

The capacitive characteristics of activated carbons—comparisons of the activation methods on the pore structure and effects of the pore structure and electrolyte on the capacitive performance

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Abstract

Fir wood-derived carbons activated with steam, KOH, and KOH + CO₂ were found to exhibit the high-power, low ESR, and highly reversible characteristics between −0.1 and 0.9 V in aqueous electrolytes, which were demonstrated to be promising electrode materials for supercapacitors. The pore structure of these activated carbons was systematically characterized by the *t*-plot method based on N₂ adsorption isotherms. Activated carbons prepared through the above three activation methods under different conditions (i.e., the gasification time of CO₂, KOH/char ratio, and activation time of steam) generally showed excellent capacitive performance in aqueous media, mainly attributed to the development of both micropores and mesopores (with the meso-pore volume ratio, $V_{\text{meso}}/V_{\text{pore}}$, ranging from 0.18 to 0.52). Scanning electron microscopic (SEM) photographs showed that the surface morphologies of honeycombed holes were found to depend on the activation methods. The average specific capacitance of the activated carbon with a combination of KOH etching and CO₂ gasification (with gasification time of 15 min) reached 197 F g^{−1} between −0.1 and 0.9 V in H₂SO₄. The capacitive characteristics of steam- and KOH-activated carbons in NaNO₃ and H₂SO₄ could be roughly estimated from the pore structure and BET surface area although the correlation may be only applicable for the fir wood-derived activated carbons. © 2005 Elsevier B.V. All rights reserved.

Keywords: Activated carbon; Activation method; BET surface area; Pore structure; Supercapacitor

1. Introduction

The physicochemical properties of activated carbons (ACs) have been found to strongly depend on the activation process and the nature of raw materials [1]. For instance, woods are ones of the most important materials for preparing ACs with particular porous characteristics, which are appropriate for the adsorption of solutes in liquid phase [2–4]. The BET surface areas and pore structures of wood-derived ACs, generally higher than those of ordinary ACs, were found to depend on the type of woods as well as the activation methods. For example, quercus agrifolia and eucalyptus woods activated with CO₂ were found to yield surface areas of 1201 and 1190 m² g^{−1} and pore volumes of 0.67 and 0.52 cm³ g^{−1}, respectively [2,3]. In addition,

rubber wood sawdust and wood flour activated with H₃PO₄ showed a BET surface area of 1780 m² g^{−1} and pore volume of 1.30 cm³ g^{−1} [4]. Accordingly, an understanding on the influences of activation variables on the physicochemical properties of ACs is very important in developing the porous structure of various carbons in both physical and chemical activation processes [5]. The above viewpoints are especially important in the development of micro- and mesopores which can be strongly related to the adsorption capability/ability of ACs for various types of chemicals, gases or liquids. Actually, the high adsorption capacity of ACs is generally attributed to the properties of specific surface area, pore volume, and porosity. Hence, recent researches usually focus on the development of ACs with desired pore structures or the possibility of new application fields [6].

Activated carbons are important industrial materials for various applications [7–11]. Recently, the relationship between the porous structures and electrochemical behavior becomes important because carbons in various forms were used as elec-

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trode materials for supercapacitors [7,12–14]. Since the cost of AC-based supercapacitors (i.e., electric double layer capacitors, EDLCs) is generally low [13], this type of energy storage devices are commercially attractive [15]. On the other hand, ACs manufactured under different conditions were found to have different pore structures and surface conditions that usually result in a loss in the electrochemically accessible surface area [12,15–17]. In addition, for the freely accessible surface areas, the specific capacitance ($\mu\text{F cm}^{-2}$) is not the same due to the presence of various functional groups [14,16]. Thus, many studies were carried out to modify the surface properties of ACs in order to optimize their capacitive performance (e.g., high power, low ESR, and high specific capacitance) [7,12–14,17,18].

For the high-power application purpose, the proportion of mesopores (i.e., $50 > \text{pore diameter} > 2 \text{ nm}$) within ACs is considered to be one of the key factors determining the capacitive performance of EDLCs since a complete array of the electric double layers can be easily established and the solvated ions can move freely within such pores. The above situations will cause a significant reduction in the equivalent series resistance (ESR) and a decrease in the electricity loss although a high proportion of mesopores will result in a loss of the specific surface area [14,16]. Moreover, the ESR is also attributable to the poor conductivity of ACs as well as the poor diffusion of solvated ions within micropores [12,15,17]. These characteristics depend mainly on the nature (e.g., graphite degree), the BET surface area, and the porous structure of carbons [12,15–18], which dictate the selection of activated carbon materials for supercapacitors [12,13,15].

The aim of this paper is to prepare various ACs from fir woods and to evaluate their applicability to supercapacitors. In addition, the physical properties such as BET surface area, pore size distribution, total pore volume, and micropore volume of carbons activated by means of three methods (i.e., steam activation, KOH etching, and KOH etching + CO_2 gasification) were systematically compared. Finally, the relationships between the physical properties and the capacitive behavior of these carbons were tried to establish.

2. Experimental details

2.1. Preparation of activated carbons with steam activation

Fir wood was dried at 110°C for 24 h and then, placed in a sealed ceramic oven with a heating rate of 5°C min^{-1} from room temperature to 450°C . In the meantime, steam generated from deionized water (Millipore, Milli-Q) in a heating tube was poured into the oven for 1.5 h. After this heating step, steam was switched from the oven into the exhaust pipes. Under such oxygen-deficient conditions, the fir wood was thermally decomposed into hydrocarbon compounds and porous carbonaceous materials. This is the carbonization process.

In the subsequent activation process, the oven was further heated to 900°C at 5°C min^{-1} and kept at this temperature for 1, 3, 5 and 7 h. At the same time, the steam generated from deionized water at a flow rate of $3 \text{ cm}^3 \text{ min}^{-1}$ was poured into the oven for activation. After activation, the resulting dried carbons

were cooled to room temperature and ground in a mill, washed with pure water, and finally dried at 130°C . They were sieved in the size ranged from 0.12 to 0.2 mm. The steam-activated ACs prepared from fir wood for 1, 3, 5 and 7 h are denoted as FWST01, FWST03, FWST05 and FWST07, respectively.

2.2. Preparation of activated carbons with KOH activation

After the carbonization step as mentioned before, a weight ratio of 0.36 between char and fir wood was obtained. The chars of fir wood were removed, crushed, and sieved to a uniform size ranging from 0.83 to 1.65 mm. These powders were then mixed with water and KOH in a stainless steel beaker with the water:KOH:char weight ratios of 2:1:2, 2:1:1, 3:4:1 and 3:6:1, respectively. After drying at 130°C for 24 h, the above mixtures were placed in a sealed ceramic oven, heated at a rate of $10^\circ\text{C min}^{-1}$ to 780°C , and kept at this temperature for 1 h. In the meantime, N_2 gas was flowed into the oven at a rate of $3 \text{ dm}^3 \text{ min}^{-1}$. The products were cooled to room temperature, washed with deionized water, and then, poured to a beaker containing 0.1 M HCl (250 cm^3) with stirring for 1 h. They were finally washed with hot water until pH of the washing solution reached 6–7 [19]. The carbons prepared from the fir wood with KOH activation at the KOH/char ratios of 0.5, 1, 4 and 6 are denoted as FWKC0500, FWKC1000, FWKC4000 and FWKC6000, respectively.

2.3. Preparation of activated carbons with KOH activation and CO_2 gasification

The same char powders handled in Section 2.2 were well mixed with water and KOH in a stainless steel beaker with a water:KOH:char weight ratio equal to 2:1:1. After drying at 130°C for 24 h, the above mixtures were placed in a sealed ceramic oven, heated at a rate of $10^\circ\text{C min}^{-1}$ to 780°C , and kept at this temperature for 1 h. In the meantime, N_2 gas was flowed into the oven at a rate of $3 \text{ dm}^3 \text{ min}^{-1}$ for various durations. When the KOH activation in N_2 reached the specified time, nitrogen gas was shut off and CO_2 gas was immediately introduced into the oven at a rate of $2 \text{ dm}^3 \text{ min}^{-1}$. The total gas flow time for nitrogen and CO_2 into the oven at 780°C was kept to be 60 min. Further treatments of these ACs were followed the same procedures handled in Section 2.2. The samples were classified according to the KOH/char ratio and the time duration of CO_2 gasification, which were denoted as FWKC1000, FWKC1015, FWKC1030 and FWKC1060, respectively (FW: fir wood; KC: KOH activation; 10: KOH/char ratio (=1.0); and the last two numbers represent the CO_2 gasification time in minutes).

2.4. Measurements of physical properties

The BET surface area of various carbons (S_p) was measured from the N_2 adsorption isotherms at 77 K with a sorptiometer (Porous Materials, BET-202A). Prior to this measurement, the samples were dried in an oven at 130°C overnight and then, quickly placed into the sample tube. After that, the tube was heated to 230°C and evacuated for 4 h until the pressure less than

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