CONTINUOUS HYDROTHERMAL SYNTHESIS OF INORGANIC PARTICLES IN SUPERCRITICAL WATER. APPLICATION TO THE BATTERY ELECTRODE MATERIAL $LiFePO_4$

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$LiFePO_4$ seems to be an excellent candidate as a cathode material for the next generation of lithium-ion batteries. A well controlled synthesis is necessary to ensure the highest performances by avoiding the grain growth. Syntheses are performed on a continuous hydrothermal reactor which allows to work from subcritical to supercritical water conditions. By offering a low viscosity, a great reactivity and a fast nucleation, nanometric powders can be produced. The as-prepared materials are fully characterized by X-Ray diffraction, surface area measurements and electron microscopy. Thus composition, particle size, morphology and aggregation state are studied. The electrochemical behaviour is studied in relation to the powders characteristics. Finally an experimental design is conducted in order to understand the influence of the experimental parameters on the final material, and to define the optimal working area.

INTRODUCTION

Lithium ion batteries are now using $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$ as positive electrode materials, which provide high voltage potentials and good reversible capacities. Recently many research groups are investigating olivine-structured $LiFePO_4$ proposed by Padhi and al [1]. Such a material is particularly attractive attention because of its high redox potential of 3.4 V, its theoretical capacity of 170 mAh/g and a good cycle property. Moreover it is less toxic than Co-, Ni- and Mn- based compounds. Various syntheses of $LiFePO_4$ for applications in lithium-ion batteries use solid-state reactions [2-5], soft chemistry [6-8] or mechanosynthesis [5-9]. In most cases electrochemical performances are poor and additives such as carbon powders are needed to improve the electronic conductivity. Also hydrothermal synthesis has succeeded preparing $LiFePO_4$ [5], [10-12]. The preparation of $LiFePO_4$ using hydrothermal reaction in batch reactors reported by Yang and al. [10] leads to micrometric powders with a grain size of about 3 μm. Smaller particles can be obtained by adding PEG [11] or carbon [12], and consequently better battery performances are observed.
The aim of this work is to present an original synthesis route that allows preparing $LiFePO_4$ without additives in a continuous way. Such a hydrothermal apparatus allows a fast reaction and the preparation of very well crystallized grains without further treatments. This process has great potentials from an industrial point of view by allowing huge production. Finally the influence of the experimental parameters on the final product is studied through an experimental design.

I - MATERIALS AND METHODS

$LiFePO_4$ powders were synthesized using a continuous hydrothermal reactor [13, 14] which allows working from subcritical to supercritical conditions.
This apparatus described Figure 1 is composed of four stages:

A – Separate storage of reactant aqueous phases

The metal salt aqueous solutions $(NH_4)_2Fe(SO_4)_2$, $6H_2O + H_3PO_4$ in (1) and the basic solution LiOH, H_2O in (3) are outgassed with N_2. They are fed into the apparatus separately.

B – Mixing point and application of sub or supercritical conditions

Before the mixing point deionized water in (2) is pressurized and heated to a temperature T_1 above the desired temperature T_2. The three pressurized streams are then combined in a mixing point just before the heated reactor, leading to a quick heating and subsequent reaction. After the reaction the solution is quenched to room temperature.

C – Filtration

The solution goes through filters of 7 µm and 2 µm that stop agglomerates.

D –The smallest particles are obtained in suspension after the back pressure regulator.

The product stopped by the filters and the suspension were then centrifuged, washed with deionized water until neutral pH and freeze-dried.

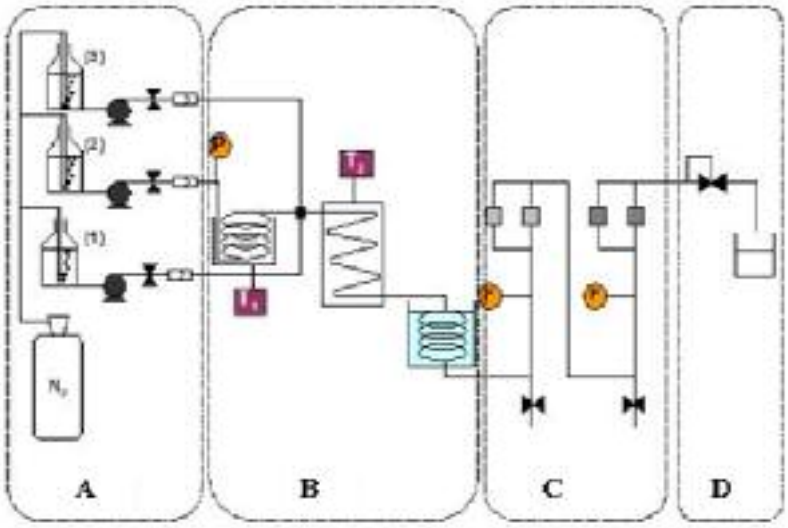


Figure 1 : The continuous hydrothermal reactor

$LiFePO_4$ powders were characterized by X-Ray Diffraction using an INEL diffractometer equipped with a curved position-sensitive detector (CPS 120 INEL), with a Co monochromatic X-ray (λ=1.7889 Å). The $LiFePO_4$ pattern was fitted with the profile analysis program TOPAS 2.1 from Brucker AXS. This profile fitting using the whole pattern decomposition is based on LeBail method.
Surface area measurements were performed using a BEL Japan apparatus with N_2 adsorbing gas. Samples (150-200 mg of powders) were outgassed at 493 K. The BET method was used to calculate the surface area values from the isotherm of nitrogen adsorption. Average particle diameters (Φ(BET) in nm) were calculated from surface area data (S(BET) in m^2/g) and the theoritical sample density (ρ in g/cm^3 ; ρ = 3.5g/cm^3 for $LiFePO_4$), using the following relationship

$$\Phi(BET) = \frac{6000}{\rho \times S(BET)} \qquad (1)$$

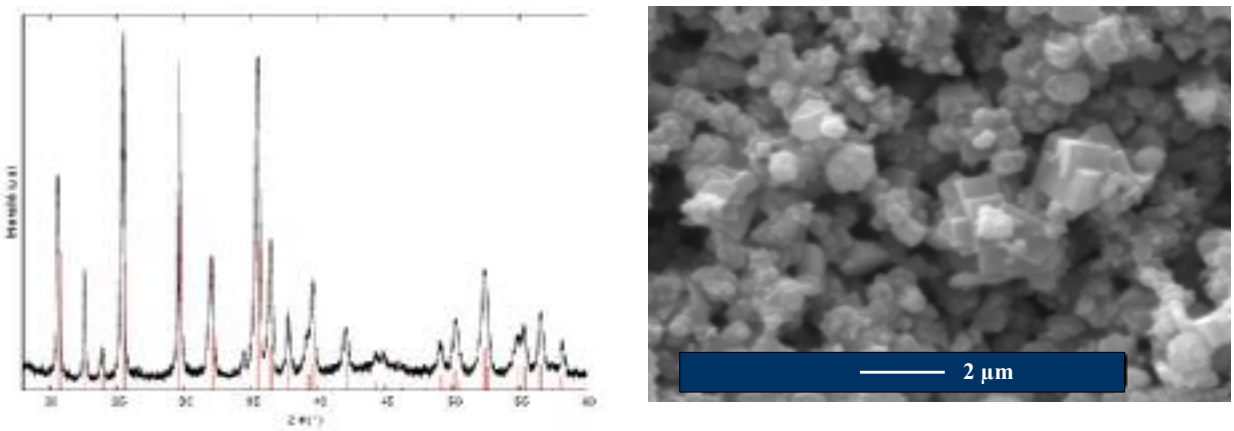
Scanning Electron Micrographs (SEM) have been performed on a JEOL JSM 6400F equipment. Particle size and size distribution was measured on a laser particle size analyser. The electrode performance was evaluated by using a galvanic cell, which was assembled in a glove box under argon atmosphere.

Finally an experimental design has been carried out using the Cornerstone DOE software. This aims at defining the optimal experimental parameters in terms of yield, grain size and agglomeration.

II – RESULTS AND DISCUSSION

$LiFePO_4$ powder synthesized on the continuous hydrothermal apparatus can be obtained within a few seconds under supercritical conditions (P = 250 bar – T = 375 °C). The powders are crystallised without any further treatment (Figure 2 a)). The crystallite size obtained from the XRD pattern is nanometric Φ(DRX) = 56 nm.

BET measurements give S(BET) = 6,7 m²/g corresponding to a particle size Φ(BET) = 256 nm. The material is non porous and as we can see on Figure 2 b) there are grains of different sizes, rounded or squared-shaped. From DRX and BET size measurements we can conclude that the material is composed of polycrystallite submicronic grains.



a) **b)**

Figure 2 : a) X-Ray diffractogram of $LiFePO_4$ powder synthesized using the continuous hydrothermal reactor in supercritical conditions. The peaks are compared to the 40-1499 ICDD card. b) SEM picture of $LiFePO_4$ powder synthesized using the continuous hydrothermal reactor in supercritical conditions.

Besides granulometry measurements Figure 3 a) shows that particles are greatly agglomerated. Finally electrochemical cycling Figure 3b) reveals a good behaviour of the material (redox potential at 3.4 V) but poor performances (only 35 % of Li exchanged). As

reported by Andersson and al. [15] a loss of capacity can be explained by the large particle sizes and the large agglomeration observed.

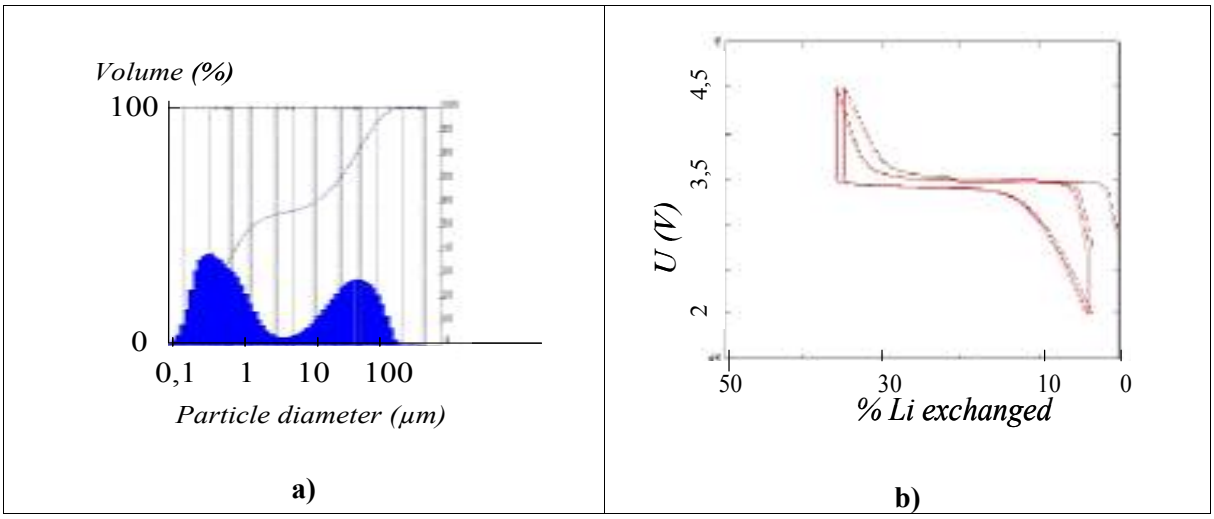


Figure 3 : a) Granulometry measurements of $LiFePO_4$ powder synthesized using the continuous hydrothermal reactor in supercritical conditions. b) Electrochemical cycling of $LiFePO_4$ powder synthesized using the continuous hydrothermal reactor in supercritical conditions.

Therefore an experimental design has been conducted to study the influence of the experimental parameters on the material grain size and agglomeration. By designing the optimal experimental parameters a well-defined material may be synthesized that shows better electrochemical performances.

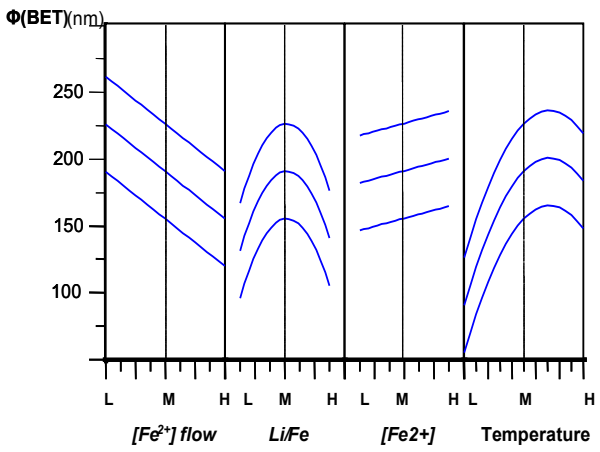
The operational parameters and desirable properties are summarized in Table 1. The pressure is fixed at 250 bar. Three levels for each factor (Low – Medium – High) are used and a quadratic model of 20 experiments was designed. The influence of each factor and the values of confidence level (R^2) are given in Table 2.

Parameters	**Responses**
Temperature (°C)	Yield (%) – maximize
$[Fe^{2+}]$ (mol/L)	Grain size Φ(BET) – minimize
$[Li^+]$ / $[Fe^{2+}]$	Agglomeration - minimize
$[Fe^{2+}]$ flow (mL/min)	

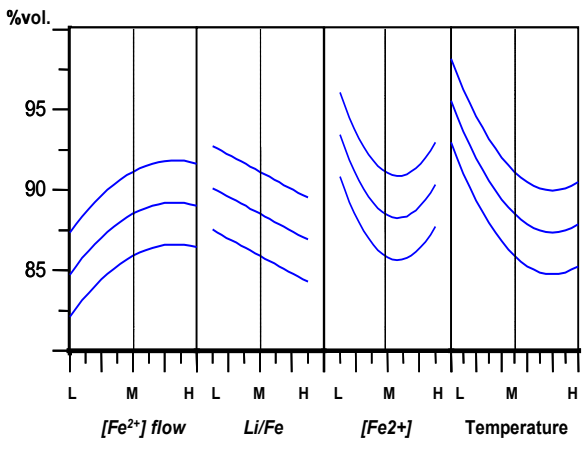
Table 1 : Experimental parameters and desirable properties

In Table 2 the predicted values for one response are obtained by varying one parameter, the three others being fixed. Around the predicted value the lowest and the highest acceptable values are given. The optimal parameters can be deduced from these curves for each factor. The highest yields are obtained for the highest flows, a temperature around the critical temperature, a medium concentration and a maximum of the ratio Li/Fe. The smallest particle sizes are obtained by applying the highest flows at the lowest temperature, and using the

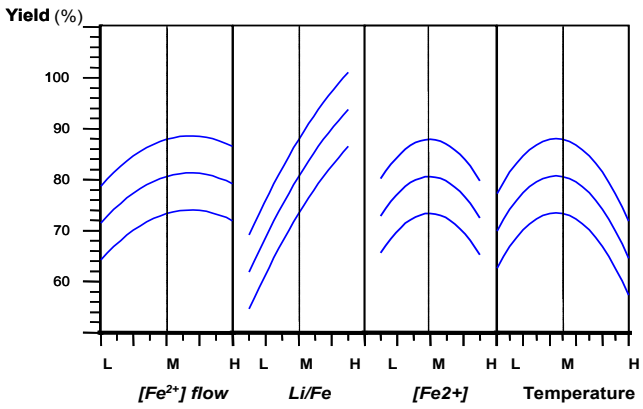
lowest concentrations and a maximum of the ratio Li/Fe. Therefore increasing the temperature leads to a grain growth, whereas increasing the setting flows leads to shorter reaction time, and consequently to a limitation of the grain growth. Finally agglomeration can be decreased by applying the slowest flows, the highest temperature, and using a medium concentration and a maximum of the ratio Li/Fe.



Φ(BET) (nm) $R^2 = 0,714$



% of the volume with grain size > 0.5 µm (agglomeration) $R^2 = 0,823$



Yield (%) $R^2 = 0,828$

Table 2 : Effect of each factor on the particle size (Φ(BET)), agglomeration state, and yield, and the value of confidence R^2 for each response.

The optimal parameters depend on the response studied; it is difficult to get at the same time the smallest grain size and the smallest agglomeration. Moreover it seems that in the range of the parameters designed here there is no condition leading to a really performing material, mainly because of the agglomeration remaining too important whatever the conditions (the percentage of the volume with grain size above 0.5 µm is more than 80 % whatever the conditions).

CONCLUSION

$LiFePO_4$ has been successfully synthesized using the continuous hydrothermal reactor. The well crystalline powders are composed of polycrystallite submicronic grains. However poor electrochemical performances are obtained that can be explained by a large grain size distribution and a great agglomeration. The influence of different factors on the grain size and the agglomeration of the material is studied through an experimental design in order to set the optimal parameters.

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