

Electronic Structure of the Cathode Material $\text{Li}_x\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ for Lithium-Ion Battery analyzed by Resonant Photoemission Spectroscopy

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1 Introduction

Olivine-type compounds LiMPO_4 [$M = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$] is one of the most promising candidates for cathode materials of the lithium-ion battery, because of its prominent properties such as low cost, high level of safety and huge power generation. Especially, the solid solution $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ has attracted much attention due to relative high potential of $\text{Mn}^{3+} / \text{Mn}^{2+}$ redox couple at 4.1 V vs. Li / Li^+ , which generates the higher energy density. Although the change in the valence states of the transition metals accompanied with the delithiation has been reported so far, the detailed electronic structure of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ has not been understood yet. Therefore, in this work, we focus on revealing experimentally the change in the electronic structure of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$, especially in the transition metal $3d$ states through the charge process by resonant photoemission spectroscopy (PES).

2 Experimental

Pristine $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ powders were synthesized by solid state reactions. Starting materials and 10 wt% carbon were mixed and sintered at 600 °C for 6 h under Ar gas flow. The characterization was performed by X-ray diffraction measurements. In order to obtain $\text{Li}_x\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ ($x = 0, 0.5, 1$), electrochemical delithiation process was carried out.

To investigate the electronic structure of Fe and Mn $3d$ states in $\text{Li}_x\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$, we have performed Fe and Mn L -edge X-ray absorption spectroscopy (XAS) and the resonant photoemission spectroscopy (PES) at BL-2C of Photon Factory. In order to avoid moisture air exposure, we transferred the samples to a load lock chamber using a grove bag filled with dry- N_2 gas.

3 Results and Discussion

Figure 1 (a) shows Fe $2p - 3d$ resonant PES spectra of $\text{Li}_x\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ measured at the photon energy of Fe $2p - 3d$ absorption edges corresponding to the Fe^{2+} (R1) and

Fe^{3+} (R2) states. The maximum intensity in the resonant PES spectra was observed at the excitation energy R1 for $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$, whereas that was observed at the excitation energy R2 for $\text{Li}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ and $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$. Figure 1 (b) shows the resonant PES spectra of LiFePO_4 and $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ measured at the excitation energy of R1, whereas Fig. 3 (c) shows those of FePO_4 and $\text{Li}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ measured at the excitation energy of R2. Comparing both resonant PES spectra at each excitation energy, we can find that both spectral-line shapes are almost identical, suggesting that the partial substitution of Fe by Mn does not influence the Fe $3d$ states significantly, which may be due to the strong localization of the Fe $3d$ states.

Acknowledgments

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)."

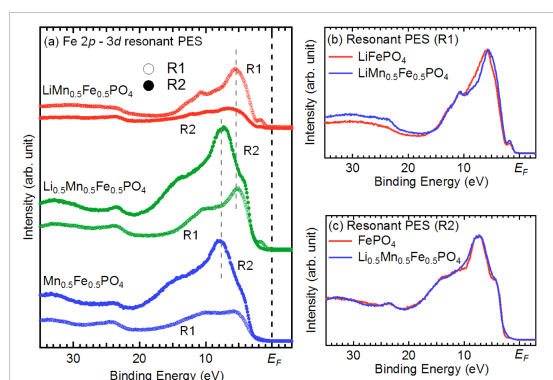


Figure 1. (a) Fe $2p - 3d$ resonant PES spectra of $\text{Li}_x\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$. (b), (c) Comparison of Fe $2p - 3d$ resonant PES spectra between $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ and LiFePO_4 measured at R1, and $\text{Li}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ and FePO_4 measured at R2, respectively.