

Time-resolved XRD Study on Phase Transition Behavior between LiFePO_4 and FePO_4

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Olivine structure lithium iron phosphate (LiFePO_4) shows a high power density. Understanding the mechanism of the phase transition can be of help in providing the origin of this fast charge-discharge ability. The material undergoes phase reactions between Li-rich $\text{Li}_{1-\alpha}\text{FePO}_4$ (LFP) and Li-poor $\text{Li}_\beta\text{FePO}_4$ (FP).¹ However, the LFP-FP phase transition model underlying battery operation has been the subject of debate for a decade. Although phase transition models such as the isotropic shrinkage core² and the “domino-cascade” models have been proposed,³ these are based on steady state results. Recently performed theoretical calculations have predicted a single-phase transition path under nonequilibrium conditions.⁴ The phase field simulation suggested dynamic suppression of the phase separation under high currents.⁵ Such transient and nonequilibrium phenomena would finish in a short time. Therefore, the mechanism in nonequilibrium condition remains unclear due to lack of experimental evidence. In this study, we investigate the dynamics of the phase transition under high-current battery operation using time-resolved XAS and XRD with emphasis on the transient emergence of a metastable crystal phase between LFP and FP⁶⁻⁸.

Carbon-coated LiFePO_4 was prepared using the hydrothermal method. For electrochemical measurements, LiFePO_4 , carbon black, and polyvinylidene fluoride were mixed at a ratio of 75:15:10 with 1-methyl-2-pyrrolidone (Wako, 99%). The slurry was coated onto an aluminum foil current collector and dried in a vacuum oven at 80°C. For *in situ* XAS and XRD measurements, three electrode cells packed with laminated Al films were prepared. Reference and counter electrodes were Li foil. The electrolyte was a 1 mol dm^{-3} solution of LiPF_6 in ethylene carbonate / ethyl methyl carbonate (3:7 volume ratio, Kishida). XAS measurements were performed on BL01B1 and BL28XU at SPring-8 (Hyogo, Japan). Fe K-edge XAS spectra were measured at room temperature in the transmission mode using two ion-chambers. The XAS spectra were acquired every 15 s during the charge reaction. *in situ* time-resolved XRD measurements were performed on a diffractometer on BL46XU and BL28XU at SPring-8 (Hyogo, Japan), using $\lambda = 0.9995 \text{ \AA}$ monochromated by a Si (111) double crystal in the transmittance mode at room temperature. The X-ray beam size was $0.5 \times 0.5 \text{ mm}^2$. The snapshot of diffraction patterns was recorded using a two-dimensional hybrid pixel array detector, PILATUS 100K, in the range of $2\theta = 18^\circ$ to 21° . The XRD pattern was obtained with 0.5 s exposure time per shot. XRD and XAS measurements were performed during the charge discharge reaction at

1700 mA/g (10C rate). The voltage range was between 2.0 V and 4.3 V (versus Li metal).

Figure 1 shows the XRD peak change during the first discharge and the second charge with a rate of 10C and relaxation process after the cycles. Before the charge, a peak at 19.15 degree can be observed, which corresponds to diffraction from the (211) and (020) planes of LFP. The charge reaction causes the appearance of peaks at 19.50 and 19.87 degrees, which reflect the (211) and (020) planes of the FP phase, respectively. In addition, an unexpected peak can be seen at 19.35 degree during the first discharge and the following charge-discharge reactions. The new peak reversibly forms and disappears in synchronization with the electrochemical cycling, and the new peak is located between the peaks of LFP and FP. These results suggest that the new peak is related to an olivine-type Li_xFePO_4 phase with an intermediate composition.

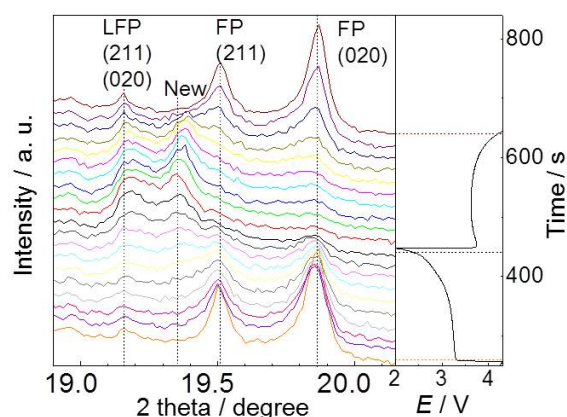


Fig. 1. Time-resolved x-ray diffraction pattern for Li_xFePO_4 during the first discharge and the second charge reaction at 10C rate.

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