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In Situ XRD and XAS of Carbon Coated Lithium Iron Phosphate Cathode Materials

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Beamline(s): X7A, X18B

Introduction: Lithium iron phosphate is a potential candidate as cathode material for rechargeable lithium batteries because of its high energy density, low raw materials cost, environmental friendliness and safety. The main limitation, for such applications, has been its poor intrinsic electronic conductivity. This limitation can be overcome to a large extent by coating the primary lithium iron phosphate particles with carbon. We have utilized in situ x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) to study the structural and electronic properties of carbon coated LiFePO_4 during electrochemical cycling. The combination of XRD and XAS is a very powerful technique for the study of electrode processes. XRD can identify phase changes during electrochemical cycling. XAS gives information on the chemistry and redox processes on the transition metal atoms in the cathode.

Results: Figure (1) shows the in situ XRD spectra obtained during electrochemical delithiation at $\sim C/12$ rate. The bottom scan was obtained at the beginning of charge while the last scan was obtained at the end of charge. It can be seen that as charging progresses new peaks corresponding to the orthorhombic FePO_4 develop at the expense of the LiFePO_4 phase. These measurements suggest a first order phase transformation from LiFePO_4 to FePO_4 on delithiation. At the end of charge more than 80% of the LiFePO_4 is converted to FePO_4 . Figure (2) shows the Fe K-edge near edge spectra obtained during charge at $\sim C/12$ rate. The positive edge shift clearly shows that on delithiation charge compensation is obtained by oxidation of Fe (II) to Fe (III). Also, a single set of "isosbestic points" is evident. Principal component analysis (PCA) reveals that this set of spectra can be well represented by two primary components, in agreement with a first order phase transition involving the LiFePO_4 and FePO_4 phases.

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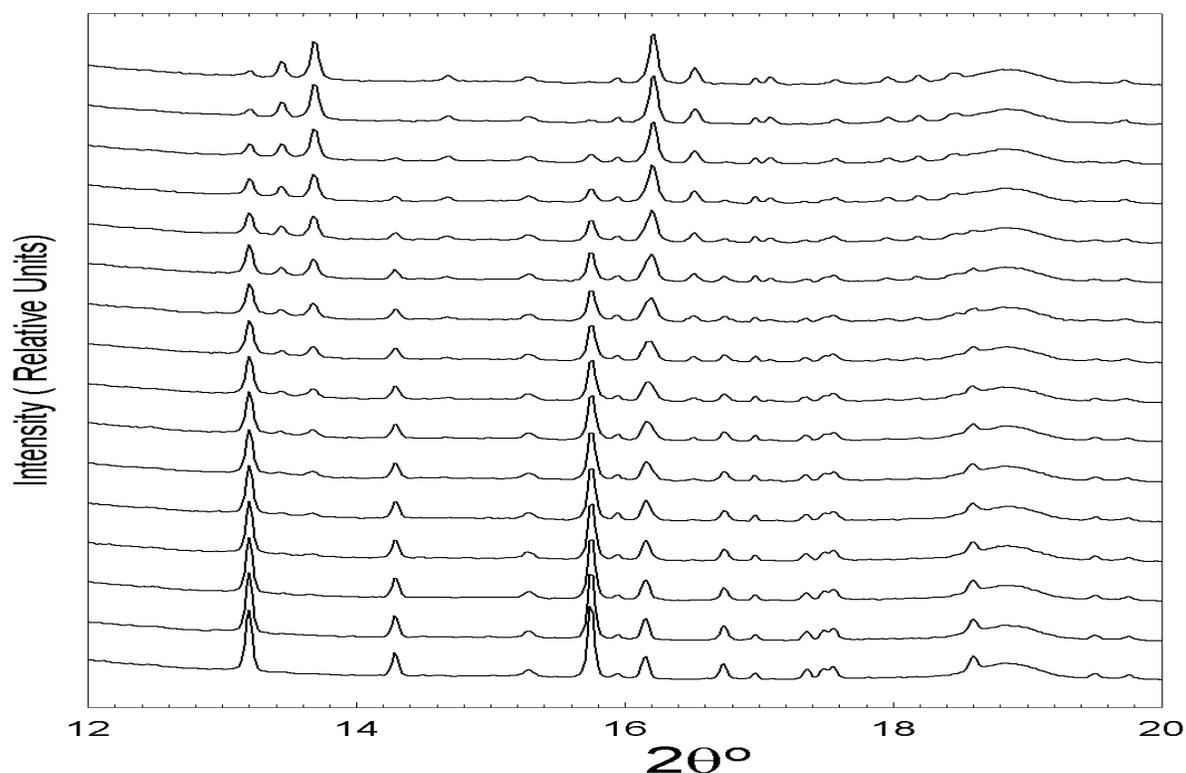


Figure 1: In situ XRD spectra illustrating the conversion of LiFePO_4 to FePO_4 during electrochemical delithiation. The data were obtained ($5^\circ < 2\theta < 35^\circ$) using monochromatic x-rays ($\lambda = 0.6907 \text{ \AA}$). Only the data in the $12^\circ < 2\theta < 20^\circ$ range is shown for clarity. The bottom scan was taken at the start of delithiation, while the top most was obtained at the end of delithiation. The first order phase transformation from the LiFePO_4 phase to FePO_4 phase is clearly evident.

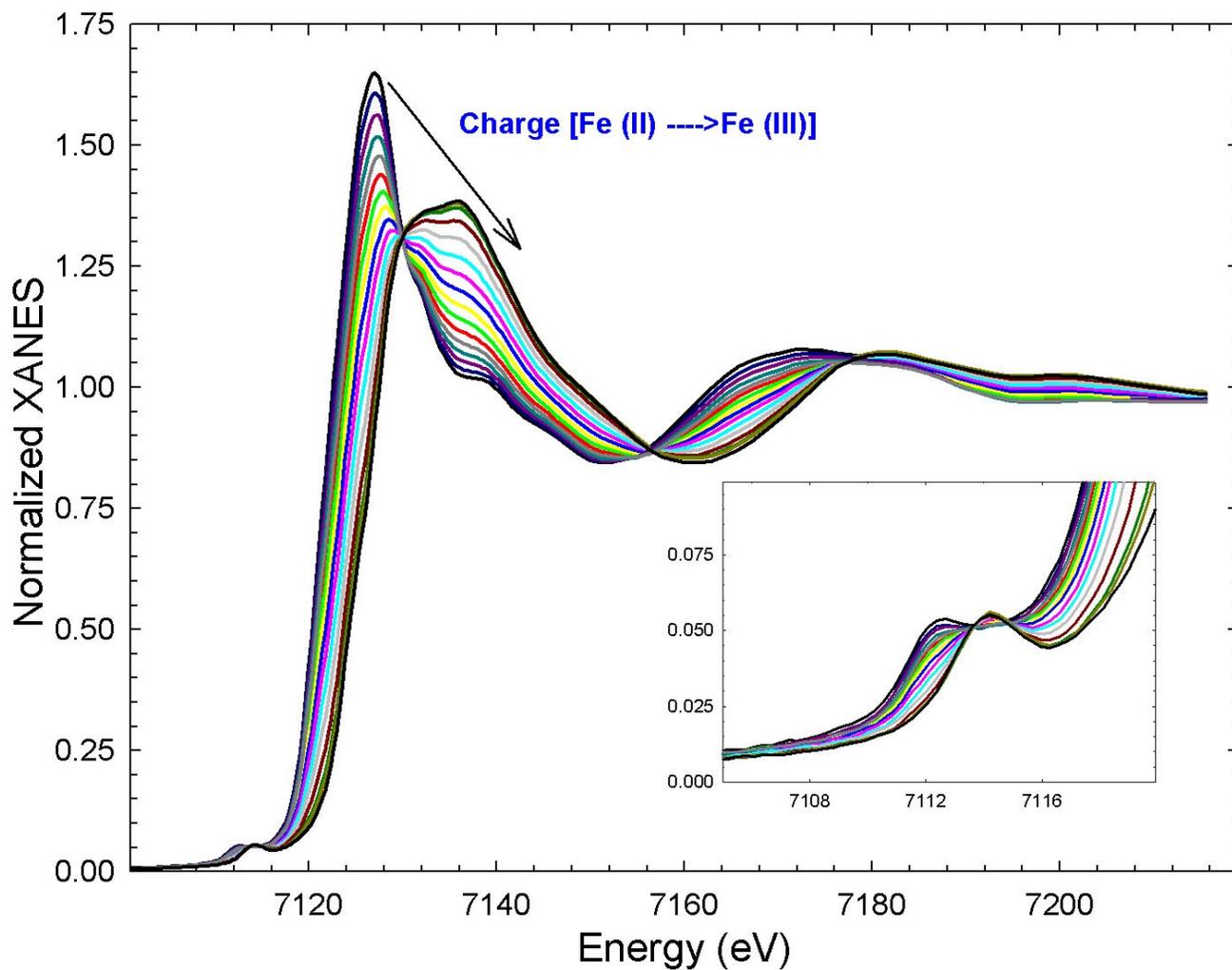


Figure 2: In Situ Fe K-edge spectra obtained during electrochemical delithiation. Every second scan is shown for clarity. PCA reveals the presence of only two primary components and is consistent with a first order phase transformation involving the LiFePO_4 and FePO_4 phases. The pre-edge region is enlarged in the inset.