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A novel concept for the synthesis of nanometric LiFePO_4 by co-precipitation method in an anhydrous environment

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Abstract

LiFePO_4 with high purity and good crystallinity was prepared by an improved environmentally benign and low-cost co-precipitation method. The precipitate was synthesized at a room temperature using technical grade reagents on ethylene glycol as a medium. LiFePO_4 precursor was characterized by TGA/DTG measurement and 650°C was found to be the optimal calcination temperature. The obtained LiFePO_4 was characterized by X-ray diffraction (XRD), Transmission Electronic Microscopy (TEM), and nitrogen adsorption/desorption measurements (N_2 -BET). The X-ray diffraction studies confirmed formation pure phase of orthorhombic LiFePO_4 (*Pnma* space group) without any impurities. The developed co-precipitation method in an anhydrous environment is environmental friendly, cheap and can be easily scalable.

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Keywords: Li-ion batteries; LiFePO_4 ; lithium iron phosphate; precipitation method.

1. Introduction

The LiFePO_4 (LFP) material with an olivine structure was first reported as promising cathode material for Li-ion batteries by Goodenough and co-workers in 1997 [1]. The reasons for interest in LiFePO_4 are its numerous advantages such as environmentally benign constituents, low price, excellent thermal and chemical stability, cycling stability and satisfactory theoretical capacity of 170 mAhg^{-1} [2]. Despite these favorable characteristics its application for high-power battery is hampered because of its poor electrical conductivity ($\sim 10^{-9}$ S cm^{-1}) and low

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lithium ion diffusivity [3]. However, it is possible to overcome limitation related with the low electronic conductivity by minimizing the particles size and coating the material with a carbon conducting layers [4,5]. In recent years, LiFePO_4 have been produced and investigated in many different preparation methods with satisfactory results. Much research has been conducted to explore the synthesis process to improve the electrochemical performance. Wide variety of synthetic methods of the olivine-type LiFePO_4 have been proposed in recent years. The most common ones are: high temperature solid state reaction [6,7], sol-gel [8], carbothermal reduction [9], supercritical hydrothermal [10] and co-precipitation [11]. The solid-state synthesis allows to obtain pure crystalline olivine-phase LiFePO_4 , but it is connected with repeated grinding to gain homogenous particles and stepwise calcination at high temperatures to prevent the formation of the impurities. Disadvantage of the described method is the formation of large particles, agglomeration and irregular morphology [6,12]. Sol-gel processing is an effective method to synthesize LiFePO_4 . This procedure enable to obtained material with good stoichiometry and control of grain size. Additionally the calcination temperatures could be lower than in ceramic powder methods. However, this type of synthesis is complex and costly. Well-crystallized LiFePO_4 can be obtained with a carbothermal reduction method by using inexpensive starting materials and conductive additives. This type of synthesis allows obtaining small particles during uncomplicated process [9,12,13]. However, it is hard to control the homogeneity of the material and the procedure is time and energy consuming. Another method for the synthesis of nano-sized LiFePO_4 is supercritical hydrothermal synthesis [10]. Application of supercritical water ensures rapid reaction rate and good reactant diffusivity [14]. During co-precipitation synthesis it is possible to optimize the particle size but because of highly reductive conditions in which phosphate reduced into phosphides the purity of samples is hard to control. Among the preparation procedures of LiFePO_4 the solid-state reaction can be applicable for mass production[15]. In order to overcome above disadvantages mentioned about solid-state method, the co-precipitation method has been proposed as an alternative for preparing LiFePO_4 . There is still a need for new synthesis procedure that reduce consumption of time, costs and allows to obtain a homogeneous material, with good electrochemical properties.

In this study, we describe a novel, simple and low-energy way synthesis method of LiFePO_4 precursors using anhydrous precipitation technique. The simple co-precipitation method is successfully introduced to prepare nanostructured olivine-type LiFePO_4 with controlled morphology and grain size.

2. Experimental

2.1. Preparation of materials

The LiFePO_4 cathode material was prepared in a two-step process. In the first step, precipitation method was used to synthesized an intermediate compound. The precursors of LiFePO_4 was obtained in nonaqueous conditions (ethylene glycol) at room temperature. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Chempur), $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ (Sigma) and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ (POCH) were used as starting reagents and were applied in an appropriate ratio. Iron (II) sulfate and lithium acetate have been dissolved in ethylene glycol (Chempur) in inert atmosphere. A green-colored solution was obtained after stirring. Then the solution of ammonium dihydrogen phosphate in ethylene glycol was added dropwise. After reaction the precipitate was separated from ethylene glycol by centrifugation, washed several times with acetone (Chempur) and dried in an air drier at 40 °C for 24h. The reaction medium can be recovered and reused after centrifugation. The use of ethylene glycol as reaction medium allow precipitation of LiFePO_4 precursor at room temperature and can provide the ability of the grain size and shape control. The second step required heat treatment of the obtained precursor. Controlled calcination was performed in inert atmosphere within temperature range 550–750 °C for 12 h.

2.2 Characterization

To determine the calcination temperature of LiFePO_4 precursor thermal gravimetry analyses (TGA/DTG) coupled with evolved gas analysis mass spectrometry (MS-EGA) were used. It was performed on Mettler-Toledo 851° thermo-analyzer (temperature range of 20–1000 °C with a heating rate of 10 °C/min). Powder X-Ray

Diffraction (XRD) was used to examine the crystalline structure of obtained LiFePO_4 materials. XRD patterns of the samples were collected with Bruker D2 PHASER X-ray powder diffractometer (Cu lamp, $\text{K}\alpha_1$ radiation = 1,54056 Å). The low-temperature nitrogen adsorption–desorption measurements were executed using ASAP 2010 Micromeritics instrument. The specific surface area of the obtained mesoporous materials was determined using BET (Braunauer–Emmett–Teller) model. The morphology of the material was studied using FEO Tecnai TF20X-Twin (200 kV) equipped with EDAX system.

3. Results and discussion

To determine the optimum conditions for the heat treatment of the obtained LFP precursor the thermo gravimetric analysis were used. TGA/DTG curves of the LFP precipitate are shown in Fig. 1a. The composition of the gases released from LFP precursor was evaluated by mass spectrometry evolved gas analysis (MS-EGA), which is shown in Fig. 1b. Decomposition process of LFP precursor terminates above 500 °C, hence the calcination was performed in the range of 550-750 °C. However, we have found the optimum temperature was 650 °C, which ensured obtaining the pure product phase.

Fig. 2 shows the X-ray diffraction data collected for LiFePO_4 materials obtained using different ratios of starting reagents. The first sample contained a stoichiometric amount of the reactants (LFP-1) and a second one contained 50% excess of lithium salts (LFP-2). In the sample LFP-1 in addition to LiFePO_4 also includes contamination, which was $\text{Fe}_2(\text{P}_2\text{O}_7)$. This impurity indicates a deficiency of lithium salts used in the reaction. In a next step a syntheses with the use of 50 % molar excess of the lithium salt was prepared. With that excess, the purity of LFP-2 was substantially improved. In the X-ray diffraction patterns all diffraction lines of the LFP-2 samples were the same as those of pure orthorhombic olivine phase LiFePO_4 .

The nitrogen adsorption/desorption isotherms of the sample LFP-2 calcined at 650 °C are shown in Fig. 3. The shape of adsorption/desorption curves indicates type IV physisorption isotherms according to the IUPAC classification. Calculated specific surface area of $5.7 \text{ m}^2 \text{ g}^{-1}$ was obtained in accordance with the BET analysis. The Barrett-Joyner-Halenda (BJH) pore-size distribution, shown in the Figure 3b, indicates the narrow distributions of the pore size where most of them have diameter about 3.8 nm. The loop in adsorption and desorption isotherm disappears suggesting the collapse of the porous structure in the sample during N_2 adsorption/desorption measurements.

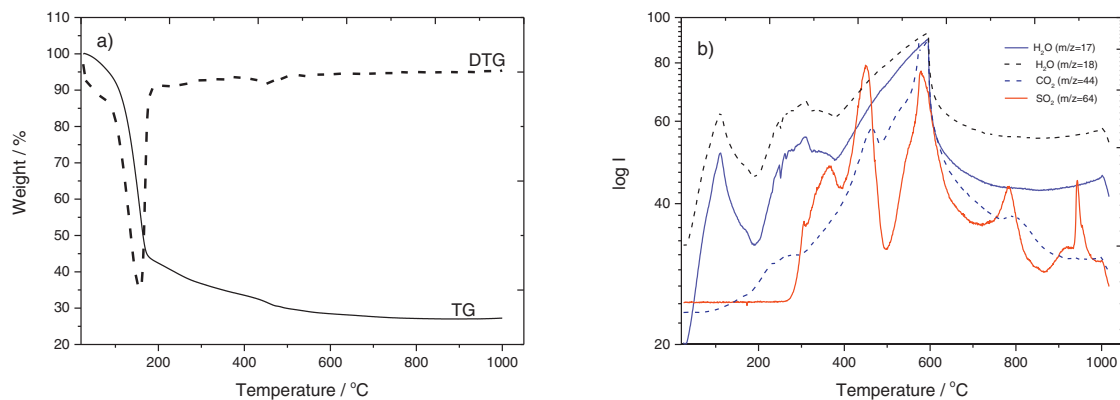


Fig. 1 Thermal analysis of LFP precursor (TGA/DTG/SDTA) conducted under argon atmosphere at heating rate of 10 °C/min, (a) TGA/DTG curves; (b) evolved gas analysis (EGA-QMS).

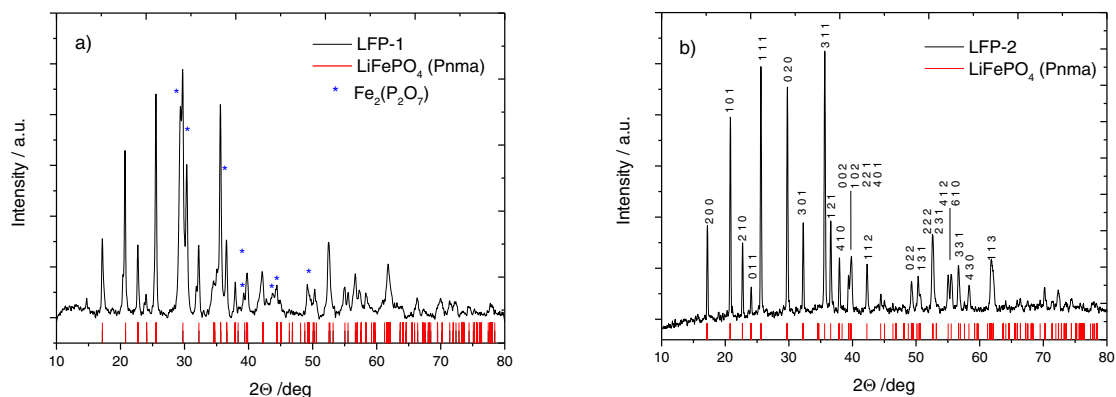


Fig. 2. XRD patterns of (a) LiFePO₄ with a stoichiometric amount of the reactants (LFP-1) and (b) LiFePO₄ contained 50% weight excess of lithium salts (LFP-2). The vertical lines (on the bottom of graphs) mark reference diffraction patterns of LiFePO₄ (with Pnma space specified in the International Center for Diffraction Data (ICDD) database with PDF 4+ code 04-015-6173).

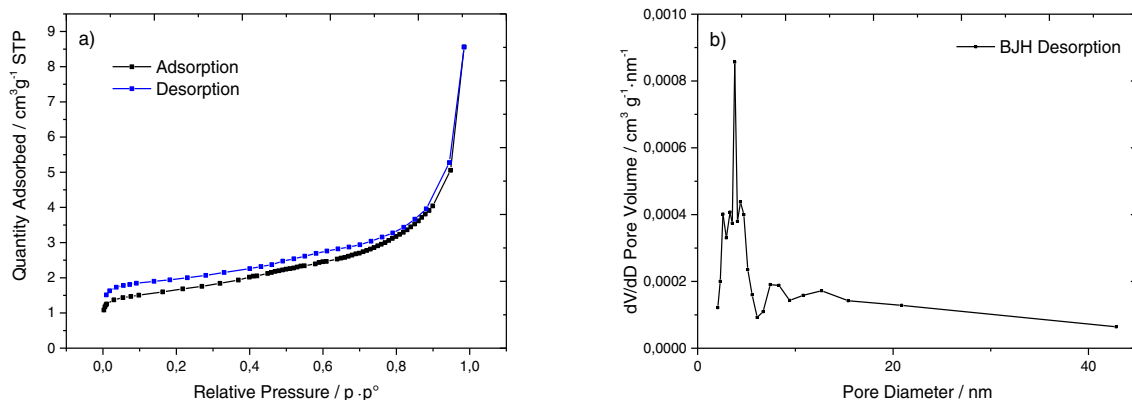


Fig. 3. Nitrogen sorption results for LiFePO₄ samples calcined at 650 °C. (a) N₂ isotherms; (b) BJH desorption pore size distribution

The TEM studies confirmed preparation of nano-crystallite LiFePO₄ composed of primary particles of 100-200 nm (Fig. 4). High-resolution transmission electron microscopy (HRTEM) (Fig. 4c) reveals presence of thin layer of amorphous LiFePO₄ on the surface of material grains. This layer probably contributes to sintering resulting in formation of larger agglomerated secondary particles. Elemental mapping by energy dispersive X-ray spectroscopy (EDS) of LFP-2 sample is shown in Fig. 4d. The homogeneous distributions of Fe, P, and O elements in the sample is confirmed. A presence of carbon traces have not been observed in the sample.

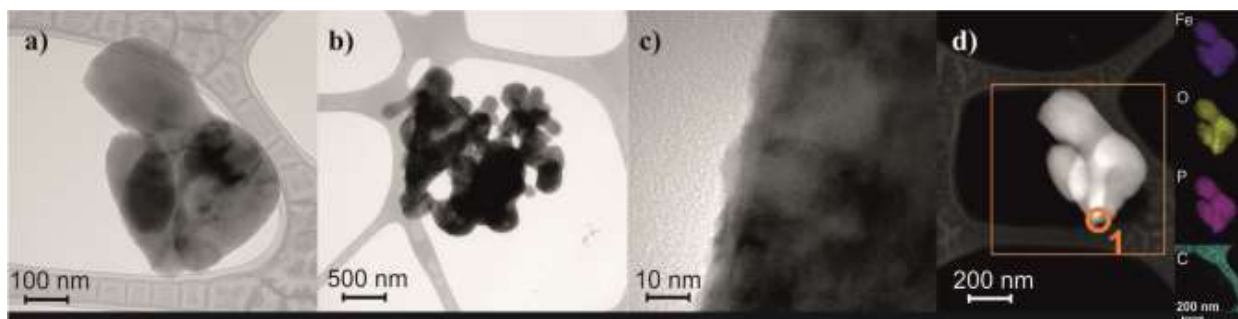


Fig. 4. TEM micrographs of LFP-2. Micrographs (a), (b) present bright field images; (c) high resolution micrograph (HREM); (d) microstructure image observed in STEM HAADF with EDS analysis from marked points

Conclusions

Pure phase fine nano-powder of LiFePO_4 , was synthesized by novel co-precipitation method in an anhydrous environment. The use of ethylene glycol as reaction medium allows precipitation of LFP precursor at room temperature and provides the ability to control the grain size and shape. The process of thermal treatment requires further optimization, which will prevent sintering LiFePO_4 grains and will ensure receipt of a homogeneous material with satisfactory electrochemical properties and morphology.

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