

Supporting Information

High rate delithiation behavior of LiFePO_4 studied by quick X-ray absorption spectroscopy

Xiqian Yu,^a Qi Wang,^a Yongning Zhou,^a Hong Li,^b Xiao-Qing Yang,^{*a} Kyung-Wan Nam,^{*a} Steven N. Ehrlich,^a Syed Khalid,^a and Ying Shirley Meng^c

^a*Brookhaven National Laboratory, Upton, New York 11973, USA.*

^b*Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China*

^c*Department of NanoEngineering, University of California San Diego, LaJolla, CA, 92093, USA.*

Tel: (+01)-631-3443663

E-mail: xyang@bnl.gov, knam@bnl.gov

1. Experimental Section

Characterization:

The LiFePO_4 powder¹ was analyzed by a scanning electron (SEM) microscope (JEOL 7600F) and a transmission electron (TEM) microscope (JEOL JEM-2100F). High quality XRD patterns were collected in transmission mode at beamline X14A of NSLS (USA.) using a linear position sensitive silicon detector. The wavelength used was 0.7748 Å.

Electrochemical measurement:

The cathode electrodes were prepared by slurring the active material, carbon black, and polyvinylidene fluoride (PVDF) at a weight ratio of 60:20:20 in *n*-methyl pyrrolidone (NMP) solvent, then coating the mixture onto Al foil. The electrochemical experiments were performed using 2032-type two-electrode coin cells. High-purity lithium foil was used as an anode. The electrolyte was 1.2 M LiPF_6 based diethyl carbonate and ethylene carbonate solution (EC: DMC = 1:1, in volume, Novolyte Inc.). The cells were assembled in an argon-filled glove box and cycled using a VMP3 BioLogic electrochemistry workstation.

Chemical delithiation:

The chemical delithiation was carried out as the following procedure: The oxidizing solution (0.5 Mol/L, 6.64 g NO_2BF_4 in acetonitrile, completely dissolved) was fed through a vertically positioned capillary at a controlled rate of 1 mL/min. The redox potential of $\text{NO}_2^+/\text{NO}_2$ is higher than the 3.4 V ($\text{Fe}^{3+}/\text{Fe}^{2+}$) redox potential for the fully extraction of Li in LiFePO_4 .

2. Principal component analysis (PCA)

Principal component analysis (PCA)² is a robust quantitative method of linear algebra, which allows us to determine the number of linearly independent components in a series of experimental spectra without making any assumption of their chemical nature or structure. Two principal components indicate that a reaction occurs without an intermediate, while three or more indicate that there are one or more intermediates. To determine the number of distinct phases during the delithiation process of LiFePO_4 , we applied PCA to a series of normalized Fe K-edge XANES spectra $\mu(E)$ collected during each individual experiment in the energy range of 7105-7145 eV. Fig. S2 presents an example where PCA was performed using 30 XANES spectra collected during chemical delithiation process. The first five components calculated by PCA, weighted by eigen

values and sorted in descending order, are displayed. The first two components clearly dominate the spectra in the edge region, which is indicative of two reaction components existed during delithiation of LiFePO_4 .

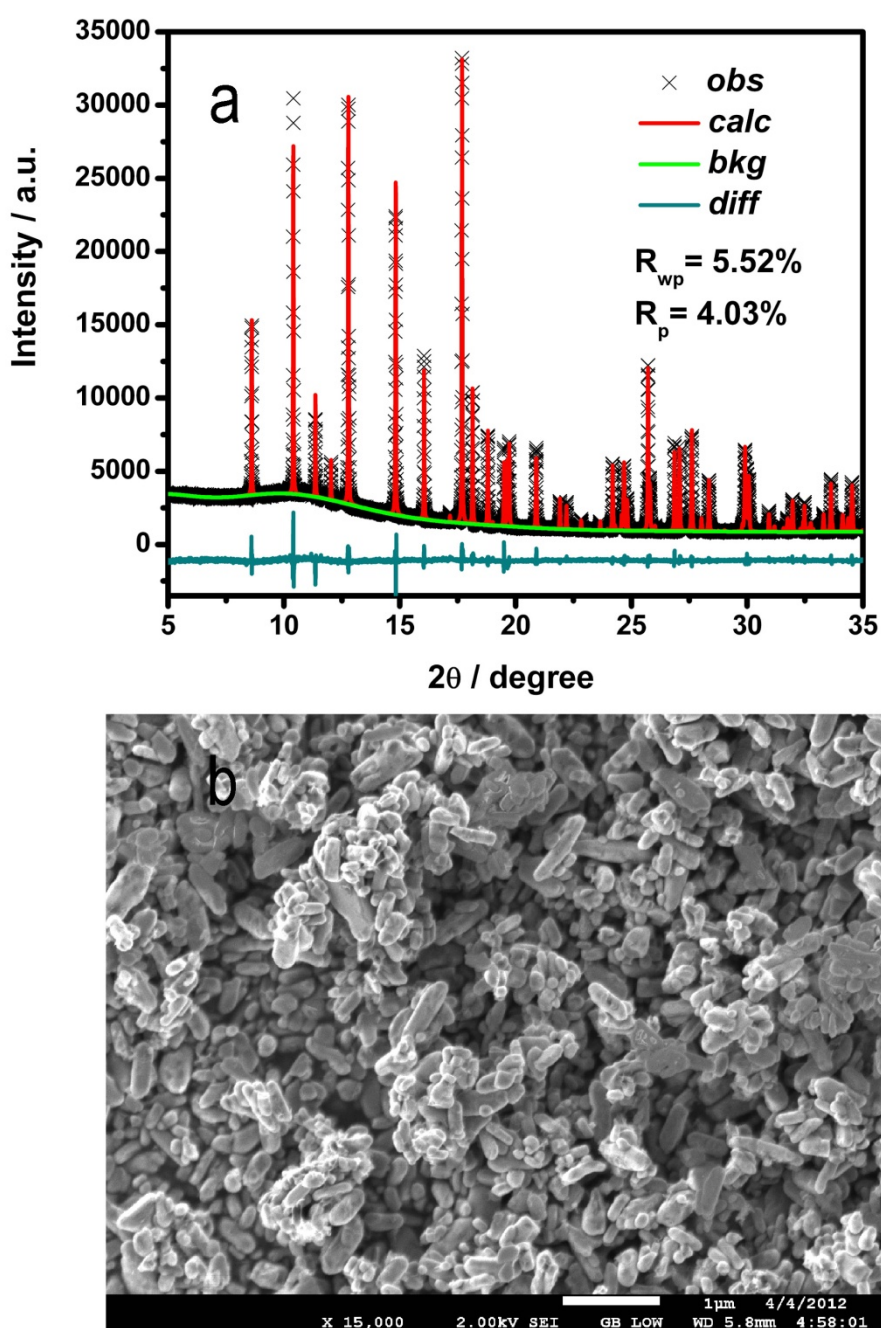


Fig. S1 (a) Rietveld refinement of the XRD pattern of LiFePO_4 with no indication of the presence of a secondary phase. (b) Scanning electron microscope (SEM) image of the LiFePO_4 sample.

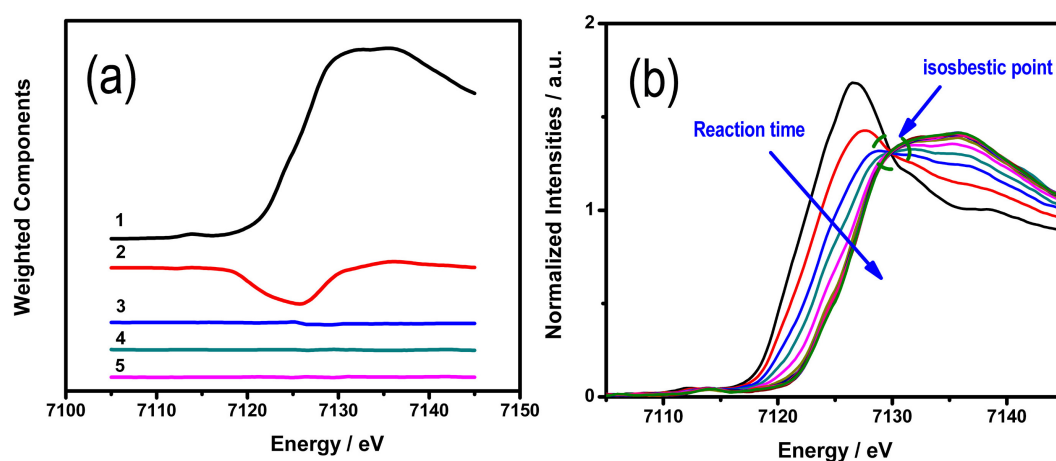


Fig. S2 (a) The first five components from PCA calculation weighted by eigenvalues. PCA calculation was performed using Fe K-edge XANES spectra $\mu(E)$ collected during chemical delithiation process. (b) Fe K-edge XANES spectra obtained during chemical delithiation process. The isosbestic point appeared on the XANES spectra indicates a two-phase reaction mechanism of LiFePO_4 to FePO_4 .

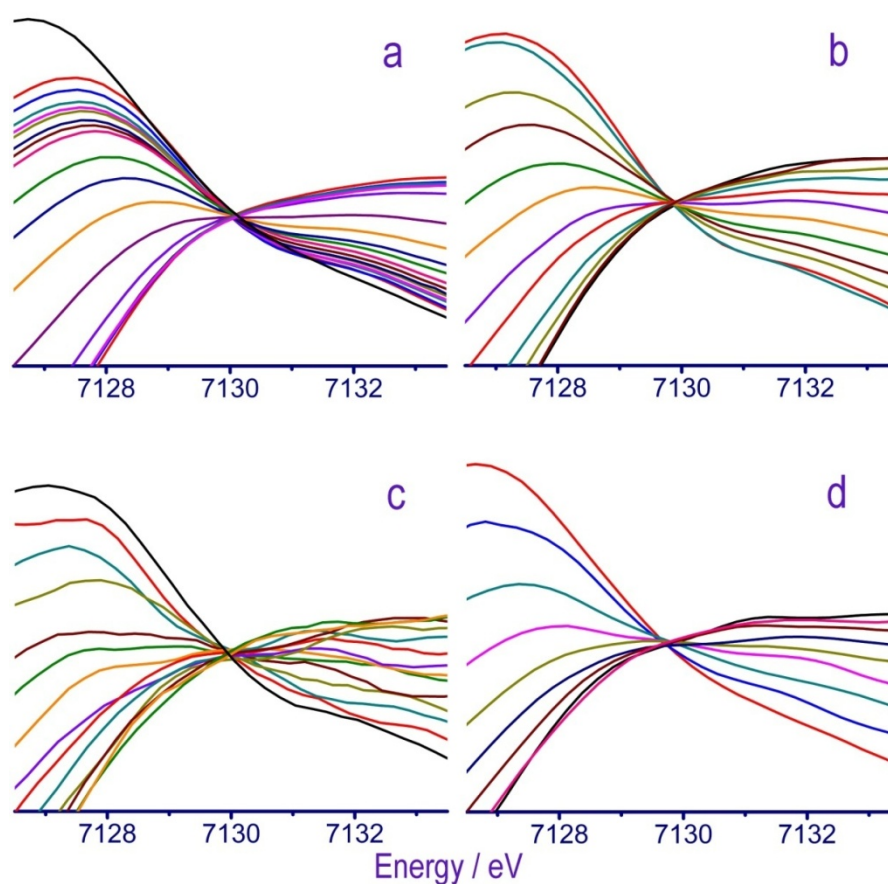


Fig. S3 Enlarged view of Fe K-edge XANES spectra of LiFePO_4 (around isosbestic point 7130eV) during charging under C-rate of (a) 0.2C, (b) 1C, (c) 10C and (d) 30C.

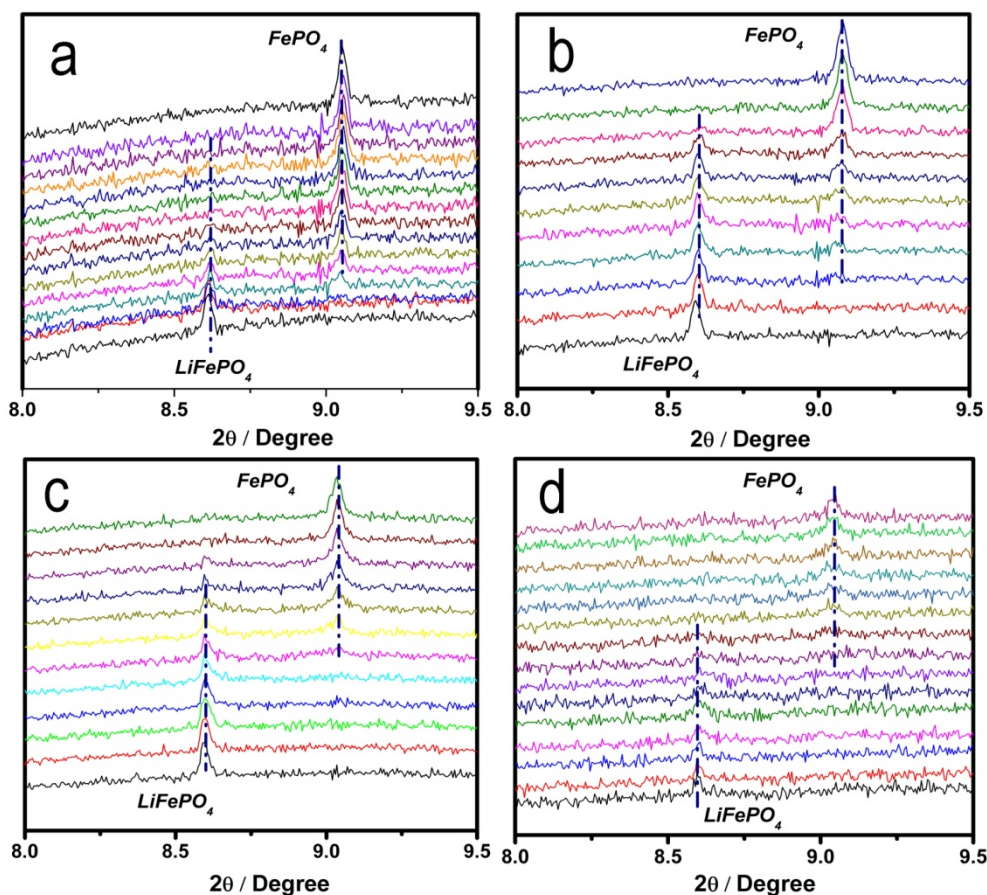


Fig. S4 The evolution of (020) reflection during LiFePO_4 charging under C-rate of (a) 0.2C, (b) 1C, (c) 10C and (d) 30C.

References

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- 2 (a) S. Beauchemin, D. Hesterberg and M. Beauchemin, *Soil Sci. Am. J.* 2002, **66**, 83; (b) S.R. Wasserman, P. G. Allen, D.K. Shuh, J.J. Bucher and N.M. Edelstein, *J. Synchrotron Radiat.*, 1999, **6**, 284; (c) A.I. Frenkel, O. Kleinfeld, S.R. Wasserman and I. Sagi, *J. Chem. Phys.*, 2002, **116**, 9449; (d) Q. Wang, J.C. Hanson and A.I. Frenkel, *J. Chem. Phys.*, 2008, **129**, 234502.