High rate performance porous carbon prepared from coal for supercapacitors

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ABSTRACT

Porous carbon with high specific surface areas up to 1851 $m^2 g^{-1}$ was prepared from coal by chemical activation. The specific capacitance of the porous carbon reaches 258 F g^{-1} at a current density of 1 A g^{-1} with about 81% capacitance retention at a current density of 30 A g^{-1}. The porous carbon exhibits good cycling durability with 92% specific capacitance retained at a current density of 2 A g^{-1} after 1000 cycles.

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1. Introduction

Porous carbon materials have been extensively studied for supercapacitor applications because of their large surface area, high conductivity and good chemical stability. Specific surface area and pore structure are two main factors in improving the capacitance of the carbon-based supercapacitors. Hence, tailoring the textural properties of porous carbon materials is of great importance in improving the electrode performance [1–3]. $ZnCl_2$ is commonly used as an activation agent for carbon materials. However, the surface area of carbon materials activated by $ZnCl_2$ is relatively low [4]. KOH activation efficiently develops high surface area and large amount of micropores [5]. In order to enhance the surface area and the amount of micropores, two-step activation using $ZnCl_2$ and KOH as activators can be adopted to prepare porous carbon with better pore structure.

Coal is the most affordable energy resource currently being consumed worldwide. Coal-based porous carbon has been widely used as supercapacitor electrodes. In this study, Coal based porous carbon was prepared by a two-step activation using $ZnCl_2$ and KOH as activation agents. The target of the activation process is aimed at enhancing surface area and micropore content of the activated carbon, thus providing a promising platform for supercapacitor electrode.

2. Experimental

Xinjiang anthracite with 29 wt% of ash content was used in this study. The anthracite was ground and sieved to a particle size of less than 75 μm. $ZnCl_2$ and anthracite (mass ratio 1:1) were thoroughly mixed, and then the mixture was placed in a tube furnace and heated from room temperature to 500 °C under nitrogen gas flow with a ramp rate of 6 °C min^{-1}. The mixture was maintained at the final temperature for 1 h before cooling down to room temperature under nitrogen atmosphere. The activated product was washed repeatedly with HCl (3 mol L^{-1}) and distilled water until the pH value of filtrate reached 7. The final product was dried at 60 °C for 12 h and the precursor was marked as AC. After that, the AC and KOH (mass ratio 1:1) were thoroughly mixed and prepared by the same activation process and the activation temperature was 800 °C. Finally, the obtained sample was marked as AC-K. For comparison, other two AC-K samples were prepared when the mass ratio of KOH to AC was 0.5:1 and 2:1 respectively. Extensive experimental details and the electrochemical measurements of the additional samples are provided within the supporting information.

Supercapacitor electrode was prepared by using porous carbon (85 wt%) as activated material, acetylene black (10 wt%) as conducting agent and polytetrafluoroethylene (5 wt%) as binder. They were mixed in ethanol to form slurry and coated on a nickel foam current collector.

Morphology of the sample was characterized by a high resolution transmission electron microscopy (JEOL 2100F). Pore structure of the sample was evaluated by the N_2 adsorption isotherms at 77 K with ASAP 2020 analyzer. Raman measurement was employed by Raman microscope (Bruker Senterra R200-L). The electrochemical performance of the sample was carried out in a 6 mol L^{-1} KOH electrolyte using a three-electrode configuration on CHI 660D electrochemical workstation in the potential range of -1.2 to -0.2 V.

3. Results and discussion

Fig. 1(a)–(c) shows the TEM images of the sample. All of the samples show a turbostratic structure and the carbon layers became
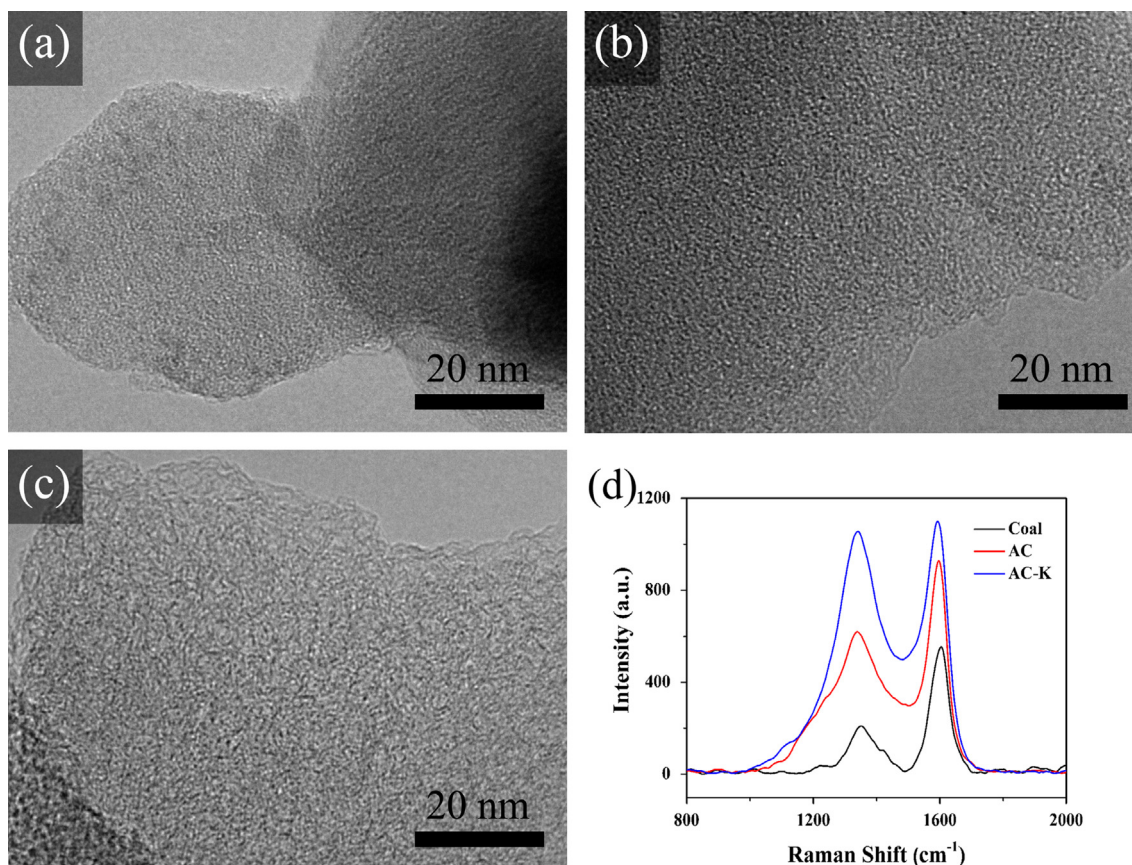
Fig. 1. (a) TEM image of coal; (b) TEM image of AC; (c) TEM image of AC-K;(d) Raman spectra of coal, AC and AC-K.
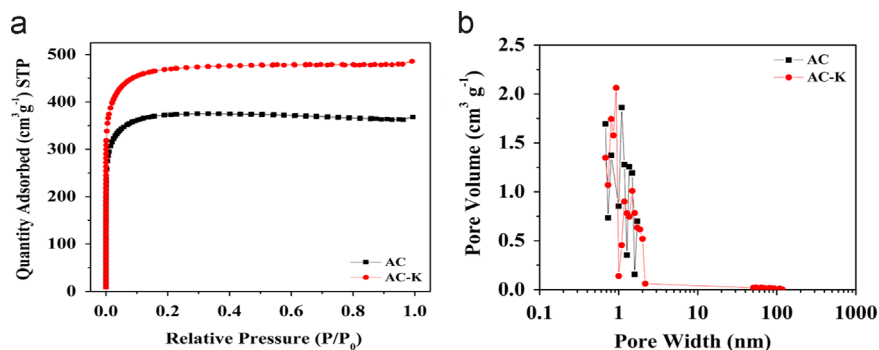

Fig. 2. (a) Nitrogen adsorption–desorption isotherms of AC and AC-K and (b) pore size distribution of AC and AC-K.

Table 1
Textural characteristics and specific capacitance of AC and AC-K at a current density of 1 A g^{-1}.

Samples	S_{BET} (m^2 g^{-1})	V_t (cm^3 g^{-1})	V_{micro} (cm^3 g^{-1})	V_{meso} (cm^3 g^{-1})	C_g (F g^{-1})
AC	1471	0.57	0.54	0.03	178
AC-K	1851	0.75	0.66	0.09	258

more disordered after KOH activation. Besides, micropores can be observed in AC and AC-K samples while barely pores can be observed in coal sample. In the chemical activation, the prominent reaction occurring between the chemical agents such as KOH and the carbon materials is mostly as follows: $6KOH+2C \rightarrow 2K+3H_2+2K_2CO_3$ [3]. The reaction of KOH with activated carbon gives birth to porous carbon with large specific surface area and micropore volume. Raman

spectra of the sample are shown in Fig. 1(d). There are two apparent peaks in the spectra for three samples, corresponding to the D band at ~ 1340 cm^{-1} and G band at ~ 1590 cm^{-1} representing disordered carbon and graphitic carbon, respectively. It can be seen that the values of I_G/I_D decrease by ZnCl$_2$ and KOH activation, indicating the reduction in degree of graphitization [6], which corresponded to the TEM observation.

Fig. 2(a) shows nitrogen adsorption–desorption isotherms of AC and AC-K. According to the IUPAC classification, the nitrogen adsorption–desorption isotherms of both samples exhibit characteristics of type I isotherms [7]. At relatively low pressure, the adsorbed volume of nitrogen increased steeply, suggesting the existence of large amount of micropores. The adsorbed volumes of AC and AC-K are around 370 cm^3 g^{-1} and 480 cm^3 g^{-1} respectively, implying that the number of micropores have increased after KOH activation. At relatively high pressures, there is no hysteresis loop on the isotherms of AC and AC-K, which indicates that a small number of