

POROSITY OF PAN - BASED ACTIVATED CARBON FIBERS

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Introduction

Activated carbon fiber (ACF) is a novel and fibrous adsorbent which is developed by carbonization and activation of organic fibers. Its unique properties are attracting attention in fundamental research and in the development of applications [1]. Typically, ACF is a kind of microporous carbonous adsorbent and its adsorption properties are associated with their porous structure and surface structural characteristics. Containing nitrogen in the structure of polyacrylonitrile (PAN) based ACFs, this introduces an interesting function as the adsorbent and catalyst [2]. In the present work, PAN-based ACFs are prepared and the results of porous structure parameters are investigated.

Experimental

PAN-based ACFs were prepared in our laboratory by continuous vertical synchronism carbonization and activation apparatus in steam, carbon dioxide and N₂ gas atmosphere. Different specific surface area samples were prepared by controlling the rate of activation.

A Micromeritics ASAP 2000 accelerated surface area and porosimetry (Micromeritics Ins. Corp. U. S. A) was used to measure nitrogen adsorption isotherms at 77.4K in the range of relative pressure from 10⁻⁶ to 1.

Results and Discussion

As illustrated by Fig. 1, the N₂ adsorption isotherms are of type I except for sample A₄. This indicated that ACFs are essentially microporous adsorbent. The exception of sample A₄ suggests that there are some meso- and macropores in its structure. The volume filling of macropores by the mechanism of capillary condensation of vapor takes place at relative pressure close to unity.

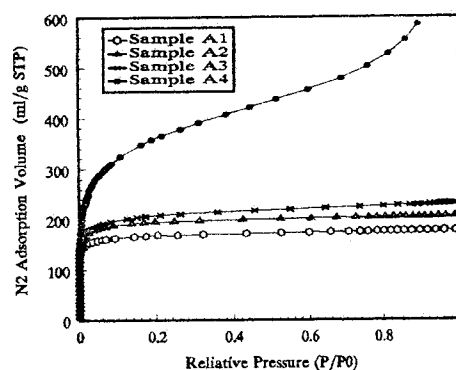


Fig. 1. N₂ adsorption isotherms for the PAN-based ACFs

The porous structure parameters derived from N₂ adsorption isotherms analysis are listed in table 1.

The micropore volume and average pore width of PAN-based ACF both increase with the rate of activation, as expected.

Table 1 Porous structure parameters of PAN-based ACFs

Sample	SSA (m ² /g)		V _{0.95} (ml)	\bar{D} (nm)	Dubinin - Astakhov			Horvath - Kawazoc	
	BET	Langmuir			S _{mi} (m ² /g)	V _{mi} (ml/g)	n	V _{mi} (ml/g)	MPD (nm)
A ₁	576	731	0.27	1.90	561	0.22	9.998	0.250	0.51
A ₂	673	847	0.32	1.89	629	0.25	9.9998	0.297	0.53
A ₃	738	891	0.36	1.94	651	0.26	6.1154	0.294	0.61
A ₄	1241	—	1.10	3.57	998	0.45	2.7819	0.480	0.73

SSA: specific surface area; V_{0.95}: The total pore volume estimated at relative pressure 0.95;

\bar{D} : according to cylindrical pore model, $\bar{D} = 4V_{0.95}/S_{BET}$; S_{mi}: micropore surface area;

V_{mi}: volume of micropore; n: exponent of Dubinin - Astakhov (0~9.9999); MPD: median pore diameter

The ultramicropore less than 1 nm are present which lead to selectivity of adsorption (molecule sieve effect).

The pore size distributions obtained by means of the regularization method according to Density Functional Theory (DFT) [3, 4] support these findings, as can be seen in Fig. 2. The sample A₂ possesses a quite amount of micropore, with small fractions of mesopores almost not macropores. The micropore size distributions are of bimodal. The sample A₄ is mesoporous, with the same bimodal micropore as the sample A₂ and small fraction of macropores. The average micropore diameter is observed to increase with increasing surface area, pore size distribution becomes broader with increasing surface area suggesting the pore widening and pore generated occur cooperatively or that pores are generated over a broad activation range and the pore widening for some pores at the expense of smaller pores [5].

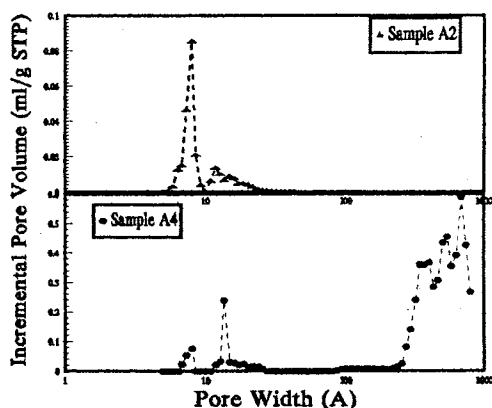


Fig. 2. Pore size distributions of PAN-based ACFs

The physical adsorption of vapor in micropore is described by the theory of micropore volume filling. The Dubinin - Radushkevich equation is the principle formula of the theory:

$$W = W_0 \exp \left[- \left(\frac{A}{\beta E_0} \right)^2 \right] = W_0 \exp \left[- \left(\frac{A}{E} \right)^2 \right]$$

Where W is current and W_0 the limited adsorption amount (ml/g). A is adsorption potential $A = RT \ln(P_0/P)$. E_0 and E are the characteristic adsorption energies for a standard vapor (usually Benzene) and adsorption vapor, respectively. β is the affinity coefficient.

The characteristic adsorption energy E for N_2 at 77.4K was determined according to D - R transformed isotherm plots in which two linear sections are apparent, as shown in Fig. 3, thus two characteristic adsorption energies are obtained.

Taking the affinity coefficient of N_2 as 0.33, the pore half - width x of slit - like micropore is calculated by using Dubinin method: $x = K/E_0 = \beta K/E$. K constant equals 12.0 KJ • nm/mol [6]. Results of D - R correlation are listed in table 2.

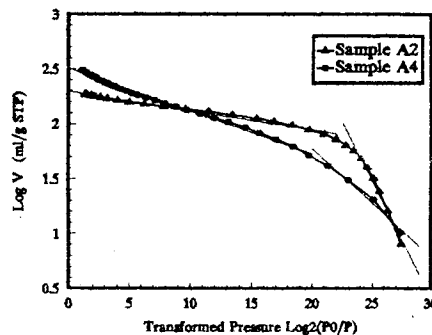


Fig. 3. Dubinin - Radushkevich plots for the adsorption N_2 at 77.4K by PAN-based ACFs

Table 2. Characteristics of porous structure of PAN-based ACFs by Dubinin - Radushkevich plots

Sample	E_1 (KJ/mol)	X_1 (nm)	r_1	E_2 (KJ/mol)	X_2 (nm)	r_2
A ₁	7.40	0.535	0.996	2.37	1.687	0.991
A ₂	5.20	0.762	0.991	2.63	1.505	0.988

r is the linear correlation coefficient.

The average pore half - width derived from the characteristic adsorption energies of N_2 isotherms are in agreement with the values from Horvath - Kawazoe equation and DFT method.

Conclusions

PAN-based ACFs are of bimodal micropores which are divided into >1 nm and <0.8 nm (ultramicropore) two sections, later occurs molecule sieve effect to lead to selectivity of adsorption. The pore size increases and pore size distributions become broader with increasing of specific surface area. The analysis results by means of different methods have a good consistency with each other.

References

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