 MLF Experimental Report	提出日 Date of Report 30th July, 2011
課題番号 Project No. 2010B0083 実験課題名 Title of experiment Crystal structure analysis of Li_2CuO_2 Cathode Material 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 10-11th December, 2010 10-12th February, 2011

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:

Li_2CuO_2 and $\text{Li}_{2-x}\text{CuO}_2$. Chemical analysis showed that average valence state of Cu was 1.97 by iodometry and ICP analysis and chemical composition was nearly stoichiometric $\text{Li}_{2.02}\text{Cu}_{1.00}\text{O}_{2.00}$.

Synthesis of samples:

The conventional solid-state reaction was used. Starting materials were chemical grade Li_2CO_3 and CuO . They were calcined at 1023 K for 24 h and sintered at 1073 K for 24 h in air. Samples for $\text{Li}_{2-x}\text{CuO}_2$ were prepared electrochemically using lithium cells with a coin-type configuration.

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

Fig. 1 shows the one of representative results of Rietveld analysis for neutron diffraction pattern of Li_2CuO_2 obtained from back surface bank at room temperature. The measurement time was for 35 minutes and the samples weight was 1.74 g. The intensity was sufficient for the following further analysis. Refinement yields a relatively good fitting by using the structure model, *S.G. Immm*. The obtained lattice parameters for orthorhombic were $a = 3.65423(11)\text{\AA}$, $b = 2.86078(9)\text{\AA}$ and $c = 9.38862(27)\text{\AA}$.

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

However, some additional peaks are clearly shown in the pattern and some of those correspond to CuO phase, which was not detected by X-ray diffraction in our laboratory. However, the magnetic property of the sample, Li_2CuO_2 confirmed that an anti-ferromagnetic behavior with Néel temperature, $T_N = 10$ K. It can therefore be presumed that here the stability is involved.

Then, analysis using a mixed model composed of Li_2CuO_2 and CuO are under investigation and for another samples including different Li content as well. With lithium-removing, LiCuO_2 phase appeared and the peaks due to CuO phase increased. At the present the Rietveld refinement doesn't progress satisfactory. The main reason is due to the structure model of CuO phase. However, this CuO phase is a key to understand the unique effect of CuO on the electrochemical activity. In this experiment, the main object is to clarify the crystal structure change of $\text{Li}_{2-x}\text{CuO}_2$ related to the electrochemical reaction, while focusing on changes in distribution of Li and oxygen. The further analysis should be needed.

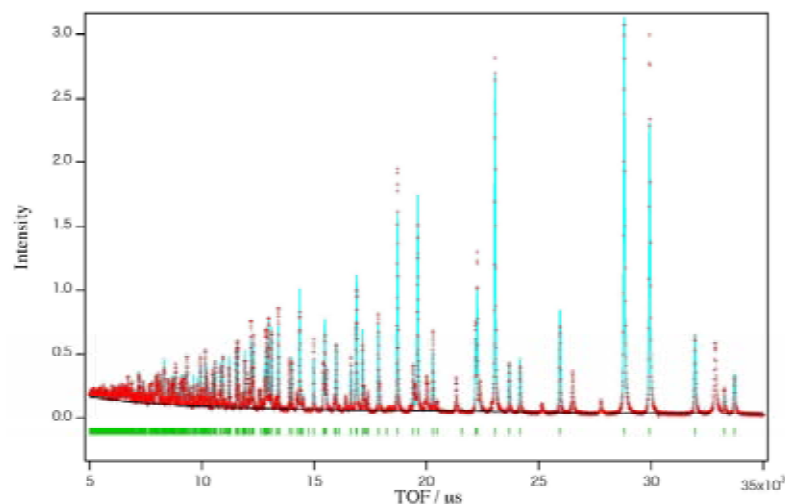


Fig.1 Observed and calculated diffraction profiles for Rietveld refinement using TOF neutron data.