

Influence of Activation Time on the Properties of Polyacrylonitrile-Based Activated Carbon Hollow Fiber

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SYNOPSIS

Activated carbon hollow fiber (ACHF) was prepared from polyacrylonitrile (PAN) hollow fiber through carbonization in nitrogen and activation with carbon dioxide. The effect of the activation time on the pore size distribution and the surface structure of the resulted ACHF was investigated. The results show that increasing the activation time at 800°C can increase the number of pores and reduce the crystal size, the tensile strength, the modulus, and the elongation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Activated carbon has porous structure and is carbonized and activated from carbonic substances such as sawdust, charcoal, coconut shell, various kind of nutshells, as well as macromolecular carbon through the process of physical or chemical activation. It contains a small quantity of hydrogen, oxygen, and some other elements.¹ It has high porosity and, hence, a very large surface area.^{2,3} Therefore, all sorts of activated carbons, whatever shapes might be, have adsorbing ability and are widely used in areas including food, pharmaceutical, chemical, national defense, agriculture, water processing, and environment-protecting industries.⁴ Recently, researches have been focused on the study of the third-generation high-performance activated carbon fiber (ACF).^{5,6} Activated carbon fiber has the advantage of uniform pore size and makes it possible to control the distribution of the porosity during production upon customer's request. In addition, ACF has the advantages of quick adsorption and desorption, light weight, and convenience for application.

Huttepain and Oberlin⁷ have observed the micropores and ultramicropores of the ACF with scanning electron microscope (SEM) and found that these micropores and ultramicropores are slit

shaped, formed by gasification of one or more individual aromatic layers of a turbostratic lamella during activation. Activated carbon fiber with such micropores is composed of individually activated carbon planes and rearranged pore structure, which result in the change in the volume, pore size, and surface in different kind of carbon materials after activation.^{3,8} Carrott and Freeman suggested that the gasification of the nongraphitized carbon existing between the graphitic surface leads to the development of the microstructure, whereas the shrinking of carbonic structure and the broadening of the distribution of microporosity occur simultaneously. Such phenomena are more important to those activated carbon with high burning off.⁹ Study of the microstructure of activated carbon and the change in the surface area of the microporosity have been conducted by Grebennikov and Fridman. They found out that the distribution of microporosity and the surface area of the ACF may vary with the raw materials as well as the conditions of activation, because the classes or kinds of the precursor of the ACF may affect the uniformity of the size of micropores, and the method and conditions of activation may affect the adsorption application of ACF.¹⁰

There is a great difference between ACHF and ACF. An asymmetrical carbon hollow fiber has a thin and dense layer of skin structure, in combination with a porous layer of finger structure with larger pores as a support to withstand the pressure. The geometry of a hollow fiber provides two flowing

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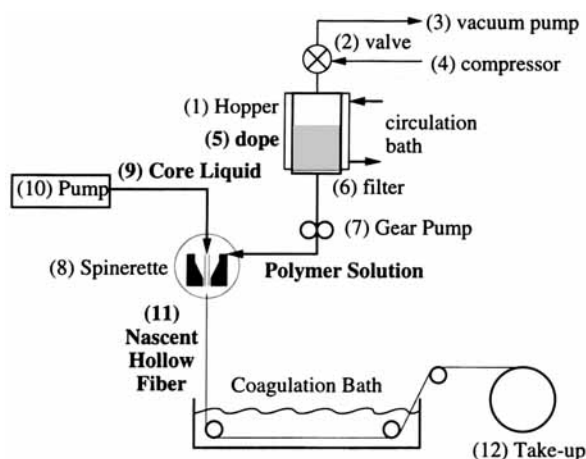


Figure 1 Schematic diagram of spinning setup for hollow fiber.

paths and enables two different streams to contact without interrupting each other's flowing. Thus, ACHF can have a higher rate of mass exchange than ACF. In addition, ACHF can also perform separation under high temperature.

Although articles of modification of hollow fiber to improve its application can be easily found, activated carbon in the shape of hollow fiber is rarely seen in the literature. Koresh and Soffer¹¹ have made carbon hollow fiber through pyrolysis for gas separation and showed high fluxes and good selectivities. The same group later obtained a patent covering the making of carbon membranes through controlled pyrolysis.¹² Schindler and Maier¹³ obtained another patent for making hollow fiber carbon membrane. In this patent, PAN hollow fiber was pretreated with hydrazine and then followed by oxidation and carbonization. The resulted carbon hollow fiber does retain the porous structure of the precursing PAN fiber, and is suitable for separation particles. Yoneyama and Nishihara have obtained a patent on the manufacturing of carbon hollow fiber from PAN-based polymers, which shows that the micropores penetrate continually from the surface of the inner wall to the surface structure of the external wall, with micropore radius ranging from 10 to 1000 nm, and of excellent thermal resistance.¹⁴ Linkov et al. have carbonized PAN hollow fiber and examined the surface structure of the resulted hollow fiber with scanning probe microscopy (SPM).¹⁵ However, all the above-mentioned processes are for producing carbon hollow fiber. Recently, we began to study the carbonization and activation of PAN hollow fiber in this research group.^{16,17}

In this article, we used carbon hollow fiber as the precursor, and used carbon dioxide as the physical activation agent to conduct the activation at 800°C. The resulted ACHF was then subjected to tests including SEM, mercury intrusion porosimetry (MIP), BET, and x-ray diffraction. The aim of this work is to study the effect of the activation time on the crystal size, mechanical properties, pore size distribution, and the surface area of the resulted ACHF, in order to serve as the basic knowledge for the manufacturing of ACHF.

EXPERIMENTAL

Preparation of PAN Hollow Fiber

Polyacrylonitrile was obtained from Aldrich. The PAN power was first dissolved in dimethyl formamide to form a 15% dope.¹⁸ Hollow fiber was spun using a dry-wet spinning setup, as shown in Figure 1, with water as the coagulation liquid. The resulted hollow fiber had an inside diameter of 400 μm and an outside diameter of 600 μm . Figure 2 shows the porous structure of the PAN hollow fiber.

Preparation of Activated Carbon Hollow Fiber

Virgin PAN hollow fiber was first oxidized at 230°C in the air for 5 h, and then carbonized in nitrogen at 1000°C. Afterwards, the carbonized fiber was activated with carbon dioxide at 800°C for a time varying from 10 to 40 min.

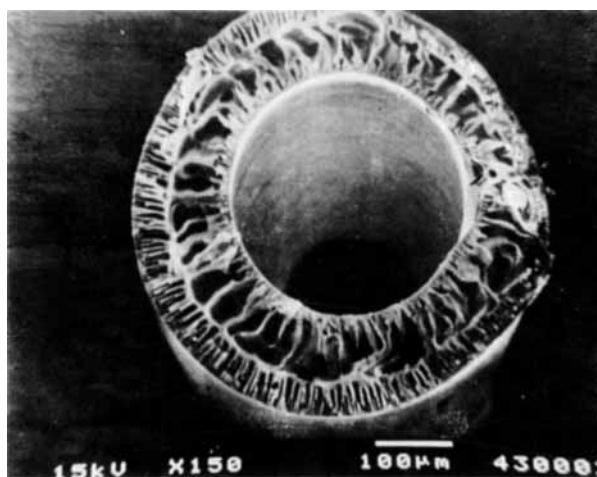


Figure 2 The cross section of virgin PAN hollow fiber ($\times 300$).

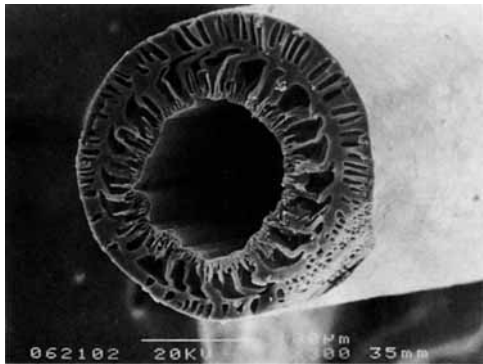


Figure 3 The cross-section of the activated carbon hollow fiber ($\times 300$).

Characterization of Activated Carbon Hollow Fiber

The mechanical properties of the fiber was determined using tensile testers (Vibro-dyn and Vibroskop, Lenzing AG) with a testing speed of 1 mm/min and a testing gauge of 10 mm. The crystal size of the fiber was determined by an x-ray diffractometer (Seintage DMS 2000) using Ni-filtered CuK_α radiation. The crystal size (L_c) was calculated from the equation:

$$L_c = \frac{k\lambda}{B \cos \theta}$$

where λ is the wavelength of CuK_α x-ray, B is the width at half-maximum intensity of the peak at $\theta = 26^\circ$, and the factor k is 0.89. An SEM (Cambridge S-360) was used to examine the cross-section and surface of the fiber. The surface area of the fiber was measured using a BET porosimeter (Quantachrome Autosorb-6). The pore size distribution of the fiber was measured with a mercury intrusion porosimeter (Quantachrome Autosorb-60) using pressure from 0 to 400 MPa.

RESULTS AND DISCUSSION

Effect of Activation Time on the Surface Structure

Grebennikov and Fridman¹⁰ presented their observation on the anisotropic activation of the carbon fiber, in which the closed pores are first opened, then the carbons in the amorphous area are sintered, and finally the carbonic layer in the crystalline lamella are sintered. This suggests that the degree of activation of ACHF can be controlled by varying the

duration of activation. Figure 3 shows the cross-section of the activated carbon fiber after activated with carbon dioxide for 10 min at 800°C. The activated

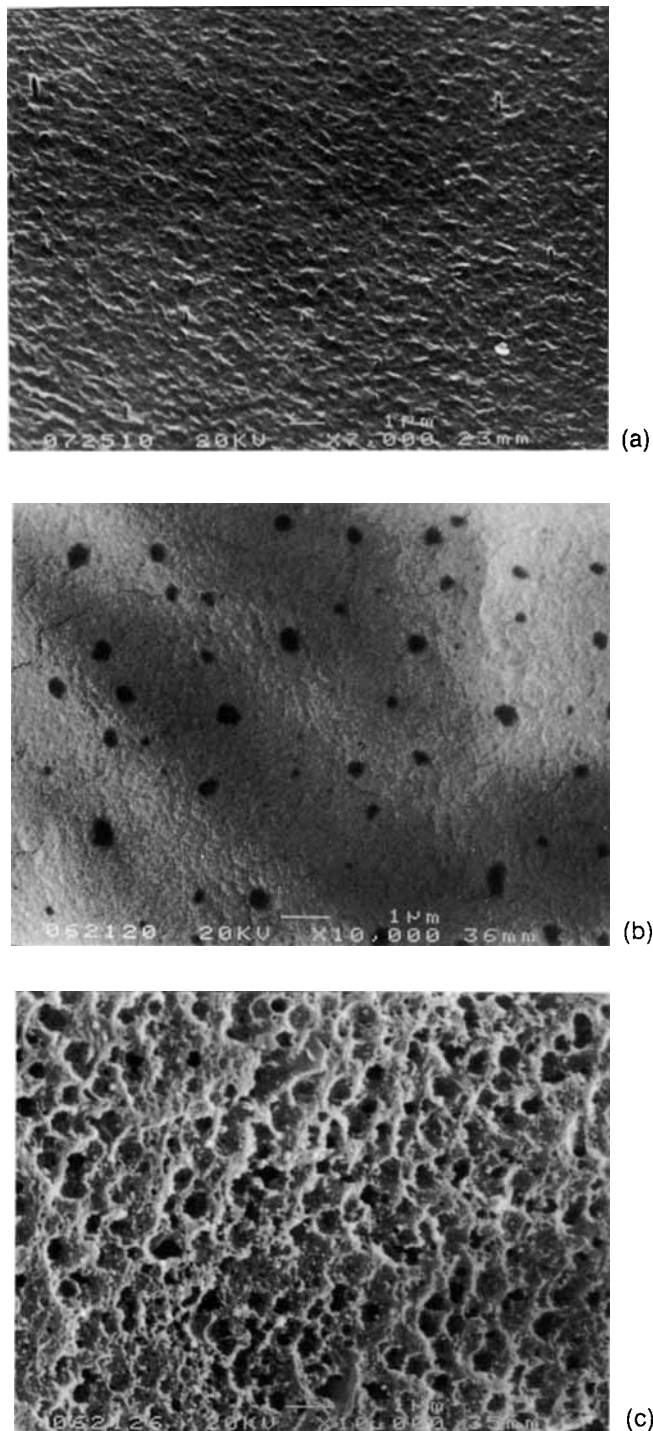


Figure 4 External surface of the activated carbon hollow fiber: (a) after being activated for 10 min ($\times 7000$); (b) after being activated for 20 min ($\times 10,000$) (c) after being activated for 40 min ($\times 10,000$).



Figure 5 The peeling off of the surface of the activated carbon hollow fiber ($\times 1000$).

carbon hollow fiber was carbonized first at 1000°C and then activated in carbon dioxide for 10 min. The appearance of ACHF is similar to that of the original PAN hollow fiber shown in Figure 2, except that the diameter and pore size was smaller. Micrograms in Figure 4 show the external surface of the resulted ACHF. For an activation time of 10 min, there is no apparent pores, but creased surface were found on the surface, as shown in Figure 4(a). After 20 min of activation, pores began to appear on the surface, as shown in Figure 4(b). This suggests that the pores in the thinner region of the skin of the hollow fiber has been activated and sintered. As shown in Figure 4(c), after 40 min of activation, the surface became composed of uniform size of pores. This indicates that the skin of the fiber was burnt off and the closed pores were opened, and the molecules in the amorphous area were broken. Before this stage, for 30 min of activation, most of the surface of the fiber was peeled off, as shown in the less magnified microgram in Figure 5.

Effect of Activation Time on the Pore Size Distribution

Figure 6 shows that the pore size distribution of the original PAN hollow fiber has two major peaks around 80 nm and 300 nm, respectively. After the activation, smaller pores (< 20 nm) appeared. For ACHF of 10 min of activation, these two peaks of the pore size distribution curve shifted to 50 nm and 200 nm, respectively, with slightly decrease in the number of pores. This is because during the carbonization process, the density of the ACHF was increased and its porosity was reduced. On the other hand, for ACHF of 20 min of activation, the pore size peaks shifted slightly to 60 nm and 230 nm,

respectively, with slightly increase in the number of pores. This suggests that during activation, the pore was opened, and more pores were created. As for ACHF of 40 min activation, those two major peaks shifted to 100 nm and 300 nm, respectively. In addition, three more peaks were found under 10 nm. This indicates that during activation, the skin of the ACHF was burnt off; hence, some of the closed pores were opened. Simultaneously molecules in the amorphous region were sintered; hence, the number of pores of certain sizes increased, while pores of other sizes disappeared.

Effect of Activation Time on the Properties

In general, the tensile strength and modulus of the carbon fiber will increased with the carbonization temperature.¹⁹ In Table I, the data show that when the PAN hollow fiber was carbonized to 1000°C , its tensile strength and modulus reached 1.43 and 83 Gpa, respectively, while the elongation was 1%. After the activation, all the tensile strength, modulus, and elongation were reduced. The longer the activation time, the greater the degree of reduction in the mechanical properties. The reason for the reduction in the mechanical properties is that during the activation, molecules were attacked by carbon dioxide; thus, the size of the crystals was reduced, as shown in Table II. Smaller crystal size resulted in weaker mechanical strength. On the other hand, the attack of carbon dioxide created more pores; thus, the sur-

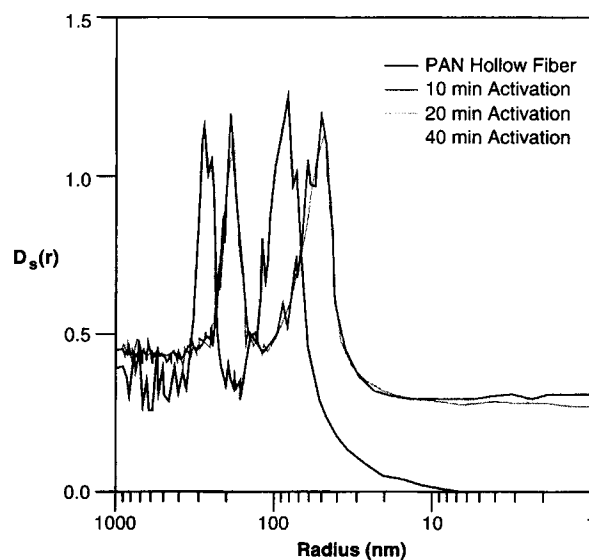


Figure 6 The pore size distribution of the activated carbon hollow fiber.

Table I The Effect of Activation Time of on the Properties of PAN-Based Activated Carbon Hollow Fiber

Sample	Activation Time (at 800°C) (min)	Tensile Strength (GPa)	Modulus (GPa)	Elongation (%)
Unactivated ^a	—	1.43	83	1.00
a	10	1.02	65	0.86
b	20	0.84	52	0.71
c	40	0.32	30.4	0.67

^a Oxidized at 230°C in the air for 7 h and then carbonized in nitrogen at 1000°C.

face area of ACHF increased with the activation time.

CONCLUSION

From the results of the activation of PAN-based carbon hollow fiber at 800°C with carbon dioxide, the longer the activation time, the smaller the size of the crystals of the fiber, the greater the surface area, and the larger the degree of reduction in the mechanical properties. When ACHF was activated for 40 min at 800°C, three peaks on the pore size distribution curve were found under 10 nm, which was because the surface of ACHF was burnt off. Therefore, the activation time should be carefully controlled in the process of manufacturing ACHF in order to achieve the desired pore size distribution and surface area.

Table II The Influence of the Time of Activation on the Crystal Size and Surface Area of PAN-Based Activated Carbon Hollow Fiber

Sample	Crystal Size Lc (nm)	Specific Surface Area (m ² /g)
Unactivated	1.20	158
a	1.15	218
b	1.03	262
c	0.81	340

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