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# Synthesis and characterization of $LiFePO_4$ prepared by sol–gel technique

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**Abstract**

$LiFePO_4$ powder was synthesized by means of a new route, using a two step process. In the first step, an intermediate compound was synthesized by the sol–gel method. This precursor compound to $LiFePO_4$ was characterized by thermal analysis (TG/DTG and DSC), Mössbauer spectroscopy, Transmission Electronic Microscopy (TEM) and Small Angle Scattering (SAXS). In the second step, the precursor was sintered and analyzed by X-ray diffraction (XRD), showing the formation of the proposed single phase material.


*Keywords:* $LiFePO_4$; Sol–gel; X-ray diffraction; Mössbauer spectrometry; TG; DSC; TEM

## 1. Introduction

The olivine-$LiFePO_4$ is a natural compound, but can also be prepared by synthetic methods. The appeal in investigating this compound is due to its electrochemical properties, since bulk $LiFePO_4$ can be used as battery cathode [1]. In order to increase the charge capacity and to improve the conductivity of this material, many works on its synthesis were performed, using different approaches as solid-state reaction [2–4], co-precipitation [5], hydrothermal synthesis [6], solution [7], emulsion-drying [8], etc. In this work a new route of synthesis, using an alcoholic colloidal suspension, was developed by a sequence of systematic chemical reactions. The advantages of this method are the low cost and the application of the produced solution in dip-coating deposition of thin films. As far as we know, there is only one attempt to prepare $LiFePO_4$ thin films, using pulsed laser deposition [9]. The possibility to deposit it as a thin film, opens up its use for microbattery technology.

## 2. Experimental

The precursor $LiFePO_4$ phase was synthesized, from stoichiometric amounts of $Li(OH)\cdot H_2O$ and $H_3PO_4$ diluted in an ethanol/water at 50% solution. Using magnetic stirring and heating at 343 K a precursor compound $LiH_2PO_4$ was formed. Then, an alcoholic (ethanol) solution of Iron(III) Acetylacetonate, $Fe(AcAc)_3$, was added to the former solution to complete the stoichiometry, maintaining the magnetic stirring and heating for approximately 1 h. The process was completed with cycles of centrifugation followed by washes with a solution of 1-butanol or a solution of propanol, both with 2% (in volume) of the surfactant Renex-95, Polibrasil®. This surfactant was chosen because it evaporates without decomposition. Four cycles were enough to peptize the precipitates. A pale blue sol was obtained after the complete washing process. The sol obtained with propanol is unstable, presenting precipitates, while the sol formed with 1-butanol is homogenous and viscous. The sol prepared with a 1-butanol solution was dried at 343 K and a very fine powder was formed. This sample was calcined at 873 K under a $N_2$ atmosphere during 2.5 h, forming the $LiFePO_4$ powder.

TG/DTG (thermogravimetry and differential thermogravimetry) curves were obtained with a thermobalance model TGA 50 (Shimadzu) in the temperature range 298–873 K, using Pt crucibles with 6.4 mg of samples, under dynamic nitrogen atmosphere (50 mL $min^{-1}$) and heating rate of 10 K $min^{-1}$. Differential scanning calorimetry (DSC) curves were obtained in a DSC-50 cell (Shimadzu) using Al crucibles with 2.4 mg of samples, under dynamic nitrogen atmosphere (100 mL $min^{-1}$) and heating rate of 10 K $min^{-1}$ in the temperature range from

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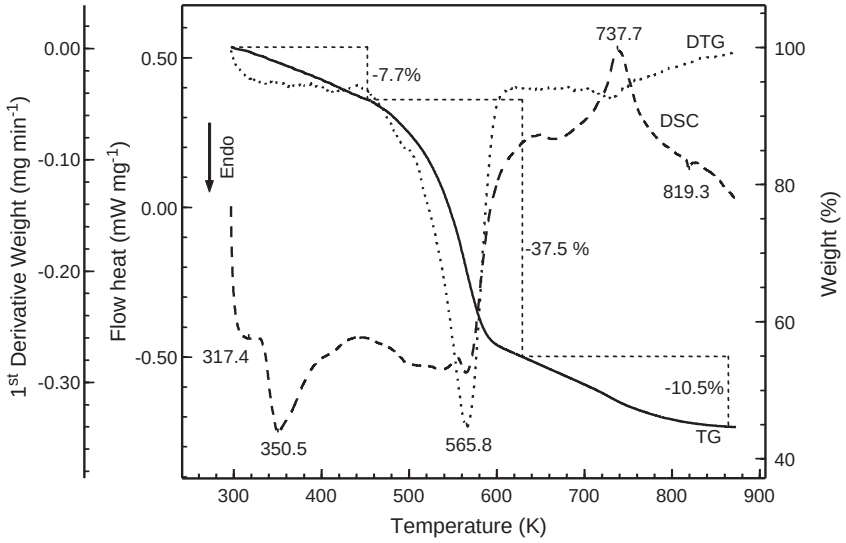


Fig. 1. TG/DTG and DSC curves of the precursor phase to $LiFePO_4$, obtained under a $N_2$ dynamic atmosphere, at a heating rate of 10 K/min.

298 to 873 K. The DSC cell was calibrated with indium (m.p. 429.6 K; $\Delta H_{fus.}=28.54$ J $g^{-1}$) and zinc (m.p. 692.6 K).

Mössbauer spectroscopy (MS) measurements were performed in transmission geometry at 294 K, in plastic sample holders, using a constant-acceleration spectrometer with a 57Co/Rh source. An α-Fe foil at 294 K was used to calibrate the isomer shifts and the velocity scale.

In order to study the particles in suspension, small angle X-ray scattering (SAXS) was utilized; the experiments were done with Cu Ká radiation (0.15418 nm), and an image plate detector to record the scattering intensity as a function of the scattering vector $q=4\pi\sin\theta/\lambda$ ($\theta$ being half of the scattering angle, and $\lambda$ the X-ray wavelength). The SAXS data were collected during 2 h at room temperature, with a power of 10 kW (50 kV and 200 mA). The sample-detector distance was 480 mm.

Micrographs were obtained in a Carl Zeiss CEM 902 transmission electron microscope at a power of 80 kV. The images were recorded with a CCD camera. The analyzed samples were prepared using 300-mesh copper grids.

The X-ray diffraction (XRD) pattern of the sample sintered at 873 K was obtained with Cu Kα radiation (0.15418 nm), using a scintillation counter and a graphite [002] bent monochromator. The data were collected in step scanning mode ($\Delta 2\theta=0.05°$) over the angular range of $15°<2\theta<85°$, with a constant counting time of 5 s per step. The structural parameters were determined by Rietveld analysis of the diffraction profiles, using the GSAS program. The spatial group setting was Pnma of synthetic triphylite $LiFePO_4$ [10].

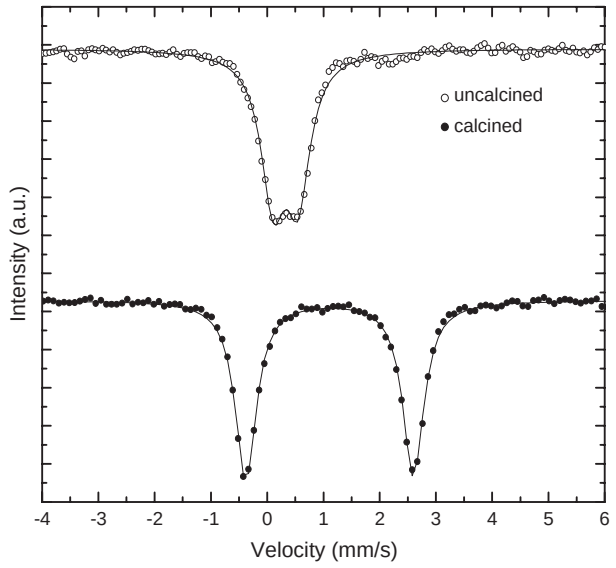


Fig. 2. Mössbauer spectra of the precursor phase to $LiFePO_4$ (open dot) and $LiFePO_4$ calcined powder sample (solid dot).

## 3. Results and discussion

TG/DTG and DSC curves (Fig. 1) of the precursor phase to $LiFePO_4$, prepared with 1-butanol at 2% in volume of Renex, show three mass loss main stages. The first one, between 298 and 453 K ($\Delta m=7.7\%$) is associated to release of physically adsorbed water and organic compounds evaporation processes. DSC curve indicates that these processes are endothermic ($T_{peak}=313$ and 350 K). The second one ($\Delta m=37.5\%$), which occurs between 453 and 633 K (DSC curve shows endothermic events), is due to surfactant thermal decomposition with carbon elemental formation. Finally, the third stage of mass loss ($\Delta m=10.5\%$) occurs of slow and gradual form above 633 K, when elemental carbon is released. DSC curve show the exothermic event ($T_{peak}=737.7$ K). The formation of the solid $LiFePO_4$ occurs above 737.7 K; this temperature is comparable to the one obtained by Franger et al. [11] using mechanochem-

Table 1
Mössbauer parameters of *as-prepared* and calcined samples, at $T=296$ K: isomer shift (IS), quadrupole splitting (QS), linewidth ($\Gamma$), and relative spectral area ($I$)

| | IS (mm/s) | QS (mm/s) | $\Gamma$ (mm/s) | $I$ (%) |
|---|---|---|---|---|
| As-prepared | 0.42(1) | 0.44(2) | 0.52(1) | 100(2) |
| Calcined | 1.21(2) | 2.98(2) | 0.44(1) | 100(2) |

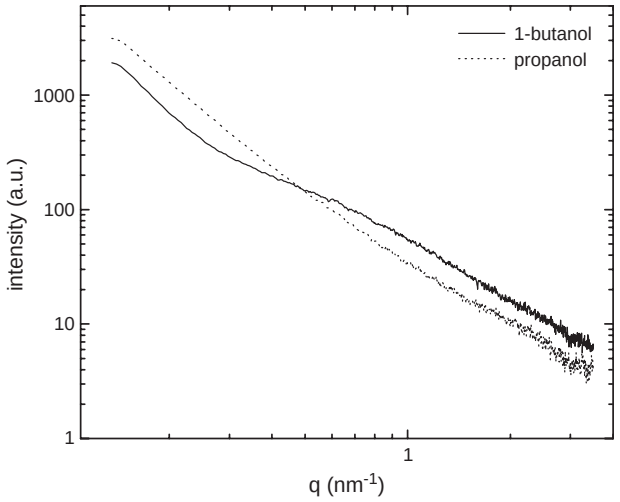


Fig. 3. SAXS data of the colloidal suspension in alcoholic solution of: 1-butanol (solid line) and propanol (dot line).

ical activation and lower than that obtained in solid-state reaction. At around 819.3 K a structural change can occur, probably, due to reorganization of the crystal lattice and this can be attributed to the endothermic event evidenced in the curve DSC.

The Mössbauer spectroscopy profiles of the precursor phase to $LiFePO_4$ and $LiFePO_4$ powder samples are displayed in Fig. 2 and the results of the analyses are listed in Table 1. The precursor phase to $LiFePO_4$ shows the hyperfine parameters characteristic of a ferric (Fe(III)) oxidation state, with quite broad line, indicating some degree of local structural disorder at the Fe sites. After calcination, the analysis shows the hyperfine parameters typical of high-spin ($S=2$ Fe(II)) ferrous ions, suggesting the reduction of this element during the calcination.

The SAXS curves of the dried colloidal suspension of the precursor phase to $LiFePO_4$ are presented in Fig. 3. The data could not be fitted with simple models, like mono or polydisperse systems of spheres [12]. The analysis of the Porod region (ln $I$ vs. ln $q$ at high $q$) shows an angular coefficient $\alpha_P<2$, indicating that the electronic contrast is not well-defined [12]. In order to elucidate the morphology of the material a direct inspection was carried out by TEM.

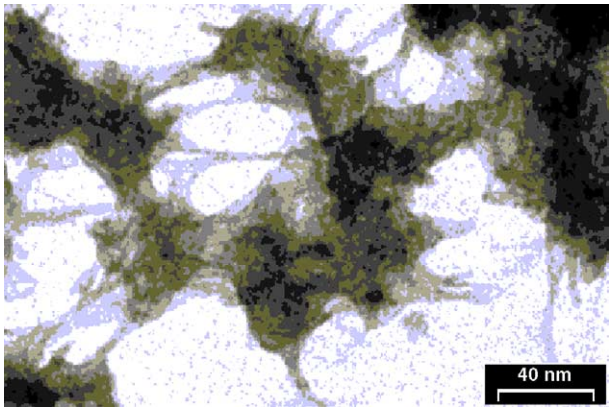


Fig. 4. TEM picture of the precursor phase to $LiFePO_4$, prepared with 1-butanol, dried at room temperature.

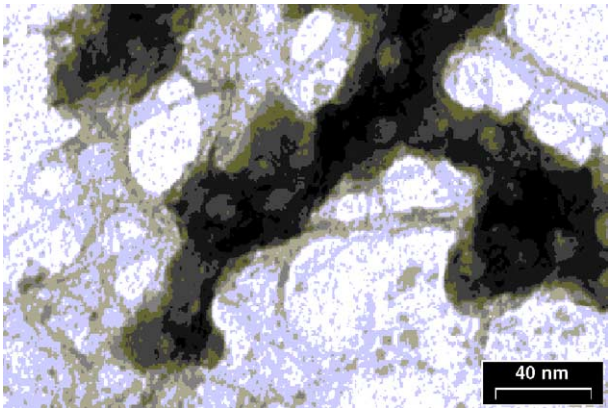


Fig. 5. TEM picture of the precursor phase to $LiFePO_4$, prepared with propanol, dried at room temperature.

Figs. 4 and 5 depict TEM pictures of the same samples measured by SAXS. Indeed, they have a complex structure, nanometer sized, formed by single particles, strings and clusters. It also observed regions with different electronic densities, corroborating the SAXS results.

The X-ray diffraction analysis of the synthesized compound (calcination at 873 K during 2.5 h) showed that it is single phase $LiFePO_4$; odd phases, which could be assigned to Fe(III) crystalline compounds, were not detected. Additionally, the peak profiles are quite narrow, indicating a well-crystallized phase (Fig. 6).

The structural parameters obtained from X-ray Rietveld refinement of the calcined material are listed in Table 2. The reliability factor ($R_{Bragg}$) found is around 3%, which indicates a good solution. The lattice parameter and atomic positions are in agreement with the ones obtained by other authors with other techniques [2–4,6,8].

The crystallite size was calculated for [020], [111] and [002] crystallographic directions using the Scherrer's formula [13], giving a mean value of 60 nm.

## 4. Conclusions

SAXS and TEM results indicate that the precursor phase to $LiFePO_4$ presents a very interconnected and complex mor-

Table 2
Parameters obtained with X-ray Rietveld refinement of the $LiFePO_4$ phase synthesized by the sol–gel method

| $LiFePO_4$ | | | | |
|---|---|---|---|---|
| Space group: Pnma | | | | |
| | a(nm) 1.03009(3) | b(nm) 0.59925(2) | c(nm) 0.46942(2) | |
| | $x$ | y | z | B ($\times 10^{-2}$ nm$^2$) |
| Li | 0 | 0 | 0 | 2.95(70) |
| Fe | 0.2825(2) | 1/4 | 0.9751(5) | 1.81(8) |
| P | 0.0953(3) | 1/4 | 0.4168(7) | 1.68(15) |
| O1 | 0.0995(9) | 1/4 | 0.7489(20) | 1.31(34) |
| O2 | 0.4564(9) | 1/4 | 0.2037(20) | 2.18(27) |
| O3 | 0.1642(7) | 0.04535(10) | 0.2857(13) | 1.61(22) |
| | | $R_{bragg}=3\%$[a] | | |

[a] $R_{Bragg}$ is the reliability factor.

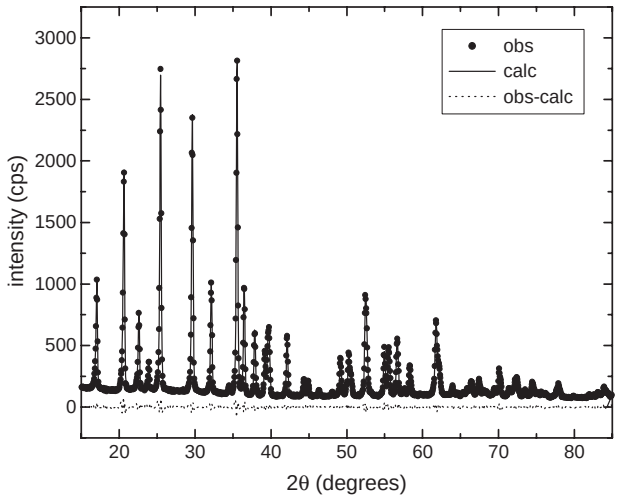


Fig. 6. Rietveld refinement of the $LiFePO_4$ powder, synthesized at 873 K during 2.5 h: experimental profile (dot ), calculated profile (line), and difference between the observed and calculated profiles (at bottom, dot line).

phology as a fiber-like structure, nanometer sized. These findings corroborate the idea that it is possible to grow denser thin films with the prepared colloidal solution.

Following the synthesis procedure, a pure well-crystallized $LiFePO_4$ solid was obtained with reduced calcination time (2.5 h).

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