

Mesopore development in PAN–ACF resulting from non-metal additives

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The narrow pore-size distribution of activated carbon fibres (ACF) limits their application in the fields concerning larger molecules, such as liquid adsorption and catalyst support. On the addition of carbon particles and organic materials to polyacrylonitrile fibres, and after stabilizing and activating, the mesoporosity in the resultant ACF has been obviously increased. Among these additives, carbon black gives the best effect. With 1 wt % carbon black I in precursor and on activating at 880 °C for 30 min, a mesoporosity of 48.2% (total pore volume 0.704 ml g⁻¹, mesopore volume 0.340 ml g⁻¹) has been obtained. The mechanism of mesopore formation is also discussed.

1. Introduction

Porous carbon materials in different forms, such as granular activated carbons (AC) and activated carbon fibres (ACF), play an important role in many industries. Among these materials, the use of ACF is currently progressing rapidly because of its high microporosity. Whilst such microporosity is the main source of the high apparent BET surface areas of ACF, the narrow pores-size distribution limits the usefulness of the material, both as a support for catalysts and as an effective means of adsorption of large molecules in a liquid phase. This has stimulated increased attention to develop a new type of ACF possessing extensive mesoporosity [1, 2].

Because the pore structure of carbonized materials is highly dependent on the precursor, selection of a proper precursor is a key factor in the production of ACF with a desired pore structure. The focus to develop mesopore ACF is now on the composition and structure of the precursor. Freeman *et al.* [3] reported the development of mesoporosity in activated charcoal cloth as a result of prior impregnation of the viscose rayon precursor with aqueous solutions containing sodium dihydrogen phosphate, and subsequent carbonization. Shimazaki [4] achieved the same result by adding TiO₂ to polyacrylonitrile (PAN) precursor. The inevitable metallic iron remaining in the resultant ACF made by the above methods limits the application of these mesoporous ACF to catalyst supports and electrodes in double-layer capacitors. The present work proposes a new way to solve this problem by using carbon particles, such as carbon black, graphite powder and activated carbon particles, and organic materials which can be dissolved in the PAN–DMSO solution such as polyvinyl alcohol (PVA), polyvinyl chloride (PVC) and polyvinyl acetate (PVAc), as the additive to PAN fibre, then by heat treatment and activation of this precursor in the

usual way. The mesoporosity is controlled by the additives and by the degree of activation through partial gasification of the carbons.

2. Experimental procedure

2.1. Sample preparation

2.1.1. Spinning

A mixture of PAN powder and carbon black particles (CB) or graphite powder, finely ground activated carbon (AC, through 320 mesh sieve), PVA, PVC, PVAc, was dissolved well in dimethylsulphoxide (DMSO), then PAN fibres were spun from this solution by the wet-spinning technique. All of the additives used in the study are commercially available. Among the four types of carbon black used, carbon black I and carbon black II are those employed in the printing industry, and the others are used in the rubber industry. Carbon black I is a toner for duplicators, carbon black II is used in printing inks. Carbon black III is a high abrasion black and carbon black IV is a general purpose black.

2.1.2. Activation

After stabilization at 240 °C for 5 h under a fixed length, the precursor fibre was cut into pieces then introduced into a vertical stainless steel furnace, and heated under a flow of nitrogen (260 ml min⁻¹) at 10 °C min⁻¹ up to the reaction temperature; steam was then introduced into the nitrogen flow. After reaction, the sample was cooled in a nitrogen flow to room temperature.

2.2. Characterization

2.2.1. Porosity

The porosities of the activated carbon fibres have been evaluated by physical adsorption of nitrogen at 77 K

using an adsorptometric apparatus ASAP 2000 (USA). From the adsorption isotherm, the micropore volume, V_{mi} , and external surface area, S_{ext} , have been calculated using the α_s method [5], taking non-graphitized non-porous carbon black adsorption data as the standard isotherm [6]. Because the amount of nitrogen adsorbed near saturation (at a relative pressure of 0.95) corresponds to the volume of micropores filled at low relative pressure and the volume of mesopores filled by capillary condensation at higher relative pressure V_{me} , the latter has been calculated by subtracting the value of V_{min} from the volume measure in the nitrogen adsorption isotherm at a relative pressure of 0.95 ($V_{0.95}$) [3]. The total surface area, S_t , has been calculated using the BET standard method, and the micropore surface area, S_{mi} , has been calculated by subtracting the external surface area from S_t . In this work, 2 and 50 nm were taken as the limits between micro- and mesopores, meso- and macropores, respectively, following the IUPAC recommendations [7].

2.2.2. Mesopore size distribution

Using the Barrett–Joyner–Halenda (BJH) method [8], the mesopore size distribution can be calculated from the desorption branch of the nitrogen isotherm.

3. Results and discussion

In the present study, two kinds of additives were used to promote the development of mesopores in PAN–ACF. One is organic material, which can be dissolved in the PAN–DMSO solution and has low carbon yield when heat treated (PVA, PVC and VA, etc.). The other is carbon particles, such as carbon black, graphite powder and finely ground activated carbon, which are all composed essentially of elemental carbon and have finer particle size, can form stable dispersions in PAN–DMSO solution by thorough milling and mixing with PAN polymer. Subsequently, a continuous PAN filament with homogeneously dispersed and dissolved additives can be spun.

3.1. Effect of organic additives

Three soluble organic materials were used as additives which led to different adsorption isotherms and pore structures of the resultant ACF. The adsorption isotherms resulting from the addition of PVA and PVAc shows a typical pattern belonging to type III, which has a hysteresis loop and the resulting ACF has prevailing mesoporosity (Table I). On the other hand, the addition of PVC leads to a type I adsorption isotherm and the ACF is nearly microporous (Fig. 1a). The decomposed temperature and carbon yield of PVA and PVAc are lower. But both the decomposed temperature and carbon yield for PVC are higher. The mesopore size distribution of the ACF fabricated from PAN fibre containing PVA, PVC or PVAc, is showed in Fig. 2a. Both ACFs from PAN fibres with PVA and PVAc have a large peak at 4.0 nm and there are few mesopores with a size larger than 4.0 nm.

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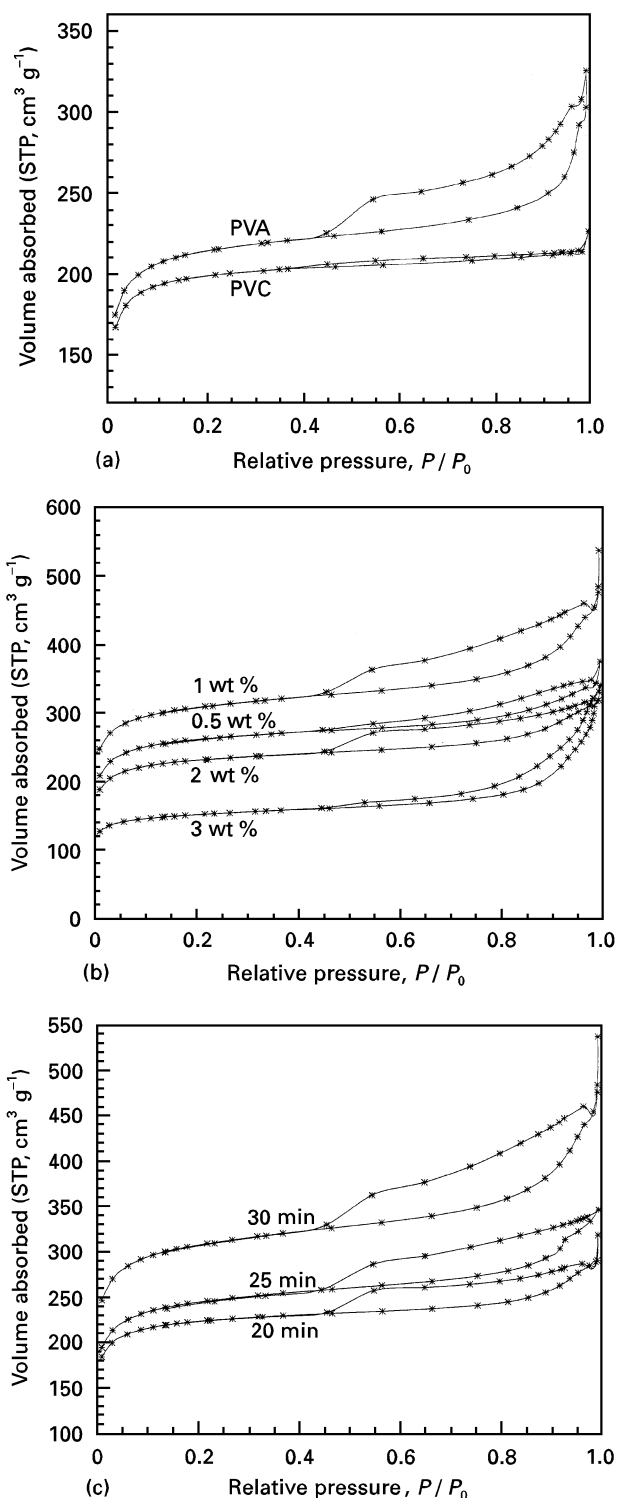


Figure 1 Nitrogen isotherm curves of ACF. (a) Precursor PAN fibres containing 1 wt % PVA and 1 wt % PVC, and activated at 880 °C for 30 min. (b) PAN fibres containing 0.5 wt %, 1 wt %, 2 wt %, 3 wt % carbon black I, and activated at 880 °C for 30 min. (c) All of the precursors containing 1 wt % carbon black I, but for activation times of 20, 25, and 30 min.

3.2. Effect of carbon additive

Six kinds of PAN fibres, containing 1 wt % carbon black I, 1 wt % graphite powder, 1 wt % finely ground activated carbon, 1 wt % carbon black II, 0.5 wt % carbon black III, 0.5 wt % carbon black IV, respectively, were prepared, then stabilized and activated at 880 °C for 30 min. All nitrogen isotherms for the resultant ACFs show hysteresis loops in all of them but the size and shapes of these loops differ from each

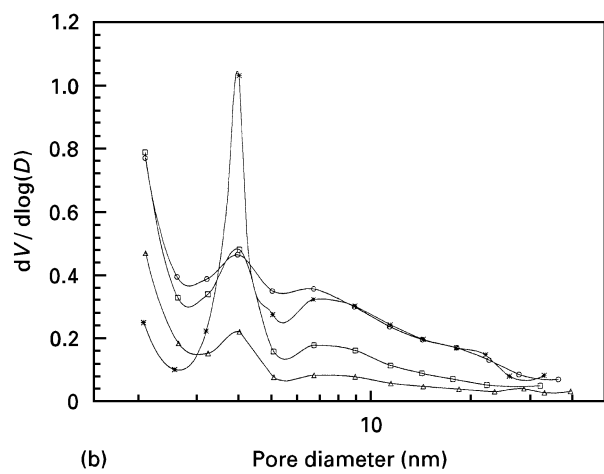
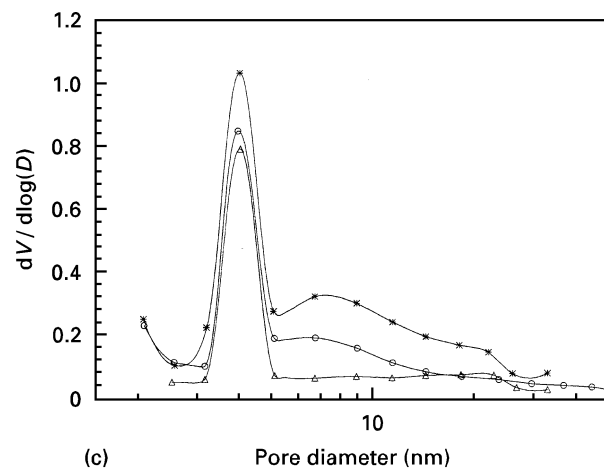
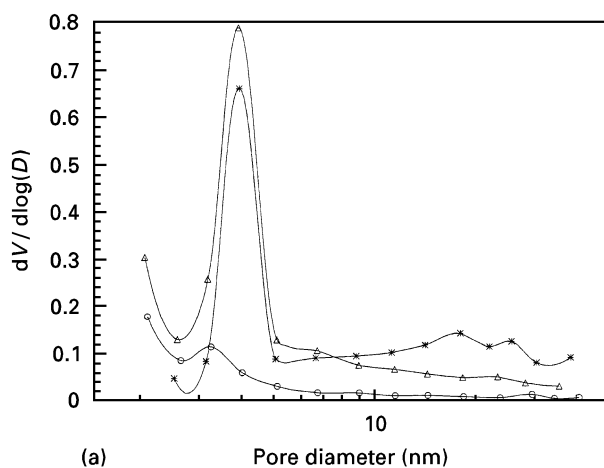


Figure 2 Mesopore size-distribution curves of ACF. (a) Precursor PAN fibres containing 1 wt % of (*) PVA, (Δ) PVAc, (\circ) PVC and activated at 880 °C for 30 min. (b) PAN fibres containing four different kinds of carbon black and activated at 880 °C for 30 min: (*) CB I, (\circ) CB II (\square) CB III, (Δ) CB IV. (c) As Fig. 1c (*) 30 min, (\circ) 25 min, (Δ) 20 min.

other, which testifies to the existence of mesopores with different content (Table I) and types. The results in Table I indicate that the addition of AC and various types carbon black leads to an abundant content of mesopores in ACF. It is shown from Fig. 2b that different types of carbon black give varied mesopore size distributions. Among them, carbon black I results in an unimodal distribution, concentrated around 4.0 nm, but carbon blacks II, III and IV yield more dispersed mesopore size distributions, e.g. two peaks exist at about 2.0 and 4.0 nm, and in the case of type II and IV there are pores over the whole range from 2.0–50 nm.

3.3. Effect of carbon black content

PAN fibre containing different amounts of carbon black I was spun, then stabilized and activated at 880 °C for 30 min. Nitrogen isotherms for the resultant ACF are presented in Fig. 1b. Although there are hysteresis loops on all of them, their shape and size are different. When the carbon black content is 0.5 wt %, the hysteresis loop is the smallest; as the carbon black content increases to 1 and 2 wt %, the hysteresis loops become larger, and when the carbon black content increases to 3 wt %, the hysteresis become smaller again and there is a rise in the isotherm at high relative pressure, which implies there are larger pores in this sample. The corresponding α_s plots derived from isotherms in Fig. 1b are illustrated in Fig. 3. As noted for the original isotherms depicted in Fig. 1b, this clearly indicates a progressive change in isotherm type as the carbon black concentration increases. Thus, when α_s was low ($0.5 < \alpha_s < 1$) the α_s plots exhibit distinct linearity over the multilayer range, allowing the calculation of the external surface areas from the slopes of the plots in this range and the micropore volumes from extrapolations of the linear region. When α_s was higher than 1.0, however, the plots in the

TABLE I The pore structure parameters of resultant ACF

| Additive | Content (wt %) | Activation temp. (°C) | Activation time (min) | S_t ($m^2 g^{-1}$) | S_{mi} ($m^2 g^{-1}$) | S_{ext} ($m^2 g^{-1}$) | $V_{0.95}$ ($ml g^{-1}$) | V_{mi} ($ml g^{-1}$) | V_{me} ($ml g^{-1}$) |
|----------|----------------|-----------------------|-----------------------|------------------------|---------------------------|----------------------------|----------------------------|--------------------------|--------------------------|
| PVA | 1.0 | 880 | 30 | 810.4 | 697.3 | 113.1 | 0.459 | 0.282 | 0.177 |
| PVAc | 1.0 | 880 | 30 | 1148.1 | 1028.8 | 119.3 | 0.585 | 0.391 | 0.194 |
| PVC | 1.0 | 880 | 30 | 754.1 | 684.3 | 69.8 | 0.329 | 0.277 | 0.052 |
| Graphite | 1.0 | 880 | 30 | 965.5 | 890.5 | 75.0 | 0.486 | 0.334 | 0.152 |
| AC | 1.0 | 880 | 40 | 1178.9 | 929.2 | 249.7 | 0.740 | 0.330 | 0.410 |
| CB(I) | 1.0 | 880 | 30 | 1157.3 | 905.6 | 251.7 | 0.704 | 0.364 | 0.340 |
| CB(II) | 1.0 | 880 | 55 | 1251.8 | 915.6 | 300.2 | 0.773 | 0.422 | 0.351 |
| CB(III) | 0.5 | 880 | 55 | 1139.5 | 884.0 | 255.5 | 0.596 | 0.468 | 0.128 |
| CB(IV) | 0.5 | 880 | 55 | 1272.3 | 1192.1 | 80.3 | 0.720 | 0.497 | 0.223 |
| CB(I) | 1.0 | 880 | 25 | 920.5 | 766.8 | 153.7 | 0.517 | 0.390 | 0.208 |
| CB(I) | 1.0 | 880 | 20 | 847.5 | 743.8 | 103.7 | 0.443 | 0.302 | 0.141 |

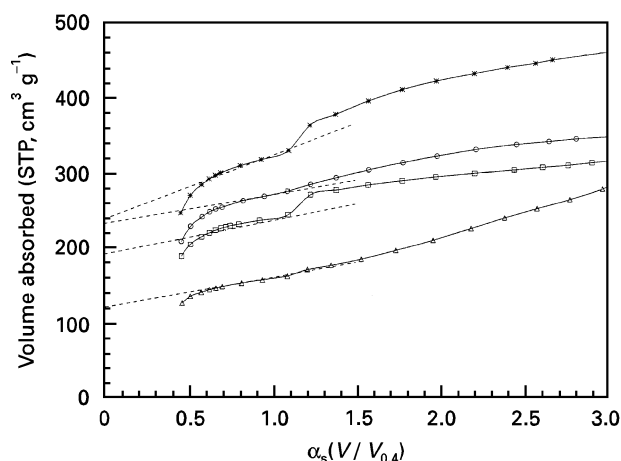


Figure 3 α_s curves for ACF (conditions as in Fig. 1b). (○) 0.5 wt %, (*) 1.0 wt %, (□) 2.0 wt %, (△) 3.0 wt %.

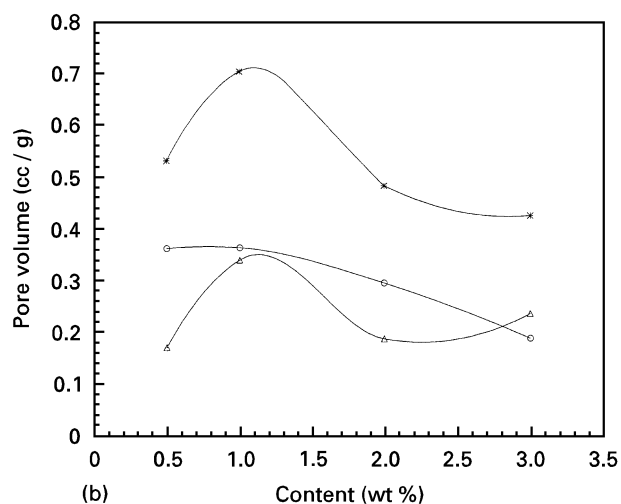
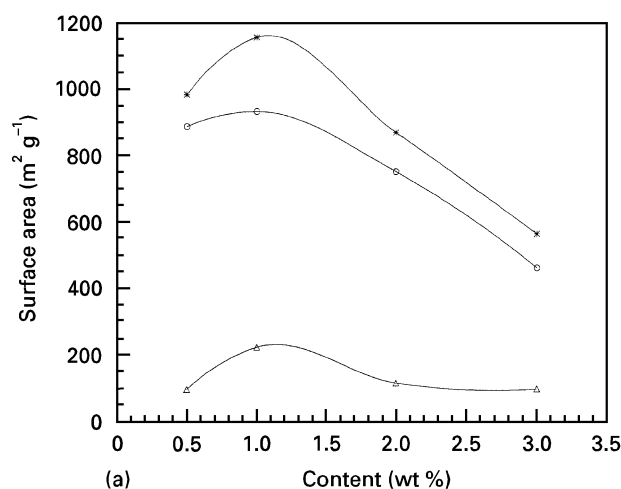


Figure 4 Pore structure parameters as a function of carbon black content (conditions as in Fig. 1b). (a) Pore surface area; (*) BET surface area, (○) micropore surface area, (△) external surface area. (b) Pore volume; (*) Total pore volume, (○) micropore volume, (△) mesopore volume.

show a distinct upward swing, indicative of capillary condensation, and the upward swing increases with the carbon black content.

Fig. 4a,b show the influence of carbon black content in PAN fibre on the porosity (Fig. 4b) and surface area (Fig. 4a) of the resulting ACF. Both total pore

surface area and volume, mesopore surface area and volume increase with carbon black content and reach a maximum at around 1 wt % then decrease again. The mesopore volume shows a slight rise at 3 wt % carbon black content, but the micropore surface area and volume show little increase at low carbon black content and an obvious decrease at high carbon black content. The result of the pore-size distribution calculation shows that all of them have a peak at about 4.0 nm. However, when carbon black contents are 1 and 2 wt %, the peak at 4.0 nm is so large that the mesopore structure can be thought to be a unimodal distribution. When the carbon black content is 3 wt %, there is a peak at 19.2 nm, which can explain the increase of the mesopore volume.

3.4. Effect of activation time

Nitrogen isotherms for ACF samples from PAN fibres with 1 wt % carbon black I subjected to activation at various times are listed in Fig. 1c. The isotherms show the progressive enlargement of hysteresis loops with activation time, which means the progressive development of mesoporosity with burn-off. From the similar shapes and some different adsorptions it can be deduced that the mesopores in these samples have the same type and different contents. The pore structure parameters are listed in Table I. The total pore volumes, mesoporosities and apparent surface areas are progressively increased with activation time. When the activation time is 30 min, the mesoporosity can reach 48.2%. The differential mesopore size-distribution curves are presented in Fig. 2c. Although the mesoporosities differ from each other, all of them have a similar shape with a peak at about 4.0 nm, but a tendency for the mesoporosity enhancement near 8.6 nm appears with increasing activation time.

3.5. The mechanism of mesopore formation

From the fact that the mesoporosities of ACF can be significantly improved by adding the carbon particles to PAN precursor, it can be proposed that mesopores develop at the interfaces of different carbon materials and micropores are formed inside the PAN-based carbon matrix. During heat treatment (stabilization and carbonization), the PAN polymer may have complex chemical reactions and shrink to some extent (according to Muller [9], when PAN fibres were heat treated in air for 5 h at 235 °C, they shrink by about 15%), but carbon additives do not. So the interface between the highly dispersed carbon particles and the carbonized PAN matrix may separate and provide a route for gas release. When there are no additives, the PAN fibres are made of uniform PAN polymer and the volatile products evolve, whenever they are formed during heat-treatment, and the routes are narrow, so the resultant ACF are microporous which means the majority of pores are narrower than 2.0 nm. However, when there are carbon additives present, the volatiles produced by PAN stabilization and carbonization may be directly deposited on to the interface between carbon black and matrix carbon, and are thus

transformed to a surface carbon layer. Otherwise, the volatile products may undergo a gas phase polycondensation reaction, leading to the formation of polyaromatic materials, which may be aggregated into so-called "droplets" and be deposited on to the surface. So the mesopores, resulting from the carbon black/PAN matrix carbon interface, are filled with amorphous carbon and become open after this carbon is gasified by steam activation. Additives PVA and PVAc decompose and leave pores in the carbon matrix, which probably play the same role as the pores between carbon additives and the matrix. These pores are also filled with amorphous carbon and this carbon can be removed by gasification. Because the mechanisms of pore formation for these two kinds of additive are similar, so the resultant mesopores have a similar size distribution which has a obvious peak at 4.0 nm.

Carbon black is a truly remarkable material having peculiar structure and texture; its manufacture is so simple but the aggregate morphology is rather complicated. Typical carbon blacks are composed of nearly pure carbon in colloidal entities of aciniform morphology, which means spherical carbon particles fused together in clusters of branched irregular shape. They have a rough surface, so polymer molecules can wet the surface to give a good blend. As mentioned above, the mesopores are developed at the interface between carbon black particles and the matrix, so the pore size is mainly effected by the carbon black particle itself and not the activation parameters, but the mesoporosity shows and inverse dependence on these two factors. With different types of carbon black (particle size, surface area and structure), the resultant ACFs have different pore-size distributions as showed in Fig. 2b. When the carbon black content is too low or high it is not effective in developing mesopores in the resultant ACF. Activation can gasify the amorphous carbon which filled the mesopores, and result in an increase of the mesoporosity. On the other hand, a longer activation time can cause the wall of micropores or mesopores to disappear and leads to an increased mesoporosity. Further research needs to be undertaken to give a more detailed explanation.

4. Conclusions

Adding certain materials to precursory PAN fibres is an effective way of improving mesoporosity in the resultant ACF. Three kinds of organic material and three kinds of carbon particles have been tested in the present paper. Among these additives, carbon

black and organic materials with low carbon yield after heat treatment (such as PVA and PVAc) are more effective.

1. When 1 wt % PVAc was added to PAN fibres and activated at 880 °C for 30 min, a mesopore volume of 0.194 ml g⁻¹ and a total pore volume of 0.585 ml g⁻¹ are obtained.

2. Both types of carbon black and their content have effects on the mesoporosity of the resultant ACF and mesopore size distribution. When 1 wt % carbon black I is added to PAN fibre, the mesopore size distribution of the resultant ACF has a unimodal distribution at 4.0 nm, a pore volume of 0.704 ml g⁻¹, and a mesopore volume of 0.340 ml g⁻¹.

3. The mesoporosity of the resultant ACF can also be determined from the activation parameters, and was found to increase with activation time.

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