MLF Experimental Report	提出日 Date of Report 2010/4/22
課題番号 Project No. 2009A0030 実験課題名 Title of experiment Crystal structure analysis of Li_2MnO_3 reduced by metal hydride – New cathode material for lithium batteries 実験責任者名 Name of principal investigator Ryoji Kanno 所属 Affiliation Tokyo Institute of Technology	装置責任者 Name of responsible person Touru Ishigaki 装置名 Name of Instrument/(BL No.) iMateria (BL No.20) 実施日 Date of Experiment 2009/11/12 – 11/13

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.

Crystal structures of Manganese compounds for lithium battery electrodes were investigated.

1. Lithium manganese oxide: Li_2MnO_{3-d}, with a space group of $C2/m$, which structure is the same as that of R3m layered rocksalt structures. The lattice constants are a=4.939 Å, b=8.540 Å, c=9.619 Å, β=99.98˚. Powder.
2. Lithium manganese phosphate hydrade: $LiMnPO_4OH$, with a space group of P-1. The lattice constants are a = 5.125 Å, b = 5.453 Å, c = 7.111 Å, α= 106.2˚, β= 108.1˚, γ= 101.2˚. Powder.

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 of Li_2MnO_{3-d} and $LiMnPO_4(OH)$ were taken at room temperature on a time-of-flight (TOF) neutron powder diffractometer at iMATERIA (BL20) using the BS (Back Scattering) bank. The specimen of ca. 1.5 cc is contained in a cylindrical vanadium cell of dimensious 10 mm inradius, 20 mm in height. These data were analyzed by Rietveld method using the program Z-Rietveld.

Results: Fig. 1 shows Rietveld analysis results using neutron diffraction data of Li_2MnO_{3-d} synthesized by a reducing method using CaH_2 with a mild condition. The structure was refined using a structure model with the $C2/m$ space group. The detailed structure is under analyzing to clarify (i) position of the oxygen vacancy, (ii) extent of vacancy ordering, (iii) extent of disordering at the lithium layer and (iv) stacking disorder perpendicular to the two-dimensional lithium layer. Fig. 2 shows Rietveld analysis results using neutron diffraction data of $LiMnPO_4OH$. The structure was refined using a structural model of $[Li]_{4i}[Mn1]_{2a}[Mn2]_{2b}[P]_{4i}[O]_{4i}$

with the space group *P*-1. Bond valence sums at different oxygen sites were calculated out of consideration of the proton site. Bond valence sum at the O1 to O4 sites were -2.0, while that of the O5 site was -1.3, indicating an electron donation of proton to oxygen. From the results, we can determine the position of protons in the lattice (4*i* site). Based on these data, we will investigate effects of protons on the structural and electrochemical properties of $LiMnPO_4(OH)$ to clarify the direction of materials design for extremely high capacity material.

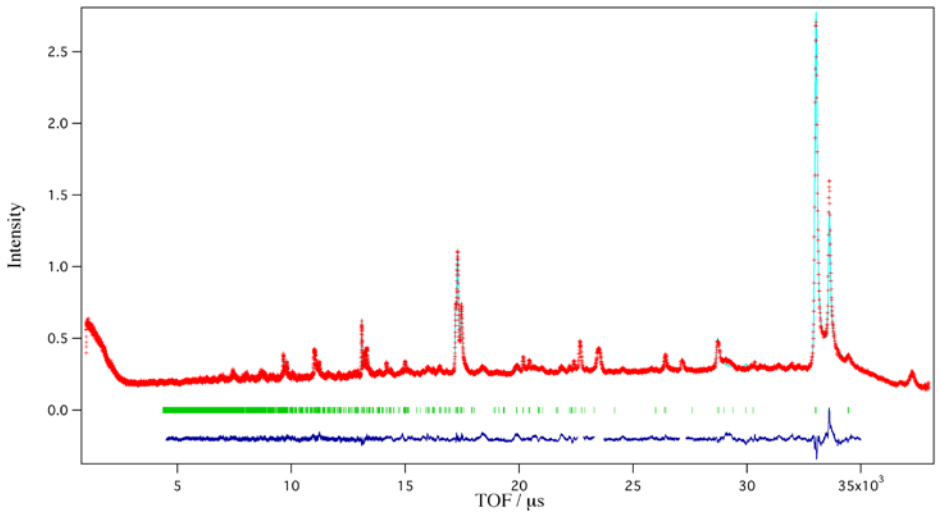

Fig. 1 Observed (plus marks), calculated (solid line), and difference (bottom) patterns for the Rietveld refinement from neutron diffraction data of Li_2MnO_{3-d}. The short vertical lines below the profiles mark the peak positions of all the possible Bragg reflections. Unit cell: *C*2/*m*, *a*=4.9343(10), *b*=8.5434(14), *c*=5.0262(8), *β*=109.279(13), R_{wp}=0.040, R_p=0.031, R_e=0.019, R_B=0.078, R_F=0.203, *S*=2.01.

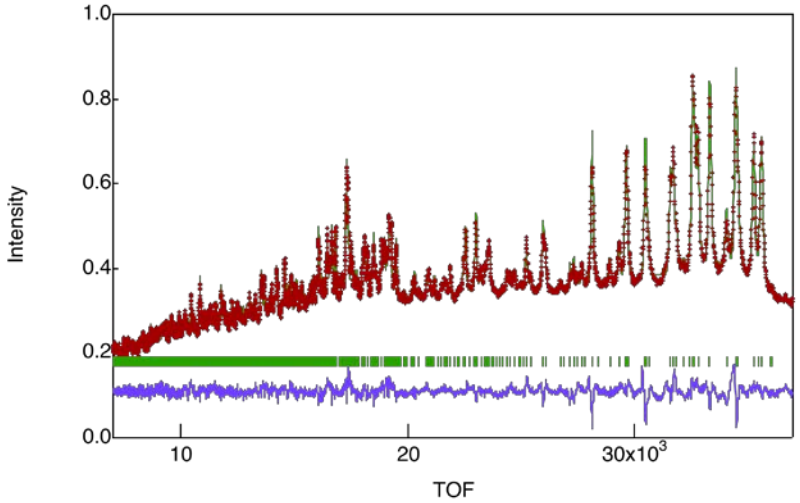

Fig. 2 Observed (plus marks), calculated (solid line), and difference (bottom) patterns for the Rietveld refinement from neutron diffraction data of $LiMnPO_4OH$. The short vertical lines below the profiles mark the peak positions of all the possible Bragg reflections. Unit cell: *P-1* (2); *a* = 5.1253(11) Å, *b* = 5.4539(11) Å, *c* = 7.1115(2) Å, *a*= 106.287(2)˚, *b*= 108.1507(8)˚, *g*= 101.282 (11)˚, *V* = 172.3(2) Å ^{3}; R_{wp} = 2.82, R_p = 2.21, R_e = 1.76, R_I = 8.71, R_F = 5.58, $S = R_{wp}/R_e$ = 1.59.