Effects of Ammonium Dibasic Phosphate Pretreatment Time on the Structure and Properties of PAN-Based Activated Carbon Hollow Fibers

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ABSTRACT: Polyacrylonitrile (PAN) hollow fibers were pretreated with ammonium dibasic phosphate aqueous solution, then further oxidized in air, carbonized in nitrogen, and activated with carbon dioxide. The effects of pretreatment time of PAN hollow fibers in ammonium dibasic phosphate aqueous solution on the microstructure, specific surface, pore-size distribution, and adsorption properties of PAN-based activated carbon hollow fibers (PAN-ACHF) were studied in this work. After the activation process, the Brunaner–Emmett–Teller (BET) surface area of the PAN-ACHF and surface area of mesopores in the PAN-ACHF increases and reaches 513 m^2 g^{-1} and 66 m^2 g^{-1} respectively, when the dipping time of PAN hollow fibers in ammonium dibasic phosphate aqueous solution is 30 min. The adsorptions to creatinine and VB$_{12}$ of PAN-ACHF are much high, reach 95% and 86% respectively, when dipping time is 30 min. The dominant pore sizes of mesopores in PAN-ACHF range from 2 nm to 5 nm. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2448–2453, 2006

Key words: polyacrylonitrile; ammonium dibasic phosphate; pretreatment time; surface area; adsorption

INTRODUCTION

Since activated carbon fibers (ACF) appeared in UK, they have been studied and produced on commercial scale for tens of years. ACF have attracted much importance all over the world owing to its special pore structure, excellent adsorption, and extensive uses.[1,2] These fibers have uniform slit-shaped micropores and great surface area. ACF are produced by carbonizing raw materials such as polyacrylonitrile (PAN), cellulose, phenolic, or pitch fibers. Recently, the PAN-based activated carbon hollow fibers (PAN-ACHF) brought on many investigators' interests,[3–8] since PAN-ACHF show the largest adsorption capacity among the carbon surfaces.

Ming-Chien Yang and Da-Guang Yu[3–6] studied the structure and properties, pore-size distribution, surface area, and mechanical properties of PAN-ACHF. Linkov et al.[7–9] reported that hollow fibers have been used for gas separation and show high fluxes and good selectivities. Schindler and Maier[10] 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.

It is well known that the activation process is essential to high performance ACF. Basically, ACF can be prepared by physical and chemical activation or a mix of both. Physical activation implies the pyrolysis of the precursor followed by the activation with gases, such as carbon dioxide, air, steam, or a mixture of them. Chemical activation consists in the pyrolysis at relatively low temperature under the presence of an activating agent. Physical activation is usually performed with steam or carbon dioxide at a temperature between 800 and 1000°C to yield microporous materials in which high surface area are developed as the carbon is burnt off.[11] In the chemical activation process, the raw material is impregnated with the chemical activating agents such as phosphoric acid, sulfuric acid or nitric acid, and consecutively pyrolyzed at a temperature between 400 and 600°C in the absence of air.[12–16] In the mix of chemical activation and physical process, the raw material is impregnated with the chemical activating agents such as phosphate, sulfate or chloride, then activated at a temperature between 800 and 900°C with activation gas.[17–19] Phosphate salts and ammonium salts are often used as chemical activating agents.[20] But it has not been known that why the two sorts of salts are more favorable than other compounds, and how they affect the yields and specific areas of ACF, etc. The effect of five different chemical activating agents including ammonium dibasic phosphate, ammonium dihydrogen phosphate, triammonium phosphate, phosphoric acid, and metaphosphoric acid on the

structure and properties of PAN-ACHF, is studied in our previous work.[21] It is indicated that the Brunaner–Emmett–Teller (BET) surface area and the adsorption ratio to mesomolecule adsorbate, VB_{12} of PAN-ACHF pretreated with ammonium dibasic phosphate reach maximum.

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. Ammonium dibasic phosphate as a pretreatment agent was used to prepare PAN-based activated carbon hollow fiber (PAN-ACHF). This study examined the effects of dipping time of PAN hollow fiber precursor in ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration for different time on the adsorption and structural properties, such as specific surface area, pore size distribution, and morphology of PAN-ACHF. We discussed the adsorption properties of the resultant PAN-ACHF to creatinine and VB_{12} whose molecular weights are 113 and 1355.4 respectively. VB_{12} is a kind of vitamin. It is the purpose of this paper to discuss what pretreatment condition provides high surface area and high adsorption ratio for the PAN-ACHF prepared from PAN hollow fibers.

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.

Original PAN hollow fibers were first dipped in ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration for different time periods. Then the pretreated fibers were dried. Afterwards, the pretreated fibers were oxidized in the air at 270°C for 2 h, carbonized in nitrogen at 900°C for 30 min, activated with carbon dioxide at 800°C for 40 min to obtain PAN-based activated carbon hollow fiber (PAN-ACHF). The pretreatment time of PAN hollow fibers in ammonium dibasic phosphate was varied from 0 to 120 min.

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_{12} 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_{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 UV–vis spectrophotometer (Shanghai Techcomp. 7500) at the wavelength of 510 nm 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 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, surface area of mesopores, and pore size distribution using an auto-adsorption apparatus (Micromeritics Tristar 3000). The surface area was calculated using the multipoint BET method. Pore volume and pore size distribution were determined from the nitrogen adsorption isotherms using the Barrett, Joyner, and Halenda (BJH) method.[22]

RESULTS AND DISCUSSION

Dipping ratio of PAN hollow fiber

Figure 2 shows the variation in dipping ratio of PAN hollow fiber with dipping time of PAN hollow fiber in the ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration. The dipping ratio was determined from a change in weight of PAN hollow fibers
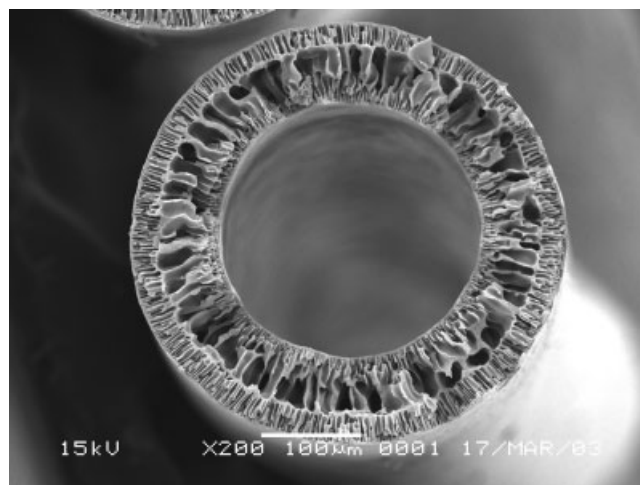
Figure 1 the cross section of original PAN hollow fiber (×200).
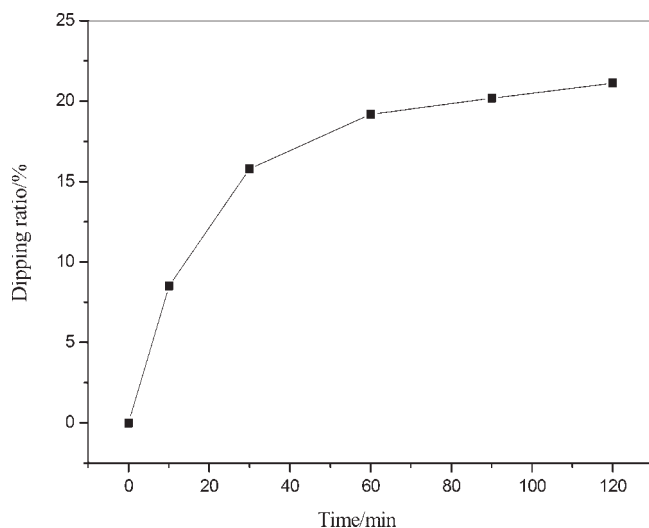
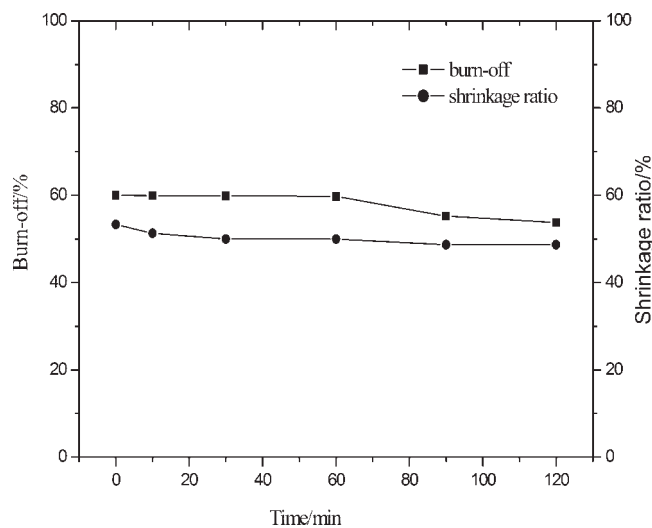**Figure 2** Dipping ratio of PAN hollow fiber versus dipping time.

before and after dipping. As shown in Figure 2, dipping ratio of PAN hollow fiber sharply increases with dipping time before 30 min, then gradually increases. It is suggested that the amount of ammonium dibasic phosphate in PAN hollow fiber increases quickly before 30 min of dipping time, then slowly increases with increasing dipping time.

Surface area and adsorption properties of PAN-ACHF

Ikegami et al.[19] studied the method for manufacture of activated carbon fiber and the result shows that activated carbon fibers of high adsorbing ability are obtained stably in short time at 900°C when fibers containing phosphorous are activated at high temperatures.

A certain amount of phosphorous compound can be processed in the preprocess to achieve a higher yield ratio of carbonization or activation. Figure 3 shows the variation in burn-off and shrinkage ratio of PAN-ACHF with dipping 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. As shown in Figure 3, the weight loss of the fibers changes little with dipping time increasing before 60 min, then decreases slowly. The shrinkage ratio changes little over all dipping time.

Ammonium dibasic phosphate as chemical activator to pretreat PAN hollow fibers, play an important role in PAN-ACHF's manufacture. It can affect the dehydrogenation and decomposition of PAN hollow fiber, and then directly affect the structure and properties of products as well as efficiency of production. Ching-Iuan Su et al.[17] reported that a certain amount of phosphorate compounds must be processed in the preprocess to achieve a higher extraction rate of carbonization or activation.


Figure 3 Burn-off and shrinkage ratio of PAN-ACHF versus dipping time. Original PAN hollow fibers were first dipped in ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration for different time. Afterwards, the pretreated fibers were oxidized in the air at 270°C for 2 h, carbonized at 900°C for 30 min, activated at 800°C for 40 min to obtain PAN-based activated carbon hollow fiber (PAN-ACHF). Then the burn-off and shrinkage ratio of the resultant PAN-ACHF were tested.

Figure 4 shows the variation in BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF with dipping time of PAN hollow fiber in the ammonium dibasic phosphate aqueous solution. As shown in Figure 4, BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF gradually increase before 30 min, and reach the maximum ($513 \ m^2 \ g^{-1}$ and $66 \ m^2 \ g^{-1}$ respectively) when dipping
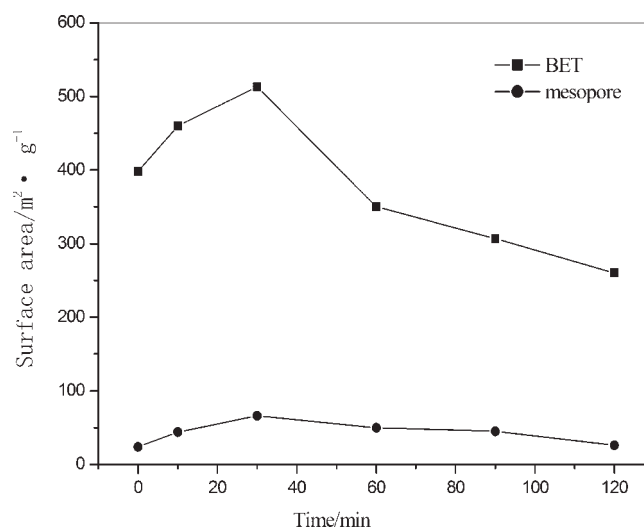
Figure 4 Surface area of PAN-ACHF versus dipping time. The preparation of PAN-ACHF is same with the illustration of Figure 3. Then BET surface areas of PAN-ACHF and surface area of mesopores in PAN-ACHF developed at different dipping time were tested.
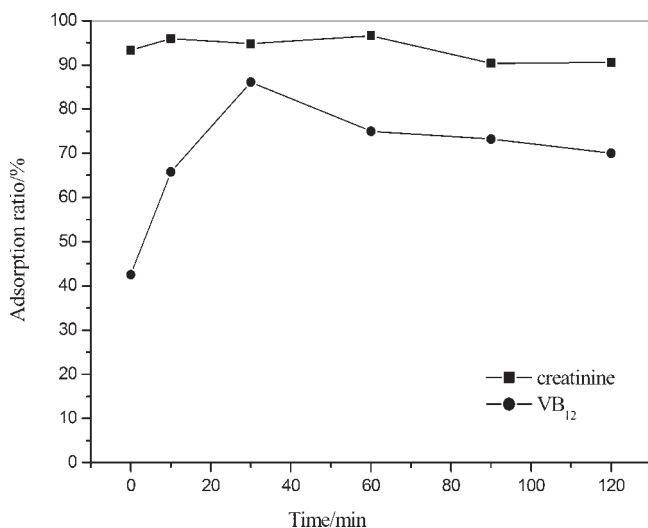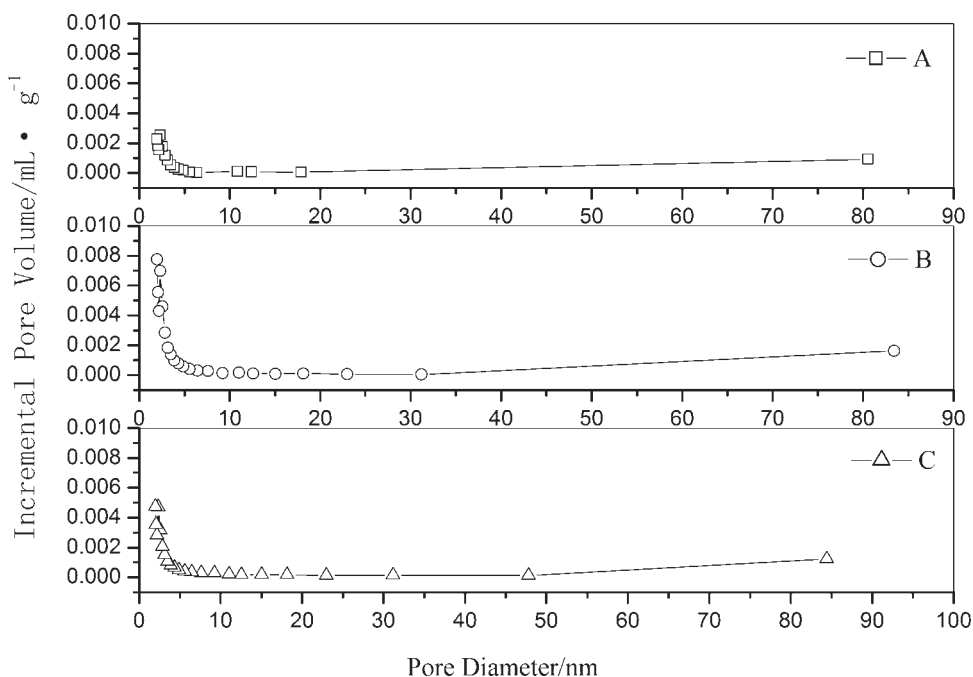
Figure 5 Adsorption ratio of PAN-ACHF versus dipping time. The preparation of PAN-ACHF is same with the illustration of Figure 3. Then the adsorption ratios of PAN-ACHF developed at different dipping time were tested.

time is 30 min, then gradually decrease. It is suggested that the number of micropores and mesopores is most in PAN-ACHF pretreated for 30 min, and the pores in PAN-ACHF are mainly composed of micropores. The ammonium dibasic phosphate coated on the surface of PAN hollow fibers is able to diffuse or migrate into the interior of hollow fiber through misaligned sheath layers and microstructural flaws and cracks in the hollow fibers with increasing temperature. Micropores

and mesopores produce on the surface and in the interior of PAN-ACHF when ammonium dibasic phosphate decomposes at lower temperature since decomposing temperature of ammonium dibasic phosphate is lower. In the later reaction, activation gas, carbon dioxide in this experiment, can easily diffuse to the interior of PAN-ACHF because of the existence of micropores and mesopores in PAN-ACHF at the beginning of activation process. Thus, a mass of micropores and mesopores produce in the interior of PAN-ACHF and the surface area of PAN-ACHF is higher. Therefore, many pores including micropores and mesopores produce in PAN-ACHF, and PAN-ACHF with high surface area was obtained when dipping time is 30 min. But, a mass of micropores and mesopores turned into macropores when dipping time is too long and there is excessive ammonium dibasic phosphate in PAN hollow fibers. Because macropores have small specific surface area, the surface area of PAN-ACHF decreases when dipping time exceeds 30 min. So, higher surface area of PAN-ACHF can be obtained when PAN hollow fibers are suitably pretreated in ammonium dibasic phosphate aqueous solution.

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 cap-

Figure 6 Pore size distribution of PAN-ACHF. The preparation of PAN-ACHF is same with the illustration of Figure 3. Then with average pore diameter increasing, incremental pore volumes of PAN-ACHF developed at different dipping time were tested.

illary 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. According to their molecule sizes, creatinine < VB_{12}, the molecule size of creatinine are less than 2 nm and primarily adsorbed by micropores (<2 nm). However, the molecule size of VB_{12} is larger than 2 nm and primarily adsorbed by mesopores (2–50 nm).

Figure 5 shows the variation in adsorption ratio of PAN-ACHF with dipping time of PAN hollow fiber. As shown in Figure 5, the adsorption ratios to creatinine are all higher than 90% over the whole dipping time. The adsorption ratios to VB_{12} gradually increase with the dipping time and reach a maximum (86%) when dipping time is 30 min, then decreases slowly. It is suggested that the number of mesopores in PAN-ACHF increases with the dipping time, and reaches the high-

est value when dipping time is 30 min. This conclusion is coincident with that concluded after Figure 4.

Pore size distribution of PAN-ACHF

Figure 6 shows the pore size distribution of the PAN-ACHF made of fiber dipped for 0, 30 min, 90 min 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 increases with dipping time, and reaches 0.0078 mL g^{-1} when dipping time is 30 min. Figure 6 shows that the incremental pore volume of mesopores gradually decreases with average diameter, and dominant pore sizes of mesopores in PAN-ACHF range from 2 nm to 5 nm. As shown in Figure 4, the surface
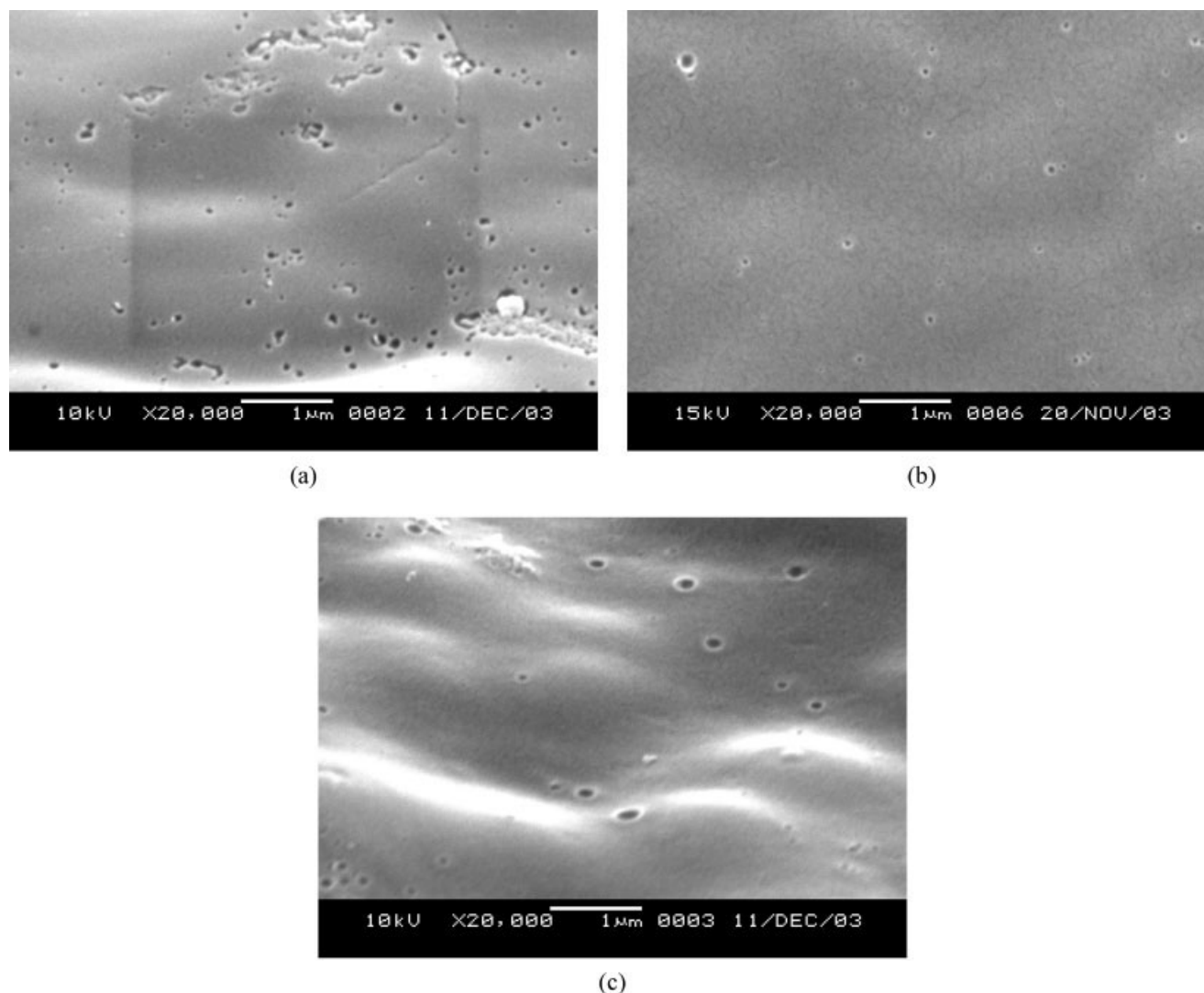
Figure 7 SEM micrographs of the external surface of PAN-ACHF(×20,000). The preparation of PAN-ACHF is same with the illustration of Figure 3. Then the SEM micrographs of the external surface of PAN-ACHF developed at different dipping time were obtained.

areas of mesopores in PAN-ACHF are much lower than that of BET surface area of PAN-ACHF. It indicates that the pores in PAN-ACHF are mainly formed by micropores and just has a small quantity of mesopores over the whole dipping time.

Morphology of PAN-ACHF

Figure 7 shows the external surface of the PAN-ACHF made of the fiber dipped for 0, 30 min, 90 min respectively. For the PAN-ACHF made of the fiber that is not dipped, there are some pores on the surface of ACHF. However, the size and distribution of pore diameter are not uniform, as shown in Figure 7(a). As shown in Figure 4, the surface area and surface area of mesopores in PAN-ACHF made of the fiber that is not dipped is lower than those in PAN-ACHF made of the fiber dipped for different time periods, although there are some uneven pores on the surface of the PAN-ACHF made of the fiber that is not dipped. It is suggested that ammonium dibasic phosphate with appropriate quantity promotes more pores, including micropores and mesopores, to produce in PAN-ACHF. After 30 min of dipping, there are some pores of uniform size, but the number of pores on the surface is few, as shown in Figure 7(b). It is suggested that the use of ammonium dibasic phosphate results in the development of porosity. After 90 min of dipping, the number of pores on the surface began to increase compared with Figure 7(b), and the size of pore diameter is bigger, as shown in Figure 7(c). It is suggested that excessive ammonium dibasic phosphate in PAN-ACHF decomposes and more macropores are produced when dipping time is 90 min.

CONCLUSIONS

Ammonium dibasic phosphate greatly promotes pores, including micropores and macropores, in PAN-ACHF when PAN hollow fiber is dipped in ammonium dibasic phosphate aqueous solution. Dipping time has little influence on the weight loss and shrinkage of resultant PAN-ACHF. When PAN hollow fibers are dipped in ammonium dibasic phosphate aqueous solution of 4% (wt %) concentration for 30 min, because of decomposing of ammonium dibasic phosphate, the number of pores within and on the surface of the resultant PAN-ACHF reaches maximum and BET surface area of PAN-ACHF and surface area of mesopores in PAN-ACHF also reach the maximum ($513 \, \mathrm{m^2 \, g^{-1}}$ and $66 \, \mathrm{m^2 \, g^{-1}}$ respectively). The adsorption ratios to creatinine are all higher than 90% over the whole dipping time. The adsorption ratios to VB_{12} gradually increase with dipping time and reach a maximum (86%) when dipping time is 30 min, then decreases slowly. The dominant pore sizes of mesopores in PAN-ACHF range from 2 nm to 5 nm.

References

1. Nakorn, W.; Hatori, S.; Nakagawa, H.; Miura, K. Carbon 2003, 41, 933.
2. Arons, G. N.; Machair, R. N.; Coffin, L. G.; Hogan, H. D. Text Res J 1974, 44, 874.
3. Yang, M.-C.; Yu, D.-G. J Appl Polym Sci 1998, 58, 185.
4. Yang, M.-C.; Yu, D.-G. Text Res J 1996, 66, 115.
5. Yang, M.-C.; Yu, D.-G. J Appl Polym Sci 1996, 69, 1725.
6. Yang, M.-C.; Yu, D.-G. J Appl Polym Sci 1996, 62, 2287.
7. Linkov, V. M.; Sanderson, R. D.; Jacobs, E. P. J Mat Sci 1994, 95, 93.
8. Linkov, V. M.; Sanderson, R. D.; Jacobs, E. P. Polym Int 1994, 35, 239.
9. Linkov, V. M.; Sanderson, R. D.; Jacobs, E. P. J Mat Sci Lett 1994, 13, 600.
10. Schindler, E.; Maier, F. U.S. Pat. 4,919,860, 1990.
11. Dawson, E. A.; Parkes. G. M. B.; Bvarnes, P. A.; Chinn, M. J. Carbon 2003, 41, 571.
12. Benaddi, H.; Bandosz, T. J.; Jagiello, J.; Schwarz, J. A.; Rouzaud, J. N.; Legras, D.; Beguin, F. Carbon 2000, 38, 669.
13. Evans, M. T. B.; Halliop, E.; MacDonald, J. A. F. Carbon 1999, 37, 269.
14. Ahmadpour, A.; King, B. A.; Do, D. D. Ind Eng Chem Res 1998, 37, 1329.
15. Freeman, J. J.; Gimblitt, F. G. R.; Roberts, R. A.; Sing, K. S. W. Carbon 1988, 26, 7.
16. Huidobro, A.; Pastor, A. C.; Rodrigues-Reinoso, F. Carbon 2001, 39, 389.
17. Su, C.-I.; Yeh, R.-S.; Wang, C.-L. Text Res J 2004, 74, 966.
18. Park, S.-J.; Kim, K.-D. Carbon 2001, 39, 1741.
19. Ikegami, S.; Hirai, M.; Izumi, K.; Shimazaki, K. U.S. Pat. 4,412,937, 1983.
20. Suzuki, M. Carbon 1994, 32, 557.
21. Sun, J.; Wu, L.; Wang, Q. J Appl Polym Sci 2005, 96, 294.
22. Rist, L. P.; Harrison, D. P. Fuel 1985, 64, 291.