


(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

 <b>MLF Experimental Report</b>	提出日 Date of Report May 31, 2014
課題番号 Project No. 2013B0197 実験課題名 Title of experiment      Crystal structure analysis of pure $\text{Li}_2\text{MnO}_3$ cathode materials with high cyclic performance 実験責任者名 Name of principal investigator Takashi Mochiku 所属 Affiliation National Institute for Materials Science	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 March 22 to 23, 2014

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.

We measured the following samples:

- (1)  $\text{Li}_2\text{MnO}_3$  cathode material before charge-discharge cycles,
- (2)  $\text{Li}_2\text{MnO}_3$  cathode material after 50 charge-discharge cycles, and
- (3) mixture of carbon black and PTFE.

The sample (2) included carbon black and PTFE to form the cathode because they are picked up from the battery cell after the charge-discharge cycles.

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.

The TOF neutron powder diffraction data of all samples were collected at room temperature using the automatic sample changer, and the data of the samples (1) and (2) were analyzed by the Rietveld refinement program Z-Rietveld. The data of the sample (2) were analyzed after the subtraction of the data of the sample (3).

The structural model is based on the  $\text{Li}_2\text{MnO}_3$ -type structure (monoclinic, space group  $C2/m$ , see Fig. 1), which can be derived by stacking  $\text{LiMn}_2\text{O}_6$  and  $\text{Li}_3$  slabs alternately along the  $c$ -axis.

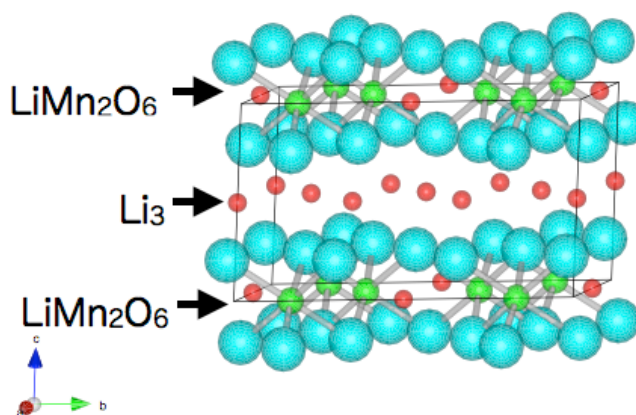


Fig. 1. Crystal structure of  $\text{Li}_2\text{MnO}_3$ .

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

Since the samples included tiny impurity phase of  $\text{LiMn}_2\text{O}_4$  spinel-type compound, the data were analyzed using two phases model ( $\text{Li}_2\text{MnO}_3$ -type and  $\text{LiMn}_2\text{O}_4$ -type).

Fig. 2 illustrated observed, calculated and difference patterns of the sample (2) plotted against the  $d$ -spacing.

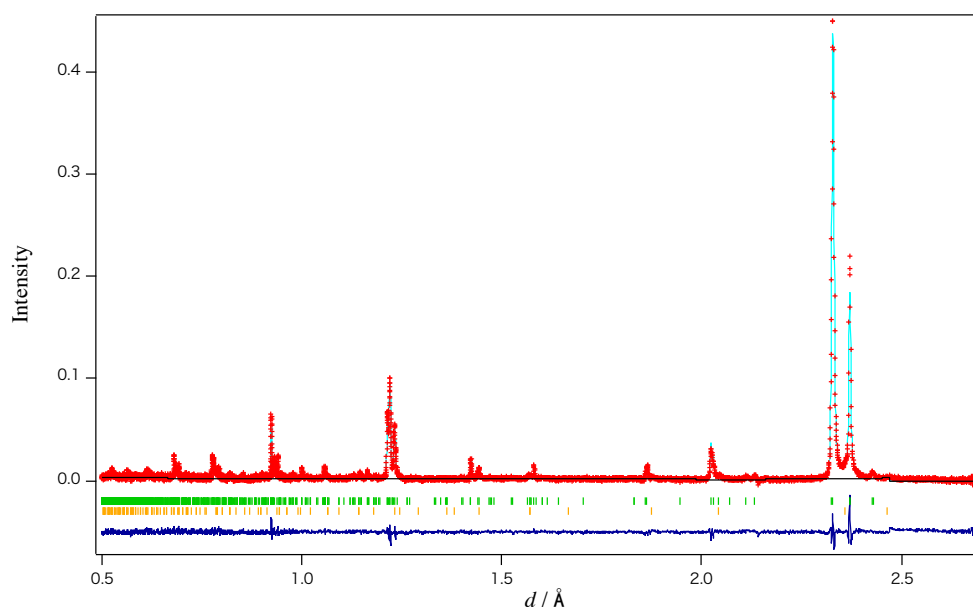


Fig. 2. Rietveld refinement pattern for  $\text{Li}_2\text{MnO}_3$  cathode material after 50 charge-discharge cycles (the sample (2)).

The above structural model is supported by the good fit between the observed and calculated patterns coupled with the low  $R$  factors ( $R_{\text{wp}} = 11.77\%$ ,  $\chi^2 = 1.79$ ). The final results of the refinements indicate that the sample (2) has atomic disorder of Li and Mn, and oxygen deficiency on the  $\text{LiMn}_2\text{O}_6$  slab, compared with the sample (1). Those structural change cause high cyclic performance of  $\text{Li}_2\text{MnO}_3$  because of activating manganese redox reaction ( $\text{Mn}^{3+}/\text{Mn}^{4+}$ ).