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J-PARC **MLF Experimental Report**	提出日 Date of Report 2022/9/24
課題番号 Project No. 2021PM2001	装置責任者 Name of responsible person Toru Ishigaki
実験課題名 Title of experiment Investigation of local structure of high capacity lithium-rich transition metal oxides during charge process. 実験責任者名 Name of principal investigator Yasushi Idemoto 所属 Affiliation Tokyo University of Science	装置名 Name of Instrument/（BL No.） iMATERIA/BL20 実施日 Date of Experiment 2022/1/26-29

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: $0.5Li_2MnO_3$-$0.5Li(Mn_{10/24}Ni_{7/24}Co_{7/24})O_2$

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 synthesized $0.5Li_2MnO_3$-$0.5Li(Mn_{10/24}Ni_{7/24}Co_{7/24})O_2$ by coprecipitation method. Phases of the samples were identified preliminarily by laboratorial X-ray diffraction measurements, and the metal compositions were evaluated by the inductively-coupled plasma atomic emission spectroscopy. The metal valences were also investigated by a redox titration. Cathode properties of the samples were investigated by a galvanostatic charge/discharge test.

0.5 g of powder samples of $0.5Li_2MnO_3$-$0.5Li(Mn_{10/24}Ni_{7/24}Co_{7/24})O_2$ were enclosed in V tubes and measured at iMATERIA with a single-frame mode. The obtained diffraction data were analyzed by the Rietveld method using Z-Rietveld software. The back scatter (BS) and special environment (SE) banks were mainly used for analysis. In the refinement, we also used synchrotron X-ray diffraction patterns measured at SPring-8 in addition to the neutron diffraction data.

Results

For the samples with $0.5Li_2MnO_3$-$0.5Li(Mn_{10/24}Ni_{7/24}Co_{7/24})O_2$ (LMNC), Rietveld refinements using neutron and synchrotron X-ray diffraction patterns were carried out. Figures 1 a) and b) show the refinement patterns neutron and synchrotron X-ray diffraction patterns. In the refinements, the cation ratios were fixed at the analytical values by the ICP-AES measurements. As can be seen in the figure, all the Bragg peaks could be attributed to the $C2/m$ space group. By refining the site occupancies, it was demonstrated that there was a cation mixing of Ni/Li on the $2c$ and $4h$ site. For this samples, charge/discharge cycle tests were performed. As a result of charge-discharge tests under various rate conditions, it was revealed that the 1C rate increased capacity the most and had the best cycle characteristics. Figures 1 (a) and (b) show the refinement patterns neutron and synchrotron X-ray diffraction patterns for LMNC after 10th cycle charge with 1C rate. Rietveld refinements shown in (c), (d) was analyzed using $C2/m$ and $R3/m$ and initial phase shown in Fig.1. From Fig.1 (c) and (d), The molar ratios of the phases $C2/m$, $R3/m$ and initial phase were found to be 0.33, 0.36, and 0.31, respectively. The results of the Rietveld analysis shown in Fig. 1 (c) and (d) indicate that the 1C rate has particularly small strain parameters for the octahedra on the $4g$ and $2c$ sites. The smaller strain parameters, especially at the 1C rate, are thought to be responsible for the improved cycle properties.
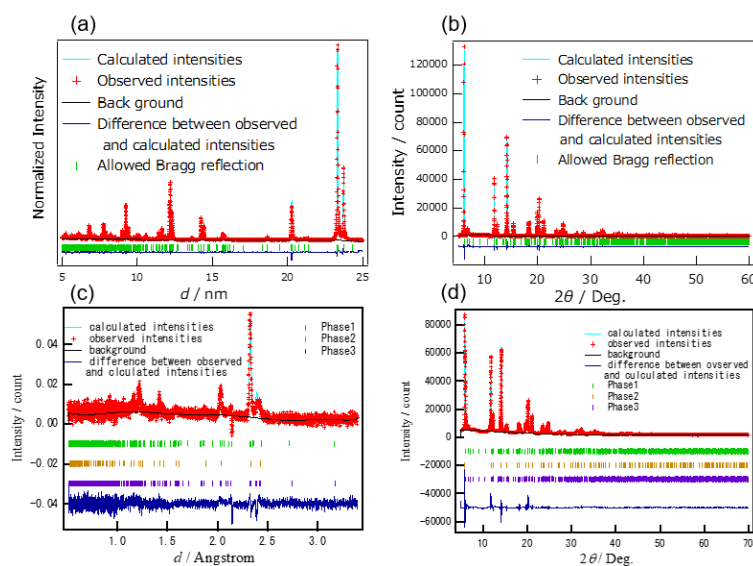

Fig.1 Rietveld refinement patterns of the pristine LMNC: (a) Neutron and (b) synchrotron X-ray diffraction and after 1C rate, 10th charge (c) Neutron and (d) synchrotron X-ray diffraction

Pair distribution function (PDF) fitting were performed for pristine LMNC using neutron total scattering data. Fig.2 (a) and (b) were shown the results of PDF fitting. In Fig.2 (a), Blue circle (G_{trunc}) indicates observed $G(r)$ from Neutron total scattering measurement, Red solid line (G_{calc}) indicates calculated $G(r)$. As can be seen in the figure, the fitting was carried out successfully. From the obtained local structure model after PDF fitting, we i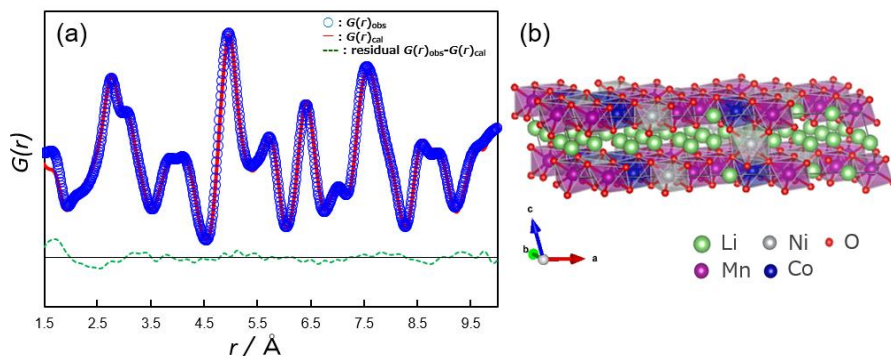nvestigated bond lengths and polyhedral distortions of MnO_6, NiO_6 and CoO_6 octahedra in detail. From the PDF analytical result, it was found that NiO_6 distortion was larger than MnO_6 and CoO_6 in pristine. Furthermore, it was suggested that the distortion of MnO_6 near Ni atom become large during charge and discharge process.

Fig.2 (a) $G(r)$ fitting patterns of pristine LMNC (Rw=12%) using Neutron total scattering data and (b) Local structure after PDF fitting.