



Cross-linked carbon network with hierarchical porous structure for high performance solid-state electrochemical capacitor



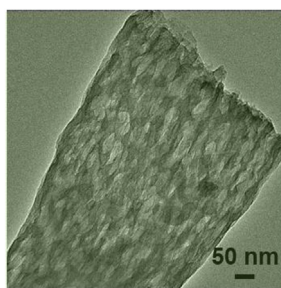
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HIGHLIGHTS

- Hierarchical porous cross-linked carbon nanofiber was prepared by electrospinning.
- The specific surface area of carbon nanofiber reaches 1144 m²/g without activation.
- Hierarchical porous structure can obviously decrease ionic diffusion resistance.
- Cross-linked structure can simultaneously improve in conductivity.
- Solid-state device exhibits excellent electrochemical performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 April 2016

Received in revised form

19 July 2016

Accepted 20 July 2016

Available online 29 July 2016

Keywords:

Hierarchical porous structure

Carbon nanofibers

Solid-state

Electrochemical capacitor

ABSTRACT

The development of portable electronics strongly requires flexible, lightweight, and inexpensive energy-storage devices with high power density, long cycling stability, and high reliability. In this work, we prepare a flexible solid-state electrochemical capacitor using cross-linked hierarchical porous carbon network as electrode material via electrospinning and carbonization process. This device can reversibly deliver a maximum energy density of 10.18 W h/kg with excellent cycling stability which achieves 95% capacitance retention after 20000 charge/discharge cycles. Moreover, it also demonstrates outstanding mechanical flexibility and excellent capacitance retention even when the device is repeatedly bended 10000 cycles under 90°. All of these results suggest its promising perspective in flexible energy storage device.

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1. Introduction

Electrical energy storage and conversion systems play a vital role in efficient and cost-effective utilization of clean energy from renewable sources [1]. Among these systems, electrochemical

capacitors (ECs) bridge the gap between batteries and electrolytic capacitors in terms of the “energy-to-power” relationship, delivering a burst of energy on the timescale from 10⁻¹–10² s [2], with outstanding cycling stability.

Porous carbonaceous materials are considered to be most promising candidate for the electrode materials of ECs because of their tunable pore size, high electronic conductivity, and large specific surface area, which may create accessible path for ionic/electronic transport and store charge by electrochemical double layer (EDLCs) effect on electrode surface [2,3]. Typically, the

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capacitance and rate capability of carbon-based ECs are believed to mainly depend on micropore features such as specific surface area, pore size, depth, and tortuosity, whereas meso- and macropores, being significantly larger than ions, are considered to facilitate ionic transport and act mostly as an electrolyte buffering reservoirs to supply electrolyte to micropores, respectively [4]. Accordingly, hierarchical porous structure with pore sizes ranging from micropore to macropore should be the suitable framework to optimize the performance of carbon electrode. However, the current strategy to build up this structure usually involves some special hard templates (silica or polystyrene sphere) [5–8], molecular [9], physical [10], or chemical activation process [11–14], which needs extra steps to template preparations and following removal of template or activation reagent, leading to excessive cost and limited perspective for large-scale production. Thus, developing a simple and efficient way to fabricate porous carbon materials with hierarchical porous structure is still a challenge.

On the other hand, the recent development of portable electronics including roll-up displays, hand-held devices, and wearable personal multi-media have been raising urgent needs for flexible and lightweight energy storage devices [15–18]. Researchers have been focusing on constructing high performance flexible solid-state ECs based on various carbon materials, including graphene [19], carbon nanotubes [20,21], and activation carbon fibers [7,22], etc., which strongly requires operational reliability and satisfactory mechanical property. In addition, the state-of-art solid-state ECs usually suffer from poor rate capability due to the lower conductivity of porous carbon nanofibers, metal catalysis graphitization, introduction graphene and carbon nanotube can improve the conductivity of carbon nanofibers [7,23,24], however, it should be noted that the contact between these nanofibers is insufficient physical contact, which exhibit large contact resistance, resulting in the decrease of conductivity of electrode [25]. To make it clearer, the conductivity of carbon monolith decreases one order of magnitude after being grinded into fine powder [26]. This is more obvious for solid-state ECs; the formation of gel layer on the surface of building blocks would further increase contact resistance and restrict electron transfer through the whole electrode to current collector [27]. The formation of cross-linked structure may be an effective way to reduce contact resistance between building blocks [28]. Therefore, cross-linked architectural with hierarchical porous structure hold great potential for high performance solid-state ECs.

In this paper, we present the fabrication of flexible cross-linked carbon nanofibers network with hierarchical porous structure (HPCNF) via one-step carbonization of electrospun polyacrylonitrile (PAN)/terephthalic acid (TPA) hybrid composite fibers. The mechanism of the formation of this hierarchical porous network can be attributed the sublimation of TPA during the pre-oxidation and carbonization and incomplete evaporation of solvent during electrospinning process. Using TPA as pore forming agent can not only obtained high specific surface area CNF with hierarchical porous structure, also need neither addition removal of template step nor activation process, which greatly simplify experiment process [7,13,14]. Moreover, the decrease in ionic diffusion resistance and simultaneous improvement in conductivity can be achieved. As a result, the as-prepared sample exhibited excellent rate capability with a specific capacitance of 165 F/g at a current density of 700 A/g. Significantly, the solid-state ECs based on HPCNF can deliver a maximum power density of 56 kW/kg and high energy density of 10.18 W h/kg, which is even higher than some carbon-based symmetrical ECs with aqueous electrolyte.

2. Experimental section

2.1. Synthesis of carbon nanofiber network

1.0 g TPA and 1.6 g PAN were added into 20.0 mL N, N-dimethylformamide (DMF) to form transparent solution after magnetic stirring for several hours. This solution was then ejected from the stainless steel capillary with a voltage of 25 kV under the feeding rate of 5.0 mL/h. The distance between the capillary and collector was 18 cm. The resulting precursor fiber was collected as a thin web on a rotating aluminum drum with the rotation speed of 360 rpm. After being pre-oxidation at 260 °C in air for 2 h and carbonized at 800 °C for 1 h in Ar atmosphere, hierarchical porous cross-linked carbon nanofibers (HPCNF) with a carbonization yield about 24% can be obtained. Non-hierarchical porous cross-linked carbon nanofibers (NHPCNF) can be obtained under the same condition as synthesis HPCNF except addition of TPA.

2.2. Preparation of flexible solid-state electrochemical capacitor

A PVA/H₃PO₄ gel electrolyte was prepared as follow: 4 g of H₃PO₄ and 4 g of PVA were added into 40 mL of deionized water under stirring and heated to 85 °C until the solution became clear. The as-prepared CNF with a size about 1 cm*2 cm (2 mg) was pressed on the gold-coated polyethylene terephthalate (PET) substrate, then the PVA/H₃PO₄ solution was slowly poured on to carbon nanofibers film. Subsequently, two electrodes were assembled together with a separator (NKK TF4050, 50 μm) sandwiched in between. After the PVA/H₃PO₄ gel solidifying at room temperature, the solid-state electrochemical capacitor was obtained.

2.3. Characterization

The morphology of precursor fibers and carbon nanofibers was analyzed by field emission scanning electron microscope (FESEM, FEI Nova 450 Nano) and transmission electron microscope (TEM, Tecnai G20). The crystal structure of carbon nanofibers was characterized by X-ray diffraction using the Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) (XRD, PhilipsX' PertPro). Specific surface area and pore structure of the fibers were measured by N₂ adsorption-desorption isotherm at 77 K on a Quantachrome autosorb iQ gas-sorption apparatus. The pore size distribution was calculated according to the Barrett-Joyner-Halenda (BJH) method. Raman spectra measurement was performed on a Renishaw-inVia Raman spectrometer using the 514.5 nm line of an Ar⁺ laser. The measurements of CV and galvanostatic charge/discharge were carried out using VMP-300 (Biologic, France). For the typical three electrode measurement, a piece of carbon nanofibers webs with mass about 0.5 mg (1.0 mg/cm²) was used as working electrode, Hg/HgSO₄, YP-50 (Kuraray Chemical, Japan), and Celgard (Celgard, USA) was used as reference electrode, counter electrode, and the separator, respectively. All the electrochemical tests were conducted in Swagelok cells (Swagelok, USA) at temperature about 20 °C. Electrochemical impedance was measured from 10 mHz to 200 KHz with a AC potential with amplitude of 10 mV.

The energy density and power density of device can be estimated using the following equations:

$$C_m = (I\Delta t)/(M\Delta V) \quad (1)$$

$$E = 0.5C_m(\Delta V)^2 \quad (2)$$

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