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Macroporous Activated Carbon Fibers from Rayon Precursors Impregnated with Phosphoric Acid

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Novel activated carbon fibers (ACFs) from rayon precursors impregnated with phosphoric acid (H_3PO_4), containing abundant macropores (pore size $>$ 50 nm), were successfully obtained. The physical properties of these ACFs were examined. The BET surface was obtained; SEM observations showed that the concentration of H_3PO_4 impregnation strongly influenced the surface morphology and the porous texture of the resulting ACFs. The shape of the pores was nearly round and we could estimate the pore size was distributed between 20 and 150 nm. Infrared spectroscopy (IR) was applied to investigate the pyrolysis process of the rayon precursors with H_3PO_4. In addition, P-containing substances, which should perhaps be acid phosphates or polyphosphates, can be observed on the surface of the resulting ACFs from SEM photos. Impregnation made the dehydration become more predominant during the pyrolysis process.

Keywords activated carbon fibers, macropores, BET surface area, SEM, IR, TGA

Introduction

In recent years, research on porous carbon materials has been very active. The forms of porous materials include the conventional activated carbon bulk, activated carbon fibers, fine carbon particles, etc. Activated carbon fibers have received considerable attention because of their high adsorption rates and capacities, easy preparation of various forms and their wide applicability (1).

According to IPUAC, pores on the surface of ACFs are classified into three types, namely macropores (pore size $>$ 50 nm), mesopores (2 nm $<$ pore size $<$ 50 nm) and micropores (pore size $<$ 2 nm). Most pores in conventional ACF including pitch-based, PAN-based and rayon-based ACF are micropores (pore size $<$ 2 nm) (2).

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It is well known that the presence of micropores is essential for the adsorption of small gas molecules in ACFs. However, when the adsorbate is a polymer, dye or vitamin, only macropores or mesopores allow the adsorption of such giant molecules and can keep even bacteria (3). For example, influenza virions measure between about 80 nm and 120 nm in diameter and the sizes of coronaviruses are between about 75 nm and 160 nm (4). We proposed to design a novel ACF with both macropores and micropores on its surface. Macropores have the function of acting as traps to capture the macromolecules such as coronaviruses, while micropores can guarantee a high specific area and grab the spikes of coronaviruses (5). There are two problems existing in the proposal. One problem is how to get the macropores. Another one is how to manufacture a macroporous ACF with a high specific area and good adsorption properties. This paper introduces a new method to alleviate these problems.

Experimental

Materials

Rayon fibers, without any surface pretreatment, were provided by Hubei Chemical Fibers Co., Ltd. The fibers were immersed in a mixed solution containing NaCl and H_3PO_4 for 9 h. The impregnation ratio of the mixed solution was mainly determined by the concentration of H_3PO_4 from 5 wt% to 20 wt%, while NaCl in the solution was always controlled at 0.125 mol/l. The impregnated samples were then taken out from the solution and dried under a flow of air at room temperature. The pretreated fibers were hung in a preoxidation furnace and heated to the predetermined temperatures 100°C, 150°C, 200°C, and 250°C (kept at each temperature for 20 min). The preoxidized fibers were then put into a carbonization-activation furnace and heated to the predetermined temperature under the protection of nitrogen gas, respectively at 600°C, 700°C, 800°C, 900°C (kept at each stage of temperature for 20 min). The fibers were activated by water steam at the temperature of 600°C (the entire process is shown in Figure 1).

Measurements

The specific surface area measurements were determined by the Brunauer-Emmett-Teller (BET) method, using nitrogen adsorbed at 77 K, calculated with a multi-point method.

Specimens were ground with KBr powder and pressed into disks. They were then analyzed by a Nicolet FTIR Nexus-670 spectrometer to measure the infrared spectra and to identify their chemical functionality.

For the evaluation of microstructure of the pores and surface morphology of the ACFs, scanning electron microscopy (SEM) was used (JSM-5600LV, Japan). The specimens were polished and sputter-coated with gold/palladium alloy after being cut to expose the cross-section.

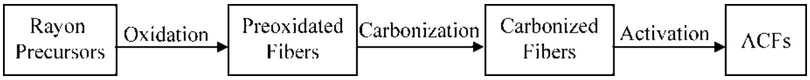


Figure 1. Flow chart for the manufacture of ACF.

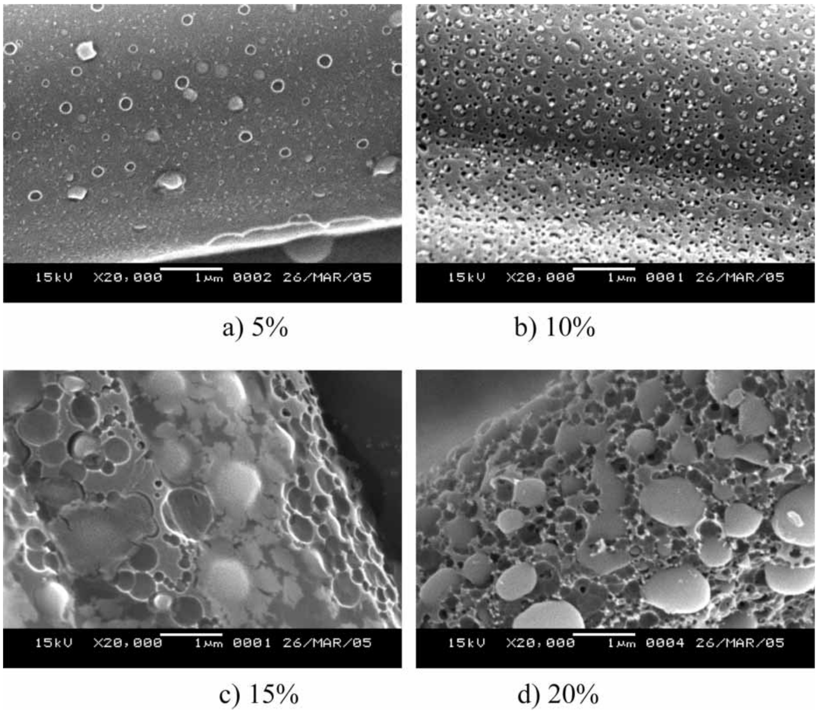
TGA analyses (TMA 7, Pekin-Elmer) were carried out on samples of the rayon precursors non-impregnated and impregnated with 5 wt% H_3PO_4 (the concentration of NaCl was 0.125 mol/l) using a 20°C/min heating rate up to 750°C and flow of 20 ml/min of N_2

Results and Discussion

Figure 2 shows a series of SEM images of rayon-based activated carbon fibers prepared from rayon precursors treated at different impregnation ratios of H_3PO_4.

At 5 wt% H_3PO_4, primarily only fibrous morphology can be seen (Figure 2(a)). Only a few pores are observed on the surface in the micrograph. As the impregnation ratio is increased to 10 wt%, porosity becomes apparent in the micrograph (Figure 2(b)) and the shape of the pores is nearly round. With the help of a computer image processing system, we can initially estimate the pore size distribution to be between 20 and 150 nm with an average value of 63 nm. It can also be seen that there are many white substances which are probably acid phosphates or polyphosphates separated out in these pores. The size of these particles is also in the range of 20–150 nm. How to accurately identify the elements of this substance is an important task in our subsequent research. The sizes of the pores become much larger when the impregnation ratio is increased to 15 wt% (Figure 2(c)), and the surface of the fiber is seriously eroded by the H_3PO_4 because of its high concentration. This can also be seen in the SEM image of ACF obtained at the impregnation ratio of 20 wt% H_3PO_4 (Figure 2(d)).

The development of pores is attributed to the reaction of rayon with H_3PO_4 (6). The concentration of H_3PO_4 has a clear effect on the morphology of the macropores. Also, the



a) 5% b) 10%

c) 15% d) 20%

Figure 2. Effect of the impregnation ratio on the surface of ACFs.

H_3PO_4 plays a positive role in the formation of micropores, which increase the specific surface area of ACF. As Figure 3 shows, the specific surface area of the ACFs increases along with the increase of H_3PO_4 concentration.

The specific surface area of porous materials can be determined from gas adsorption measurements. Although increasing the impregnation ratio is beneficial regarding the specific surface area development (Figure 3), the use of large amounts of acid is harmful for the strength of the obtained macroporous ACF, and the fibrous morphology is progressively eroded. Therefore, the optimal concentration of H_3PO_4 solution should be 10 wt% to reach a compromise between porosity development and the fibrous morphology structure.

Figure 4 shows the infrared spectra of rayon precursors impregnated with 10 wt% concentration of phosphoric acid at different temperature stages of preparation. There are two shoulders (at 1064 cm^{-1} and 991 cm^{-1}, respectively) in the spectra of all oxidized samples. These shoulders are attributable to phosphorous and phosphocarbonaceous compounds (6). Thus, one at 1064 cm^{-1} can be assigned to the P-O symmetrical vibration in a chain of P-O-P (polyphosphate) (6–9). The shoulder at 991 cm^{-1} can be assigned to the P-O-C asymmetric stretching, interaction between aromatic ring vibration and P-C (aromatic) stretching and/or symmetrical stretching of PO_2 and PO_3 in phosphate-carbon complexes (7). The intensities of these two peaks increase at the beginning of the oxidation, then decrease with the increase of oxidation temperature. Therefore, P-containing carbonaceous structures like acid phosphates and polyphosphates may be formed in the samples carbonized in the presence of H_3PO_4.

At the same time, the IR adsorption bands due to C-H vibrations at 2925 cm^{-1} and 2893 cm^{-1} have similar changes through the whole process. They are larger at 150°C than at 20°C, but essentially missing at 250°C, and remain missing while the sample was carbonized. Before the activation, all the spectra exhibit a band at 1640 cm^{-1} that can be assigned to the C=C stretching vibration in polynuclear aromatic compounds (6). Unfortunately, it is impossible to obtain quantitative information from the FTIR scans performed in this study.

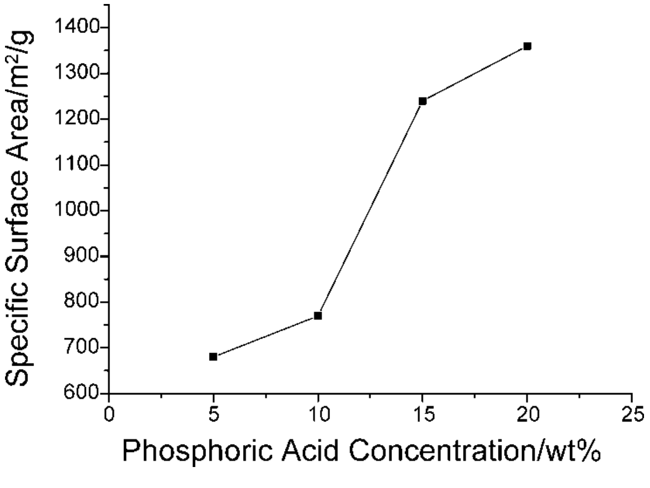


Figure 3. Effect of the H_3PO_4 concentration on the specific surface area of ACFs.

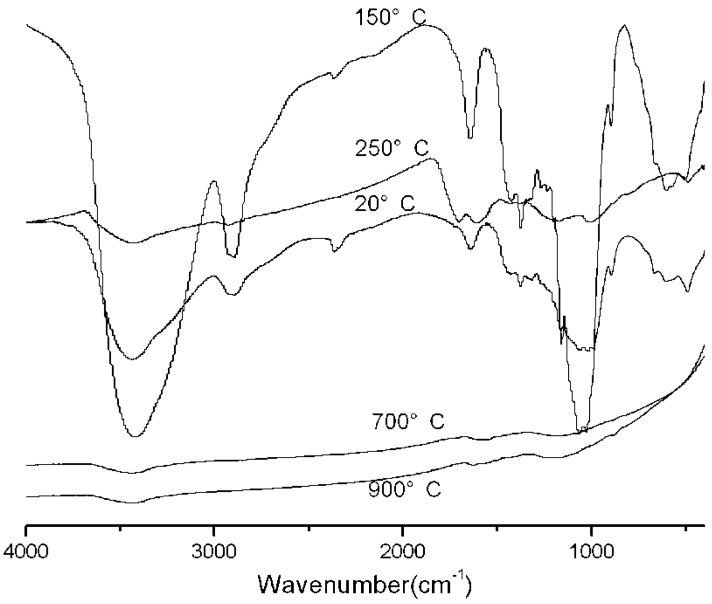


Figure 4. FTIR spectra of ACFs at different stages of preparation.

The thermal behavior of the rayon precursors was analyzed by TGA. Figure 5 shows the TGA plots for the rayon precursors impregnated with 5 wt% H_3PO_4 and unimpregnated, respectively. One can find slight weight losses in both materials due to the evaporation of adsorbed water at temperatures below 100°C. The weight loss due to decomposition starts at a lower temperature for the impregnated sample than the

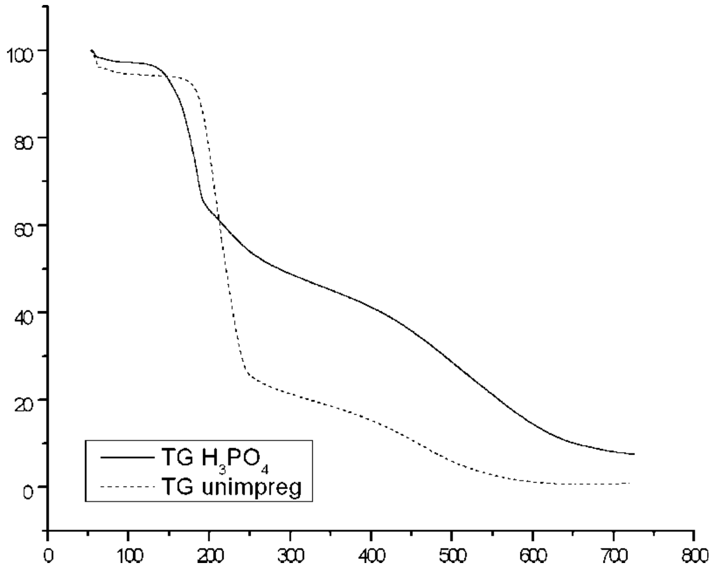


Figure 5. TGA curves for unimpregnated and 5 wt% H_3PO_4 impregnated rayon precursors.

unimpregnated one (10). There is a continuous weight loss with increasing temperature up to over 700°C for the impregnated material, whereas the weight loss for the non-impregnated material reaches almost 100% above 550°C.

Conclusions

The concentration of the phosphoric acid had a strong effect on the formation of the macropores and the morphology of rayon-based ACF. The specific area of the ACF was also determined by the concentration of the phosphoric acid. During the process, intermediate products, which possessed P-containing functionalities like acid phosphates and polyphosphates, were observed. Impregnation of rayon precursors with H_3PO_4 modified the pyrolysis process, dehydration becoming more predominant. A novel macroporous ACF with a high specific area had been successfully manufactured from rayon precursor pretreated with H_3PO_4 solution at a concentration of 10 wt%.

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References

1. Liben, Y. and Anbu, Y. (2002) *The Application Technology of Activated Carbon*, South East University Press: Nanjing, 76
2. Lu, W. and Chung, D.D.L. (1996) *Mat. Res. Soc. Symp. Proceedings*, 431: 393–398.
3. Kyotani, T. (2000) *Carbon*, 38: 269–286.
4. Kamps, B.S., Hoffmann, C. http://www.SARSReference.com/.
5. Wu, Q-L., Gu, S-Y., Zhang, Z-H., et al. (2004) *J. Functional Mat. (Chinese), Supplement*, 2085–2093.
6. Suarez-Garcia, F., Martinez-Alonso, A., and Tascon, Juan. M.D. (2004) *Carbon*, 42: 1419–1426.
7. Puxiy, A.M., Poddubnaya, O.I., Matinez-Alonso, A., Puziy, A.M., Poddubnaya, O.I., Martínez-Alonso, A., Suárez-García, F., and Tascón, J.M.D. (2002) *Carbon*, 40: 1493–1505.
8. Bourbigot, S., Le Bras, M., and Delobel, R. (1995) *Carbon*, 33: 283–294.
9. Fu, R., Liu, L., Huang, W., Fu, R., Liu, L., Huang, W., and Sun, P. (2003) *J. Appl. Polym. Sci.*, 87: 2253–2261.
10. Huidobro, A., Pastor, A.C., and Rodriguez-Reinoso, F. (2001) *Carbon*, 39: 389–398.