



## Synthesis of microcrystalline LiFePO<sub>4</sub> in air



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### ABSTRACT

In this paper a method for the synthesis of nano-sized microcrystalline LiFePO<sub>4</sub>, which is particularly suitable for the production of high energy density electrodes, was developed. The method is characterized by the fact that it provides for the solid state reaction of anhydrous FePO<sub>4</sub> with lithium acetate. The method is easy to implement and, above all, does not involve the need to operate in a controlled environment, since the material may be synthesized directly in air by mixing anhydrous FePO<sub>4</sub> with lithium acetate. This latter is simultaneously used as a reducing and lithiating agent. Anhydrous FePO<sub>4</sub> is prepared by dehydrating iron phosphate hydrate, which is in turn prepared by means of the spontaneous precipitation thereof from a solution of FeSO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>, using H<sub>2</sub>O<sub>2</sub> as the oxidizing agent. The FePO<sub>4</sub> used as the precursor is characterized by thermogravimetry and its morphology is investigated by SEM microscopy. The structure of LiFePO<sub>4</sub> is characterized by X-Ray diffraction and its morphology investigated by SEM microscopy. Finally, the LiFePO<sub>4</sub> is used to fabricate composite electrodes that are electrochemically tested in lithium cells.

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### 1. Introduction

Lithium iron phosphate (LiFePO<sub>4</sub>) is emerging as one of the most interesting cathode materials for the production of lithium-ion batteries. LiFePO<sub>4</sub> can be used not only in connection with consumer electronics products, but also in connection with other areas in which lithium batteries have not yet reached their full commercial potential, such as, for example, in the field of stationary electricity accumulation. LiFePO<sub>4</sub> may be synthesized with various methods and, consequently, various synthetic procedures may be found in literature, which include: 1) solid state reaction [1]; 2) sol-gel [2]; 3) hydrothermal synthesis [3]; 4) co-precipitation [4], and 5) heating with a microwave oven [5] and various other methods. Many of these methods use FePO<sub>4</sub> as a precursor. The use of FePO<sub>4</sub> as a precursor gives rise to two possible synthetic routes. The first consists in the reduction and simultaneous lithiation of FePO<sub>4</sub>. The second consists in a two-step process, in which the first step is the reduction of FePO<sub>4</sub> and the second is the lithiation thereof. A typical reagent used for the reduction and simultaneous lithiation of FePO<sub>4</sub> is lithium iodide (LiI). Prosini et al. [6] first prepared LiFePO<sub>4</sub> by using LiI. The effect of LiI being used for improving the electrochemical performance of LiFePO<sub>4</sub> has been recently studied by Kuo et al. [7]. Shiratsuchi et al. [8] have also carried out the reduction and simultaneous lithiation of FePO<sub>4</sub> with LiI in acetonitrile. The FePO<sub>4</sub> precursor was, in turn, synthesized by starting from an equimolar aqueous suspension of iron powder and P<sub>2</sub>O<sub>5</sub>.

A second possibility for obtaining LiFePO<sub>4</sub> by commencing from FePO<sub>4</sub> consists in the use of two different compounds, one of which is a reducing agent and the other a lithium source. Studies to this effect may be found in literature, which have been conducted by using different reducing agents and lithium sources. For example, amorphous LiFePO<sub>4</sub> has been obtained by the chemical reduction and subsequent lithiation of FePO<sub>4</sub> by means of the use of ascorbic acid as the reducing agent and lithium acetate as a source of lithium [9,10]. Chen et al. [11] prepared a LiFePO<sub>4</sub>/C composite by heating a mixture of resorcinol-formaldehyde as a reducing agent and lithium acetate dihydrate as a lithium source in nitrogen atmosphere. Zheng et al. [12] prepared amorphous LiFePO<sub>4</sub> via the lithiation of FePO<sub>4</sub>·xH<sub>2</sub>O by using oxalic acid as a reducing agent and lithium carbonate as a lithium source. Mi et al. [13] used polypropylene as the reducing agent (and carbon source) in a solid state reaction for the carbo-thermal production of LiFePO<sub>4</sub>, with lithium carbonate as the lithium source. Li et al. [14] used, instead, citric acid and lithium carbonate. Zhao et al. [15] used glucose and lithium acetate, while Wang et al. [16] used sucrose and lithium nitrate. Yao et al. [17] used various lithium salts including lithium carbonate, lithium hydroxide, lithium acetate and lithium citrate as secondary lithium sources for the synthesis of lithium iron phosphate/carbon composites with cheap iron sources in the form of Fe and FePO<sub>4</sub>.

All these synthesis methods have been carried out under inert or reducing atmosphere. Only Zhang et al. [18] prepared LiFePO<sub>4</sub> in air by starting from a mixture containing PEG 20000 as the carbon source, lithium carbonate as the lithium source, ammonium phosphate as the phosphate source and iron (II) oxalate as the iron source.

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In this paper is described the solid state synthesis of  $\text{LiFePO}_4$ , commencing from  $\text{FePO}_4$ , as well as the simultaneous use of lithium acetate used both as a reducing agent and a lithium source. The main purpose of this work is to produce the material by starting from inexpensive precursors and using a method which is easy to implement and which, above all, does not involve the need to operate in a controlled environment, since such synthesis may be carried out directly in air. This result has been achieved by perfecting a process for the preparation of microcrystalline  $\text{LiFePO}_4$  that is based on the preparation of a mixture of amorphous and anhydrous  $\text{FePO}_4$  with lithium acetate, as well as in the subsequent heat treatment for the purpose of obtaining microcrystalline  $\text{LiFePO}_4$ . Such material has been found to be particularly suitable for using as a cathode in lithium batteries.

## 2. Experimental

### 2.1. Material preparation

De-ionized water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) produced by a Milli-Q water production system (Millipore, Bedford, MA) was used to prepare all the solutions. Ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Aldrich, ACS reagent, >99.0%), phosphoric acid ( $\text{H}_3\text{PO}_4$ , Carlo Erba analytical grade), lithium acetate dihydrate ( $\text{LiCOOCH}_3 \cdot 2\text{H}_2\text{O}$ , Aldrich, ACS reagent, >99.0%), sodium hydroxide (NaOH, Carlo Erba, analytical grade), hydrogen peroxide 50% weight (Reagent grade, Ashland Chemical Italiana) were used as received.  $\text{FePO}_4 \cdot 3\text{H}_2\text{O}$  was synthesized by spontaneous precipitation from an 1:1 M aqueous solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4$ , using 50 wt.% hydrogen peroxide as the oxidizing agent. Anhydrous  $\text{FePO}_4$  was obtained by heating hydrated  $\text{FePO}_4$  ( $\text{FePO}_4 \cdot 3\text{H}_2\text{O}$ ) in a tubular furnace at  $300^\circ\text{C}$  under air for 15 min. Crystalline  $\text{LiFePO}_4$  was obtained by heating a 1:1 M mixture of anhydrous  $\text{FePO}_4$  and lithium acetate in a tubular furnace at  $550^\circ\text{C}$  under air for 30'. This time was chosen because it allows to obtain a crystalline material without the concomitant occurrence of oxidative processes. After the heat treatment, the material was allowed to cool to room temperature. In a typical experiment, a solution of sodium hydrogen phosphate was prepared by adding a solution formed by dissolving 8.06 g of sodium hydroxide [ $\text{NaOH}$ , MW = 40, 0.2015 m] in 50 ml of water to a solution containing 19.72 g of phosphoric acid [MW = 98, 0.2012 m] in 500 ml. The solution was allowed to cool at room temperature and then it was added with 55.70 g of ferrous sulfate heptahydrate [ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , MW = 278, 0.2003 m]. The volume of the solution was brought up to 800 ml with deionized water. The solution was filtered to remove any precipitate. 10 ml of hydrogen peroxide at 50 wt.% d = 1.197 g / ml (equal to 11.97 g of solution, 5.985 g of  $\text{H}_2\text{O}_2$ , MW = 34, 0.176 m) diluted with 20 ml of water was added dropwise to the solution to oxidize the iron (II) to iron (III). The solution was left under vigorous stirring for 1 h, then left to settle. The solution was filtered and the solid was taken up with 300 ml of water and placed under stirring for a few minutes and filtered again. Further experimental details can be found in prior publications [6–19]. The solid was allowed to rest several days in the dry room. After this period of time the weight of the solid was 35.33 g. 1.6 g of the material [ $\text{FePO}_4 \cdot 3\text{H}_2\text{O}$  MW = 204.8, 7.8 mm] was placed in a crucible and heated at  $300^\circ\text{C}$  for 1 h. After heating, the weight dropped down to 1.16 g. [ $\text{FePO}_4$  MW = 150.8, 7.7 mm]. The material was crushed in a mortar with 0.904 g of lithium acetate dihydrate ( $\text{LiCOOCH}_3 \cdot 2\text{H}_2\text{O}$ , MW = 102, 8.8 mm, ratio Li / Fe = 1.17). The mixture was placed in an alumina crucible. The crucible was covered with an aluminum foil and inserted in a tubular furnace, which in turn was placed in an oven preheated to  $550^\circ\text{C}$ . The tubular furnace was a quartz tube of 4 cm in diameter and 50 cm in length. The quartz tube was inserted in the oven for about 2/3 of its length. The reaction was carried out for 30 min under stagnant air. 1.22 g of a light gray product were obtained after cooling [ $\text{LiFePO}_4$ , MW = 157.8, 7.7 mm, yield = 100%].

### 2.2. Thermal characterization

Thermal stabilities were verified in air and nitrogen using a simultaneous TG-DTA (Q600 SDT, TA Instruments) equipped with the Thermal Solution Software (version 1.4). The temperature was calibrated using the nickel Curie point as the reference. The mass was calibrated using ceramic standards provided with the instrument. High purity aluminum oxide was used as the reference material. Open platinum crucibles (cross-section =  $0.32 \text{ cm}^2$ ) were used to contain the samples. The experiments were performed on 10–12 mg samples that were stored, handled, and weighed in a dry-room. The thermal stability was investigated by heating the samples from room temperature up to  $850^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . The onset temperature was calculated by thermal analysis software (Universal Analysis version 2.5) as the intersection between the extrapolated baseline weight and the tangent through the inflection point of the weight vs. temperature curve.

### 2.3. Scanning Electron Microscopy

The morphology of the materials was evaluated by a AURIGA, CrossBeam Workstation dual column Focused Ion Beam – Secondary Electron Microscope (SEM).

### 2.4. XRD characterization

Phase identification was performed by XRD analysis using a Rigaku MiniFlex diffractometer with  $\text{Cu K}\alpha$  radiation. The Scherrer's formula was used to evaluate the crystallite dimensions.

### 2.5. Electrochemical characterization

The active material and the carbon (Super P, MMM Carbon) were weighted in a 4.4:1 ratio and mixed in a mortar. Teflon, used as a binder, was added and the resulting blend was mixed in the mortar for obtaining a plastic like material. Composite cathode tapes were made by roll milling the plastic material to reduce the thickness to about  $150 \mu\text{m}$ . The final compositions of the cathode tape was: active material 75 wt.%, carbon 17 wt.% Teflon 8 wt.%. The electrodes were punched in form of disks with a diameter of 8 mm. The electrode weights ranged from 12.0 to 13.0 mg corresponding to an active material mass loading of  $18.0\text{--}19.5 \text{ mg cm}^{-2}$ . The capacity of the electrodes was approximately 1.53–1.65 mAh. The electrodes were assembled in sealed cells formed by a polypropylene T-type pipe connector with cylindrical stainless steel (SS316) current collectors. A lithium foil was used both as anode and reference electrode and a glass fiber as a separator. The cells were filled with ethylene carbonate/diethyl carbonate 1:1  $\text{LiPF}_6$  1 M electrolyte solution (Merck, battery grade). The cycling tests were carried out automatically by means of a battery cycler (Maccor 4000). Material handling, composite cathode preparation, cell assembly, test and storage were performed in a dry room (R.H. < 0.2% at  $20^\circ\text{C}$ ).

## 3. Results and discussion

### 3.1. Material preparation

Anhydrous iron (III) phosphate is prepared by dehydrating iron phosphate hydrate, which is in turn prepared by means of the spontaneous precipitation thereof from a solution of iron (II) sulfate and sodium phosphate, using hydrogen peroxide as the oxidizing agent (reaction 1). The sodium hydrogen sulfate, that forms during the double exchange reaction as shown in Eq. (1), has a concentration of about 3 g/100 mL, less than the solubility equilibrium (28 g/100 mL at room temperature). For this reason it should be completely dissolved in water and easily removed by filtration. Nevertheless a small amount of sulfur is found in the precipitate as confirmed by EDS analysis. The presence of sulfur in the precipitate can be explained considering that a small amount of

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