



Full Length Article

Freeze-drying synthesis of three-dimensional porous LiFePO₄ modified with well-dispersed nitrogen-doped carbon nanotubes for high-performance lithium-ion batteries



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ARTICLE INFO

Article history:

Received 13 September 2016

Received in revised form

22 December 2016

Accepted 27 December 2016

Available online 27 December 2016

Keyword:

Porous LiFePO₄

Nitrogen-doped carbon nanotube

Freeze-drying

Positive electrode

Lithium-ion battery

ABSTRACT

The three-dimensional porous LiFePO₄ modified with uniformly dispersed nitrogen-doped carbon nanotubes has been successfully prepared by a freeze-drying method. The morphology and structure of the porous composites are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), and the electrochemical performances are evaluated using the constant current charge/discharge tests, cyclic voltammetry and electrochemical impedance spectroscopy. The nitrogen-doped carbon nanotubes are uniformly dispersed inside the porous LiFePO₄ to construct a superior three-dimensional conductive network, which remarkably increases the electronic conductivity and accelerates the diffusion of lithium ion. The porous composite displays high specific capacity, good rate capability and excellent cycling stability, rendering it a promising positive electrode material for high-performance lithium-ion batteries.

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1. Introduction

In recent years, the increasing demand for electric vehicles (EVs), hybrid electric vehicles (HEVs) and energy storage systems has given rise to the increased production of lithium-ion batteries (LIBs), which have occupied a large share of the rechargeable battery market [1–3]. The performances of LIBs, especially their power capability, are greatly dependent on the ionic and electronic transport kinetics of the electrode materials [4,5]. Since discovered in 1997 [6], the olivine-type LiFePO₄ has been deemed to be one of the most promising positive electrode materials for LIBs, owing to its advantages of high theoretical capacity (170 mAh g⁻¹), low cost, high safety and long cycle life [6,7]. The major restrictions for the widespread application of LiFePO₄ are still the sluggish kinetics of the lithium-ion diffusion and the poor electronic conductivity [6,8,9]. The poor electronic conductivity is mainly caused by the large band gap of the pristine LiFePO₄, while the structural defects may obstruct the one-dimensional lithium-ion diffusion [10,11]. Many efforts, such as coating with a conductive layer [12–14], doping with the alien atoms [15,16], reducing the particle size

and optimizing the morphology [11,17,18], have been devoted to overcome the disadvantages and enhance the electrochemical performances of LiFePO₄.

Among the numerous approaches, reducing the size of LiFePO₄ particles to nanoscale is regarded as an efficient way, as the diffusion pathway for lithium ion is shortened and the rate capability is improved [15]. Though the size reduction can indeed increase the performance of LiFePO₄, this improvement is achieved at the expense of the tap density and the volumetric capacity, and both of which are important in the practical battery application [4,9]. Compared to the nanomaterials, the three-dimensional porous electrode materials have attracted great attention in recent years for the relatively high tap density and large specific surface area. The bicontinuous walls and pores in a porous active material can provide continuous electron and ion transport paths through the active phase (walls) and the electrolyte phase (pores), greatly improving the electrochemical Li-insertion properties [19,20].

On the other hand, though carbon coating is a low-cost method to increase the electronic conductivity of LiFePO₄, it is usually difficult to get an uniform and continuous coating layer to achieve the satisfactory rate performance [21,22]. In recent years, the highly conductive carbon nanotubes (CNTs) with an unique quasi-one-dimensional morphology have been considered as promising additives to efficiently improve the conductivity of LiFePO₄ [10,23]. In comparison to the pristine nanocarbon, the nitrogen-doped

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materials present further enhanced physicochemical properties and can remarkably improve the electron transport and lithium-ion diffusion kinetics of LiFePO_4 , because the dopants provide more electron carriers in the conduction band, and the introduced nitrogen-containing functional groups increase the interactions between the nanocarbon and LiFePO_4 , thus enhancing the affinity and wettability to the electrolyte [4,24,25].

In this work, we synthesized the three-dimensional porous LiFePO_4 materials modified with the uniformly dispersed nitrogen-doped carbon nanotubes (N-CNTs) by a freeze-drying method, which includes mainly three stages: rapid freezing, vacuum freeze-drying and heating treatment. The freeze-drying approach has been widely used in the material synthesis, and presents advantages on the designing and tuning of the morphology and surface properties of the target product [26–29]. An early work on the freeze-drying synthesis of LiFePO_4 was conducted by Palomares et al. [26], where the precursor solution was drop-by-drop frozen in the liquid nitrogen and finally a fine powder of LiFePO_4/C was obtained. In contrast, in this work, the whole precursor solution is instantly frozen under the liquid nitrogen and the final product displays a three-dimensional porous bulk morphology. Moreover, the nitrogen-doped carbon nanotubes can be homogeneously incorporated into the porous LiFePO_4 framework during the freeze-drying process. In the three-dimensional porous LiFePO_4 composite materials, the continuous pores serve as channels for the fast Li^+ supply and the N-CNTs can facilitate the fast electron transfer. Owing to the unique and novel structures, the synthesized porous $\text{LiFePO}_4/\text{N-CNTs}$ composite demonstrates a specific capacity of 159 mAh g^{-1} at the rate of 0.1C, a rate performance with a capacity of 72 mAh g^{-1} at a high rate of 10C, and a high capacity retention of 96.7% after 500 charge/discharge cycles, which are superior to the pristine LiFePO_4 and the $\text{LiFePO}_4/\text{CNTs}$ composite and are promising for application in the lithium-ion power batteries.

2. Experimental

2.1. Synthesis of materials

The $\text{LiFePO}_4/\text{N-CNTs}$ composite material was synthesized via a freeze-drying method using LiH_2PO_4 (Aladdin, China), $\text{FeC}_6\text{H}_5\text{O}_7$ (Aladdin, China) and the nitrogen-doped carbon nanotubes (N-CNTs) (Chengdu Organic Chemicals Co. Ltd., China) as the raw materials. Typically, the stoichiometric LiH_2PO_4 and $\text{FeC}_6\text{H}_5\text{O}_7$ (corresponding to 0.02 mol of LiFePO_4) were separately dissolved in 20 ml of distilled water with stirring. These two solutions were mixed together and 50 mg of N-CNTs were added, and then the mixture was stirred until a uniform black suspension was obtained. The suspension was instantly frozen with the liquid nitrogen and then dried at -55°C in a vacuum freeze dryer (FD-1A-50, Shanghai Binlon Instrument Co. Ltd.) for 48 h. Finally, the solidified precursor was transferred into a tubular furnace (SK2-2-12Q, Wuhan Yahua Electric Furnace Co. Ltd.) and heated in a reducing atmosphere (H_2/Ar , 10/90) to 650°C with a heating rate of $5^\circ\text{C}/\text{min}$ and remained for 10 h. For comparison, the pristine LiFePO_4 and the $\text{LiFePO}_4/\text{CNTs}$ composite were also prepared by the same procedures, without using the nanocarbon or with the N-CNTs replaced by CNTs, and the samples are abbreviated as LFP, LFP/CNTs and LFP/N-CNTs.

2.2. Characterization of materials

The X-ray powder diffraction (XRD) analysis was conducted by using a Xpert Pro MPD diffractometer with the $\text{Cu K}\alpha$ radiation ($\text{K}\alpha = 0.15418 \text{ nm}$) and the diffraction data were collected from 10° to 90° at a step of $10^\circ/\text{min}$. The morphologies of the LiFePO_4

composite materials were observed by a scanning electron microscopy (SEM, PHILIPS XL30TMP) at an acceleration voltage of 15 kV and the element distributions were explored by the energy dispersive X-ray spectroscopy (EDX, OXFORD IET200). The microstructures of the LiFePO_4 composite materials were investigated by a transmission electron microscopy (TEM, FEI Tecnai G20) at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a VG Multilab 2000 apparatus. Thermogravimetric measurements (TG) were carried out on a Pyris Diamond TG/DTA instrument (STA449/6/G, NETZSCH) in air at a rate of $10^\circ\text{C}/\text{min}$ from room temperature to 1000°C . The nitrogen adsorption and desorption isotherms were measured on Autosorb-1-MP/LP, the Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area (S_{BET}), and the pore size distributions were derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) model.

2.3. Electrochemical measurements

The coin cells (type 2032) were assembled in a pure argon-filled glove box with the content of H_2O and O_2 less than 1 ppm. Lithium foil was used as the counter electrode and the porous polypropylene membrane (Celgard 2400) as the separator. The electrolyte was 1 M LiPF_6 dissolved in the solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volumetric ratio of 1:1. To make the working electrodes, the active material, super P and polyvinylidene fluoride (PVDF) with the weight ratio of 80:12:8 were mixed in N-methylpyrrolidone (NMP) to produce a slurry, which was then coated on an aluminum foil and dried at 100°C for 12 h in a vacuum oven. The coin cells and all the materials and chemicals for cell assembly (including the lithium foil, aluminum foil, electrolyte, conductive carbon, PVDF and NMP) were purchased from the Poxon company of China. The specific capacity of the material was calculated based on the mass of LiFePO_4 ($\sim 1 \text{ mg}$, not including the carbon) in the cathode. Galvanostatic charge/discharge tests were performed on a battery test system (Neware BTS 5V 50 mA) at different rates ($1\text{C} = 170 \text{ mA g}^{-1}$) in the voltage range of 2.5–4.0 V. Cyclic voltammograms (CV) were recorded at various scan rates of 0.1, 0.2, 0.5 and 1 mV s^{-1} on the CHI 660D electrochemical workstation in the voltage range of 2.5–4.2 V. EIS measurements were performed over the frequency range of 0.01 Hz and 100 MHz with an applied perturbation signal of 10 mV. All the electrochemical tests were carried out at room temperature.

3. Results and discussion

The pristine LFP and the LFP composites were prepared by a freeze-drying method. Fig. 1 illustrates the synthesis process of the porous LFP/N-CNTs composite. Typically, LiH_2PO_4 and $\text{FeC}_6\text{H}_5\text{O}_7$ were dissolved in distilled water, then the N-CNTs were added. After well dispersed in the homogeneous precursor solution, rapidly frozen and freeze-dried under vacuum, the N-CNTs were uniformly incorporated and immobilized in the solidified precursor, as shown in Fig. 1a, b. The highly crystalline three-dimensional porous LiFePO_4 materials were then obtained after suitable calcination, as illustrated in Fig. 1c, with the N-CNTs uniformly incorporated as in the precursor. As displayed in Fig. 1d, in such a composite, the interlaced nitrogen-doped carbon nanotube networks facilitate the fast electron transfer and the continuous pores serve as channels for the fast Li^+ supply.

The phase composition and crystal structure of the porous LFP, LFP/CNTs and LFP/N-CNTs materials are identified by the XRD analysis, as shown in Fig. 2. The diffraction patterns of all the three samples match well with the standard orthorhombic olivine structure of LFP with a Pnma space group [30]. The diffraction peaks are

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