

Synthesis of LiFePO₄ via a Novel Carbon-Free
Precipitation Method

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Abstract

Lithium iron phosphate (LiFePO₄) is a promising alternative cathode material for LiCoO₂¹⁻², which applications are limited by resource availability and safety issues³. However, the full potential of the material is difficult to achieve due to its limited electrical conductivity and low rate of Li⁺ ion diffusion that together may limit the battery performance.

Two broad strategies have been employed to increase the electrical conductivity and improve the Li⁺ diffusion kinetics. One strategy is to decrease the LiFePO₄ particle size to nanometre levels which consequently decreases the diffusion length, for both electrons and Li-ions in the phosphate structure. The other strategy is to manufacture LiFePO₄ particles coated with a conductive phase, such as carbon, which improves the electronic contact between the particles⁴⁻⁷. However, the carbon in LiFePO₄ phase appears to modulate not only the electric conductivity but also the crystallite sizes and thus reduces the distance for Li⁺ transport in the phosphate structure. Furthermore, carbon may improve the phase purity of the final product because during high temperature synthesis, carbon acts as a reducing agent and thus minimizes the likelihood of oxidation of Fe²⁺ to Fe³⁺. Therefore, the addition of some form of carbon during synthesis may have three synergistic effects on the electrochemical performance of the cathode material; yields phase-pure LiFePO₄, enhances its electronic conductivity and retards the crystallite growth, which in turn improves Li⁺ diffusion rate. It is worth noting that not all carbons are equal. For example, if sp³-bonded carbon coatings are formed *in situ* during the pyrolysis of the carbon containing precursors used for the synthesis of LiFePO₄ then the electron conductivity may not increase. However, these carbons may have a beneficial effect on the material properties because they may precipitate at the crystallite interfaces, limit the crystal sizes of the phosphate particles and hence decrease the Li⁺ diffusion path-lengths. Preferably, the carbon coating should contain mainly sp² bonded carbons with delocalized π electrons in order to improve the electronic conductivity and modulate crystallite sizes of the phosphate product. Despite aforementioned advantages, the role of the carbon on the electrochemical performance of LiFePO₄ is yet to be fully understood.

It is therefore important to investigate the effect of various nanocarbons in particular sp² and sp³ bonded on the crystallite size, particle morphology and electrochemical performance of phosphate product. However, the reported methods of solution-derived LiFePO₄ always contain some form of residual carbon derived either from the carbon containing solvent and/or from the precursor materials. The aim of this work is to develop a new protocol for LiFePO₄ synthesis by precipitation from carbon-free precursors in carbon-free aqueous environment and to investigate the crystallization behaviour and particle morphology of the LiFePO₄ phase. For this purpose, a new co-precipitation method to

synthesize LiFePO₄ using, LiOH·H₂O, NH₄H₂PO₄ and FeSO₄·7H₂O as starting materials has been developed. The precipitation sequence and methodology as well as the role of intermediates *en route* to LiFePO₄ and the phase purity of LiFePO₄ in both argon and mixed argon/hydrogen atmospheres has been investigated in detail using, thermal analysis XRD, SEM, FTIR and Raman spectroscopic techniques. A mechanism of formation of phase-pure carbon free LiFePO₄ is proposed and the role of synthesis atmosphere on the phase transformations and the effect of evolving gaseous species on the likelihood of oxidation of Fe²⁺ to Fe³⁺ are discussed. The optimal synthesis conditions (temperature, time and atmosphere) are also summarized.

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