Hydrothermal synthesis of $LiFePO_4$ particles with controlled morphology

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Abstract. Lithium iron phosphate was prepared by hydrothermal synthesis using $LiOH{\cdot}H_2O$, $FeSO_4{\cdot}7H_2O$, $(NH_4)_2HPO_4$, and aminoterephthalic acid (ATPA) as raw materials. The effects of ATPA concentration on particle morphology and electrochemical property were investigated. The samples were characterized by scanning electronic microscope (SEM), X-ray powder diffraction (XRD), infrared absorption spectroscopy (IR) and elemental analysis. The results showed that the particles exhibit a rod-like morphology in the absence of ATPA. When ATPA is added to the system, the particles crystallize as hexagonal plates. An increase in the ATPA concentration leads to the formation of structures with a more complex hierarchical arrangement of structural elements. The resulting particles are expected to serve as a cathode material for industrial needs in electric vehicles (EVs), hybrid electric vehicles (HEVs), and other mobile or portable electrical devices.

1 Introduction

Among the Li ion battery materials, the olivine-structured cathode $LiFePO_4$ material has attracted considerable attention. Extensive studies have focused on this material due to its low cost, non-toxicity, environmental safety, cycling stability [1], high theoretical capacity (170 mAh g^{-1}) [2] and charge potential (3.45 V versus Li^+/Li). However, a separation of the FeO_6 octahedra by PO_3^{4-} ions in the $LiFePO_4$ structure reduces its electronic conductivity, and a slightly distorted hexagonal close-packed oxygen array provides limited channels for Li-ion diffusion [3]. The poor electronic conductivity and slow diffusion of lithium ions [4, 5] impede rate capability, a critical parameter for high power applications [6, 7].

In this context, tremendous efforts have been made in recent years to overcome these problems in three aspects: enhancing the surface electron conductivity (by conductive agent coating) [8, 9]; increasing Li-ion conductivity in the bulk (by cationic doping) [10, 11]; and especially decreasing the Li-ion transport path (by reducing the particle size) [12]. Isam et al. [13] reported that the Li^+ ions preferably move along the *b*-axis rather than along the *a*- or *c*-axis in crystals with the orthorhombic space group *Pnma* due to the lowest Li^+

⁻ Corresponding author: zima@solid.nsc.ru migration energy. Gaberscek et al. [14] presented a theoretical model to explain why the ionic conductivity (ca. 10^{-11}-10^{-10} S cm^{-1} at RT) of $LiFePO_4$ is much smaller than the electronic conductivity (>10^{-9} S cm^{-1} at RT), which implies that the mass transport of Li^+ is crucial for improving the kinetic issues. Therefore, it presents a possible way to enhance the kinetics of $LiFePO_4$ electrode material through controlling the nanostructure of $LiFePO_4$ with small scale along the *b*-axis, which may afford the $LiFePO_4$ material excellent performance with high rate capability owing to a shortened lithium ion diffusion path length. Recently, much progress has been made in this respect. Liu et al. [15] adopted a solvothermal method to prepare carbon coated $LiFePO_4$ nanoparticles (~50 nm along the *b*-axis), which could have a discharge capacity of ~155 mAh g^{-1} at a 0.1 C rate. Vittal et al. [16] adopted solvothermal method to synthesize $LiFePO_4$/C particles with ethylene glycol as a solvent. In fact, it was shown that the use of organic reagents is critical to tune particle size and morphology due to the adsorption of molecules of these substances on the surface of the particles during their growth.

In the present work $LiFePO_4$ particles were synthesized with controllable *b*-axis thickness through tuning the concentration of aminoterephthalic acid in a hydrothermal way. Experiments show that by increasing concentration of ATPA from 0.0028 moles to 0.0083 moles, the $LiFePO_4$ morphology evolves from hexagonal plates to plate assemblies - the structures with a more complex hierarchical arrangement of structural elements, while in the absence of ATPA, only $LiFePO_4$ rods were obtained. The aim of this work was to obtain $LiFePO_4$ powders with controlled morphology under hydrothermal conditions. Further, it is planned to investigate their electrochemical properties.

2 Experimental Method

The synthesis of $LiFePO_4$ particles was carried out using $LiOH \cdot H_2O$, $FeSO_4 \cdot 7H_2O$, $(NH_4)_2HPO_4$ as starting reagents. In a typical procedure, these reagents were mixed in the mass ratio 1:3:2.5 with 25 ml of distilled water at room temperature. The mixture transformed into a homogeneous solution, to which aminoterephthalic acid (ATPA, $C_8H_7NO_4$) was added in amount of 0.0028, 0.0056 or 0.0084 mole. After magnetic stirring, the specimen was transferred into a 40 ml PTFE-lined stainless steel autoclave and held in an oven at 180 ^oC for 24 h. After the hydrothermal reaction, the autoclave was cooled to room temperature and the resulting precipitate was separated by centrifugation, then washed several times with distilled water and dried in air at 80 ^0C for 10 h.

The resulting powders were characterized by X-ray powder diffraction (XRD) using a D8 Advance diffractometer with monochromatic CuK_α radiation. The lattice parameter refinement was performed by the Rietveld method. The infrared (IR) absorption spectra have been measured by an Infralum FT-801 Spectrometer in a region of 1750–500 cm^{-1}. Scanning electron microscopic analysis (SEM) was carried out using TM-1000 (Hitachi) with an accelerating voltage of 15 kV, equipped with an energy dispersive X-ray (EDX) spectrometer.

3 Results and Discussion

The XRD patterns of synthesized powders are shown in Fig. 1. The XRD patterns clearly show the single-phase structure of all synthesized samples without any observable impurity phase. All of the diffraction lines could be indexed to an orthorhombic system of $LiFePO_4$ with the *Pnma* space group (ICDD, Card 83-2092). The refined lattice parameters of $LiFePO_4$ are a = 1.03226 nm, b = 0.60025 nm, c = 0.46974 nm, and V = 0.29107 nm^3,

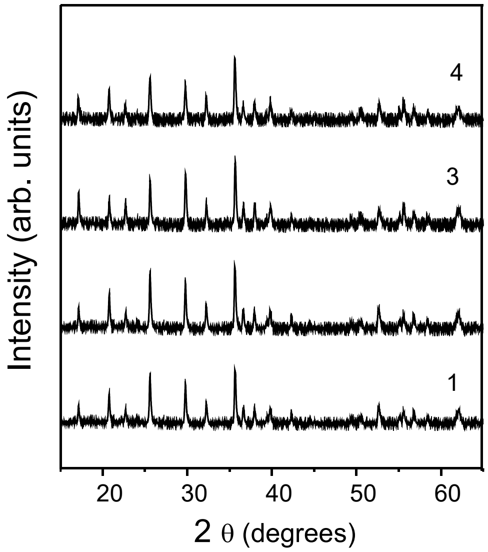

Fig. 1. Diffraction patterns of powders obtained without additive (1) and in the presence of ATPA in an amount of 0.0028 (2), 0.0056 (3), and 0.0084 (4) mole.

which are in good agreement with the literature values [17, 18]. In addition, the olivine-type phase structure of the $LiFePO_4$ was confirmed by IR spectroscopy. The IR spectra of the synthesized powders are shown in Fig. 2. As shown in Fig. 2, the shoulders at 947 cm^{-1} and the band at 970 cm^{-1} are assigned to the symmetric P–O stretching vibration of the PO_4^{3-} group, while the rest three bands at 1060, 1098 and 1138 cm^{-1} are due to the asymmetric P–O stretching vibrations. The asymmetric bending OPO mode splits into four bands at 544, 583, 632 and 648 cm^{-1}.

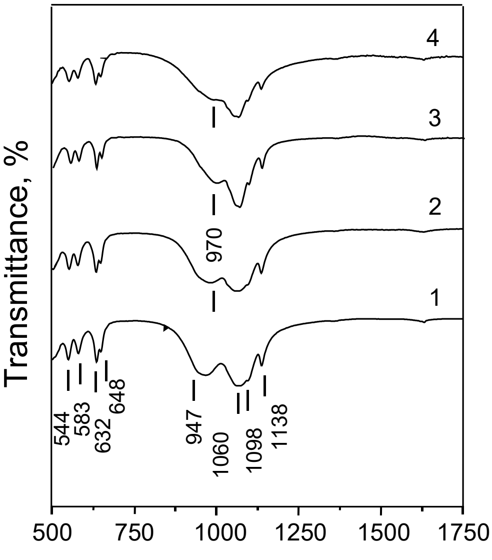

Fig. 2. The IR spectra of powders obtained without additive (1) and in the presence of ATPA in an amount of 0.0028 (2), 0.0056 (3), and 0.0084 (4) mole.

The morphology of the as-prepared particles $LiFePO_4$ is shown in Fig. 3. It can be clearly seen that powder obtained without ATPA is composed of rods with ~1 μm thickness (Fig. 3a). When 0.0028 mole of ATPA is added to the reaction mixture, hexagonal plates are formed (Fig. 3b). The thickness of these plates is about 300-500 nm and a length in the range from ~1.5 μm to ~3 μm. When a higher concentration of ATPA (0.0056 mole) is used, a hierarchical assembly of hexagonal plates in three-dimensional structures is observed, as shown in Fig. 3c. In such structures, one can see hexagonal plates with a thickness of about 100 nm. The content of such thin nanoplates increases in sample synthesized with 0.0084 moles of ATPA (Fig. 3d). Therefore, with the increasing concentration of ATPA, the $LiFePO_4$ morphology evolves from sufficiently thick hexagonal plates to thinner plate assembles which form structure with a more complex hierarchical arrangement of individual structural elements. Similar the variations in morphology can be associated with the influence of ATPA on the nucleation process and the growth rate of $LiFePO_4$ particles.

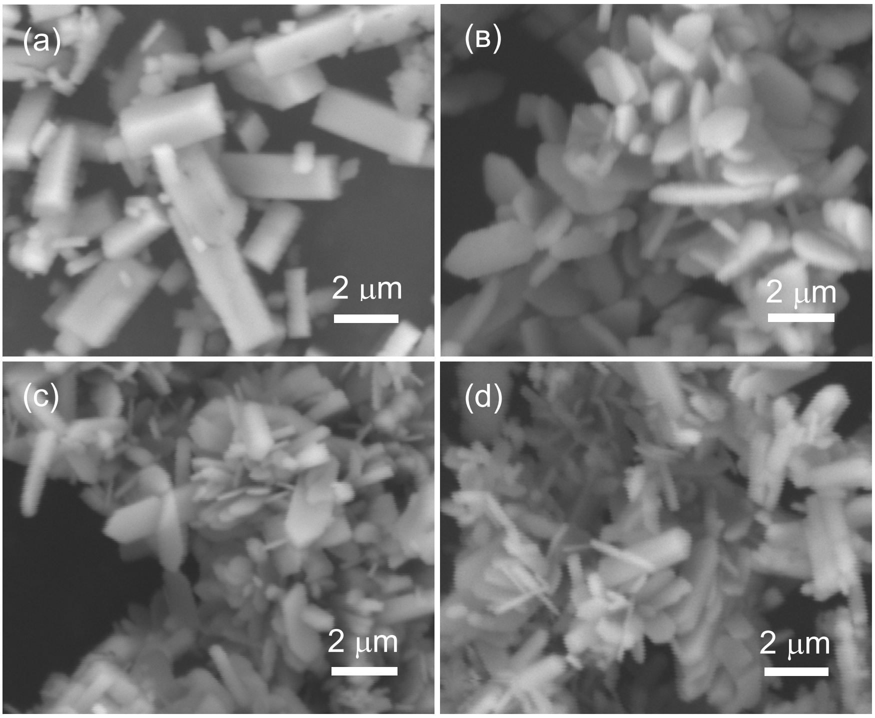

Fig. 3. SEM images of $LiFePO_4$ particles obtained without additive (a) and in the presence of ATPA in an amount of 0.0028 (b), 0.0056 (c), and 0.0084 (d) mole.

4 Conclusions

In summary, $LiFePO_4$ particles were synthesized with controlled morphology just by altering the concentration of aminoterephthalic acid under hydrothermal conditions. As a result, increasing concentration of ATPA from 0.0028 moles to 0.0083 moles, the $LiFePO_4$ morphology evolves from hexagonal plates to plate assemblies which form the structures with a more complex hierarchical arrangement of structural elements. Further, it is planned to investigate their electrochemical properties.

The work was carried out with the financial support of the RFBR grant No. 20-58-53055.

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