$LiFePO_4$ and Li^+ addition rate during synthesis: Combining X-ray diffraction and spectroscopy techniques to determine average and local structure

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$LiFePO_4$ (LFP) as a cathode material in lithium-ion batteries has a number of advantages including a long cycle life, a long calendar life and can be used at high discharge currents. A low cost, low energy hydrothermal synthetic route is being investigated where homemade Teflon bombs are used in an oven at 120ºC to synthesise LFP. During synthesis an aqueous LiOH solution is added dropwise to a $FeSO_4$–H_3PO_4 solution. All solutions are constantly purged with nitrogen during this step to prevent any oxidation. Interestingly it was determined that the rate at which the Li^+ solution was added to the Fe^{2+} solution (while being stirred at a constant speed) influenced the final product. The addition rate was set to one drop every 1, 2, 3, 4 and 5 seconds. If the Li^+ was added too slowly a mixture of phases (LFP and Li_3PO_4) was formed and when it was added too fast a completely different final phase was formed. In the latter case no LFP was identified using PXRD, but Raman spectroscopy (RS) showed that non-crystalline LFP was present in the sample together with other phases. A range of different techniques have been combined to probe the effect of the different addition rates on the local and average environments. It was determined that the 3sec addition rate was the optimum rate. Synchrotron X-ray diffraction (SXRD) with Rietveld refinement was used to characterize the average structures of the different environments **(Figure 1)**. Mössbauer spectroscopy (MS) was used to probe the effect of Li^+ addition on the local environment. Although no impure phases were identified using SXRD in the samples synthesised with the optimum addition rate, MS indicated that there was amorphous phases present. MS also showed that there was more than one Fe environment present in the sample. The major phase is Fe^{2+} in a distorted octahedral environment ($LiFePO_4$). The other three contributions to the total Fe in the sample are due to either structural defects, distortions or disorder [1]. X-ray absorption spectroscopy (XAS), in particular extended X-ray absorption fine structure (EXAFS) **(Figure 2)** used to determine what the effect of the different addition rates on the local structure is.

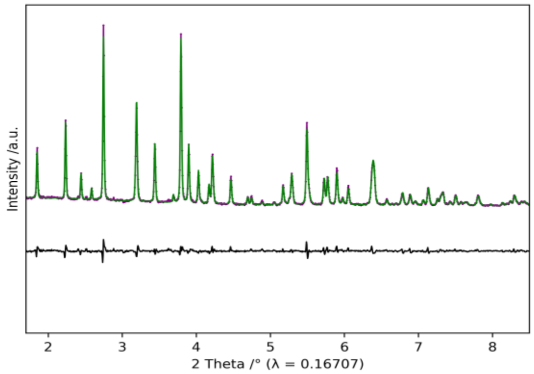

Figure 1. SXRD with Rietveld refinement of the optimum addition rate showing a single phase.

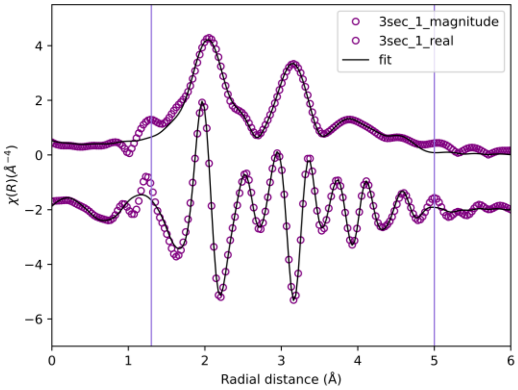

Figure 2. Comparison between the experimental and the theoretical fit of the magnitude and real space Fourier Transform for the 3sec sample.

[1] Amisse, R. *et al.* Singular Structural and Electrochemical Properties in Highly Defective $LiFePO_4$ Powders. *Chem. Mater.* **27**, 4261–4273 (2015).

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