

# Effects of Activation Time on the Properties and Structure of Polyacrylonitrile-Based Activated Carbon Hollow Fiber

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**ABSTRACT:** Polyacrylonitrile (PAN) hollow fibers were pretreated with ammonium dibasic phosphate, then further oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. The effects of activation time of a precursor fiber on the microstructure, specific surface area, pore-size distribution, and adsorption properties of PAN-based activated carbon hollow fibers (PAN-ACHF) were studied in this work. The BET surface area of PAN-ACHF and surface area of mesopores gradually increase with activation time extending, and reach the maximum values, 780 and 180 m<sup>2</sup> g<sup>-1</sup>, respectively, when fibers are activated at 800°C for 100 min. The adsorption ratio to creatinine changes little with activation time extending and all values over all activation

time are above 90%. The adsorption ratio to VB<sub>12</sub> gradually increases with activation time extending before 60 min, and then becomes relatively constant from 60 to 100 min. The number of pores on the surface of PAN-ACHF increases with activation time extending. The amount of mesopores in PAN-ACHF made of fibers activated for different time increases with activation time extending and the dominant pore sizes of mesopores in PAN-ACHF range from 2 to 5 nm. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2565–2569, 2006

**Key words:** activation time; polyacrylonitrile; activated carbon hollow fiber; adsorption properties

## INTRODUCTION

Needs for porous materials in industrial application and in our daily life are increasing. Porous carbon materials, especially those containing micropores or mesopores, are being used in various applications such as adsorbent and catalyst supports.<sup>1</sup> Activated carbon fibers have played a major role in adsorption technology over the last few years. These fibers have uniform slit-shaped micropores and great surface area. Activated carbon fibers are produced by carbonizing raw materials such as polyacrylonitrile (PAN), cellulose, phenolic, or pitch fibers. Although the porous carbon materials such as activated carbon fibers were usually prepared by chemical and/or steam activation treatments, the control of pore size needs a careful regulation of the activation condition. Recently, the PAN-based activated carbon hollow fiber (PAN-ACHF) has brought on many investigators' interests,<sup>2–7</sup> since PAN-ACHF shows the largest adsorption capacity among the carbon surfaces.

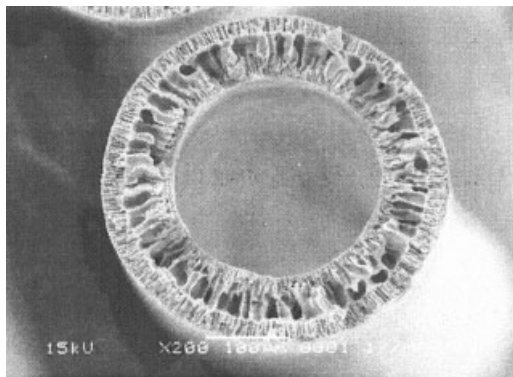
Ming-Chien Yang and Da-Guang Yu<sup>2–5</sup> studied the structure and properties, pore-size distribution, surface area, and mechanical properties of PAN-ACHF. Linkov et al.<sup>8</sup> reported that hollow fibers have been

used for gas separation and show high fluxes and good selectivities. Schindler and Maier<sup>9</sup> obtained a patent for making hollow carbon fiber membrane, in which the PAN hollow fiber was pretreated with hydrazine and followed by oxidation and carbonization, and was suitable for separating particles.

Commonly, most commercially available activated carbons are extremely microporous and of high surface area, and consequently they have high efficiency for the adsorption or removal of low-molecular-weight compounds.<sup>10–12</sup> The mesoporous activated carbons are expected to be excellent adsorbents for the removal and recovery of mesomolecular weight compounds. Tamai et al. developed highly mesoporous activated carbon fiber with high BET surface area by activating pitch containing small amount of organo rare earth metal complexes with steam activation<sup>13–15</sup> and described the adsorption of different mesomolecular weight compounds (e.g., acid, direct, and basic dyes) on the mesoporous activated carbon fiber obtained from pitch containing yttrium acetylacetonate.<sup>16</sup> It is not reported about PAN-ACHF containing micropores and mesopores.

In this research, the PAN hollow fibers were dipped in ammonium dibasic phosphate aqueous solution, oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. This study examined the effects of activation time of stabilized PAN hollow fiber precursor on the adsorption and structural properties,

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**Figure 1** The cross section of virgin PAN hollow fiber ( $\times 200$ ).

such as specific surface area, pore-size distribution, and morphology of PAN-ACHF. We discuss the adsorption properties of the resultant PAN-ACHF to creatinine and VB<sub>12</sub>. According to their molecule sizes, creatinine < VB<sub>12</sub>, the molecule size of creatinine is less than 2 nm and primarily adsorbed by micropores (<2 nm). However, the molecule size of VB<sub>12</sub> is larger than 2 nm and primarily adsorbed by mesopores (2–50 nm). There are various types of pores in the ACHF. Macropores have small specific surface area and are thus insignificant to adsorption. However, these pores control the access of adsorbate and also serve as the space for deposition. Mesopores provide channels for the adsorbate to the micropores from the macropores and simultaneously adsorb matter of mesomolecules. As reported in the literature, mesopore can function a capillary condensation; thus, it is indispensable for the adsorption of liquid and gas. Micropores determine the adsorption capacity of the ACHF and primarily adsorb the matter of micromolecules. It is the purpose of this article to discuss what activation process condition provides high surface area and high adsorption ratio for the PAN-ACHF prepared from PAN hollow fibers.

## EXPERIMENTAL

PAN (a copolymer of acrylonitrile (92 wt %), methyl methacrylate (6 wt %), itaconic acid (2 wt %)) hollow fiber spun by dry-wet spinning setup was used as the precursor. The resultant hollow fiber had an inside diameter of 400  $\mu\text{m}$  and an outside diameter of 500  $\mu\text{m}$ . Figure 1 shows the porous structure of the PAN hollow fiber.

Virgin PAN hollow fiber was first dipped in ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration for 30 min. Afterwards, the pre-treated fiber was oxidized in the air at 230°C for 5 h, carbonized in nitrogen at 900°C for 70 min, and activated at 800°C for different time.

A scanning electron microscope (SEM) (JEOL Model JSM-5600LV) was used to examine the cross section and external surface of fibers.

Adsorption study to creatinine and VB<sub>12</sub> was carried out by a static process. A known quantity of the PAN-ACHF was immersed in a known volume of aqueous solution at 37°C for 24 h. The amount of creatinine and VB<sub>12</sub> adsorbed was determined by the concentration difference before and after immersion in the solution. The creatinine and VB<sub>12</sub> concentrations of the solution were determined with a UV/Vis spectrophotometer (Shanghai Techcomp Corp. 7500) at the wavelength of 510 and 361 nm, respectively. Absorbency of creatinine and VB<sub>12</sub> in the aqueous solutions reflects the difference of solution concentration. Then, the adsorption ratio was calculated as follow:

adsorption ratio (wt %)

$$\frac{\text{absorbency before adsorption} - \text{absorbency after adsorption}}{\text{absorbency before adsorption}} \times 100\%$$

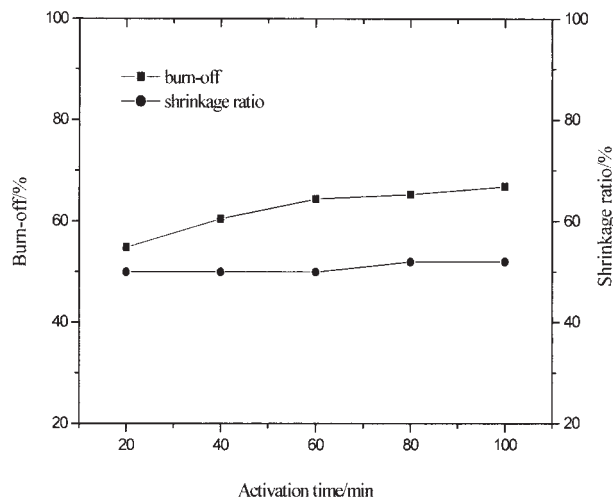
Samples of PAN-ACHF were characterized by measuring specific BET surface area, surface area of mesopores, and pore-size distribution using an auto-adsorption apparatus (Micromeritics Tristar 3000). The surface area was calculated using the multi point BET method. Pore volume and pore-size distribution were determined from the nitrogen adsorption isotherms using the Barrett, Joyner, and Halenda method.<sup>17</sup>

## RESULTS AND DISCUSSION

### Surface area and adsorption properties of PAN-ACHF

The activation step during activation process is to create pores within the consolidated carbon structure by etching effects. The interaction of activating agents with the carbon structure inevitably alters the surface chemical structure as well as the microstructure of the resultant ACHF, and therefore bears significant impact on the properties of ACHF.

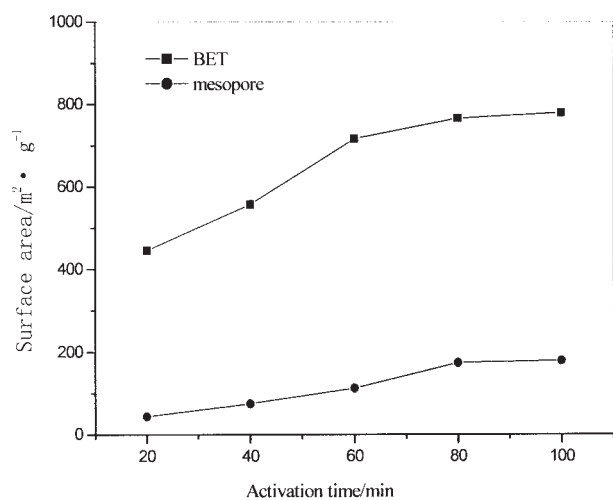
Figure 2 shows the variation in burn-off and shrinkage ratio of PAN-ACHF with activation time of activated carbon hollow fiber. The weight loss and shrinkage ratio were determined from a change in weight and length before and after activation. We found that the weight loss of the fibers increases with activation time. The weight loss increases slowly before 60 min, and then increases little. The shrinkage ratio changes little and is about 50% over all activation time. When the carbon fibers were heated in carbon dioxide, the carbon composition in the fiber reacted with the carbon dioxide and evolved carbon monoxide.<sup>18</sup> This



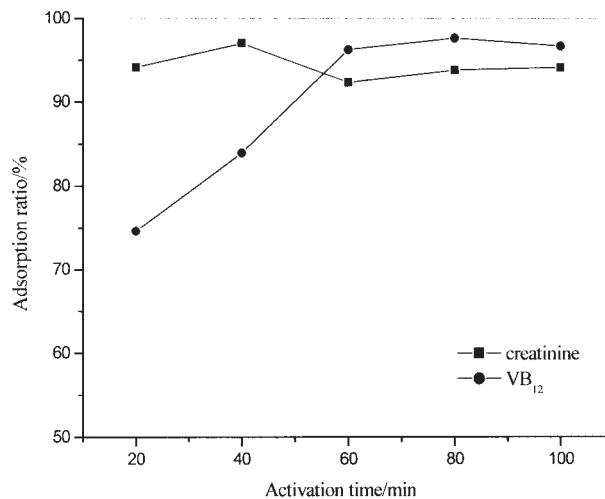
**Figure 2** Burn-off and shrinkage ratio of PAN-ACHF versus activation time. Virgin PAN hollow fibers were first dipped in ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration for 30 min. Afterwards, the pretreated fibers were oxidized in the air at 230°C for 5 h, carbonized at 900°C for 70 min, activated at 800°C for different time to obtain PAN-ACHF. Then the burn-off and shrinkage ratio of the resultant PAN-ACHF were tested.

reaction led to a decrease in the weight of the resultant activated carbon hollow fibers, as shown in Figure 2. And this reaction processes more completely with activation time extending.

Figure 3 shows the variation in BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF with activation time. The carbon structure of the PAN-based carbon fibers in low carbonization temperature is composed of mainly two types of car-



**Figure 3** Surface area of BET and mesopores versus activation time. The preparation of PAN-ACHF is same with the illustration of Figure 2. Then, BET surface areas of PAN-ACHF and surface area of mesopores in PAN-ACHF developed at different activation time were tested.



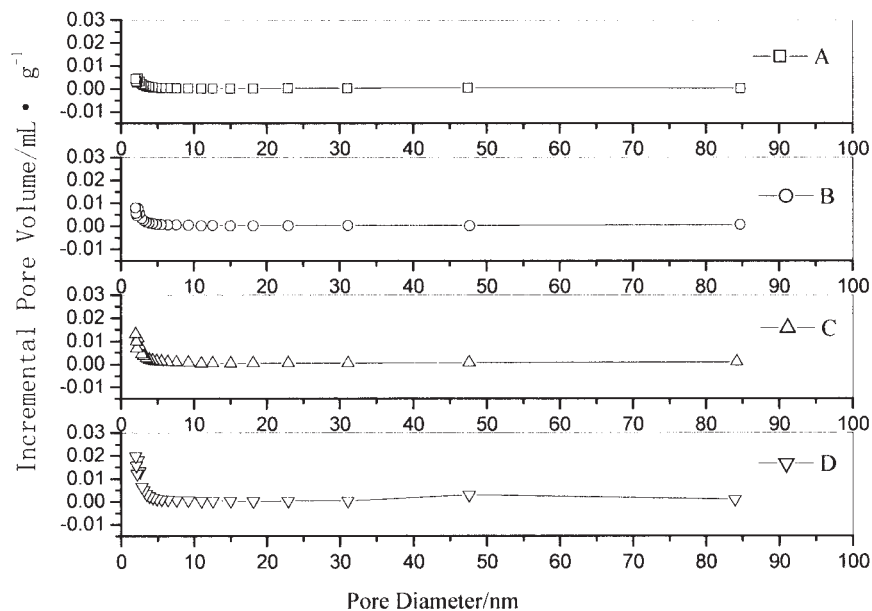
**Figure 4** Adsorption ratio of PAN-ACHF versus activation time. The preparation of PAN-ACHF is same with the illustration of Figure 2. Then, the adsorption ratios of PAN-ACHF developed at different activation time were tested.

bon basal planes, graphitic-like basal planes and edge planes. During activation, activating agents react preferentially with carbons at the edge planes, or nonregular parts of the carbon structures. As this proceeds, pores are created and formed within the consolidated carbon structure. This reaction became more complete and developed more pores with activation time extending. As shown in Figure 3, BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF gradually increase before 80 min, then increase slowly, and reach the maximum, 780 and 180 m<sup>2</sup> g<sup>-1</sup>, respectively, when activation time is 100 min. This significant increase in surface area may be due to two aspects: new pores were created upon extending activation time, and pore drilling and pore deepening effects.<sup>19</sup> It is suggested that the further development of the porosity on extending activation time and the amount of micropores and mesopores in PAN-ACHF reach the maximum when activation time is 100 min.

Figure 4 shows the variation in adsorption ratio of PAN-ACHF with activation time of activated carbon hollow fibers. The adsorption ratio to creatinine changes little with activation time extending and all values over all activation time are above 90%. The adsorption ratio to VB<sub>12</sub> gradually increases with activation time extending before 60 min, and then becomes relatively constant from 60 to 100 min. It is suggested that activation time has more obvious effect on adsorption ratio to VB<sub>12</sub> than on that to creatinine.

#### Pore size distribution of PAN-ACHF

Figure 5 shows the pore-size distribution of the PAN-ACHF made of fiber activated at 800°C for 20, 40, 60, 80 min, respectively. Because of the limits of appa-



**Figure 5** Pore-size distribution of PAN-ACHF. The preparation of PAN-ACHF is same with the illustration of Figure 2. Then, with average pore diameter increasing, incremental pore volumes of PAN-ACHF developed at different activation time were tested.

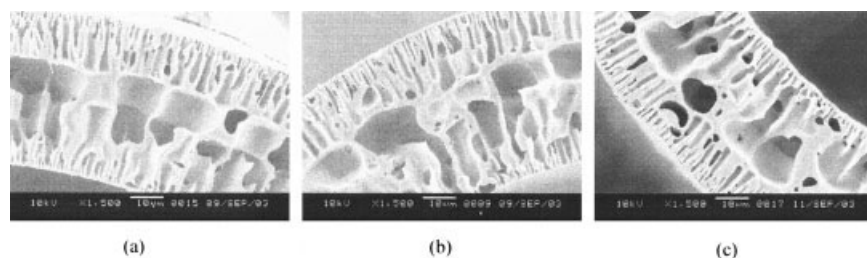
tus, pore diameters of less than 2 nm could not be tested. However, the distribution of mesopores (2–50 nm) and macropores (>50 nm) can be observed from Figure 5. As shown in Figure 5, the value of starting incremental pore volume increases with activation time extending, and reaches the maximum, 0.01987 mL g<sup>-1</sup>. As shown in Figure 3, the surface area of mesopores in PAN-ACHF activated at 800°C for 100 min also reach the maximum, 180 m<sup>2</sup> g<sup>-1</sup>. It indicates that the amount of mesopores in PAN-ACHF increases with extending activation time, which is coincident with the conclusion concluded after Figure 3.

### Morphology of PAN-ACHF

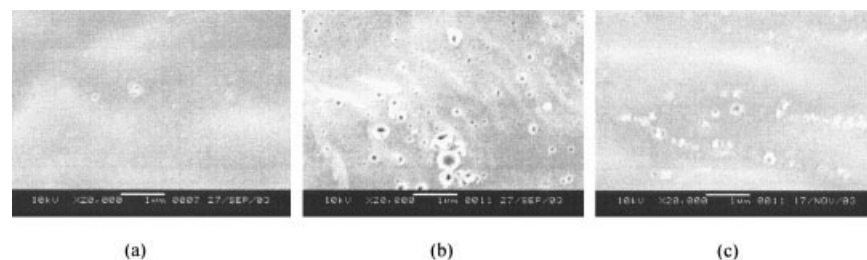
Figure 6 shows the cross section of the PAN-ACHF made of the fiber activated at 800°C for 20, 40, 80 min, respectively. The cross-sectional shapes of PAN-ACHF in Figures 6(a)–6(c), difinger-like porous struc-

ture, are preserved after activation with CO<sub>2</sub> and similar. When the carbon fibers were heated in carbon dioxide, the carbon composition in the fiber reacted with the carbon dioxide and evolved carbon monoxide. This reaction led to a decrease in the diameter of the resultant activated carbon fibers. As shown in Figures 6(a)–6(c), the diameter of PAN-ACHF for 80 min of activation obviously decreases when compared with that for 20 and 40 min of activation. It means that the longer the activation time, the more the reduction of carbon composition in PAN-ACHF.

Figure 7 shows the external surface of the PAN-ACHF made of the fiber activated at 800°C for 20, 40, 80 min, respectively. For activation time of 20 min, there are few pores on the surface of PAN-ACHF, as shown in Figure 7(a). It is suggested that there is not enough time to promote the diffusion of CO<sub>2</sub> into the amorphous region to react with carbon when activation time is short. After 40 min of activation, there are



**Figure 6** SEM micrographs of the cross-sections of PAN-ACHF ( $\times 1500$ ) (activation time of a, b, c is 20, 40, 80 min, respectively). The preparation of PAN-ACHF is same with the illustration of Figure 2. Then, the SEM micrographs of the cross-sections of PAN-ACHF developed at different activation time were obtained.



**Figure 7** SEM micrographs of the external surface of PAN-ACHF ( $\times 20,000$ ) (activation time of a, b, c is 20, 40, 80 min, respectively). The preparation of PAN-ACHF is same with the illustration of Figure 2. Then, the SEM micrographs of the external surface of PAN-ACHF developed at different activation time were obtained.

more pores on the surface of ACHF and the sizes of pores are more uniformed, as shown in Figure 7(b). It indicates that the external surface and the thinner region of the skin of the hollow fibers have been activated. The number of pores on the surface of ACHF continually increases after 80 min of activation, as shown in Figure 7(c). It indicates that the attack of carbon dioxide created more pores on the surface of ACHF and in the ACHF with activation time extending.

### CONCLUSIONS

The BET surface area of PAN-ACHF and surface area of mesopores gradually increase with activation time extending, and reach the maximum values, 780 and  $180 \text{ m}^2 \text{ g}^{-1}$ , respectively, when fibers are activated at  $800^\circ\text{C}$  for 100 min. The adsorption ratio to creatinine changes little with activation time extending and all values over all activation time are above 90%. The adsorption ratio to  $\text{VB}_{12}$  gradually increases with activation time extending before 60 min, and then becomes relatively constant from 60 to 100 min. After the activation process, the cross-sectional shape of ACHF, difinger-like porous structure, is preserved. The number of pores on the surface of PAN-ACHF increases with activation time extending. The amount of mesopores in PAN-ACHF made of fibers activated for different time increases with activation time extending

and the dominant pore sizes of mesopores in PAN-ACHF range from 2 to 5 nm.

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