

EFFECTS OF MODIFIED SOLID STATE SYNTHESIS ON PHYSICO-CHEMISTRY AND ELECTROCHEMICAL PROPERTIES OF LiFePO_4 MATERIAL

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ABSTRACT: LiFePO_4 compound was prepared by a modified protocol of solid state reaction method. Analysis of the structure and morphology of the synthesized material shows that the used protocol of synthesis can lead to the formation of a product with a relatively good purity and an average particle size of about 200 nm. The reduction of the particle size of LiFePO_4 by the modified protocol leads to much better electrochemical performances than those of LiFePO_4 prepared by classical protocol of solid state reaction. The use of this modified protocol may provide an easy way for industrial production of LiFePO_4 cathode material in the lithium ion batteries.

Keywords: Li-ion batteries; LiFePO_4 ; Solid-state reaction; X-ray diffraction.

RESUME: Le composé LiFePO_4 a été préparé par un protocole modifié de la réaction à l'état solide. L'analyse de la structure et de la morphologie du matériau synthétisé montre que le protocole utilisé pour la synthèse peut mener à la formation d'un produit ayant une pureté relativement élevée et des particules d'environ 200 nm de taille moyenne. La réduction de la taille des particules par le protocole modifié mène à des performances électrochimiques meilleures que celles obtenues pour LiFePO_4 préparé par le protocole classique de la réaction à l'état solide. L'utilisation de ce protocole modifié peut constituer un chemin aisé pour la production industrielle du matériau LiFePO_4 d'électrode positive dans les batteries aux ions lithium.

Mots clés: Batteries Li-ion; LiFePO_4 ; Réaction à l'état solide; diffraction des rayons X.

1. INTRODUCTION

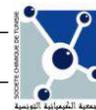
For the development of lithium-ion batteries, the research of new electrode having an improved electrochemical performance has been a matter of numerous researches. Lithium iron phosphate LiFePO_4 with an ordered olivine structure is intensively studied as a promising cathode material due to its low cost, relatively high theoretical specific capacity of 170 mAh.g^{-1} , safety and stability [1, 2]. LiFePO_4 has a lithium intercalation voltage of about 3.4 V versus lithium metal [3].

The main drawback with LiFePO_4 is the low electronic and lithium-ion conductivities [4-7]. Another aspect concerns the material purity; the 1D Li channels make the olivine performances sensitive to impurities and stacking faults that block these channels.

Various synthesis and processing approaches have been carried out to overcome the conductivity problems, which include doping with "supervalent" cations [8, 9], synthesizing LiFePO_4 with small particle size [10-12] and/or coating with conductive additives such as carbon [13-18] and metal powders [19].

In this work, we report on the synthesis of LiFePO_4 with small particle size using the solid-state reaction, widely used for mass production, with classic and modified protocols. The structural characteristics and electrochemical performances of the synthesized LiFePO_4 are discussed.

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2. EXPERIMENTAL

2. 1. Synthesis of samples

A major difficulty of the synthesis of orthophosphate LiFePO_4 is the existence of two oxidation degrees of iron in nature, namely Fe (II) and Fe (III). The ability to control the size and crystallinity of the particles during the synthesis process is crucial. The two protocols of solid-state reaction used to grow this material are:

2. 1. 1. Classical protocol

The LiFePO_4 powder was prepared by mixing the reactants iron (II) oxalate $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, lithium carbonate Li_2CO_3 and ammonium dihydrogen-phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ in a ratio of Li:Fe:P = 1:1:1 with minimum of acetone in the mortar. The initial heating and synthesis were performed in a tubular furnace under N_2 atmosphere with the following four stages of time/temperature regimes: 1.5 h at 100 °C (to remove water from the system), 2 h at 260 °C (to decompose iron oxalate) and 3h at 350 °C (to remove gaseous products and to initiate the synthesis). The final heating was performed at 700 °C for 10 h. The sample obtained in this manner is hereafter named LFP1.

2. 1. 2. Modified protocol

The reactants ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ in ratio of Li:Fe:P = 1:1:1) were mixed thoroughly with high purity ethanol and were stirred under high purity argon for 24 h. Ethanol was eliminated by using rotary evaporator. Thermal treatment was performed in two stages under high purity argon flow. The precursor powders were first annealed at 350°C for 3 h in order to drive away the gases and to initiate the synthesis, then reground and annealed at 700°C for 10 h. The final product is referred to LFP2 sample.

2. 2. Structural and morphological characterization

The crystalline phases of LiFePO_4 powders were identified by X-ray diffraction (XRD) using a Philips X'Pert PRO diffractometer equipped with a Copper or cobalt anticathode at room temperature. The Rietveld refinement of the X-ray powder diffraction patterns was performed using TOPAS 4.2. Microstructural observation was performed using a scanning electron microscope PHILIPS XL30 and an analytical transmission electron microscope FEI Tecnai G2 operating at 200 kV with a LaB_6 filament. ^{57}Fe Mössbauer experiments were performed in transmission geometry at 300 K using a constant-acceleration spectrometer with a ^{57}Co source. The spectra were analyzed using the MOSFIT program [20] and the values of isomer shift calibration were quoted relative to that of $\alpha\text{-Fe}$ at 300 K.

2. 3. Electrochemical characterization

Electrochemical measurements were performed at room temperature in cells fabricated with the LiFePO_4 cathode, metallic lithium anode, 1M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 volume ratio and the separator was fiber filter. The positive electrode was prepared by mixing the active material with acetylene black and binder (polyvinylidene fluoride, PVDF, dissolved in N-methyl-2-pyrrolidone, NMP) in a weight ratio of 80:10:10. The mixture was pressed onto stainless steel mesh used as current collector and dried under vacuum at 80 °C for 16 h. The laboratory cells were assembled in an argon-filled glove box. Charge and discharge tests were performed using a Digatron BTS 600 battery testing system with different rates and voltage cut-off positions at room temperature.

3. RESULTS AND DISCUSSION

The X-ray patterns of LFP1 and LFP2 samples obtained by the two different preparation protocols are reported in Fig. 1. The Rietveld refinement results of the XRD pattern of the LFP1 sample are shown in Fig.1a and Table 1, XRD shows additional peaks attributed to Li_3PO_4 impurity phase ($\approx 24^\circ$ and 29°) and some other unknown peaks shown by an asterisk. Quantitative phase analysis and Rietveld refinement performed by TOPAS 4.2 lead to 94.8(5) % for LiFePO_4 and 5.2(5) % for Li_3PO_4 of weight composition. The Rietveld refinement results of the XRD pattern of the LFP2 sample are shown in Fig.1b and Table 2, all diffraction peaks can be attributed to an

ordered olivine LiFePO_4 structure with orthorhombic lattice ($Pnma$). The sharp peaks and the unit cell volume ($V = 291.3(3) \text{ \AA}^3$) indicate a good crystallinity [21]. An efficient criterion for the crystal quality is the unit cell volume which must be in the range $[291.0 - 291.5] \text{ \AA}^3$ for LiFePO_4 [22]. There is no evidence for the formation of crystalline or amorphous carbons.

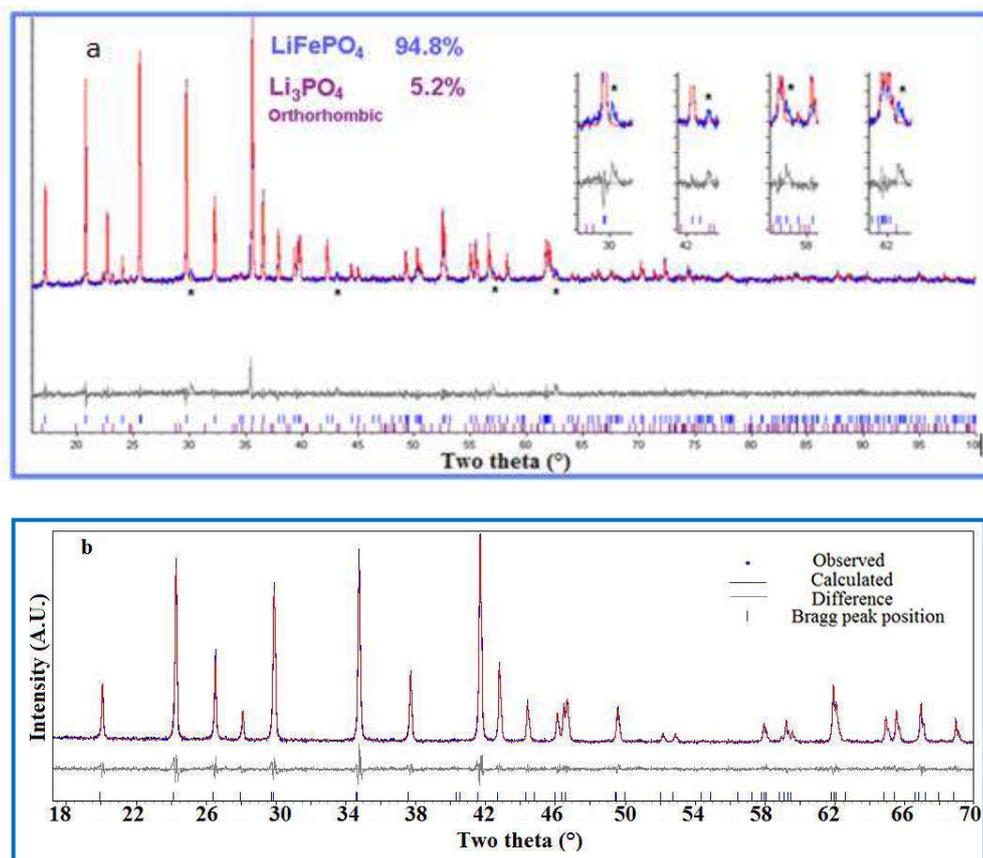


Figure 1: The XRD patterns of: (a) LFP1 and (b) LFP2 samples.

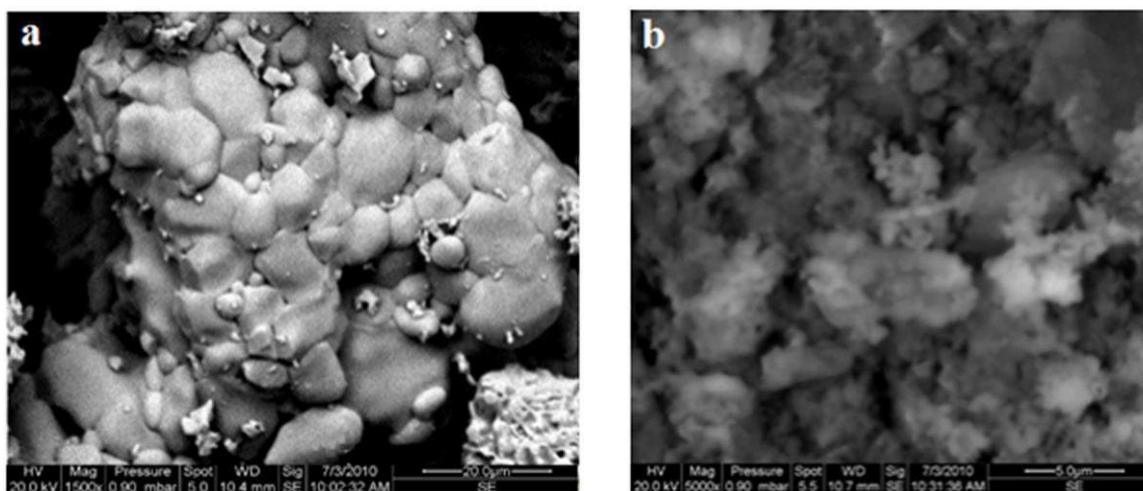
Table I: Results of structural analysis obtained from X-ray Rietveld refinement of LFP1 sample.

Structure 1: LiFePO_4						
Phase formula	LiFePO_4	Space group			$Pnma$	
a (\AA)	10.325(2)	Crystallite Size (nm)			704(31)	
b (\AA)	6.005(1)					
c (\AA)	4.695(2)					
Cell Volume(\AA^3)	290.8(8)	Lorentzian contribution			704(31)	
		Crystal Density (g.cm^{-3})			3.64(2)	
Site	Np	x	y	z	Occ.	B_{eq}
Li	4	0	0	0	0.95(2)	1
Fe	4	0	0	0	0.024(8)	1
Fe	4	0.2828(3)	$\frac{1}{4}$	0.9753(8)	1.012(7)	1
P	4	0.0969(5)	$\frac{1}{4}$	0.417(2)	1	1
O1	4	0.093(2)	$\frac{1}{4}$	0.743(3)	1	1
O2	4	0.450(2)	$\frac{1}{4}$	0.203(3)	1	1
O3	8	0.164(1)	0.042(2)	0.281(2)	1	1

Table II: Results of structural analysis obtained from X-ray Rietveld refinement of LFP2 sample.

Structure: LiFePO ₄						
Phase formula	LiFePO ₄		Space group		Pnma	
a (Å)	10.329(3)	Cell Mass (g)		631.1(2)		
b (Å)	6.007(2)	Crystallite Size (nm)				
c (Å)	4.695(2)	Lorentzian contribution		202.6(55)		
Cell Volume (Å ³)	291.3(2)	Crystal Density (g.cm ⁻³)		3.597(2)		
Site	Np	x	y	z	Occ.	B _{eq}
Li	4	0	0	0	1.000(61)	1
Fe	4	0.28243	¼	0.97600	1.005(66)	1
P	4	0.09500	¼	0.41880	1	1
O1	4	0.09610	¼	0.74850	1	1
O2	4	0.45830	¼	0.20620	1	1
O3	8	0.16580	0.04600	0.28510	1	1

Fig. 2 shows scanning electron microscopy (SEM) micrographs of the LFP1 and LFP2 particles. It reveals that the LFP2 sample (Fig. 2b) is composed of relatively uniform fine particles, with a size ranging from 100 to 300 nm, which were much smaller than those of the LFP1 (Fig. 2a), with average size ranging from 1 to 20 μm . These SEM micrographs show the influence of the modified protocol used. Such a result is usually induced by the presence of organic species with more homogeneous in size and with less evidence of coalescence between the grains to form agglomerated particles [14, 15], but also with micrometric size when the solid state reaction is used. This indicated that the homogenization of reactants by stirring the mixture in ethanol leads to smaller reagents particles preventing particle growth during sintering. These smaller particles which shortened the diffusion path for Li ions were expected to contribute to improved electrochemical properties of the LFP2 compound. It was demonstrated that the electrochemical performance of the electrode is greatly influenced by particle size and morphology of the particles [23].

**Figure 2:** SEM micrographs corresponding to: (a) LFP1 sample and (b) LFP2 sample.

For a better characterization of the micro-structural state of these particles, transmission electron microscopy observations were carried out on the prepared LFP2 powder (Fig. 3). The sample was uniform and composed of non-spherical particles with a size of about 200 nm. This has not been reported yet for solid state reaction, and the particle size is smaller than that reported in the

literature [24, 25]. The uniform morphology and size are due to the homogenization of the starting material by stirring in ethanol for several hours. Note that the average particle size of the synthesized LFP2 sample is in agreement with the obtained crystal grain size calculated from XRD patterns, implying that the particles are in an individual state and not formed from the agglomeration of several grains.

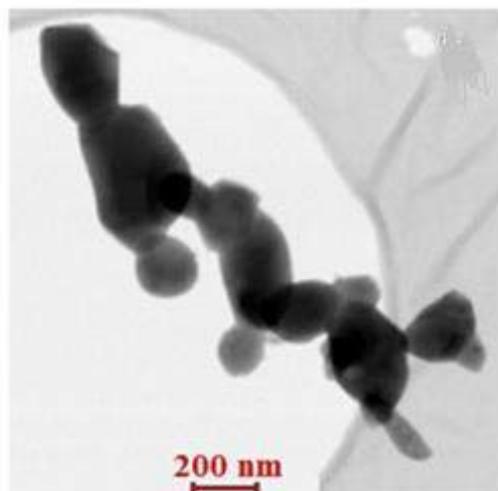


Figure 3: TEM bright field image of crystallized LFP2 sample.

Mössbauer spectroscopy more sensitive than X-ray diffraction for Fe atoms location was used to detect Fe^{3+} impurities. The Mössbauer spectra for LiFePO_4 crystals have been measured by some researchers [10, 26] and the values of isomer shift δ and quadrupole splitting Δ have been reported ($\delta = 1.20\text{--}1.22$ mm/s and $\Delta = 2.95\text{--}2.98$ mm/s). The ^{57}Fe Mössbauer spectrum of the prepared LFP2 recorded at room temperature is shown in Fig. 4 and the results indicate only one quadrupole doublet. The mean values of the hyperfine parameters, $\delta = 1.23$ mm/s and $\Delta = 2.96$ mm/s, are assigned to Fe^{2+} ions with a high spin configuration of 3d electrons and the asymmetric local environment at the Fe in LiFePO_4 as explained by Yamada *et al.* [10], the low line width $\Gamma = 0.34$ mm/s value is due to the formation of LiFePO_4 crystals. We note the absence of Fe^{3+} , any incidence of Fe^{3+} would result in a weak and closely spaced doublet located in between the very strong Fe^{2+} doublets, as was seen in the work of Prince *et al.* [26].

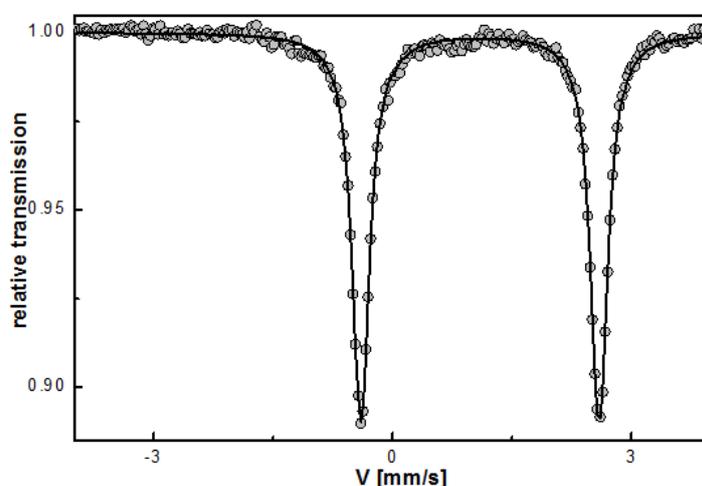


Figure 4: Mössbauer spectrum of the synthesized LFP2 sample. The spheres represent the experimental data, whereas the solid line shows the total fit.

The charge and discharge curves of synthesized LFP1 and LFP2 samples shown in Fig. 5 were carried out at C/20. In both cases, the plateaus were observed in the charge and discharge curves at a potential of about 3.5V versus Li/Li⁺. This electrochemical behavior corresponds to the solid-state redox of Fe^{2+/3+} in the LiFePO₄ accompanied with Li⁺ ion extraction and insertion [1]. The initial discharge capacity of LFP1 sample based on the weight of the active material was 13 mAhg⁻¹ (Fig. 5a) which is considerably smaller than the theoretical capacity (170 mAhg⁻¹). On the other hand, the initial discharge capacity of LFP2 sample was 85 mAhg⁻¹ (Fig. 5b). The very small discharge capacity of the LFP1 sample is probably due to the relatively large particle size and the low electronic conductivity of LiFePO₄. The smaller particle size of LFP2 particles which is helpful for accessibility of the redox centers is favorable to achieve larger capacity.

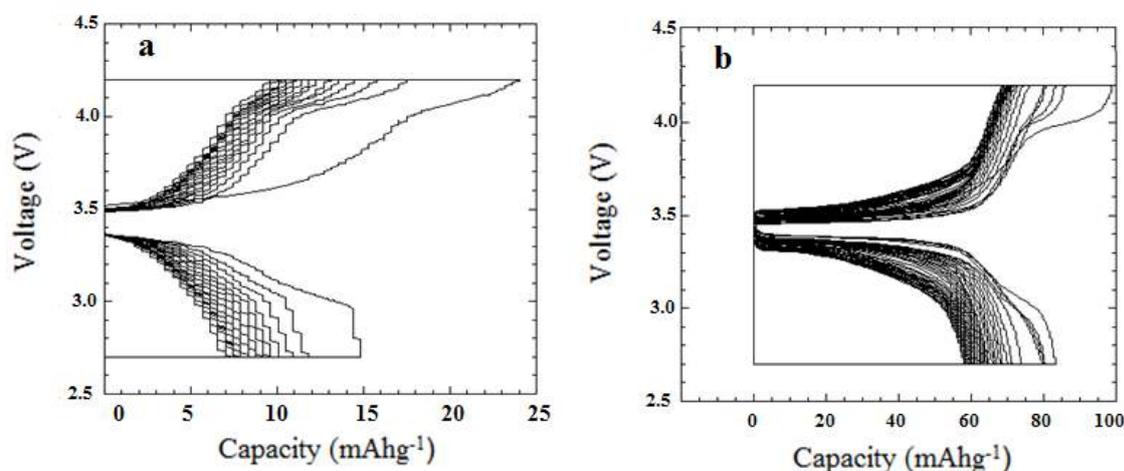


Figure 5: Charge and discharge curves of LFP1 (a) and LFP2 (b) prepared by solid state reaction.

4. CONCLUSIONS

This paper describes a modified protocol of solid state reaction for preparing homogeneous nanometric LiFePO₄ powders. The effects of the modification of synthetic experimental protocol on the properties of the LiFePO₄ compound were investigated. DRX analysis, SEM and TEM images revealed that the size of the LiFePO₄ particles was significantly reduced by stirring the reactants in ethanol for 24 h under argon atmosphere. The particles obtained in this way show a good crystallinity with a particle size of about 200 nm and a relatively good purity compared to the particles obtained by the usual solid state reaction. The improved electrochemical properties were attributed to the reduced LiFePO₄ particle size. This simple preparation method may provide an easy way for industrial production of the LiFePO₄ cathode materials for the lithium-ion batteries.

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