

# Comparison between different $\text{LiFePO}_4$ synthesis routes and their influence on its physico-chemical properties

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## Abstract

$\text{LiFePO}_4$  powders were synthesized under several different conditions (solid state reactions at high temperatures, co-precipitation in aqueous medium, hydrothermal synthesis or mechanochemical activation). The samples were characterized by X-ray diffraction (XRD), chemical titration and their electrochemical performance were investigated in terms of cycling behavior. We also report, in this work, the benefit of introducing an electronic conductor precursor (typically a sucrose) during or after the synthesis in order to overcome the poor charge transfer associated with the lithium iron phosphate.

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## 1. Introduction

Since the pioneering works of Padhi et al. [1], mixed orthophosphates  $\text{LiMPO}_4$  (M: Mn, Fe, Co, Ni) isostructural to olivine are intensively studied as lithium insertion compounds for lithium batteries [2–6]. Indeed, their theoretical specific capacity (170 mAh/g) combined with a discharge voltage between 3.4 and 4.8 V versus  $\text{Li/Li}^+$ , lead to very high energy densities. Among these materials,  $\text{LiFePO}_4$  is one of the most promising compounds due to the inexpensive price of the starting materials, the relative lack of toxicity, and the intermediate voltage value (3.45 V versus  $\text{Li/Li}^+$ ) at which it operates.

At this time, the main obstacle for reaching the theoretical performances of  $\text{LiFePO}_4$  at ambient temperature is its very low electronic conductivity. Two possible means to overcome this major problem were recently explored:

- (i) the synthesis of a  $\text{LiFePO}_4$ /electronic conductor composite compound,
- (ii) the achievement of a small and homogeneous particle size distribution.

To succeed in preparing such fine and homogeneous particles of lithium iron phosphate, we have performed several syntheses, under different conditions: solid state reactions, co-precipitations in aqueous medium, hydrothermal conditions

with various reactants and mechanochemical activations. We present here the results obtained upon optimization of each procedure.

## 2. Experimental

X-ray diffraction (XRD) experiments were performed with a Siemens D5000 diffractometer using  $\text{Cu K}\alpha$  radiation. The pictures of our materials were obtained with a Philips XL 30 scanning electron microscope. The thermal analysis (TGA/DSC) was made with a Netzsch STA 409 analyzer. The electrochemical studies were carried out in two electrode cells.

Thin film electrodes were manufactured for electrochemical testing of the samples by casting on an aluminium current collector a *N*-methylpyrrolidone (NMP) slurry of the  $\text{LiFePO}_4$  active material (85 wt.%) mixed with a carbon (Super P—MMM Carbon) conductive additive (10 wt.%) and a polyvinylidene fluoride (Solef 6020—Solvay) binder (5 wt.%).

These film-type  $\text{LiFePO}_4$  electrodes were assembled in electrochemical cells with lithium metal as counter electrode separated by a polypropylene felt imbedded by an electrolyte consisting of a 1 M  $\text{LiPF}_6$  solution in an ethylene carbonate–diethyl carbonate (EC–DMC, 1/1) mixture.

The assembly of the cell prototypes was carried out in a dry glove box, under argon. The cathode performance were investigated in terms of charge–discharge curves and cycle life. These cycling tests were run by an Arbin instrument.

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### 3. Results and discussion

The solid state reaction was performed using stoichiometric amounts of iron(II) oxalate  $\text{FeC}_2\text{O}_4$ , di-ammonium hydrogenophosphate  $(\text{NH}_4)_2\text{HPO}_4$ , and lithium carbonate  $\text{Li}_2\text{CO}_3$ . The reaction was carried out under inert atmosphere to prevent the formation of  $\text{Fe}^{3+}$  compounds as impurities. The intimately ground mixture of the starting materials was first decomposed at  $250^\circ\text{C}$  for 3 h in order to drive away the gases. The mixture was then reground and put back in the furnace at  $550^\circ\text{C}$  for 12 h under argon before being cooled slowly to room temperature.

The XRD diagram (Fig. 1b) shows parasitic peaks due to impurities such as iron(II, III) pyrophosphates (or phosphides when the thermal treatment is made above  $700^\circ\text{C}$ ). The use of a reductive gas like  $\text{Ar} + 3\% \text{H}_2$  does not reduce the amount of impurities, since the complete reduction of iron(III) into iron(II) occurs parallel to the reduction of phosphates entities into phosphides. Pure  $\text{LiFePO}_4$  phase was never observed when starting from other Fe(II) sources (acetate, sulphate, ...). In fact, whatever the iron(II) salt used, thermal

treatments, under argon above  $500^\circ\text{C}$ , lead systematically to the formation of crystallized Fe(III) species. This synthetic route is not convenient for the preparation of pure  $\text{LiFePO}_4$ .

The co-precipitation technique consisted of adding lithium hydroxide into a solution containing ferrous ions and phosphoric acid. The precipitate obtained was washed with water, dried under vacuum and heat-treated at  $550^\circ\text{C}$  for 12 h under inert atmosphere.

The XRD diagram (Fig. 1c) shows the presence of several poly-phosphate entities (such as lithium pyrophosphate,  $\text{Li}_4\text{P}_2\text{O}_7$ ) probably due to the use, for this synthesis, of commercial phosphoric acid which could be already polymerized as follows:  $2\text{H}_3\text{PO}_4 \rightarrow \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$  and gives, in lithium-rich medium, the low temperature form  $\text{Li}_4\text{P}_2\text{O}_7$ . The mixture could be treated for 5 days by an aqueous  $1 \text{ mol l}^{-1}$  solution of acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ), which dissolves  $\text{Li}_4\text{P}_2\text{O}_7$ , but this treatment makes the procedure longer and more laborious [7]. This route is not convenient for the preparation of pure  $\text{LiFePO}_4$ .

$\text{LiFePO}_4$  was also obtained by hydrothermal synthesis using either fresh iron(II) phosphate  $\text{Fe}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$  and

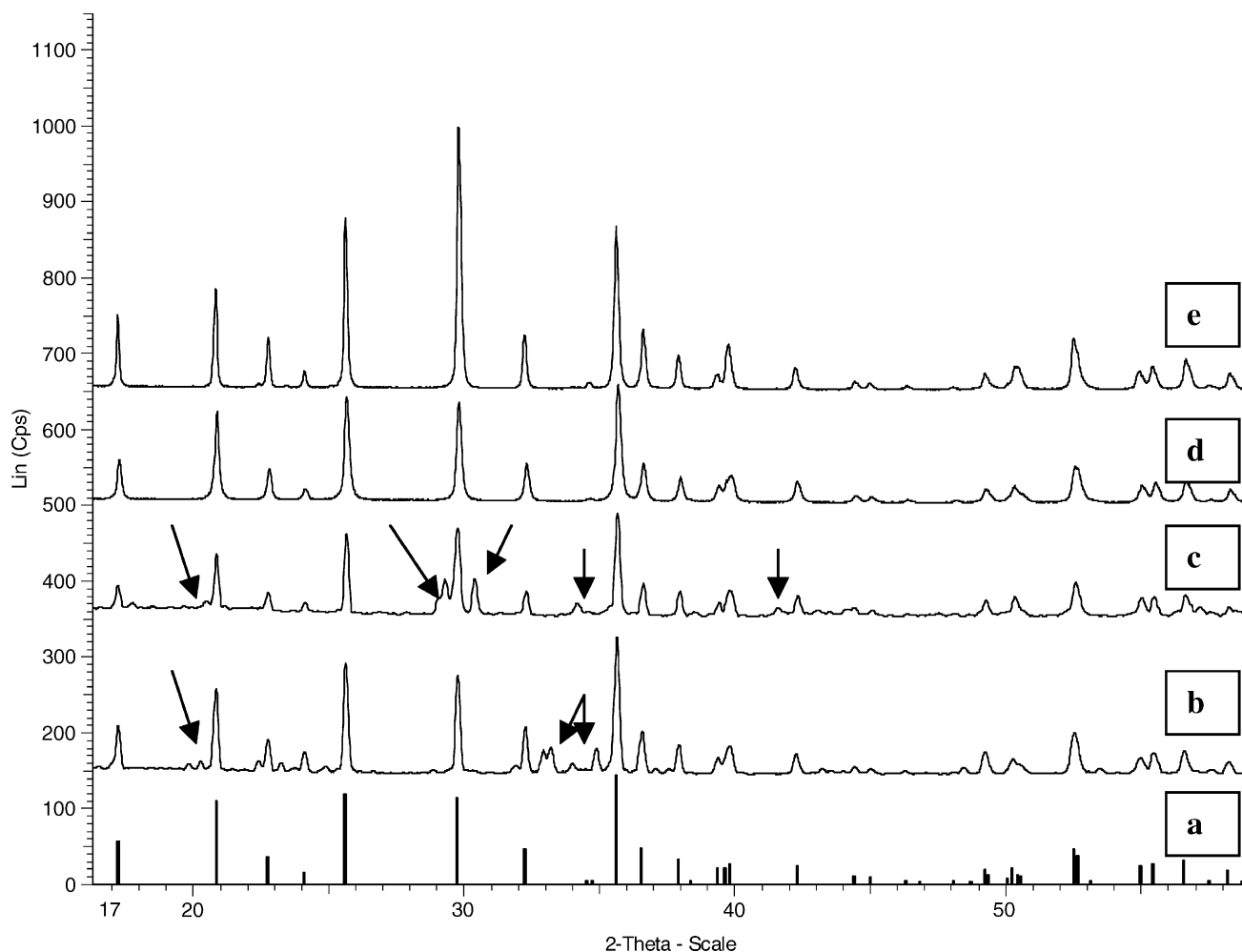


Fig. 1. XRD patterns of (a) theoretical  $\text{LiFePO}_4$ ; (b) solid state  $\text{LiFePO}_4$ ; (c) co-precipitation  $\text{LiFePO}_4$ ; (d) HY1 or HY2  $\text{LiFePO}_4$  and (e) mechanochemical  $\text{LiFePO}_4$  after heat treatment at  $600^\circ\text{C}/15 \text{ min}$  (the arrows point out peaks due to impurities).

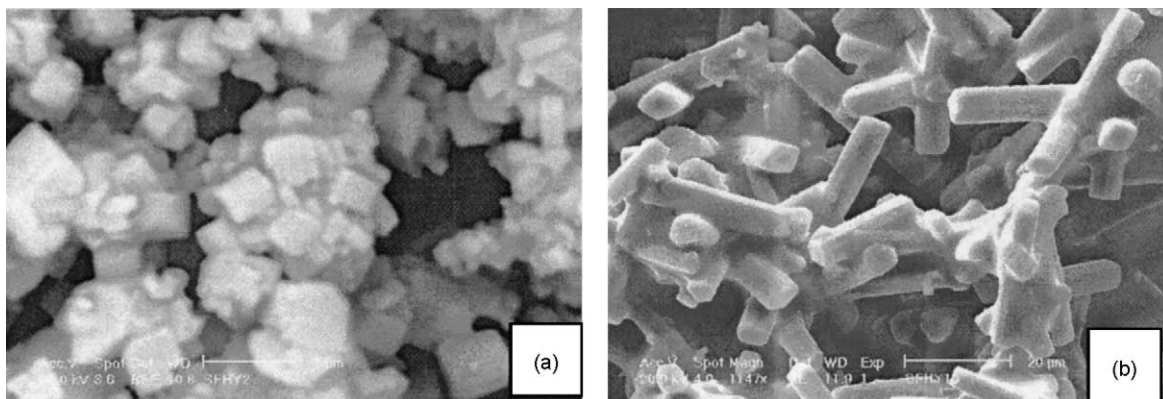


Fig. 2. SEM pictures of hydrothermal  $\text{LiFePO}_4$  obtained: (a) via HY1 and (b) via HY2.

tri-lithium phosphate  $\text{Li}_3\text{PO}_4$  (method HY1) [8,9] or iron(III) nitrilotriacetate  $\text{FeNTA}$  (see preparation in Section 5) and lithium hydrogenophosphate  $\text{Li}_2\text{HPO}_4$  (method HY2) as precursors. In both cases, the synthesis was performed in a PARR 4842 autoclave. The reactants were introduced in 800 ml of demonized and deoxygenized water. Then, the reactor was sealed and a purge of the dead volume with argon was made in order to overcome undesired oxidizing reactions. The conditions applied were: 220 °C, 24 bars. After 1 h, the mixture was cooled to ambient temperature. The powder was then filtered, washed with demonized water and dried at 60 °C under vacuum.

X-ray diffraction patterns of the powders show an absence of parasitic peaks whatever the synthesis route chosen (HY1 or HY2), and there is a good correspondence with the reference  $\text{LiFePO}_4$  pattern, demonstrating that single phase is obtained with no evidence of impurities (Fig. 1d).

Depending on the synthesis conditions, the particle size of the final  $\text{LiFePO}_4$  powder samples were within a few micrometers range ( $\varnothing \# 1 \mu\text{m}$  when using the HY1 method) (Figs. 2a and 3) from several micrometers ( $\varnothing \# 30 \mu\text{m}$  when using HY2) (Figs. 2b and 3).

These  $\text{LiFePO}_4$  powders can then be heat-treated, under nitrogen, in presence of an organic compound (typically a sucrose) in order to deposit a thin layer of carbon onto the particles and improve the contact C– $\text{LiFePO}_4$  and thereafter the efficiency of the electronic transfer to the material. The optimized thermal treatment is reached at 550 °C/12 h with less than 5 wt.% of carbon. The specific capacity is very dependent on the particle size. The most promising behavior was observed for the material with the thinnest grains (obtained from the HY1 method), which is consistent with recent works showing that the kinetic of the lithium diffusion into the host lattice is very slow. A way to bypass this

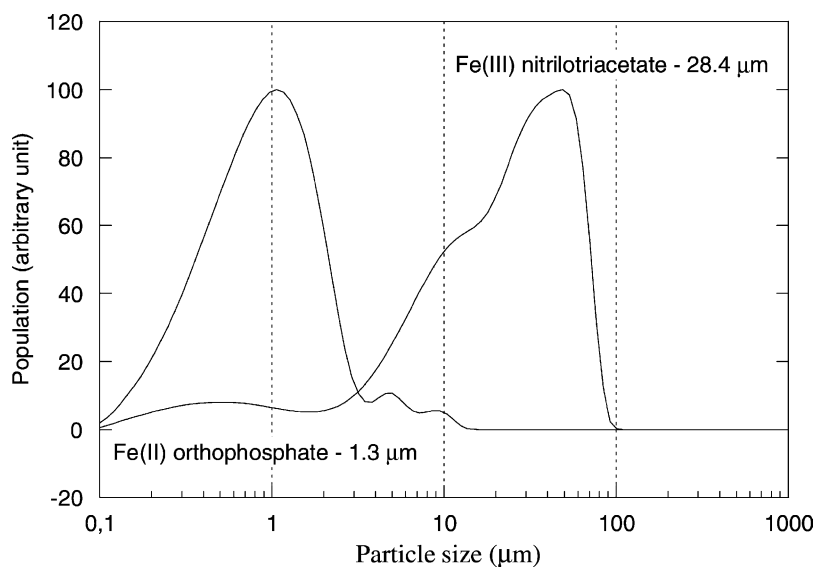


Fig. 3. Grain size distribution of the hydrothermal  $\text{LiFePO}_4$  depending on the initial synthesis reactants (iron orthophosphate for HY1 or iron nitrilotriacetate for HY2).

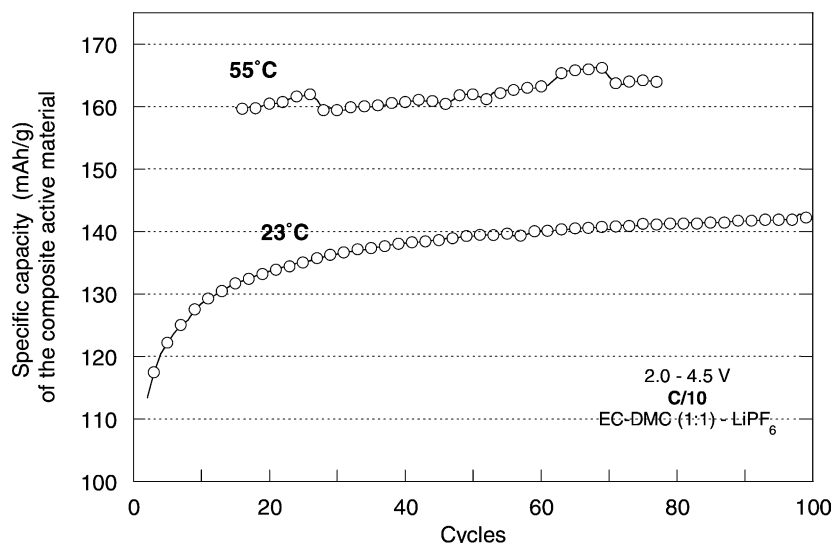


Fig. 4. Specific capacity of the hydrothermal (HY1)  $\text{LiFePO}_4$  in function of the cycle numbers and the temperature of the experiment.

limitation may consist in operating at medium–high temperature. Several authors have demonstrated the validity of this approach by cycling their cells between 55 and 80 °C [2,10].

In the present work, if the operating temperature of the tests is increased, for example up to 55 °C, the theoretical capacity of 1 mole  $\text{Li}^+$  per mole of  $\text{LiFePO}_4$  is achieved, for both optimized composite materials (Fig. 4).

The last route envisaged here for the synthesis of pure  $\text{LiFePO}_4$  was a mechanochemical activation. It was performed using dry iron(II) phosphate  $\text{Fe}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$  and tri-lithium phosphate  $\text{Li}_3\text{PO}_4$  as starting materials [8,9]. The powders (~20 g) were ball milled for 24 h in a planetary mill (Retsch S1000) with agate vessels and the electronic

conductor additive precursor (sucrose) was incorporated initially with the two reactants. The resulting product is heat-treated at 550 °C, under nitrogen, for 15 min. This thermal treatment is necessary to crystallize the final compound  $\text{LiFePO}_4$  and to decompose the organic additive into native carbon which will coat the particles (Fig. 1e).

The main benefit of this synthesis route is the activation of the mixture because of a very intimate grinding of the reactants on the molecular level. The temperature of the thermal treatment necessary for the crystallization of the compound can be then decreased (crystallization is observed at 432 °C for the activated mixture, and 502 °C for the unactivated) (Fig. 5) and the duration of this treatment

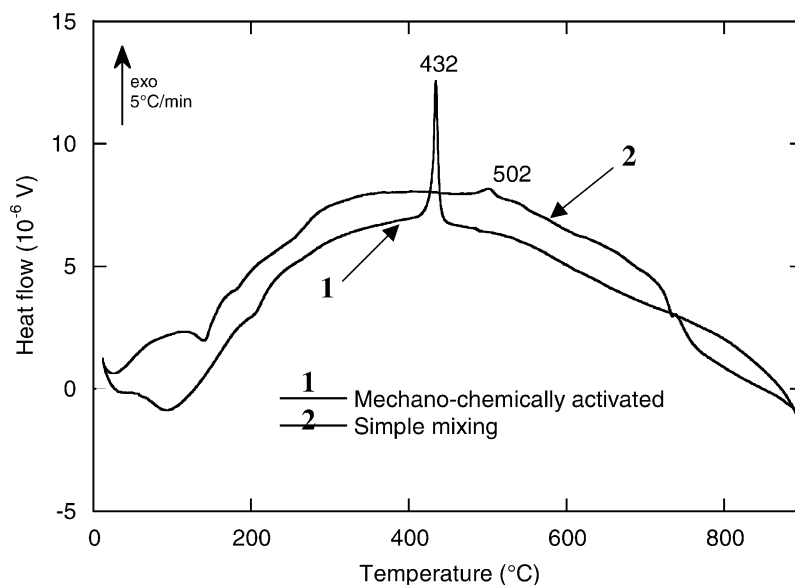


Fig. 5. Comparison between the DSC signals of the mechanochemical activated mixture and the simple manual mixing.

can also be shortened which is interesting if the goal is to keep small grain size (Fig. 6).

Indeed, the higher the temperature of the thermal treatment is performed, the larger the particles of  $\text{LiFePO}_4$  are observed from X-ray diffraction patterns (Fig. 7).

As mentioned above, the slow kinetics of the lithium diffusion into this cathodic material makes unable to use those large grains. This point is clearly shown again when comparing the cycling performances of several samples heat-treated at different temperatures (from 500 to 700 °C/15 min). The optimal sintering temperature seems to be here reached for 600 °C/15 min (with less than 5 wt.% of carbon) since the capacity retention is important even at high current rate (125 mAh/g at C-rate). There is probably a compromise between the crystallinity, the grain size of  $\text{LiFePO}_4$  and the decomposition of sucrose into native carbon onto the particles (Fig. 8).

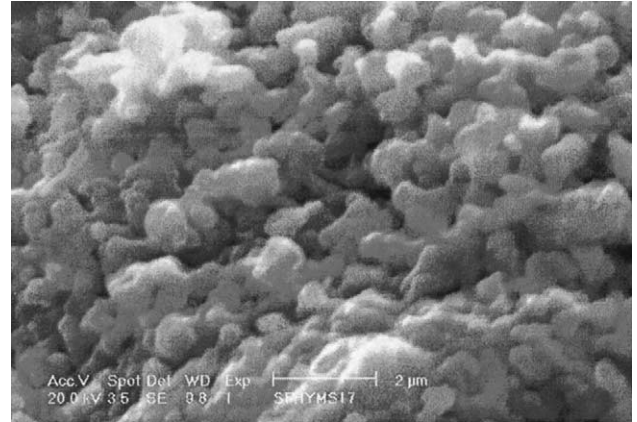


Fig. 6. SEM picture of mechanochemical  $\text{LiFePO}_4$  obtained after treatment at 600 °C/15 min.

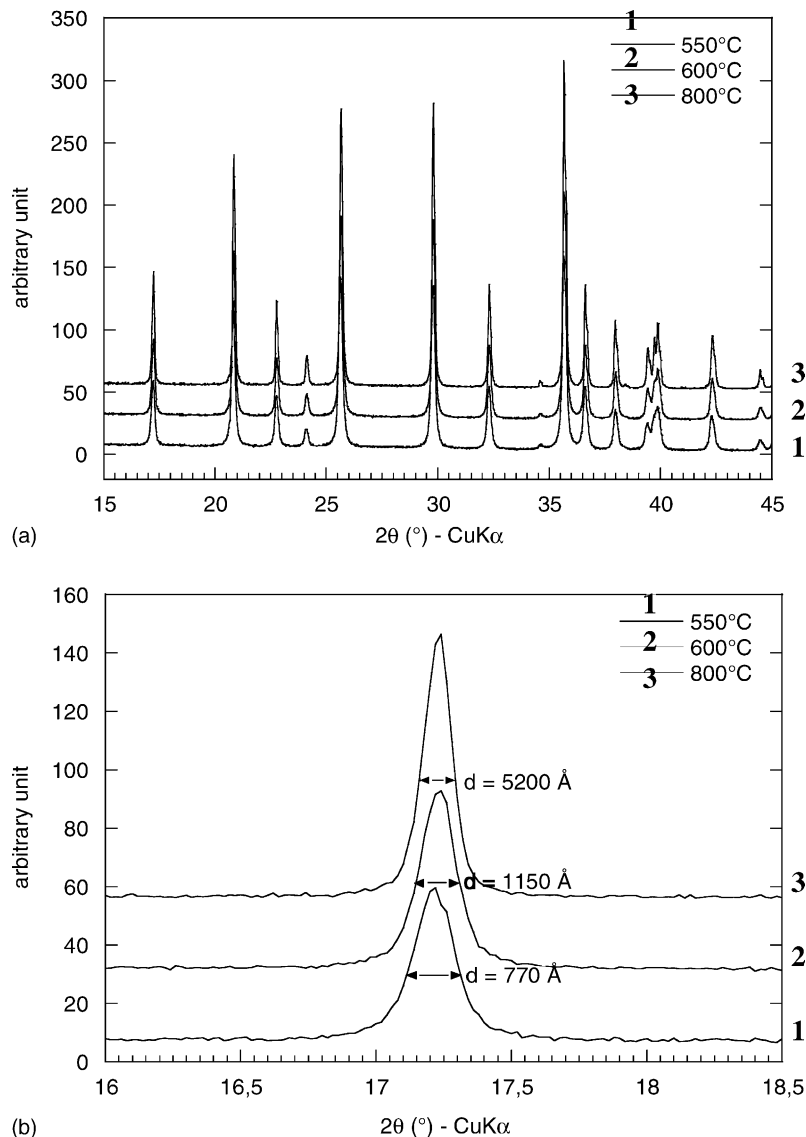


Fig. 7. XRD patterns of the mechanochemical  $\text{LiFePO}_4$ : (a) in function of the heat treatment after grinding and (b) zoom between 16 and 19° ( $2\theta$ ).

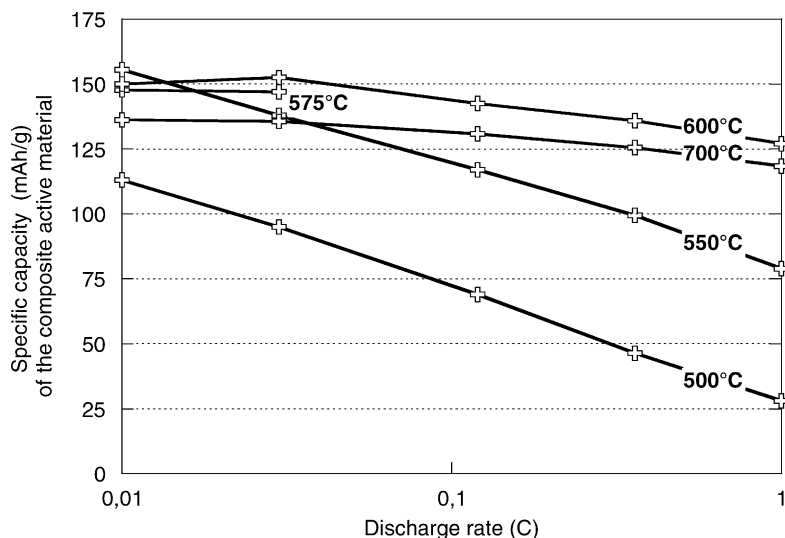


Fig. 8. Evolution of the specific capacity of the mechanochemical LiFePO<sub>4</sub> in function of the temperature of the heat treatment operated after grinding and the C-rate imposed for charge–discharge processes.

More measurements are needed to understand the mechanism of lithium insertion into this very promising cathodic material for secondary lithium battery.

#### 4. Conclusion

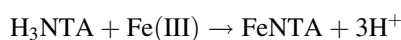
Different synthesis routes have been explored for the preparation of LiFePO<sub>4</sub> and two of them produced pure, well crystallized and homogeneous particles (the hydrothermal and the mechanochemical activation). However, the mechanochemical activation process gives the optimum composite material since a very stable specific capacity as high as 150 mAh/g at C/5 is obtained. The electronic conductor additive seems to be more efficient when incorporated during the very beginning of the synthesis (probably due to a better homogeneity of the mixture). The carbon content of our optimized composite material is less than 5 wt.% compared with the 15–20 wt.% reported in the literature.

Recent work performed in our laboratory concerning partial substitution of iron by other elements are very promising in terms of enhancement of the conductivity of the material and allow reaching the theoretical specific capacity even at very fast rate (*work to be published*).

#### 5. Annexe

The preparation of the iron(III) nitrilotriacetate complex (FeNTA) is described here: 17 g of iron(III) sulphate, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, are added with 8 g of nitrilotriacetic acid (H<sub>3</sub>NTA: N(CH<sub>2</sub>CO<sub>2</sub>H)<sub>3</sub>) in 500 ml of demonized water and boiled

at 100 °C for 1 h to react as follows:



The yellow precipitate of FeNTA is then washed with cold demonized water and dried at 30 °C for 12 h.

Nitrilotriacetate complexes are known to be degraded by thermal treatments with reducing properties. Here, for example, the ulterior decomposition of the FeNTA complex during the hydrothermal synthesis (HY2) would make possible the reduction of the iron(III) entities into iron(II) and the formation of the desired compound LiFePO<sub>4</sub>.

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