MLF Experimental Report	提出日 Date of Report 2012.03.25
課題番号 Project No. 2012B0176 実験課題名 Title of experiment Relaxation analysis of electrode materials for Li-ion secondary battery 実験責任者名 Name of principal investigator Takeshi Yao 所属 Affiliation Kyoto University	装置責任者 Name of responsible person Toru Ishigaki 装置名 Name of Instrument/（BL No.） BL-20 実施日 Date of Experiment 2012.12.11 09:00 ~ 2012.12.12 09:00

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.

- Name of sample : Lithium titanate
- Chemical formula : $Li_{4/3+x}Ti_{5/3}O_4$ (x=0 and 0.5)

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.

$Li_{4/3}Ti_{5/3}O_4$ with median diameter of 20.5 μm (LT-017, Ishihara Sangyo, Ltd, Japan) was used for this experiment. Lithium was electrochemically inserted into the $Li_{4/3}Ti_{5/3}O_4$ at 25 ℃ using an Ar-sealed three-electrode glass beaker cell. For working electrode, the $Li_{4/3}Ti_{5/3}O_4$ powder was mixed with AB (Acetylene Black, Surface area: 133m^2g^{-1}, Denkikagaku Kogyo Corp., Ltd) as a supplemental conductor and PTFE powder as an adhesive agent in a weight ratio of 0.7:0.3:0.05. The mixture was ground, spread and pressed onto a nickel mesh as a current collector. Lithium metal was used for the counter and reference electrode. 1M ethylene carbonate and a 1,2-dimethoxyethane solution (1:1, v/v) of lithium perchlorate ($LiClO_4$ EC/DME, Kishida chemical Corp., Ltd) was used for the electrolyte. The electrode fabrication and the cell assembly were carried out under argon gas system. The samples were discharged from the natural potential of approximately 3 V (vs. Li/Li^+) at a current density of 1C. The amount of Li estimated by integrating the current was x= 0.50 in terms of $Li_{4/3+x}Ti_{5/3}O_4$. After the required electrochemical conditions were attained, the circuits were opened immediately. And the working electrode was detached from the glass beaker cell and set in a vanadium cell in an argon gas system and this was used for neutron diffraction test.

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

Due to limitation of measuring time, we made samples with several relaxation time (10, 25, and 50 hours) after the lithium insertion. Neutron powder diffraction was measured at room temperature for all specimens. The obtained neutron diffraction patterns were analyzed by the Rietveld method by using N-RIEVEC program coded by T. Yao. Two phases Rietveld analysis was conducted based on $Li_{4/3}Ti_{5/3}O_4$ and $Li_{7/3}Ti_{5/3}O_4$. The crystal structure of both phases was represented by the space group *Fd-3m*. The peaks derived from the nickel collector observed in the patterns were evaluated as background and excluded from the analysis (Figure 1).

Figure 1 shows one example of the fitting results of the sample after the lithium insertion followed by the relaxation time of 10 h. Using the refined scale factors and lattice parameters of two phases, relative mole fraction changes in the process of relaxation were calculated with the following equation [1].

$$M_p = S_p(ZV)_p / \sum_{i=1}^{n} S_i(ZV)_i$$

where M_P, S, Z, and V are the relative mole fraction of phase p in a mixture of n phases, the Rietveld scale factor, the number of formula units per unit cell and the unit cell volume, respectively.

After lithium insertion, the mole fraction of $Li_{4/3}Ti_{5/3}O_4$ phase increased and that of $Li_{7/3}Ti_{5/3}O_4$ phase decreased as the increase of the relaxation time. At the Li insertion process, it is considered that $Li_{7/3}Ti_{5/3}O_4$ phase including lithium defects favorable lithium diffusion formed during the lithium insertion process. On the relaxation process after the lithium insertion, it is considered that the defective $Li_{7/3}Ti_{5/3}O_4$ phase separated to $Li_{7/3}Ti_{5/3}O_4$ phase without lithium defects and $Li_{4/3}Ti_{5/3}O_4$ phase.

By the neutron diffraction tests for the various lithium insertion samples as a function of lithium insertion rate and amount, we would like to investigate more about the relaxation behaviors of $Li_{4/3}Ti_{5/3}O_4$ electrode for the development of the electrode material.

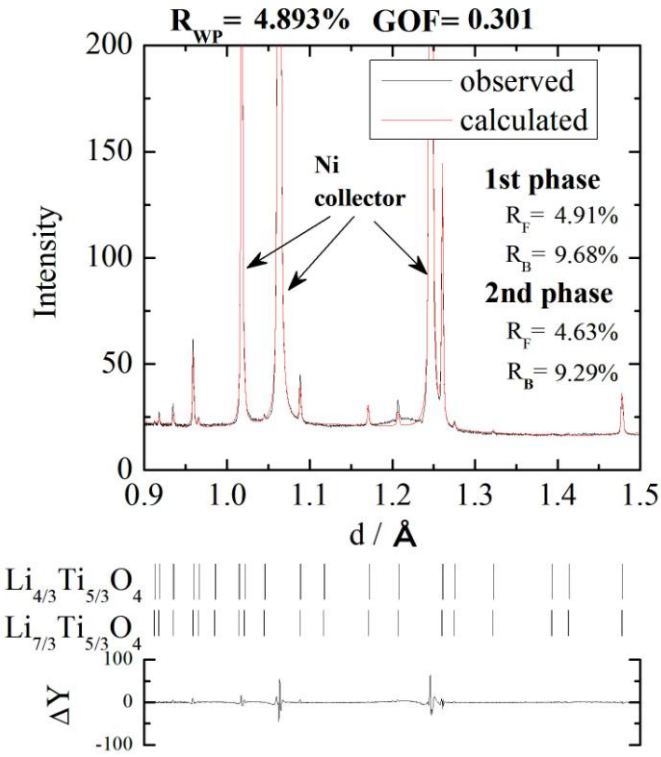

Fig. 1 Result of the Rietveld analysis : Relaxation time of 10 h.

Reference

[1] Roderick J. Hill, in *The Rietveld Method*, R. A. Young, Editor, p 95, Oxford Univ. Press, Oxford (1995).