



# Preparation of activated carbon hollow fibers from ramie at low temperature for electric double-layer capacitor applications



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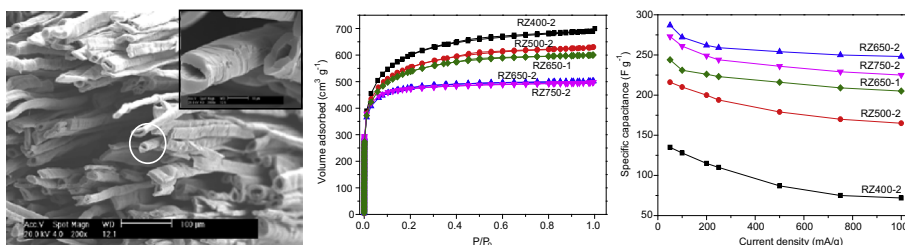
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## HIGHLIGHTS

- Ramie was used to prepare activated carbon hollow fibers (ACHFs) for the first time.
- The precursor fibers were activated by simple single-stage ZnCl<sub>2</sub> activation.
- Surface area, pore structure and conductivity are keys to electrochemical properties.
- The ACHFs showed a specific capacitance of 287 F g<sup>-1</sup> and good cycling performance.
- The ramie-based ACHFs have good prospect in large-scale EDLC application.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Activated carbon hollow fibers (ACHFs) with high surface area were prepared from inexpensive, renewable ramie fibers (RFs) by a single-step activation method under lower temperature than that of other reports. The effects of activation conditions on the pore structure and turbostratic structure of ACHFs were investigated systematically. The results show that ACHFs surface area decreased but micropore volume and conductivity increased as the increase of activation temperature and activation time. The electrochemical measurements of supercapacitors fabricated from these ACHFs electrodes reveal that the electrochemical properties improved with the enhancing of activation degree. However, too high activation temperature can make the ion diffusion resistance increase. It suggests that pore structure and conductivity are as important as surface area to decide the electrochemical performances of ACHFs electrode materials. A maximum capacity of 287 F g<sup>-1</sup> at 50 mA g<sup>-1</sup> was obtained for the ACHFs electrode prepared under suitable conditions.

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## 1. Introduction

It is well known that porous carbon materials offer a wide range of applications in separation/purification of liquids and gases, gas storage, and catalytic processing owing to their large surface area

and porosity. In recent years, investigations on the porous structures and electrochemical behaviors of porous carbons have been ignited by their using as electrode materials for electric double layer capacitors (EDLCs) or supercapacitors in worldwide. So far, for carbon materials used in EDLCs, various type porous carbons have been reported in the literatures, such as granular/powdery carbon (Liang et al., 2009), spherical carbon (Li et al., 2007), fibrous carbon (Zhai et al., 2011) and so on. Compared with other shapes

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activated carbons (ACs), activated carbon fibers (ACFs) have a number of advantages over them, which make them attract increasing interest. For example, the principal merit of ACFs is their micropores open directly to the exterior (Momma et al., 1996; Yue et al., 2002). While, for other shapes of ACs, their porosity decreases from macro to meso and to microporosity along the external surface towards the interior. Hence, the adsorption rate, as well as the adsorption capacity of ACFs, will be much higher than those of other shapes ACs. In addition, other advantages of ACFs, including light weight, high-strength, fatigue endurance and thermal resistance, also promoted ACFs to be a widely studied strategic material (Macia-Agullo et al., 2007; Wang and Inagaki, 1999). In the studies of ACFs, some researchers found a kind of carbon fibers with the hollow structure (Jiang et al., 2007; Wang et al., 1998; Yang and Yu, 1996). Because of this unique shape, activated carbon hollow fibers (ACHFs) possess larger surface area and higher adsorption and desorption rate comparing to solid carbon fibers, which is more preferable for commercial application.

Up to now, the precursors used to produce ACHFs mainly include polyacrylonitrile (Hu et al., 2009), pitch (Choi et al., 2001), and phenol–resin (Suzuki, 1994), which usually are extracted from coal or petroleum, all belonging to nonrenewable resources. And more, the production process of ACHFs based on these precursors must undergo a stabilization step under 200–400 °C for several hours before carbonization and activation at higher temperature. Now, natural biomaterials based ACs have been become researching focus due to these precursors using for electrode materials of EDLCs are abundant, renewable, cheap and environmental friendly (Balathanjigaimani et al., 2008; Elmouwahidi et al., 2012; Farma et al., 2013; Guo et al., 2003; Ismanto et al., 2010; Kim et al., 2006; Li et al., 2011; Nabais et al., 2011; Rufford et al., 2008; Subramanian et al., 2007; Wang et al., 2011). For example, Rufford et al. (2008) used waste coffee beans as raw material to produce ACs with a specific capacitance as high as 368 F g<sup>-1</sup>. The good electrochemical performance of the carbon materials was attributed to a well developed porosity and the presence of electrochemically active quinone oxygen groups and nitrogen functional groups. Elmouwahidi et al. (2012) prepared ACs for supercapacitor electrodes by KOH-activation of argan seed shells and the obtained highest capacitance was 355 F g<sup>-1</sup> in 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> within a three-electrode cell. The good electrochemical performance of the carbon was attributed to the large surface area, appropriate and well-developed micro-mesopore texture, and N content. Kim et al. (2006) prepared activated carbons from bamboo by chemical activation. The results illustrated that the carbon with higher mesopore fraction showed higher capacitance in organic electrolyte and desirable rate capability in aqueous electrolyte. Subramanian et al. (2007) prepared ACs from banana fibers using chemical activation with ZnCl<sub>2</sub> and KOH. The resulted ACs displayed good electrochemical properties in neutral electrolyte. They thought different activating agents can affect the structure of obtained ACs and further influence the double-layer formation and the associated capacitance of EDLCs. However, as far as we know, most of these reported ACs need to be fabricated at high carbonization and activation temperature (800–1000 °C) and only resulted in granular or powdery shape ACs.

As one of the strongest natural fibers, ramie has a tensile strength eight times higher than that of cotton and seven times greater than that of silk (Sen and Jagannatha Reddy, 2011). Ramie fiber (RF) is a unique absorbent owing to its inner hollow structure. Moreover, it is even known especially for its ability to hold shape and reduce shrinking. More recently, some investigations have reported that the cellulose of natural materials could coordinate with zinc ions and then were degraded under low activation temperature with the catalysis of zinc ions (Guo et al., 2003; Kalderis

et al., 2008; Khelfa et al., 2008; Lv et al., 2012; Qian et al., 2007; Rufford et al., 2010; Yue et al., 2002; Zhang et al., 2010).

Herein, ramie fibers-based ACFs retaining the original hollow shape of precursor were prepared by a single-step activation method at low temperatures. The effects of the activation temperature and activation time on pore development, crystallite structure and subsequently electrochemical performance are discussed intensively.

## 2. Experimental

### 2.1. Preparation of activated carbon hollow fibers (ACHFs)

RFs obtained from Tianhao Chemical Co., Ltd., Hangzhou were previously cut into about 5 mm long and dried in the oven for 6 h at 100 °C. Then the dried fibers were impregnated in 20% wt. zinc chloride solution and dehydrated in an oven at 80 °C for 2 h. The ZnCl<sub>2</sub> impregnated RFs were placed in a stainless steel boat and pyrolyzed in a horizontal tubular furnace under the nitrogen flow. The temperature was ramped from ambient temperature to final temperature (400–750 °C) at a heating rate of 5 °C min<sup>-1</sup> with retention time of 1 h and 2 h. The activated samples were washed in 1 mol L<sup>-1</sup> HCl, rinsed in distilled water to neutral, filtered and then dried to obtain the ACHFs. Then these samples were labeled to as RZ followed by the pyrolysis temperature and holding time; for example, RZ400-2 represented pyrolysis temperature of 400 °C and activation for 2 h. Similarly, the sample treated at 650 °C for 1 h was denoted as RZ650-1.

Thermal gravimetric analysis (TGA) coupled with derivative thermogravimetry analysis (DTG) was conducted with Rigaku Plus TG8120 analyzer in order to determine the pyrolysis behaviors of RF and ZnCl<sub>2</sub>-impregnated RF. The samples (5–8 mg) were heated from room temperature to 800 °C at a heating rate of 10 °C min<sup>-1</sup> in flowing nitrogen. The surface morphologies of ACHFs were characterized by field Philips XL30 scanning electron microscopy (SEM). X-ray diffraction (XRD) was carried out on a Rigaku D/max 2500v/PC system with CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Fourier transform infrared spectra (FTIR) of RF and ACHFs samples were recorded from an Nicolet Magna-IR 560 FTIR spectrophotometer using the KBr disk method. Thirty-two scans were taken of each sample recorded from the range 4000–400 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup> in the transmission mode. The N<sub>2</sub> adsorption–desorption isotherms of ACHFs were measured at 77 K using ASAP2020 (Micromeritics, USA) in order to determine the specific surface areas and pore structure parameters. Prior to measurement, samples were outgassed overnight at 300 °C in a vacuum oven. The BET equation was used to calculate the specific surface areas and the pore size distribution was calculated based on the density functional theory (DFT).

### 2.2. Electrochemical measurements

The sheet-type electrode was prepared by mixing ACHFs (85 wt.%), acetylene black (10 wt.%) and PTFE (5 wt.%), kneading and then rolling to nickel grid that serves as a current collector. Then the electrodes were dried in a vacuum oven at 100 °C for 12 h to remove the solvent totally. A couple of the sample electrodes were separated by a glass paper fiber wetted with the 6 mol L<sup>-1</sup> KOH solution. The three layers were then pressed in a coin-type cell (LIR 2430). Electrochemical measurements of the sample electrode were determined by two-electrode system without reference electrode using the test cell. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on CHI 604A electrochemical analyzer (Shanghai, China) controlled by a computer. Cyclic voltammograms were re-

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