

# Surface Analyses of Polyacrylonitrile-Based Activated Carbon Fibers by X-ray Photoelectron Spectroscopy

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## SYNOPSIS

In this work, polyacrylonitrile (PAN)-based activated carbon fibers (ACFs) were developed by the common processes of stabilization, carbonization, and steam activation. Those fibers were successively subjected to heat treatment in a vacuum at high temperature and reactivation in steam. The changes in specific surface area and surface chemical characteristics were studied. The vacuum treatment reduced the surface area dramatically, while the surface nitrogen decreased after activation in steam and the surface oxygen was lowered upon the vacuum treatment. By curve-fitting the X-ray photoelectron spectroscopy (XPS) of C1s, O1s, and N1s, it was shown that the forms and compositions of the oxygen-containing functionalities seemed not to be affected significantly by the above-mentioned heat-treatment processes, whereas the nitrogen-containing functionalities showed some changes with these treatments. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Because of their excellent surface properties, high adsorption capacity, and great flexibility in converting into a wide variety of textile forms, activated carbon fibers (ACFs) have attracted increasing attention. An advantage of fibrous active carbon over powdered carbon is the higher bulk volume of the former, which can lead to higher adsorption and desorption rates due to the more open structure.<sup>1-3</sup> Because of the nitrogen atoms contained therein, the activated carbon fibers developed from polyacrylonitrile (PAN)-based fibers have some specific features in industrial application. Conversion of activated carbon fibers from PAN-based precursor fibers usually include three steps: (1) oxidative stabilization, which transforms the linear structure of PAN fibers into a partially cyclized ladder structure; (2) higher-temperature carbonization, which develops a consolidated, graphiticlike carbon structure; and (3) activation treatment. During the activation treatment, high porosity is formed within the material through the interaction of activating agents

(usually oxidizing medium like steam, carbon dioxide, etc.) with carbon structures. By this interaction, the surface chemical properties are altered or transformed to some extent. It has been accepted that the efficiency and potential of ACFs in the application areas is greatly determined by their porosities, surface areas, as well as surface chemical structures. Thus, it is important to understand the transformation or variation of the surface chemical structure of carbon fibers during the activation process.

In the present study, activated carbon fibers were developed from PAN-based fibers by oxidative stabilization, carbonization, and steam activation. Then, those fibers were heat-treated in a vacuum at a high temperature, followed by being reactivated in steam. The variation of surface chemical structures (surface atomic compositions and surface functionalities) of the fibers along these processes was carefully investigated by XPS analyses.

## EXPERIMENTAL

A special grade of PAN-based fiber tow (Courtelle Fiber, Courtauld Ltd., UK) containing 6000 filaments was used in this work. The PAN fibers were

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**Table I** Specific Surface Areas of the Fibers

	Sample			
	A	B	C	D
Specific surface area (m <sup>2</sup> /g)	0.6	383	1.3	815

A: Initial fiber; B: activated at 830°C for 1 h in steam-argon mixture; C: obtained by treating B in a vacuum at 850°C for 40 min; D: obtained by treating C under the same conditions as B for 0.5 h.

stabilized and carbonized using a continuous process. The stabilization constitutes four furnaces with temperatures of 215, 230, 255, and 300°C, respectively. The processing rate is about 10 m/h. The stabilized fibers were carbonized by passing through a furnace with temperature increasing from 300 to about 900°C in an argon atmosphere (sample A). Three parts of sample A were activated in a mixture of steam-argon at about 830°C for 1 h simultaneously using a batch method (sample B). Two parts of sample B were then heat-treated under a vacuum ( $\sim 7 \times 10^{-4}$  mbar) at about 850°C for 40 min (sample C). One part of sample C was reactivated in the same conditions as was sample B but with 0.5 h in activation time.

The surface area of the fibers was measured by adsorption of nitrogen at 77 K with application of the BET equation using a domestically manufactured surface area analyzer. XPS measurements were carried out in a VG ESCALAB MK II system with a spherical sector analyzer. The base pressure was  $1 \times 10^{-9}$  mbar. A MgK $\alpha$  radiation source ( $h\nu = 1253.6$  eV) was used in the XPS measurements with the overall energy resolution of 1.0 eV. The experiments were conducted on a fiber bundle.

## RESULTS AND DISCUSSION

### Surface Composition

The results on the variation of specific surface area of carbon fibers upon activation, vacuum treatment, and reactivation are listed in Table I. It can be seen that the surface area of carbon fibers shows a certain extent of increase after the first activation. With the vacuum treatment at high temperature, the surface area of the activated carbon fibers decreases significantly. While on reactivation, the surface area increases markedly. Sandle and Sudershan Rao<sup>4</sup> observed a similar decrease in the surface area when active carbons underwent heat treatment in a vac-

uum at high temperature. It should be noted that the duration for the reactivation treatment was about half of the first activation treatment. However, the increase in surface area was more significant during the reactivation than during the first activation. It is thus suggested that heat treatment in a vacuum led to a decrease in open porosity or converted the open porosity to close porosity. The subsequent reactivation treatment caused the opening up of this closed porosity and, therefore, led to a more significant increase in the surface area.

The surface atomic compositions of the fibers by XPS analysis are given in Table II. The initial activation causes an obvious decrease in surface nitrogen. While on reactivation, the decrease in surface nitrogen is more evident. These observations suggest that the activation treatment in steam helps the elimination of nitrogen from the carbon structures.<sup>5</sup> It is known there are still some amount of nitrogen left in the structures of carbon fibers, which exist in various types of nitrogen functionalities after the carbonization treatment. These functionalities were bounded or attached to the edge parts of the carbon structures. During activation treatment, these edge parts would be preferentially attacked by the oxidizing agents, which probably led to the removal of these edge structures. Due to this effect, the surface nitrogen level decreased upon activation treatment. Table II shows that the heat treatment in a vacuum seems to lead to an increase in the surface nitrogen. One reason may be that the vacuum treatment brought about the release of trapped products and the associated oxygen groups, thus resulting in exposure of the new nitrogen functionalities residual in the fiber structure. On the other hand, an obvious decrease in the surface oxygen is observed during the process of heat treatment in a vacuum. This indicates that this treatment somewhat reduces the surface oxygen complexes. With reactivation in steam, as from sample C to D, the surface oxygen shows a trend of increase, indicating the reformation of some carbon oxygen complexes or functionalities on the fiber surface.

**Table II** Surface Composition (Atomic %) of the Fibers

Sample	C	O	N	N/C	O/C
A	84.3	7.0	8.7	0.10	0.083
B	86.2	7.0	6.7	0.078	0.082
C	86.6	5.7	7.6	0.088	0.066
D	88.5	6.6	4.9	0.055	0.075

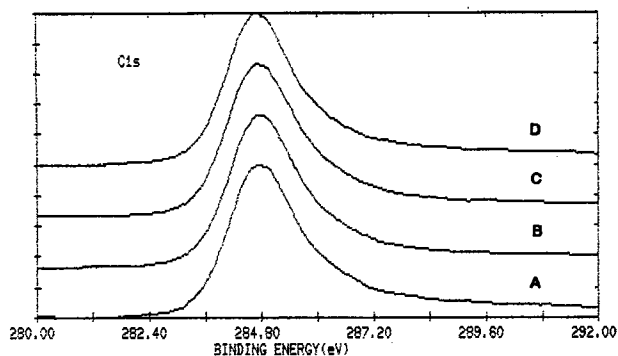


Figure 1 XPS C1s spectra of the fibers.

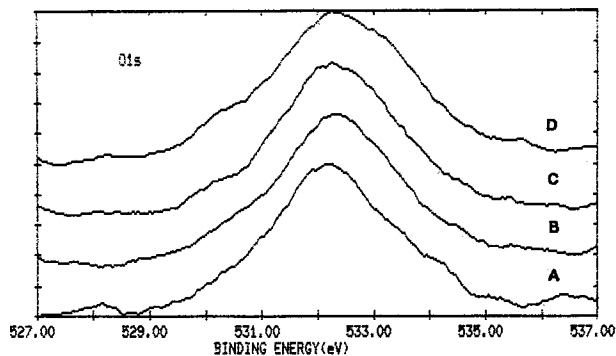


Figure 2 XPS O1s spectra of the fibers.

### Surface Functionalities

The XPS C1s, O1s, and N1s spectra of the surfaces of four fiber samples (A–D) are shown in Figures 1, 2, and 3, respectively. No significant difference in C1s and O1s spectra between fiber samples exists. However, all C1s peaks show a quite obvious chemical shift toward the high binding energy side. These indicate that there exist various carbons in different circumstances on the surfaces of the fibers. The O1s spectra show a high value in the half-width, suggesting a different chemical structure of oxygen on the fiber surfaces. Combining the observations on the C1s and O1s spectra, it is implied that there are different forms of carbon–oxygen functionalities on both carbon fibers and the activated carbon fibers. The N1s spectra in Figure 3 indicate that not only does nitrogen exist in various functionalities on the surfaces, but also that these nitrogen functionalities vary to some extent from initial activation to final reactivation.

To clarify the forms of different functionalities and the variation of these functionalities with the heat-treatment processes, the curve-fitting procedures on the C1s, O1s, and N1s spectra of four fiber samples were performed. Typical results are shown in Figure 4. A C1s spectrum contains a major peak at a binding energy of about 284.7 eV. This peak can be probably attributed to graphitic carbons. In addition, a series of chemically shifted peaks are observed at the high-binding energy side of this main peak. Three peaks are generally observed, which occurs at binding energies of about 286.1, 287.5, and 289.1 eV, respectively. These peaks can be assigned to C—O (ether/hydroxyl), C—N, C—O (carbonyl), and COOH (carboxylic) functionalities, respectively.<sup>6–8</sup> A typical O1s envelope appears to contain mainly three chemically shifted peaks. The peak at a binding energy of about 531.3 eV is attributable to C=O groups in carboxylic acids or esters.<sup>6,9</sup> The

peak at 532.3 eV is probably due to C—O in carboxylic acids or C=O in quinone groups, while the peak at 533.6 eV is tentatively assigned to the C—O bond in an aliphatic ketone or alcohol.<sup>6,9</sup> Thus, based on the C1s and O1s spectrum analyses, it can be inferred that on the surface of fibers either before or after activation there are present several forms of carbon–oxygen functionalities. The activation, vacuum treatment, and reactivation did not significantly vary the forms of these carbon–oxygen functionalities. The curve-fitting of C1s envelopes of four fiber samples was performed and the results on compositions of different functionalities present on the surfaces of fibers are listed in Table III.

The N1s envelope contains four chemically shifted peaks. The binding energy values of the peaks for the surface of four fiber samples are given in Table IV. The low binding energy, which gives a peak at  $\sim 399$  eV, is indicative of aromatic amine ( $\text{PhNH}_2$ ) and/or imine ( $\text{C}=\text{NH}$ ). The peaks at 399.0–400.0 eV can be attributed to amide functionalities.<sup>10–12</sup> The peaks observed between binding energies of 400 and 401 eV were ascribed to aliphatic amine (about 400.4 eV),<sup>12</sup> while the peak around 401.4 eV is probably due to protonated amine ( $\text{NH}^{3+}$ ).<sup>12</sup> The high binding energies are character-

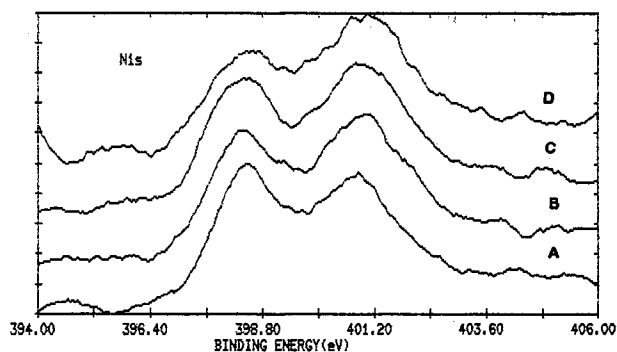
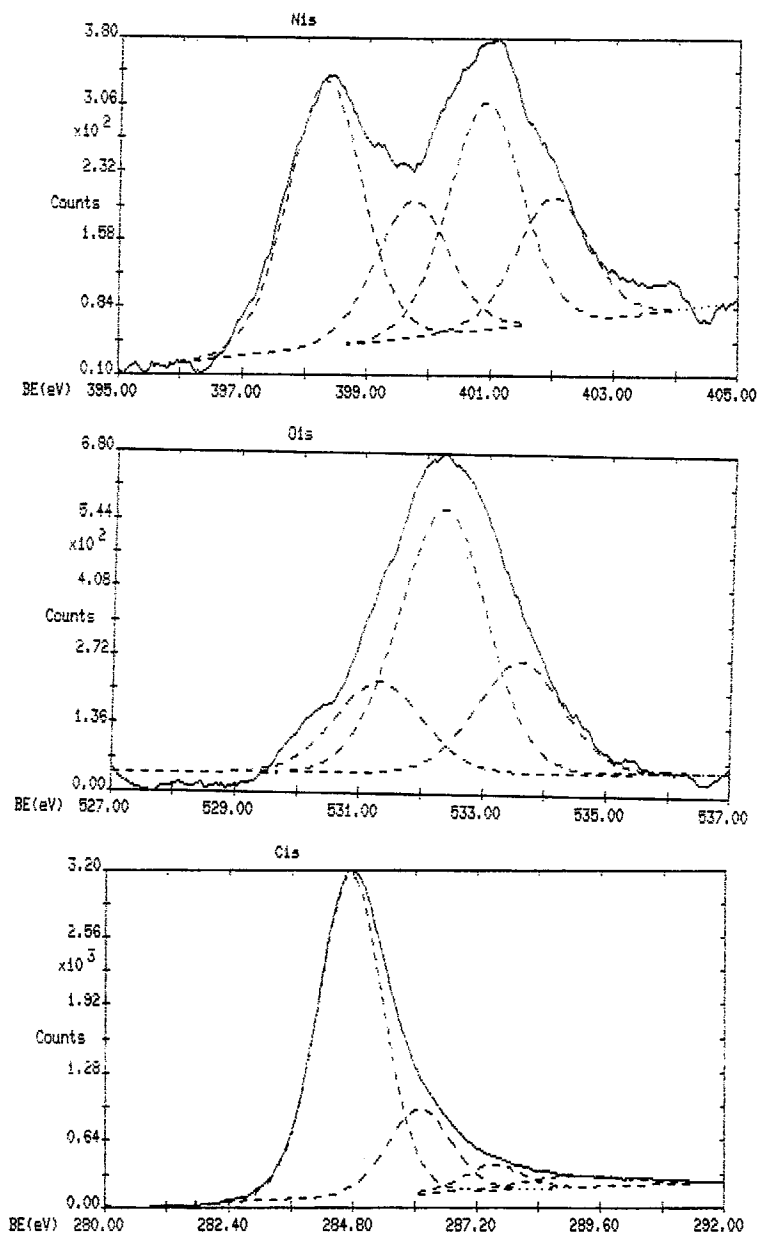


Figure 3 XPS N1s spectra of the fibers.



**Figure 4** Typical curve-fit spectra of XPS C1s, O1s, and N1s peaks envelopes.

istics of an ammonium ion which has been reported to give a peak at a binding energy of  $\sim 402.8$  eV.<sup>12,13</sup> The decrease in intensity of the lower binding energy peak with subsequent activation, vacuum treatment, and reactivation could indicate the gradual elimination of aromatic amine and/or imine species during these processes. It may be because these groups are bound to the carbon structures at basal plane edge sites. Therefore, during heat treatment, either in activation or vacuum treatment, these sites would be preferentially removed or altered. The development of a peak at high binding energy (around 401

eV) is probably due to the formation of protonated amine.

## CONCLUSIONS

1. The specific surface area of carbon fibers showed an obvious increase with steam activation. However, with vacuum treatment at high temperature, the surface area of the activated carbon fibers decreased significantly.

**Table III XPS Curve-fit Data for C<sub>1s</sub> Photoelectron Peaks**

Sample	C—C		C—O or C—N		C=O		O=C—O	
	B.E. <sup>a</sup>	%	B.E. <sup>a</sup>	%	B.E. <sup>a</sup>	%	B.E. <sup>a</sup>	%
A	284.7	68.2	286.1	20.1	287.5	5.9	289.1	5.9
B	284.7	71.6	286.1	18.9	287.5	5.3	289.1	4.2
C	284.7	67.8	286.0	20.3	287.4	6.4	289.1	5.4
D	284.7	74.1	286.2	12.5	287.4	8.0	289.4	5.4

<sup>a</sup> Binding energy (eV).

While on reactivation, the surface area increased markedly.

- The surface nitrogen level of carbon fibers showed an evident decrease upon initial activation. Upon reactivation, this decrease in surface nitrogen was observed to be more significant. The results indicated that steam interaction with fibers (either carbon fibers or activated carbon fibers) can eliminate nitrogen from the carbon structure. However, heat treatment in a vacuum appeared to cause the increase in the surface nitrogen content.
- The heat treatment in a vacuum gave rise to a decrease in the surface oxygen level of activated carbon fibers. This indicated that the vacuum treatment somewhat reduced the surface oxygen complexes. When reactivated in steam, the surface oxygen increased.
- The curve-fitting of XPS C<sub>1s</sub>, O<sub>1s</sub>, and N<sub>1s</sub> spectra showed that on the surface of activated carbon fibers were presented various forms of oxygen-containing and nitrogen-containing functionalities. The forms and composition of the oxygen-containing functionalities were not significantly affected by the present heat-treatment processes, while the nitrogen functionalities showed some variance. The intensity of the lower binding energy peak gradually decreased when sub-

jected to heat treatment. This suggested that the elimination of aromatic amine and/or imine species occurred during these processes. The development of a peak at high binding energy (around 401 eV) could be probably due to the formation of protonated amine.

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**Table IV Nitrogen 1s Photoelectron Energies (B.E., eV) of the Fibers**

Sample	B.E. <sub>1</sub>	B.E. <sub>2</sub>	B.E. <sub>3</sub>	B.E. <sub>4</sub>
A	398.4	399.8	401.0	402.5
B	398.3	399.7	400.9	402.0
C	398.2	399.7	401.0	402.3
D	398.4	399.8	401.2	402.8