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# Metal organic frameworks derived porous lithium iron phosphate with continuous nitrogen-doped carbon networks for lithium ion batteries



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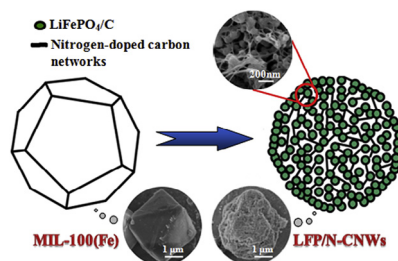
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## HIGHLIGHTS

- 3D porous LFP/N-CNWs was synthesized using MIL-100(Fe) as template and raw material.
- LFP/N-CNWs composite possess a high BET surface area of 129 m<sup>2</sup> g<sup>-1</sup>.
- LFP/N-CNWs shows excellent capacity and rate performance comparing with LFP/CNWs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Lithium iron phosphate (LiFePO<sub>4</sub>) nanoparticles embedded in the continuous interconnected nitrogen-doped carbon networks (LFP/N-CNWs) is an optimal architecture to fast electron and Li<sup>+</sup> conduction. This paper, for the first time, reports a reasonable design and successful preparation of porous hierarchical LFP/N-CNWs composites using unique Fe-based metal organic framework (MIL-100(Fe)) as both template and starting material of Fe and C. Such nitrogen-doped carbon networks (N-CNWs) surrounding the lithium iron phosphate nanoparticles facilitate the transfer of Li<sup>+</sup> and electrons throughout the electrodes, which significantly decreases the internal resistance for the electrodes and results in the efficient utilization of LiFePO<sub>4</sub>. The synthesized LFP/N-CNWs composites possess a porous structure with an amazing surface area of 129 m<sup>2</sup> g<sup>-1</sup>, considerably enhanced electrical conductivities of 7.58 × 10<sup>-2</sup> S cm<sup>-1</sup> and Li<sup>+</sup> diffusion coefficient of 8.82 × 10<sup>-14</sup> cm<sup>2</sup> s<sup>-1</sup>, thereby delivering excellent discharge capacities of 161.5 and 93.6 mAh·g<sup>-1</sup> at 0.1C and 20C, respectively.

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## 1. Introduction

With the rapid depletion of traditional fossil fuels and continually worsened environmental pollution, there is a greatly increased demand for the clean and efficient energy storage devices. Because

of the excellent safety performance, long cycle life, high operational voltage and energy density, lithium ion batteries (LIBs) have already been used in many portable electronic products over other energy storage technologies in recently years [1,2]. As a preferred cathode materials for LIBs, the lithium iron phosphate (LiFePO<sub>4</sub>) has attract considerable attention owing to its merits of high theoretical discharge capacity (~170 mAh·g<sup>-1</sup>), acceptable operating voltage (3.42 V), low price, environmental benignity and superior safety [3,4]. However, the drawbacks involving extremely low electronic con-

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ductivity ( $\sim 10^{-9}$  S  $\text{cm}^{-1}$ ) and  $\text{Li}^+$  conductivity ( $\sim 1.8 \times 10^{-14}$   $\text{cm}^2 \text{S}^{-1}$ ), which result in poor electrochemical performance and hinder the commercial application of  $\text{LiFePO}_4$  [5]. Therefore, many efforts have been directed towards increasing the purity and crystallinity [4,6], incorporating supervalent ions, modifying the crystal structure [7], morphology [8,9] and particle size of  $\text{LiFePO}_4$  [10,11], or creating a fast electron conductive surface, such as phosphorus-doped carbon layers [12] aiming to enhance the electronic conductivity and reduce the  $\text{Li}^+$  diffusion resistance.

It is widely accepted that the power capability of  $\text{LiFePO}_4$  depends on the kinetics during the  $\text{Li}^+$  insertion/extraction process, which involves three steps: (i) electron and  $\text{Li}^+$  diffusion between the electrode and electrolyte, (ii) charge transfer reactions in the cathode-electrolyte interface, and (iii)  $\text{Li}^+$  diffusion within the electrolyte. Among these reported approaches, fabricating a three-dimensional (3D) porous  $\text{LiFePO}_4/\text{C}$  architecture with host  $\text{LiFePO}_4$  nanoparticles embedding in the guest carbon frameworks (CNWs) is the most efficient one to fast electronic and  $\text{Li}^+$  conduction [13–17]. That is because the carbon networks can bridge the embedded  $\text{LiFePO}_4$  nanoparticles to overcome the low electron transfer, and the adequate porosity of carbon framework promotes the rapid movement of  $\text{Li}^+$  for high-rate capabilities. Currently, a variety of synthetic technologies have been applied to synthesize porous LFP/CNWs composites. Template approaches is one of the well-studied and easy methodology to tune the morphology and structure of  $\text{LiFePO}_4$  with desired architecture. Both soft and hard templates, including tartaric acid [17], carbon monolith [18], colloidal crystal [19], and triblock copolymer [20], have already been utilized to synthesize porous carbon frameworks for loading  $\text{LiFePO}_4$  nanoparticles.

Metal-organic frameworks (MOFs), a fantastic porous crystalline compound which compose of metal ions connected by bridges of organic molecules, have already been attracted considerable interests not only because of their large surface area, controlled pore size and distribution, but also because of their potential applications in hydrogen storage, gas adsorption and separations, catalysis, sensing, as well as photonics and magnetic [21–23]. At present, MOFs have been attempted to be utilized as both a template and starting materials for the preparation of tuneable framework composites, carbon nanotubes, and some other inorganic materials. For instance, well interconnected 3D hierarchically porous networks (AS-ZC-800) were successfully formed using microporous Zn-based ZIF-8 particles as template [24]. The prepared unique AS-ZC-800 strategy with a large BET surface area  $\sim 2972$   $\text{m}^2 \text{g}^{-1}$  exhibits high performance as a super capacitor electrode. In addition, a HPCN-S with 3D hierarchically porous nanostructure was prepared by encapsulating sulfur (S) into the porous carbon nanoplates (HPCN) which derived from the pyrolysis reaction of metal-organic frameworks (MOF-5). The resultant HPCN-S composites with a high specific capacity deliver an initial discharge capacity of 1177  $\text{mAh}\cdot\text{g}^{-1}$  and final 730  $\text{mAh}\cdot\text{g}^{-1}$  after 50th cycle at 0.1C [25].

Herein, for the first time, we report a reasonable design and a successful preparation of hierarchically porous LFP/CNWs composites using unique Fe-based metal organic framework MIL-100(Fe) as a porous template and the starting material of Fe and C. The metal organic framework MIL-100(Fe) has already been utilized as a template to synthesize  $\gamma\text{-Fe}_2\text{O}_3/\text{C}$  [26] and magnetic  $\text{CoFe}_2\text{O}_4$  [27] previously. Thereafter, the prepared LFP/CNWs composites were mixed with melamine to synthesize nitrogen-modified LFP/N-CNWs composites, expecting to further increase the electrical conductivity and consequently enhance the electrochemical performance of  $\text{LiFePO}_4$  cathodes materials. It is worthwhile noting that the XRD, SEM and TEM characterizations indicate that both of the LFP/CNWs and LFP/N-CNWs composites exhibit a 3D porous architecture with  $\text{LiFePO}_4$  nanoparticles uniformly embed in the continuous carbon framework. Compared with the LFP/CNWs sample, nitrogen-doped LFP/N-CNWs sample show superior elec-

trochemical performance in terms of high discharge capacity, good rate capability and excellent capacity retention which is promising for the applications in LIBs.

## 2. Experimental

### 2.1. Materials

$\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ,  $\text{LiH}_2\text{PO}_4$ ,  $\text{NH}_4\text{F}$  and  $\text{C}_3\text{N}_3(\text{NH}_2)_3$  were purchased from Guang Fu Fine Chemical Research Institute (Shanghai, China). Benzene trimesic acid (BTC) was purchased from Sigma-Aldrich Co. LLC (Shanghai, China). All of the materials were of analytical grade and were used without further purification. Deionized water was used throughout the process.

### 2.2. Synthesis of MIL-100(Fe)

MIL-100(Fe) was synthesized according to the literature of Seo et al. [28]. The entirely dissolved  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  aqueous solution was loaded into a vessel, followed by benzene trimesic acid (BTC) powder. The resultant composition of the reactant mixture was 1  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ : 0.67 BTC:  $x$   $\text{H}_2\text{O}$  ( $x = 55\text{--}280$ ). After stirred for 1 h at ambient temperature, the reactant mixture was shifted into a Teflon-lined pressure crystallizer and then heat treated at 160  $^\circ\text{C}$  for 12 h. After reaction, the obtained suspension was filtered, and then washed using deionized water at 80  $^\circ\text{C}$  for 3 h and hot ethanol at 65  $^\circ\text{C}$  for 3 h until no detected colored impurities in the filtrate. To further purification, a 70  $^\circ\text{C}$   $\text{NH}_4\text{F}$  aqueous solution was utilized to purified MIL-100(Fe) for 3 h. The final solids were then dried under air at 80  $^\circ\text{C}$  for 12 h.

### 2.3. Synthesis of LFP/CNWs and LFP/N-CNWs

The synthetic procedure of LFP/CNWs and LFP/N-CNWs is shown in Scheme 1. In a typical synthesis of LFP/CNWs, 6.51 g of the as-prepared MIL-100(Fe) was dispersed in 50 mL ethanol. Next, 4.08 g  $\text{LiH}_2\text{PO}_4$  was dissolved in 100 mL ethanol and added into the MIL-100(Fe) turbid liquid under stirring. The molar ratio of Fe/Li is controlled as 1:1. The mixed ethanol solution was evaporated at 80  $^\circ\text{C}$  for 4 h after been stirred for 24 h at room temperature. The resulting solid product was transferred into a tubular furnace and heat to 600  $^\circ\text{C}$  for 5 h at the heating speed of 2  $^\circ\text{C min}^{-1}$  in reducing atmosphere (10%  $\text{H}_2$  + 90% Ar). The nitrogen-doped LFP/N-CNWs was prepared via carbonization of the nitrogen-containing  $\text{C}_3\text{N}_3(\text{NH}_2)_3$  using the following procedure: 0.4672 g  $\text{C}_3\text{N}_3(\text{NH}_2)_3$  is mixed with 4 g of the as-prepared LFP/CNWs in 60 mL ethanol solvent, and then the mixtures were stirred at 60  $^\circ\text{C}$  for 24 h. The final solids were dried under vacuum at 80  $^\circ\text{C}$  for 10 h before calcination under a  $\text{N}_2$  atmosphere at 600  $^\circ\text{C}$  for 4 h.

### 2.4. Materials characterization

The crystal structure was identified by X-ray diffraction (XRD, Rigaku D/max 2500 V/PC) with a  $\text{Cu-K}\alpha$  radiation source. The diffraction data were collected in a  $2\theta$  range from 5 $^\circ$  to 70 $^\circ$  with each step of 0.017 $^\circ$ . The surface morphology of the crystal was observed by a scanning electron microscopy (SEM, Hitachi Ltd., Japan, Model S-4800) with an X-ray energy dispersive spectroscope (EDS). The surface texture and morphology of the crystal were observed by a transmission electron microscope (TEM, JEM-2010 FEF, Japan). The specific surface area was measured by a  $\text{N}_2$  adsorption-desorption method using a Brunauer-Emmett-Teller (BET) analyzer, a Nove 2000e (Quantachrome Instruments, USA). X-ray photoelectron spectroscopy (XPS) measurement was carried out by a PHI5000 Versa Probe spectrometer. The analyzer pass energy for survey and detailed elemental scans were set to 187.85 eV and 46.95 eV, re-

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