

Octagonal prism shaped lithium iron phosphate composite particles as positive electrode materials for rechargeable lithium-ion battery



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ABSTRACT

For the first time, octagonal prism shaped lithium iron phosphate (LiFePO₄) composite particles supported on the multi-walled carbon nanotubes (MWNTs) (denoted as OP-LiFePO₄/MWNTs) are prepared by using a boiling reflux assisted calcination method. Interestingly, spherical LiFePO₄ composite particles (indexed as S-LiFePO₄/C) are produced by the same procedure in the presence of activated carbon. It is observed that the edge length of OP-LiFePO₄ particles is about 400 nm as compared to the particle size of S-LiFePO₄ (~150 nm) sample. Cyclic voltammetry (CV) tests demonstrate that at the scan rate of 0.5 mVs⁻¹ the potential separation of the OP-LiFePO₄ sample (about 250 mV) is much smaller than that of S-LiFePO₄ (about 443 mV). More importantly, the initial discharge capacities at 0.1 and 1.0 C for the OP-LiFePO₄/MWNTs are 160.58 and 116.71 mAhg⁻¹, higher than that of S-LiFePO₄/C (151.29 and 95.69 mAhg⁻¹ at 0.1 and 1.0 C).

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1. Introduction

Lithium ion batteries (LIBs) are one of the most advanced secondary rechargeable energy storage devices due to its higher power and energy density [1–3]. The development of higher energy LIBs is essential for the further commercialization of portable electronic devices [4], such as laptops, personal digital assistants, cellular phones, and automobiles [5]. Recently, olivine structured lithium iron phosphate (LiFePO₄) has been thought as a promising cathode candidate for the higher power LIBs especially since its discovery by Goodenough group [6]. LiFePO₄ has a theoretical specific capacity of 170 mAh g⁻¹ and a relatively high redox potential of 3.4 ~ 3.5 V vs. Li/Li⁺ arising from the chemical valence transition of the Fe²⁺/Fe³⁺ couple [7,8]. However, the disadvantages of LiFePO₄ including the lower electronic conductivity (10⁻⁹ S cm⁻¹) and lower lithium ion diffusion coefficient (10⁻¹⁸ m² s⁻¹) effectively limit its wide applications [9,10]. Thus, many methods have been developed to resolve above problems. Summarily, the following three solutions were proposed so far, (i) anchoring a conductive layer on the surface of the particles; (ii) doping a second (or third) metal ion into the

lattice of crystallite LiFePO₄; (iii) controlling the morphologies of the resultant LiFePO₄ particles.

Up to now, many works concerning the morphologies of the LiFePO₄ particles have been published. For example, Xing et al. [11] reported the synthesis of LiFePO₄ particles that have a 3D conductive network and porous structure, and he addressed that the as-prepared sample could deliver a discharge capacity of 95 mAh g⁻¹ at a rate of 20 C. Sun et al. [12] synthesized LiFePO₄ microspheres that consist of nanoplates or nanoparticles by using a novel solvothermal method, and after mixing with carbon materials the products exhibited larger discharge capacity values (140 mAh g⁻¹ at 0.1 C) and better cycling performance (110 mAh g⁻¹ at 5 C and 86 mAh g⁻¹ at 10 C after 1000 cycles). Chen et al. [13] fabricated the monodisperse porous LiFePO₄/C microspheres with a diameter range of 1.0 ~ 1.5 μm via a microwave-assisted hydrothermal approach combined with carbothermal reduction. Wang et al. [14] fabricated nano-sized core-shell structured LiFePO₄/C nanocomposites using polyaniline (PANI) as the carbon precursor. Lim et al. [15] synthesized the nanowire and hollow particles of LiFePO₄, in which the nanowire sample showed a discharge capacity of 157 mAh g⁻¹ at 0.2 C and the hollow sample exhibited a discharge capacity of 165 mAh g⁻¹ at 0.2 C. Muraliganth et al. [16] reported that the LiFePO₄ nanorods could be prepared by a rapid microwave-solvothermal method within 5 minutes at the temperature of 300 °C. Zhou et al. [17]

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described the synthesis of a highly-conductive 3D carbon nano-tube network interlaced with porous LiFePO_4 through an in-situ sol-gel process, which exhibited a discharge capacity of 159 mAh g^{-1} at the current density of 10 mA g^{-1} . Toprakci et al. [18] prepared the $\text{LiFePO}_4/\text{CNT}/\text{C}$ composite nanofibers through a combined method (electrospinning and sol-gel techniques), and the as-prepared samples displayed large capacity value (165 mAh g^{-1} at 0.1 C), extended cycle life, and excellent rate capability. It can be deduced from above publications that the carbon sources played a key role in controlling the morphology of the resultant LiFePO_4 particles. To the best of our knowledge, there is no paper reporting the preparation of octagonal prism shaped LiFePO_4 huge particles and the method of boiling reflux assisted calcination process as well.

In this communication, MWNTs and activated carbon have been utilized as carbon sources in the boiling reflux assisted calcination process for preparing LiFePO_4 , with an intention to evaluate the influence of carbon sources on the morphologies of the resultant samples. As a result, octagonal prism shaped and spherical particles of LiFePO_4 were produced, respectively, in the presence of MWNTs and activated carbon. The obtained LiFePO_4 composites have been characterized by Fourier transform infrared (FT-IR), X-ray diffraction (XRD), Energy Dispersive X-Ray Spectroscopy (EDX), and scanning electron microscope (SEM). The electrochemical performances of the LiFePO_4 composites as cathode materials for the LIBs are evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge measurement.

2. Experimental

$\text{LiOH}\cdot\text{H}_2\text{O}$ (99.0 wt%), phosphoric acid (H_3PO_4 , 85 wt%), $\alpha\text{-Fe}_2\text{O}_3$, activated carbon, oxalic acid ($\geq 99.5 \text{ wt}\%$), and glucose were all obtained from Tianjin Yongda Chemical Reagent Co., Ltd (China). Acetylene black, polyvinylidene fluoride (PVDF, binder), N-methyl-2-pyrrolidone (NMP), electrolyte solution (ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC)=2: 5: 11 (volume) with $1 \text{ mol L}^{-1} \text{ LiClO}_4$), and polypropylene (PP, $M_w = 2400$) were purchased from Tianjin Liangnuo S&T Development Co., Ltd (China). Multi-walled carbon nanotubes (MWNTs) with an average diameter of $30 \sim 50 \text{ nm}$ were purchased from Shenzhen Nanotech Port Co., Ltd. (China). All of the chemicals were analytical grade and used as-received without any further treatment. Doubly distilled water was used to prepare the aqueous solutions.

The procedure for the preparation of LiFePO_4 composites filled with MWNTs or activated carbon is as follows. Starting materials of $\text{LiOH}\cdot\text{H}_2\text{O}$, H_3PO_4 , $\alpha\text{-Fe}_2\text{O}_3$ and MWNTs in a molar ratio of 1.1: 1: 0.5: 0.6 were mixed with 90 mL distilled water in a three-neck round-bottom flask. 5 g of oxalic acid and 0.4 g glucose were added into the above suspension solution, and then the suspension solution was heated to boiling reflux, and this process was kept for about one hour until the solution volume became $30 \sim 40 \text{ mL}$. It should be noted that after the boiling reflux process, a green solution was obtained, indicative of the Fe^{2+} formation. After cooling down to the room temperature, the solution was placed in an oven and dried at 150°C for 3 h. Subsequently, the produced powders were ground in a mortar and pressed into a slice with a diameter of around 1 cm. And then the samples were transferred into a crucible that was covered by carbon powders. Finally, the crucible was placed in an electronic furnace at 700°C for 5 h. The final product was denoted as OP- $\text{LiFePO}_4/\text{MWNTs}$. The products mixed with activated carbon were also fabricated according to the same procedure, and correspondingly, the resultant samples were named as S- LiFePO_4/C .

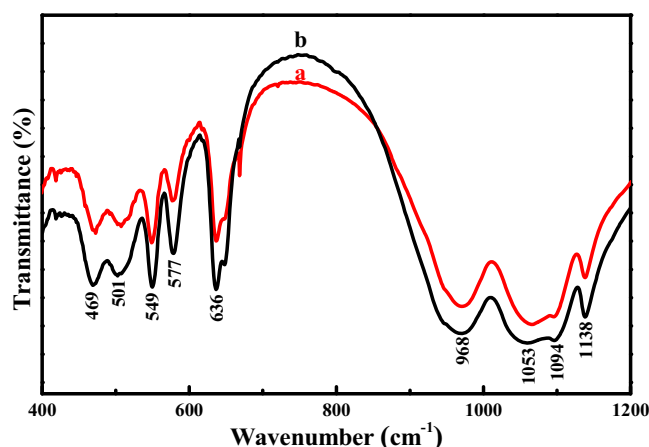


Fig. 1. FT-IR spectra of (a) OP- $\text{LiFePO}_4/\text{MWNTs}$ and (b) S- LiFePO_4/C samples.

Fourier transform infrared (FT-IR) spectra of the samples were obtained on a JASCO 8900 (Hitachi Ltd., Japan) in the range of 400 to 1200 cm^{-1} at a resolution of 4 cm^{-1} . X-ray diffraction (XRD) analysis was carried out with a Bruker AXS D8 ADVANCES with a $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). Data were collected in a range of 15 to 75° . The morphologies of the synthesized products were observed on a field emission scanning electron microscope (SEM, S-4800, Hitachi Ltd., Japan). Energy Dispersive X-ray Spectroscopy (EDX) spectrum analysis was carried out on an instrument of EDAX (PV-9900, USA).

Electrochemical measurements were carried out on a CHI 660B electrochemical workstation (Shanghai Chenhua Apparatus, China) connected to a personal computer. In the EIS measurement, the excitation voltage applied to the cells was 5 mV and the frequency range was from 0.1 to $1 \times 10^5 \text{ Hz}$. All the experiments were carried out at room temperature.

The cathode was prepared as follows. The fabricated OP- $\text{LiFePO}_4/\text{MWNTs}$ or S- LiFePO_4/C powders, polyvinylidene fluoride (PVDF), acetylene black were mixed in n-methyl-2 pyrrolidone (NMP) solution with a weight ratio of 8: 1: 1. After the above slurries were uniformly coated on the aluminum foil with a diameter of 10 mm , the prepared electrodes were put into a vacuum oven and dried at 120°C for 12 h. After that, the dried samples were pressed by hydraulic presser at 5 MPa and cut into disks before transferring into a nitrogen-filled glove box. Two-electrode electrochemical cells, consisting of lithium metal foil as the negative electrode, Celgard 2400 separator, and an electrolyte of 1 M LiClO_4 in ethylene carbonate (EC):diethyl carbonate(DEC):dimethyl carbonate (DMC) (2:5:11, vol.), were assembled in a nitrogen-filled glove box. The electrochemical cycle tests were performed using a CT-3008W-5V20mA-S4 testing system (Shen Zhen Newware Technology Ltd., China) at various rates ($1 \text{ C} = 170 \text{ mAh g}^{-1}$) between 2.75 and 4.2 V at room temperature.

3. Results and discussion

Fig. 1 shows the FT-IR spectra of OP- $\text{LiFePO}_4/\text{MWNTs}$ and S- LiFePO_4/C samples. The main absorption bands are in the region of $400 \sim 1200 \text{ cm}^{-1}$. The strong bands at 636 , 968 , 1053 , 1094 , and 1138 cm^{-1} correspond to the symmetrical and asymmetrical vibration of PO_4^{3-} [19]. The peaks located at 469 , 501 , 549 , and 577 cm^{-1} are assigned to the bending vibration of P-O band. These characteristic peaks (469 , 501 , 549 , 577 , 636 , 968 , 1053 , 1094 , and 1138 cm^{-1}) are consistent with the results of LiFePO_4 in the literature [19] very well. Fig. 2 shows the EDX spectra of $\text{LiFePO}_4/\text{MWNTs}$ and LiFePO_4/C samples. Only Fe, P, O elements are observed in the OP- $\text{LiFePO}_4/\text{MWNTs}$ and S- LiFePO_4/C samples, indicating that there

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