



# Facile low-temperature polyol process for LiFePO<sub>4</sub> nanoplate and carbon nanotube composite



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## ABSTRACT

Crystalline LiFePO<sub>4</sub> nanoplates were incorporated with 5 wt.% multi-walled carbon nanotubes (CNTs) via a facile low temperature polyol process, in one single step without any post heat treatment. The CNTs were embedded into the LiFePO<sub>4</sub> particles to form a network to enhance the electrochemical performance of LiFePO<sub>4</sub> electrode for lithium-ion battery applications. The structural and morphological characters of the LiFePO<sub>4</sub>-CNT composites were investigated by X-ray diffraction, Fourier Transform infrared spectroscopy, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy. The electrochemical properties were analyzed by cyclic voltammetry, electrochemical impedance spectroscopy and charge/discharge tests. Primary results showed that well crystallized olivine-type structure without any impurity phases was developed, and the LiFePO<sub>4</sub>-CNT composites exhibited good electrochemical performance, with a reversible specific capacity of 155 mAh g<sup>-1</sup> at the current rate of 10 mA g<sup>-1</sup>, and a capacity retention ratio close to 100% after 100 cycles.

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## 1. Introduction

Lithium-ion batteries are now common in consumer electronics, and considered to play an important role in the hybrid electric vehicles (HEV) and plug-in HEV (PHEV) in the near future. Though, there are still many technical problems to be solved regarding the large-scale applications, and the developments of lithium-ion batteries are mainly focusing on the intrinsic safety, energy density, durability, and cost [1,2]. Typically, a suitable cathode material is significant to the performance of the whole system. Recently, olivine-type lithium iron phosphate (LiFePO<sub>4</sub>) has been researched thoroughly due to its potential applicability as the next generation cathode material for lithium-ion power batteries [3].

LiFePO<sub>4</sub> owns many advantages when compared to conventional cathode materials such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub>, which has a relatively high theoretical capacity of 170 mAh g<sup>-1</sup> and a suitable voltage-region of 3.4–3.5 V. Besides, LiFePO<sub>4</sub> is durable,

inexpensive, environmentally compatible and structurally stable [2,3]. Owing to the special architecture, bulk LiFePO<sub>4</sub> shows low electronic conductivity, slow lithium ion diffusivity, and poor rate performance [4]. Generally, coating or integrating the LiFePO<sub>4</sub> with conductive agents, doping foreign metal ions in the LiFePO<sub>4</sub> particles, and decreasing the size of LiFePO<sub>4</sub> particles are helpful to improve its electronic conductivity and ion diffusivity [3,5–8]. To overcome the potential agglomeration and dissolution of nanoparticulate electrode materials for long term application, recently, plate like LiMPO<sub>4</sub> (M = Fe, Mn, Co) have attracted attention for the short diffusion path of lithium ions in the vertical directions and good structure stability during cycling, and various synthesis methods have been reported, for example, solvothermal method [9,10], hydrothermal method [11], supercritical fluid method [12], etc. In addition, insertion of CNTs into LiFePO<sub>4</sub> particles provides particular routes for electrons to pass and makes for fast lithium ions supply, in this way CNTs can improve the intrinsic electric conductivity and ion diffusivity of LiFePO<sub>4</sub> [2,13–16]. For large-scale industrial applications, low processing cost and easy manufacturing are also the primary requirements for the synthesis methods [17].

In this paper, we designed and synthesized a novel nano-composite of plate like well-crystallized LiFePO<sub>4</sub> and multi-walled CNTs with a single-step low temperature polyol process

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( $\sim 270^\circ\text{C}$ ), without using any subsequent heat treatments or inert gas, as shown in Fig. 1a and b. This kind of new composite combines the manifold benefits of CNTs (including high electronic conductivity, special tubular nanoscale morphology, anti-corrosion ability and high surface area) and plate like cathode materials, to create a novel nanocomposite with facile electron and  $\text{Li}^+$  transport paths and yield a good composite cathode for lithium-ion batteries (Fig. 1c and d). The composites were characterized using a series of characterization techniques and electrochemical tests, as will be detailed in the following sections. Though the single-step low temperature polyol process is convenient, low-cost and scalable, the produced nanocomposites exhibit good electrochemical properties and yields promising metrics for potential large-scale practical applications in lithium-ion batteries.

## 2. Experimental

### 2.1. Material preparation

Multi-walled carbon nanotubes (Chengdu Alpha Nano Technology Co. Ltd) were functionalized via the mixed acid method in order to remove the impurities and acquire excellent dispersion in the polyol medium.  $\text{LiFePO}_4$ -CNT nanocomposites were obtained by using a polyol process as follows: first of all, the CNTs were added into 200 ml of triethylene glycol (TEG) and a homogeneous dispersion was achieved by an ultrasonic process for 30 min. Then,  $\text{Fe}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  (molar ratio of 1:1:1, and all chemicals purity  $>99\%$ ) were directly dissolved into the dispersion, by mechanical agitation for 30 min at room temperature, in a three-neck round flask connected with a mechanical stirring unit and a refluxing unit. Next, the mixed dispersion was heated to above its boiling point ( $\sim 270^\circ\text{C}$ ) with a heating rate of  $12^\circ\text{C min}^{-1}$  and maintained for 18 h under stirring and refluxing, as depicted in Fig. 1a. After cooling down, the products were separated from the solvent via centrifugation. In order to remove the organic residue and other remaining impurities, the products were washed with deionized water and acetone several times. Finally, the  $\text{LiFePO}_4$ -CNT composite powder was dried in a vacuum oven at  $100^\circ\text{C}$  for 24 h. Analogously, the pristine  $\text{LiFePO}_4$  was synthesized by the same procedure except CNTs were not added.

### 2.2. Material characterization

XRD measurements were characterized by an ARL X'TRA advance diffractometer with filtered  $\text{CuK}\alpha$  radiation, and the experimental diffraction samples were collected at room temperature by step scanning in the range of  $10^\circ \leq 2\theta \leq 80^\circ$ . The Raman spectroscopy of the  $\text{LiFePO}_4$ -CNT composite was obtained in an HR800 UV Raman micro-spectrometer (JOBIN YVON, France) using the green line of an argon laser ( $\lambda = 514.53 \text{ nm}$ ) as excitation source. Fourier transform infrared spectroscopy (FT-IR, AVATAR-360) of the pristine  $\text{LiFePO}_4$  or the composite  $\text{LiFePO}_4$ -CNT powders was recorded from  $4000$  to  $400 \text{ cm}^{-1}$  by the KBr pellet method. The specific surface area of each sample was characterized by  $\text{N}_2$  adsorption at the liquid nitrogen temperature using a BELSORP II instrument. Prior to analysis, the samples were treated at  $200^\circ\text{C}$  for 3 h in vacuum to remove the surface adsorbed species. SEM measurements were examined by a Hitachi S-4800 field-emission scanning electron microscope. TEM measurements were studied by a JEOL JEM-200CX transmission electron microscope. The elemental composition of the samples was investigated on an elemental analyzer (ELEMENTAR VARIO EL III). The charge-discharge tests of the cells were recorded over the voltage range of  $2.5$ – $4.0 \text{ V}$  using a NEWARE BTS ( $5 \text{ V}$ ,  $50 \text{ mA}$ ) computer-controlled battery test station at different rates at room temperature. CV tests were performed over the voltage range between  $2.5$  and  $4.2 \text{ V}$  using a Princeton Applied Research PARSTAT 2273 advanced electrochemical system at the scanning rate of  $0.1 \text{ mV s}^{-1}$ , and EIS measurements were examined over the frequency range between  $1 \text{ MHz}$  and  $100 \text{ mHz}$  by using the same Princeton 2273 electrochemical system with an applied perturbation signal of  $10 \text{ mV}$ .

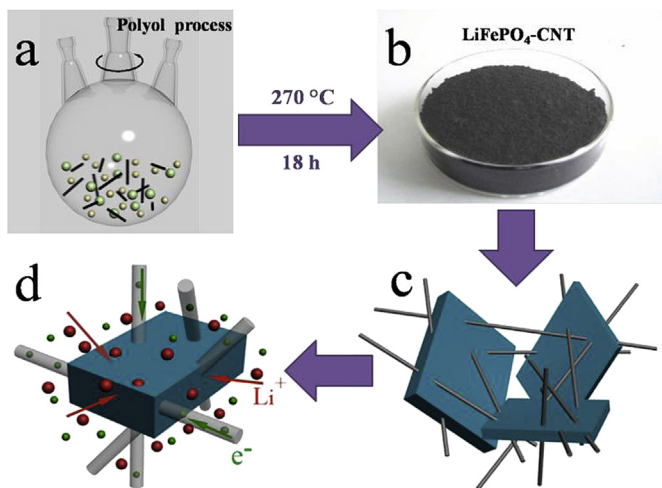
### 2.3. Electrochemical test

The electrochemical performance of  $\text{LiFePO}_4$  and  $\text{LiFePO}_4$ -CNT composites was performed with coin shape cells while metallic lithium film was used as the counter and reference electrode. Microporous polypropylene film (Celgard 2400) was used as the separator. The liquid electrolyte consisted of a solution of  $1 \text{ M LiPF}_6$  in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1, v/v).  $80 \text{ wt.}\%$   $\text{LiFePO}_4$  (or  $\text{LiFePO}_4$ -CNT),  $15 \text{ wt.}\%$  conductive carbon Super P (NCM HERSBIT Chemical Co. LTD., China) and  $5 \text{ wt.}\%$  polyvinylidene fluoride (PVDF) binder were mixed in *N*-methyl pyrrolidinone (NMP) thoroughly and then pasted onto pure aluminum foil ( $10 \mu\text{m}$ ) to fabricate working electrodes. The electrode was dried in a vacuum oven at  $100^\circ\text{C}$  for 12 h before electrochemical examination. The cells were assembled in a glove box filled with pure argon.

## 3. Results and discussion

### 3.1. Microstructure characterizations

XRD patterns of the as synthesized  $\text{LiFePO}_4$  and  $\text{LiFePO}_4$ -CNT composite are shown in Fig. 2. Both patterns could be indexed to an orthorhombic olivine-type structure (space group:  $\text{Pnma}$ ). The XRD measurement results demonstrate that no unwanted impurities were found and the products were very well crystallized, even the polyol process was carried at a temperature as low as  $\sim 270^\circ\text{C}$  and without using any inert gases or subsequent heat treatments. This is a good point in consideration of the material synthesis cost for practical large-scale applications, as even so far various methods and processes have been developed to prepare  $\text{LiFePO}_4$  based materials, most of them have to be calcined (as the solid phase synthesis) or post heat-treated (as the hydrothermal synthesis) at  $\sim 700^\circ\text{C}$  in an inert atmosphere ( $\text{Ar}$  or  $\text{N}_2$ ), to get the stable olivine-



**Fig. 1.** (a) Depiction of the polyol process in a three-neck round flask; (b) Photograph of the produced plate like well-crystallized  $\text{LiFePO}_4$  and multi-wall CNT composites; (c) Illustrations of the  $\text{LiFePO}_4$  and CNT composite, and (d) is the enlarged zone from (c) showing the mechanisms of accelerated electron transport and ion diffusion.

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