

PREPARATION OF ACF WITH HIGH SPECIFIC SURFACE AREA BY $K_2Cr_2O_7$ SOLUTION PRETREATED

Xiu-Jun Liu¹, Bing Pan¹, Tong-Qi Li²

1.School of Material Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin, 300160, China

2.National Key Laboratory of Advanced Functional Composite Materials, Aerospace Research Institute of Materials and Processing Technology, Beijing, 100076, China

Abstract

The specific surface area of polyacrylonitrile-based (PAN) carbon fiber is less than $2m^2g^{-1}$ before activation, but it can be increased with different methods. By using the PAN-based carbon fibers as materials, they are impregnated by potassium dichromate solution first, and then are activated by vapor of water under N_2 flow protection at $850^\circ C$. The specific surface area is characterized by BET. The pretreatment time, the concentration of potassium dichromate solution and the activation time are investigated. The results show that the specific surface area after activation decreases with increasing impregnated time. In addition, the specific surface area increases gradually with the increasing concentration of potassium dichromate solution. As the activated time increases, the specific surface area increases rapidly. The specific surface area of carbon fiber which is pretreated and then activation is higher than not. We get the optimum experimental condition from experiments. The specific surface area of activated carbon fiber is up to $1023 m^2g^{-1}$ under the condition of 10% potassium dichromate solution, 0.5h of pretreatment, and 2h of activation time.

Keywords: activation; carbon fibers; impregnation

1. Introduction

Because of excellent porosity (high surface area and large pore volumes) and special surface (hydrophobic) properties, porous carbon-based materials have been widely used as adsorbents, catalysts, and catalyst supports^[1]. Among the porous carbonaceous materials, activated carbon fibers (ACFs) have extended surface area, high adsorption capacity, and fast adsorption/desorption rate than the usual granulated activated carbons and so can adsorb a mass of chemical substances in gas and liquid phases^[2-4]. ACFs are profusely used as adsorbents for pollution control and are widely used in air and water purification, solvent recovery, etc^[5, 6]. Otherwise, Activated carbon fibers are popular materials for the electrode of the electric double-layer capacitor because of their high specific surface areas and conductivities^[7]. The surface area is especially important, so that ACFs with larger surface area are quite attractive for use as capacitor electrodes. ACF is a microporous carbonaceous adsorbent, which is developed from organic precursors such as polyacrylonitrile (PAN), cellulose, phenol, or pitch fibers.

The specific surface area of carbon fiber is very little which is less than $2m^2g^{-1}$ before activation, but it can be increased either by physical activation or chemical activation. The physical activation method involves carbonizing the precursors at a high temperature and then activating in an oxidizing atmosphere such as carbon dioxide or steam. Chemical activation involves carbonizing the parent material impregnated with zinc chloride, potassium hydroxide or phosphoric acid at a lower temperature^[8].

In this paper, PAN-based carbon fibers were used as materials that were impregnated by potassium dichromate solution and then activated by vapor water. We researched the influence of the specific surface area of carbon fibers in terms of impregnated time, concentration of the potassium dichromate solution and activation time. We found the proper conditions to increase the specific surface area of carbon fibers.

2. Experimental

2.1 Samples

PAN-based carbon fibers (T300B, 6000filaments, Toray Co. Ltd)

2.2 Pretreatment and Activation

The samples were cleaned and soaked by deionized water for 48 hours and replaced water every several hours to remove the additives from the samples surface. Then they were dried to use later.

The dried samples were impregnated by potassium dichromate solution of different concentration for different hours and cleaned again and again then dried for hours at $110^\circ C$. The pretreated samples were put in activation stove, heating from room temperature to $600^\circ C$ under the protection of nitrogen gas at the rate of $10^\circ Cmin^{-1}$, then to $850^\circ C$ at the rate of $5^\circ C min^{-1}$. Deionized water was joined at the speed of $2ml min^{-1}$. When water was evaporated, steam entered into activation stove and the samples were activated for different time. Later cooled to room temperature under the protection of nitrogen gas then determined the specific surface area.

2.3 Determination of the specific surface area

The specific surface area was measured in 3H / 2000 type automatic N₂ adsorption instrument made by Beijing Huihaihong nanometer ST. Co., Ltd. By using activated carbons as reference materials, adsorbing nitrogen gas at the atmosphere of liquid nitrogen and then desorbed with water at 60°C. The samples were dehydrated and degassed in vacuum drier before measurement.

3. Results and discussion

3.1 Effect of impregnated time

The dry samples were impregnated by potassium dichromate solution for different time and activated with vapor for 0.5 hours. The influence of impregnated time on the specific surface area after activation was observed.

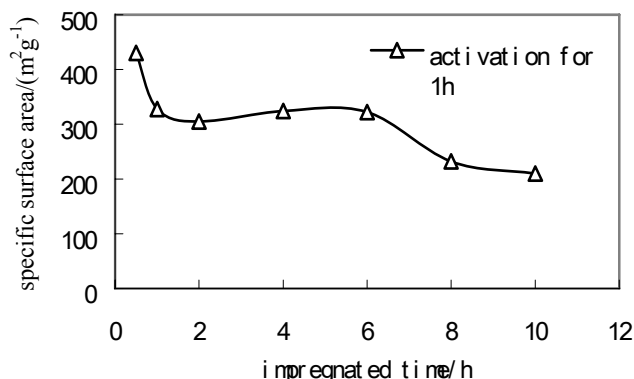


Fig.1 Relationship between specific surface area and impregnated time

The variation of specific surface area with impregnated time after activation is shown in Fig.1. It shows that the specific surface area of the samples after activation decreased with increasing impregnated time. In contrary with the samples that the specific surface area is less than 2m²g⁻¹, it increased obviously after activation. That is because the carbon fibers had defects to some extent and potassium dichromate is a kind of strong oxidizer so that those defects could be oxidated to form microporous after impregnation. Microporous contributed to specific surface area most so it could be increased enormously after activation. Potassium dichromate continued to oxidize the pores as the impregnated time increased. When the samples were activated at high temperature, adjacent microporous can polymerize into mesoporous or macroporous so as to decrease the specific surface area. So it can get to the best effect on condition that the samples were impregnated for 0.5h by potassium dichromate solution and then activated by vapor.

3.2 Effect of the concentration of potassium dichromate solution

PAN-based carbon fibers were impregnated by 5%, 8% and 10% potassium dichromate solution respectively, then activated with vapor for 1 hour and measured the specific surface area. The variation curve was shown in figure 2.

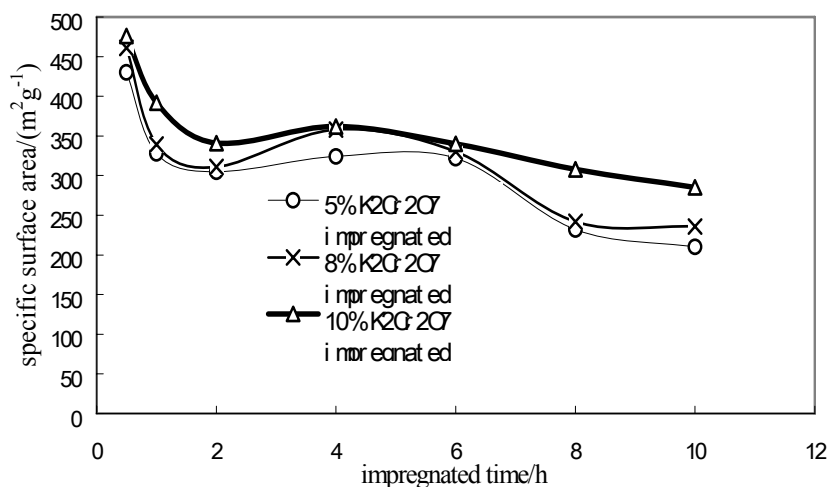


Fig.2 Relationship between specific surface area and impregnating solution concentration

As seen in Fig.2 , the specific surface area increased with the increasing impregnated time. That is because as the concentration of potassium dichromate solution increased, more surface defects were oxidized to microporous per hour and area. More active groups were shaped on the surface so that the specific surface area could be ascended after activation.

3.3 Effect of activation time

The samples were activated for 0.5h, 1h, 1.5h and 2h, and then measured the specific surface area. The variation curve was shown in fig.3.

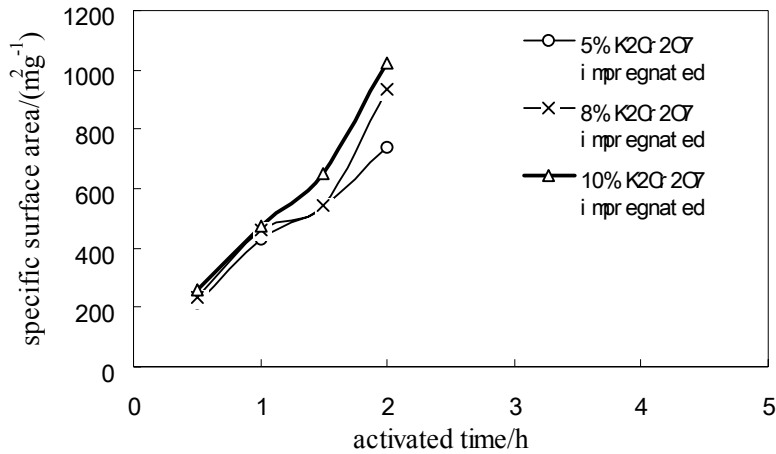


Fig.3 Relationship between specific surface area and activated time

In Fig.3, it can be observed that the surface area increased along with the increasing activated time, which could be explained with physical activation mechanism. Physical activation mechanism is in terms of three basic processes^[9]—gasification of nongraphitic carbon and heteroatoms, reaction of graphitic carbon, and reordering of the graphitic layer planes. At the beginning of activation, the amorphous carbon blocking off pores was ablated and the hole was opened up. Further activation, carbon in different part of crystal lattices on surface reacted in different rates so that carbon in dislocation and brim left surface in the form of gas oxides and new pores shaped. In depth activation, these pores were widening. Therefore, their specific surface area increased along with the increasing activation time.

3.4 Effect of pretreatment

The carbon fibers were pretreated by 10% potassium dichromate solution for 0.5h and activated by vapor for different time. Then the specific surface area was measured. In contrast to the carbon fibers that were not pretreated, we can get the variation curve shown in figure 4.

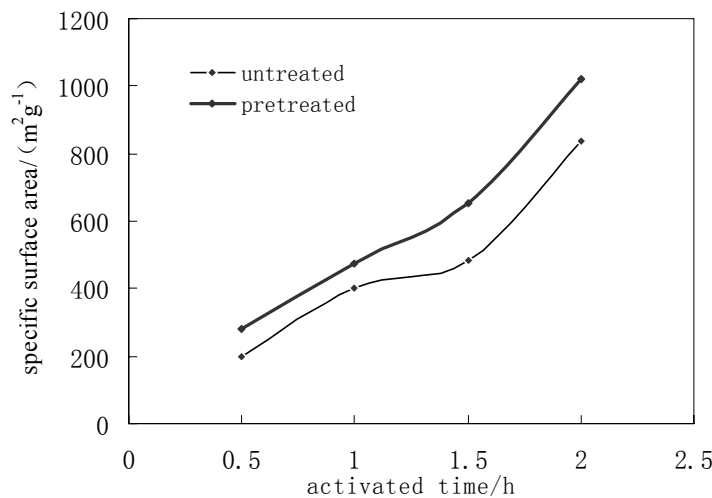


Fig.4 Relationship between specific surface area and pretreatment

In contrast with activation by vapor directly, the specific surface area of pretreated carbon fibers was larger. The high specific surface area was attained from pretreatment and then activation.

4. Conclusions

The present research studied the effect of impregnation time, the concentration of potassium dichromate solution, and activation time to specific surface area. As could be seen, pretreated by potassium dichromate solution the specific surface area after activation decreased with the increasing impregnated time increased. And it increased with the increasing concentration of potassium dichromate solution and activation time. In addition the specific surface area of pretreated carbon fibers can be higher than the ones that were not pretreated. According to the impregnation, the specific surface area increased enormously than before. It was found that the specific surface area of activated carbon fiber is up to $1023 \text{ m}^2\text{g}^{-1}$ under the condition of 10% potassium dichromate solution, 0.5h of impregnation, and 2h of activation time.

References

- [1] Z M Wang, N Yamashita, Z X Wang, *et al.* Air oxidation effects on microporosity, surface property, and CH_4 adsorptivity of pitch-based activated carbon fibers. *Colloid and Interface Science*, 2004, 276: 143-150.
- [2] Soo-Jin Park, Byung-Jae Park, Seung-Kon Ryu. Electrochemical treatment on activated carbon fibers for increasing the amount and rate of Cr (VI) adsorption. *Carbon*, 1999,37: 1223-1226.
- [3] Jinchuan Xie, Xuhui Wang, Jiyong Deng. Modifying the pore structure of Pit-ACF with the chemical vapor deposition of methane and propylene. *Microporous and Mesoporous Materials*, 2004,76: 167-175.
- [4] Jinchuan Xie, Xuhui Wang, Jiyong Deng. Pore size control of Pitch-based activated carbon fibers by pyrolytic deposition of propylene. *Applied Surface Science*, 2005,250: 152-160.
- [5] Soo-Jin Park, Byung-Joo Kim. Influence of oxygen plasma treatment on hydrogen chloride removal of activated carbon fibers. *Journal of Colloid and Interface Science*, 2004,275: 590-595.
- [6] Weiming Lu, D D L Chung. Preparation of conductive carbons with high surface area. *Carbon*, 2001,39: 39-44.
- [7] Keiichi Okajima, Keigo Ohta, Masco Sudoh. Capacitance behavior of activated carbon fibers with oxygen-plasma treatment. *Electrochimica Acta*, 2005,50: 2227-2231.
- [8] Zhongren Yue, Christian L. Mangun, James Economy. Preparation of fibrous porous materials by chemical activation 2: H_3PO_4 activation of polymer coated fibers. *Carbon*, 2002,40: 1181-1191.
- [9] P J M Carrott, J J Freeman. Evolution of micropore structure of activated charcoal cloth. *Carbon*, 1991, 29: 499-506.