MLF Experimental Report	提出日 Date of Report 2011.1.24
課題番号 Project No. 2010A0083 実験課題名 Title of experiment Neutron Powder Diffraction Studies of Lithium Battery Electrode Materials with Tunnel Structure 実験責任者名 Name of principal investigator Norihito KIJIMA 所属 Affiliation National Institute of Advanced Industrial Science and Technology	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/（BL No.） Super HRPD (BL08) 実施日 Date of Experiment 2010.11.24 ～ 2010.11.25

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.

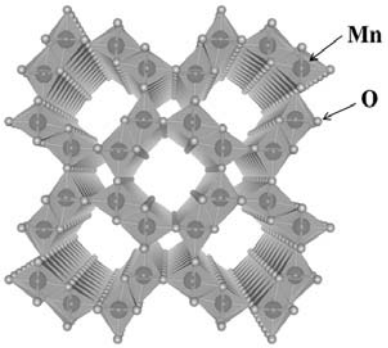
Sample

Name of sample: α-MnO_2 (hollandite-type manganese dioxide)

Chemical formula: $MnO_2 \cdot nH_2O$

Physical form: powder specimen

*Hollandite-type structure is shown in right figure.



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.

Sample preparation

An α-MnO_2 specimen was prepared by the precipitation method using ozone oxidation. Fourteen grams of $MnSO_4 \cdot 5H_2O$ was dissolved in 600 cm^3 of a 3 mol/dm^3 solution of H_2SO_4; subsequently, this solution was heated up to 80 ºC while being stirred at 200 rpm. The solution was bubbled by a mixture of O_3 and O_2. After bubbling the gas for 3 h; the product was filtered off and washed with deionized water until washings were practically free from H_2SO_4. It was then freeze-dried in an evacuated bottle for about 10 h using a freeze-dryer. Scanning electron microscopy and transmission electron microscopy images of the α-MnO_2 specimen showed that surfaces of particles were covered almost uniformly with needle crystals which were elongated parallel to the *c*-axis, i.e., along the direction of the tunnel.

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

Measurements and Structure Analysis

Neutron diffraction data were taken on a high-resolution time-on-flight (TOF) neutron powder diffractometer Super HRPD at the J-PARC (Japan Proton Accelerator Research Complex). The sample was contained in a cylindrical vanadium can with inner diameter of 10 mm, and the intensity data were collected at room temperature.

Intensity data used for the refinement covered a wide Q range corresponding to lattice-plane spacings between 0.25 and 3.8 Å. The diffraction data were analyzed by the Rietveld method with a computer program package, Jana2006. The refinement of the structure was carried out in the space group $I4/m$ with Mn, O1, and O2 on the 8h sites (x,y,0) and O3 on the 2b site (0,0,1/2). The coherent scattering lengths used were -3.730 fm for Mn and 5.803 fm for O.

Results

The diffraction data showed the fairly high background, which is due to the marked incoherent scattering from H atoms in the tunnel space. Some reflections exhibited anisotropic profile broadening, which stems from stacking faults along the needle axis. No systematic relations could be found among diffraction indices, hkl; and full-widths at half-maximum.

Figure 1 shows the preliminary result of the Rietveld-refinement patterns for the TOF neutron powder diffraction data of the α-MnO_2 specimen. The resulting R factors reached R_{wp} = 4.90 %, R_p = 3.75 %, R_B = 7.12 %, and R_F = 3.91 %. The lattice constants are a = 9.84942(13) Å and c = 2.85252(3) Å. In this preliminary refinement, no H atoms were considered. Detailed structure analyses are in progress and these results will be published elsewhere.

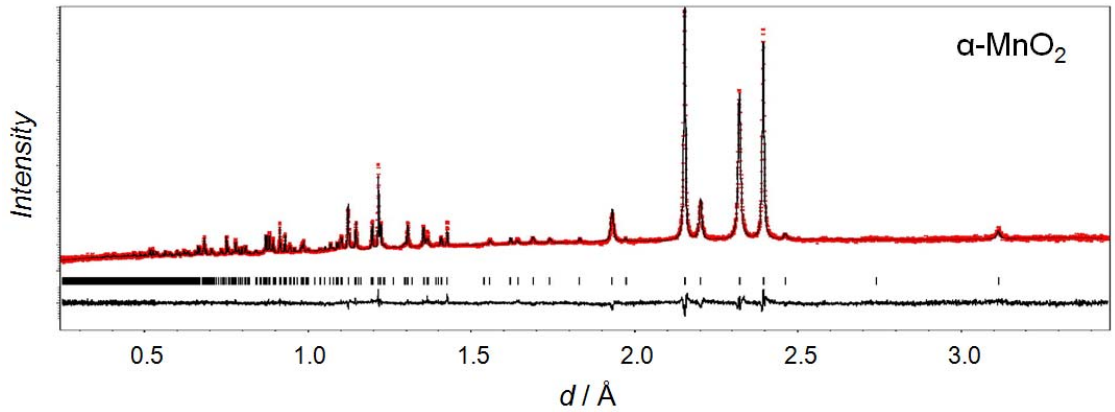


Fig. 1 Rietveld-refinement patterns for the TOF neutron powder diffraction data of the α-MnO_2 specimen at room temperature. Observed diffraction intensities are represented by multiple (×) marks, and the calculated pattern by the solid line. Differences between the observed and calculated intensities are given near the bottom. Short vertical marks below the observed and calculated patterns indicate the positions of allowed Bragg reflections.