

Conversion of Polyacrylonitrile Fibers to Activated Carbon Fibers: Effect of Activation

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SYNOPSIS

Polyacrylonitrile (PAN)-based activated carbon fibers were developed with the idea of increasing their potential and efficiency in industrial applications. The PAN-based fibers were first oxidized in air in a continuous multistage stabilization process, and then subjected to a continuous, low temperature carbonization and activation treatment in a mixture of steam and argon. The effect of the activation condition on the specific surface area, elemental composition, as well as the morphological structure of activated carbon fibers was studied. The surface area of the carbon fibers increased remarkably after the steam activation. It was found that steam activation promoted the elimination of nitrogen from the fiber. The bulk oxygen content of the fibers increased upon activation, probably due to formation of carbon-oxygen functionalities on the surface of the activated carbon fibers. The surface oxygen level of activated carbon fibers was greater than the bulk analysis of oxygen. It was observed that activation decayed the order of the carbon structure. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Activated carbon fibers (ACFs) are highly microporous solids and have better adsorption characteristics, such as larger adsorption capacity and higher adsorption and desorption rates, than granulated active carbons.¹⁻³ Owing to the nitrogen atoms contained therein, the ACFs evolved from polyacrylonitrile (PAN)-based fibers bear some specific adsorption features, and therefore have gained much attention recently.^{4,5}

The conversion of PAN fibers to ACFs usually include three steps: a low temperature thermoxidative stabilization, which forming a ladder structure to withstand subsequent high temperature annealing; a higher temperature carbonization to obtain a consolidated, graphiticlike carbon structure; and an activation treatment by an oxidizing atmosphere to create micropores. The first two steps are also encountered in the manufacture of PAN-based carbon

fibers on which a large amount of work has been done to get a better understanding of the underlying mechanisms and to acquire high-quality carbon fibers.⁶⁻¹¹ The activation step in ACF production is to create pores within the consolidated carbon structure by etching effects. The interaction of activating agents with the carbon structure inevitably alters the surface chemical structure as well as the microstructure of the resulting ACFs, and therefore bears significant impact on the application potential of ACFs. Therefore, it was deemed necessary to get a better understanding of the various processes and mechanisms involved in the conversion of ACFs from PAN-based fibers so as to choose suitable processing conditions to produce ACFs of desirable properties with high productivity and low cost. To this end, a sequence of experiments were conducted in our laboratory preparing ACFs from PAN-based fibers through a continuous process. During this set of studies, it was attempted to carbonize and activate PAN-based oxidized fibers in the same furnace, with activating mainly in the higher temperature region. The purpose of this choice was detailed in an earlier

report.¹² PAN-based fibers were first oxidized in air in a continuous multistage stabilization process, and then passed through a long quartz tube in which both carbonization and activation were performed. In this report, the effect of the activation condition, especially the amount of activating agent used, on the surface properties and morphological structure of the resulting ACFs is addressed.

EXPERIMENTAL

A special grade of PAN fiber tows (COURTELLE fiber, Courtaulds Ltd., U.K.) containing 3,000 filaments of 1.22 dtex was used in this work.

The apparatus for the continuous manufacture of activated carbon fibers from PAN-based fibers is similar to that reported in the literature.⁸ The continuous stabilization was performed in four independent furnaces, with each set to a specific temperature. The temperature profiles are as follows: 215, 230, 250, and 295°C, respectively. The feeding rate into the first stabilization furnace was controlled at about 8 m/h. After stabilization, the fiber tow was continuously passing through a furnace in which the carbonization and activation was functioning. The detailed description of this step was reported elsewhere.¹² The temperature profile adopted in this step is shown in Figure 1. A short U-shaped tube extended into the furnace from the outlet end, that is, the higher temperature end. Steam was obtained by vaporization of distilled water and then introduced into the furnace through an orifice situated at about the position of the end of the U-shaped tube. Oxygen-free argon of constant flow was purged through both ends of the furnace as the protective atmosphere. The concentration of steam was controlled by the flow rate of the water, which was varied in this work. It was the aim of this study to evaluate the influence of the concentration of the activating agent on the surface characteristics, such as surface area and surface chemical structure, of PAN-based ACF thus obtained through a continuous carbonization and activation process.

Bulk elemental analysis of fiber sample was carried out with a Perkin-Elmer 240C Elemental Analyzer. The fiber was examined for carbon, hydrogen, and nitrogen. The oxygen content was determined by difference.

The specific surface area (Brunauer-Emmett-Teller or BET method) of ACFs was measured by adsorption of nitrogen at 77 K using a domestically manufactured ST-03 Surface Area Analyzer.

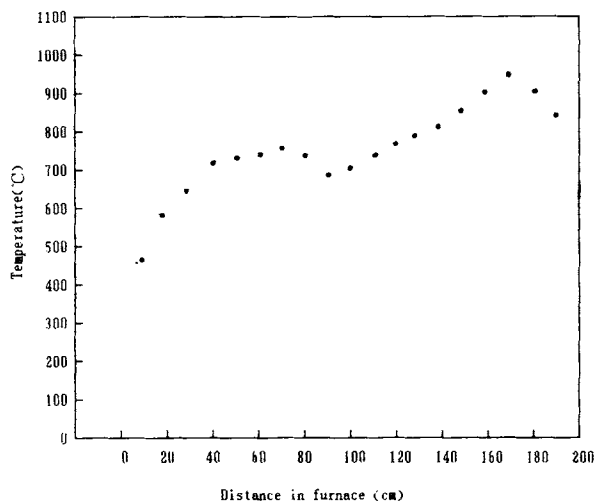


Figure 1 Temperature profile on carbonization and activation process.

The X-ray photoelectron spectroscopy analysis (XPS) on the fiber surface was done on a VG ESCALAB MKII. The surface atomic concentrations were calculated from integrated areas under the N1s, O1s, and C1s peaks in XPS spectra.

A rotating anode X-ray diffractometer, D/MAX- γ A, with Ni-filtered $\text{CuK}\alpha$ -radiation, was used to measure the stacking size, L_c , which was calculated by Scherrer formula.⁸ The data obtained is relative and provides a basis for comparison.

The morphology of the fiber surface and cross sections were observed on a Hitachi S-650 scanning electron microscope.

RESULTS AND DISCUSSION

Effect of Activation on Surface Area

The carbon structure of the PAN-based carbon fibers in low carbonization temperature are composed of mainly two types of carbon basal planes, graphiticlike basal planes and edge planes. During activation, activating agents react preferentially with the carbons at the edge planes, or nonregular parts of the carbon structures. As this proceeds, pores are created and formed within the consolidated carbon structure. The further development of the porosity on increasing the extent of activation, which usually yields increasing burn-off, depends on the mechanism of carbon removal via active site formation and the reactive rate of the reaction in the direction

Table I Specific Surface Area of Activated Carbon Fibers

Sample Code	a	b	c	d
Flow rate of water (g/min)	0	0.36	0.49	0.61
Specific surface area by BET (m ² /g)	Neg	613	716	900
Iodine number (mg/g)	19.3	985.9	1082.6	1237.4

Neg, negligible.

parallel to the plane of the graphitic layers compared to carbon removal in the direction perpendicular to this plane.¹³ Pores having an effective width less than 2 nm are defined as micropores; those having an effective width between 2 and 50 nm are defined as mesopores; those having width of larger than 50 nm are defined as macropores. As various pores are formed and created, the surface area of the carbon fibers is increased during activation. Table I shows the effect of activation on the iodine adsorption capacity and surface area of PAN-based ACFs via the continuous, concomitant carbonization and activation process. The surface area and iodine capacity increase remarkably after the activation. With the further increase in amount of activating agent (steam), the surface area and iodine capacity increase significantly. This indicates that the surface area of ACFs increases with an increase in the extent of activation. This significant increase in surface area may be due to two aspects: new pores were created upon increasing extent of activation, and pore drilling and pore deepening effects.¹³

Effect of Activation on Elemental Composition

The results of bulk elemental content and elemental composition of ACFs with activation are given in Table II. It can be seen that the bulk analysis of nitrogen content and N/C ratio decrease with activation. Comparing the bulk nitrogen content and N/C ratio of sample A (no activation) with those of sample B (with activation), both values decrease. Because the carbonization and activation was concomitant in the same furnace, this observation indicates that during the activation process nitrogen continued to be eliminated. Furthermore, the elimination of nitrogen was promoted in the case of steam activation. From sample B to D, the bulk analysis of nitrogen of ACFs decreases. The inference is that the steam activation enhanced the evacuation of nitrogen from the ACFs. Based on these results, it is assumed that the nitrogen containing moieties or functionalities of the fibers might act as active sites in the process of activation. As is known, activating agents preferentially interact with the edge or nonregular parts of the carbon structures when activation occurs, which leads to etching or removal of these pieces. In the carbonization of PAN-based oxidized fibers, the formation and stacking of carbon basal planes is due to crosslinking and polycondensation reactions between relatively stable, nitrogen containing heterocyclic aromatic structures. This implies that nitrogen containing parts were at the edges of the carbon basal planes. In addition, it was found that there were various forms of nitrogen containing functionalities bound to the carbon structures.¹⁴ Thus, during activation, these parts might perform as active sites and were preferentially attacked by activating agents. Due to this interaction, the elimination of nitrogen was promoted.

Table II Bulk Elemental Analysis and XPS Surface Analysis Data

Sample Code	Flow Rate of Water (g/min)	Bulk Elemental Analyses							XPS Surface Analyses			
		Atomic Content (wt %)				Atomic Ratios			Atomic Ratios		FWHM of C _{1s} peaks (eV)	Stacking Size by WAXD Lc (nm)
		C	H	N	O	[H]/[C]	[N]/[C]	[O]/[C]	[N]/[C]	[O]/[C]		
A	0	75.8	1.8	16.7	5.7	0.29	0.19	0.056				1.34
B	0.12	76.3	2.4	8.0	13.3	0.38	0.090	0.13	0.052	0.23	2.2	1.27
C	0.25	80.0	2.5	4.8	12.7	0.38	0.051	0.12	0.052	0.19	2.2	1.11
D	0.49	83.0	2.6	2.7	11.7	0.38	0.028	0.11	0.025	0.26	2.3	1.07

FWHM, full-width at half maximum.

The bulk analysis of oxygen content and O/C ratio in Table II show a complex trend. With activation (sample A to B), oxygen content increases. While increasing the extent of activation as from sample B to D, the oxygen content shows a slight decrease. When carbon fibers were heat treated during steam activation, the reaction between the water molecules and the disorganized parts of the carbon structures led to formation of various types of carbon-oxygen complexes. These complexes became the origin of oxygen containing functionalities. As this process proceeded, additional oxygen was thus introduced onto the fibers, causing an increase in oxygen content. On the other hand, it was conceived that the carbons attached by oxygen functionalities belonged to nonregular carbons situated at the edges of the carbon basal planes. Thereafter, during heat treatment in activation, these sites behaved as active sites or sites of attack of water molecules. As this happened, the carbon-oxygen functionalities were partially destroyed or converted, which causes a decrease in oxygen content. Therefore, the outcome of this competition related to the formation and elimination of oxygen containing functionalities largely determined the surface chemical structure of the ACFs, and naturally the oxygen content variation. As seen in Table II, it seems that when carbon fibers were first exposed to heat treatment in steam (sample A to B), bulk oxygen content increases, which is probably due to some oxygen functionalities being induced onto fibers by activation.

To get further insight into the effect of activation on chemical composition of ACFs, XPS was used to obtain information on the surface chemical composition of the ACFs. The spectral shapes of the C1s spectra of the XPS of three ACFs (samples B-D) are compared in Figure 2. All C1s peaks show significant broadening. A large chemical shift toward the higher binding energy side can be observed. These observations are mainly due to various types of carbon-heteroatom (oxygen and nitrogen) functionalities bound to the surface carbons of the ACFs. The surface elemental composition of ACFs detected by XPS is listed in Table II, together with values of full-width at half maximum (FWHM) of three C1s peaks. The surface N/C ratio decreases from sample B to D, indicating that with an increase in concentration of steam, nitrogen content decreases. This trend in surface nitrogen variation is similar to that of the bulk analysis of ACFs (Table II). This observation supports the before-mentioned inference that steam activation accelerates the elimination of nitrogen from the fibers. Comparing the nitrogen

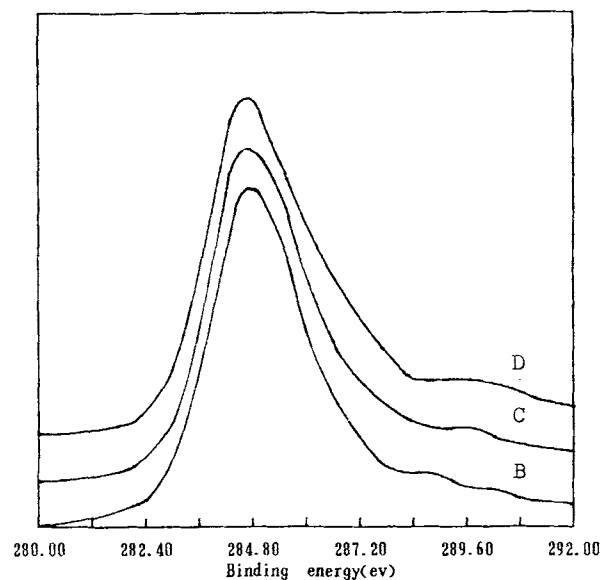


Figure 2 XPS C1s spectra of activated carbon fibers.

ratio of the surface and that of the bulk, it seems that the bulk nitrogen level is higher than that at the surface. At a low extent of activation (sample B), this difference in nitrogen level is obvious. Although further evidence is needed to obtain a convincing conclusion, this observation may be explained on the basis of carbonization and activation, respectively. As is known, during carbonization treatment of PAN-based oxidized fibers, nitrogen elimination occurs as heterocyclic aromatic rings undergo crosslinking and condensation reactions. This process leads to formation and stacking of carbon basal planes, which are the basic elements of the consolidated carbon structures of carbon fibers, because the nitrogen elimination is directly related to the extent of stacking of the carbon basal plane, the latter being the symbol of the degree of carbonization. Evidence has shown that PAN-based carbon fibers have higher orientation and larger crystallites on the surface or sheath region than that in the interior of the fiber.¹⁵ This difference in radial structure, termed as a two-phase structure, is originated from the initial oxidative stabilization treatment, with the outer sheath formed from the outer region with a higher extent of stabilization, and the core from the partially stabilized inner part of the fiber. This indicates there exists a gradient in the degree of carbonization from the surface to the core region during or after carbonization, which suggests a similar gradient in the extent of nitrogen elimination, that is in the outer region; a higher degree of car-

bonization corresponds to a higher extent of nitrogen elimination; and in the inner region, a lower degree of carbonization corresponds to a lower extent of nitrogen elimination. As a result, the nitrogen content on the surface of the carbon fibers is supposed to be less than that in the inner region. Therefore, the bulk analysis of nitrogen is higher compared to that on the surface. Second, as discussed above, activation by steam helps in evacuating nitrogen from the carbon structures, because activation was mainly functioning on the surface layer of the fiber. Consequently, this interaction caused more loss of nitrogen on the surface. As a result, the nitrogen content on the surface was more reduced, different from that in the bulk.

Comparing the surface O/C ratio with that of bulk analysis, the surface oxygen is greater than the bulk analysis of oxygen. This may suggest that during steam activation some oxygen containing functionalities were induced onto the fiber surface, making the level of oxygen on the fiber surface higher than the bulk. As the concentration of steam increases (sample B–D), the surface oxygen level of the ACFs shows no significant variation. It is accepted that the characteristics of these oxygen and nitrogen containing functionalities on the surface of the fiber have significant influence on the adsorption features and efficiency of resulting ACFs. Recent studies by a Chinese research group on ACFs showed that the surface of ACFs have redox function.^{16,17} For example the Au³⁺ could be reduced to Au on the surface of ACFs. These discoveries render new application potential to the ACFs, and symbolize the significance and necessity of careful understanding and investigation of the surface characteristics, including the various functionalities, of the ACFs.

Effect of Activation on Morphological Structure

The data on variation of stacking size of ACFs measured by WAXD is given in Table II. With activation and increase in concentration of steam, the stacking size generally decreases. This indicates that steam activation has a degrading effect on the carbon structures due to its etching interaction. From the FWHM values of the C1s peaks of XPS spectra in Table II, some aspect on the surface order of ACFs can be shown. It was established that a carbon material with a less complete graphite structure on the surface showed a broader C1s spectrum, that is, a higher FWHM value.¹⁸ Thus, FWHM can be an indication of the extent of the order of the carbon

structure on the fiber surface layer. The high FWHM values of ACFs (Table II) indicate a highly disordered structure on the surface of ACF. Besides, it seems that the severe activation by steam (as in sample D) has a further disordering effect on the surface of ACF. Combining the results on variation of stacking size and FWHM values of ACFs, it appears that the steam activation has a degrading effect on the order of the carbon structure. The more vigorous the activation, the more obvious the degrading effect.

The morphology on surfaces and cross sections of ACFs are revealed by SEM in Figure 3. It is obvious that as the extent of activation increases, the diameter of the fiber decreases, indicating more parts of structure being etched and removed during activation. The roughness on the surface of the fiber seems to decrease from sample A to D, especially at a high extent of activation (sample D). This is probably due to the etching effect of activation that removed the outermost layer of the fiber surface, thus smoothing the fiber surface. Examining the cross sections of the fibers in Figure 3, a similar observation can be seen: the fiber diameter decreases significantly as the extent of activation increases. The roughness on the cross sections also shows a decreasing trend with activation. This result may be because the activation treatment increases the brittleness of the fiber because it creates a lot of pores within the carbon structure. Thus, the fracture behavior of ACFs, especially with a high extent of activation, might more likely be brittle failure. As a result, the fracture surface on cross sections of the fiber appears smooth.

CONCLUSIONS

1. The surface area of the carbon fibers increased very remarkably after the steam activation process. With increase in steam concentration, the surface area increased significantly.
2. The activation treatment was found to promote the elimination of nitrogen. This might be due to the steam interaction with nitrogen-containing moieties that were attached or bounded to the carbon basal structures. The bulk level of the nitrogen content of the ACFs seemed higher than that at the surface. Further evidence is being sought to draw a convincing conclusion.

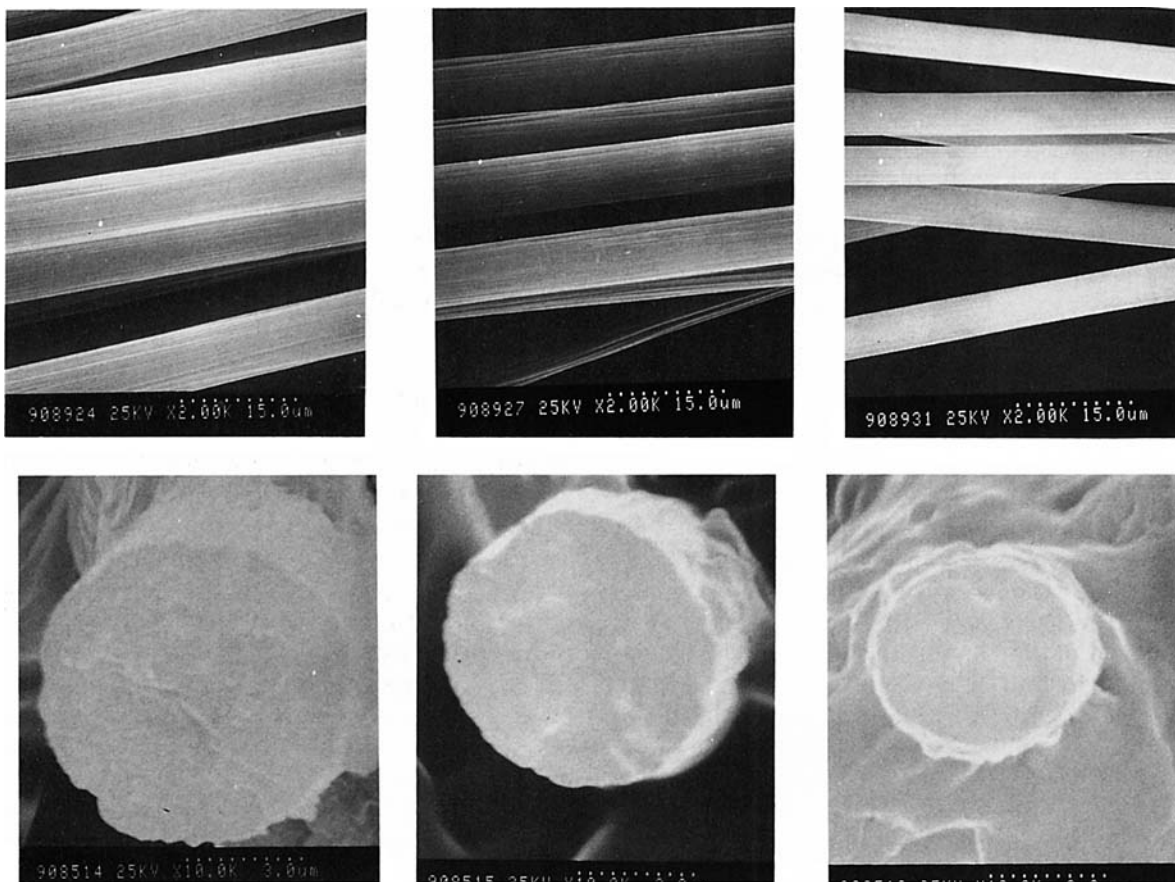


Figure 3 SEM photographs of the sample surfaces and cross sections.

3. The effect of steam activation on the oxygen content of ACFs depended on a competition between two reverse processes: formation of carbon-oxygen functionalities and elimination of these functionalities. Upon activation, the bulk oxygen content of the fiber increased, probably due to some oxygen-containing functionalities being induced onto the fiber surface. The surface oxygen content of ACFs was greater than the bulk analysis of oxygen.
4. Steam activation had a degrading effect on the order of the carbon structure. The fiber diameter decreased with an increase in activation.

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