



# Synthesis, characterization and electrochemical performances of LiFePO<sub>4</sub>/graphene cathode material for high power lithium-ion batteries



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## ABSTRACT

LiFePO<sub>4</sub>/graphene (LiFePO<sub>4</sub>/G) cathode with exciting electrochemical performance was successfully synthesized by liquid phase method. LiFePO<sub>4</sub> nanoparticles wrapped with multi-layered graphene can be fabricated in a short time. This method did not need external heating source. Heat generated by chemical reaction conduct the process and removed the solvent simultaneously. The LiFePO<sub>4</sub>/G were analyzed by X-ray diffraction (XRD) analysis, scanning electron microscope (SEM), transmission electron microscopy (TEM), magnetic properties analysis and electrochemical performance tests. The LiFePO<sub>4</sub>/G delivered a capacity of 160 mAh g<sup>-1</sup> at 0.1C and could tolerate various dis-charge currents with a capacity retention rate of 99.8%, 99.2%, 99.0%, 98.6%, 97.3% and 95.0% after stepwise under 5C, 10C, 15C, 20C, 25C and 30C, respectively.

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## 1. Introduction

At present, Li-ion batteries have been recognized as alternative energy sources for electrical vehicles (EVs) and hybrid electrical vehicles (HEVs) [1]. It is well known that the cathode materials have a significant influence on the electrochemical performance of the batteries, and among those cathode materials, LiFePO<sub>4</sub> has received much attention due to its high theoretical specific capacity (170 mAh g<sup>-1</sup>), low material cost, natural abundance, better environmental compatibility, thermal stability in the fully charged state and good cycle stability, and especially, superior safety [2].

However, the lithium ion diffusion rate and electrical conductivity (10<sup>-9</sup> S cm<sup>-1</sup>) of LiFePO<sub>4</sub> are poor. These fatal drawbacks limit the practical use of LiFePO<sub>4</sub> in Li-ion batteries for EVs and HEVs [3,4]. To improve Li-ion diffusion within LiFePO<sub>4</sub> and the LiFePO<sub>4</sub>/FePO<sub>4</sub> interface, nano-sized LiFePO<sub>4</sub> particles were designed, thus Li-ion insertion/extraction pathway were effectively shorten [5–10]. To enhance electronic conductivity, carbon coating is widely applied and systemically studied [11–14], but still far from satisfaction. The newly born graphene attracts great attentions recently because of its superior conductivity, flexible structure. And more importantly, high surface area of graphene

(theoretical value of 2630 m<sup>2</sup> g<sup>-1</sup>) [15,16] may offer an improved interfacial contact.

To improve the rate performance and cycle stability of LiFePO<sub>4</sub>, graphene-modified LiFePO<sub>4</sub> composite has been developed as Li-ion battery cathode materials. The graphene is considered to be the best conductive material so far and its raw material, graphite, is widespread in the world. However, no significant improvement in rate performance compared with conventional carbon coated LiFePO<sub>4</sub>, because the LiFePO<sub>4</sub> nanoparticles were only loosely loaded on graphene sheets, thereby resulting only in a limited enhancement in electron conductivity [17,18]. In this work, we demonstrated a liquid phase method to synthesis LiFePO<sub>4</sub> coated with graphene (LiFePO<sub>4</sub>/G). Heat could be generated during synthesis process and external heating source was needn't, meanwhile the solvent could be removed simultaneously. This method can solve the shortcoming of solid-phase method with high energy consumption. Moreover, it did not require high cost equipments for precursor mixing. It is also a new approach for the liquid phase synthesis of other nano-materials. We successfully fabricated LiFePO<sub>4</sub> particles coated with a discontinuous layer of graphene, whose thickness was less than 4 nm. It is one of the key factors for the outstanding electrochemical performance of LiFePO<sub>4</sub>/G [19]. The LiFePO<sub>4</sub>/G shows exciting performance with highly capacity retention rate after various dis-charge currents.

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## 2. Experimental

### 2.1. Synthesis of LiFePO<sub>4</sub>/G

LiFePO<sub>4</sub>/G was synthesized by liquid phase method as described below. CH<sub>3</sub>COOLi·2H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> were used as the raw materials. All chemicals used in our work were analytical grade. Firstly, the CH<sub>3</sub>COOLi·2H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in the mixture of distilled water and ethanol, (3/1, V/V), and secondly added the water solution of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>. The proportion of elements in the above solution is Li:Fe:PO<sub>4</sub>:C = 1:1:1:1. Then the mixture was stirred at room temperature for 1 h. After that, solution of ammonium nitrate (5 wt.% of the obtained LiFePO<sub>4</sub>) was added. After the mixture was stirred for 30 min at room temperature and subsequently the interior exothermic reaction was occurred. As the solution temperature was gradually increased, the solvent was slowly evaporated. Finally, a primrose yellow solid as a precursor phase of LiFePO<sub>4</sub> was obtained by liquid phase method.

The dried precursor were treated at 300 °C for 1 h then was heated to 600 °C for 2 h under a N<sub>2</sub>/C<sub>2</sub>H<sub>2</sub>/CH<sub>4</sub> (90:5:5, V/V/V) atmosphere, and then cooled slowly to obtain LiFePO<sub>4</sub>/G (G < 2%).

### 2.2. Physical characterization

The X-ray powder diffraction data were collected on a Bruker D8 ADVANCE diffractometer with Cu-Kα<sub>1, 2</sub> radiations operating at 40 kV and 40 mA at room temperature. Measurements were done over the 2θ range of 5–90° with a scanning step width of 0.02° and 1 s time per step for each sample. Raman spectra were recorded on a JY HR800 Raman spectrophotometer. FTIR absorption spectra were recorded with a Fourier-transform interferometer (NICOLET 6700FT-IR) over a wave number range of 400–4000 cm<sup>-1</sup> at a spectral resolution of 1 cm<sup>-1</sup>. Scanning electron microscopy (SEM) imaging was carried out using a Hitachi S-4800 microscope with an operation voltage of 5 kV. Transmission electron microscopy (TEM) observations were performed with a Hitachi H-7000 microscope at an accelerating voltage of 100 kV. Magnetic measurements were carried out with a fully automated magnetometer (MPMS-5S from Quantum Design) using an ultra-sensitive Superconducting Quantum Interference Device (SQUID) in the temperature range 4–300 K. Impurities content left in the sample was measured by inductive coupled plasma emission spectrometer (ICP). The accurate content of graphene in the LiFePO<sub>4</sub>/G composite was measured by HCS-140 high frequency infrared carbon-sulfur analyzer (1.7 wt.%).

### 2.3. Coin-type cell and 26,650 batteries

LiFePO<sub>4</sub>/G, Super-P, and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10 were mixed in N-N-Methyl-2-pyrrolidone (NMP) and stirred for 2 h to make the slurry. After which the slurry was pressed onto Al foil. After vacuum drying at 120 °C for 24 h, CR2032 coin cells were using lithium metal as the anode and 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in EC:DMC:EMC (1:1:1, V/V/V) as the electrolyte, and Celgard 2300 porous polypropylene film as the separator. CR2032 coin cells charge/discharge tests were performed between 2.0 and 3.8 V vs Li/Li<sup>+</sup> at various C rates on a BTSDA 5V5 mV battery tester.

Column 26,650 lithium ion batteries, nominally diameter 26 mm, high 65 mm, which were assembled to investigate the electrochemical performances of LiFePO<sub>4</sub>/G high power batteries. The nominal capacity of the batteries was designed to be 3200 mAh. The batteries used the prepared LiFePO<sub>4</sub>/G as the cathode, graphite as the anode, and polyethylene as a separator. The

cathode consisted of 85 wt.% LiFePO<sub>4</sub>/G, 7 wt.% Super-P and 8 wt.% polyvinylidene fluoride (PVDF). The graphite anode consisted of 90 wt.% composite graphite, 5 wt.% Super-P, 5 wt.% styrene-butadiene rubber. 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in EC:DMC:EMC (1:1:1, V/V/V) as the electrolyte. The anode, cathode, and separator were rolled together to form the battery core and then the core was set into a 26650-type steel shell. The electrolyte was thereafter injected and the batteries were sealed with a sealing machine. The formation and charge–discharge tests of batteries were performed by using the BTSDA lithium-ion battery testers.

## 3. Results and discussion

### 3.1. Physical characterization

#### 3.1.1. XRD and Raman analysis

The XRD spectra of the LiFePO<sub>4</sub>/G are shown in Fig. 1. The structure is belonging to orthorhombic olivine (*Pnma*) space group with the parameters: *a* = 10.35 Å, *b* = 6.02 Å and *c* = 4.70 Å. The diffraction patterns perfectly match the standard orthorhombic LiFePO<sub>4</sub> (JCPDS #40-1499), indicating that the obtained samples are highly crystalline. Furthermore, the addition of graphene has no effects on the crystal structure of LiFePO<sub>4</sub>. In a word, a pure phase of olivine structured LiFePO<sub>4</sub>/G was successfully synthesized by the liquid phase method.

Further information for the structure of LiFePO<sub>4</sub>/G can be supported by the Raman spectra (Fig. 2). The peaks at about 1345 cm<sup>-1</sup> (D band) and 1578 cm<sup>-1</sup> (G band) are observed in the composites. The intensity ratio of D and G band, *I*<sub>D</sub>/*I*<sub>G</sub>, is a reflection of sp<sup>2</sup>-hybridized carbon atoms [20]. The sp<sup>2</sup>-hybridized carbon atoms take an important role for the good conductivity of graphene. Therefore, the Raman results consistent with the XRD results further demonstrated the formation of LiFePO<sub>4</sub>/G composites.

#### 3.1.2. FTIR spectroscopy

FTIR spectroscopy is a probe of vibrations of molecular edifices and is thus a good means of investigating the surface on a local scale. The FTIR spectrum of LiFePO<sub>4</sub>/G is shown in Fig. 3. Two typical bands appear at 372–647 cm<sup>-1</sup> and 945–1139 cm<sup>-1</sup>, corresponding to intra-molecular symmetric O–P–O bending and antisymmetric P–O stretching respectively, which related to the (PO<sub>4</sub>)<sup>3-</sup> group in the LiFePO<sub>4</sub> phase [21]. The weak peak between 1200 and 1600 cm<sup>-1</sup> are related to the discrete graphene of carbon coating vibration [22]. The H–O–H bending band and intra-molecular

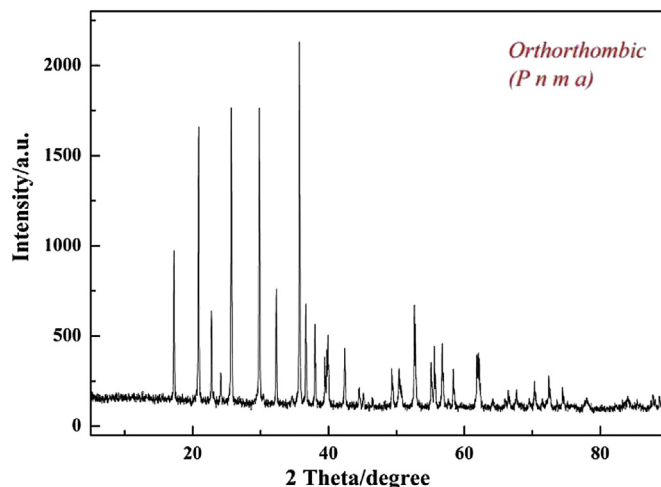


Fig. 1. XRD patterns ( $\lambda$  Cu Kα<sub>1</sub>) of the LiFePO<sub>4</sub>/G powder.

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