Superior lithium storage in nitrogen-doped carbon nanofibers with open-channels

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HIGHLIGHTS

- Nitrogen-doped carbon nanofibers are prepared by an electrospinning process with 2-step carbonization.
- The addition of waste poly(vinyl butyral) induces the open channels on the surface of nanofibers.
- The urea plays a role in the increases of the nitrogen contents of nanofibers.
- The carbon nanofibers exhibit high reversible capacity and long-term cycling stability.

GRAPHICAL ABSTRACT
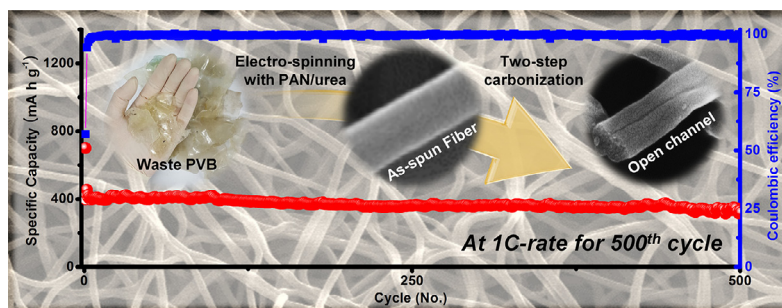
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ABSTRACT

Increasing porosity and nitrogen doping are the most effective strategies for enhancing lithium storage in carbon-based anodes for lithium-ion batteries (LIBs). In this study, we prepare nitrogen-doped carbon nanofibers with open channels (N-CNFO) using a simple electrospinning method with subsequent two-step carbonization using polyacrylonitrile, waste poly(vinyl butyral) (W-PVB), and urea. The W-PVB induce open channels including pores of various sizes, and the urea increase the nitrogen content of the carbon fibers. N-CNFO exhibit excellent electrochemical properties as an anode material for LIBs, including high reversible capacity (734 mA h g^{-1} at 0.2 C), superior rate capability (388 and 358 mA h g^{-1} at 3 C and 5 C, respectively), and excellent cycling performance (330 mA h g^{-1} at 1 C after 500 cycles). These properties are imparted to the material owing to the high electrical conductivity of the web structure, the increased number of active sites derived from the open channel structure, and the high nitrogen content, specifically that of N-5 species. This facile synthesis using a waste resource may offer a new direction for the design of superior carbon-based anode materials for high-energy LIBs.

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1. Introduction

Lithium-ion batteries (LIBs) are recent common power sources and their stable cycling performance and safety of use make them suitable for portable energy storage devices that need to be continuously charged/discharged many times a day. However, the energy and power density of LIBs are insufficient for the large rechargeable batteries required for plug-in hybrid electric vehicles (PHEVs), pure electric vehicles (PEVs), and energy storage systems (ESSs). Graphite, which is currently the most common material used for anodes in LIBs, maintains a stable layer structure during intercalation by lithium ions, but suffers from a low theoretical capacity (372 mA h g^{-1}) and poor rate performance due to limited lithium-ion diffusivity within carbon layers. To overcome these weaknesses, many researchers have employed nanotechnology to

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develop carbon materials such as graphene nanosheets, aligned carbon nanotubes, carbon aerogels, and activated carbon as anodes for LIBs [1–3]. Nanostructured carbon material-based anodes exhibit electrochemical properties far superior to those of their parent material; however, nanotechnological processes are typically complex and cost ineffective due to the additional chemical treatments and harsh synthesis conditions required, and are thus unsuitable for mass production [4–7].

Electrospinning, which is a well-known, simple, and economical technique for the preparation of concatenated nanofibers on a large scale, is often used in the development of one-dimensional nanostructures consisting of ceramics, metals, carbon, or their composites. Recently, carbon nanofibers prepared using electrospinning and subsequent carbonization have been utilized as high-performance anodes for LIBs owing to the improved electron transfer capabilities imparted by their web-like structures [8–10]. In addition to the fundamental web structures possible, electrospinning can be coupled with pyrolysis to produce porous carbon nanofiber materials. In this process, bicomponent polymer nanofibers prepared with electrospinning are simply pyrolyzed, and no treatment with expensive and/or hazardous chemicals is necessary.

Pores in the carbon nanofibers act not only as reservoirs for the adsorption of lithium ions, but also provide an efficient pathway for their diffusion, leading to an improved number and distribution of active sites [11,12]. Thus, porous carbon nanofibers exhibit the excellent electrochemical properties required for LIB anode materials. For example, polyacrylonitrile (PAN)/poly(methyl methacrylate) (PMMA)-derived porous carbon nanofibers have been reported to exhibit a discharge capacity of 354 mA h g^{-1} after 100 cycles at a current density of 200 mA g^{-1} [13]. Also, both PAN/poly-L-lactic acid (PLLA)-derived porous carbon nanofibers and PAN/styrene acrylonitrile resin (SAN)-derived porous hollow carbon nanofibers have been reported to exhibit higher discharge capacities (435 mA h g^{-1} after 50 cycles and 474 mA h g^{-1} after 20 cycles, respectively, at a current density of 50 mA g^{-1}) than the theoretical capacity of graphite [14,15].

Doping the carbon matrix with heteroatoms such as nitrogen, sulfur, phosphorous, and boron is another way to improve the electrochemical properties of carbon-based anodes. Nitrogen doping is particularly attractive for LIBs because nitrogen has a smaller atomic radius and higher electronegativity than those of carbon [16]. Furthermore, nitrogen-doped carbon structures have extrinsic defects that enhance lithium intercalation, and surface nitrogen functionalities that provide many active sites for lithium-ion adsorption, both of which are favorable for lithium storage systems [17,18]. Recently, Bhattacharjya et al. [19] reported that nitrogen-doped carbon nanoparticles show not only a 17% higher discharge capacity than that of the corresponding undoped carbon nanoparticles at a low current density of 0.1 C, but also at the higher current density of 1 C, which is ca. two-times higher than that of commercial graphite. Thus, nitrogen doping is regarded as a promising method to overcome the weakness of carbon-based anodes for LIBs.

Poly(vinyl butyral) (PVB) is commonly used in laminated glass as an adhesive because of its high light transmittance and superior adhesion properties. Every year, ca. 65% of the PVB produced worldwide is consumed by safety glass production for automobiles, and a large amount of waste PVB (W-PVB) is generated from disused automobiles [20]. Unfortunately, most of the W-PVB from windshield glass is buried in landfill sites and not recycled because processes for separating PVB sheets from windshield glass are expensive, and it is difficult to remove impurities such as plasticizers and the high water content from W-PVB [21]. For these reasons, the development of high-value-added materialization technologies using W-PVB is necessary for environmental protection.

Herein, we synthesize nitrogen-doped carbon nanofibers with open channels (N-CNFO) from urea-containing PAN/W-PVB bicomponent nanofibers via simple electrospinning followed by two-step carbonization. W-PVB is vaporized during the carbonization, generating unique open-channel structures that have the appearance of deep scars on the surface of the nanofibers, while urea acts as a nitrogen source. N-CNFO synthesized by this facile and cost-effective method exhibit high performance as an anode for LIBs. The unique open channels and the nitrogen incorporated into the carbon matrix impart the material with a higher reversible capacity than the theoretical capacity of graphite at both low and high current densities, and excellent cycling stability.

2. Experimental

2.1. Synthesis of carbon nanofibers with open channels (CNFOs)

W-PVB was separated from windshield glass by shredding and hammer crushing, then washed with deionized water and dried at room temperature. To prepare spinnable PAN/W-PVB blend solutions, PAN and W-PVB were dissolved in N,N-dimethylformamide (DMF) at a concentration of 9.1 wt% under vigorous stirring. Blend solutions with different PAN/W-PVB weight ratios (100:0, 80:20, 50:50, and 30:70) were poured into 10 mL syringes and used for electrospinning over a potential range from 12 to 20 kV at an extrusion rate of 0.4 mL h^{-1} (at low potentials) and 1.2 mL h^{-1} (at high potentials). The distance between the target and the tip of the needle was 10 cm. After electrospinning, the bicomponent nanofibers collected on the grounded aluminum foil were transferred into an alumina crucible and heated to 280 °C for 2 h in air using a tube furnace for oxidative stabilization. The stabilized nanofibers were then placed into a tube furnace and carbonized by increasing the temperature to 500 °C at a heating rate of 50 °C min^{-1} for 2 h, and then further increasing the temperature to 800 °C at a heating rate of 10 °C min^{-1} for 2 h under nitrogen. Final products were named CNF, CNFO20, CNFO50, and CNFO70, corresponding to the materials prepared with W-PVB weight ratios of 0, 20, 50, and 70%, respectively.

2.2. Synthesis of nitrogen-doped carbon nanofibers with open channels (N-CNFOs)

Urea was dissolved in DMF under ultrasonic agitation for 20 min. Then, PAN and W-PVB were dissolved in the prepared urea solution with vigorous stirring. Solutions with different PAN/W-PVB/urea weight ratios (80:20:20, 80:20:30, and 80:20:40) were poured into 10 mL syringes and used for electrospinning at a voltage of 14 kV and an extrusion rate of 1.2 mL h^{-1}. After electrospinning, the PAN/W-PVB bicomponent nanofibers containing urea were exposed to the same conditions used for the heat treatment of the CNFOs for oxidative stabilization and carbonization. The final products were named N20-CNFO, N30-CNFO, and N40-CNFO, corresponding to the urea weight ratio used in their preparation, i.e., 20, 30, and 40%, respectively.

2.3. Materials characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Ultima III diffractometer with CuKα radiation (λ = 1.5406 Å). The morphologies of the samples were characterized using field emission scanning electron microscopy (FESEM, Hitachi, S-4300) and transmission electron microscopy (TEM, FEI Tecnai, G2-F30). Pyrolysis behaviors of PAN and W-PVB were observed by thermal gravimetric analysis (TGA, NETZSCH, STA 409 PC/PG). Specific surface areas were calculated by the