

Effects of Oxidation Time on the Structure and Properties 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 oxidation time of PAN hollow fiber precursor on the microstructure, specific surface, pore size distribution, and adsorption properties of PAN-based activated carbon hollow fiber (PAN-ACHF) were studied in this work. Both of specific surface area and adsorption ratio to VB_{12} reach maximums when PAN hollow fibers are oxidized for 5 h in air. The adsorption ratios for creatinine are

all higher than 90% over all oxidation time. After 5 h of oxidation, the number of pores on the surface obviously increases, and the pore size is uniform. After 7 h of oxidation, the number of macropores in PAN-ACHF increases. The dominant pore sizes of mesopores in PAN-ACHF range from 2 to 5 nm. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 470–474, 2007

Key words: oxidation; polyacrylonitrile; activated carbon hollow fiber; adsorption properties

INTRODUCTION

Activated carbon fiber (ACF) has played a major role because it 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.^{1–4} Recently, the polyacrylonitrile (PAN)-based activated carbon hollow fiber (PAN-ACHF) has brought on many investigators' interests,^{5–8} since PAN-ACHF shows the largest adsorption capacity among the carbon surfaces.

The structure of the pores and their size distribution are largely predetermined by the nature of the raw material and its carbonization history.⁹ One of the most important steps in developing PAN carbon fibers is oxidation. During the stabilization stage, the following process are believed to take place: (1) cyclization of nitrile groups leading to hydronaphthiridine rings, (2) oxidative dehydrogenation leading to a certain degree of aromatization, and (3) oxidation of hydronaphthiridine rings leading mainly to acridone and some other structures.¹⁰

In this work, the PAN hollow fibers were dipped in ammonium dibasic phosphate aqueous solution, then oxidized at 230°C for different time ranging from 1 to

7 h, followed by carbonization in nitrogen and activation with carbon dioxide. This study examined the effects of oxidation time of PAN hollow fibers on the adsorption and structural properties, such as specific surface area, pore size distribution, and morphology of the PAN-ACHF.

EXPERIMENTAL

PAN (a copolymer of acrylonitrile, methyl methacrylate, itaconic acid) hollow fiber spun by dry-wet spinning setup was used as the precursor. The resultant hollow fiber had an inside diameter of 400 μm and an outside diameter of 500 μm . Figure 1 shows the porous structure of the PAN hollow fiber.

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 at 230°C for different time in air respectively, carbonized at 900°C for 30 min in nitrogen, and activated at 800°C for 40 min with carbon dioxide. A scanning electron microscope (SEM) (JEOL Model JSM-5600LV) was used to examine the cross section and external surface of fibers.

Burn-off and shrinkage ratio of PAN-ACHF were determined from a change in weight and length before and after activation. The PAN hollow fibers were cut to 15 cm in length and were weighed before activation. Then the length and weight of the PAN-ACHF were tested after activation. The burn-off and shrinkage ratio were calculated as follows:

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$$\text{Burn-off (wt \%)} = \frac{\text{Weight before activation} - \text{Weight after activation}}{\text{Weight before activation}} \times 100\%$$

$$\text{Shrinkage ratio (\%)} = \frac{\text{Length before activation} - \text{Length after activation}}{\text{Length before activation}} \times 100\%$$

Adsorption study for creatinine and VB₁₂ was carried out by a static process. The creatinine aqueous solution was prepared by adding 20 mg of creatinine to 1000 mL of distilled water and the VB₁₂ aqueous solution was prepared by adding 20 mg of VB₁₂ to 1000 mL of distilled water. Then 100 mg of PAN-ACHF was immersed in 20 mL of creatinine aqueous solution and 100 mg of PAN-ACHF was immersed in 20 mL of VB₁₂ aqueous solution at 37°C for 24 h. The amount of creati-

nine and VB₁₂ adsorbed was determined by the concentration difference before and after immersion in the solution. The creatinine and VB₁₂ concentrations of the solution were determined with a UV/vis spectrophotometer (Shanghai Techcomp 7500) at the wavelength of 510 and 361 nm, respectively. Absorbency of creatinine and VB₁₂ in the aqueous solutions reflects the difference of solution concentration. Then the adsorption ratio was calculated as follows:

$$\text{Adsorption ratio (wt \%)} = \frac{\text{Absorbency before adsorption} - \text{Absorbency after adsorption}}{\text{Absorbency before adsorption}} \times 100\%$$

Samples of PAN-ACHF were characterized by measuring specific BET surface area 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 (BJH) method.¹¹

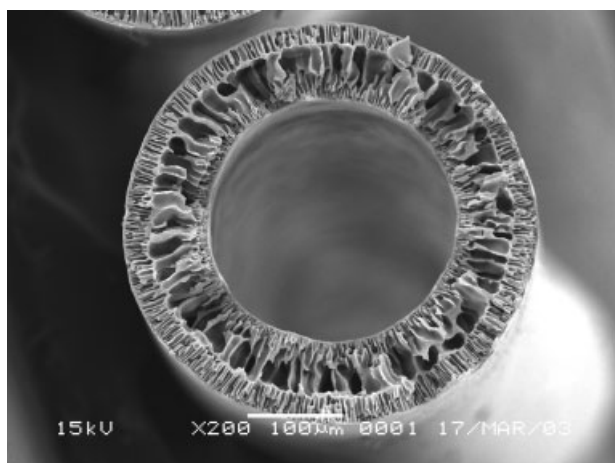


Figure 1 The cross section of virgin PAN hollow fiber ($\times 200$).

RESULTS AND DISCUSSION

Surface area and adsorption properties of PAN-ACHF

Pyrolysis of PAN fibers, the stabilization process, is necessary to develop the ACFs. The stabilization process of PAN fibers for transformation of the ladder polymer is best achieved in air (or in an oxygen-containing atmosphere) between 200 and 300°C to obtain stabilized fibers.

Figure 2 shows the variation of burn-off and shrinkage ratio of PAN-ACHF with oxidation time. The burn-off and the shrinkage ratio were determined from a change in weight and length before and after activation, and the calculation formulae are shown in Experimental section. As shown in Figure 2, the burn-off of PAN-ACHF slowly increases with oxidation time increasing from 1 to 5 h and then changes little. And the shrinkage of PAN-ACHF almost does not change with oxidation time increasing.

Figure 3 shows the variation of specific surface areas of PAN-ACHF with oxidation time. As shown in Figure 3, the surface area increases with oxidation time increasing, reaches a maximum ($666 \text{ m}^2 \text{ g}^{-1}$) when oxidation time is 5 h, and then decreases. It is suggested that with oxidation time increasing, more and more molecule chain scission in the hollow fibers occurs and these region of chain scission are attacked to develop into pores during the activation stage. Thus, the

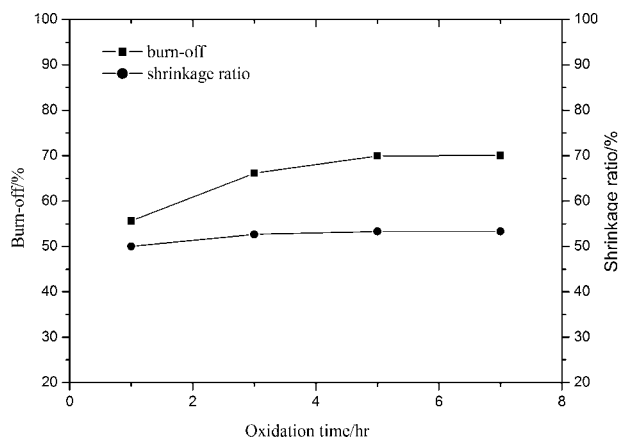


Figure 2 Burn-off and shrinkage ratio of PAN-ACHF versus oxidation time (the samples are pretreated with ammonium dibasic phosphate of 4% (wt %) concentration for 30 min, oxidized at 230°C for different time, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).

specific surface area of the resultant PAN-ACHF increases with oxidation time increasing. But, if oxidation time is too long, a lot of chain scission occurs, which develop into many larger pores during the activation stage, thus the specific surface area decreases. In the activated carbon, macropores (>50 nm) have small specific surface area and micropores (<2 nm) have large specific surface area.¹² It indicates that choosing proper oxidation time can increase surface area of PAN-ACHF.

Figure 4 shows the variation of adsorption ratio with oxidation time. The adsorption ratios to creatinine are all higher than 90% over all oxidation time. The adsorption ratio to VB₁₂ increases with oxidation time increasing from 1 to 5 h, reaches a maximum (96%),

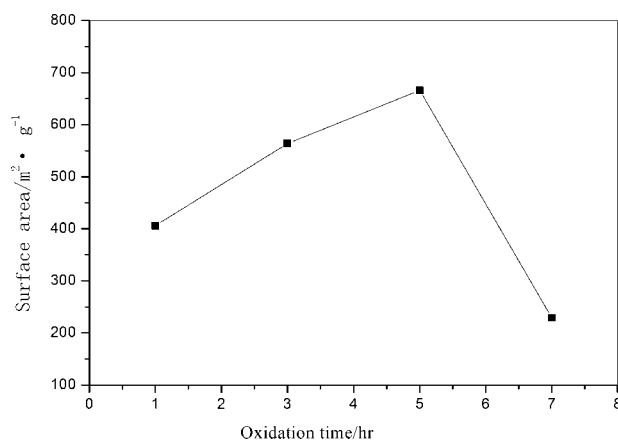


Figure 3 Specific surface area of PAN-ACHF versus oxidation time (the samples are pretreated with ammonium dibasic phosphate of 4% (wt %) concentration for 30 min, oxidized at 230°C for different time, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).

and then decreases. According to their molecule sizes, creatinine < VB₁₂, the molecule size of creatinine is less than 2 nm and primarily adsorbed by micropores (<2 nm). However, the molecule size of VB₁₂ is larger than 2 nm and primarily adsorbed by mesopores (2–50 nm). It indicates that there are more mesopores in PAN-ACHF made of the fibers oxidized at 230°C for 5 h than for other time.

Morphology of PAN-ACHF

When the PAN fibers were heated, ladder-polymer began to form above 200°C. Because both inner and outer surface of the hollow fibers were attacked by oxygen, the morphology of oxidized hollow fibers (OHF) is different from oxidized solid fibers. Dense ladder structure was formed in the skin region of the wall of OHF, whereas the original microvoid and finger-like structure was driven toward the inner region of the wall.¹³

Figure 5 shows the external surface of the PAN-ACHF made of the fiber oxidized at 230°C for 1, 3, 5, and 7 h, respectively. As shown in Figures 5(a) and 5(b), the number of pores on the surface is few when oxidation times are 1 and 3 h, respectively. This is because when the fibers are oxidized for short time, less scission of the molecular chains on the surface of the fibers occurs during oxidation and the occurrence of chain scission facilitates the formation of the pores. After 5 h of oxidation, the number of pores on the surface obviously increases, and the pore size is uniform, as shown in Figure 5(c). It is suggested that more scission of the molecular chains on the surface of the fibers occurs during oxidation when the fibers are oxidized for long time. These regions of chain scission are more likely to be attacked and to develop into pores during

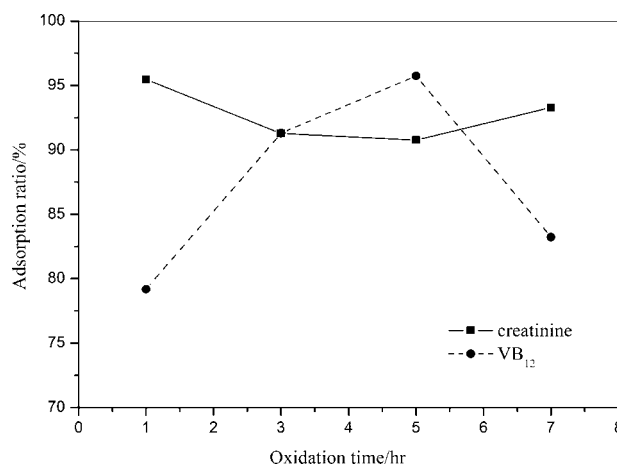


Figure 4 Adsorption ratio of PAN-ACHF versus oxidation time (the samples are pretreated with ammonium dibasic phosphate of 4% (wt %) concentration for 30 min, oxidized at 230°C for different time, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).

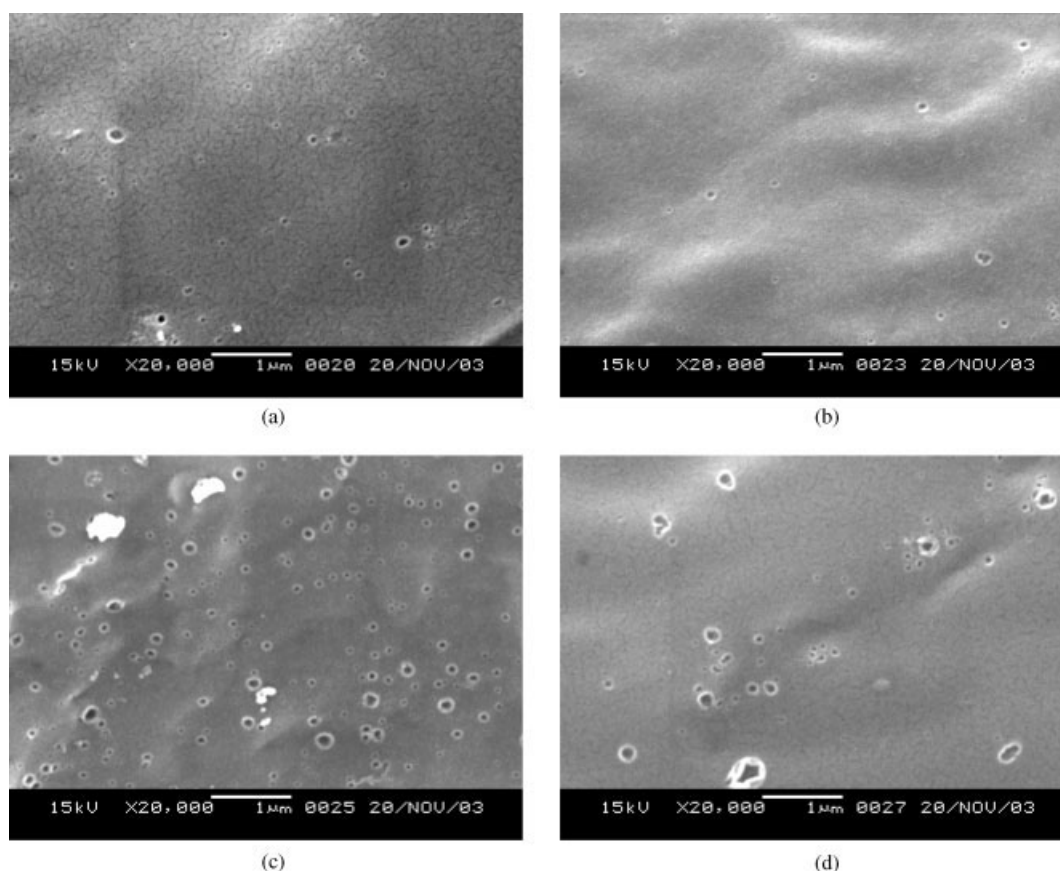


Figure 5 SEM micrographs of the external surface of PAN-ACHF ($\times 20,000$) oxidation time of (a), (b), (c), and (d) is 1, 3, 5, and 7 h, respectively (the samples are pretreated with ammonium dibasic phosphate of 4% (wt %) concentration for 30 min, oxidized at 230°C for different time, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).

the activation stages. After 7 h of oxidation, the number of pores on the surface decreases; however, the diameter of pores increases. This is probably because when the oxidation time is too long, a large quantity of chain scission not only on the surface of the fibers but also in the inner of the fibers has occurred during oxidation. Hence the pores gradually move toward the center of the wall of the hollow fibers and become larger.

Pore size distribution of PAN-ACHF

Figure 6 shows the pore size distribution of PAN-ACHF made of the fibers oxidized for 1, 3, 5, and 7 h, respectively. Because of the limits of apparatus, 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 by Figure 6. As shown in Figure 6, the maximum of incremental pore volume reaches 0.0093 mL g^{-1} when oxidation time is 5 h. Figure 6 shows the incremental pore volume of mesopores gradually decreases with average diameter, and dominant pore sizes of mesopores in PAN-ACHF range from 2 to 5 nm. The number of macro-

pores in PAN-ACHF made of the fibers oxidized for 7 h is higher than others, as shown in Figure 6, which is consistent with the analysis about surface area and

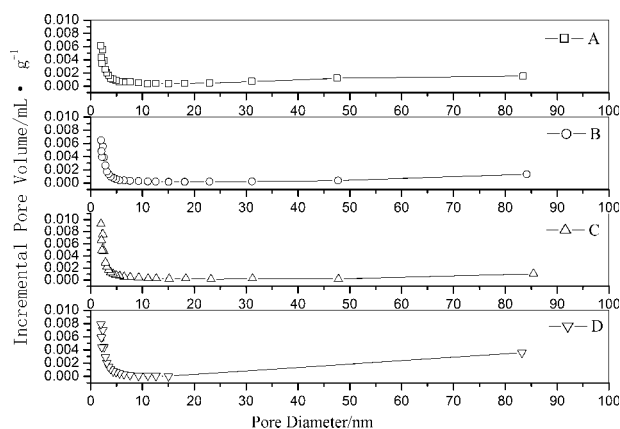


Figure 6 Pore size distribution of PAN-ACHF oxidation time of A, B, C, and D is 1, 3, 5, and 7 h, respectively (the samples are pretreated with ammonium dibasic phosphate of 4% (wt %) concentration for 30 min, oxidized at 230°C for different time, carbonized at 900°C for 30 min, and activated at 800°C for 40 min).

morphology. Moreover, a mass of micropores is existed in PAN-ACHF.

CONCLUSIONS

With oxidation time increasing, more and more molecule chain scission in the hollow fibers occurs and these region of chain scission are attacked to develop into pores during the activation stage. But, if oxidation time is too long, a lot of chain scission occurs, which develop into many larger pores during the activation stage, thus the specific surface area decreases. Both specific surface area and adsorption ratio to VB_{12} reach maximum when PAN hollow fibers are oxidized for 5 h in air. The adsorption ratios for creatinine are all higher than 90% over all oxidation time. After 5 h of oxidation, the number of pores on the surface obviously increases, and the pore size is uniform. After 7 h of oxidation, the number of macropores in PAN-ACHF increases. The

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

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