

Electronic Structure of the Cathode Material Li_xFePO_4 for Lithium-Ion Battery analyzed by Resonant Photoemission Spectroscopy

Shodai KUROSUMI¹, Naoka NAGAMURA¹, Satoshi TOYODA^{1,2}, Koji HORIBA^{1,2,3}, Hiroshi KUMIGASHIRA^{1,3,4}, Masaharu OSHIMA^{1,2,3}, Sho FURUTSUKI⁵, Shin-ichi NISHIMURA⁵, Atsuo YAMADA⁵, Noritaka MIZUNO¹

¹Department of Applied Chemistry, The University of Tokyo, Japan

²Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Japan

³Synchrotron Radiation Research Organization, The University of Tokyo, Japan

⁴Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, Japan

⁵Department of Chemical System Engineering, The University of Tokyo, Japan

Introduction

Olivine-type iron compound LiFePO_4 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. In order to understand the electronic conduction properties and charge/discharge mechanism, many researchers have devoted their efforts to the study of the electronic structure in LiFePO_4 . Although many theoretical investigations into the electronic structure have been performed, there are few experimental studies for investigating directly the electronic structure of LiFePO_4 . Therefore, in this work, we focus on revealing experimentally the change of the electronic structure of Li_xFePO_4 ($x = 0, 0.6, 1.0$), especially in the Fe $3d$ states through the Li intercalation/deintercalation.

Experimental

The $\text{Li}_{1.0}\text{FePO}_4$ powder was synthesized from a stoichiometric mixture of Li_2CO_3 , $\text{Fe}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$. After 10 wt% (as a final product) conductive carbon was added, the mixture was thoroughly mixed and ground by a conventional planetary milling apparatus. The $\text{Li}_{1.0}\text{FePO}_4$ composite was obtained by sintering at 600°C under Ar gas flow. In order to obtain the composites FePO_4 and $\text{Li}_{0.6}\text{FePO}_4$, the chemical lithiation/delithiation were carried out.

To investigate the electronic structure of Fe $3d$ states in Li_xFePO_4 , we have performed Fe $2p - 3d$ X-ray absorption spectroscopy (XAS) and the resonant photoemission spectroscopy (PES) at BL-2C of the Photon Factory.

Results and Discussion

Figure 1 (a) shows Fe $2p - 3d$ XAS spectra of Li_xFePO_4 . The energy position of the main peak shifts from 708.1 eV in $\text{Li}_{1.0}\text{FePO}_4$ to 710.2 eV in FePO_4 due to the valence change from Fe^{2+} to Fe^{3+} . Subsequently, Fe $2p - 3d$ resonant PES spectra were measured for each sample with excitation energies denoted by R1 and R2 in Fig. 1 (a) corresponding to the positions of the main peaks of

the XAS spectra derived from Fe^{2+} and Fe^{3+} , respectively. Figure 1 (b) shows the resonant PES results on Li_xFePO_4 . The maximum intensity in the resonant PES spectra was observed at the excitation energy R1 for $\text{Li}_{0.6}\text{FePO}_4$ and $\text{Li}_{1.0}\text{FePO}_4$, whereas at the excitation energy R2 for FePO_4 . Compared between the resonant PES spectra for Fe^{2+} and Fe^{3+} , the spectral line-shape drastically changes in the wide region of valence bands. These results suggest that not only occupation of one spin-down Fe $3d$ band located at the binding energy of about 2 eV, but also the electronic structure of fully-occupied spin-up Fe $3d$ bands changes accompanied with the Li intercalation/deintercalation process.

Acknowledgments

This work 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)."

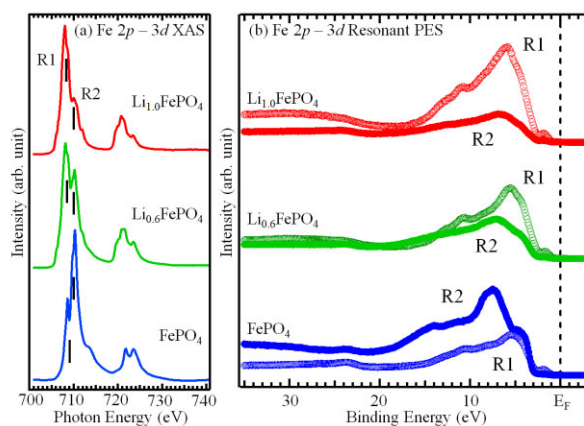


Figure 1. (a) Fe $2p - 3d$ XAS spectra of Li_xFePO_4 (b) Fe $2p - 3d$ resonant PES spectra of Li_xFePO_4 measured at the photon energy of Fe $2p - 3d$ absorption edge indicated by R1 and R2 in Fig. 1 (a).

*oshima@sr.t.u-tokyo.ac.jp