Effects of activation temperatures on the surface structures and supercapacitive performances of porous carbon fibers

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ABSTRACT

Activated carbon fibers (ACFs) with uniform sub-nanometer pores (mainly < 1 nm) are obtained using a simple KOH chemical activation approach at lower temperature. The effects of activated temperature, especially lower temperature, on the morphology, structures, surface chemical states, pore structures, and supercapacitive performances of the ACFs are systematically investigated. The ACFs activated at 550 °C as the electrode material of supercapacitors exhibit superior specific capacitance (427 F g^{-1} at 0.1 A g^{-1}), good rate performance (294 F g^{-1} at 10 A g^{-1} and 248 F g^{-1} at 20 A g^{-1}), and excellent cycle stability (91.9% capacitance retention after 1000 cycles) in 6 M KOH aqueous solution. The outstanding charge storage capabilities are due to the suitable and larger specific surface area, high proportion of micropores and proper pore size. In addition, appropriate oxygen-containing functional groups also play important roles. Therefore, the high capacitance of activated carbon fibers is a synergy of pseudocapacitance and double-layer capacitance.

1. Introduction

Activated carbon fibers (ACFs), as the generation of activated carbon after the powdered activated carbons (ACs) and granular ACs [1, 2], offer a wide range of applications in catalysis, electrode, purification and separation [3, 4], owing to their fibrous shape, large surface area and porosity. ACFs align pores along the external surface towards the interior and show narrow distribution. Compared to powdered or granular activated carbons, the unique fibrous sharp of ACFs present a lower diffusion resistance to bulk flows and higher adsorption-desorption kinetics [5].

ACFs are commonly synthesized by chemical and physical methods. Compared to the physical approach, chemical activation has significant advantages, such as higher specific surface area, well-controlled porosity and lower activation temperature [6]. Chemical activation with KOH is an effective method to prepare ACFs with extensive porosity, large specific surface area as well as high yield [6, 7]. Activation temperature plays critical roles in the structure of final activated carbon fibers. During the activation process, the main products are H₂, H₂O, CO, CO₂, potassium oxide (K₂O) and potassium carbonate (K₂CO₃) [8]. With the increasing of activation temperature, the activation reactions intensify and the produced K₂CO₃ will further decompose to form CO₂.

As heat treatment reaches 760 °C (the boiling point of potassium), the metallic potassium formed by the reduction of potassium compound would be efficiently intercalated onto the carbon hexagonal structure of graphite [9]. In addition, oxygen-containing surface groups could be introduced via the reaction with KOH, which may generate the faradic reaction resulting in pseudocapacitance [10].

In previous studies, most of researchers are used to choosing higher activation temperatures (700–900 °C), when using KOH as an activating agent. Yang et al. have carbonized bamboo after surface activation using KOH for energy storage applications [11]. The highest specific capacitance (258 F g^{-1} at a current density of 0.1 A g^{-1} in 6 M KOH electrolyte) can be obtained by KOH activation at 800 °C. Xie et al. have used KOH activated packaging polystyrene foam waste for high energy density supercapacitor [12]. The activated carbon with KOH heat-treated at 700 °C exhibited high specific capacitance of 339 F g^{-1} at current density of 0.05 A g^{-1}. Huang et al. have researched ACFs with different pore structure have been prepared from wood sawdust using the KOH activation method [13]. The sample activated at 850 °C exhibited the highest single electrode gravimetric (225 F g^{-1} at a current density of 0.5 A g^{-1}). Its ability to retain capacitance corresponding to 10 A g^{-1} and 6 M KOH was 85.3%. Guo et al. used hierarchical porous carbon from sulfonated pitch and studied the effect of the KOH

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activation on the porosity and the specific surface area [14]. These porous carbons, which obtained by surface activation of the carbonized pitch with KOH heat-treated at 800 °C, have the highest specific capacitance of 263 F g^{-1} at 0.05 A g^{-1}.

In this work, mesophase pitch-based carbon fibers were used as the raw materials. By chemical activation with KOH, activated carbon fibers with uniform sub-nanometer pores (mainly < 1 nm) can be obtained. We focus on investigating the effects of activation temperatures (450–850 °C) on the pore structure, surface chemical property and electrochemical performances of ACFs, especially lower activation temperatures.

2. Experimental

2.1. Raw materials

A commercial naphthalene-derived mesophase pitch, provided by Mitsubishi Gas Chemical Corporation, was directly used as a raw material to produce the pitch fibers by melt spinning. This type of mesophase pitch is 100% anisotropic and has a softening point of 265 °C High orientation of lamelliform molecules within the mesophase fibers is easy to achieve, which is beneficial for producing carbon fibers with higher conductivity by post-treatment [15, 16]. Molten mesophase pitch was extruded through a spinneret with 255 holes of 300 mm diameter under pressurized nitrogen of 0.2 MPa at a spinning temperature of 320 °C. The extrudates were then drawn through a winding drum at rotational speed of 100 m min^{-1} controlled by a servo motor to form round-shaped pitch fibers. The as-spun pitch fibers were stabilized at 240 °C for 20 h in a flowing oxygen atmosphere. The stabilized fibers have a slightly higher carbonization yield of about 84%. Finally, the stabilized fibers were treated at 450 °C to obtain the raw carbon fibers.

2.2. Preparation of ACFs

The as-prepared mesophase pitch-based carbon fibers (CFs) were used as raw materials and subsequently activated to produce ACFs using KOH as an activating agent with KOH/carbon fiber ratios of 4/1. The activation temperatures varied from 450 °C to 850 °C. Typically, the pitch-based fibers carbonized at 450 °C were firstly cut into lengths of 3 cm to facilitate the following treatment. 1 g of pitch-based CFs was added into 40 mL of 10% KOH, followed by sonicated for 1 h. The fully immersed carbon fibers were dried at 100 °C for 12 h. Then the mixtures were heated at target temperature for 1 h with a heating rate of 3 °C min^{-1} under nitrogen flow (400 mL min^{-1}) in a vertical furnace. After activation, the samples were washed repeatedly with 10% HCl solution and deionized water until pH value of the supernatant reached 7. The purified samples were dried in an oven at 100 °C overnight. Then the weight of the dried sample was measured in order to calculate the activation yield. The obtained activated carbon fibers were denoted as ACFs-T, where T represented the corresponding activation temperature.

2.3. Characterizations

Morphologies of the ACFs were characterized by TESCAN VEGE 3 SBH-Easy Probe scanning electron microscope (SEM). High-resolution transmission electron microscopy (HR-TEM) of the ACFs was tested by JEM-2100. The Philips X Pert MPD Pro diffractometer was used to study X-ray diffraction (XRD) patterns with CuKα radiation (λ = 0.154056 nm) operated at 30 mA and 40 kV, using step sans to obtain XRD patterns with a step size of 8 °C min^{-1} in the 2θ range from 10° to 90°. Raman spectra were measured using Confocal Raman Microspectroscopy (RenishawRM-1000) equipped with Ar$^+$ laser excitation (λ = 532 nm) to examine the graphitic structure of the ACFs.

Fourier transform infrared (FTIR) spectrometry was carried out in a Shimadzu IR-Prestige-21 spectrometer using KBr pellet technique over the wavenumber ranges from 400 to 4000 cm^{-1}. X-ray photoelectron

spectroscopy (XPS) analysis was obtained from a Thermo Fisher K-Alpha 1063 with a monochromatized Al Kα X-ray source.

The pore structure of the ACFs was characterized by the physical adsorption of nitrogen at 77 K on ASAP 2020 system (Micromeritics). Before analysis, the samples would be degassed for 8 h at 350 °C in vacuum. On the basis of the nitrogen adsorption results, the specific surface area (SSA) and the pore size (D) were calculated by applying Brunauer-Emmet-Teller (BET) equation and Density Function Theory (DFT) method. The t-plot equation was used to calculate micropore volume (V_{micro}) [13]. Total pore volume (V_t) was calculated based on the nitrogen adsorption volume at the maximum relative pressure.

2.4. Electrochemical measurements

The supercapacitor tests were performed by a symmetrical two-electrode system. The electrode slurry was prepared by mixing and grinding ACFs, carbon black and polytetrafluoroethylene (PTFE, 60 wt % suspension in water) at a mass ratio of 80:10:10 in an agate mortar. The resultant slurry was rolled into thin film (ca. 6 μm in thickness) and coated onto the nickel foam to punch into 12 mm diameter electrodes, subsequently pressed at 10 MPa for 10 s and dried at 60 °C for 12 h under vacuum. Before the electrochemical test, the electrodes were soaked overnight in 6 M KOH aqueous electrolyte under vacuum. The symmetrical two-electrode coin-cell was assembled with two similar mass carbon electrodes, separated by polypropylene membrane in 6 M KOH aqueous electrolyte. All electrochemical measurements were carried out at 24 ± 1 °C.

The galvanostatic charge/discharge tests were conducted on Neware battery test system in a potential range of 0–1 V, and a current density of 0.1 A g^{-1}, 0.2 A g^{-1}, 0.5 A g^{-1}, 1 A g^{-1}. The specific capacity was calculated based on the capacitance per unit mass excluding conductive material and binder (F g^{-1}).

The gravimetric capacitance of the electrode (C, F g^{-1}) was evaluated from the discharge curve according to Eq. (1) [17]:

$$C = \frac{2I\Delta t}{\Delta V} \tag{1}$$

where C is the specific capacity of the two-electrode supercapacitor (F g^{-1}), and I is the discharge current density (A g^{-1}) which was normalized by the mass of a single electrode, ΔV is the discharge voltage between the Δt period.

The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) at higher current densities (2 A g^{-1}, 5 A g^{-1}, 10 A g^{-1}, 20 A g^{-1}) were collected using CHI660D electrochemical workstation. All the ACFs electrodes were investigated in a 6 M KOH solution.

3. Results and discussion

3.1. Morphology and structure of ACFs

Fig. 1 presents the SEM images of the original CFs and ACFs activated at different temperatures to investigate the effects of KOH activation on the surface morphology of carbon fibers. The original CFs (Fig. 1a) manifest round and smooth surface. Fig. 1(b–f) show the SEM images of ACFs activated with KOH at different temperatures. All the ACFs samples keep the complete fiber morphology and show obvious and abundant etched texture, generated by KOH etching and further decomposition of volatile substances in the raw materials [18]. Fig. 2 shows the TEM images of the ACFs-550 and ACFs-750. It can be observed that the carbon layer orientation is disorder, indicating the ACFs-550 and ACFs-750 is mainly amorphous carbon structures.

XRD patterns of the KOH-activated ACFs are depicted in Fig. 3a. There are an observable broad peak at 2θ ≈ 23° and a very weak peak at 2θ ≈ 43° for all prepared samples, ascribed to the crystal planes diffraction of (002) and (100) of carbon, irrespectively. The lower position of the corresponding peaks as well as their broader full width at