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COMMUNICATION

High rate delithiation behaviour of LiFePO₄ 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

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A novel *in situ* time-resolved synchrotron X-ray absorption spectroscopy (XAS) was introduced for the dynamic studies during fast chemical and electrochemical delithiation of LiFePO₄. The lithium diffusion in LiFePO₄ and the reaction mechanisms for both processes were investigated. This approach opens new opportunities for dynamic studies of various energy storage systems.

High charge–discharge is a critical property required for lithium-ion batteries (LIB) powering hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEV) with short charging and acceleration times. An in-depth understanding of the relationship between the structural changes and the dynamic electrochemical performance of these batteries is the key to achieving this goal. Various *in situ* techniques have been developed and applied to study the structural changes relating to the delithiation and lithiation of electrode materials of LIB during electrochemical cycling, such as X-ray diffraction (XRD),¹ X-ray absorption spectroscopy (XAS),² neutron powder diffraction (NPD),³ nuclear magnetic resonance (NMR),⁴ and transmission X-ray microscopy (TXM).⁵ Although these techniques have provided important information about the structural changes during low or intermediate rate cycling, the reports on studies and tool development for high rate cycling are quite limited. Recently, taking advantage of the high intensity beam, *in situ* synchrotron X-ray diffraction was used to explore the crystalline structural changes of LiFePO₄ during chemical delithiation with excellent temporal resolution for dynamic studies.⁶ In this communication, we report the results of using another novel approach, *in situ* quick X-ray absorption spectroscopy (XAS), for studying the high rate delithiation behaviour of LiFePO₄. Quick XAS can dynamically monitor the oxidation state of Fe, which is directly related to the content of Li in LiFePO₄. In contrast, the XRD can only probe the new crystal phase, which can be delayed with respect to the changes in the Li content caused by the nucleation and growth rate of the new phase.

LiFePO₄, first reported by Padhi *et al.*,⁷ is a very promising cathode material for lithium ion batteries. The high rate capability⁸ of LiFePO₄ is scientifically interesting and practically important, considering its electronic insulator⁹ nature and mediocre ionic transport property.¹⁰ The important issues are how fast the Li⁺ can be extracted out and what are the controlling factors of this process. In addition, the phase transition reaction mechanism still remains controversial.¹¹ Here we report the results of applying *in situ* quick XAS to study the high rate delithiation behaviour of LiFePO₄ with sub-second temporal resolution for the first time. These results could shine some light on answering the dynamic issues and provide new tools to study them.

The LiFePO₄ sample was obtained from Pacific Northwest National Lab. with phase purity and morphology as illustrated in Fig. S1 (ESI†). The LiFePO₄ particle sizes are uniformly distributed with the smallest dimension of about 300 nm. Both chemical⁶ and electrochemical delithiation methods were used. The quick XAS experiment was performed at beamline X18A of the National Synchrotron Light Source (NSLS, BNL). Up to 16–17 XAS spectra were recorded in a 30 second time interval, with the best achievable temporal resolution of 2 seconds per scan. 8 successive spectra were merged into one to get a better signal-to-noise ratio. Therefore, the real temporal resolution in this work is about 15 seconds.

Fe K-edge XANES spectra of Li_xFePO₄ at 0 second and 120 seconds of chemical delithiation are plotted in Fig. 1a, showing a clear edge shift to higher energy. The detailed quick XAS spectra during chemical delithiation for a total time of 200 seconds are plotted in Fig. 1b using a colour scale for the spectrum intensity. With increasing reaction time, the Fe K-edge continuously shifts to a high energy (from 7120 eV to 7130 eV), indicating the oxidation of LiFePO₄ to FePO₄. The chemical delithiation reaction was completed within a very short period of time: no further changes in the XANES feature can be observed after 120 seconds. To further examine the reaction dynamics, quantitative analysis was applied. In order to decide the number of reaction components during delithiation of LiFePO₄ to be used in the linear combination fitting (LCF), the principal component analysis (PCA) was used. As can be seen from Fig. S2(a) (ESI†), only two important components dominate the spectra in the edge region, which is consistent with the isosbestic point¹² observed in Fig. S2(b)† on the XANES spectra

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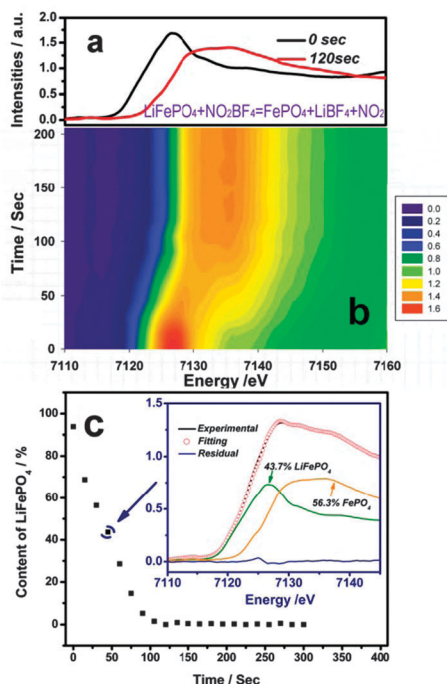


Fig. 1 (a) Fe K-edge XANES spectra of pristine LiFePO_4 and after 120 second chemical delithiation; (b) the evolution and (c) linear combination fitting of Fe K-edge XANES spectra during *in situ* chemical delithiation of LiFePO_4 . Inset: example of the detailed linear combination fitting result of the XANES spectrum collected after chemical delithiation for 45 seconds.

indicating two reaction components during delithiation of LiFePO_4 . This is in good agreement with the well accepted “two-phase reaction” mechanism in the literature. Therefore, the linear combination fitting (LCF) using the spectra of the two end members (LiFePO_4 and FePO_4) was processed to estimate the Li content in Li_xFePO_4 at a certain reaction stage, plotted as a function of reaction time in Fig. 1c. As can be seen from Fig. 1c, more than 90% of LiFePO_4 had been converted to FePO_4 after 120 seconds, showing the excellent ionic transport property of this particular LiFePO_4 sample during chemical delithiation. The inset of Fig. 1c presents an example of the observed spectrum plotted with its LCF after 45 seconds of reaction. The best fit is composed of 43.7% of LiFePO_4 and 56.3% of FePO_4 . A low χ^2 value of 0.8% indicates an excellent linear fit. Such high quality reproduction of data in the whole series of spectra further validates the two-phase assumption of this reaction process.

The *in situ* quick XAS measured during chemical delithiation can monitor the Li content changes limited by the ionic transport only, without the effects of electronic conduction issues such as C-coating, carbon additives and current collectors. However, it cannot fully reflect the electrochemical process in battery cells and the content of Li could not be verified by the capacity reached as in electrochemical delithiation. Therefore, *in situ* quick XAS was also performed during electrochemical delithiation of the same sample using constant voltage charge at 4.3 V. Electrochemical delithiation of LiFePO_4 should be similar to chemical delithiation if one assumes that the electron transport in both LiFePO_4 and FePO_4 is faster than ion transport.¹³ Therefore, an electrode made by mixing 20% of conducting carbon was used in order to ensure good electronic conductivity.

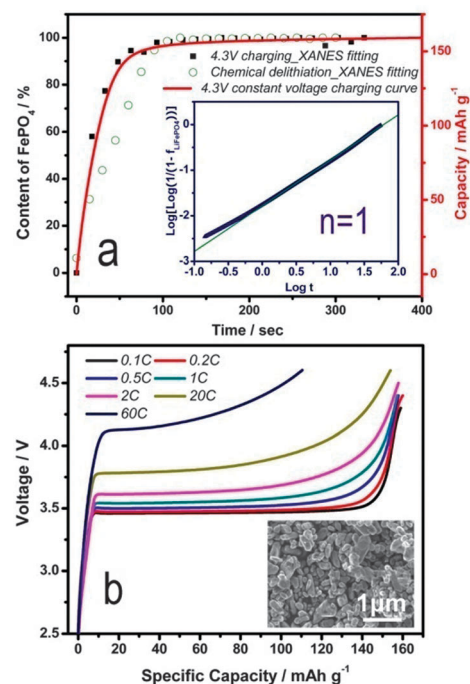


Fig. 2 (a) Comparison of fast delithiation of LiFePO_4 between *in situ* chemical delithiation and 4.3 V constant voltage charging; solid square symbols represent the FePO_4 content obtained from XANES linear combination fitting and the red solid line is the integrated charge capacity recorded during 4.3 V constant voltage charging. The FePO_4 content scale on the left side is one-to-one related to the capacity scale on the right. Inset: determination of the Avrami exponent by fitting a constant voltage charging curve with the Johnson–Mehl–Avrami–Kolmogorov equation; (b) charge curve of LiFePO_4 at different C-rates.

The data collection and processing followed the same procedure as that for the chemical reaction and the results are plotted in Fig. 2.

As shown in Fig. 2a, during electrochemical delithiation, the FePO_4 content estimated from LCF of XANES spectra (solid square symbols) are quite close to those calculated from the integrated charge capacity curve (red line) recorded during constant voltage charging, demonstrating the reliability and accuracy of the LCF analysis. For both chemical and electrochemical delithiation reactions, LCF results show that more than 60% of the Li^+ can be extracted from LiFePO_4 within 1 minute. The kinetic property of electrochemical delithiation at constant voltage charging is as good as that of chemical delithiation, showing that the Li^+ transport is the main governing factor for both reactions. When samples with excellent Li^+ transport kinetics are used (as in this study), most of the Li^+ can be extracted out within 1 minute through constant voltage charging. This is verified by the excellent rate capability during constant current charge shown in Fig. 2b. Even with a rate as high as 60 C (60 C = 1/60 or 1 minute charge), 120 mAh g^{-1} specific capacity can be achieved, which is consistent with the LCF results for chemical and electrochemical delithiation (constant voltage charging).

The kinetics of the LiFePO_4 to FePO_4 phase transition was analyzed by using the Johnson–Mehl–Avrami–Kolmogorov equation (also named JMAK equation).¹⁴

$$f = 1 - \exp(-kt)^n, \quad (1)$$

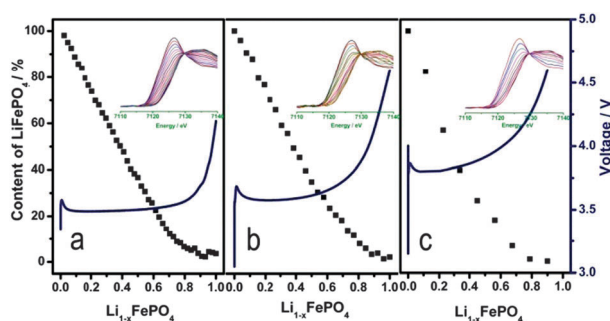


Fig. 3 Linear combination fitting of Fe K-edge XANES spectra of LiFePO₄ charged at a C-rate of (a) 1 C (b) 10 C and (c) 30 C. The black dot line is obtained from XANES LCF, and the blue line is the charging curve; inset figures are the corresponding *in situ* XANES spectra.

where f is the fraction of FePO₄, k is a rate constant and n depends on the phase growth geometry. The Avrami exponent n increases with the dimensionality of growth. Typically, an n value of 1–2 is indicative of one dimensional growth. Allen *et al.* applied this theory to the electrochemical discharge curve of the LiFePO₄ based system.¹⁵ By using the fraction of FePO₄ obtained from LCF for both chemical and electrochemical delithiation in Fig. 2a, the curve fitting of eqn (1) is plotted in the inset of Fig. 2a and $n = 1$ is obtained, indicating the one-dimensional growth of FePO₄ in LiFePO₄. Assuming that the delithiation kinetic is controlled by lithium diffusion (*i.e.* along the b axis), the apparent diffusion coefficient can be roughly estimated by eqn (2) regardless of particle morphology and diffusion geometry.

$$\tau \sim (d/2\pi)^2/D_{\text{Li}^+} \quad (2)$$

Considering that the shortest diffusion distance of the investigated LiFePO₄ is about 150 nm and the total delithiation reaction time is 120 seconds, the determined apparent D_{Li^+} is estimated to be $1.9 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. This value is close to the recent reported data obtained from chemical delithiation of LiFePO₄ single crystal.¹³

The charge curve and contents of FePO₄ in LiFePO₄ obtained by LCF during constant charge at 1 C, 10 C, and 30 C rates are plotted in Fig. 3 with *in situ* quick Fe K-edge XANES spectra plotted in the insets. Isosbestic points¹² at 7130 eV (enlarged images shown in Fig. S3, ESI†) are observed in all cases, indicating that the delithiations are two-phase reactions at different charging rates. The LCF results shown in Fig. 3 also support a two-phase reaction mode for all three C-rates used for this particular sample. Results from a separate *in situ* X-ray diffraction study shown in Fig. S4 provide further support for this model.

In conclusion, we have shown that time-resolved XAS carried out *in situ* during chemical and electrochemical reaction is capable of dynamically monitoring the two-phase transition behaviour between LiFePO₄ and FePO₄. The apparent Li⁺ diffusion coefficient of LiFePO₄ was estimated in the magnitude of $10^{-13} \text{ cm}^2 \text{ s}^{-1}$. The XAS technique, with the capability of probing a specific element, can provide information on both electronic structure and local structure of the material. The application of quick XAS on the high rate delithiation of LiFePO₄ reported in this work opens new opportunities for studying the dynamic process of lithium batteries with excellent time resolution. Further development of this *in situ* XAS

approach in combination with *in situ* XRD will provide more powerful tools for investigating many reactions in energy storage and other chemical reaction systems.

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