Study on Dynamics of Structural Transformation during Charge/Discharge of $LiFePO_4$

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In-situ synchrotron XRD was conducted to study the structural transformation of $LiFePO_4$ during charge/discharge by using beam-line 01-C2 in National Synchrotron Radiation Research Center, Taiwan, ROC, and an X-ray source of 0.10223 nm in wavelength was employed. XRD spectra were acquired during the charge/discharge tests carried out at 55°C.

Fig. 1a shows the synchrotron XRD patterns of selected 2θ range acquired during a discharge/charge cycle under 1C rate with an intermittent rest period, while the corresponding voltage curve is shown in Fig. 1b. The structure transformation can be monitored by, for instance, following the evolution of the (211) and (020) reflection peaks of the end compounds, as marked in Fig. 1a. As shown, the XRD pattern show only the $FePO_4$ structure before the 8th measurement during discharge, and then transformed rapidly into that of the $LiFePO_4$-structure during the period between the 9th and11th measurements, when the test was switched to rest. The inset shown in Fig. 1a plots the intensities of the (020) peaks of the $LiFePO_4$- and $FePO_4$-structures, respectively, confirming the delayed $FePO_4$-to-$LiFePO_4$ transformation until near the end of discharge.

Similarly, during charge, the crystal structure of the electrode remained as the $LiFePO_4$-structure until near the end of charge, and then transformed abruptly to the $FePO_4$-structure upon reaching another rest period (Fig. 1a, b). It is important to note that, both the discharge and charge voltage curves (Fig. 1b) exhibit a flat-plateau region, where the XRD patterns show essentially only one structure. A plateau typically observed over the middle capacity region of an either charge or discharge voltage curve has been considered as a signature of the two-phase reaction nature, namely

$$LiFePO_4 \leftrightarrow e^- + Li^+ + FePO_4,$$

of the present electrochemical system.

In summary, in-situ synchrotron XRD study has revealed the complex nature of the transformation dynamics during charge/discharge of $LiFePO_4$ electrode, which can not be predicted from current understanding of the equilibrium phase relations. The transformation dynamics, in turn, could have a significant impact on the cycling performance of the electrode. Comparison between the XRD and electrochemical data have indicated that the two-phase reaction nature of the electrochemical lithiation/delithiation processes is not governed by crystallographic consideration but more likely by localized electron/ion site coulombic interaction.

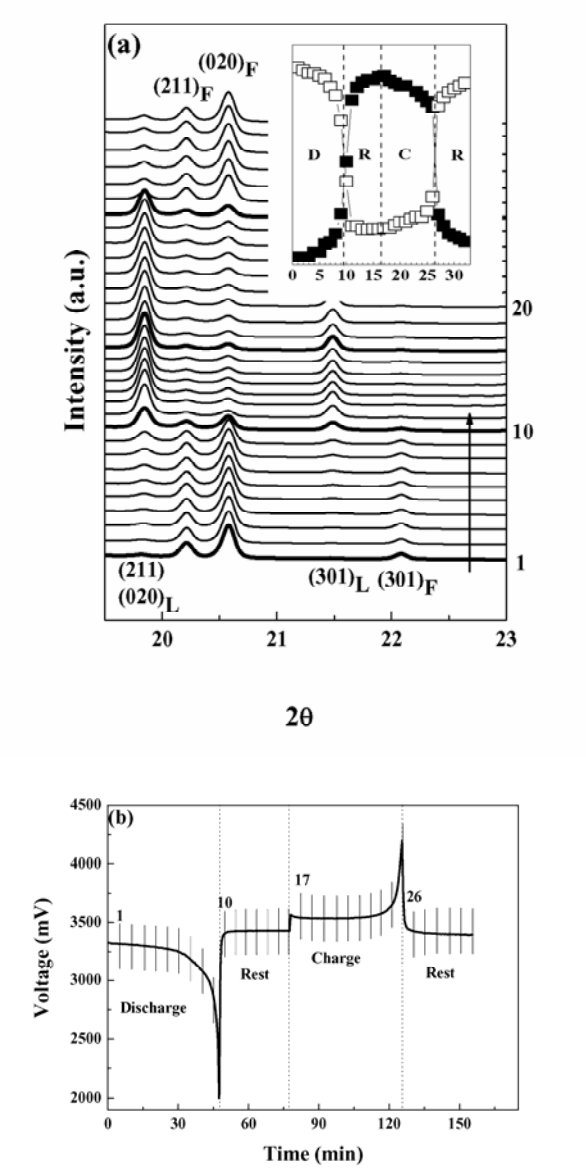

Figure 1. XRD and electrochemical data for charge/discharge test of at 1C rate at 55 °C with an intermittent rest period. (a) Synchrotron XRD patterns. The subscripts F and L indicate respectively reflections from the $FePO_4$- and $LiFePO_4$-structures. The bold curves mark the onset of different stages (C for charge; D, discharge; R, rest) within a test cycle. The inset shows the XRD peak intensities of $LiFePO_4$ (020) (■) and $FePO_4$ (020) (□) versus the measurement number. (b) Voltage curve. The numbers shown along the right-axis in (a) and within the figure in (b) index the XRD measurement number.