

Phase Decomposition and Valence Change during Delithiation in Olivine-type $\text{LiFePO}_4/\text{FePO}_4$ System

- An Application of Simultaneous XRD and XAFS Measurements -

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The olivine-type lithium iron phosphate (LiFePO_4)[1] has been attracted great attention for positive electrodes of Li-ion batteries by largely improving its electron conductivity by carbon coating[2]. This material is characterized by the two-phase reaction of LiFePO_4 (LFP) and FePO_4 (FP). These two phases have the same structure symmetries with different lattice parameters. There is about 6.8% volume change between these two phases. Thus, the battery reaction is affected by large coherent strain, which is yielded due to the phase change.

In the present study, we experimentally determined the valence change from Fe(II) to Fe(III), and the phase decomposition from LFP to FP during delithiation by the simultaneous in situ XANES and resonant X-ray diffraction (XRD) measurements. The present measurements were carried out at the beam line BL-28XU (the Kyoto University-NEDO RISING beam line), SPring8. By simultaneously measuring the information on valence and structure in the same location of the sample by XANES and XRD, respectively, we can reveal a change of active materials inherent in the battery reaction without being affected by the reaction inhomogeneity due to various causes in batteries. The experimental relations between the volume fractions of Fe(II) and LFP, and Fe(III) and FP in Fig. 1 were determined from the experimental time dependence of the volume fractions of Fe (II) and Fe(III) by XANES and those of LFP and FP by XRD.

The relation in Fig. 1 provides us a new insight into the structure transition from LFP to FP under the influence of the large coherent strain. Namely, at the initial stage of the phase decomposition, the nucleation and growth of the FP phase in the LFP matrix is suppressed due to the large coherent strain. At a point (E in Fig. 1) where the volumes of the LFP phase and the FP phase are equal, the influence of the strain energy on the phase decomposition is reversed and the growth of the FP phase is accelerated at the latter stage. In our presentation, we also introduce the battery reaction analysis by the combination of XANES and resonance X-ray powder diffraction.

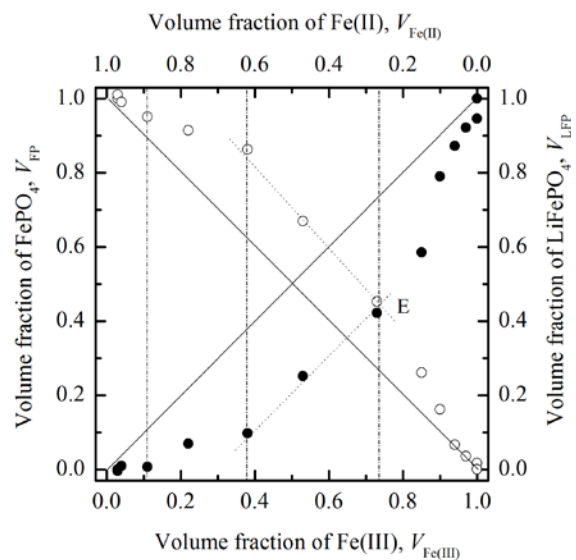


Fig. 1. Changes of the volume fractions of LFP (V_{LFP}) and FP (V_{FP}) vs. the volume fraction of Fe(III) ($V_{\text{Fe(III)}}$).

[1] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, J. Electrochem. Soc. 144, 1188 (1997).
[2] A. Yamada, S. C. Chung, and K. Hinokuma, J. Electrochem. Soc. 148, A224 (2001).