

Comparison about the Structure and Properties of PAN-Based Activated Carbon Hollow Fibers Pretreated with Different Compounds Containing Phosphorus

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Abstract: Polyacrylonitrile (PAN) hollow fibers were pretreated with five different compounds containing phosphorus, including ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, and then further oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. The effects of different compounds containing phosphorus as pretreating agents on the properties and structure of the resultant oxidized hollow fibers, carbon hollow fibers, and activated carbon hollow fibers are discussed. Comparing the Brunauer-Emmett-Teller (BET) surface area of PAN-activated carbon hollow fibers (ACHF) pretreated with five different compounds, ammonium diba-

sic phosphate > triammonium phosphate > ammonium dihydrogen phosphate > phosphoric acid > metaphosphoric acid, and the surface area of mesopores in PAN-ACHF pretreated with ammonium dibasic phosphate reaches maximum, $174 \text{ m}^2 \text{ g}^{-1}$. The adsorption ratio to mesomolecule adsorbate, VB_{12} , of PAN-ACHF pretreated with ammonium dibasic phosphate also reaches maximum, 97.7 wt %. Moreover, the dominant pore sizes of PAN-ACHF range from 2 to 5 nm in diameter. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 294–300, 2005

Key words: polyacrylonitrile; oxidized hollow fibers; carbon hollow fibers; activated carbon hollow fibers; compound

INTRODUCTION

Because of their excellent surface properties and adsorption capacity, activated carbon fibers have attracted increasing attention. An advantage of fibrous activated carbon over a finely divided, activated, powdered carbon is the higher bulk volume of the former, which can lead to higher adsorption rates because of the more open base structure.^{1–3} Therefore, activated carbon fibers have been widely used in various areas such as water treatment,^{4,5} the removal of SO_x and NO_x ,^{6,7} and the adsorption of toxic gases.^{8,9} Recently, the polyacrylonitrile-based activated carbon hollow fiber (PAN-ACHF) has brought on many investigators' interests,^{10–15} because PAN-ACHF shows the largest adsorption capacity among the carbon surfaces.

The active carbon in fiber form developed recently is increasingly applied in various areas. Active carbon fibers (ACFs) have unique characteristics compared to granular or powdered, activated carbons.¹⁶ The fibrous form is also favored because of the ease in handling when it is used in membranes or hollow forms by newly developed molding techniques. The inherent advantage of a favorable membrane surface area to

total separator unit volume is a well-established principle for hollow fiber applications. There have been numerous applications of hollow fiber technology to separation and purification in both industry and medicine, including the preparation of drinkable, high-quality water for the electronics and pharmaceutical industries, treatment of secondary effluent from sewage and processing plants, gas separation for industrial application, hemodialyzers, and the controlled release of a drug to mention only a few applications.¹⁷

Yang and Yu^{10–13} studied the structure and properties, pore-size distribution, surface area, and mechanical properties of PAN-ACHF. Linkov et al.¹⁸ reported that hollow fibers were used for gas separation and showed high fluxes and good selectivities. Schindler and Maier¹⁹ 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, suitable for separating particles.

In this research, the PAN hollow fibers were first dipped in ammonium dibasic phosphate aqueous solution, ammonium dihydrogen phosphate aqueous solution, triammonium phosphate aqueous solution, phosphoric acid aqueous solution, and metaphosphoric acid aqueous solution, respectively. Afterwards, the pretreated fibers were oxidized in the air at 230°C for 5 h, carbonized in nitrogen at 900°C for 70 min, and activated with carbon dioxide at 800°C for 80 min.

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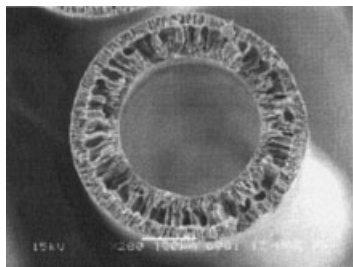


Figure 1 SEM micrographs of the cross section of virgin PAN hollow fiber ($\times 200$).

This study examined the effects of pretreatment with five different compounds containing phosphorus on the adsorption and structural properties, such as specific surface area, element analysis, pore size distribution, and morphology of PAN-based oxidized hollow fiber (PAN-OHF), PAN-based carbon hollow fiber (PAN-CHF), and PAN-based activated carbon hollow fiber (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 $400\ \mu\text{m}$ and an outside diameter of $500\ \mu\text{m}$. Figure 1 shows the porous structure of the PAN hollow fiber.

Virgin PAN hollow fibers were first dipped in ammonium dibasic phosphate aqueous solution, ammonium dihydrogen phosphate aqueous solution, triammonium phosphate aqueous solution, phosphoric acid aqueous solution, and metaphosphoric acid aqueous solution (the concentrations of all aqueous solution are 4 wt %) for 30 min, respectively. Afterwards, the pretreated fibers were oxidized in the air at 230°C for 5 h, carbonized in nitrogen at 900°C for 70 min, and activated with carbon dioxide at 800°C for 80 min.

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

Elemental analysis was carried out with an elemental analyzer (Elementar Americas, Inc., vario EL III). The oxidized hollow fibers were analyzed for carbon, nitrogen, and hydrogen content.

The aromatization index (AI value) of PAN-OHF was determined by an X-ray diffractometer (Rigaku, D/MAX-B) and was estimated by the formula²⁰

$$\text{AI}/\% = \frac{I_a}{I_a + I_p}$$

where I_a is the diffraction intensity of the aromatic structure at $\theta = 26^\circ$ and I_p is the diffraction intensity of the PAN crystal at $\theta = 17^\circ$.

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

adsorption ratio (wt %)

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

Samples of PAN-CHF and PAN-ACHF were characterized by measuring specific BET surface area and pore size distribution by using an auto-adsorption apparatus (Micromeritics Tristar 3000). The surface area was calculated by using the multipoint BET method. Pore volume and pore size distribution were determined from the nitrogen adsorption isotherms by using the Barrett, Joyner, and Halenda (BJH) method.²¹

RESULTS AND DISCUSSION

Properties and morphology of PAN-based oxidized hollow fibers

Aromatic index and element analysis of PAN-based oxidized hollow fibers

The incorporation of phosphorus to the fiber is effected in the form of a phosphorus compound. Oguwa et al.²² reported that, by adding the phosphorus compounds, the activation yield at the activation treatment of the fibers can be increased as well as the strength, abrasion, resistance, and adsorptive property of ACF can be improved. By adding phosphorus, the reaction of phosphorus and carbon produces diversified byproducts that continuously flee from the surface of fibers and pores are formed.

An important step in preparing activated carbon fibers from PAN fibers is to oxidize the precursor at $200\text{--}300^\circ\text{C}$ in air. It will convert the precursor to an infusible stable ladder polymer for subsequent higher temperature processing. In this work, we pretreated PAN hollow fibers with five different compounds containing phosphorus and compared the properties and morphology of five resultant oxidized fibers.

Table I shows the shrinkage ratio and aromatic index (AI value) of five fibers. As shown in Table I, we

TABLE I
The Properties and Elemental Analysis of PAN-Based Oxidized Hollow Fibers

Sample	A	B	C	D	E
Shrinkage ratio/%	37.3	30.0	30.0	30.0	30.0
AI value/%	52.4	52.7	53.3	44.5	57.6
C%	48.34	47.09	52.90	47.47	46.55
N%	14.60	15.39	16.16	13.81	13.54
H%	2.213	2.374	2.486	2.860	2.665

Samples of A, B, C, D, and E are pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively.

can see that the shrinkage ratios of five PAN-OHFs are approximately same and just the shrinkage ratio of sample A (fibers pretreated with ammonium dibasic phosphate) is a little high. The AI value is used as the reference value for the degree of stabilization.²³ A higher AI value indicates that there are more ladder polymers converted from $C\equiv N$ bonds in PAN fibers.²⁴ The AI values of samples A, B, and C change little; that of sample D is the lowest, and that of sample E is the highest. It means that the degree of stabilization of PAN-OHF pretreated with metaphosphoric acid is higher than others. Generally speaking, the AI value of fibers is controlled between 0.45 and 0.55 to obtain stabilized fibers. If the AI value is less than 0.41, it means that the degree of stabilization is low and the resultant oxidized fibers could not be carbonized ul-

teriorly. If the AI value is more than 0.60, it means that the degree of stabilization is too high and immoderate, and the resultant carbonization yield is low. So, it indicates that samples A, B, and C (fibers pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, and triammonium phosphate, respectively) have moderate AI value.

Morphology of PAN-based oxidized hollow fibers

Figure 2 shows the cross section of the PAN-OHF pretreated with five different compounds. The cross-sectional shape of OHF in Figure 2(a–e), di-finger-like porous structure, is preserved after oxidation. It means that the oxidation process keeps the hollow shape of virgin hollow fibers and is necessary to develop the carbon hollow fibers and activated carbon hollow fibers.

Properties and morphology of PAN-based carbon hollow fibers

Surface area of PAN-based carbon hollow fibers

During the stage of carbonization, the hydroxyl groups present in the oxidized PAN fibers start crosslinking condensation reactions, which help in reorganization and coalescence of the cyclized sections. This crosslinking probably fixes the structure of the polymer, whereas the remaining linear segments become either cyclized or undergo chain scission evolving the gaseous products. This cyclized structures un-

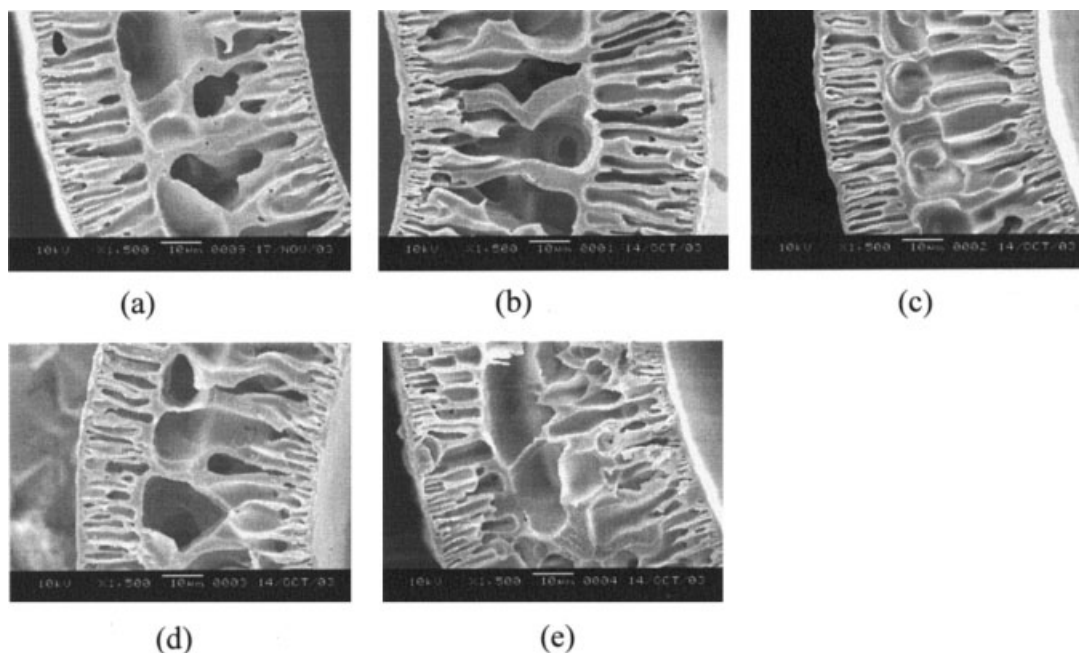


Figure 2 SEM micrographs of the cross sections of PAN-OHF ($\times 1500$). Samples of a, b, c, d, and e are pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively.

TABLE II
The Properties of PAN-Based Carbon Hollow Fibers

Sample	A	B	C	D	E
Weight loss/%	45.1	42.6	43.1	38.4	38.3
Shrinkage ratio/%	52.0	45.3	46.7	45.3	44.0
BET surface area/m ² g ⁻¹	59	4.1	5.8	2.9	13.7

Samples of A, B, C, D, and E are pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively.

dergo dehydrogenation and denitrogenation and fuse a heterocyclic ring system.²⁵

The carbonization of oxidized fibers is also an important step in preparing activated carbon fibers from PAN fibers. By adding different compounds containing phosphorus to the surface of PAN hollow fiber, the weight loss and shrinkage ratio of the resultant carbon hollow fiber are different. As shown in Table II, the weight losses of PAN-CHF pretreated with phosphoric acid and metaphosphoric acid are lower than others. However, the shrinkage ratio of PAN-CHF pretreated with ammonium dibasic phosphate is higher than the other four fibers.

Morphology of PAN-based carbon hollow fibers

Figure 3 shows the cross section of the PAN-CHF pretreated with five different compounds. The cross-sectional shape of PAN-CHF in Figure 3(a–e), di-finger-

like porous structure, is preserved after carbonization. It means that the carbonization process ulteriorly keeps the hollow shape of the virgin hollow fiber and is necessary to develop the activated carbon hollow fibers.

Properties and morphology of PAN-based activated carbon hollow fibers

Surface area and adsorption properties of PAN-based activated carbon hollow fibers

During the carbonization stage of carbon fiber, formation of carbon basal planes was due to the crosslinking reaction, and noncarbon elements evolved. The mechanical strength was increased, but the surface area was reduced and hence was unsuitable for adsorption applications. By activating in CO₂ at high temperature, micropores and mesopores suitable for adsorption purpose would appear on the surface and the interior of the carbon fiber.²⁶ By adding different compounds containing phosphorus to the surface of PAN hollow fibers, the properties of the resultant PAN-ACHF are different such as weight loss, shrinkage ratio, surface area, pore size distribution, and adsorption ratio. As shown in Table III, the weight loss of PAN-ACHF pretreated with ammonium dibasic phosphate is the highest and that of ACHF pretreated with phosphoric acid is the lowest. The shrinkage ratio of PAN-ACHF pretreated with ammonium dibasic phosphate is a little higher than others. Adsorption ratio to creatinine of PAN-ACHF pretreated with metaphos-

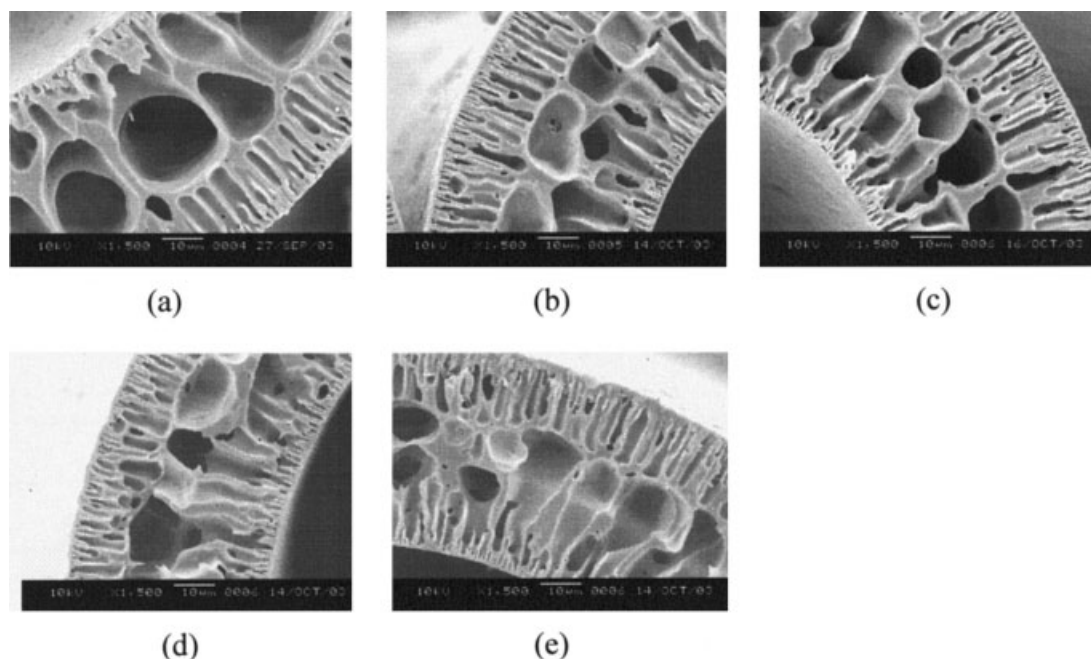


Figure 3 SEM micrographs of the cross sections of PAN-HCF ($\times 1500$). Samples of a, b, c, d, and e are pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively.

TABLE III
The Properties of PAN-Based Activated Carbon Hollow Fibers

Sample	A	B	C	D	E
Weight loss/%	60.4	59.7	60	54.8	57.5
Shrinkage ratio/%	52.0	49.3	49.3	49.3	49.3
BET surface area/m ² g ⁻¹	766	659	705	451	428
Surface area of mesopores/m ² g ⁻¹	174	104	93	71	75
Adsorption ratio to creatinine/%	93.8	97.3	89.5	89.5	97.6
Adsorption ratio to VB ₁₂ /%	97.7	93.4	94.3	94.7	97.2

Samples of A, B, C, D, and E are pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively.

phoric acid is the highest, and that to VB₁₂ of PAN-ACHF pretreated with ammonium dibasic phosphate is the highest. Moreover, the BET surface area of PAN-ACHF pretreated with ammonium dibasic phosphate is the highest and reaches 766 m² g⁻¹, and correspondingly, the surface of mesopores reaches 174 m² g⁻¹. It indicates that the number of micropores and mesopores in PAN-ACHF pretreated with ammonium dibasic phosphate is the highest among five PAN-ACHF pretreated with different compounds.

Pore size distribution of PAN-based activated carbon hollow fibers

Figure 4 shows the pore size distribution of the PAN-ACHF pretreated with five different compounds. Because of the limits of apparatus, pore diameters < 2 nm could not be tested. However, the distribution of mesopores (2–50 nm) and macropores (>50 nm) can be observed in Figure 4. As shown in Figure 4, the

dominant pore sizes of mesopores range from 2 to 5 nm in diameter, and PAN-ACHF pretreated with ammonium dibasic phosphate has the maximum of incremental pore volume. It is suggested that among five different compounds containing phosphorus, ammonium dibasic phosphate is the best pretreating agent to develop the BET surface area, surface of mesopores, adsorption properties, and so on of PAN-ACHF.

Morphology of PAN-based activated carbon hollow fibers

Figures 5 and 6 show the cross section and external surface of the PAN-ACHF pretreated with five different compounds. The cross-sectional shape of PAN-ACHF in Figure 5(a–e), di-finger-like porous structure, is preserved after activation. As shown in Figure 6, obvious holes can be observed on the external surface of PAN-ACHF pretreated with ammonium diba-

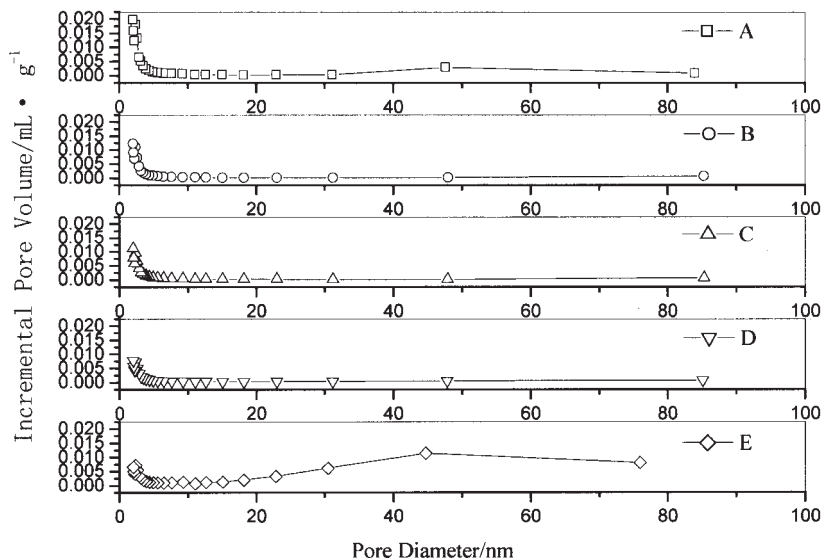


Figure 4 Incremental volume of PAN-ACHF pretreated with different compounds. Samples of A, B, C, D, and E are pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively.

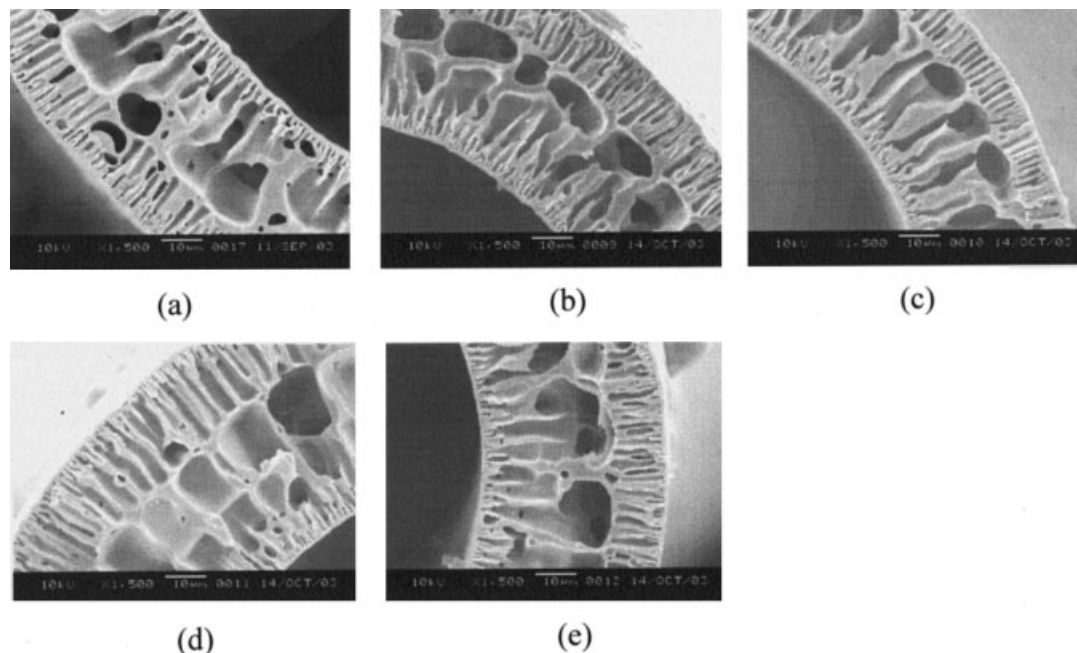


Figure 5 SEM micrographs of the cross sections of PAN-ACHF ($\times 1500$). Samples of a, b, c, d, and e are pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively.

dic phosphate. It means that the external surface and the thinner region of the skin of the hollow fiber were activated; the skin of the fiber was burned off, and the molecules in the amorphous area were broken. The closed pores were open. On the external surface of

PAN-ACHF pretreated with phosphoric acid, there are no obvious pits. On other external surface of samples, holes or pits cannot be observed (white matter on the surface is compounds not reacted). It means that CO_2 cannot diffuse deeper to cause activation in the

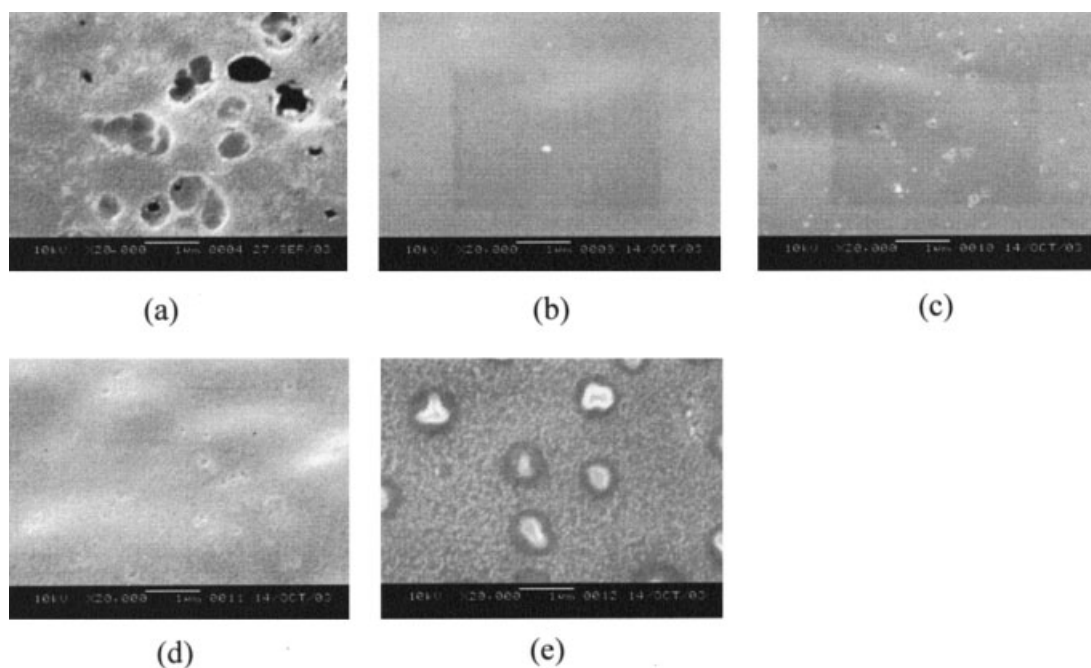


Figure 6 SEM micrographs of the external surface of PAN-ACHF ($\times 20,000$). Samples of a, b, c, d, and e are pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively.

depth of the hollow fibers when PAN hollow fibers were pretreated with ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid.

CONCLUSION

PAN hollow fibers were pretreated with ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid, respectively. Then, pretreated PAN hollow fibers were oxidized, carbonized, and activated to obtain PAN-OHF, PAN-CHF, and PAN-ACHF, in that order. Compared to the BET surface area of PAN-ACHF pretreated with five different compounds, ammonium dibasic phosphate > triammonium phosphate > ammonium dihydrogen phosphate > phosphoric acid > metaphosphoric acid, and the surface area of mesopores in PAN-ACHF pretreated with ammonium dibasic phosphate reaches maximum, $174 \text{ m}^2 \text{ g}^{-1}$. The adsorption ratio to mesomolecule adsorbate, VB_{12} , of PAN-ACHF, pretreated with ammonium dibasic phosphate also reaches maximum, 97.7 wt %. Moreover, the dominant pore sizes of PAN-ACHF range from 2 to 5 nm in diameter.

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