 <b>MLF Experimental Report</b>	提出日 Date of Report 3rd October, 2013
課題番号 Project No. 2012A0116 実験課題名 Title of experiment Crystal Structure Analysis of Cu-containing Cathode Materials for Lithium-ion Batteries 実験責任者名 Name of principal investigator Yoshinori ARACHI 所属 Affiliation Kansai University	装置責任者 Name of responsible person Professor Dr. Toru Ishigaki 装置名 Name of Instrument/(BL No.) i-MATERIA/BL-20 実施日 Date of Experiment 25-26th October, 2012

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.

**Samples:**

The investigated samples were  $x = 0 - 0.1$  in  $\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$  and mainly for  $x = 0, 0.1, 0.2, 0.3$  and  $0.4$ .

**Synthesis of samples:**

The sample was prepared by combination of co-precipitation and solid state reaction. The co-precipitates were obtained from  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  by dropping 1 M LiOH solution. After heating dried co-precipitates at 873 K for 6 h in air Cu and Ni oxides were obtained. They were mixed with chemical grade  $\text{Li}_2\text{O}$  and pellets were made by the pressing under a pressure of 0.49 MPa and sintered at 1073 K for 24 h under  $\text{N}_2$  flow.

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**

Neutron diffraction data were collected at room temperature on the time-of-flight (TOF) neutron powder diffractometer installed in BL-20, i-MATERIA with pulsed spallation neutron source at Japan Photon Accelerator Research Complex (J-PARC). The specimen (ca. 1 g) was contained in a cylindrical vanadium cell having a radius 6 mm and height 60 mm. The structural parameters were refined by Rietveld analysis using the computer program *Z-Rietveld*.

**Experimental results**

All of peaks in the obtained neutron diffraction patterns for  $x = 0 - 0.4$  in  $\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$  could be indexed with a single orthorhombic lattice. On the other hand, the patterns for  $x > 0.4$  included considerable impurity phases such as NiO or Li-containing compounds. The compositional dependence of the calculated lattice parameters are summarized. A linear relationship is observed and a lattice parameter of  $a$  increased, those of  $b$  and  $c$  decreased contrastingly in the orthorhombic lattice according to Vegard's law.

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

The lattice parameters of  $b$  and  $c$  are related to those of length parallel to planer square  $\text{CuO}_4$  with the oxygen atoms at the corners and the copper atom in the center. The decreases of these lengths are attributed to substitution of smaller ionic radius of divalent Ni ion ( $0.55 \text{ \AA}$ ) for larger divalent Cu ion ( $3d_z^2 3d_{x^2-y^2}^1$ ) ( $0.57 \text{ \AA}$ ). The increase in lattice parameter of  $a$  arises from an electrostatic repulsion between  $3d_z^2$  of divalent Ni ion ( $3d_z^2 3d_{x^2-y^2}^0$ ) with Jahn-Teller effect. Therefore, we confirmed a solid solution of  $\text{Li}_2\text{CuO}_2$ - $\text{Li}_2\text{NiO}_2$  system between  $x = 0$  and  $0.4$  in  $\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$  except for  $x = 0.4$  included trace amount of NiO phase. Then, we carried out Rietveld refinements for all samples consisting of a single phase and a representative result for  $x = 0.4$  is shown in Figure 1. Refinement yields a good fitting by using the structure model, S.G.  $Immm$ . The refined lattice parameters for orthorhombic was  $a = 3.6838(0) \text{ \AA}$ ,  $b = 2.8244(0) \text{ \AA}$ ,  $c = 9.2314(1) \text{ \AA}$ . Based on the obtained occupation factor of Cu site, a substitution of divalent Ni ion to divalent Cu ion was confirmed.

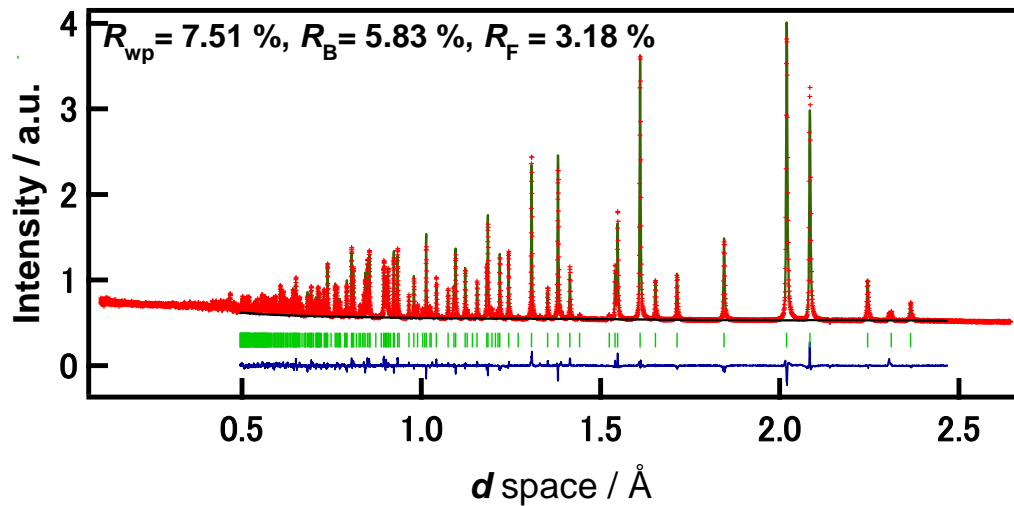


Fig.1 Rietveld refinement of neutron diffraction pattern for  $x = 0.4$  in  $\text{Li}_2\text{Cu}_{1-x}\text{Ni}_x\text{O}_2$ .