



Full Length Article

High capacitive performance of hollow activated carbon fibers derived from willow catkins



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ARTICLE INFO

Article history:

Received 11 August 2016

Received in revised form 23 October 2016

Accepted 24 October 2016

Available online 25 October 2016

Keywords:

Supercapacitor

Willow catkins

Potassium hydroxide activation

Hollow activated carbon fibers

ABSTRACT

In this paper, we prepared three different kinds of hollow activated carbon fibers (HACFs) from willow catkins (WCs), phenolic- and pitch-based hollow fibers, respectively. The morphology, pore structure, surface chemical composition and electrochemical properties of these hollow fibers were studied in parallel. Due to its high-hollow, cost-effective as well as eco-friendly nature, HACFs derived from WCs can be served as excellent electrode materials for electrochemical energy storage devices. Electrochemical measurements illustrate that the WCs derived HACFs exhibit not only high specific capacitance of 333 F g^{-1} at 0.1 A g^{-1} but also considerable rate capability with a retention of 62.7% (209 F g^{-1} at 10 A g^{-1}). Symmetric supercapacitor devices that using WCs derived HACFs as electrodes deliver a maximum energy density of $\sim 8.8 \text{ Wh kg}^{-1}$ at power density of 50 W kg^{-1} and good cycling performance with 95.5% retention over 3000 cycles at 5 A g^{-1} in 6 M KOH aqueous electrolytes.

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1. Introduction

Climate change and energy consumption of non-renewable fossil fuels have greatly affected the development of economy and circulation of ecological environment. With the increasing need for portable electronic devices and the development of hybrid electric vehicles, environmentally-friendly and powerful energy resources are highly demanded. Electrochemical capacitors (ECs) or supercapacitors have attracted increasing attention in energy storage due to the high power density, rapid charge/discharge capability and long cycle life, etc. [1–3]. Based on the energy storage mechanism, supercapacitors can be divided into two categories: electrochemical double layer capacitance (EDLC) involving physical adsorption of ions from electrolyte and pseudocapacitance involving reversible faradaic redox reactions [4,5]. Currently, most commercial supercapacitors are EDLCs ascribed to their relatively low cost and prominent durability [6–8]. Carbon-based materials including activated carbons and carbon nanomaterials (CNTs, Graphenes) are most widely used as electrodes because of the superior physical and chemical properties, such as low cost, diverse

forms (powders, fibers, tubes, sheets, monoliths, aerogels, composites, etc.) [9–17], ease of processability, controllable porosity, and rich electrochemical active sites. Besides, in terms of both power delivery rate and energy storage capacity, proper control over the specific surface area and pore size suitable to appropriate type of electrolyte solution are vital to ensure a good performance of EDLCs.

In general, commercial activated carbons are the most widely used electrode materials in supercapacitor application. However, most of them are particles and may have different pore structures such as microporous, mesoporous or hierarchical porous that means the coexist of micropores ($< 2 \text{ nm}$), mesopores ($2\text{--}50 \text{ nm}$) and macropores ($> 50 \text{ nm}$), which is ascribed to different preparation processes and different raw materials used. Generally speaking, the mesoporous and hierarchical porous activated carbons offer relatively low specific capacitance ($< 200 \text{ F g}^{-1}$) in aqueous electrolytes due to their relatively broad pore size distribution but low micropores content. It is well known that the energy storage occurs primarily in micropores [18,19]. Carbon materials in the form of fiber may be more effective to produce activated carbon with more micropores which will lead to shortened transport distance for ions from the electrolyte to micropores [20,21]. Hollow micro-/nano-structures are of great interest as a unique family of functional materials with well-defined interior voids and functional shells [22,23]. Their unique structural virtue such as large

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surface area, high pore volume, and low density endows them with the potential application in many aspects, including catalysis, gas sensors, energy conversion, and storage systems [24–27]. Therefore, there has been an increasing demand for simple and controllable synthesis of hollow nanostructured materials [28,29]. In particular, one-dimensional (1D) hollow tubular structures have been considered as promising hollow structures. e.g. the hollow macro-chamber can ensure ion transportation at high rates and plays the important role of ion reservoir. Lou [22] et al. prepared series of binary-metal sulfides with hollow tubular structures that exhibited excellent electrochemical properties. Therefore, it is also become very attractive to prepare activated carbon fibers with hollow tubular structures, which combines the advantages of activated carbon fibers and peculiar 1D hollow tubular structure.

Besides, when considering the potential scale of supercapacitor applications. Biomass is a cost-effective carbon precursor because it's an environmentally friendly and renewable resource with abundant availability [30–32]. The microstructure and chemical compositions of carbon precursor from biomass have great effect on the morphology, pore structure and surface chemical functional groups of the final porous carbonaceous materials. The cotton-based carbon fibers (CCFs) with hollow tubular structure prepared by carbonizing the cotton fibers in ammonia inherit the natural hollow structure of the cotton fibers. The CCFs have high specific surface area up to $778.6 \text{ m}^2 \text{ g}^{-1}$ and high nitrogen content (3.3 at.%). The maximum specific capacitance of the CCFs are 355 F g^{-1} at 1 A g^{-1} , 245.3 F g^{-1} at 0.8 A g^{-1} and 181.3 F g^{-1} at 0.2 A g^{-1} in KOH, H_2SO_4 and Na_2SO_4 electrolytes, respectively [33]. Du [20] et al. prepared activated carbon hollow fibers from cheap and renewable ramie fibers by ZnCl_2 activation. The activation temperature and activation time both have significant effect on the surface area, micropore volume and conductivity, further influence the electrochemical properties. A maximum capacity of 287 F g^{-1} at 50 mA g^{-1} was obtained under suitable conditions. Jin [21] et al. prepared activated carbon fibers from wood-derived fibers by melt-spinning process of mixture of waste wood shavings, phenol and phosphoric acid, curing and followed by a simple one-step process of carbonization and water vapor activation. The sample with optimal structure exhibits a high specific capacitance of 280 F g^{-1} at 0.5 A g^{-1} as well as excellent rate capability in $1 \text{ M H}_2\text{SO}_4$ and high capacitance retention of 99.3% over 2000 charge-discharge cycles.

In our previous reports, we prepared three-dimensional network like structured porous activated carbon by using willow catkins as raw materials and one-step KOH chemical activation process without pre-carbonization, the as-prepared activated carbon exhibited good electrochemical properties [34]. However, the original hollow fiber-like structure of willow catkins were destroyed seriously due to the KOH etching strongly, as a result, the obtained samples became power-like morphologies. So, how to maintain the original hollow fiber-like structure of willow catkins in the final samples appears to be very important. Herein, we report novel hollow activated carbon fibers from biomass willow catkins by a two-step process of pyrolysis and KOH activation. For contrast, the other two artificial HACFs were also fabricated by melt-spinning of high-molecular polymer phenolic resin and pitch, followed by pre-carbonization and KOH activation under the same process parameters. The morphology, pore structure, surface chemical composition and electrochemical properties of the samples were studied. The as-prepared willow catkins derived HACFs show unique high-hollow tubular structure, high microporous specific surface area ($1067 \text{ m}^2 \text{ g}^{-1}$), concentrated pore size distribution ($0.7 \sim 1.2 \text{ nm}$), abundant surface heteroatom-doped functional groups (2.39 wt.% N and 16.41 wt.% O species) and thus display excellent electrochemical performances in KOH aqueous electrolyte.

2. Experiments

2.1. Preparation of WCs derived HACFs

The preparation process of WCs derived HACFs was shown in Fig. 1. The WCs were cleaned with acetone and deionized water to remove the surface adherent impurities and dried at 80°C . The dried WCs were pyrolyzed at 500°C for 2 h under nitrogen flow with a heating rate of 5°C min^{-1} in horizontal tubular furnace to obtain hollow carbon fibers. Then, the hollow carbon fibers were mixed with KOH with the mass ratio of 1:1 and the mixture was treated at 700°C for 2 h under nitrogen flow with a heating rate of 5°C min^{-1} . After being cooled down to room temperature, the mixture was washed with 1 M HCl and deionized water alternately until the filtrate reached to neutral. The final samples were obtained after drying in vacuum at 80°C overnight and labeled as willow-HACFs.

2.2. Preparation of phenolic-based HACFs

The thermoplastic phenolic resin was used as raw material to prepare hollow phenolic fibers by melt spinning techniques with hollow spinneret at 150°C . Then, the obtained hollow phenolic fibers were cured in hexamethylenetetramine solution for 10 min, and pre-carbonized at 500°C for 2 h under nitrogen flow with a heating rate of 5°C min^{-1} in horizontal tubular furnace. Then, the phenolic derived hollow carbon fibers were mixed with KOH at mass ratio of 1:1 and pyrolyzed at 700°C for 2 h under nitrogen atmospheres at heating rate of 5°C min^{-1} . The ultimate samples were named as phenolic-HACFs.

2.3. Preparation of pitch-based HACFs

Similar to the preparation of phenolic-based HACFs, the pitch-based HACFs were fabricated by melt spinning techniques with isotropic pitch as raw material and the spinning temperature is 355°C followed by pre-oxidization at 300°C for 3 h and pyrolyzation at 500°C for 2 h. Then, the pitch-based hollow carbon fibers were mixed with KOH at mass ratio of 1:1 and heat-treated at 700°C for 2 h under nitrogen atmospheres at heating rate of 5°C min^{-1} . The final pitch derived hollow activated carbon fibers were denoted as pitch-HACFs.

2.4. Sample characterization

The microstructures and morphologies of the three kinds of HACFs were performed with field emission scanning electron microscopy (FE-SEM) on a JEOL JSM-7001F microscopy at an accelerating voltage of 10 kV. Nitrogen sorption isotherms and physical properties were examined by ASAP 2020 physisorption apparatus at 77K. The samples were degassed at 250°C for 5 h prior to the measurement. The surface area was calculated by Brunauer-Emmett-Teller (BET) method based on the nitrogen adsorption data in the P/P_0 range corresponding to linear region. The pore size distribution (PSD) was obtained by non-local density functional theory (NLDFT) method with an assumption of slit pore model [35]. X-ray photoelectron spectra (XPS) was measured on a Kratos AXIS Ultra DLD spectrometer with Al target, $\text{K}\alpha$ radiation, from a double anode X-ray source.

2.5. Electrochemical measurements

Both three-electrode and Two-electrode configurations were adopted to evaluate the capacitive properties of the as-prepared HACFs on a CHI 660C electrochemical workstation (Shanghai Chenhua Instruments Co., China). In three-electrode system, the

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