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Construction of ultrathin N-doped carbon shell on LiFePO₄ spheres as enhanced cathode for lithium ion batteries

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ABSTRACT

Developing advanced cathode is playing a crucial role in the advancement of lithium ion batteries (LIBs). In this work, we report a novel one-step spray drying method for fabrication of N-doped carbon (N-C) coated LiFePO₄ spheres forming LiFePO₄/N-C spheres composite. Thin N-C layer of about 5 nm was coating on the surface of LiFePO₄ spheres. The electrochemical properties of LiFePO₄/N-C spheres composite have been thoroughly studied as cathode of LIBs. The LiFePO₄/N-C spheres composite delivers discharge capacities of 160, 143 and 115 mAh g⁻¹ at 1 C, 5 C and 20 C, respectively, much better than unmodified LiFePO₄ cathode. A high discharge capacity of 159 mAh g⁻¹ is preserved with 99% capacity retention after 1000 cycles at 1 C. The enhanced performance is due to the introduction of N-C shell with improved electrical conductivity and structural stability.

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1. Introduction

High performance electrochemical energy storage devices are important for advancement of modern electronics and electric vehicles [1–3]. Of power sources candidates, Li ion batteries (LIBs) have attracted great attention due to large energy density and high working voltage. Though layered LiCoO₂ has been commercialized as cathode material, but it suffers from relatively low safety and high price. Therefore, olivine lithium iron phosphate (LiFePO₄) energy and are widely used as alternative cathode due to its high theoretical capacity (170 mAh g⁻¹) [4–7], low cost, long cycle life, and high operating voltage. Nevertheless, the commercial application of LiFePO₄ cathode is hindered by low electronic and ion conductivities. In view of these disadvantages, rational modification strategy must be taken to enhance its performance [8–10].

Great efforts have been made by using nanostructure design, doping with cations, and conductive coatings. Among them, the conductive coating strategy has been demonstrated the most successful. To date, carbon materials (rGO [11], amorphous carbon [12], carbon nanotube [13], etc.) have been used to enhance the performance of LiFePO₄ with high capacities. The carbon layer can not only improve the conductivity of electrode resulting in better reaction kinetics, but also serve as a barrier to suppress the aggregation of possibly pulverized active materials during cycling

[14–16]. Then, the carbon layer effectively limits the volume expansion, thus increasing their structure stability leading to enhanced cycling. But the current modification method of carbon is also not perfect. The thickness of conductive carbon coating is difficult to control. If it is too thick, the performance of LiFePO₄ cathode will be undermined due to the blocking effect for Li ion. In addition, high carbon content would decrease the energy density and power density [17–20].

Traditional solid-state reaction is always used to prepare LiFePO₄ cathode, but it is not controllable with size and morphology. Moreover, the carbon layer formed by the solid-state reaction is not homogeneous. In parallel with this method, facile spray drying method has aroused great interest because of low cost, high efficiency, high tap density and easy processing. Generally, spherical LiFePO₄ spheres are prepared by the spray drying method. In spite of this progress, the carbon coating is still necessary. In recent years, it is reported that heteroatom doping, especially, nitrogen doping in carbon can increase reactive sites and decreases the energy barrier of ion penetration. Up to now, there is no report on the fabrication of N-doping carbon on LiFePO₄ spheres as cathode of lithium ion batteries.

In this work, N-doping carbon layer is constructed on the LiFePO₄ spheres forming LiFePO₄/N-C sphere composites via one-step spray drying method. Compared to the unmodified counterpart, the LiFePO₄/N-C sphere composites present excellent electrochemical performance with high-rate capability and cycling stability. Enhanced reaction kinetics are proven due to improved electron transfer and fast ion diffusion. Our results provide

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reference for construction of other high-performance cathodes of LIBs.

2. Experimental

The N-C coated LiFePO_4 was synthesized by a spray drying method using stoichiometric Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ and dopamine as starting materials. They were dissolved in distilled water. The resulting solution was fed into a commercial spray-dryer to produce homogeneous precursor powders. The inlet air temperature was 220°C , and the exit air temperature was kept in the range of $90\text{--}110^\circ\text{C}$. The precursor powders were annealed at 600°C for 4 h in a nitrogen-argon mixture to obtain $\text{LiFePO}_4/\text{N-C}$ spheres composite. For comparison, pure LiFePO_4 spheres were prepared as the same parameters without N-C coating.

The microstructures and morphologies of the as-deposited samples were characterized by X-ray diffractometer (XRD, Rigaku D/max 2550 PC, Cu Ka), X-ray photo-electron spectroscopy (XPS, PHI 5700), scanning electron microscopy (SEM, Hitachi S-4700), and transmission electron microscopy (TEM, Tecnai G2 F20 at 200 kV).

Electrochemical performances were performed by assembling CR2025 coin cells for galvanostatic charge/discharge testing. The cell consisted of a lithium foil anode and a $\text{LiFePO}_4/\text{N-C}$ cathode separated by a polypropylene microporous separator (Cellgard 2300), 1 M LiPF_6 in ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1 in volume) as the electrolyte (the electrolyte was LB-302, which was purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co.). The cathode was made of 80 wt.% $\text{LiFePO}_4/\text{N-C}$, 4 wt.% polyvinylidene fluoride (PVDF) as a binder and 16 wt.% acetylene black, which were dispersed in 1-methyl-2-pyrrolidinone (NMP), and the resultant slurry was then spread onto the circular disc aluminum foil. After drying in an oven at 60°C , the cathode was pressed to achieve good adherence between the coated material and the aluminum foil. The coin cells were

assembled inside a glove box filled with high-purity argon gas (99.9995% purity). The galvanostatic charge/discharge measurements were performed on LAND battery test system at different current densities between the potential of 2.5–4.2 V at room temperature. Cyclic voltammetry (CV) tests were conducted on a CHI600D electrochemistry workstation at a scan rate of 0.1 mV s^{-1} in the potential range of 2.5–4.2 V. Electrochemical impedance spectroscopy (EIS) results were obtained from the frequency range of 100 kHz–10 mHz with the excitation voltage of 5 mV.

3. Results and discussion

Fig. 1 shows SEM images of LiFePO_4 spheres and $\text{LiFePO}_4/\text{N-C}$ sphere composites. It is seen that the LiFePO_4 sample prepared by the spray drying method shows spherical morphology. The obtained LiFePO_4 spheres exhibit diameter of 1–2 μm (Fig. 1a–b). Moreover, the LiFePO_4 spheres possess porous structure, suggesting that this porous structure will not block the transfer of electrolyte. For the $\text{LiFePO}_4/\text{N-C}$ sphere composites, the spherical morphology is well preserved. And the size does not change much. It is indicated that the developed spray drying method does not have harmful effect on the morphology. In addition, as shown in Fig. 1c, the size distribution is very uniform, demonstrating the high quality of the final samples.

TEM image of the LiFePO_4 sample confirms the spherical shape with size of 2 μm (Fig. 2a). After coating of N-C layer, the sphere shape is well maintained. Note that only an ultrathin N-C layer of 1.6 nm is coated on the surface of LiFePO_4 spheres (Fig. 2b–c). The small thickness is favorable for achieving both high electrical conductivity and fast ionic conductivity. HRTEM image of the $\text{LiFePO}_4/\text{N-C}$ spheres composite is shown in Fig. 2c. It is seen that highly crystalline LiFePO_4 is uniformly coated by the intimate N-C layer of $\sim 1.6\text{ nm}$. In addition, the N-C layer is amorphous. The presence of N-C layer is also supported by the homogeneous EDS elemental maps of Fe, P, C and N, respectively (Fig. 2d). This N-C

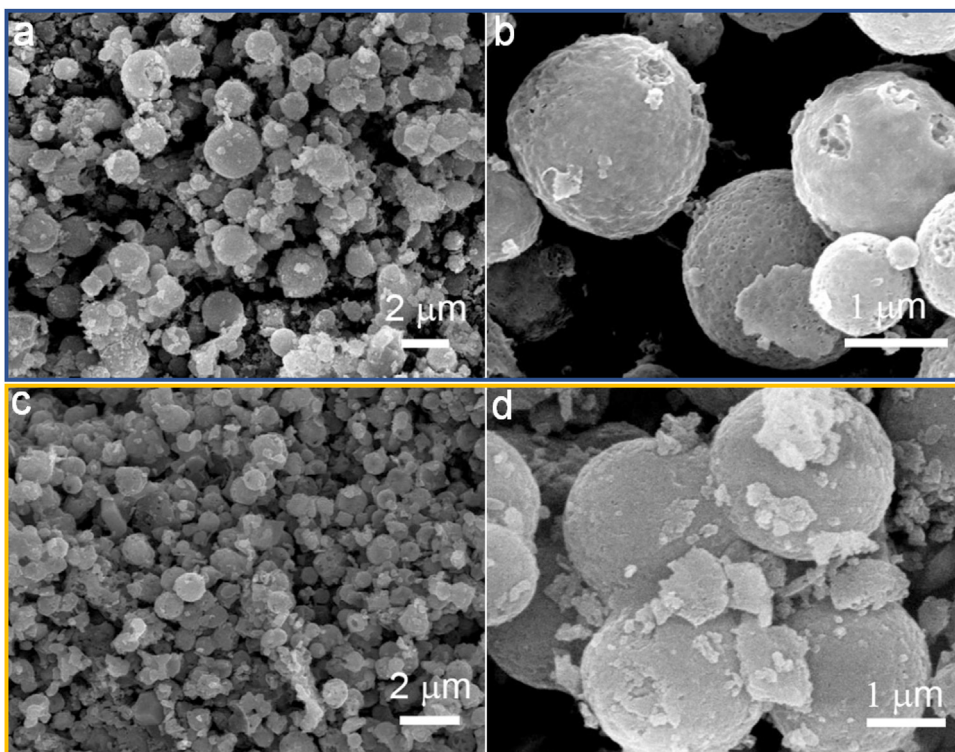


Fig. 1. SEM images of (a, b) LiFePO_4 spheres and (c, d) $\text{LiFePO}_4/\text{N-C}$ sphere composites.

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