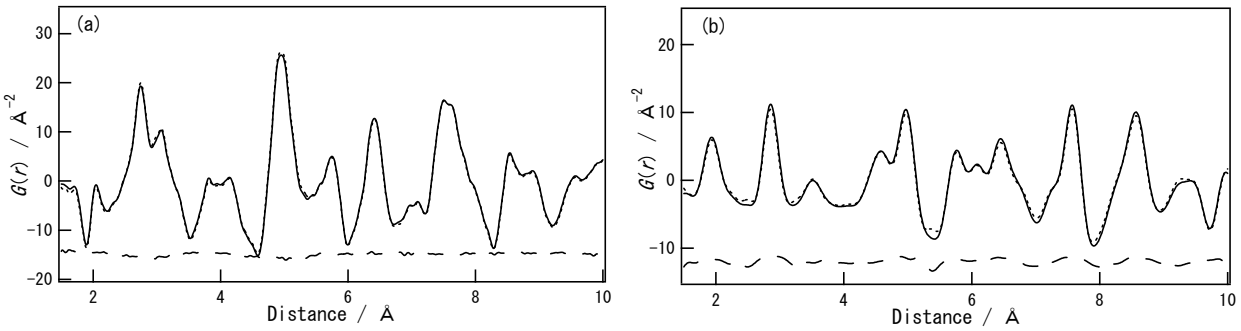


Fig. 1 Fitting patterns obtained by the pair distribution function (PDF) analysis for $0.4Li_2MnO_3$-$0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ using both (a) neutron and (b) synchrotron X-ray $G(r)$ simultaneously ($R_w$=6.10 %). Solid, dotted and broken lines represent experimentally-obtained pattern, calculated data and the residual, respectively.

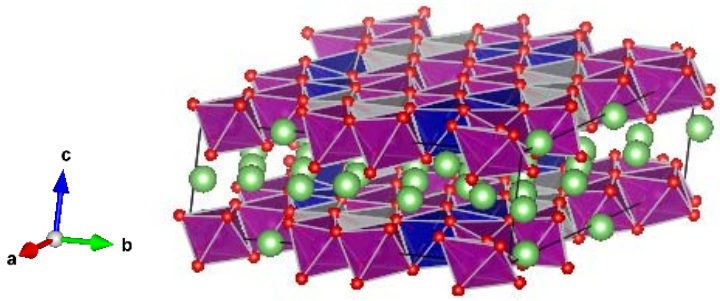


Fig. 2 Atomic configuration refined by the PDF analysis. Green and red spheres mean Li and O. Purple, gray and blue octahedrons represent Mn-$O_6$, Ni-$O_6$ and Co-$O_6$, respectively.