

Crystal structure analysis of $\text{Li}_2\text{MP}_2\text{O}_7$ ($M = \text{Fe}, \text{Mn}$)

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1 Introduction

Cathode materials of lithium-ion battery (LIB) have many issues of safety and performance improvements. Development of new cathode materials can solve such stagnant of LIB performance. Lithium transition-metal phosphates are the most prominent material group for cathode active materials for lithium ion battery. Recently Adam *et al.* discovered a new material $\text{Li}_2\text{MnP}_2\text{O}_7$, which have a completely new crystal structure[1]. This class of material $\text{Li}_2\text{MP}_2\text{O}_7$ is expected for the cathode material as its ideal Li/M ratio of 2, which means availability of larger battery capacity. Following the Adam's work, we started to synthesize $\text{Li}_2\text{FeP}_2\text{O}_7$ and tried to characterize the structure and battery performances.

2 Experiment

Powder XRD experiment were performed by using a two-axis diffractometer with multiple-detector system installed at the beam-line 4B2 of Photon Factory (PF), High Energy Accelerator Organization (KEK) in Tsukuba[2]. The diffraction patterns were collected in asymmetric reflection geometry where the incident angle was fixed at 3° . The recorded pattern of each detectors were merged by an Igor Pro macro system developed by Ida[3]. Rietveld refinement of the powder diffraction patterns were conducted by TOPAS-Academic (Ver. 4.1).

3 Results and Discussion

Fig.1 shows Rietveld refinement patterns of $\text{Li}_2\text{MnP}_2\text{O}_7$ and $\text{Li}_2\text{FeP}_2\text{O}_7$. The both patterns were successfully refined with $P2_1/c$ space group and a structural model, which is based on Adam's model[1]. The good ness of fit (S) and reliability indices were converged to reasonable values (see Fig.1) by including a small amount of impurities ($< 2\text{wt}\%$ in total). These structures are essentially isomorphic, while the peak intensity ratios are significantly different. Origin of such differences are originated from the significant disordering of cation position. Detailed Rietveld and Fourier analysis suggests that an anti-site type defect between a specific crystallographic site of Li and Fe is the most reasonable model for describing the cation disorder. Surprisingly the crystal structure of $\text{Li}_2\text{FeP}_2\text{O}_7$ have never been reported. Thus our report was the first synthesis and structure determination of $\text{Li}_2\text{FeP}_2\text{O}_7$ [4].

Recently we found that the $\text{Li}_2\text{MnP}_2\text{O}_7$ is electrochemically active, although the previous studies showed negligible performance at the conventional voltage

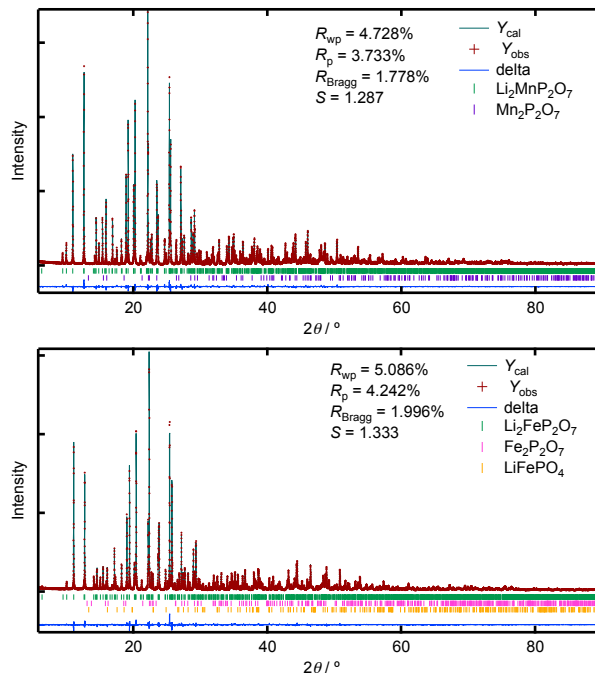


Fig. 1: Rietveld refinement patterns of $\text{Li}_2\text{MnP}_2\text{O}_7$ (top) and $\text{Li}_2\text{FeP}_2\text{O}_7$ (bottom).

range of 2.0 - 4.5 V. The average redox potential was 4.45 V vs. Li, which is the highest value among manganese phosphate materials. This activity was achieved by careful optimization of the material. Details of electrochemical data and structural analysis will be reported elsewhere[5].

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