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Nanoconfinement of red phosphorus nanoparticles in seaweed-derived hierarchical porous carbonaceous fibers for enhanced lithium ion storage

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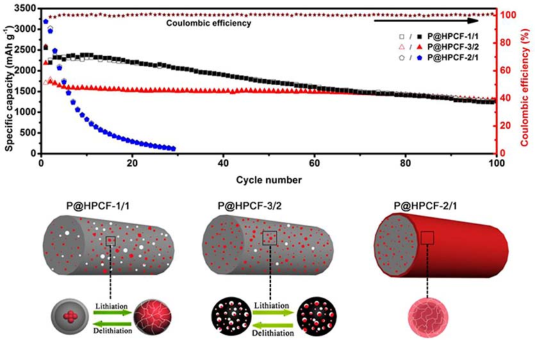
HIGHLIGHTS

- Seaweed-derived hierarchical porous carbonaceous fibers confine Red P nanoparticles.
- Red P nanoparticles filled in micropores and gradually extended to larger pores.
- Incorporation of appropriate content of red P showed outstanding performance.
- Higher reversible capacity, excellent cycle life and rate performance were achieved.

GRAPHICAL ABSTRACT

We confined red P nanoparticles into the seaweed-derived porous carbonaceous fibers with hierarchical pores where the small micropores are used to confine the red P nanoparticles and the large mesopores are beneficial for the increased contact of electrolyte. The P@HPCF-3/2 showed an outstanding performance with the reversible capacity maintaining at 1300 mAh g^{-1} after 100 cycles.



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ABSTRACT

Red phosphorus has come to our attention as the anode material for lithium-ion batteries with high theoretical specific capacity of 2596 mAh g^{-1} due to its earth-abundant and low-cost. However, it suffers from low electroconductivity and large volume expansion, resulting in serious capacity fading. In this study, we confined red phosphorus nanoparticles into the hierarchical porous carbonaceous fibers to enhance its cycling stability. Red phosphorus nanoparticles preferentially filled in the micropores and gradually extended to the larger pores. The optimized electrochemical performance benefits from hierarchical pores filled with the appropriate content of red phosphorus, where the small micropores are used to confine the red phosphorus nanoparticles and the large mesopores are beneficial for the increased contact of electrolyte. This can remit excessive volume change and

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facilitate the contact area of electrolyte effectively. Thus, the P@HPCF-3/2 displays outstanding cycle performance with a superior high reversible capacity (1300 mAh g^{-1} after 100 cycles at 1 A g^{-1}).

1. Introduction

Lithium-ion rechargeable batteries (LIBs) have served as energy sources for a wide category of energy storage devices, including hybrid electric vehicles (HEV), smart grids, and portable electric vehicles [1–6]. Graphite, as a traditional anode material for LIBs, only has a unsatisfactory theoretical specific capacity of 372 mAh g^{-1} and poor energy density, which could not meet the requirements for high gravimetric and volumetric energy density [7–8]. Development of more novel electrode materials [9–11], especially the anode materials is particularly important [12–17]. Phosphorus (P) is a good candidate anode material for LIBs with a super high storage capacity (Li_3P, 2596 mAh g^{-1}) [18–21]. Solid P has three main allotropes: white, black and red. White P is toxic, unstable and flammable due to its tetrahedral P_4 structure, which limit it as an effective anode material. Black P is similar to the two-dimensional structure of graphene with high electrical conductivity and chemical stability, but it is generally synthesized under extreme conditions, such as high temperature and high pressure [22,23]. Red P is a commercial available, environmental friendly and thermal stable material. Unfortunately, red P is facing two major problems as an anode material for LIBs as follows: (1) poor electronic conductivity ($\sim 1 \times 10^{-14}$ S cm^{-1}); (2) a huge volume change (about 300% expansion) during the charge/discharge process, resulting in fast capacity fading [24,25]. In order to overcome both drawbacks, some effective approaches have been proposed, such as reducing the size of red P particles to buffer volume expansion and promote the ion diffusion effectively; compositing the conductive substrates with red P to enhance electrical conductivity and reduce electrochemical impedance.

The porous carbon materials such as carbon nanotubes [25], activated carbon [26], black carbon, and graphene [27,28] are believed to be ideal carriers to load red P due to their excellent electrical conductivity and abundant porous structure [29–35]. Some studies have shown that micropores (< 2 nm) are preferential to adsorb red P nanoparticles due to their stronger adsorption force [26,29]. However, the channel block induced by red P confinement results in the decrease of contact with electrolyte and thus reduces the ion transport capacity [33]. This would lead to the larger internal resistance and poor cycle performance. Apparently, it is an ideal design to use a hierarchical porous carbonaceous (HPC) material as substrate for confinement of red P nanoparticles, where the small micropores are used to confine red P nanoparticles and the large mesopores are beneficial for the increased contact of electrolyte.

Herein, HPC fibers were synthesized by using calcium algniate fibers (CAFs) as precursors. Different contents of red P were incorporated into the HPC fibers (P@HPCF) by vaporization-condensation method. It was found that red P nanoparticles preferentially filled in the micropores and gradually extended to the larger pores. When evaluated as anode for LIBs, the P@HPCF-3/2 exhibited outstanding cycle performance with a superior high reversible capacity (1300 mAh g^{-1} after 100 cycles at 1 A g^{-1}). Apparently, the HPCF loaded with optimum content of red P is beneficial to confine and disperse red P nanoparticles preferably, shorten the transmission distance of ions, remit excessive volume change and facilitate the contact area of electrolyte effectively in ion de-intercalation process.

2. Experimental

2.1. Preparation of HPCF

The original materials, CAFs, were pyrolyzed at 900 °C for 1 h under a argon flow in a tube furnace. After cooling to ambient temperature, the carbonized CAFs were obtained and transferred to beakers with 1 M HCl solution overnight to remove CaO and make more abundant porous structure. Finally, the HPCF were obtained by washing with ultra-pure water and dried thoroughly in an oven at 60 °C.

2.2. Preparation of P@HPCF-x

The commercial red P powder was washed with distilled water at 200 °C for 10 h to remove possible oxides on the surface. The processed red P and HPCF were weighed with different proportions (weight ratio of red P and HPCF was 1/1, 3/2, and 2/1), transferred to a 10 mm diameter quartz tube and then vacuum-sealed [36]. Afterwards, the quartz tube was put into a tube furnace, then heated to 550 °C and held at that temperature for 2 h under air. Subsequently, the tube furnace was cooled to 280 °C and maintained for 40 h (Fig. S1). The composites were acquired after cooling to room temperature and washed with CS_2 to remove white P. The materials obtained are denoted as P@HPCF-x (x = 1/1, 3/2, and 2/1).

2.3. Characterization

The X-ray diffraction (XRD, DX2700, China) was applied to characterize the phase structure of composites operating with Cu Kα radiation at a scan rate of 3° min^{-1}. The specific surface area and pore size analysis were determined by nitrogen adsorption and desorption isotherms using the Brunauer-Emmett-Teller (BET) method (3H-2000PS2 analyzer). Thermogravimetric analysis (TGA) data were got in argon with a heating rate of 10 °C min^{-1} by using an EXSTAR TG 6300 instrument. X-ray photoelectron spectroscopy (XPS) spectra was measured using an ESCALab250 electron spectrometer in a high-vacuum chamber with monochromatic Al Kα radiation. The Raman spectroscopy was conducted on a spectrometer (Renishaw) at room temperature. The microscopic feature of all samples were examined by the field-emission scanning electron microscopy (FESEM; JSM-7001F) and transmission electron microscopy (TEM; FEI Tecnai 20 TEM). And the SEM energy dispersive X-ray spectroscopy (EDS) element mapping was measured to observe element distribution.

2.4. Electrochemical tests

The electrochemical performance was measured by CR2016-type coin cells, in which metallic lithium was employed as the counter electrodes. The as-prepared P@HPCF-x composites were mixed with acetylene and polyvinylidene fluoride (PVDF) at a ratio of 80:10:10 (wt %) to form a slurry by using N-methyl-2-pyrrolidone (NMP) as a solvent. Subsequently, the working electrode was fabricated by pasting the resultant slurry equably onto a copper foil substrate and then dried in a vacuum oven at 100 °C overnight. After pressed, the active material mass loading of the electrode was about 1.5–2.0 mg cm^{-2}. All cells were assembled in a purity argon-filled glove box, using polypropylene (Celgard 2500) as separator. And the electrolyte solution consisted of 1 M $LiPF_6$ in ethylene carbonate (EC)-diethyl carbonate (DEC)-dimethyl carbonate (DMC) (1: 1: 1, in weight). The charging and discharging performances were conducted on a LAND CT2001A with the voltage ranging from 0.01 to 2.0 V. Cyclic voltammetry (CV) measurement was conducted at a sweep rate of 0.1 mV s^{-1} on a CHI 760E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was tested on fresh cell in the frequency ranging from 0.01 Hz to 100 k Hz.