Electronic Structure of the Cathode Material Li$_2$Fe$_{1-x}$Mn$_x$PO$_4$ for Lithium-Ion Battery Studied by Resonant Photoemission Spectroscopy

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1 Introduction
A pyrophosphate ion compound Li$_x$Fe$_{1-x}$PO$_4$ is a newly designed polyanionic-cathode material for a Li-ion battery [1]. Compared to olivine formula LiFePO$_4$, Li$_x$Fe$_{1-x}$PO$_4$ has some superior characteristics such as reversible electrochemical activity without any particle-downsizing/carbon coating, a two-dimensional channel for Li-diffusion, and the potential of a 2-electron redox reaction. In addition, with partial substitution of Mn for Fe sites in Li$_x$Fe$_{1-x}$PO$_4$, the Fe$^{2+}$/Fe$^{3+}$ redox potential upshifts to 4 V [2]. In order to clarify changes in the electronic structures, especially Fe 3d partial density of states (DOS), of Li$_x$Fe$_{1-x}$Mn$_x$PO$_4$ with Mn substitution, we have performed resonant photoemission spectroscopy (PES) experiments for Li$_x$Fe$_{1-x}$Mn$_x$PO$_4$.

2 Experiment
Li$_x$Fe$_{1-x}$Mn$_x$PO$_4$ ($x = 0, 0.25, 0.5, 0.75$) powder samples were synthesized by conventional solid-state reactions. Starting materials and carbon additives were mixed and sintered at 600°C for 12 h under Ar gas flow.

Before PES measurements, electrochemical charge/discharge processes were carried out. The working electrodes were formulated by mixing of Li$_x$Fe$_{1-x}$Mn$_x$PO$_4$, carbon black and polyvinylidene fluoride binder. After three charge/discharge cycles, the cells were completely discharged for full lithiation.

Spectroscopic experiments were performed at BL-2C. We transferred the electrodes to a UHV load lock chamber of PES equipment using an Ar-filled transfer chamber without any exposure to moisture air.

3 Results and Discussion
Figure 1 shows Fe 2p - 3d resonant photoemission spectra on Li$_x$Fe$_{1-x}$Mn$_x$PO$_4$ ($x = 0$ and 0.5). Fe 3d partial DOS on Li$_x$Fe$_{1-x}$Mn$_x$PO$_4$ obtained by RPES spectra are similar to those on olivine formula LiFePO$_4$ [3] and LiFe$_{x}$Mn$_{1-x}$PO$_4$ [4]. We found that a sharp peak around 2 eV derived from Fe 3d down spin states shifts to the higher binding energy with Mn substitution. This suggests that the shift of Fe 3d down spin states accompanied with Mn substitution is the origin of high redox voltage in Li$_x$Fe$_{1-x}$Mn$_x$PO$_4$.

![Fig. 1: Fe 2p - 3d resonant photoemission spectra on Li$_x$Fe$_{1-x}$Mn$_x$PO$_4$.](image)

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