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Preparation of porous carbons by hydrothermal carbonization and KOH activation of lignite and their performance for electric double layer capacitor

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ABSTRACT

A series of porous carbons (PCs) were obtained from Shengli lignite (SL) via hydrothermal carbonization (HTC) pre-treatment and followed by chemical activation with KOH. The effects of preparation parameters including HTC temperature, KOH-hydrochar ratio and activation temperature on pore structure and the electrochemical performances of PCs were investigated in details. The PCs are mainly micropores structure according to the N_2 adsorption-desorption isotherms test and the highest specific surface area (SSA) is up to 3162 $m^2 g^{-1}$. The SSA and total pore volume of PCs with HTC pre-treatment are larger than that without HTC treatment. The electrochemical performances of the symmetric electric double layer capacitor (EDLC) fabricated from these PC electrodes were tested by galvanostatic charge-discharge, cyclic voltammetry and electrochemical impedance spectroscopy. All the PCs as electrode for EDLC exhibit ideal capacitive behaviors in 6 M KOH electrolyte. The specific capacitance of 200-HTC-800-3 can reach as high as 295 $F g^{-1}$ at the current density of 40 $mA g^{-1}$ and still retained 210 $F g^{-1}$ at the current density of 10 $A g^{-1}$. It also shows excellent electrochemical cycle performance that after 15000 cycles the specific capacitance value almost not decay. The processes used to produce the PCs can reduce the energy consumption compared to the traditional carbonization-activation method.

1. Introduction

As a highlight energy storage device, supercapacitors have attracted much attention due to their high power densities, fast charge-discharge rates, long cycling life and excellent stability [1–4]. Supercapacitors have a wide range of applications, such as hybrid electrical vehicles, communication devices, portable devices and electronic devices [5,6]. According to the storage mechanism, the supercapacitors can be classified into two categories, electric double layer capacitor (EDLC) and pseudocapacitor [7]. EDLC shows that the double layer is formed at the electrode/electrolyte interface to storage energy, while pseudocapacitor exhibits the reversible redox reaction in the electrodes [8,9].

The electrochemical performances of EDLC are affected by the surface property and specific surface area (SSA). Porous materials with high SSA and appropriate porosity distribution are beneficial to the improvement of electrochemical performances. Porous materials with excellent electrical conductivity and porous structure are widely used for EDLC, such as porous carbons (PCs) [10–12], carbon nanotubes (CNTs) [13,14], graphene sheets [15,16], carbon aerogels [17] and carbon nanofibers [18]. Among that, PCs are always one of the most investigated electrode materials because of the large SSA, moderate cost and good electrical properties. The PC electrode materials were mainly prepared from biomass wastes, coal, pitch, petroleum and their derived products through chemical activation or physical activation. While in a variety of raw materials, coal is still main material for PCs due to its easy availability, low cost and high carbon contain.

Hydrothermal carbonization (HTC) is an alternative thermochemical synthesis method to produce functional carbon materials with high concentrations of oxygenated functional groups [19–21]. The hydrochar rich in oxygenated functional groups makes it suitable for a lot of applications, such as adsorption [22], drug delivery [23], catalyst supporter [24,25] and PCs synthesis [26,27]. Furthermore, the presence of oxygen groups in the precursor improves the activity of activating agent and thus causes the

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increase in the porosity of the activated carbon [27,28]. Hydrothermal treatment is environmentally friendly as the reactions are carried out in the enclosed system conditions.

Recently, several researchers synthesized the PCs and carbon spheres through hydrothermal treatment with biomass [29–31]. It is well-known that low-rank coal, such as lignite, have high moisture, low calorific value and high volatiles, which are not suitable for coking raw materials. Lignite are frequently carbonized and upgraded by HTC treatment [32,33]. However, the PCs derived from the lignite with HTC treatment and applied in EDLC are rarely reported.

In this study, lignite were used as the raw material to prepare PCs by two-step method. Firstly, lignite were HTC pre-treated in Teflon-lined autoclave and then the hydrochar was activated with KOH. The PCs were characterized by the pore size analyzer, X-ray diffractometer (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectrometer (FTIR). The PCs were used as electrode material to investigate the electrochemical properties of EDLC in 6 M KOH aqueous electrolyte by galvanostatic charge-discharge (GCD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Materials

Shengli lignite (SL) from Xilin Gole of Inner Mongolia, China were used as the raw material in this study. The proximate and ultimate analyses of SL were listed in Table 1. Analytical grade KOH was provided by Xilong Chemical Co. Ltd.

2.2. Preparation of PCs

The PCs were prepared through two-stage process involving HTC and chemical activation with KOH. 5.0 g of SL and 40 mL deionized water were added to a 100 mL Teflon-lined autoclave and heated at a prescribed temperatures of 160, 180, 200 and 220 °C for 8 h. After the autoclave was cooled down to room temperature, the resulted product was filtered and washed by deionized water several times followed by desiccation at 100 °C for 24 h. The obtained hydrothermal produce was denoted as T-hydrochar, where T represents for the HTC temperature. The hydrochar was then mixed with KOH and activated in a horizontal tube furnace with a heating rate of 10 °C min^{-1} up to the final temperature (600, 700, 800 and 900 °C) and held for 90 min under Ar atmosphere. After cooling down, the activated sample was washed with 2 M HCl and subsequently washed several times with hot deionized water and finally with cooling deionized water until neutral. Then the sample was dried at 150 °C in vacuum for 3 h. The obtained PC was named as T-HTC-X-Y, where T represents the HTC temperature, X represents the finial heating temperature and Y represents the mass ratio of KOH and hydrochar. AC-800-3 was that the SL was directly activated with KOH at the temperature 800 °C and the KOH/SL ratio of 3. The yield of PCs was estimated by Eq. (1).

$$Y = \frac{M_1}{M_2} \times 100\% \qquad (1)$$

Where M_1 is the weight of PCs, M_2 is the weight of SL.

2.3. Characterization

SEM images were obtained using a Merlin Zeiss to observe the morphology of the samples. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer with Cu Kα radiation. The surface functional groups were analyzed by a Nicolet Magna 560 FTIR spectrometer. Raman analysis were carried out on a Bruker Senterra Raman Spectroscopy with 532 nm laser excitation. N_2 adsorption-desorption isotherms were measured at −196 °C with a Gold APP V-Sorb 4800TP instrument. The SSA was obtained by applying the Brunauer-Emmett-Teller (BET) method. Micropore surface area and micropore volume were calculated by using the t-plot method. Total pore volume was determined at a relative pressure P/P_0 of 0.99. The pore size distribution was calculated from N_2 sorption data using Density Functional Theory (DFT) model method. Thermogravimetric (TG) analysis of SL and 200-hydrochar were measured by a Mettler-Toledo TGA/DSC1 analyzer. Transmission electron microscope (TEM) images were carried out with an FEI Tecnai G2 F20 microscope. X-ray photoelectron spectroscopy (XPS) data were collected in Thermo ESCALAB 250Xi apparatus.

Table 1
Proximate and ultimate analyses of SL.

Proximate analysis (wt%)				Ultimate analysis (wt%, daf)				$S_{t,d}$	H/C
M_{ar}	A_d	VM_d	FC_d^b	C	H	N	O^b		
12.8	18.7	43.6	37.7	67.5	4.9	1.3	25.8	0.5	0.9

A: ash; M: moisture; FC: fixed carbon; VM: volatile matter; ar: as received basis; d: dried basis; $S_{t,d}$: total sulfur in dried basis; ^{b} Calculated by difference.

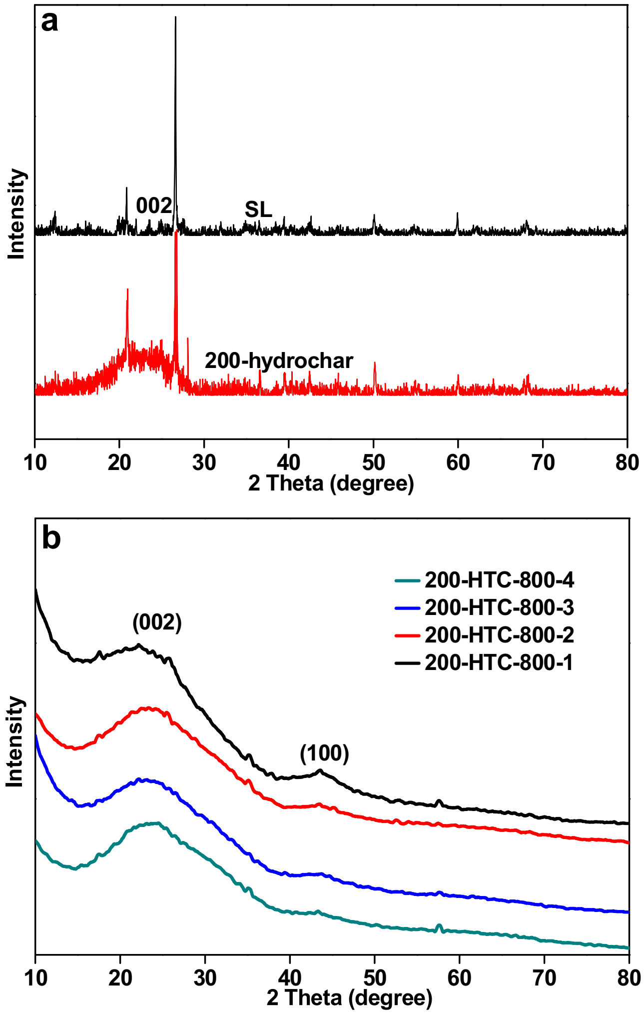

Fig. 1. XRD patterns of SL and 200-hydrochar (a) and PCs from different KOH-hydrochar ratios (b).