

Thermostability of Li_xFePO_4

Joanna Dodd^{1,2}, Rachid Yazami^{1,3}, and Brent Fultz¹

¹California Institute of Technology
Mail Stop 138-78
Pasadena, CA 91125, USA

²Quallion LLC
12744 San Fernando Rd
Sylmar, CA 91342, USA

³CNRS-UMR 5631
38402 St Martin d'Hères, France

Lithium iron phosphate (LiFePO_4) is an attractive positive active material for rechargeable lithium ion batteries. It is especially favorable for its safety characteristics: it has very high thermostability and is non-toxic. It also has a theoretical capacity of 170mAh/g, with a working voltage of 3.5V vs Li/Li^+ [1]. The present work reports new results on the thermostability of Li_xFePO_4 at elevated temperatures and at different states of charge from $x = 0$ to 1.

Chemical delithiation enables the study of pure LiFePO_4 , without the addition of binder or conductor. This was performed by use of aqueous solutions composed of different amounts of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), depending on the desired amount of delithiation. As expected, the x-ray diffraction (XRD) measurements show that the starting material, LiFePO_4 , begins as the triphylite phase, which is an orthorhombic structure. As it is delithiated, a two-phase mixture results, with triphylite as well as another orthorhombic phase, heterosite, which is the phase for FePO_4 . Figure 1 is a plot of XRD spectra for several Li_xFePO_4 samples. The triphylite and heterosite phases can also be distinguished via Mossbauer spectrometry. The iron valency varies between the two phases, with Fe^{2+} in the triphylite phase, and Fe^{3+} in the heterosite phase. Figure 2 shows the Mossbauer spectra of the same series of samples as shown in Figure 1. The phase fractions determined by XRD and Mossbauer spectrometry results were in good agreement with each other, and with the chemical compositions measured by intercoupled plasma (ICP) analysis, assuming a two-phase mixture of triphylite and heterosite.

Li_xFePO_4 is much less reactive under heating, compared with other more conventional cathode materials, such as LiCoO_2 . In fact, even a fully charged Li_0FePO_4 cathode, in contact with electrolyte, only results in a small exothermic peak at around 250-350°C for a scan from 100 to 400°C [2,3]. In the present work, the stability of Li_xFePO_4 for various values of x was investigated, by heating samples in an argon-filled tube furnace, and then performing XRD and Mossbauer analysis. The fully lithiated material, LiFePO_4 , is very stable, even up to 800°C. However, delithiated samples were not as stable. By heating to 500°C, the FePO_4 heterosite phase began to change into a new phase, $\text{Fe}_7(\text{PO}_4)_6$, which is a triclinic structure. For intermediate x , between 0 and 1, upon heating, the composition is relatively unstable, and generally tends towards either triphylite or heterosite, depending upon which was dominant initially.

Phase transformations upon heating, as well as the nature of these changes will be discussed. This study of phase formation is important to the understanding of the thermodynamics of this cathode system.

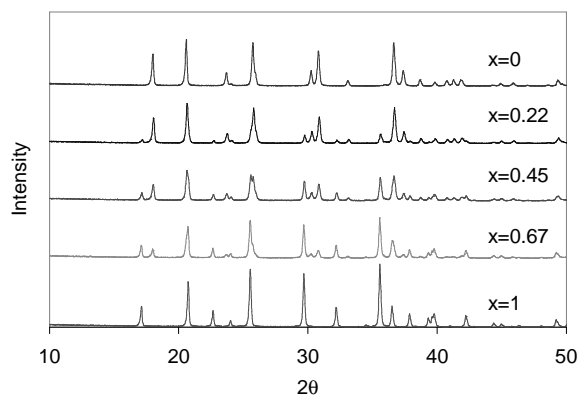


Figure 1. XRD spectra obtained from samples of various lithiation, Li_xFePO_4 for $x = 0$ to 1.

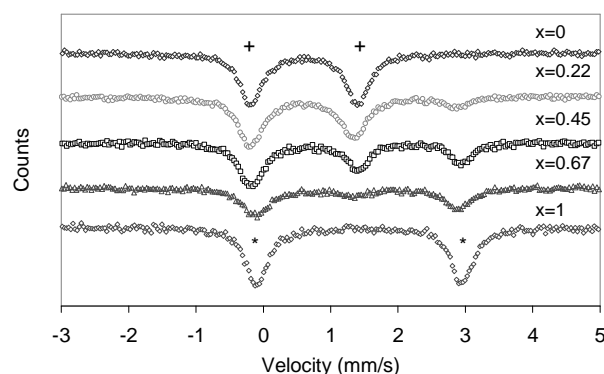


Figure 2. Mossbauer spectra of Li_xFePO_4 for $x = 0$ to 1. Fe(II) is the valency of LiFePO_4 (*), while Fe(III) is the valency of the fully delithiated state (+).

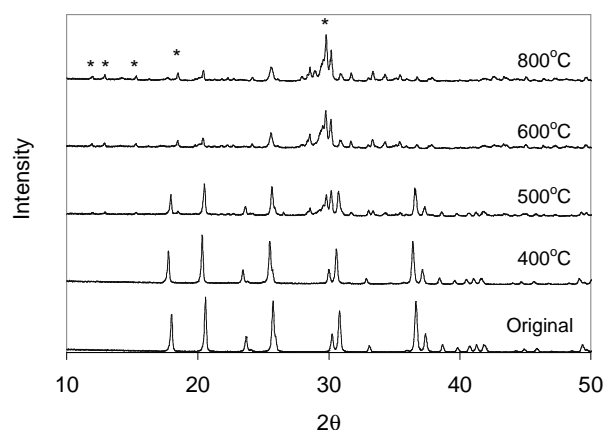


Figure 3. XRD of FePO_4 samples. Shown are spectra for a sample with no heat treatment, as well as samples heat treated to 400, 500, 600 and 800°C. Peaks from the phase $\text{Fe}_7(\text{PO}_4)_6$ are indicated by asterisks.

References

1. Padhi AK, Nanjundaswamy KS, Goodenough JB. *J. Electrochem. Soc.* **144** (1997) 1188
2. Takahashi M, Tobishima S, Takei K, Sakurai, Y. *Solid State Ionics* **148** (2002) 283.
3. MacNeil DD, Lu Z, Chen Z, Dahn, JR. *J. Power Sources* **108** (2002) 8.