

Chemistry and electrochemistry of lithium iron phosphate

Charlotte Benoit · Sylvain Franger

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Abstract We report here several synthesis routes and their respective drawbacks/advantages for the preparation of pure LiFePO_4 . We demonstrate the possibility of using LiFePO_4 for electrochemical applications, with respect that an effective carbon coating was realized onto the smallest particles. Actually, to bypass the weak ionic conductivity of lithium iron phosphate, the thinnest would be the particles; the highest would be the performance under severe electrochemical conditions.

Keywords Lithium batteries · LiFePO_4 · Syntheses · Nanoparticles · Carbon coating

Introduction

A natural compound, LiFePO_4 (triphylite), able to reversibly insert/deinsert one lithium ion per iron atom (theoretical capacity = 170 mAh g^{-1}) [1] at 3.5 V/Li (which makes it stable in almost all electrolytes commonly used in lithium batteries) becomes, today, one of the most attractive material even if it is penalized by a very poor intrinsic conductivity.

Indeed, in a lithium cell, the electrochemical extraction of lithium from LiFePO_4 is accompanied by a direct transition to FePO_4 , in which the Fe^{2+} ions are oxidized to Fe^{3+} , leaving the olivine FePO_4 framework intact.

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C. Benoit · S. Franger (✉)
Solid State Physico-Chemistry Group,
Institute for Materials and Molecular Chemistry,
ICMMO/UMR CNRS 8182, University Paris XI,
15 avenue Georges Clémenceau,
91405 Orsay Cedex, France
e-mail: sylvain.franger@u-psud.fr

Therefore, during charge and discharge of the cell, LiFePO_4 electrodes are actually composed of two separate phases, LiFePO_4 and FePO_4 , which are both poor electronic conductors because they each contain iron cations with just one oxidation state ($2+$ or $3+$, respectively).

Therefore, to obtain acceptable energy and power from the lithium cells, it has been necessary to use small LiFePO_4 particles, coated or in intimate contact with electronically conductive carbon.

A major improvement to this material was actually proposed by Ravet et al. [2]. The increase of the global electronic conductivity was achieved by synthesizing olivine/carbon composites. It leads to practical specific capacity approaching the theoretical value of 170 mAh g^{-1} at room temperature.

These pioneer works have clearly shown that “conductive” LiFePO_4 was a very promising active compound for positive electrodes in secondary lithium batteries. The polyanionic array gives the material an excellent structural stability in the charged state, making it a safe material for batteries [3], and finally, the low cost of raw material should lead to a cheap intercalation compound.

However, it seems that the improved electronic conductivity did not improve the battery performance as high as expected, but the rate capabilities of batteries can also be enhanced by reducing the particle size of electrode materials, as it is well established that the rate capabilities of Li-ion batteries are limited by solid-state diffusion of Li^+ within the electrode materials. The use of nanostructured cathodes can then improve the intercalation behavior because of the shorter diffusion distances in nanoparticles [4, 5].

The optimization of the carbon coating onto the particles (for the enhancement of the electronic conductivity) and the reduction of the crystallites size (to overcome the weak ionic conductivity) are unambiguously both major keys to

make lithium iron phosphate a powerful positive electrode material.

We have, thus, performed, in our group, several series of syntheses using different processes to improve the physico-chemical properties of the LiFePO_4 material [6–13]. The main aim is to make it usable in a battery that could work at ambient temperature and at relatively high current densities (superior to C rate).

For that purpose, we have mainly centered our research on:

1. The preparation of the most homogeneous and the thinnest particles possible
2. The synthesis of an intimate composite material “ LiFePO_4 |electronic conductor”

The results obtained are presented and discussed in the following sections.

Experimental: syntheses and physico-chemical characterizations of LiFePO_4

Coprecipitation techniques

To efficiently obtain LiFePO_4 , we considered, as Delacourt [14] did, that the most appropriate domain of pH was the one corresponding to the simultaneous precipitation of Li_3PO_4 and $\text{Fe}_3(\text{PO}_4)_2$, as these compounds are already known as good precursors for LiFePO_4 [6–7, 15].

The reactants used were $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, LiH_2PO_4 , LiOH , H_2O , and HNO_3 (68 vol.%).

LiH_2PO_4 (0.1 M) and LiOH (1 M) were mixed in deionized and deaerated water, and the initial Li_3PO_4 precipitate was dissolved with the addition of a small amount of nitric acid. Freshly grounded $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ powder was then added to the latter solution ($[\text{Fe(II)}]=0.1 \text{ M}$).

Chemical coprecipitation in aqueous medium

The pH was slightly increased by the addition of a sodium hydroxide (4 M) solution until $\text{pH}=9$.

The precipitates were separated from the solution by centrifugation, rinsed several times with deionized and deaerated water, and dried at room temperature under vacuum during 12 h.

The X-ray diffraction (XRD) patterns of this mixture confirms the formation of both $\text{Fe}_3(\text{PO}_4)_2 \cdot x \text{H}_2\text{O}$ and Li_3PO_4 .

This powder was then activated (ball milled) under inert gas during 12 h and heated at $600 \text{ }^\circ\text{C}$ during 15 min under argon atmosphere.

The final product obtained after this heat treatment contains LiFePO_4 and $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$. The presence of this

iron(III)-based phase was evidenced by chemical titration, XRD, and Mössbauer spectroscopy. The amount of this parasitic phase can be decreased by an ulterior thermal treatment at $850 \text{ }^\circ\text{C}$ (1 h) under a CO/CO_2 gas flow (dioxygen partial pressure= $4 \cdot 10^{-17} \text{ atm}$; Benoit and Franger, in preparation).

The ratio $\text{Fe(II)}/\text{Fe(III)}$ in the sample goes, thus, from 0.62 to 0.95 (chemical titration). However, the grains tend to grow drastically during this treatment (Fig. 1a). It is actually difficult to maintain a small particle size when heating at elevated temperature.

Another way to decrease the formation of iron (III) during the synthesis consists in using a specific iron (II) complexing agent, *o*-phenanthroline, to make the $\text{Fe(III)}/\text{Fe(II)}$ redox potential higher.

By using $[\text{o-phen}]=10^{-2} \text{ M}$ and after five steps of rinsing (the complexing agent is difficult to eliminate from the powders), we can successfully obtain LiFePO_4 with less Nasicon phase ($\sim 20 \text{ mol\%}$). However, the ratio $\text{Fe(II)}/\text{Fe(III)}$

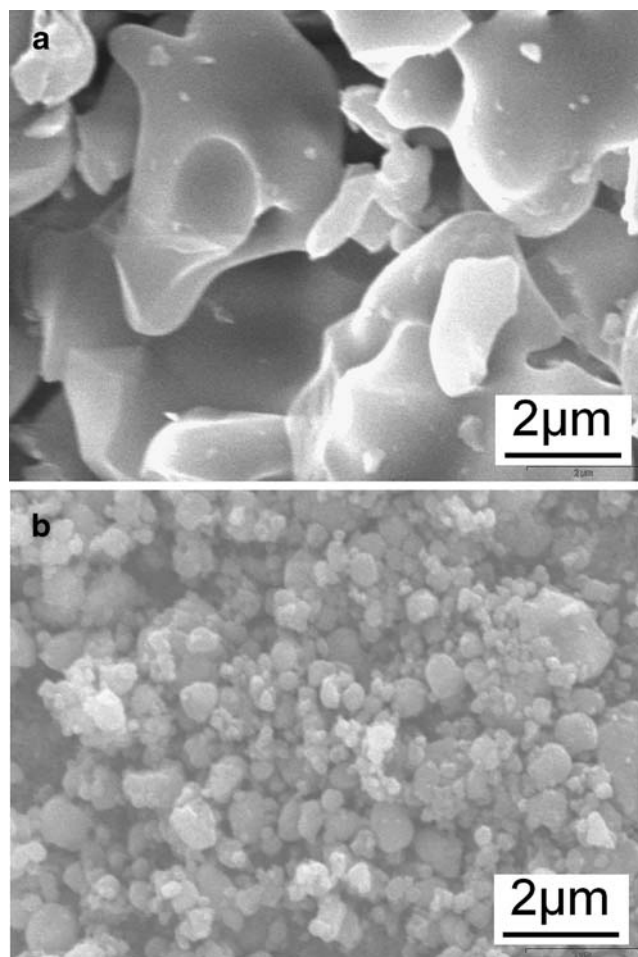


Fig. 1 a SEM picture of LiFePO_4 obtained by a simple chemical coprecipitation technique followed by a heat treatment under a CO/CO_2 gas flow ($850 \text{ }^\circ\text{C}$, 1 h); b SEM picture of LiFePO_4 obtained by an electrochemically assisted coprecipitation technique

(III) in the sample is still too low, almost 0.85 (chemical titration).

Electrochemically assisted coprecipitation

For electrochemical coprecipitation, a galvanostat was used as controlled current generator. The experimental cell consisted in two platine wire electrodes in separated compartments. When applying a constant current (~25 mA) through the cell, the pH near the cathode slightly increases because of the consumption of proton at this electrode (water reduction). Dihydrogen is also simultaneously produced at the cathode, and it protects the dissolved iron (II) ions in the electrolytic solution by limiting their oxidation with the oxygen.

After 10 days of current application, the pH has reached the value of 7. The experiment is stopped; the solid is centrifuged and rinsed several times and dried under vacuum during 12 h.

No diffraction peaks are observed when performing XRD experiment on the so-obtained powder.

The solid is then treated by mechanical activation (ball milled) during 12 h and sintered at 600 °C during 15 min under argon.

XRD patterns of the final product show the presence of pure LiFePO₄ with no secondary crystallized phase (Benoit and Franger, in preparation). This was confirmed by Mössbauer and magnetic measurements (only traces of the Nasicon phase, <1%). This procedure seems to be more convenient to obtain the desired olivine phase with both a good purity and nanosized particles (Fig. 1b).

Hydrothermal syntheses

Starting from an iron(II) source: HY1 process

LiFePO₄ was obtained by hydrothermal synthesis using fresh iron (II) phosphate Fe₃(PO₄)₂·5H₂O (homemade) and commercial tri-lithium phosphate Li₃PO₄ (method HY1) as precursors.

The synthesis was performed in a 1-l PARR 4523 autoclave. The reactants were introduced in 800 ml of deionized and deaerated water. Then, the reactor was sealed, and a purge of the dead volume with argon was made 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 de-ionized water, and dried at 60 °C under vacuum.

XRD patterns of the powders show an absence of parasitic peaks, and there is a good correspondence with the reference LiFePO₄ patterns, demonstrating that single phase is obtained with no evidence of impurities. This last

assertion was, moreover, confirmed by a chemical titration (Fe(III)<1%).

However, a close examination of the HY1 diffraction diagram shows there are almost 5% iron atoms in the lithium sites. These iron atoms essentially block diffusion of the lithium ions, as the diffusion is fast only along the tunnel and not between them [16, 17]. Similar results for hydrothermally synthesized LiFePO₄, i.e., an excess of iron in the structure, have also been reported by Yang et al. [18, 19]. Firing these materials at 700 °C resolves this phenomenon but enhances, in the same time, the growth of the particles which is, once again, penalizing to keep small grain size.

Starting from an iron(III) source: HY2 process

LiFePO₄ was also obtained by hydrothermal synthesis using iron (III) nitrilotriacetate FeNTA (homemade, see preparation in [7, 10]) and lithium hydrogenophosphate Li₂HPO₄ (method HY2) as precursors.

The synthesis was performed in the same conditions as for HY1.

XRD patterns of the powders show an absence of parasitic peaks, and there is a good correspondence with the reference LiFePO₄ patterns, demonstrating that single phase is obtained with no evidence of impurities. Moreover, the diffraction diagram for HY2 is quite identical to that of ordered triphylite, and the calculated lattice parameters are in good agreement with the expected ones [7, 10].

The LiFePO₄ solid building mechanism is different in that case compared to that observed with the HY1 process, as the medium is here under constant reducing conditions (because of the degradation of the nitrilotriacetic molecules). The HY2 route leads directly to ordered LiFePO₄ without any ulterior thermal treatment.

Depending on the synthesis conditions (initial reactants and cooling process), the particle sizes of the final LiFePO₄ samples were within a few micrometers range (Ø~1 µm when using the HY1 method and rapid cooling; Fig. 2a) from several micrometers, Ø~30 µm when using HY2 and slow cooling; Fig. 2b).

It can be then noticed by taking these last results into consideration that hydrothermal methods are particularly interesting for the particles size tailoring.

Mechanochemical activation

General procedure

Another route envisaged here for the synthesis of pure LiFePO₄ was a mechanochemical activation. It was performed using dry iron (II) phosphate Fe₃(PO₄)₂·5H₂O (homemade) and commercial tri-lithium phosphate Li₃PO₄ as starting materials. The powders were ball milled during

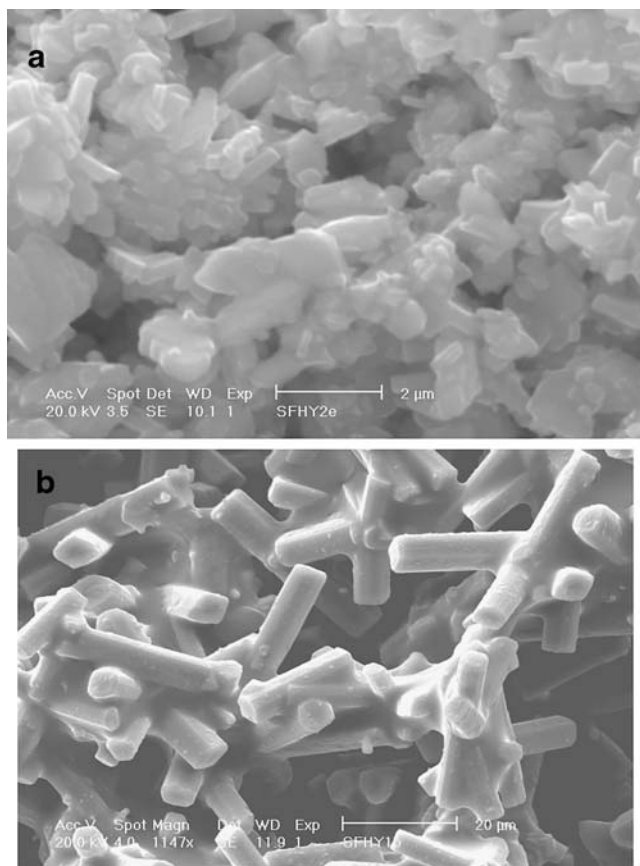


Fig. 2 **a** SEM picture of LiFePO_4 obtained by the HY1 hydrothermal process (rapid cooling); **b** SEM picture of LiFePO_4 obtained by the HY2 hydrothermal process (slow cooling)

24 h in a planetary mill (Retsch S1000) with agate vessels. The resulting product was heat treated, under argon. This thermal treatment is necessary to crystallize the final compound LiFePO_4 .

The main benefit of this synthesis route is the activation of the mixture because of a very intimate grinding of the reactants. The temperature of the thermal treatment necessary for the crystallization of the compound is then decreased (crystallization is observed at $432\text{ }^\circ\text{C}$ for the activated mixture in spite of $502\text{ }^\circ\text{C}$ for the unactivated one) [7], and the duration of this treatment can also be shortened to limit the final grain size.

Moreover, this intimate mixing of the reactant allows to obtain pure LiFePO_4 in a single step thermal treatment, with a grain size as low as 50 nm (Fig. 3).

Elaboration of C-LiFePO₄ composite active material

The aforementioned experiment can also be performed by adding a carbon source (typically a carbohydrate compound, such as glycogen, cellulose, or polyacrylonitrile) to the main reactants at the very beginning of the procedure, i.e., just before ball milling.

In this way, the decomposition of the carbohydrate compound that will occur during the thermal treatment will give birth to native carbon. The latter will then coat the LiFePO_4 particles [2, 13] and enhance the conductivity of the final material.

Moreover, the formation of reducing conditions during heating prevents any parallel parasitic oxidation reaction and, thus, allows to ensure the maintenance of a maximum iron (II) rate in the compound.

Discussion: improving electrochemical properties of lithium iron phosphate

Coating of the particles

Pure LiFePO_4 is known to be a very bad conductor ($\sigma = 2.10^{-9}\text{ S cm}^{-1}$) [13]. To enhance its weak intrinsic electronic conductivity, a carbon coating seems to be necessary. As for all other mixed conductors, there is an interplay between electronic and ionic conductivities.

To produce the optimal effect, the concentration of the mobile ions, c_{Li} , should be high compared to the concentration of the electronic species, c_e . However, c_{Li} should not be very much larger than c_e to keep the transference number of the electrons close to 1 (to produce fast equilibration of the electrode).

These requirements are somewhat contradictory but may best be fulfilled if the mobility of the small number of electrons is very large compared to the mobility of the lithium ions.

In this favorable case, the electrons move ahead of the ions and, in this way, generate an internal electric field in which the ions are accelerated and the electrons are slowed down to maintain electroneutrality of the crystal lattice. One can then understand that, if the concentration of

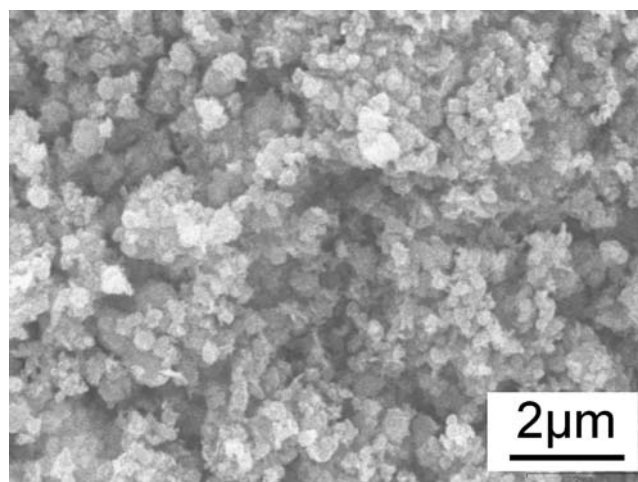


Fig. 3 SEM picture of LiFePO_4 obtained by a mechanochemical activation technique

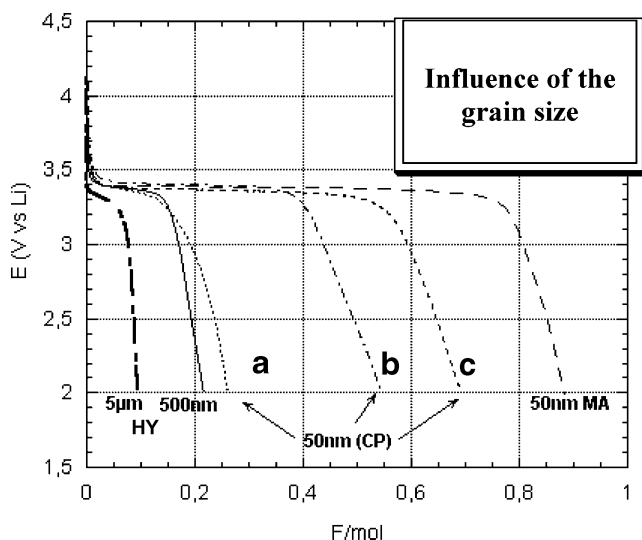


Fig. 4 Electrochemical performance of LiFePO₄ samples obtained by different synthesis methods (*HY* hydrothermal syntheses, *CP* coprecipitation, *MA* mechanochemical activation) in function of their particle sizes: *a* chemical CP, *b* chemical CP with 10⁻² M *o*-phen, *c* electrochemically assisted CP

electrons is too large, a small backward diffusion of this large number would compensate the electrical field. In other words, the electronic species would shield the electrical field from the lithium ions. The electrical field exerts the maximum enhancement of the lithium ions motion if the concentration of electrons is small, which can be achieved with a controlled coating onto the particles. This explains how it is possible to transform efficiently the electrochemical kinetics of triphylite (from a slow to a quasi-rapid system) by enhancing the electronic (and subsequently the ionic) conductivity [13].

Despite the treatments described above, the ionic diffusion ($\tilde{D}_{Li} = 5.10^{-14} \text{ cm}^2\text{s}^{-1}$) remains at a low value for an insertion compound [6, 13, 20].

Another way to improve drastically the ionic conductivity could be a partial doping of the pristine olivine structure with hetero-atoms (Zr, Nb...) to create defects, as suggested by Chung et al. [21]. However, it seems that the incorporation of external elements into the triphylite structure is still discussed [22, 23]. There are actually strong evidence for the formation of very conductive Fe₂P (>10⁻¹ S cm⁻¹) and/or amorphous composite (Zr, Nb, C, O, P) coating around the LiFePO₄ particles instead, which would lead to the aforementioned considerations.

We tried ourselves a partial substitution of the olivine structure with boron [9, 12]. From a crystallographic point of view, there is effectively no evidence for the incorporation of this element into the pristine crystal lattice. However, electrochemical measurements performed onto this “composite” material have revealed an enhancement of the ionic conductivity, as the lithium diffusion coefficient is ten times higher in the case of boron-based electrode than

for C-coated material. If we assume the presence of a boron-based wrap around the triphylite particles, more conductive than the carbon one, this improved electrochemical behavior can be then easily explained by the aforementioned considerations. This better ionic conductivity was, moreover, clearly observed in real cycling conditions. We have indeed pointed out a complete lack of capacity fading when multiplying the operating current density of the cell by 5.

Reduction of the particle size

Finally, the simplest (and probably the most promising) way to bypass the weak ionic conductivity of the triphylite remains the decrease of the particle size to have the shortest diffusion pathway for the lithium ions and then to maintain good cycling kinetics, even at high current densities.

Figure 4 shows the electrochemical performance of several LiFePO₄ compounds in function of their particles sizes. The faradic output corresponding to the insertion process ($\eta = \frac{x}{1}$, where *x* is the lithium content in the Li_{*x*}FePO₄ material) is indeed clearly dependant of this dimensional parameter. The efficiency of the insertion seems to be optimal when the crystallite size is within the range of the maximum length of the lithium diffusion pathway (*L*), the latter being imposed by the current density chosen for the cycling experiment.

L values can be estimated from the integrated form of the first Fick’s law (in one-way and semi-infinite diffusion conditions, $L = \sqrt{2\tilde{D}_{Li}t}$), and we have reported in Table 1 some calculated values of the maximum length of the lithium diffusion pathway *L* in function of the cycling rate (the diffusion coefficient mean value was taken as $\tilde{D}_{Li} = 5.10^{-14} \text{ cm}^2\text{s}^{-1}$) to compare them with some common particle radii.

To obtain, thus, good electrochemical performance even at high rates (>C rate), it is necessary to have real nanosized particles (<100 nm), if not, it is obvious that only a small part of the crystallite is accessible for the lithium ions,

Table 1 Efficiency of the electrochemical process in function of the particle size for a given C-rate

Cycling rate	<i>L</i> _{max} (nm)	Efficiency (<i>L</i> _{max} /particle radius; %)			
		1 µm	0.5 µm	100 nm	10 nm
C/20	850	85	100	100	100
C/10	604	60	100	100	100
C/5	425	43	86	100	100
C	190	19	38	100	100
2C	134	13	26	100	100
4C	94	9	18	94	100

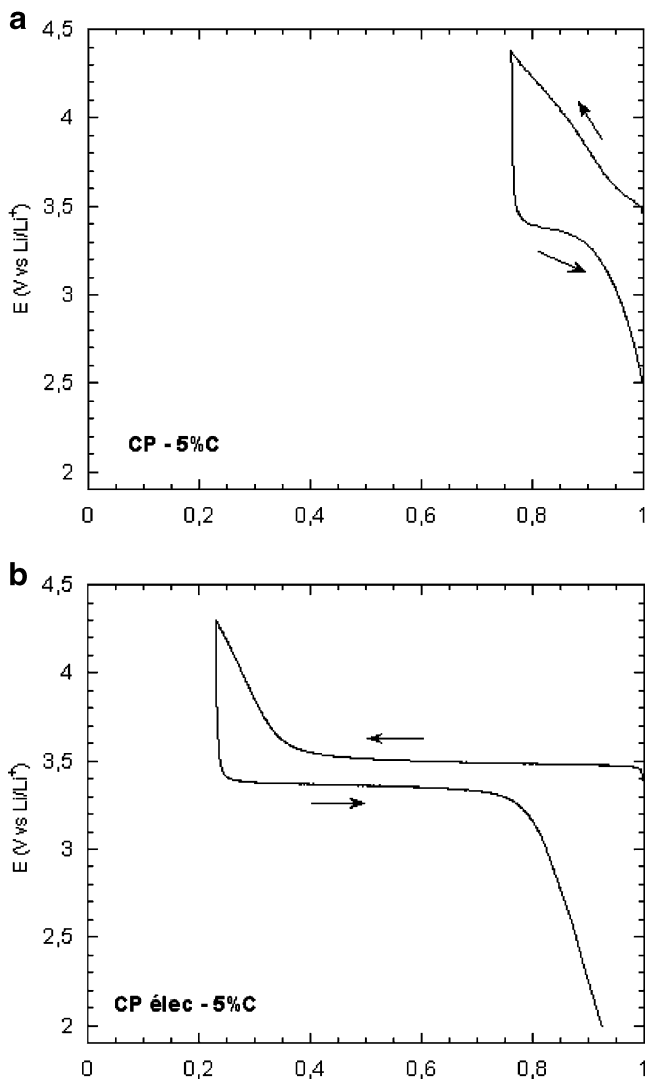
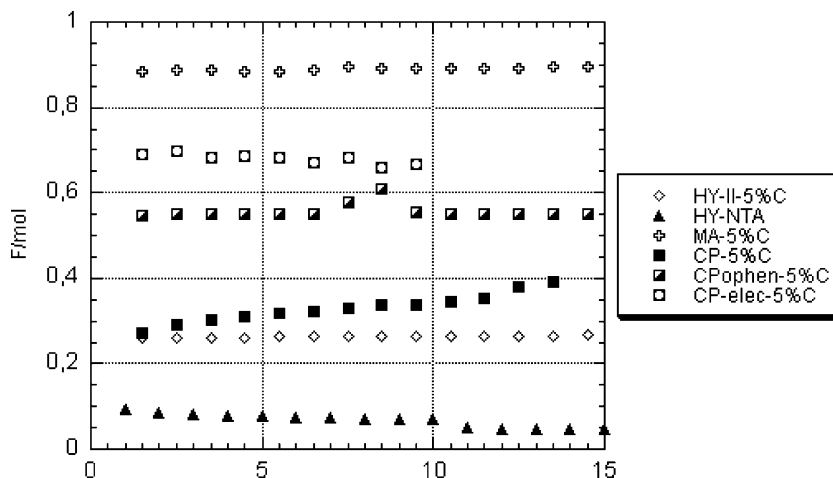


Fig. 5 Galvanostatic curves (C/10) of composite C-LiFePO₄ obtained by **a** a chemical coprecipitation technique followed by a heat treatment under a CO/CO₂ gas flow (850 °C, 1 h) and by **b** an electrochemically assisted coprecipitation technique

Fig. 6 Electrochemical behavior of different LiFePO₄ samples in function of the number of cycles (C/10, 25 °C)



which consequently leads to a reduced overall efficiency ($\eta \ll 1$).

Therefore, the need for small particles size of LiFePO₄ is quite well demonstrated.

However, even for small particles (50 nm), other considerations must be taken into account because the electrochemical performance (Fig. 4) seem also sensitive to intrinsic defects, as it will be illustrated in the next section.

Practical electrochemical behavior of optimized LiFePO₄

The electrodes were manufactured for electrochemical testing of the samples by casting on an aluminum current collector a *N*-methylpyrrolidone (NMP) slurry of the 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 electrodes (thickness, ~0.35 mm) were assembled together in commercial type 2 electrodes cells (\varnothing 16 mm button cells) separated by a polypropylene felt imbedded by an electrolyte consisting of a 1-M LiPF₆ solution in an ethylene carbonate–dimethyl carbonate (EC–DMC, 1:1 vol.) mixture.

The assembly of the cell prototypes was carried out in a dry glove box under argon.

The cell performance was investigated both in terms of charge–discharge curves and cycle life.

For the first charge of CP–5%C (Fig. 5a), the electrochemical behavior is that of a pseudo-solid solution: We cannot indeed recognize the well-defined plateau (at 3.5 V vs Li) usually observed for LiFePO₄.

In the contrary, for CP–Elec–5%C (Fig. 5b), a large plateau is observed at 3.5 V vs Li, which means that the insertion and deinsertion of lithium ions corresponds here to the well-known biphasic process.

These different behaviors (both in terms of fingerprint and capacity) can be caused by an incomplete crystallo-

graphic order and/or the presence of intrinsic structural defects [iron (III) + lithium vacancy replacing iron (II) + Li⁺].

Actually, such defects in the crystal lattice have been evidenced by magnetic measurements (deviation between susceptibility direct measurements and derivation of the magnetization curves) and will be precisely detailed in another publication (Benoit et al., in preparation).

This explains the trends shown in Fig. 6.

In one hand, we can observe that, for a given C rate (here C/10), the more important is the grain size (HY samples), the less is the specific capacity (between 0.1 and 0.25 F/mol).

In the second hand, however, this comment should be moderated for nanosized particles (CP and MA samples), as the specific capacity varies from 0.3 to 0.9, whereas all grains exhibit quite identical size distribution (almost 50 nm). The variations observed here are caused by different amounts of intrinsic crystalline defects between the samples.

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