Solid state synthesis of LiFePO₄ studied by in situ high energy X-ray diffraction

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Received 22nd November 2010, Accepted 13th January 2011
DOI: 10.1039/c0jm04049e

The phase evolution and crystal structure transition of materials during solid-state synthesis of LiFePO₄ were investigated by in situ high energy X-ray diffraction. It was found that the solid state reaction forming LiFePO₄ started at a very low temperature, and LiFePO₄ was clearly observed when the reaction temperature was above 173 °C. In situ X-ray diffraction data also revealed that several impurities appeared when the reaction temperature was above 400 °C. These impurities were successfully indexed with ex situ X-ray diffraction as Li₃PO₄, Fe₂P, and Fe₃P.

Introduction

Research efforts are in progress worldwide to develop reliable, high-performance cathode materials for advanced lithium-ion batteries, paving the way to a secure and sustainable energy future. Among these massive research efforts, there have been reports on low reproducibility of some cathode materials, large discrepancy on cathode performance from group to group, and intense debate on criteria to guide material discovery and design. It is impossible to resolve these issues without a systematic understanding of the structure–property relationship of candidate cathode materials. For instance, LiFePO₄ was first reported by Goodenough and coworkers as a potential cathode material for lithium-ion batteries in 1997,1,2 Because of its low electronic conductivity3,4 and Li⁺ mobility, the LiFePO₄/FePO₄ interfaces,3,5 the major improvement on power capability of LiFePO₄ was not reported until recently that extremely high rates could be achieved with LiFePO₄ by chemical doping of metal supervalent to Li in nano-structured LiFePO₄ or off-stoichiometry synthesis to generate a special surface coating.6 However, the mechanism of the performance improvement is still under debate, and a guideline for successful material design has not been established yet.

It is common practice now to develop nano-structured materials to mitigate the low bulk conductivity of LiFePO₄ by reducing the diffusion length of Li ions.5–8 Furthermore, a conductive carbon coating using various fabrication processes and carbon sources is also widely used to promote the electronic conductivity of olivine materials.9–12 Besides these incremental improvements, a major improvement was reported by Chiang and coworkers, who improved the electronic conductivity of LiFePO₄ by a factor of ~10³ by doping metal supervalent to Li⁺ site, such as [Li₀.₉⁹Nb₀.₀₁]FePO₄.5 However, this doping mechanism was seriously questioned by subsequent studies from different groups.3,13,14 Using X-ray diffraction and neutron diffraction data, Nazar et al. reported that the supervalent doping of Li⁺ site is possible, but offered no evidence connecting the supervalent doping to the dramatic electronic conductivity improvement.15 Nazar et al.16 studied the surface of carbon-coated LiFePO₄ synthesized at 600 °C using Mössbauer and X-ray photoelectron spectroscopy, and observed some impurity components other than simple carbon coating on the LiFePO₄ surface. They believed that the impurity was a mixture of Li₃PO₄, FeP, and Fe₂P, and that the iron phosphate coating was the key contributor to the dramatic boost in the electronic conductivity of the LiFePO₄ particles.16 Aiming at understanding the structure–property relationship of LiFePO₄, Ceder et al. used first principle calculations to predict the Li–Fe–P–O₂ phase diagrams for different synthesis environments,17 and believed that a Li₃PO₄ coating was the key factor in the performance enhancement.6 As pointed out by Ceder et al., the solid state reaction for LiFePO₄ synthesis is a complicated process that depends on the reducing environment and stoichiometry of the starting materials. Experimental effort to validate these theoretical predictions has not been reported yet.

In this work, in situ high energy X-ray diffraction (HEXRD) was used to investigate the phase formation and crystal structure
evolution during solid state synthesis of LiFePO$_4$ using carbothermal reduction process.$^{18}$

**Experimental**

**In situ experiment**

The precursor, FePO$_4$·2H$_2$O, was first dehydrated by heating at 500 °C for 6 h in air atmosphere for accurate measurement of iron in the raw material. The anhydrous FePO$_4$ was then mixed with Li$_2$CO$_3$ and sugar by ball-milling in water with zirconia balls. This mixing was done for 2 hours with a rotation speed of 450 rpm. The molar ratio of Li$_2$CO$_3$ : FePO$_4$ : sugar was 0.51 : 1 : 0.1. Sugar was used as (i) the reduction agent to convert Fe(III) to Fe(II) during solid state reaction, and (ii) the precursor of carbon coating on LiFePO$_4$ particles, on which the carbon coating further acts as the reduction agent to partially decompose LiFePO$_4$ into other impurities at a temperature above 400 °C. About 2% excess Li$_2$CO$_3$ was added with an initial expectation to compensate for the loss of Li$_2$O during solid state reaction; this aspect will be discussed later.

After the ball milling, the mixture was dried at 120 °C for 5 hours and pressed into pellets about 2 mm in thickness. Some crystalline water can be there in the sample due to the low drying temperature and direct exposal of samples to the ambient air. The pellet was sandwiched between an alumina can and a platinum cover with holes ($\Phi = 1$ mm) on the centers of both can and cover. The sample was then placed vertically in a programmable furnace with glass windows and Ar was used as the protective gas. The sample was heated up to 600 °C with a heating rate of 2 °C per minute. The in situ XRD experiment was carried out at the sector 11 of Advanced Photon Source (APS) of Argonne National Laboratory, the wavelength of X-ray used was pre-set to 0.107805 Å (fixed wavelength for this station). The high energy X-ray source at about 0.1 Å was selected for its excellent penetration capability to detect structural changes on bulk part of the sample. The high flux of X-ray beam at APS is a major advantage to carry out fast experiments at one spectrum per minute. During the course of solid state synthesis, a high energy X-ray hit the sample horizontally (see Fig. 1), and a 2D X-ray detector was used to collect the X-ray diffraction (XRD) profiles using a transmission mode with a speed of one spectrum per minute.

The collected 2D pattern was then integrated into conventional 1D data (intensity vs. 2θ) for final data analysis and fitting with GSAS (general structure analysis software). Rietveld refinement using GSAS was carried out to perform (1) background and zero point calibration, (2) X-ray source profile calibration, (3) cell parameter optimization and (4) Li–Fe inter-mixing analysis for LiFePO$_4$.

**Ex situ experiment**

After the in situ experiment, the sample was further heated to 650 °C and sintered for 10 hours to accumulate more impurities. After the sample was cooled to room temperature, the XRD pattern of the sintered sample was collected with the integration time set to one minute, the same as used for the in situ experiment. The ex situ XRD pattern was then analyzed with GSAS to identify the formula and structures of the impurities.

**Results and discussion**

Fig. 2a shows the XRD pattern of the mixed starting material before heat treatment. The sample was prepared by simple drying of the wet mixture. The starting materials were not well crystallized, showing broadened peaks. We compared the peak positions and intensities of the XRD pattern against those for each individual component found in the inorganic crystal structure database (ICSD). As shown in Fig. 2b and c, most of the diffraction peaks can be well indexed by FePO$_4$ ($P3_21_1$, space group # 152) and Li$_2$CO$_3$ ($C12/c1$, space group # 15). Fig. 2a also shows four minor peaks (marked by asterisks) that we were not able to index, and they were believed to belong to the sugar added in the mixture, since these peaks disappeared during the solid state synthesis. Fig. 2d shows the peak positions and relative intensities of the expected product, LiFePO$_4$ ($Pnma$, space group # 62). The (200) peak of LiFePO$_4$ at about 1.2° can be used as the characteristic peak to index the existence of LiFePO$_4$. Similarly, FePO$_4$ can be specifically indexed by its strong (100) peak at about 1.41°, and Li$_2$CO$_3$ can be indexed using its (110) peak at about 1.48°. Fig. 2a also shows four extra diffraction peaks that are marked by asterisks and that are indexed by sucrose (C$_{12}$H$_{22}$O$_{11}$) (Card # 000-024-1977 in the Powder
Fig. 3 shows the contour plot of the in situ HEXRD patterns during the solid state synthesis of LiFePO$_4$ with the temperature increasing from 32 °C to 600 °C at a heating rate of 2 °C per minute. All peaks shifted slightly to a lower angle with the increase of the reaction temperature. This shift is primarily caused by the thermal expansion of the crystals and is not conclusive evidence for the phase transformation. The first clear indication of a phase change occurred during the initial heating up to 200 °C. Because the diffraction intensity from the sample is very low in the temperature range between 125 °C and 200 °C, detailed diffraction patterns at various temperatures from 32 °C to 205 °C are illustrated separately in Fig. 4. This figure clearly shows that the (200) peak of LiFePO$_4$ at about 1.2° appeared when the temperature was above 164°, and that the (102) peak of FePO$_4$ at 1.41° disappeared at about 134 °C. However, the (100) peak of Li$_2$CO$_3$ at 1.48° steadily decreased with the reaction temperature and did not completely disappear until 205 °C.

A possible explanation of this low diffraction intensity zone is as follows. The hydrated iron phosphate (FePO$_4$·$x$H$_2$O) started to lose its crystalline water as the temperature increased and formed nano-clusters of dehydrated FePO$_4$, leading to a rapid decrease of the peak intensity. After the normalizing the intensity of (200) peak, no obvious peak broadening was observed from 32 °C to 164 °C. Therefore, it was believed that FePO$_4$ was formed in amorphous state. When the temperature was above 164 °C, solid state reaction among amorphous FePO$_4$, Li$_2$CO$_3$, and sugar started led to gradual consumption of Li$_2$CO$_3$ and accumulation of LiFePO$_4$.

To confirm our speculation that the solid state reaction can occur at a temperature as low as 164 °C, we performed thermal gravimetric analysis (TGA) on a fresh sample in an Ar environment with a heating rate of 1 °C per minute. The weight loss and derivative weight loss of the sample are plotted in Fig. 5 as a function of the sample temperature. The top panel of Fig. 5 shows a slow but accelerated weight loss during the initial heating, which can be related to the dehydration of starting material as proposed above to explain the HEXRD patterns. After that, a sharp major reaction was observed at about 173 °C, leading to about 5% weight loss in 10 minutes. Combining the XRD patterns (Fig. 4) and the TGA data (Fig. 5), we can draw the conclusion that the reaction at this low temperature was related to the solid state reaction that formed LiFePO$_4$, and that the major weight loss was due to the loss of CO$_2$ from Li$_2$CO$_3$ and oxidation of sugar to balance the reduction of Fe(III) to Fe(II). We believe that the liquid sugar, whose melting point is about 155 °C, facilitated the diffusion of Li(I) into the FePO$_4$ nano-clusters, so that the solid state reaction occurred at such low temperature.

Fig. 3 Contour plot of XRD patterns collected during the solid state synthesis.

Fig. 4 XRD pattern of the material during the initial stage between room temperature and 200 °C, showing the progress of the solid state reaction.

Fig. 5 TGA analysis of starting material in Ar with a heating rate of 1 °C min$^{-1}$. 

Diffraction Files of the International Center for Diffraction Data).
The TGA data in Fig. 5 show a continuous multiple-step reaction from initial heating up to about 580 °C, after which the sample weight stabilized. The weight loss curve of Fig. 5 shows poor resolution between reactions, and hence the derivative curve versus sample temperature was calculated and is shown in the bottom panel. Besides the solid state reaction to form LiFePO$_4$, peaks at 173 °C, four minor broad peaks can be seen at 237 °C, 306 °C, 431 °C, and 503 °C. As later confirmed by ex situ XRD, the peaks at above 400 °C are associated with the reduction of LiFePO$_4$ by carbon and generate a mixture impurity of Li$_3$PO$_4$, Fe$_2$P, and Fe$_3$P. In the scope of this work, we were not able to collect conclusive evidence to index the carbonization reaction of sugar during the synthesis. The carbonization of sugar may have occurred in the temperature window between 200 °C and 350 °C. More experimental study in this temperature window needs to be conducted to confirm our speculation.

Fig. 6A shows the XRD pattern collected when the sample was heated up to 299 °C along with the simulated XRD pattern for LiFePO$_4$. An excellent fit was obtained by using the cell parameters shown in Fig. 6A, with very small fitting residue. The XRD pattern and its fit clearly indicate the formation of pure LiFePO$_4$ at low temperature. Rietveld refinement was carried out on XRD patterns collected in the temperature window from 200 °C to 600 °C (the XRD pattern not shown). The XRD pattern collected at 201 °C shows some minor peaks that cannot be fit by the simulated XRD pattern for LiFePO$_4$. These peaks represent some residues from the starting materials since the solid state reaction was not fully complete yet. Other XRD patterns collected from 251 °C to 501 °C were all well fitted, and their corresponding lattice parameters are shown in Fig. 6B. All three parameters showed a strong linear correlation with each other, and all increased linearly with the temperature. These trends are believed to be caused by the thermal expansion of the lattice, leading to the shift of the diffraction peaks to lower angles (see Fig. 2).

It was also found that the fitting residues increased steadily with the temperature above 400 °C, and most of the residue peaks are centered in a small 2θ range between 2.0° and 3.0°. Hence, a contour plot from the XRD patterns was prepared to show the diffraction peaks in this narrow 2θ range. As shown in Fig. 7, several peaks appeared when the temperature was above 400 °C, suggesting emergence of new impurities when synthesizing LiFePO$_4$ at high temperature. In addition, these weak peaks all appeared as left shoulders of major diffraction peaks of LiFePO$_4$, and the impurities also showed less thermal expansion than LiFePO$_4$. As a consequence, these weak peaks finally merged into the strong peaks of LiFePO$_4$ as the temperature increased, making them difficult to be observed. Our interest is to accurately index the formula and structure of the impurities. Therefore, the sample after the in situ experiment was further heated up to 650 °C and sintered at 650 °C for 10 hours to accumulate more impurities to ease the structural analysis. The ex situ XRD pattern was collected at room temperature to obtain better resolution between LiFePO$_4$ and the impurities. Fig. 8 shows the ex situ XRD pattern as well as its fit using four species: LiPO$_4$ (Pnnm), Fe$_2$P (P62m), Fe$_3$P (I4), and LiFePO$_4$ (Pnma). The experimental and simulated patterns agreed well, as shown in Fig. 8a. The XRD pattern shows no evidence of the FeP impurity that was proposed by Nazar et al.\cite{5}

Fig. 9 shows a simplified Li–Fe–P ternary phase diagram to help understand the results from the ex situ XRD pattern.\cite{16} In the starting material, 2% excess Li$_2$CO$_3$ was added to compensate for the potential loss of Li$_2$O during the high temperature reaction and to obtain stoichiometric LiFePO$_4$, shown at the center of the phase diagram (Fig. 9). Fig. 8 shows that the extra impurities detected are Fe$_2$P, Fe$_3$P, and Li$_3$PO$_4$, which are also labeled in Fig. 9. Also note in Fig. 9 that the composition of LiFePO$_4$ is sitting right outside the triangle formed by Fe$_2$P,
impurity is generally a mixture of several species, and the specific effect of each component on the electrochemical performance has not been conclusively quantified yet. It is of great importance to selectively synthesize LiFePO₄ cathode materials with different impurity contents to isolate and quantify the impact of each component, including the carbon coating. As mentioned above, it is difficult to carry out quantitative analysis on the impurities using in situ XRD data, and more research effort is needed to carry out ex situ experiments and to quantitatively establish the electrochemical performance and the evolution of impurities, as well as the carbon coating.

Conclusion

In situ high energy X-ray diffraction was deployed to study the phase evolution during the solid state synthesis of LiFePO₄. The solid state reaction occurred at a temperature as low as 173 °C, and impurities including Li₃PO₄, Fe₂P, and Fe₃P emerged when the synthesizing temperature was above 400 °C. We believe that this in situ technique is a powerful tool for studying the structure–property relationship of electrode materials and can be easily applied to other classes of materials.

Acknowledgements

Research at Argonne National Laboratory was funded by US Department of Energy, FreedomCAR and Vehicle Technologies Office. Argonne National Laboratory is operated for the US Department of Energy by UChicago Argonne, LLC, under contract DE-AC02-06CH11357. This work was also supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2009-C1AAA001-0093307).

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