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Flute type micropores activated carbon from cotton stalk for high performance supercapacitors

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HIGHLIGHTS

- FTMAC material has been successfully obtained from cotton stalk.
- FTMAC material exhibits on ordered flute type pores structure.
- The FTMAC-based electrode could deliver a high specific capacitance of 254 F g^{-1}.
- Symmetric supercapacitor can deliver a high energy density of 18.14 Wh kg^{-1}.

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ABSTRACT

Flute type micropores activated carbon (FTMAC) has been successfully obtained from cotton stalk via KOH-chemical activation method. The synthesized carbon material exhibits an ordered pore structure with high specific surface area of 1964.46 m^2 g^{-1} and pore volume of 1.03 m^3 g^{-1}. The assembled FTMAC-based electrode delivers a high specific capacitance of 254 F g^{-1} at a current density of 0.2 A g^{-1} in 1 M H_2SO_4 aqueous electrolyte. It still can maintain 221 F g^{-1}at a current density of 10 A g^{-1}, demonstrating a good rate capacity (87% retention), as well as long cyclic stability of 96% capacitance retention after 10000 charging and discharging cycles at current density of 1 A g^{-1}. Moreover, the symmetric supercapacitor can deliver a high energy density of 18.14 W h kg^{-1} and a power density of 450.37 W kg^{-1} which is operated in the voltage range of 0–1.8 V.

1. Introduction

Mobile electrical device and vehicle have attracted more attention in energy storage and conversion [1,2], due to the scarcity of fossil fuels and its environmental issues. Supercapacitors are known as the most promising energy storage systems due to their fast charge and discharge time, long life cycle and higher specific power density than the most widely commercial application lithium ion batteries [3–5]. At the same time, the disadvantages of supercapacitors including much lower energy density and higher production cost than lithium ion batteries [6,7], which need to be addressed. Thus, a number of studies have been actuated to exploring new advanced electrode materials for supercapacitors [8].

Carbon-based supercapacitor storage mechanism has fast physical absorption and desorption [9]. Therefore, the development of porous carbon materials can effectively overcome the obstacle of low energy density of supercapacitor [8,10]. Carbon materials, ranging from activated carbon [11], carbon nanotubes [12], carbon aerogel [13], graphene [14–17], carbon foam [18] and biomass-derived porous carbons [9,19–21], have been reported for

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electrode materials. Biomass-derived activated carbon has been regarded as a promising electrode material for supercapacitors due to their sustainable development characteristics, low cost, high specific surface area and good conductivity [22]. In general, KOH activation can generate micropores and small mesopores of various carbon frameworks [23]. The mechanism of KOH activation carbon materials is as the following equation (1):

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \quad (1)$$

The Xinjiang Production and Construction Corps is an agricultural province in China, and its cotton annual production is up to 1.5 million tons [11]. Cotton stalk as a waste byproduct has become a big issue. Generally, cotton stalk is dumped or burned in the field which resulting with ash and hazardous gaseous that pollutes the environment. However, cotton stalk contains a lot of cellulose, hemicelluloses and lignin. In this work, we demonstrate a green route to fabricated flute type micropores activated carbon by the chemical activation method for supercapacitors electrode from cotton stalk as raw material. Meanwhile, the ordered pore structure on the carbon particle surface prepared by using KOH as activating agent can improve its apparently surface area of activated carbon. This unique structure can be beneficial to enhance the electrochemistry performance of supercapacitors.

2. Experimental

2.1. Materials

The cotton straw used in this work was from local cotton fields. All chemicals in the present work were analytical reagent grades and were used as received without further purifications.

2.2. Pretreatment of cotton stalk

Firstly, the cotton stalk was sheared into small pieces and subsequently washed with distilled water and then dried at 100 °C overnight. Cotton stalk was crushed and screened with a 200 mesh. This material was first treated with an alkaline hydrolysis, according to the reported method [24]. The lignin and hemicelluloses was removed. The cotton stalk was kept at 80 °C in 4% mass fraction of sodium hydroxide solution and acetic acid for 4 h, respectively. Then, the cotton stalk was immersed into sodium chlorite solution again for one week until the color of sample became white [13]. The obtained white samples were washed thoroughly with deionized water until almost neutral (pH 6.5) and finally dried at 50 °C overnight.

2.3. Preparation of flute typed micropore activated carbon

The obtained white samples (16.55 g) were then carbonized in a tube furnace under a N_2 flow and with a heating rate of 5 °C min^{-1} at 800 °C for 1 h. Then, samples were cooled down to room temperature at the rate of 5 °C min^{-1}. The carbonized samples (3.12 g) were washed several times with deionized water and dried at 50 °C for 12 h. The obtained carbon samples (0.5 g) were mixed with solid KOH under various weight ratios and the mixture sample was heated to 800 °C for 2 h under a continuous N_2 flow. The obtained samples were washed thoroughly with deionized water and 10 wt% HCl solution under vigorous stirring for 24 h to remove the residual chemicals thoroughly. Then the samples were further washed thoroughly with a lot of deionized water and dried at 50 °C for 12 h. These samples are referred to as FTMAC-2 (0.24 g), FTMAC-3 (0.25 g), FTMAC-4 (0.17 g), FTMAC-5 (0.21 g) and FTMAC-6 (0.15 g) (2–6 are KOH and carbonized cotton stalk weight ratios).

2.4. Characterization

The morphology and microstructure of the flute typed activated carbon was observed by a Scanning Electron Microscope (JSM 6490-LV from JEOL), and a High Resolution Transmission Electron Microscopy (HRTEM) from a FEI Tecnai G20. The Raman spectroscopy of porous carbon was carried out using a Laser confocal MicroSpectroscopy (LabRAM HR800) with the 512 nm line of a He-Ne laser as excitation source. The X-ray diffraction spectra (XRD) measurements were measured using a Bruker D8 advance X-ray diffractometer with Cu Kα radiation source ($\lambda = 1.5406$ Å) in the scanning angle range of 10–90° at scanning rate of 10° min^{-1} at 40 mA and 40 kV. The BET surface area analysis was conducted by obtaining nitrogen adsorption isotherm with Micromeritics ASAP 2020 instrument at 77 K.

2.5. Electrochemical measurements

The electrode thin sheets were prepared by porous carbon materials (80 wt%), acetylene black (10 wt%) and polytetrafluoroethylene (PTFE, 10 wt%) binder. Then the mixture was homogenized in a mortar, adding a few drops of absolute alcohol and the resultant paste was rolled into uniform thin sheets electrode of 8 mm diameter using tablet press and dried at 110 °C for 4 h. The mass loading of the active materials in each electrode was around 1.6 mg. Symmetrical supercapacitor was made of two quality similar electrodes on the hydrophilic carbon paper and separated by a piece of polypropylene membrane in a stainless steel plate. 1 M H_2SO_4 was used as the electrolyte. Electrochemical performance measurements were carried out in a two-electrode system by a cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) on a CHI 604E electrochemical workstation. The charge-discharge performance of supercapacitors was studied on a CHI 760E electrochemical workstation. CV test of the two-electrode cell and three-electrode test were investigated between 0.8 V and 0 V. Saturated calomel electrode (SCE) reference electrode and Pt counter electrode were used in the three-electrode testing systems. EIS measurements were performed by an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz at the open circuit potential. The tests of cycle life were performed on a land cell taster (Land, CT-2001A).

According to the charge/discharge curves, the specific capacitance of electrodes can be calculated based on the following equation:

$$C_m = \frac{I_d \times \Delta t}{\Delta V \times m} \quad (2)$$

Where C_m (F g^{-1}) is specific capacitance, I_d (mA) is the discharge current, Δt (s) is the discharge time and ΔV (V) is the discharge voltage range, m (mg) is the mass loading of active materials based on both electrodes.

Energy density E (Wh kg^{-1}) and power density P (W kg^{-1}) were calculated according to the following equations:

$$E = \frac{1}{2} C_m \times \Delta V^2 \times \frac{1}{3.6} \quad (3)$$

$$P = \frac{E}{\Delta t} \times 3600 \quad (4)$$

Where as C_m (F g^{-1}) is specific capacitance based on mass loading of active materials in both electrodes, ΔV (V) is the discharge voltage range that is exclusive of the IR drop, Δt (s) is the discharge time.