



Centrifugally-spun carbon microfibers and porous carbon microfibers as anode materials for sodium-ion batteries



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HIGHLIGHTS

- Centrifugal spinning is performed to fabricate porous carbon microfibers.
- Porous carbon microfibers are evaluated as anode material in sodium-ion batteries.
- Specific capacity of porous carbon microfibers at the 200th cycle is 242 mAh g⁻¹.
- Porous carbon microfibers show stable cycling performance of 89% over 200 cycles.

ARTICLE INFO

Article history:

Received 18 May 2016

Received in revised form

11 July 2016

Accepted 19 July 2016

Keywords:

Sodium-ion battery

Centrifugal spinning

Porous carbon microfibers

Capacity retention

Coulombic efficiency

ABSTRACT

Natural abundance and low cost of sodium resources bring forward the sodium-ion batteries as a promising alternative to widely-used lithium-ion batteries. However, insufficient energy density and low cycling stability of current sodium-ion batteries hinder their practical use for next-generation smart power grid and stationary storage applications. Electrospun carbon microfibers have recently been introduced as a high-performance anode material for sodium-ion batteries. However, electrospinning is not feasible for mass production of carbon microfibers due to its complex processing condition, low production rate and high cost. Herein, we report centrifugal spinning, a high-rate and low-cost microfiber production method, as an alternative approach to electrospinning for carbon microfiber production and introduce centrifugally-spun carbon microfibers (CMFs) and porous carbon microfibers (PCMFs) as anode materials for sodium-ion batteries. Electrochemical performance results indicated that the highly porous nature of centrifugally-spun PCMFs led to increased Na⁺ storage capacity and improved cycling stability. The reversible capacity of centrifugally-spun PCMF anodes at the 200th cycle was 242 mAh g⁻¹, which was much higher than that of centrifugally-spun CMFs (143 mAh g⁻¹). The capacity retention and coulombic efficiency of the centrifugally-spun PCMF anodes were 89.0% and 99.9%, respectively, even at the 200th cycle.

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1. Introduction

Exploring clean and sustainable energy sources is very crucial for the human society because our world is facing ever-growing global warming and inevitable energy crisis. Since harvesting natural energy sources such as wind, solar and hydropower are mainly depend on environmental conditions, they must be efficiently stored during the energy sourcing pick time for use when needed

[1–3]. Rechargeable batteries store the energy efficiently without greenhouse gas emission and have been considered as one of the most promising technologies for renewable energy storage [4,5]. Because of their distinguished features, including high energy density, durable cycling stability and good power performance, rechargeable lithium-ion batteries have been counted as the most preferred battery technology for portable devices and electric vehicles [6,7]. However, ever growing cost of lithium due to limited reserves of lithium element in the earth crust hinders the use of lithium-ion batteries for large-scale applications, such as smart power grids and stationary energy storage [3,8]. Nowadays, ambient temperature sodium-ion batteries are regarded as one of

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the most promising alternatives to lithium-ion batteries for large-scale applications, due to the low cost and abundance of sodium resources [9,10]. However, insufficient energy density and poor cycling stability of current sodium-ion batteries prevent their practical implementation for advanced energy storage systems. The development of anode materials with enhanced capacity and cycling stability for sodium-ion batteries will be critically important for technological improvements on smart electric grids and stationary energy storage [11–13].

Discovering an appropriate anode material with adequate Na-insertion capacity and cycling capability is extremely crucial because the radius of Na ions (~1.09 Å) is much larger than that of Li ions (~0.74 Å), which makes intercalation and deintercalation processes of sodium-ion batteries quite distinctive than those of lithium-ion batteries [14,15]. Graphite is a good example to indicate the importance of this matter. As pointed out in many similar studies, although graphite is a widely-used anode material in current lithium-ion batteries, it can barely store sodium ions in its layer structure [16]. On the other hand, hard carbon has been reported as a convenient anode for Na insertion because of its disordered nature and wide interlayer distance [17]. Recently, transition metals (e.g., tin, antimony, and germanium) and their oxides, which intercalate Na ions based on conversion mechanism and exhibit much higher capacities than that of graphite, have been studied as potential anode materials for Na-ion batteries [18,19]. However, insertion of sodium ions into these anodes results in large volumetric change, which leads to severe pulverization and demolishing of electrical contact between the active material and carbon conductor [15,20]. These drawbacks bring together intense capacity loss during the sodium insertion and extraction processes. Currently, reducing the size of active materials into the nanoscale range is considered as one of the most efficient methods for eliminating the volume change problem [20,21].

Recently, micro- and nanostructured carbonaceous materials, such as nanospheres, nanotubes, and microfibers, have been widely examined as anode material for lithium-ion and sodium-ion batteries [22]. Among these micro- and nanostructured carbonaceous anodes, carbon microfibers (CMFs) and CMF-based composites have drawn great attention due to their high cyclability and rate capability features. Most CMFs and CMF-based composites introduced for lithium-ion and sodium-ion batteries have been synthesized through the electrospinning of polymer precursor fibers and subsequent carbonization processes [18,22,23]. Although the electrospinning method is versatile for altering fiber diameter and morphology, it is not considered an appropriate approach for mass production of CMFs because of its low production rate, high cost, complex processing condition and safety concern [24,25]. In recent years, centrifugal spinning has gained great attention as a low-cost and highly efficient alternative method for synthesizing microfibers for large-scale applications [26]. To this end, centrifugal spinning has been widely investigated to fabricate both polymeric and inorganic micro and nanofibers for different applications such as mechanical enforcement, tissue engineering, and energy storage [27–30]. Herein, we report the preparation of CMFs as an anode material for sodium-ion batteries by the centrifugal spinning of polyacrylonitrile (PAN) precursor, followed by carbonization. To increase the active sites for Na storage, porous carbon microfibers (PCMFs) were also fabricated by the centrifugal spinning and carbonization of a mixture of PAN and polymethyl methacrylate (PMMA) precursors. During the carbonization process, PAN was pyrolyzed to carbon while PMMA was thermally degraded to form nanoscale pores in the resultant carbon microfiber matrix. Electrochemical performance studies reveal that the high porosity of centrifugally-spun PCMFs resulted in increased Na⁺ storage capacity and improved cycling stability. At the 200th cycle, the

reversible capacity of centrifugally-spun PCMF anodes was 242 mAh g⁻¹, which was much higher than that of centrifugally-spun CMFs (143 mAh g⁻¹). The capacity retention and coulombic efficiency of the centrifugally-spun PCMF anodes were 89.0% and 99.9%, respectively, even at the 200th cycle. These results demonstrate that centrifugal spinning is a promising alternative to electrospinning in fabricating PCMF anode materials with increased Na⁺ storage capacity and improved cycling stability.

2. Experimental

2.1. Chemicals

Polyacrylonitrile (PAN, Pfaltz & Bauer Inc., 150,000 g mol⁻¹), polymethyl methacrylate (PMMA, Aldrich, 120,000 g mol⁻¹) and *N,N*-dimethylformamide (DMF, Aldrich) were used without further purification.

2.2. Centrifugal spinning of PAN and PAN/PMMA precursor fibers

PAN and PAN/PMMA precursor fibers were fabricated by centrifugal spinning of PAN and PAN/PMMA blend solutions, respectively. To this end, two different DMF solutions of 15 wt% PAN and 15 wt% PAN/PMMA blend (PAN-to-PMMA mass ratio = 1/1) were prepared and mechanically stirred for 24 h at 70 °C. PAN and PAN/PMMA precursor fibers were fabricated by using a lab-scale centrifugal spinning device. Fig. 1 shows the schematic illustration of the centrifugal spinning apparatus and the fabrication process of PAN and PAN/PMMA precursor fibers. The centrifugal spinning device used in this study was composed of a perforated Teflon spinneret placed in the center of the spinning apparatus, a motor connected to the spinneret to provide high-speed rotation, a speed controller to tune the rotational speed of the spinneret, and a series of fiber collector rods placed radially in the outer perimeter of the Teflon spinneret. The spinneret was in a cylindrical shape with 1.5 cm in radius and 2 cm in height, and it had two nozzles with inner diameter of 0.4 mm on the sidewall. The distance from the spinneret to rod collectors was 10 cm. For the fabrication of centrifugally-spun PAN and PAN/PMMA precursor fibers, PAN/DMF and PAN/PMMA/DMF solutions were loaded into the Teflon spinneret and the rotation was started. Spinning process of PAN/DMF and PAN/PMMA/DMF solutions was performed with a rotational speed of 4000 rpm at room temperature. Centrifugally-spun precursor fibers were collected on aluminum rods placed around the spinneret.

2.3. Synthesis of nonporous and porous carbon microfibers

CMFs and PCMFs were prepared by the thermal treatment of centrifugally-spun PAN and PAN/PMMA precursor fibers. During preparation, PAN and PAN/PMMA fibers were initially stabilized in air atmosphere at 280 °C for 5.5 h with a heating rate of 5 °C min⁻¹ and further carbonized at 700 °C for 2 h in argon environment with a heating rate of 2 °C min⁻¹, during which PAN was converted to carbon while PMMA was thermally decomposed to form nanoscale pores in the carbon matrix.

2.4. Structure characterization

The morphology of centrifugally-spun CMFs and PCMFs was investigated by field emission scanning electron microscope (FE-SEM, FEI Verios 460L) and scanning transmission electron microscope (STEM, JEOL 2000FX). The structure of microfibers was examined by Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 470) and wide angle X-ray diffraction (WAXD, Rigaku

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