

Design and facile synthesis of nitrogen-doped carbon decorated LiVPO₄F nanocrystals as superior cathode for lithium-ion batteries



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ABSTRACT

In this study, nitrogen-doped carbon is coated on LiVPO₄F electrode for the first time via a simple chemical refluxing process, using ethylenediamine (EDA) as the carbon and nitrogen source. The structure, morphology and microstructure of the as-prepared electrode are characterized by XRD, XPS, Raman spectra, SEM and TEM. The uniform coating of nitrogen-doped carbon improves the electronic conductivity of LiVPO₄F. As cathode material for lithium-ion batteries, the nitrogen-doped carbon coated LiVPO₄F composite exhibits superior rate capability and excellent cycle performance over the carbon coated LiVPO₄F. The electrode delivers an initial discharge capacity of 109.6 mAh g⁻¹ at high rate of 10 C and 103.1 mAh g⁻¹ of capacity is retained after 100 cycles. Thus, this novel modification method of nitrogen-doped carbon coating is highly effective and could be widely used to optimize the electronic conductivity of other electrode materials for lithium-ion batteries.

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1. Introduction

With urgent requirements of large-scale energy storage, hybrid electric vehicles (HEVs) and electric vehicles (EVs), rechargeable lithium-ion batteries have been extensively researched [1]. Nowadays, the development of advanced electrode materials with high reversible capacity and excellent rate capability, as well as sufficient cycling stability, are critical for the next generation of lithium-ion batteries [2,3]. Among the various cathode materials [4–9], the new fluorophosphate electrode, LiVPO₄F, has gained great interest due to its high voltage, good rate capacity, long cycle life and good safety features [10].

LiVPO₄F is isostructural with the naturally-occurring mineral tavorite, LiFePO₄·OH or amblygonite, LiAlPO₄F, crystallizing with a triclinic structure (space group P) [11,12]. It shows excellent lattice stability and good thermal stability with electrolyte owing to the consolidus covalent-bonded crystal structure. Moreover, tavorite LiVPO₄F has a relatively high potential of 4.2 V (vs. Li⁺/Li) and a theoretical capacity of 155 mAh g⁻¹ from a one-electron V³⁺/V⁴⁺ redox. However, like many other cathode materials, the electronic conductivity of the pristine LiVPO₄F is poor (10⁻¹¹ S cm⁻¹ [13]), limiting its application in high power density batteries. Up to now, numerous strategies have been investigated with the aim of improving the electronic conductivity of LiVPO₄F, including the metal ion doping [14,15], and carbon or other conductive materials coating [9,10,16–18]. All of these methods, especially the carbon coating, have greatly improved the

electrochemical performances of LiVPO₄F electrode, including the discharge capacity, rate capability and cycle stability. Nevertheless, the comprehensive performances of LiVPO₄F still need to be further improved for practical applications.

It is proved that heteroatom doping has an enhancing effect on the electronic conductivity and electrochemical activity of carbon-based materials [19–21]. A carbon coating can effectively improve the electrochemical performance of the electrode when nitrogen is introduced in the carbon structure as a dopant [22]. Recently, the nitrogen-doped carbon has been used to modify the LiFePO₄ [23,24], Li₃V₂(PO₄)₃ [25] and TiO₂ [26] electrode materials. The results reveal that the nitrogen-doped carbon coated electrode materials can further improve the electronic conductivity, Li-ion diffusion through the carbon layer, and the charge transfer at the interface, which contribute significantly toward a good reversible capacity and an enhanced rate capability of the electrodes. To the best of our knowledge, there is no reports about the fabrication of nitrogen-doped carbon coated LiVPO₄F, and the effects of nitrogen-doped carbon on the electrochemical performance of LiVPO₄F have not been investigated.

In this study, we firstly report the synthesis of nitrogen-doped carbon coated LiVPO₄F nanocomposite via a simple chemical refluxing process, using EDA as the carbon and nitrogen source. Various analytical methods, including XRD, XPS, Raman spectra, SEM and TEM, are performed to investigate the chemical composition, morphology and microstructure of the sample. We demonstrate that the as-prepared electrode would exhibit significant improvements in electronic conductivity and electrochemical performance when used as the cathode material for lithium-ion batteries.

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2. Experimental

2.1. Material preparation

The pristine LiVPO_4F sample was prepared via a sol–gel route using LiF , V_2O_5 , $\text{NH}_4\text{H}_2\text{PO}_4$ and citric acid (reducing agent) as the starting materials. In a typical procedure, the $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gel was firstly synthesized through a simple method reported by Wei's group [9]. Then, stoichiometric LiF , $\text{NH}_4\text{H}_2\text{PO}_4$ and citric acid were added to the above $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ hydro-gel under magnetic stirring for 5 h at room temperature. The mixture was heated at 80°C for several hours with vigorous stirring to evaporate the water until a gel was obtained. The gel precursor was then dried at 100°C in a vacuum oven. Finally, the gel powder was ground, and preheated at 300°C for 4 h and then annealed at 650°C for 6 h in flowing Ar atmosphere by using a tube furnace to obtain the pristine LiVPO_4F sample.

The synthetic process used to prepare nitrogen-doped carbon coated LiVPO_4F sample ($\text{LiVPO}_4\text{F}/\text{N-C}$) is schematically illustrated in Fig. 1. Typically, the as-prepared pristine LiVPO_4F and cetyltrimethylammonium bromide (CTAB) were dispersed in the EDA solution with continuous stirring and refluxing at 120°C for 48 h. Then, the precipitate (LiVPO_4F covered by EDA) was obtained by centrifugation at 6000 rpm and dried at 70°C in a vacuum oven overnight. Finally, the obtained powder was calcined at 600°C for 5 h in a furnace purged with Ar gas. For comparison, the carbon coated LiVPO_4F ($\text{LiVPO}_4\text{F}/\text{C}$) was also successfully prepared by the sol–gel method. During the synthetic process, the citric acid was used as both reducing agent and carbon source.

2.2. Material characterization

XRD of the samples was performed on a Bruker powder diffraction system (model D8 Advanced) with a $\text{Cu-K}\alpha$ radiation source. The particle morphology was observed using SEM (Philips XL 300) and TEM (JEOL 2100F). Raman spectra were carried out on a laser Raman spectrometer (Dongwoo DM500i, Japan) with the 514 nm line of an Ar ion laser as the excitation source. X-ray photoelectron spectroscopy (XPS) was collected on a K-Alpha system with a monochromatic Al K α (1486.6 eV) anode.

2.3. Electrochemical measurements

The electrochemical performances were tested with CR2032 coin cells assembled in a glovebox filled with pure argon gas. The cathodes were prepared by mixing the active materials, super P and polyvinylidene fluoride (PVDF) in a weight ratio of 85:10:5 in NMP solvent to form a homogeneous slurry, which was uniformly coated on an Al foil and then dried in a vacuum at 120°C . The circular cathode disc with a diameter of 1.4 cm was punched from the aluminum foil. The mass loading of each electrode plate was around $2.5\text{--}2.8\text{ mg cm}^{-2}$. A Celgard 2400 membrane was used as a separator and a lithium

metal served as the anode. The electrolyte used for testing was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, volume). All cells were aged for 6 h before charge/discharge to ensure full absorption of the electrolyte into the electrodes. The coin cells were charged and discharged between 3.0 and 4.5 V at different current rates on the electrochemical test instrument (CT2001A, Wuhan Land Electronic Co. Ltd., China) at room temperature (25°C). The charge/discharge capacities were calculated based on the LiVPO_4F material. The electrochemical impedance spectroscopy (EIS) tests were performed using a CHI660D electrochemical working station (Shanghai, China) in a frequency range of 10 kHz to 10 mHz with an applied amplitude of 5 mV.

3. Results and discussion

In order to confirm the effects of N–C coating on the crystal structure of LiVPO_4F , XRD patterns of the as-prepared $\text{LiVPO}_4\text{F}/\text{C}$ and $\text{LiVPO}_4\text{F}/\text{N-C}$ samples were performed and the results are shown in Fig. 2. As illustrated in Fig. 2, it is clear that there is no difference between the XRD results of the two samples, and the refined patterns fit very well with the crystal structure of amblygonite LiAlPO_4F and tavorite $\text{LiFePO}_4 \cdot \text{OH}$. All the diffraction patterns of both samples show a triclinic structure (space group P, JCPDS card No. 42-1412) which are consistent well with the previously reported papers [12,16,27]. Besides, no evidence of the carbon related patterns are detected by XRD which can be attributed to that the residual carbon is amorphous. The above XRD results reveal that the nitrogen doped into the carbon layer does not have an effect on the crystal structure of LiVPO_4F material.

Fig. 3 shows the SEM images of $\text{LiVPO}_4\text{F}/\text{C}$ and $\text{LiVPO}_4\text{F}/\text{N-C}$ particles. It can be noted that the primary particles of both samples are less than 200 nm in size. The smaller particles, which have a larger surface area, increase the electrode/electrolyte contact area and promote greater Li^+ diffusion between the cathode and electrolyte during the electrochemical reaction, resulting in high-rate performance [28]. The C and N–C coating layers on the LiVPO_4F particles can be clearly observed by TEM, and the results are illustrated in Fig. 4(a–c) and (d–f), respectively. Both the C and N–C coating layers present short range ordered amorphous structures, and the coating layers are approximately 5 nm in thickness. These stable conducting coating layers can effectively enhance the surface electronic conductivity of LiVPO_4F and ensure a good electronic connection between the LiVPO_4F particles.

To confirm the difference in the defect level between the C and N–C coating layers for the $\text{LiVPO}_4\text{F}/\text{C}$ and $\text{LiVPO}_4\text{F}/\text{N-C}$ composites, the Raman spectra were performed. It can be found from Fig. 5(a) that both samples exhibit two peaks of a D-band and G-band, which are located at about 1337 cm^{-1} and 1582 cm^{-1} , respectively. The G-band stands for the presence of graphite carbon, whereas the D-band is attributed to the disorders or defects in the graphite structure [29].

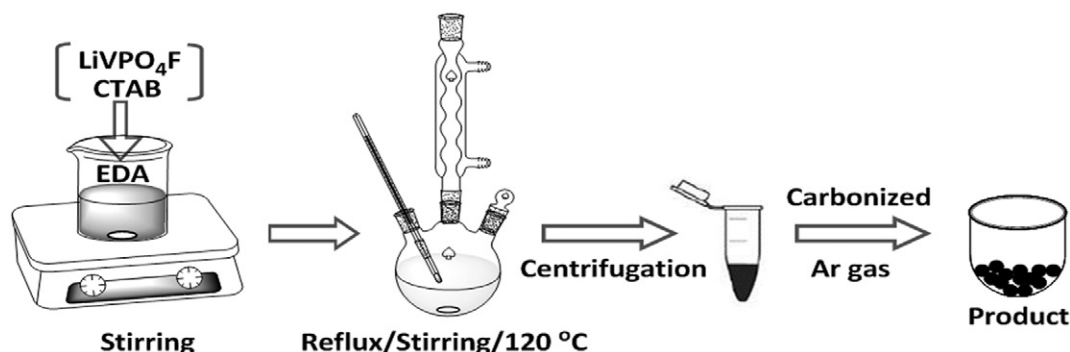


Fig. 1. Schematic drawing of the preparation for the nitrogen-doped carbon decorated LiVPO_4F sample.

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