

PREPARATION OF ACTIVATED CARBON FIBERS FOR XENON ADSORPTION I: EFFECT OF ACTIVATION TEMPERATURE ON PORE STRUCTURE

Chen Shuixia, Zeng Hanmin

Materials Science Institute, Zhongshan University, Guangzhou 510275, China
Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Zhongshan University, Guangzhou 510275, P. R. China

Introduction

Xenon isotopes are products of nuclear fission. The nuclear plant operation may release radioactive xenon to environment, thus result in serious damage to the environment and human health. Therefore, the adsorption and concentrating of xenon has practical application in radioactive waste gas purification. Moreover, the monitor of xenon isotopic, derived from nuclear explosion or nuclear accident, is also one of effective tools for the examination of nuclear explosion. Our previous works^[1,2] showed that activated carbon fiber has higher adsorption amount and selectivity for xenon, and that the adsorption amount is determined not only by the specific surface area, but also by the pore size distribution. Thus to control proper pore size of ACF is the key step for the improvement of the adsorption capacity of ACF for xenon. In this paper, a series of sisal-based activated carbon fibers were prepared under different condition. The effects of carbonization and activation conditions on porous structure of ACFs were investigated for purposes of providing effective preparing process of ACF for xenon adsorption.

Experimental

Sisal fiber treated with 5%NaOH was impregnated with $(\text{NH}_4)_2\text{HPO}_4$ for 24 hours, then the fiber was heated under inert atmosphere to high temperature for carbonizing, then, while kept at that temperature, a stream of steam was introduced to oven for activation. The carbonization – activation temperature were 750, 800, and 900°C, the resulted ACFs were noted as SACF750, SACF800,and SACF900.

The nitrogen adsorption isotherms on SACFs at 77K were measured with an OMNISORP 360 adsorbmeter, and were used to evaluate the porous structure of SACF.

Results and Discussion

Adsorption isotherms

Nitrogen adsorption isotherms of ACFs activated under different temperature are shown in Fig. 1. They are all type I. There is a steep nitrogen

adsorption at lower relative pressure p/p_0 , and then to a gradual plateau at higher relative pressure, which suggests high microporosity of these SACFs. In all isotherms, there is also a hysteresis loop at higher p/p_0 , indicating the existence of some mesoporosity^[3]. The size of hysteresis loop indicates the difference of micropore volume.

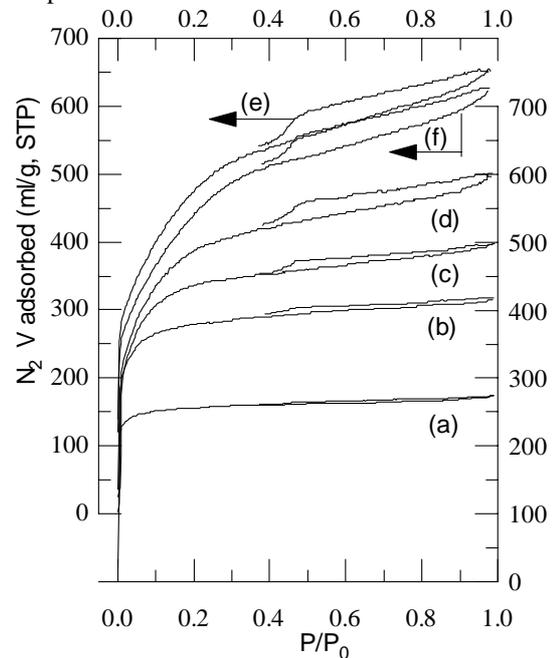


Fig. 1 Adsorption-desorption isotherms of N_2 on SACFs (a) SACF750; (b) SACF800; (c) SACF820; (d) SACF840; (e) SACF870; (f) SACF900

Table 1 Parameters of porosity of SACFs

sample	S_{BET} (m^2/g)	V_t (ml/g)
SACF750	819.8	0.4233
SACF800	1247.8	0.6494
SACF820	1439.5	0.7767
SACF840	1691.5	0.9372
SACF870	1713.0	1.0106
SACF900	1597.7	0.9594

The specific surface area, S_{BET} , of SACFs was calculated based on BET method (p/p_0 between 0.05~0.30). The adsorption amount at $p/p_0=0.95$ was

converse into the total volume of SACFs V_t taking the density of liquid nitrogen as 0.808 g/cm^3 . The results are shown in table 1. The surface areas and total volumes increase significantly with activation temperature; and at as high as 900°C activation, there is a drop in both surface area and pore volume.

t-plots and mesopore volume

The microporosity of SACF can be characterized using t-plots. Fig. 2 shows the t-plots for nitrogen isotherms on above SACFs. The standard thickness values of nitrogen adsorbed on carbon black^[4] were used to construct the t-plots. All t-plots have a steep uprising at the very beginning, and then bend at about $0.25\sim 0.5 \text{ nm}$ to reach a plateau. The steep uprising represents the nitrogen filling in micropores of ACF, and the glacial plateau represent the multi-layers adsorption of nitrogen on mesopores.

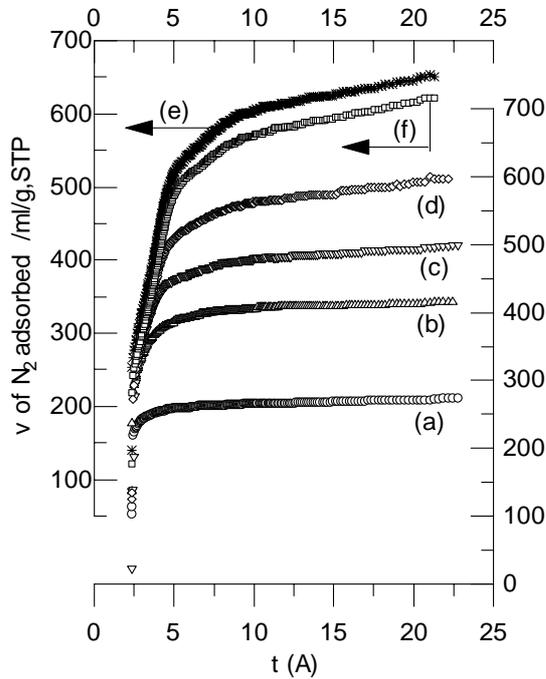


Fig. 2 t-plot for SACFs (a) SACF750; (b) SACF800; (c) SACF820; (d) SACF840; (e) SACF870; (f) SACF900

According to the definition of adsorption thickness t , the adsorption on porous materials with both micropores and mesopores can be described as follow:

$$V = V_{mi}^0 + V_{me} = V_{mi}^0 + \frac{V_m}{t_m} \cdot t \quad (1)$$

where V is adsorption amount at adsorption layer thickness t , V_{mi}^0 is micropore volume, V_m is single-layer adsorption amount, t_m thickness of single molecule layer adsorbed. Therefore, a straight line of V against t can be drawn, and from the intercept of the line, the micropore volume $V_{mi,t}$ can be calculated; similarly, the single layer adsorption amount V_m and surface area of mesopore $S_{me,t}$ would be calculated

from the slope of the line.

$$V_{mi}(ml/g) = V_{mi}^0(ml/g, STP) \times 0.001546 \quad (2)$$

$$S_{me}(m^2/g) = t_m \cdot b = 0.354 \times 4.36 \times b(ml/g, STP) \quad (3)$$

The calculated results are shown in table 2. the mesopore volume $V_{me,t}$, by subtracting total pore volume V_t in table 1 with micropore volume $V_{mi,t}$, is also listed in table 2. The results indicate that micropore dominate in SACF, and mesopore only take up a small portion.

Table 2 Parameters of porosity of SACFs by t-method

sample	$V_{mi,t}$ (ml/g)	$S_{me,t}$ (m^2/g)	$V_{me,t}$ (ml/g)
SACF750	0.3694	14.4	0.0269
SACF800	0.6108	16.5	0.0386
SACF820	0.7053	32.5	0.0714
SACF840	0.8067	58.6	0.1305
SACF870	0.8719	67.2	0.1387
SACF900	0.8150	71.6	0.1444

DR-plots and multi-stage distribution of micropores

By combining Polanyi's adsorption potential theory and micropore filling theory, Dubinin proposed a DR equation to describe the adsorption isotherm for porous carbon with unique pore size distribution^[5]:

$$\ln W = \ln W_0 - B \left(\frac{T}{\beta} \right)^2 \ln^2(p_0/p) \quad (4)$$

where W is adsorption amount at relative pressure p/p_0 , W_0 is total volume of micropores, T is temperature, B and β are coefficients.

Kaneko et al^[6] divide the DR-plot into L, M, H and S regions in order of increasing p/p_0 , and assumed this characteristic of DR plot is caused by the different micropore structure. They proposed that the micropore sizes should be integral multiples of ca. 0.35 nm of the thickness of the graphitic layer, as the micropores of ACF should arise from defaults of graphitic layers on activation. Considering the thickness of adsorbed nitrogen molecule is 0.35 nm , micropores of 0.4 , 1.1 , and 1.4 nm were denoted as bilayer-, trilayer- and four-sized micropores. The L region correspond to the adsorption in bilayer-sized pores; M region correspond to monolayer adsorption in tri- and four-layer-sized pores; and H region correspond to the filling of nitrogen in the gaps between the micropore walls coated by nitrogen monolayer.

The DR-plots for nitrogen adsorption isotherms of the above SACFs were shown in Fig. 3. It is evident that DR-plot for nitrogen adsorption on each SACF is different from one to another. Besides a linear section with very steep slope at $p/p_0 > 0.5$ (S region), all DR-plots also have additional 1 to 3 linear

regions with different slopes. DR-plots of SACF activated at higher temperature (SACF870 and SACF900) are composed of L, M, H linear regions, DR-plots of SACF820 and SACF840 are composed of L, M, and those of SACF750 and SACF800 activated at lower temperature are composed of only L region. The intercept of each linear region would represent the volume of micropore in certain pore size range. The calculated results are shown in table 3. The results reveal that the increase of activation temperature brings the shift toward larger pore size and the increase of pore volume. though extra high temperature (over 900 degree in this case) will result in the drop of pore volume, the supermicropores components with wider pore size increase.

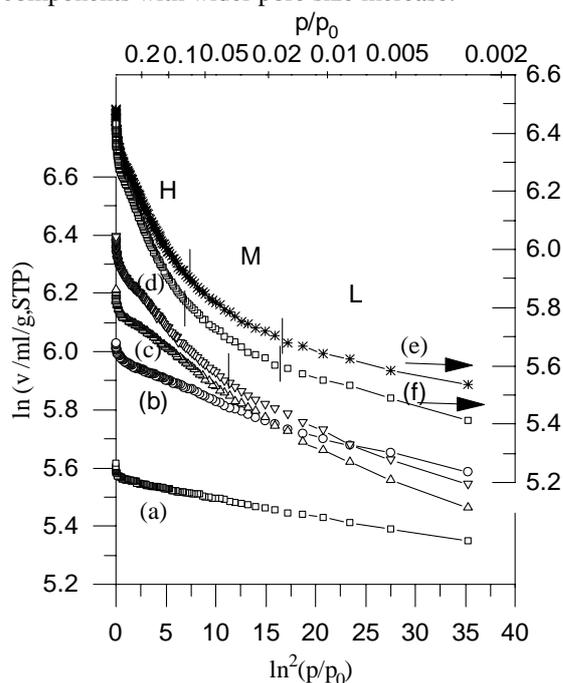


Fig.3 DR plot for SACFs (a)SACF750; (b) SACF800;(c) SACF820;(d) SACF840; (e) SACF870; (f) SACF900

Tab.3 pore volume of SACFs by DR method

sample	$W_{0.1}$ (ml/g)	$W_{0.2}$ (ml/g)	$W_{0.3}$ (ml/g)	ΣW_0
SACF750	0.403	-	-	0.403
SACF800	0.607	-	-	0.607
SACF820	0.664	0.055	-	0.719
SACF840	0.657	0.170	-	0.827
SACF870	0.522	0.149	0.243	0.914
SACF900	0.491	0.122	0.223	0.836

Effect of activation temperature on pore development

From the above analysis it has been noticed that sisal based activated carbon fibers activated with steam are dominated by micropores. While activation temperature is under 800 °C, pore structure of SACF is dominated by micropore narrower than 1.1 nm (ultramicropore). With the increase of activation temperature, the micropore is widened; both ultramicropores and supermicropores exist in SACFs. And while activation temperature is over 870°C, micropores is further broadened, some mesopores were created in SACFs. The above results indicate that the activation temperature can be used to effectively control the development of pores of ACFs. And in order to prepare ACFs with unique ultramicropores in favor of xenon adsorption, the activation temperature should be under 800°C, certainly, prolonging activation duration is necessary for higher pore volume and surface area.

References

1. Deng Jiyong, Zeng Hanmin, Zhang Haotao, and Zhang Lixing, Xenon adsorption on activated carbon fibers. *Chinese J. Materials Research*, 2000,14(2):179-182
2. Deng Jiyong, Zeng Hanmin, and Zhang Lixing, Studies on xenon adsorption behavior on activated carbon fibers I: effect of raw materials on adsorption properties. *Chinese J. Ion Exchange & Adsorption*. 1999,15(5):464-467
3. P. J. M. Carrott, R. A. Roberts, K. S. W. Sing, Adsorption of nitrogen by porous and non-porous carbons. *Carbon*, 1987, 25(1): 59-68
4. F. Rodriguez-Reinoso, J. M. Martin-Marinez, C. Prado-Burguette et al, A standard adsorption isotherm for the characterization of active carbon *J. Phys. Chem.*, 1987, 91:515-516
5. M. M. Dubinin, Adsorption properties and microporous structures of carbonaceous adsorbents. *Carbon* 1987, 25(5): 593-598
6. K. Kakei, S. Ozeki, T. Suzuki, K. Kaneko, Multi-stage micropore filling mechanism of nitrogen on microporous and micrographitic carbons. *J. Chem. Soc. Faraday Trans. I*, 1990, 86(2): 371-376

Acknowledgements

We are grateful to the financial support by Natural Science Foundation Committee of Chinese government (grant No. 50073029), and by Guangdong Provincial Natural Science Foundation (001276).