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Biochar-based carbons with hierarchical micro-meso-macro porosity for high rate and long cycle life supercapacitors

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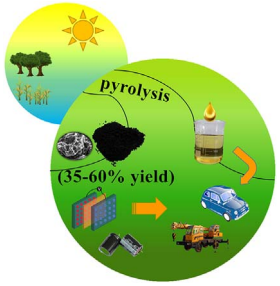
HIGHLIGHTS

- The corn straw biochar is used as precursor for preparation of porous carbon.
- The biochar-based carbons possess typical hierarchical porosity.
- The BBC-4 carbon exhibits high rate performance and outstanding cyclic stability.
- BBC-4 carbon could steady work at 1.6 V in Na_2SO_4 electrolyte over 3000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of supercapacitors with high energy density and power density is an important research topic despite many challenging issues exist. In this work, porous carbon material was prepared from corn straw biochar and used as the active electrode material for electric double-layer capacitors (EDLCs). During the KOH activation process, the ratio of KOH/biochar significantly affects the microstructure of the resultant carbon, which further influences the capacitive performance. The optimized carbon material possesses typical hierarchical porosity composed of multi-leveled pores with high surface area and pore volume up to 2790.4 $m^2 g^{-1}$ and 2.04 $cm^3 g^{-1}$, respectively. Such hierarchical micro-meso-macro porosity significantly improved the rate performance of the biochar-based carbons. The achieved maximum specific capacitance was 327 F g^{-1} and maintained a high value of 205 F g^{-1} at a ultrahigh current density of 100 A g^{-1}. Meanwhile, the prepared EDLCs present excellent cycle stability in alkaline electrolytes for 120 000 cycles at 5 A g^{-1}. Moreover, the biochar-based carbon could work at a high voltage of 1.6 V in neutral Na_2SO_4, and exhibit a high specific capacitance of 227 F g^{-1}, thus giving an outstanding energy density of 20.2 Wh kg^{-1}.

1. Introduction

The development of new and efficient energy storage devices is a critical component of utilization of sustainable energy. Supercapacitors [1], lithium ion batteries [2] and some other rechargeable batteries [3,4] are considered to be promising energy storage devices. In particular, the supercapacitors have got lots of attentions due to their exceptional power density, ultra-long cycle life, good convertibility and extensive storage applications prospects [5–7]. According to the work mechanism, supercapacitor could be divided into pseudo-capacitors

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and electrochemical double layer capacitors (EDLCs). Pseudo-capacitive materials, such as transition metal oxides, conductive polymer and their composites, store energies by reversible redox reaction of the electroactive species, and could give very high specific capacitance. However, these electrode materials generally possess poor cycle performance, low conductivity and high price. Moreover, the pseudo-capacitive materials are always used to asymmetric supercapacitors matching with a carbon electrode materials. The above facts limit the practical application of these materials. Differently, EDLCs store energies by the electrostatic charge uptake at the electrolyte/electrode interfacial regions, and exhibit superior long-term cycle performance.

However, the much low energy densities (approximately 5 Wh kg^{-1}) of commercial EDLCs have hindered their wide applications [8,9]. In order to improve performance and expand application fields, researchers are exploring new electrode materials for supercapacitors. Porous carbons have recently aroused great passion due to their large surface area, stable chemical properties, high conductivity, cheap, availability and structure adjustable [10].

Generally, the performance of carbon materials in EDLCs is highly dependent on the migration and adsorption of ions inside nanopores, which are largely determined by the pore structure of the material. Porous structure could be designed and developed by many methods, such as physical [11] or chemical activation [12], polymer blend carbonization [13], soft template [14] and hard template [15] associated with carbonization or activation [16]. Chemical activation is an effective and low-cost way to develop porous structure, which operate at lower temperature and in shorter activation time. KOH [17–20], NaOH [21], H_3PO_4 [22] and $ZnCl_2$ [23] are generally selected as activation agents for chemical activation.

In recent years, waste biomass, such as abandoned coffee beans [24], starch [25], apricot shell waste [26], sugarcane bagasse [27–29], rice husk [30], peanut shell [31], wood [32], potato starch [33] and rubber wood sawdust [34], as precursors in the preparation of carbon materials for EDLCs have gained much attention due to their huge reserves and economical [35]. Generally, residual biomass accounts for 10% of the global energy storage [36]. According to full estimate, the potential of annual biomass is predicted to be as high as 1.08×10^{11} toe (tons of oil equivalent), which is almost 10 times of the world's current energy requirement [37,38]. The large-scale utilization of biomass resources can largely ease the fossil crisis, which has become the major driver of the biomass energy research. We can stored this energy by biomass pyrolysis to produce biomass fuels which can be readily transported and effectively utilized. The product of biomass pyrolysis were biodiesel, biochar, and gas [39,40]. The biochar is the main solid product which has a large yield about 35–60 wt% [36,41]. The applications of biochar contain adsorbent, soil fertilizer and agricultural by-product/waste recycling [42]. Considering the broad scale of supercapacitor utilizations, developing carbon electrode materials from renewable biochar is of high application prospects [43].

In this work, the corn straw biochar are used to be prepared porous carbon materials for high performance supercapacitors. As shown in Fig. 1, the biochar are prepared by a flash pyrolysis of corn straw which is one of most common straws in north China. After a KOH activation process, biochar-based porous carbons (BBCs) are prepared. These carbons are proved to possess typical hierarchial porosity composed of multi-leveled pores. The prepared BBCs samples are applied as electrodes materials of supercapacitor, and show excellent capacitive performance in aqueous electrolytes (6 M KOH, 1 M H_2SO_4 and 1 M Na_2SO_4 electrolyte): a very high specific capacitance up to 327 F g^{-1}, outstanding rate performance with a high specific capacitance of 205 F g^{-1} at 100 A g^{-1}, high work voltage up to 1.6 V and ultrahigh energy density of 20.2 Wh kg^{-1} in neutral electrolyte, and impressive long-term stability up to 120 000 cycles.

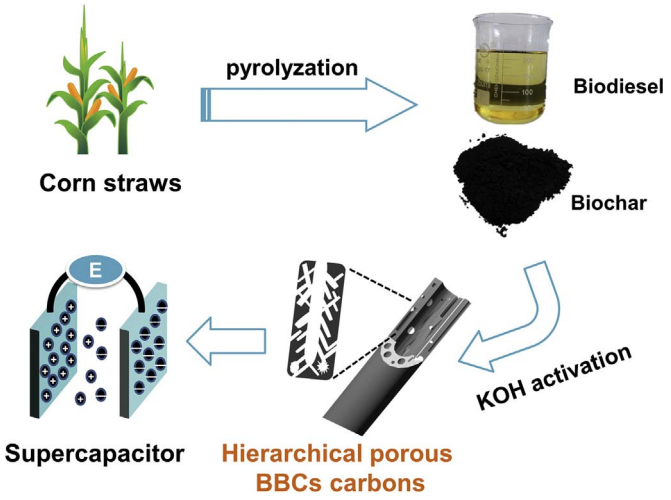

Fig. 1. Illustration for biochar-based porous carbon materials.

2. Experimental section

2.1. Material preparation

Corn straws are gathered from farmland of north China and thoroughly washed to remove impurities. All the chemical reagent, including KOH, Na_2SO_4, H_2SO_4 and polytetrafluoroethylene (PTFE) emulsion etc. are analytical pure and are purchased from Sinopharm Chemical Reagent Co., Ltd. The pyrolysis reactor was a home-made fluidized bed, which can heat corn straw in an inert atmosphere. The biochar were obtained as a solid residue in a yield about 40% via a flash pyrolysis of corn straws on a home-made fluidized bed at a temperature of 450 °C. Biodiesel was collected in a beaker and the separated biochar was the raw material in this study [44].

The biochar-based carbons were prepared from corn straw biochar via a KOH activation method. The typical procedure of biochar-based carbons is that: 100–200 mesh of biochar powder are firstly mixed with different proportion of KOH and small amount of H_2O. The use of H_2O is to dissolve the KOH and obtain an even mixture of KOH with the biochar. The obtained mixture was placed in carbonization furnace tube, heated to 800 °C at a heating rate of 5 °C min^{-1} under N_2 flow, and further maintained for 1 h. After cooling down to the room temperature, the black solid residue were repeatedly washed by 1 M HF, 1 M HCl and distilled water to be neutral. For convenience, the prepared carbon samples are named as BBC-x, in which BBC and x stand for biochar-based carbon and the weight ratio of KOH/biochar (1, 2, 3 and 4), respectively.

2.2. Material characterization

Micro morphology of the BBC-x were observed by scanning electron microscope (SEM, Sirion 200 FEI, Netherlands) and transmission electron microscope (TEM, JEM2100, JEOL, Japan). Element composition and their atom binding states were characterized by energy dispersive spectroscopy (EDS, INCA Energy spectrometer, Netherlands) and a X-ray photoelectron spectroscopy (XPS, Escalab 250, USA). X-ray diffraction (XRD) patterns of the carbon materials were conducted on a Brucker D8 Advance diffractometer with Cu Kα radiation. Raman spectra were collected by a LabRAM HR800 from JY Horiba. The electronic conductivity was measured by a ST-2722 Semiconductor resistivity tester (Lattice Electronics Co. Ltd., Suzhou, China). And the data of electronic conductivity was calculated from the average of three measurements. The porosity of the prepared carbon materials was analyzed by an ASAP 2020 nitrogen sorption system (Micrometitics, USA). The carbon materials were degassed at 350 °C for 4 h before