MLF Experimental Report	提出日 Date of Report 2023/5/1
課題番号 Project No. 2022PM2004 実験課題名 Title of experiment Crystal structure analysis of spinel type $Mg(Ni,Co,Mn,Al)_2O_4$ as a cathode material for magnesium rechargeable battery. 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 2022/5/24-25 2022/06/22-23 2022/12/20-21 2023/03/02-03

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: $MgCo_{2-x-y-z}Ni_xMn_yAl_zO_4$ (x = 0.4, 0.5, 0.6; y = 0.4, 0.6, 0.8; z = 0, 0.1, 0.3)
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 $MgCo_{2-x-y-z}Ni_xMn_yAl_zO_4$ (x = 0.4, 0.5, 0.6; y = 0.4, 0.6, 0.8; z = 0, 0.1, 0.3) by reverse co-precipitation method. The samples phases 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 $MgCo_{2-x-y-z}Ni_xMn_yAl_zO_4$ with particularly good cathode properties are crushed were enclosed in V tubes and measured at neutron diffraction experiments using 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.

Results

Among $MgCo_{2-x-y-z}Ni_xMn_yAl_zO_4$ in x=0.2, y=1.0, z=0.3, especially with Al substitution showed higher capacity retention after repeated cycles in charge-discharge tests than x=0.25, y=0.25, z=0 without Al substitution. Rietveld refinements using neutron diffraction patterns were carried out for $MgCo_{2-x-y-z}Ni_xMn_yAl_zO_4$ (x=0.2, y=1.0, z=0.3). Figure 1 show the refinement patterns neutron diffraction patterns. In this refinements, the ratios of several metal atoms were fixed at the analytical values by the ICP-AES measurements. As can be seen in the figure, all the Bragg peaks could be assign to the *Fd*-3m space group. By refining the site occupancies, it was demonstrated that there was a cation mixing of Co and Mn atoms to the 8*a* site. As a result of Rietveld analysis using neutron diffraction measurements, the sample with x=0.2, y=1.0, z=0.3 shown in Fig.1 b) was better than the sample with x=0.25, y=0.25, z=0 shown in a). It was revealed that the occupancy of Mg on the *8a* site increased and the cation mixing of transition metals decreased. Thus, it is clear that the cycle properties were improved in the sample x=0.2, y=1.0, z=0.3 over the sample of x=0.25, y=0.25, z=0, especially during charge and discharge, because the transition metal occupancy of the *8a* site, which is involved in the diffusion of Mg, was reduced. Z-MEM was performed on the samples with the best cycle properties (x=0.2, y=1.0, z=0.3) using neutron diffraction to visualize the nuclear density at each site. As a result, the presence of atoms was confirmed at the *16c* site, which is not a normal spinel-type site. The *R*-factor was thus lowered as a result of the analysis using a model that included the *16c* site, and the results of the analysis are considered more accurate.

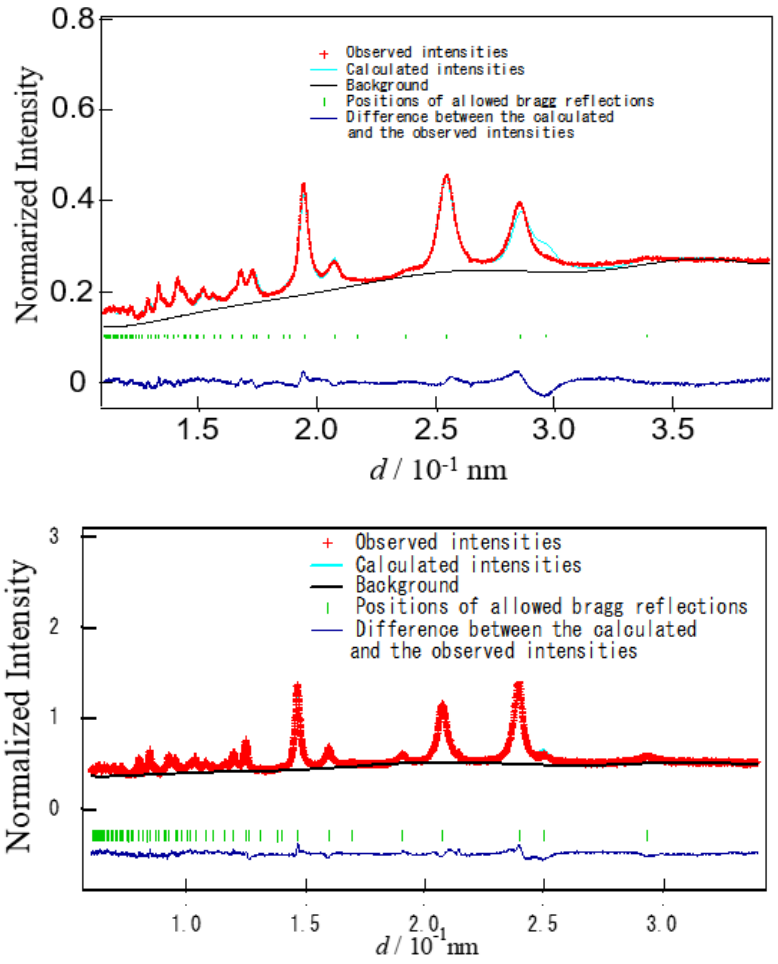

Fig. 1 Rietveld refinement patterns of $MgCo_{2-x-y-z}Ni_xMn_yAl_zO_4$ in a) x=0.25, y=0.25, z=0, and b) x=0.2, y=1.0, z=0.3 using neutron diffraction.