Journal of Analytical and Applied Pyrolysis 105 (2014) 116–121

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

KOH activation of a HyperCoal to develop activated carbons for electric double-layer capacitors

Xiao-Yan Zhao [a], Shan-Shan Huang [a], Jing-Pei Cao [a,b,*], Shao-Chen Xi [a], Xian-Yong Wei [a], Junpei Kamamoto [b], Takayuki Takarada [b]

[a] Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), China University of Mining & Technology, Xuzhou 221008, Jiangsu, China
[b] Division of Environmental Engineering Science, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515, Japan

ARTICLE INFO

Article history:
Received 25 May 2013
Accepted 13 October 2013
Available online 27 October 2013

Keywords:
HyperCoal
Activated carbon
EDLC
Capacitance
Pore size

ABSTRACT

A series of activated carbons (ACs) was prepared from HyperCoal by conventional and direct KOH activation methods, and was used as electrodes in electric double-layer capacitors (EDLCs) using 0.5 M $TEABF_4$/PC as the electrolytic solution. The effects of carbonization temperature (CT), activation temperature (AT) and KOH/sample ratio on BET surface area, average pore size and capacitance of ACs were investigated in this study. Nitrogen adsorption isotherms of all ACs indicated that the pores in ACs were mainly micropores. The BET surface area and capacitance decreased with raising CT from 500 to 900 °C, while the highest BET surface area of 2540 $m^2 g^{-1}$ and maximum capacitance of 46.0 $F g^{-1}$ were achieved at CT of 500 °C and AT of 800 °C in conventional activation. On the contrary, in the direct activation, the BET surface area and the capacitance increased with the increase of AT and KOH/sample ratio, getting the maximum value of 2440 $m^2 g^{-1}$ and 44.4 $F g^{-1}$, which is comparable with that of conventional method, at AT of 800 °C and KOH/sample ratio of 4.0. Such a procedure provides a cost-effective approach to preparation of high performance activated carbons from HyperCoal for EDLC.

1. Introduction

Electric double-layer capacitor (EDLC), using activated carbons (ACs) as electrode materials, is recognized as an efficient storage device for electric power, due to its high power density, large capacity, low leakage current, simple charging and discharging process and long cycle life [1,2]. AC electrode is widely preferred [3] due to its excellent properties such as easy processability, high abundance, low cost, corrosion resistance and high endurance at high operating temperatures [4]. The ideal ACs for EDLC electrodes are required to have a high surface area and an optimal pore size distribution that are important to high specific capacitance of EDLC [5,6]. Particularly, raw materials and activation methods are two of the most important factors which may influence the final structure and cost of ACs.

Although the use of various biomass, resin and polymer materials to produce ACs becomes one of the hot topics [7–9], coal is still the main material for ACs at present. The coal with too much ash has a great impact on the quality of ACs. For example, it not only affects the mechanical strength of products, but also reduces the adsorption capacity and chemical characteristics [10]. When the coal derived ACs are used as EDLC electrode materials, the impurities or ash will compromise the EDLC performance [11]. In these cases, since ash materials causes various problems, it is necessary to remove it before ACs preparation. HyperCoal is an ash-less coal obtained by a mild thermal extraction of coal (HyperCoal process), has lower water content and softening point and higher liquidity than the raw coal, which shows significant advantages in energy saving, environmental protection and good prospects for development [12]. The utilization of HyperCoal at present is mainly concentrated on the gasification [13] and liquefaction [14], but as materials to produce ACs for EDLC electrode is rarely reported.

The main objective of the present work is to investigate the applicability of ACs derived from HyperCoal as supercapacitor electrodes. ACs were prepared from HyperCoal by conventional 2-step carbonization/KOH-activation and single step direct KOH-activation at argon atmosphere, which have the well developed textual properties on the ACs surface for application as a EDLC electrode material. The effects of carbonization temperature, activation temperature and KOH/sample ratio on the yield, BET surface area, pore structure, capacitance and their relationship of the prepared ACs were systematically investigated.

* Corresponding author at: Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), China University of Mining & Technology, Xuzhou 221008, Jiangsu, China. Tel.: +86 516 83591059; fax: +86 516 83591059.
E-mail addresses: beyondcao@hotmail.com, beyondcao_2000@163.com (J.-P. Cao).

0165-2370/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jaap.2013.10.010

Table 1
Proximate and ultimate analyses of HyperCoal.

Proximate analysis (wt%, d)			Ultimate analysis (wt%, daf)				
Ash	VM	FC	C	H	N	S	O[a]
0.03	37.8	62.17	83.5	5.4	2.2	0.6	8.3

[a] By difference; d, dry basis; daf, dry and ash free basis.

2. Materials and methods

2.1. Materials

The HyperCoal used in this study is produced from Gregory coal by Kobe Steel, Ltd., Japan. Detailed information in regard to the HyperCoal production has been described in detail [12]. It was pulverized to pass through a 200-mesh sieve (<75 μm) followed by drying at 107 °C for 24 h and then stored in an airtight container before use. Table 1 shows the proximate and ultimate analyses of the HyperCoal sample.

2.2. Preparation and characterization of ACs

The conventional 2-step carbonization/KOH-activation method consists of the following sequential steps:

- The sample was carbonized in a muffle furnace under Ar flow at a heating rate of 10 °C min^{-1} and was held at the prescribed temperature between 500 °C and 900 °C for 2 h. The char was mixed with KOH in a KOH/sample ratio of 4 and then activated at 800 °C for 2 h under Ar flow. After completion of the heat treatment, the sample was allowed to cool to room temperature. The resultant material was washed with 2 M HCl solution, rinsed with distilled water until neutral and then dried at 200 °C in vacuum for 2 h. The ACs prepared by conventional activation were designated as AC-*X*, where *X* represents the final carbonization temperature.

The single step direct KOH-activation method implies:

- The HyperCoal was directly activated with KOH in the temperature range of 500–800 °C without carbonization in the same manner as above. Different KOH/sample ratios between 2 and 4 at activated temperature of 800 °C were investigated as well. The ACs prepared by direct activation were designated as AC-r-*Y*, where *Y* represents the final activation temperature or KOH/sample ratio. All subsequent data are expressed as the averages of values that were obtained from repeated experiments.

The porous texture and the BET surface area of all the ACs samples were characterized by nitrogen adsorption and desorption studies at 77 K (BELSORP-max, Japan).

2.3. Preparation of electrode and capacitance measurements

A mixture of 87 wt% AC, 10 wt% acetylene black, and 3 wt% PTFE binder was pressed into pellets (13 mm in diameter) as the electrodes. Then, the electrodes were dried under vacuum at 200 °C for 2 h. A button-type capacitor was assembled with two AC electrodes using 0.5 M $TEABF_4$/PC as the electrolyte. The capacitors were galvanostatically cycled between 0 and 2.5 V on a Land cell tester at a constant current discharge mode. The capacitance (*C*) of a single electrode was determined with the formula $C = IdT/2dV$ (1), where *I* is the discharge current, *dT* is the discharge time variation, and *dV* is the voltage variation in discharge.

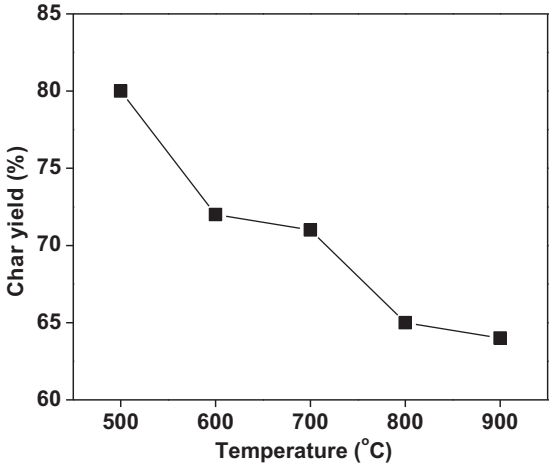

Fig. 1. The char yields of HyperCoal at different temperatures.

3. Results and discussion

3.1. Conventional activation method

As shown in Fig. 1, raising temperature from 500 to 900 °C decreased the char yield because of the progressive pyrolysis conversion. However, the rate of declination in the range of 800–900 °C is not as fast as that in the range of 500–800 °C. The results show that most of volatile matter from HyperCoal was evolved at about 800 °C.

The adsorption isotherms of N_2 on the prepared ACs at 77 K are shown in Fig. 2. In all cases, the obtained results correspond to typical type I isotherms microporous carbons according to the IUPAC classification [15]. When P/P_0 is 0.39 and 1.00, all of ACs represent different adsorption of micropores and total pores respectively, due to various pore structures. The ACs prepared at lower carbonization temperature show larger adsorption amounts.

As shown in Fig. 3, the ACs obtained at lower temperature show higher BET surface area value. The BET surface area almost keeps constant until 700 °C and then decreases sharply from 2440 to 1110 $m^2 g^{-1}$. This explains that the pores enlarge up to this temperature. Above 700 °C, the excess enlargement induces combination of pores, resulting in an increase in mesopores, and a decrease of

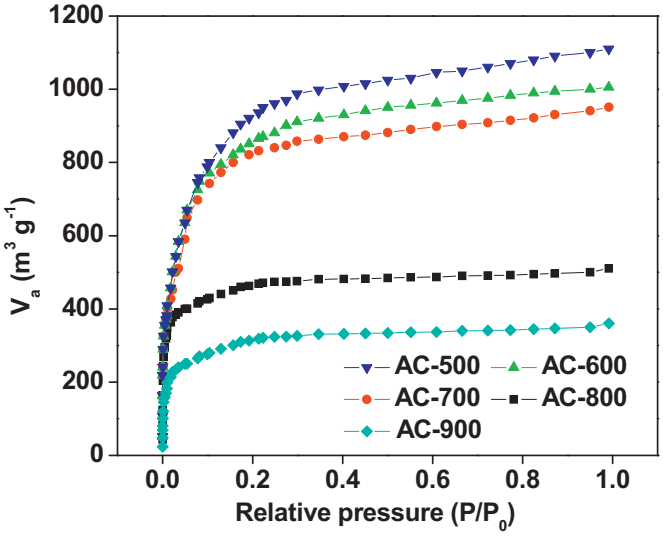

Fig. 2. The nitrogen adsorption isotherms of the ACs at different temperatures.