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Short communication

Solution blowing of continuous carbon nanofiber yarn and its electrochemical performance for supercapacitors

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HIGHLIGHTS

- A facile spinning-based process was reported as novel nanofiber yarn fabricating method.
- Aligned polyacrylonitrile precursor nanofiber yarn was prepared using the process.
- Carbon nanofiber yarn (CNFY) was prepared as one-dimensional supercapacitor electrode.
- The CNFY electrode possessed high conductivity, large specific capacitance and perfect cyclic performance.

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ABSTRACT

A facile spinning-based process was presented as a new method to fabricate continuous nanofiber yarn. In this process, a funnel-like nanofiber net with aligned structure was formed to collect nanofibers and the net was twisted and attenuated to the nanofiber yarn. The morphologies and structures of the prepared polyacrylonitrile (PAN) nanofiber yarn and PAN-based carbon nanofiber yarn (CNFY) were examined. The PAN and carbon nanofibers were well aligned, with average diameters of 231 and 136 nm, respectively. The electrochemical properties of CNFY were studied. The results showed that CNFY possessed high conductivity, mass specific capacitance (15.8 Fg^{-1} at the current density of 2 Ag^{-1}) and extremely excellent cycling performance at high current density (only 8.8% capacitance loss after 1200 cycles at a high rate of 2 Ag^{-1}), which imply the potential application of CNFY as a novel electrode for supercapacitors.

1. Introduction

Because of their high power density, long life cycle, and low environmental impact, supercapacitors have been considered as promising power sources for electronic systems and upcoming electric vehicles [1]. Carbon-based materials with various micro-textures, which include activated carbon, carbide-derived carbon, carbon nanotubes, carbon nanofibers, and grapheme [2–4], are widely used as electrodes because of their large specific surface area, high flexibility and good electrochemical stability. Carbon electrodes are commonly prepared through blending of carbon and binder, and they are used in planar sheet structures [5]. Carbon nanotubes and graphene were recently fabricated as yarn for supercapacitor electrode [6]. Their well-aligned structure, which has been proven effective in improving their performance, enables them to provide numerous channels for ion and current transport and thus decrease resistance and improve energy density [7]. Moreover, one dimensional (1D) electrodes have potential applications in microelectronics, functional clothing textile, and highly integrated equipment [8]. Comparing with carbon nanotube and graphene yarn whose fabrication is complicated, carbon nanofiber yarn (CNFY) can be easily spun from continuous carbon nanofibers. These carbon nanofibers can be easily obtained from precursor polymers with the spinning-based method [9,10] and can be directly used as self-standing carbon electrodes without using any binders as in the case of CNFY.

Solution blowing process has been recently reported as an innovative nanofiber spinning process. In this process, polymer solution streams are blown to nanofibers only using a high-speed gas flow. To date, several natural and synthetic polymers have been solution blown into nanofibers [11]. With its high solution feed rate, solution blowing is efficient in producing nanofiber nonwoven mats and is expected to be developed further as an important method for the mass production of nanofibers.

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The study introduced a modified solution blowing process to directly fabricate continuous nanofiber yarn. Polyacrylonitrile (PAN) was used as a precursor to obtain aligned CNFY, which was suggested as a novel binder-free, unidimensional electrode with high performance for supercapacitors. The forming process and the electrochemical properties of CNFY as a supercapacitor electrode were systematically investigated.

2. Experimental

2.1. Description of the setup and experimental procedure

The experimental setup used in this study is illustrated in Fig. 1, which is a modification of our previous setup [12]. The previous mesh-like collector was replaced with a new collecting system which included a rotary disk, a thread guide tube, and a bobbin. The bobbin and thread guide tube were particularly crossed fixed on a vertical shaft, which rotated in the same direction as the collector but at a different speed. Initially, one end of the guide yarn was tied to the bobbin, and the other end was inserted through the thread guide tube and was hung about 10 cm over the disk as a free end. The spinning procedure briefly described as follows: 12 wt.% PAN solution in DMF was supplied to the nozzle to spin nanofibers which were collected between the rotary disk and the free end of the guide yarn. Then, the guide yarn was pulled upward by the bobbin on which the twisted nanofibers were continuously wound as a yarn. The spinning conditions are listed in Table 1.

2.2. Heat treatment

The stabilization of the as-prepared PAN nanofiber yarn was performed in a tube quartz furnace (Zhonghuan Co, Ltd., Tianjin, China). The yarn was first heated up at a rate of 1 °C min^{-1} and kept at 240 °C in air during 1 h for the oxidative stabilization. Afterwards, the samples was further heated for carbonization under nitrogen atmosphere at a rate of 5 °C min^{-1} and finally maintained at 1000 °C for 1 h.

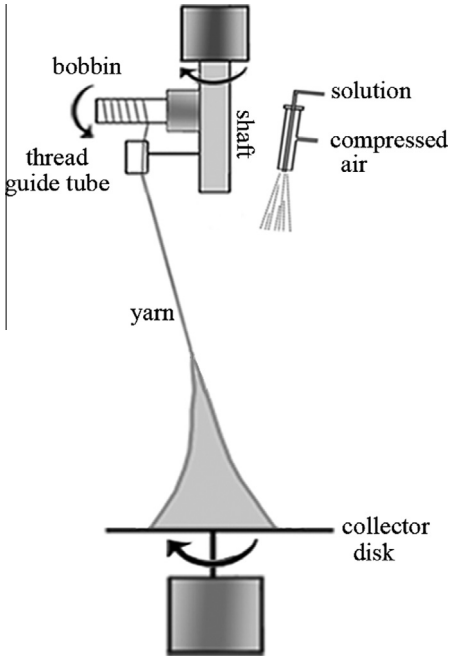

Fig. 1. Solution blowing process with a modified collecting system for nanofiber yarn fabrication.

Table 1
Spinning conditions for solution blowing.

Parameters	Value
Solution feeding rate	12 mL/h
Air pressure supplied to the annual nozzle	0.05 MPa
Capillary diameter	0.5 mm
Collector distance	50 cm
Bobbin line speed	7.8 cm/min
Collector disk rotary speed	25 rpm
Shaft rotary speed	100 rpm

2.3. Electrochemical tests

The electrochemical measurements were performed in a three electrode cell system with 6 M KOH aqueous solution as electrolyte. The working electrodes were fabricated by fixing and connecting one end of the CNFY to a nickel wire by silver paint [6]. Here the CNFY functioned as the working electrode without any other binder or current collector. Platinum foil and saturated calomel electrode (SCE) electrode were used as counter electrode and reference electrode, respectively. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were carried out on CHI760D electrochemical workstation (Chenhua Co, Ltd., Shanghai, China). The impedance behavior of the CNFY electrode was tested in a frequency range of 10 mHz–100 kHz with an alternating current (AC) potential amplitude of 5 mV.

3. Results and discussion

3.1. Fabrication of the aligned PAN precursor nanofiber yarn

In solution blowing process, the nanofibers are generated as the spinning solution stream is pushed into the high-speed air flow field, accompanied with the evaporation of the solvent [11,12]. For this specially designed setup, the fibers are collected on the rotary disk as a nonwoven mat and meanwhile, adhered to the free end of the guide yarn and formed fiber links between the guide yarn and the collector disk. Then, a 3D aligned net with a funnel shape was formed (Fig. 2a) and subsequently twisted and attenuated to the yarn because of the combination of the withdrawing force of the bobbin and the rotation of the disk and the shaft. As shown in Fig. 2b and c, the fibers were well aligned and uniform without microscopically identifiable beads and/or beaded nanofibers and the average fiber diameters were approximately 231 nm. The key point of the process was the formation of the stable funnel-like nanofiber net. After this net was formed, the nanofibers were deposited on the surface of the rotary nanofiber net, and continuously fabrication of the nanofiber yarn resulted.

This process is similar to conventional open-end spinning in the textile industry. In open-end spinning, fibers are collected on a small surface and pulled as a thin layer to constantly add to the open end of the forming yarn. The thin layer is attenuated and then twisted into the yarn [13]. In our modified solution blowing process, the nanofibers were deposited on the surface of the net and continuously wrapped into the yarn that was wound onto the bobbin. The process, which includes nanofiber formation, collection, twisting and winding, offers a new formation process of continuous nanofiber yarn.

3.2. The structure and electrochemical properties of CNFY

The PAN precursor yarn was converted to CNFY through the following stabilization and carbonization treatment. As shown in Fig. 2d, the morphologies of the carbonized PAN nanofibers were