Photon Factory Activity Report 2012 #30 (2013) **B**

BL-2C/2011S2-003

Electronic Structure of the Cathode Material $Li_2Fe_{1-x}Mn_xP_2O_7$ for Lithium-Ion Battery Studied by Resonant Photoemission Spectroscopy

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1 Introduction

A pyrophosphate ion compound $Li_2FeP_2O_7$ is a newly designed polyanionic-cathode material for a Li-ion battery [1]. Compared to olivine fomula $LiFePO_4$, $Li_2FeP_2O_7$ 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 $Li_2FeP_2O_7$ the Fe^{3+}/Fe^{2+} redox potential upshifts to 4 V [2]. In order to clarify changes in the electronic structures, especially Fe 3*d* partial density of states (DOS), of $Li_2Fe_{1-x}Mn_xP_2O_7$ with Mn substitution, we have performed resonant photoemission spectroscopy (PES) experiments for $Li_2Fe_{1-x}Mn_xP_2O_7$.

2 Experiment

$Li_2Fe_{1-x}Mn_xP_2O_7$ (x = 0, 0.25, 0.5, 0.75) powder samples were sytnesized 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 $Li_2Fe_{1-x}Mn_xP_2O_7$, carbon black and polyvinylidene fluoride binder. After three charge/discharge cycles, the cells were completely discharges 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 2*p* - 3*d* resonant PES spectra on $Li_2Fe_{1-x}Mn_xP_2O_7$ (x = 0 and 0.5). Fe 3*d* partial DOS on $Li_2Fe_{1-x}Mn_xP_2O_7$ obtained by RPES spectra are similar to those on olivine fomula $LiFePO_4$ [3] and $LiFe_{0.5}Mn_{0.5}PO_4$ [4]. We found that a sharp peak around 2 eV derived from Fe 3*d* down spin states shifts to the higher binding energy with Mn substitution. This suggests that the shift of Fe 3*d* down spin states accompanied with Mn substitution is the origin of high redox voltage in $Li_2Fe_{1-x}Mn_xP_2O_7$.

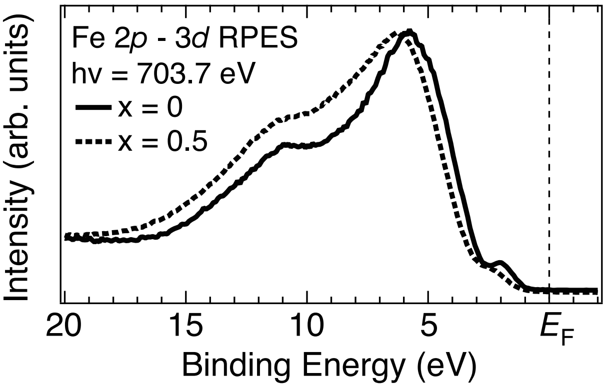

Fig. 1: Fe 2*p* - 3*d* resonant photoemission spectra on $Li_2Fe_{1-x}Mn_xP_2O_7$.

Acknowledgement (option)

This research is supported by the Japan Society for the Promotion of Science (JSPS) through its "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)."

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