

Vanadium Powers the Lithium-Ion Battery

*This report features the work of Chih-Hao Lee, and his co-workers published in J. Power Sources **270**, 449 (2014).*

A Li battery based on LiFePO_4 (LFP) prevails in applications in electric vehicles because of its property of superior safety after a car collision and low cost, but the poor conductivity of LFP prevents it from popular applications. To solve the problem, LFP of sub- μm size should be used. In addition, doping with a supervalent cation (Zr, Nb, V, Cr, and Ni etc.) has proved to be an efficient way to improve the electrochemical performance, including the intrinsic electronic conductivity, the Li-ion diffusivity and the durability.¹ The influence of added vanadium on the structural evolution and electrochemical performance of 50-nm LFP powder was systematically investigated with X-ray powder diffraction (XRPD) and X-ray absorption near-edge structure (XANES) *in situ*.²

With a small proportion of a vanadium additive, both the highly disordered and inactive triphylite phase³

and the remnant heterosite phase are significantly decreased, especially upon higher C-rate cycling or after cycling many times. These vanadium additives also facilitate the reversibility of heterosite and triphylite phase transitions on the cathode, therefore the cycle stability of this Li battery.

To understand the influence of a vanadium additive on the chemical state changes of Fe ion in a local structural region (short-range ordering) at varied rates of charging (0.2 C, 0.5 C and 1 C) as shown in Fig. 1, the phase fraction changes were estimated with linear combination function analysis.

Figures 2(a)-(b) illustrate the evolution of intensities of signals for (301) reflections for $\text{LiFePO}_4/\text{FePO}_4$ (LFP/FP) and $\text{LiFePO}_4:\text{V}/\text{FePO}_4:\text{V}$ (LFPV/FPV) at varied C-rates,

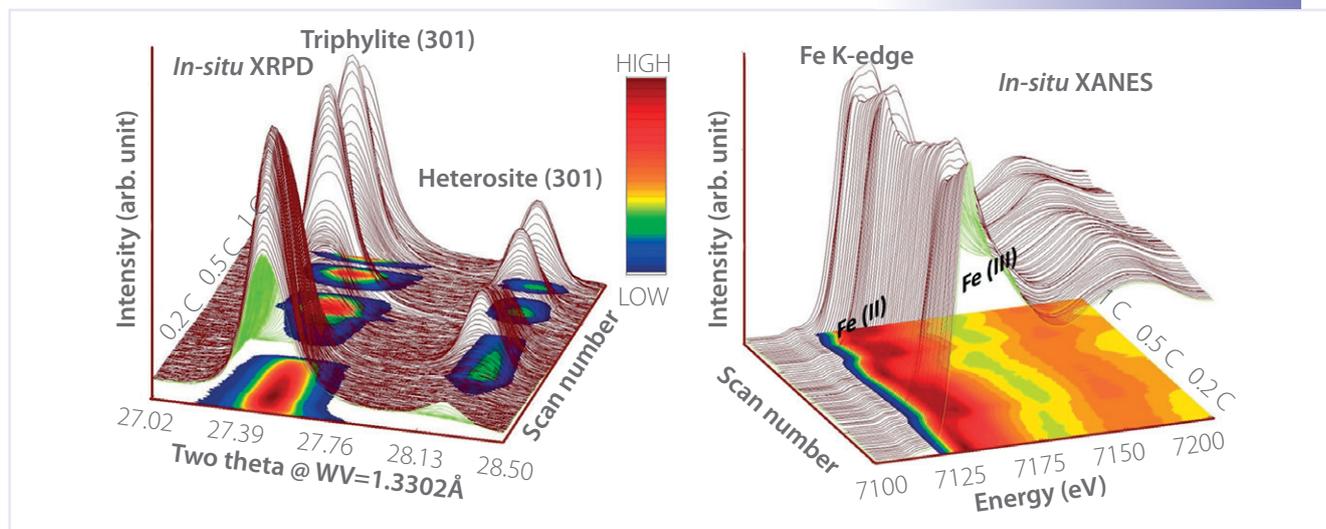


Fig. 1: XRPD and XANES are measured *in situ* to investigate the chemical states and phase evolution of a LiFePO_4 cathode with and without a vanadium additive.

including the potential curves and the relative variation of LFP and FP phase fractions during charging and discharging. The phase fractions of LFP and FP are obtained from the integrated area of (301) reflections relative to that at the beginning of charging and discharging of 0.2 C. In Fig. 2(a), significant portions of the FP phase remnants are found at the end of electrochemical cycles for 0.5 C and 1 C, indicating the incomplete charge/discharge cycle on increasing the C-rate. In contrast, as shown in Fig. 2(b), such remnant phenomenon is almost absent in LFPV, indicating an easy triphylite and het-

erosite phase transformation.

To portray the full scheme of structural evolution, XANES was employed *in situ* to obtain the variation of electronic structure on these two cathode materials upon charge and discharge cycling. Clear isosbestic points are observed in the real-time absorption spectra, which provide a direct indication of two mixed phases. It also shows a two-phase transition mechanism for the delithiation/lithiation reaction of LFP (LFPV).

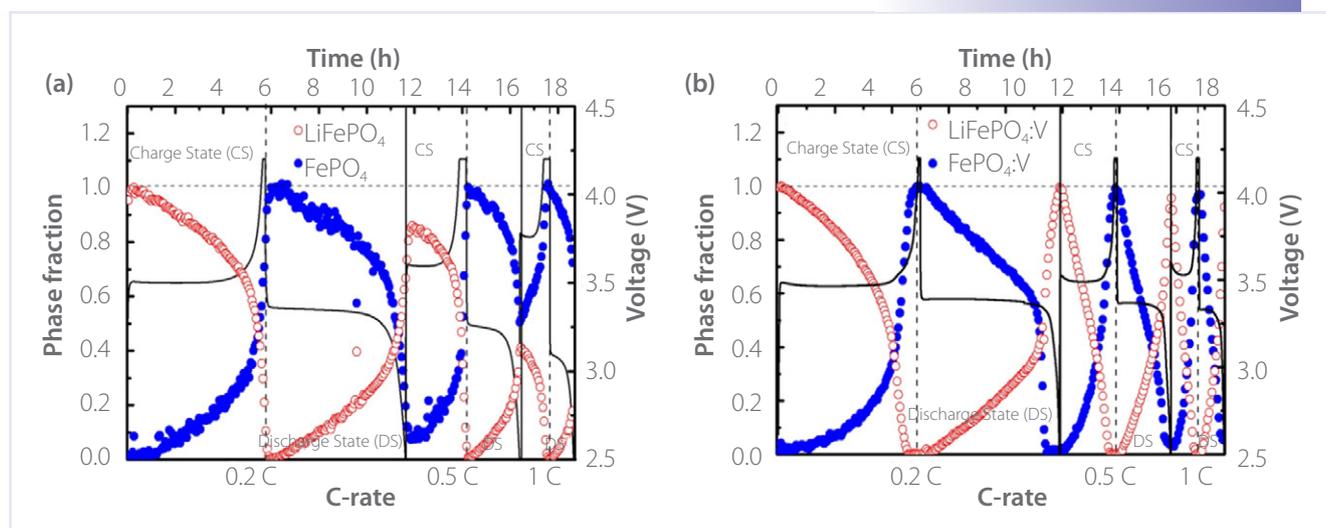


Fig. 2: Variation of phase fractions of (a) LFP/FP and (b) LFPV/FPV estimated from XRPD patterns *in situ* at rates 0.2 C, 0.5 C and 1 C of charge and discharge. The corresponding electrochemical charge and discharge curves are denoted with solid lines.

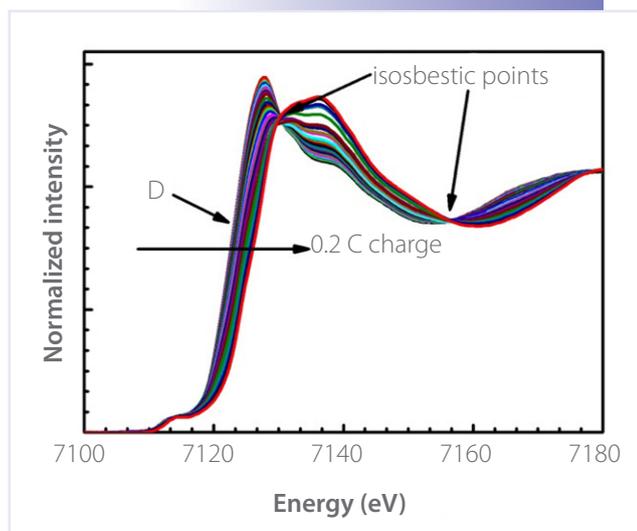


Fig. 3: Normalized Fe K-edge XANES spectra *in situ* at charge rate 0.2 C. D is the position of the absorption edge of each XANES spectrum.

The energy shift of the edge shoulder (D) is generally proportional to the oxidation state of Fe. The absorption edge of Fe shifts to increased energy as the volume of the cell increases. This condition indicates the transformation of Fe(II) into Fe(III), which corresponds to a phase transition from LFP to FP upon delithiation. During lithiation, the changes of Fe oxidation states are reversible; it can hence serve as an index to estimate the chemical oxidation state of Fe in our work. In the case of a small

C-rate, the position of D is found to shift reversibly from 7123.7 to 7127.5 eV in a single charge-discharge cycle. This effect indicates a reversible transition of chemical state of Fe ions in LFP during delithiation and lithiation. The range of energy shift of D is progressively narrowed from 3.8 eV to 2.3 eV on increasing the C-rate from 0.2 C to 1.0 C. This condition implies an irreversible chemical redox reaction with rapid rates of charging and discharging at the LFP cathode. In contrast, with a vanadium additive, this narrowing phenomenon is almost absent, even at large C-rates, as clearly shown by the range of shift of the edge position (D) in a complete electrochemical charge-discharge cycle. The chemical environments of LFPV are reversible during the charge and discharge cycling.

As Fig. 4(a) shows, the chemical state of Fe was found to transfer symmetrically between LFP and FP during the charge and discharge cycling at a small C-rate (0.2 C). This result, which refers to the equilibrium redox kinetics for Fe ions to accept and to donate charge to their local coordination when bulk LFP/FP phases are driven with a small current density, is expected. The redox kinetics of Fe become progressively unbalanced on increasing the C-rate to more than 0.5. In this case,

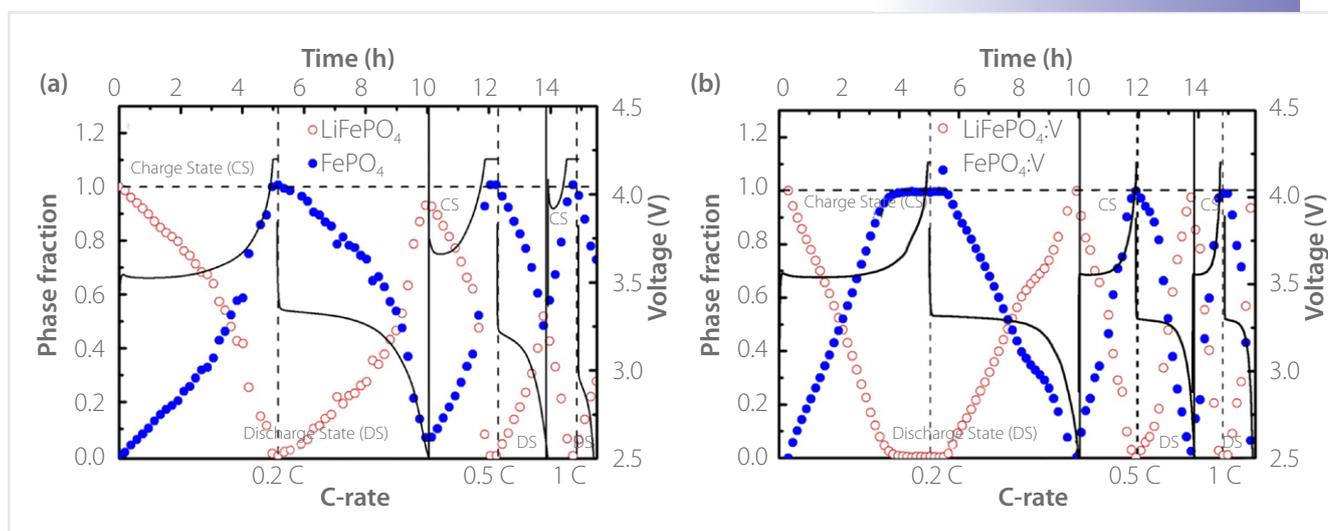


Fig. 4: Results of linear-combination fitting analysis of Fe K-edge spectra for (a) LFP/FP and (b) LFPV/FPV at charge and discharge rates 0.2 C, 0.5 C and 1 C.

an incomplete chemical state of Fe ions from FP to LFP is found. Presumably, this unbalanced transition of the chemical state of the Fe ion can be attributed to a presence of a substantial energy barrier (i.e. solid electrolyte interface layer) that hinders a transition of chemical state of Fe and Li ion diffusions between FP and LFP during the charge and discharge cycles of a Li battery at a large C-rate. In contrast (see Fig. 4(b)), a perfectly symmetric transition of the Fe chemical state between LFPV and FP was found even on charging or discharging the LIB cycling at 1.0 C. Such a phenomenon provides direct evidence to prove that vanadium additives substantially decrease the energy barrier and thus facilitate the redox chemical kinetics of Fe to accept and to donate their valence charge during the transition of chemical state between LFPV and FP in a LIB.

Compared to the FP to LFP phase transition (see Fig. 5), the extents of reversible LFP estimated from XANES are much greater than those of XRPD analysis; the phenomenon is especially evident at discharge rates greater than 0.5 C. The nearly recovered valence state of Fe is direct evidence that a substantial amount of highly disordered triphylite phase is found after completing a charging and discharging cycle as the crystalline phase recovery is incomplete. In contrast, with the vanadium additive (see Fig. 5(b)), this phenomenon is not significantly observed: the crystalline triphylite phase is fully recovered.

In summary, from the results of testing half-cell Li batteries, we found that, during discharge, the greater is its rate, the more the highly disordered LFP phase is formed. This irreversible LFP to FP phase transition results in capacity losses during the charge and discharge cycle. In contrast, the remnant effects are insignificant for the case of Li battery with a LFPV cathode. These values are significantly smaller than that in LFP without added vanadium. The highly reversible phase transformation is explicable as a formation of easy paths for diffusion in the presence of Li vacancies in an adequate proportion

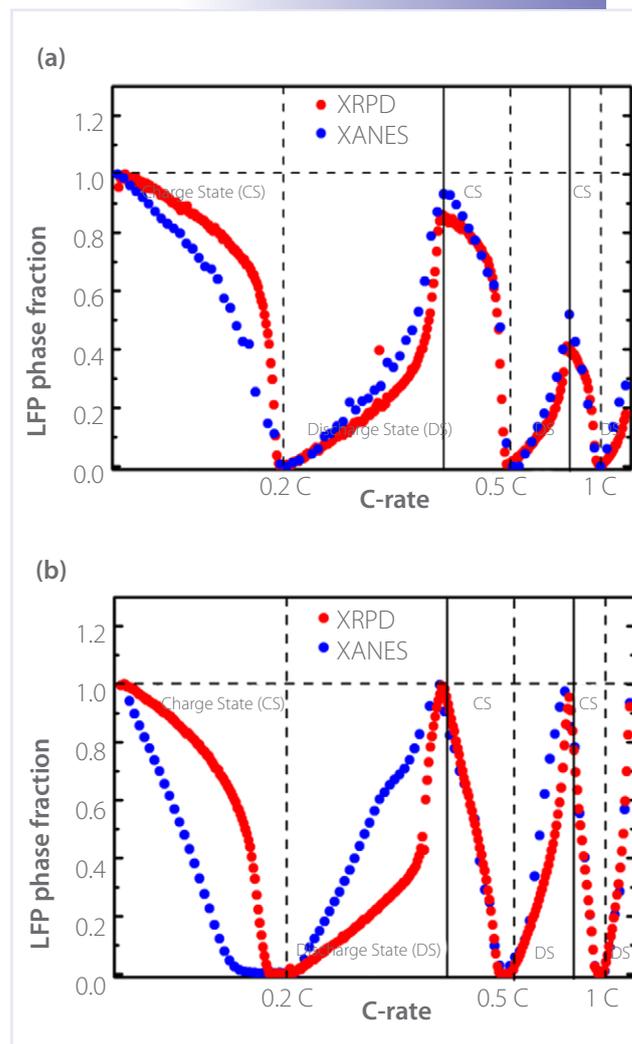


Fig. 5: Relative amounts of (a) LFP and (b) LFPV versus charge/discharge rate (0.2 C, 0.5 C and 1 C) as obtained from XRPD and XANES data.

(vacancy effect), due to charge balance of incorporation of supervalent vanadium in LFP during the electrochemical redox cycles. (Reported by Chih-Hao Lee)

References

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