

Superior potassium storage in chitin-derived natural nitrogen-doped carbon nanofibers

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ABSTRACT

Potassium ion batteries (KIBs) are drawing intensive attention as the next-generation energy storage technology, owing to their similar electrochemical properties to lithium system and rich abundance of potassium resources. The carbonaceous materials with low cost, nontoxicity and high safety have been considered as promising candidates for KIBs anodes. However, they still suffer from several problems, such as poor cycling and rate capability, complex activation process steps and multiple procedures to import heteroatoms doping. Herein, the N-doped carbon nanofibers (NCFs) are fabricated by direct pyrolysis of bio-waste chitin, which is the second most abundant biopolymer throughout nature. The as-prepared NCFs used as KIBs anodes, without any additional activation steps, are systematically investigated for the first time. They deliver high capacity, excellent rate capability and long-term cycling stability, which benefit from the multiple synergistic effects of suitable interlayer spacing, heteroatom doping and unique one dimensional mesoporous structure. With the spotlight of environmental friendliness, low cost and high energy density in energy storage field, the chitin-based NCFs demonstrate great potential for future low-cost energy storage applications.

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1. Introduction

The demand for lithium ion batteries (LIBs) in portable electronic devices, electric vehicles and smart grids keeps growing steadily due to their long cycling life and high energy density. However, the expensiveness and relative scarce existence of lithium resources make it challenging to be deployed in large-scale energy storage systems [1–10]. Consequently, tremendous interests in pursuing high-performance earth abundant metal ion batteries come into being. Potassium ion batteries (KIBs), based on the wide availability and low-cost of potassium, have drawn enormous attention in recent years [11–19]. The redox potential of potassium is -2.92 V (vs standard hydrogen electrode (SHE)), close to that of lithium (-3.01 V), suggesting similar electrochemical behaviors; It is lower than that of sodium (-2.71 V), indicating a higher operating voltage with comparable low cost [20–22]. These intriguing

features suggest that KIBs with high voltage, low cost and high energy density are potential substitute for sodium ion batteries (SIBs) and even LIBs.

The carbonaceous materials are the most attractive materials for KIBs anode due to their particularly low cost and high natural abundance [23–27]. For graphite, it allows reversible K^+ ions insertion/extraction in the electrochemical environment, delivering a high specific capacity of 273 mAh g^{-1} , close to its theoretical value of 279 mAh g^{-1} . However, poor cyclability and rate capability appear simultaneously due to its large volume expansion [28,29]. Activated graphite was fabricated by an etching method, enlarging inter-planar spacing so that ion diffusion efficiency can be enhanced [30]. Non-graphitic carbon, such as hard carbon microspheres and carbon nanofibers prepared by the pyrolysis of artificial organic precursor hold a high initial capacity, which benefit from high diffusion coefficient of K^+ ions in the particular structure [31–33]. However, considering their complicated, time-consuming synthesis procedures as well as poor cycling and rate ability caused by large ionic radius of potassium (1.33 Å), the large-scale application of carbon-based anodes in KIBs remains challenging.

Herein, a novel concept for synthesizing nitrogen-doped carbon

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nanofibers (NCFs) have been proposed by using bio-waste chitin as raw materials. Chitin, the second most abundant biopolymer after cellulose, possesses many absorbing properties such as low-cost, renewability, natural nitrogen-containing functional groups and intrinsic fibrous structure, demonstrating great superiority over other biomass materials [34,35]. Besides, chitin-derived NCFs used as KIBs anode is free from any extra-activation steps, which greatly shorten the synthesis period. Further, the as-prepared NCFs electrode exhibited a high specific capacity, an outstanding rate capability, as well as long-term cycle life (Fig. 1). Significantly, our work reveals the interrelationship between NCFs electrochemical performance and synergistic effects of interlayer space, heteroatom doping and unique one dimensional (1D) structure. It is believed that based on the incorporate heteroatom doping and the unique morphologies, the renewable chitin-derived advanced carbon materials will be a promising electrode material candidate for the low-cost, large-scale practical application of KIBs.

2. Experiment

2.1. Materials synthesis

Synthesis of the NCFs: The N-doped carbon nanofibers were prepared via a facile direct pyrolysis of pure chitin (Sigma, C9213) in tubular furnace (heating rate: $5\text{ }^{\circ}\text{C min}^{-1}$) under Ar atmosphere. The carbonization temperatures were kept at 500, 700, and $900\text{ }^{\circ}\text{C}$ for 2 h, yielding the fabricated carbonized chitin samples denoted as NCF-500, NCF-700 and NCF-900, respectively.

2.2. Materials characterization

Atomic force microscopy (AFM) was performed using a Bruker Dimension Icon Microscope, and the samples were dispersed on a mica plate for the test. To characterize the morphology of the carbon samples, scanning electron microscopy (SEM) (7500F, JEOL), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) (JEOL JEM-2100F) were used. The X-ray diffraction spectra (XRD) were recorded using a Rigaku Dmax 2200 X-ray diffractometer with Cu $K\alpha$ radiation. Thermogravimetric analysis was conducted at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 flow, using a Netzsch Sta449F3 thermal analyzer. The nitrogen sorption

isotherms of the carbon samples was measured at 77 K using an ASAP 2460. The apparent surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore-size distribution plots were recorded from the desorption branch of the isotherms based on the Barrett-Joyner-Halenda (BJH) model. Raman spectroscopy measurements were performed on a LabRAM HR800 system with an excitation wavelength of 633 nm. The silicon peak at 520 cm^{-1} was used as a reference. X-ray photoelectron spectroscopy measurements (XPS) were performed on an ESCALAB 250 XPS system (Thermo Fisher Scientific). The spectra were referenced to the C 1s binding energy of 284.6 eV and analyzed using X-peak software. The electrical conductivity was measured using the four-point method on a Kunde KDY-1 system (Guangzhou, China).

2.3. Electrochemical measurements

The electrochemical properties for both half cells and full cells were carried out *via* stainless-steel coin cells (CR2016) in a glove box under Ar atmosphere. The electrodes were obtained with 80% as-synthesized NCFs, 10% acetylene black, and 10% Na-alginate binder [36] to form slurry and cast on Cu foils using a doctor blade and dried in a vacuum at $100\text{ }^{\circ}\text{C}$ overnight. Using glass fiber membrane as the separator, potassium metal as the anode, and 0.8 M KPF_6 (Sigma Aldrich) in a solvent mixture of ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume) as the electrolyte. Cyclic voltammetry (CV) of NCFs coin cells were tested using an electrochemical workstation (CHI660C, China) at a scan rate of 0.3 mV s^{-1} in the voltage range of 0.01–2 V (vs. K/K^+). The galvanostatic charge/discharge experiments were studied in a potential range of 0.01–2 V (vs. K/K^+) using a multichannel battery testing system (Land CT 2001A). The EIS measurements are performed on an electrochemical workstation (CHI660D) using an open circuit voltage with an amplitude of 5 mV, in the frequency range from 10^{-1} kHz to 10^5 Hz. The electrode active material loading was about $0.9\text{--}1.3\text{ mg cm}^{-2}$.

3. Results and discussion

The surface feature of raw chitin was characterized by AFM (Fig. 2a and Fig. S1), which reveals that chitin possesses smooth surface morphology, consisting of fine nanofibers in a uniform

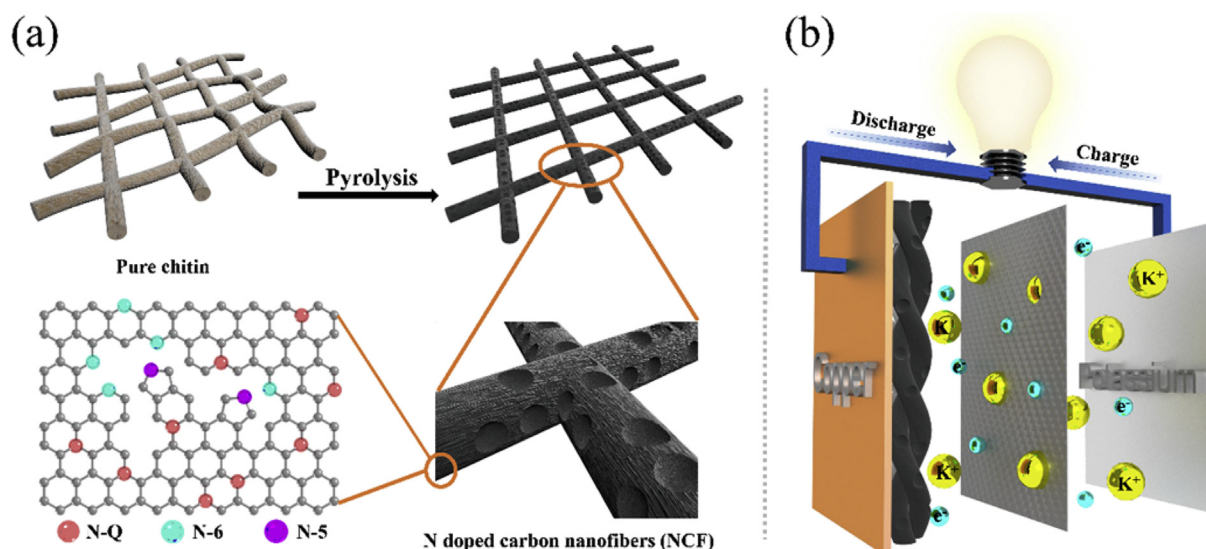


Fig. 1. Schematic illustration for the synthesis of a) the NCFs and b) their application in KIBs. (A colour version of this figure can be viewed online.)

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