

Diffraction Anomalous Fine Structure Analysis of LiFePO₄-FePO₄ Two Phase Reaction

Tetsuro Ikeya^a, Ryoji Matsui^a, Junya Furutani^a, Toshiaki Ina^b, Tomoya Uruga^b, Yuki Oriksa^a

^a *Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga, 525-8577 Japan*

^b *Japan Synchrotron Radiation Research Institute, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198 Japan*

E-mail: sc0047vp@ed.ritsumei.ac.jp

Rate capability of lithium-ion batteries is one of important characteristics. Charge-discharge reaction proceeds by repeated insertion and extraction of lithium ions into the electrode active material. In the active material, crystal structure change due to ion diffusion continuously occurs, and its behavior may be different from the reaction mechanism obtained from the steady state analysis. Elucidation of the phenomenon in the non-equilibrium condition leads to guidance for development of high rate active materials. We have analyzed the dynamic phase change in the two phase system between LiFePO₄ and FePO₄ during charge-discharge by operando X-ray diffraction method [1]. While the diffraction peak position does not change during two phase reaction, the position measured during charge-discharge reaction at 1C rate continuously changes. However, the valence state of LiFePO₄ and FePO₄ phases has not been clearly understood. Since XRD gives only average crystal data, it was impossible to detect directly the valence state of two-phase individually. In this study, the diffraction anomalous fine structure (DAFS) analysis was applied to discuss the electronic structure change in each crystal during the two-phase reaction.

Li_xFePO₄ samples were prepared by electrochemically lithium extraction from LiFePO₄ electrode. Two-electrode cell using LiFePO₄ composite electrode and lithium metal with 1M LiPF₆ / EC:EMC was constructed. Charged cell was disassembled and washed in an Ar-filled glove box. The prepared Li_xFePO₄ electrodes were used for DAFS measurements. The measurement was performed on BL01B1 at SPring-8 (Hyogo, Japan). The diffraction pattern near Fe K-edge were measured using a two-dimensional hybrid pixel array detector, PILATUS 100K.

In the LiFePO₄-FePO₄ two phase system, the X-ray absorption edge energy of Fe K-edge shifts towards the higher energy during charging. This corresponds to the valence change of Fe from divalent to trivalent. Fig. 1 shows the corresponded spectra of LiFePO₄ and FePO₄ from DAFS measurements. The absorption edge of FePO₄ was observed on the high energy side as compared with the LiFePO₄ electrode. This change is almost the same value as observed in X-ray absorption spectra, indicating that the electronic states of LiFePO₄ and FePO₄ can be individually observed by the DAFS method.

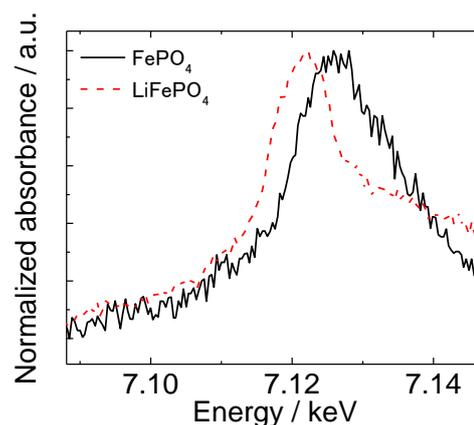


Fig. 1 Analyzed DAFS spectra of LiFePO₄ and FePO₄.

References:

[1] Y. Oriksa, T. Maeda, Y. Koyama, H. Murayama, K. Fukuda, H. Tanida, H. Arai, E. Matsubara, Y. Uchimoto, Z. Ogumi, *Chem. Mater.*, **25**, 1032-1039 (2013).