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 MLF Experimental Report	提出日 Date of Report 2018/3/22
課題番号 Project No. 2017A0039 実験課題名 Title of experiment Crystal Structure Refinement and Electrochemical Properties of the Spinel-Type New Cathode Material of $\text{MgCo}_{2-x}\text{Ni}_x\text{O}_4$ for Magnesium Secondary 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 2017/5/22 2017/10/30 - 2017/11/01

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: $\text{MgCo}_{2-x}\text{Ni}_x\text{O}_4$ ($x = 0.2, 0.3, 0.4, 0.6, 0.8, 1.0$) Physical form: Powder
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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 <p>MgCo_2O_4 and $\text{MgCo}_{2-x}\text{Ni}_x\text{O}_4$ ($x = 0.2, 0.3, 0.4, 0.6, 0.8, 1.0$) were synthesized by a reverse coprecipitation method and subsequently solid state reaction at 350 °C. The samples were identified by powder X-ray diffraction measurements, and their metal compositions were evaluated by Inductively Coupled Plasma (ICP) emission. In order to clarify how the substitution of Ni to Co affected the electrochemical properties after charge and discharge in detail, we performed charge and discharge tests with a 5 mA/g. First of all, we focused on the structure changes after the first discharge in this work, and thus prepared electrodes after the first discharge, for neutron diffraction measurements.</p> <p>Neutron diffraction patterns of the synthesized powders and these cathodes were measured by iMATERIA. Each cathode after the discharge was separated from an Al substrate, and then loaded into a V can. The measurements were carried out at room temperature with a SF mode, and data were collected by using all the banks. Crystal structures of the cathodes were refined by a Z-Rietveld program. For the pristine powders, we also performed the analysis using the Synchrotron X-ray diffraction with BL19B2 at SPirng-8.</p>
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2. 実験方法及び結果(つづき) Experimental method and results (continued)

Results

The synthesized $\text{MgCo}_{2-x}\text{Ni}_x\text{O}_4$ ($x = 0.2, 0.3, 0.4, 0.6, 0.8, 1.0$) were identified by XRD and ICP. The XRD patterns were characteristic of the broad peak derived from small particle size. Since the neutron diffraction patterns also weak diffraction peaks in spite of relatively long measured time, the Rietveld analyses were performed using the both data from neutron diffraction in SE bank and from synchrotron XRD at SPring-8. The analyzed profiles of $\text{MgCo}_{1.7}\text{Ni}_{0.3}\text{O}_4$ were shown in Fig. 1.

The site occupancies at $8a$ and $16d$ sites regarded as Mg site and transition metal (Co, Ni) site, respectively, were refined with the constraints on the mixing of Mg, Co and Ni. Although the tendency between the Ni compositions and the cation mixing contents was not obtained in the results of Rietveld analysis using only neutron diffraction data, the linear correlation was clearly recognized by using the neutron and the synchrotron X-ray diffraction data (Fig. 2). Since the neutron can distinguish Ni from Co and the synchrotron X-ray gives the strong diffraction peaks over wide d range, the collaborative use of neutron and X-ray is extremely effective for the structural refinement of the $\text{MgCo}_{2-x}\text{Ni}_x\text{O}_4$.

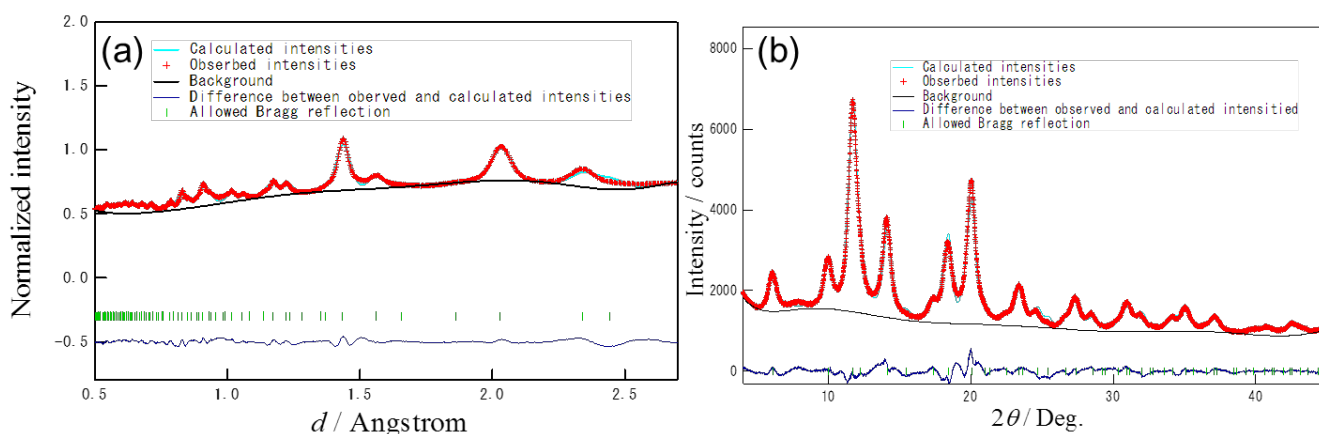


Fig. 1 Rietveld analysis for (a) neutron diffraction data and (b) synchrotron XRD data of $\text{MgCo}_{1.7}\text{Ni}_{0.3}\text{O}_4$. The reliability factors in R_{wp} were 1.87 % and 4.35 % for neutron diffraction and synchrotron XRD, respectively.

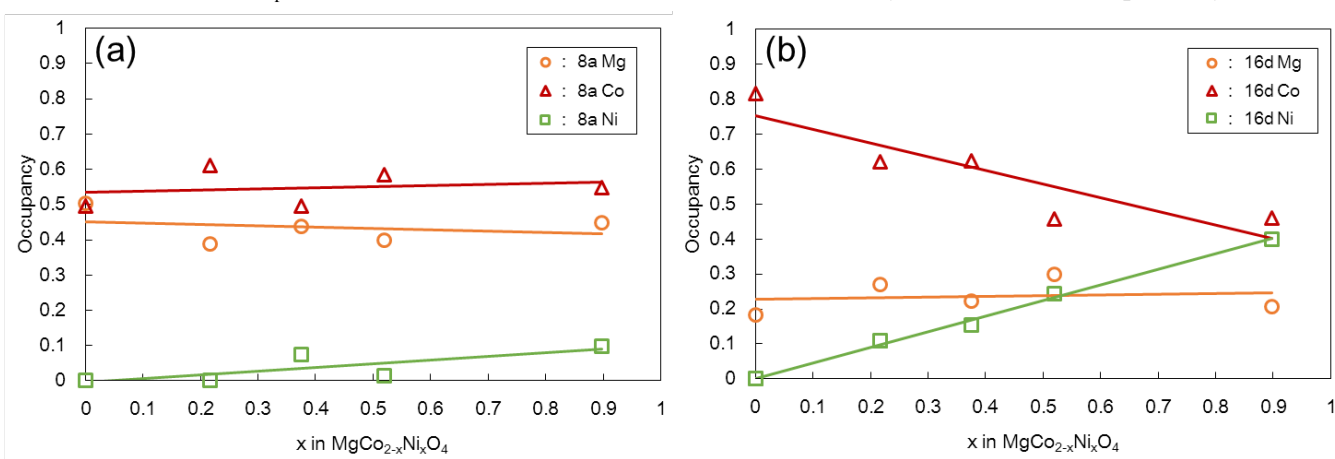


Fig. 2 Refined occupancies at (a) $8a$ site and (b) $16d$ site for the Ni compositions. The structure refinements were performed using the neutron and the synchrotron diffraction data.