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X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. 22. Comparison between Surface Treatment of Untreated and Previously Surface-Treated Fibers

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IM7 PAN-based carbon fibers, with a proprietary surface treatment applied by the manufacturer, were analyzed by X-ray photoelectron spectroscopy (XPS). The surface treatment applied by the manufacturer was removed by heating in a vacuum. The fibers detreated in this manner were then subjected to electrochemical treatment. The electrochemical behavior of the as-received fibers and detreated fibers were measured and analyzed. When the same electrochemical treatment was applied to the as-received fibers with their commercial surface treatment intact, a different surface chemistry was observed for the detreated fibers. This study shows that the surface chemistry of treated fibers depends closely on the initial surface chemistry of the fibers and its detreatment. This work shows the importance of using untreated or detreated fibers as precursors for applying reproducible surface treatment so that one can understand and control the surface chemistry of fibers and their interfacial interaction in composites.

1. Introduction

Carbon fiber composites are now widely used as structural materials in a variety of applications, particularly in the aerospace industry. Carbon fibers are commonly used as reinforcement materials in such composites because of their high strength, high stiffness-to-weight ratio, and their resistance to corrosion and high temperatures.[1−4] However, as the performance requirements of composites increase, the need to control the interaction between the reinforcing fibers and the matrix material has also become much more important. Previous studies have shown that the nature of the fiber surface significantly affects the adhesion at the interface.[5] It is now generally accepted that the surface treatment of carbon fibers is an essential step in the manufacture of composite materials because a treatment of this type promotes better adhesion between the fiber and matrix phases involved.[6−9]

Carbon fibers are graphitic in nature and in their untreated mainly graphitic state have very low surface reactivity with hydrophilic matrixes. Untreated carbon fibers are usually characterized by a low surface area and lack of chemical functionality on the fiber surface, resulting in poor wetting of the fiber surface by the matrix phase of the composite. This often leads to a low interlaminar shear strength, affecting the other desirable mechanical properties of the material.[10] It is thus common for manufacturers to apply some form of proprietary surface treatment to the fibers. Such a treatment usually results in an improvement in the fiber-matrix adhesion for the chosen matrix material. Electrochemical treatments are widely used as treatment methods. Nitric acid, among other electrolytes, has been used for many years as an electrolyte for such treatments.[9,11] The investigation of the effect of such treatments on the surface chemistry of the fibers have been the subject of extensive examination by many research groups,[12−20] including our own group.[7, 21−24]

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X-ray photoelectron spectroscopic (XPS) studies of a thin layer of resin coated onto the surface of a carbon fiber have been effectively used to model and study the interfacial properties of a composite.[25−37] However, for such a study to be feasible, it is necessary to know the exact nature of the chemical entities present on the fiber surface and matrix phase, so that the mode of interaction with the matrix phase can be accurately predicted. Surface treatments applied by the manufacturer are invariably proprietary for a special matrix phase, and without knowing the exact history of the fiber, it is impossible to predict the nature of its bonding to the resin phase. It is thus necessary to improve the surface chemistry of the fibers by further treatment or removal of original surface compounds before further treatment. Removal of a manufacturer's surface treatment is not straightforward, especially if a size has been applied,[38] and in this work we use a high-temperature treatment under vacuum to perform the task. This study will focus on a comparison between the surface chemistry that results when untreated carbon fibers are electrochemically oxidized and manufacturer surface-treated carbon fibers that are subjected to the same electrochemical oxidation. We generate the "untreated" carbon fibers by removing the manufacturer's surface treatment by heating in vacuo.

2. Experimental Section

2.1. Sample Preparation. The carbon fibers used for this study were obtained from Hercules and had been previously surface-treated to the level of one standard industrial treatment, which is proprietary (Hercules IM7(3K)-unsized). This treatment had produced enough surface functionality that the fiber no longer behaved as if the surface were untreated. Care was taken to prevent contamination of the fibers by manual handling and the fiber tows used were harvested from a part of the spool not directly in contact with the protective plastic packaging.

Electrochemical oxidation of the fibers was carried out in a special three-electrode glass cell constructed for this purpose. Details of the cell have been published in earlier work from this group.[22] A 1.0 M solution of nitric acid was used as the electrolyte and a 6-cm tow of the carbon fibers was used as the working electrode (4 cm was immersed in the solution). Oxidation was conducted in the potentiostatic mode. A standard calomel electrode (SCE) was used as the reference electrode in the electrochemical cell. A 4-cm tow of the fiber was potentiostatically oxidized at voltages ranging from 0.5 to 3.0 V with respect to SCE. Nonuniform treatment is common in the potentiostatic mode when shorter polarization times are used.[39] The polarization was thus carried out over a 20-min time period to ensure that all parts of the fiber tow were oxidized in a uniform and reproducible manner.

2.2. Sample Detreatment. The experiment was conducted in a vacuum, which is required to prevent carbon oxidation and its resulting mass loss. The commercially treated IM7 fibers were cut from the spool in separate tows ≈6 cm in length and put into a silica glass tube with an inner diameter of 2 mm. The tube was pumped down below 1.0×10^{-2} Torr and sealed. The sealed tube was heated in a resistance furnace over 1100 °C for 30 min and then cooled slowly.

2.3. Voltammetry of Fibers. Multicyclic voltammograms were run on a Bioanalytical Systems, Inc. CV-50 W equipped with a PC using the same electrochemical cell, counter electrode, reference electrode, and electrolyte (1 M HNO_3) that was used for the electrochemical surface treatment of the fibers. The scan rate of the cyclic voltammetry was at 10 mV/s with a sensitivity of 10 mA/V. The 4-cm long IM7 carbon fibers were immersed in the electrolyte. The system uses computer control to perform the electrochemistry and collect the data. Four nonstop consecutive cycles were collected for each sample. The two sample types studied were commercially received IM7 fibers and detreated IM7 fibers. Multiple samples were run for each type of fiber to ensure reproducibility of the experiment, though we report the data for one experiment below.

2.4. Surface Analysis. XPS spectra were collected on an AEI (Kratos) ES200B X -ray photoelectron spectrometer, which operates at base pressures of approximately 10^{-8} Torr. Data were collected using the fixed analyzer transmission (FAT) mode with a pass energy of 50 eV using achromatic Mg $K\alpha_{1,2}$ X-radiation (1256.3 eV, 240 W) having a linewidth of 0.7 eV. The energy scale of the spectrometer was calibrated using copper,[40,41] and the C 1s binding energy of the graphitic peak was fixed at 284.6 eV for calibration purposes.

Curve fitting of the core-level XPS spectra was carried out using a nonlinear least-squares fitting program with a Gaussian−Lorentzian (G/L) fitting function[42] and a nonlinear background.[43] The G/L mix was assumed to be 0.5 for all peaks except for the main graphitic peak, where it was given a value of 0.84 with an exponential tail.

3. Results and Discussion

This study focused on the examination of the oxidation behavior of the surface-treated IM7 fibers when subjected to potentiostatic oxidation. Because the as-received surface treatment is proprietary, it is important to determine the surface chemistry of the fiber after commercial treatment. The sample designations given in Table 1 will be used throughout this paper, except where otherwise noted. Sample (a) represents the fiber as-received from the manufacturer or the fiber that we detreated, while samples (b)−(f) are fiber samples that have been subjected to electrochemical oxidation at various voltages ranging from 0.5 to 3.0 V.

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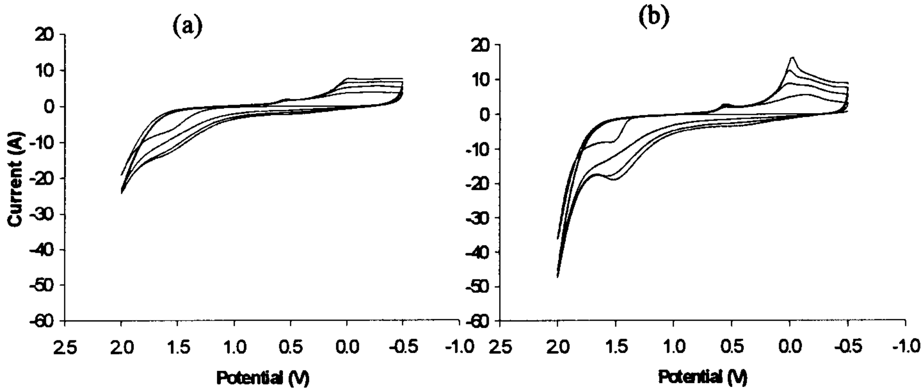

Figure 1. The voltammograms of (a) as-received IM7 carbon fibers and (b) detreated IM7 fibers measured at 10 mV/s in 1 M HNO_3 electrolyte.

Table 1. Description of Samples Studied

designation	description of electrochemical treatment
(a)	commercially treated or as-detreated, rinsed in distilled water
(b)	0.5 V/1.0 M HNO_3, rinsed
(c)	1.0 V/1.0 M HNO_3, rinsed
(d)	1.5 V/1.0 M HNO_3, rinsed
(e)	2.0 V/1.0 M HNO_3, rinsed
(f)	3.0 V/1.0 M HNO_3, rinsed

3.1. Detreatment of Surface-Treated Carbon Fibers. It is well-known that surface treatment can be removed by heating carbon fibers in vacuo to high temperatures. Indeed, this approach has been used[44] to investigate the surface treatment of carbon materials by monitoring the emitted gases by mass spectrometry. We have used this approach to produce carbon fibers surfaces with no surface functionality in a number of studies. For example, we have compared an untreated carbon fiber at ambient temperature with one heated in vacuo at 1400 °C to determine residual surface functionality on untreated carbon fibers, monitoring the evolved gases by mass spectrometry.[7] We have used the heating in vacuo of untreated carbon fibers that have been surface-treated as a means of removing the surface treatment,[45] including the development of a special apparatus to monitor the effects of oxygen ion bombardment and the subsequent removal of the resulting surface functionality.[46] In this paper we have used this approach to remove the surface treatment applied by the manufacturer so that we could produce samples whose surface chemistry was equivalent to untreated carbon fiber for subsequent surface treatment.

3.2. Voltammograms of the As-Received and Detreated Fibers. The electrochemical behavior of a material is associated with its surface chemical composition. The detreated fiber will be largely graphitic in nature, with the initial oxide functionality of the as-received commercially treated fibers removed. The cyclic voltammograms for the as-received and the detreated fibers are shown in Figure 1. While we know that the surface chemistry of the two fibers is different, it is important to investigate the subsequent electrochemical oxidation and reduction of the fibers in the cyclic voltammetric process. If these cyclic voltammograms were the same then it would indicate that electrochemical surface treatment is indifferent to the initial surface chemistry. Not surprisingly we find that this is not the case, and indeed there are substantial differences in the cyclic voltammograms for the two fiber types. For both as-received and detreated fibers, the current changes only slightly when the potential sweeps between 0 and 1.0 V. However, when the potential sweeps from 1.0 to 1.5 V, the cyclic voltammograms show a different peak position, shape, and intensity for each fiber type. In the case of the as-received fibers, the peak was less intense than that of the detreated fibers. The current is clearly greater for the detreated fibers than the as-received fibers in this region. Furthermore, when the potential reaches 2.0 V, the current is much larger for the detreated fibers, indicating more oxygen evolution from the fiber surface.

The peaks in the range 1.5−1.6 V are consistent with our observation of fiber surface oxidation discussed in the following discussion, and the peaks in the range from 0.5 to −0.3 V is consistent with the reduction of these oxidized features. The fact that there is a steady increase in current as the number of cycles increases leading to an almost symmetric voltammogram about the potential axis is consistent with the formation of reversible and irreversible oxidation products on the surface. This observation is consistent with our surface analysis studies to be discussed below and would be compatible with the formation of reversible and irreversibly formed oxide on the basal plane sites of the carbon fiber. Put another way, once the fiber surface is oxidized, only a certain amount of this oxide can be removed by electrochemical reduction. Another example of this system is found for the electrochemical oxidation of iridium metal.[47] An important conclusion from this observation is that electrochemical reduction alone would not be an effective method for detreating commercially treated carbon fibers.

3.3. Electrochemical Oxidation Results of Commercially Treated IM7. *3.3.1. Survey Spectra.* The overall spectra for the fibers are shown in Figure 2. As expected, the as-received fiber shows a dominant C 1s peak, as do the oxidized samples. However, there is also

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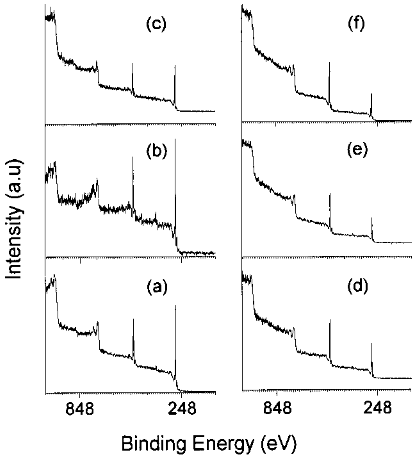

Figure 2. XPS survey spectra of commercially treated IM7 carbon fibers and the same fibers electrochemically oxidized in 1 M HNO_3 in potentiostatic mode for 20 min. The labels (a)−(f) are described in Table 1.

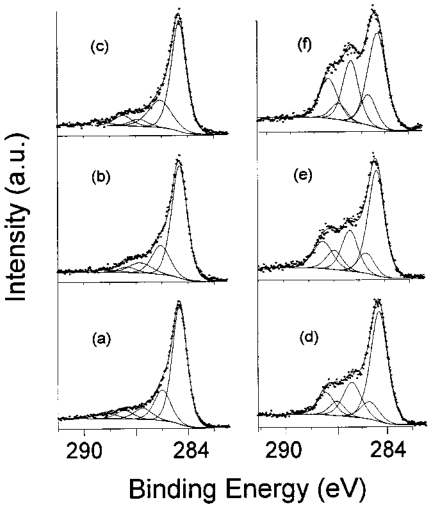

Figure 3. XPS C 1s spectra of commercially treated IM7 carbon fibers and the same fibers electrochemically oxidized in 1 M HNO_3 in potentiostatic mode for 20 min. The labels (a)−(f) are described in Table 1.

a fairly intense peak at ≈530 eV corresponding to the O 1s peak. This level of oxidation is much higher than what would normally be observed for an untreated carbon fiber and clearly results from the surface treatment applied by the manufacturer. A small amount of nitrogen is seen in the survey spectra because the fibers used are PAN-based fibers. The oxidized fibers show an increasing amount of O 1s intensity and changes in the O 1s/C 1s area ratio as the potential increases.

3.3.2. C 1s Region. The curve-fitted C 1s region XPS spectra for the samples are given in Figure 3. The spectrum for the as-received sample (a) is dominated by a peak at 284.6 eV, which corresponds to the main graphitic peak of the fiber. However, the spectrum does not have the characteristically narrow peak shape normally associated with an untreated graphite fiber. The relative broadness of the peak and the presence of weak features to the high binding energy side of the main peak indicate that the surface treatment may have introduced various oxidized organic species onto the surface.[38] The binding energies and designations used for these peaks are given in Table 2.

Table 2. Chemical Shift, fwhm, and Relative Area of C 1s XPS of IM7 Carbon Fibers (As-Received) Electrochemically Treated in HNO_3 at Potentiostatic Mode for 20 min

		as-received (a)	0.5 V (b)	1.0 V (c)	1.5 V (d)	2.0 V (e)	3.0 V (f)
peak 1	CS (eV)	0	0	0	0	0	0
(C−C)	fwhm (eV)	1.34	1.42	1.39	1.58	1.53	1.86
	area (%)	64.5	65.3	61.4	55.0	48.5	42.1
peak 2	CS (eV)				0.75	0.75	0.75
(β-C)	fwhm (eV)				1.72	1.53	1.58
	area (%)				9.2	9.3	11.5
peak 3	CS (eV)	1.35	1.44	1.45			
(C−OH)	fwhm (eV)	1.48	1.63	2.11			
	area (%)	18.4	19.3	23.3			
peak 4	CS (eV)				2.15	2.10	2.25
(HBS)	fwhm (eV)				1.72	1.53	1.58
	area (%)				18.4	18.6	23.1
peak 5	CS (eV)	2.85	3.03	3.10	3.35	3.35	3.3
(C=O)	fwhm (eV)	1.63	2.01	1.63	1.34	1.53	1.53
	area (%)	7.3	8.7	4.8	6.3	8.8	6.1
peak 6	CS (eV)	4.25	4.05	4.30	4.25	4.25	4.15
(COOH)	fwhm (eV)	1.53	1.64	1.63	1.57	1.81	1.81
	area (%)	5.3	3.8	6.9	11.1	14.8	17.2
peak 7	CS (eV)	5.75	5.88	6.20			
($\pi-\pi^*$)	fwhm (eV)	1.91	2.86	1.91			
	area (%)	4.6	2.9	3.7			
C_{ox}/C_{tot}	area ratio	35.5	34.7	38.6	35.8	42.2	46.4

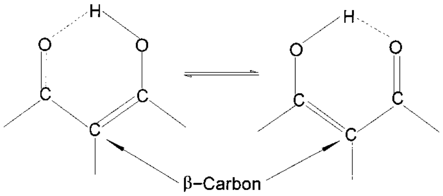

Figure 4. Diagram for hydrogen-bridged structure (HBS) oxide showing the position of the β-carbon.

The peaks due to oxidized carbon were assigned on the basis of previous studies[7] and the values given previously. These features are the graphite carbon (peak 1), β-carbon (peak 2), hydroxide (C−OH) (peak 3), hydrogen-bridged structure (HBS) oxide groups (peak 4), carbonyl (C=O) (peak 5), and carboxyl (COOH) (peak 6) and $\pi-\pi^*$ shake-up (peak 7). The HBS group was first reported by us in 1985[21] and has a binding energy between that of the hydroxide and carbonyl groups.[21,38] Figure 4 shows the arrangement of the HBS group and the position of the β-carbon atom. The β-carbon atom that results from the HBS group is fitted to all the spectra, with its intensity fixed as half of that of the HBS group (because there are two HBS carbons for each β-carbon). We believe that the HBS group is the principal oxidized feature on IM7 fibers that have been detreated and subsequently oxidized in nitric acid. This is the case for other high graphitic carbon fibers.[27,39,48]

The curve fits performed for the as-received fiber are shown in Figure 3a. This figure shows the presence of three oxide peaks at chemical shifts (CS) of 1.35, 3.5, and 4.2 eV, which correspond to hydroxide (C−OH), carboxylate (C=O), and carboxyl or carbonate (COOH or CO_3^{2-}) functionalities, respectively. The formation of these species and the increase in the area ratio of the

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O 1s/C1 s peaks are compatible with the fiber becoming oxidized as a result of the manufacturer's surface treatment. When the as-received fibers are oxidized potentiostatically at 0.5 and 1.0 V, the C−OH functionality is further increased on the surface, the C═O functionality is decreased, and the COOH functionality is increased in relative intensity. When the fibers are oxidized at potentials over 1.5 V, the spectra can be fitted to three oxide components with a CS of about 2.15, 3.35, and 4.25 eV, respectively. The component corresponding to C−OH (CS: 1.4 eV) disappears. As the polarization potential increases, the main carbon component decreases, the C═O (CS: 3.0 eV) remains unchanged, and COOH (CS: 4.25 eV) increases steadily. The fact that the cyclic voltammogram (Figure 1) is very different at 1.5 V than at 1.0 V, with more current at the former potential is consistent with this being due to oxide formation which leads to two species that not only are of different chemical compositions but also are formed on the surface in larger amounts (consistent with the increase in chemically shifted species in the C 1s region and an increase in the O 1s/C 1s area ratio).

The peak with a CS of 2.15 eV, resulting from oxidation of C−OH and C═O groups, is often observed in the electrochemical treatment of carbon fibers and corresponds to the HBS structure, and the fits include the β-peak in the fit. The "graphitic" carbon peak develops a hydrocarbon character because of the high level of oxidation on the fibers and does not show the large exponential tail associated with untreated fiber surfaces.

3.3.3. O 1s Region and N 1s Region. The O 1s spectra for the as-received fiber (a) and the oxidized fibers ((b)−(f)) are shown in Figure 5(I). The spectra consist in all cases of two dominant features occurring at ≈533 eV (−OH and −C−O−C−) and 531.5 eV (HBS and ═O). The former corresponds to the single bond between carbon and oxygen atoms and the latter to a double bond between these atoms. The curve-fitting results for the O 1s spectra are shown in Table 3. For polarization potentials of 0.5 and 1.0 V, the amount of oxygen changed slightly and the relative concentration of the oxygen component peaks remained similar to the as-received sample, although the total amount of oxygen-containing species increased. In this case the single-bonded component (−OH and −C−O−C−) concentration is more than that of the double-bonded one (HBS and ═O). The single-bonded group falls in relative intensity and the double-bonded group increases steadily in relative intensity as the polarizing potential voltage is increased, which is in good agreement with the spectral changes observed in the C 1s region because of the conversion of the −OH and −C−O−C− groups and ═O group into the HBS group. These results also indicate that the commercially treated fibers have a critical oxidation point being 1.0 V.

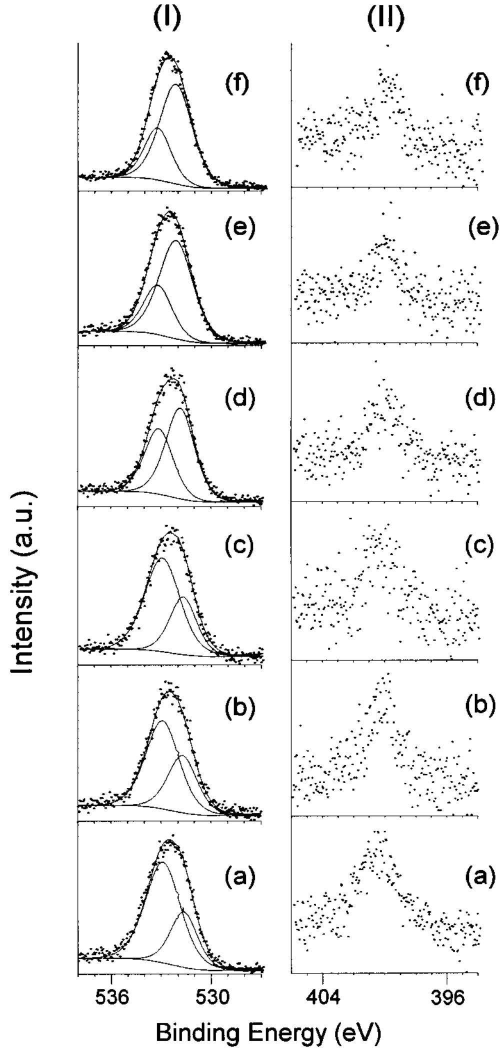

Figure 5. XPS O 1s (I) and N 1s (II) spectra of commercially treated IM7 carbon fibers and the same fibers electrochemically oxidized in 1 M HNO_3 in potentiostatic mode for 20 min. The labels (a)−(f) are described in Table 1.

Table 3. Binding Energy (BE, eV), fwhm (eV), and Relative Area (%) of O 1s XPS of IM7 Carbon Fibers (As-Received) Electrochemically Treated in 1 M HNO_3 in Potentiostatic Mode for 20 min

		as-received (a)	0.5 V (b)	1.0 V (c)	1.5 V (d)	2.0 V (e)	3.0 V (f)
peak 1	BE	532.8	532.9	532.9	532.8	533.2	533.2
(C−O)	fwhm	2.49	2.38	1.91	2.06	2.00	1.91
	area	70.0	63.8	67.9	41.3	39.6	29.6
peak 2	BE	531.6	531.7	531.7	531.5	532.1	532.1
(C═O)	fwhm	1.93	2.08	2.49	2.00	2.39	2.29
	area	30.0	36.2	32.1	58.7	60.4	70.4

The N 1s region spectra of carbon fibers are shown in Figure 5(II). The N 1s peak is positioned at a binding energy of about 401 eV and does not change during the polarization process of the fibers in nitric acid. The lack of any significant change in either the N 1s peak shape and position indicates that the oxidation process does not alter the chemical environment of the nitrogen atom. This implies that the carbon atoms which are oxidized into oxidized carbon are far from the nitrogen atoms.

3.3.4. Valence Band Region. Figure 6 represents the valence band spectra for the as-received (a) and the oxidized fibers ((b)−(f)). The significance of this region lies in the fact that information that cannot be obtained in the core region may often become available when a detailed analysis of the valence band is carried out.[49−51]

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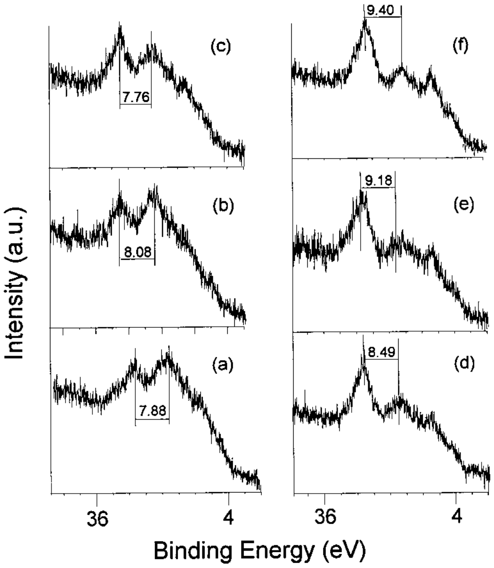

Figure 6. XPS valence band spectra of commercially treated IM7 carbon fibers and the same fibers electrochemically oxidized in 1 M HNO_3 in potentiostatic mode for 20 min. The labels (a)−(f) are described in Table 1.

The region also probes somewhat more deeply into the carbon fiber because of the higher kinetic energy of the electrons. The spectrum for the as-received sample in (a) shows an intense peak at ≈25 eV, corresponding to an orbital that is predominantly O 2s in character, though significant O 2s character is found at lower binding energy. In addition, there is also a peak at 18 eV representing a significant amount of the C 2s intensity which is to be expected for a sample that is mostly carbon. The relative intensities of the O 2s and C 2s regions indicate that there is a fairly high level of surface oxidation in the case of the as-received fiber sample. Further, the separation of the principally O 2s features peak from the C 2s peak in the valence band can be used to determine the exact nature of the functionalities present on the surface. On the basis of previous work involving Xα calculations on substituted coronene,[50] it was determined that C−OH-type functionality produces the lowest separations while C═O, −C−O−C−, and COOH functionalities show separations that are slightly higher. The valence band thus allows us to distinguish between −COH and −C−O−C− functionality, and in this case we can assume that the −COH functionality identified in the core region (C 1s and O 1s) is in this form rather than in the form of −C−O−C− because of the position of the O 2s peak. When both −C−OH and −C−O−C− functionality was present, we observed *two* peaks in the valence band region (e.g., when carbon fibers are oxidized in an ammonium carbonate electrolyte[11]). The valence band spectrum for the as-received fiber in Figure 6 has an O 2s−C 2s separation of 7.88 eV. The O 2s−C 2s separation of oxidized carbon fibers is increased with increasing polarization potential from 8.08 to 9.40 eV except in the case of a 1.0-V polarization potential. These separations indicate that the oxidized products have changed from a single-bonded to double-bonded oxidized species.

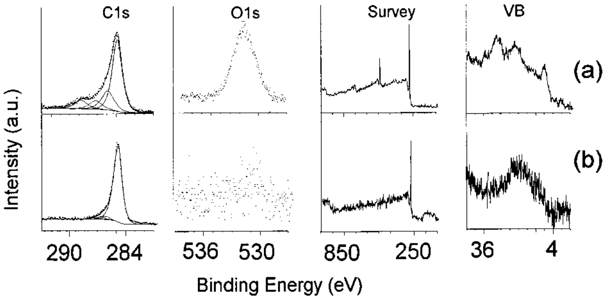

Figure 7. XPS spectra of as-received IM7 carbon fibers (a) and as-detreated IM7 carbon fibers (b).

3.4. Fiber Detreatment Results. In view of the difficulties encountered in oxidizing the commercially surface-treated fibers and the relative uncertainty associated with a proprietary treatment of this type, we concluded that it was better to begin the electrochemical process with an untreated fiber surface. We thus removed the commercially applied surface treatment to obtain a sample with a surface that resembled an untreated fiber. This was achieved by the method described in the Experimental Section.

Figure 7 shows the spectra obtained for the as-received fibers and those obtained for the same fibers following detreatment. The C 1s core level spectrum for the detreated fiber is significantly different from that of the surface-treated fibers. The main graphitic peak at 284.6 eV is considerably narrower and has the characteristic peak shape normally associated with untreated fiber surfaces. Further, no features at higher binding energies are observed in the C 1s region, indicating that much of the little oxygen-containing functionalities are present on the surface. The successful removal of the manufacturer-applied surface treatment is further demonstrated by the absence of any significant signal in the O 1s region and also by the lack of an O 1s signal in the overall spectrum for this sample. The valence band spectrum also does not demonstrate the characteristic O 2s feature at 25 eV, confirming that all oxygen-containing functionalities on the fiber surface have been successfully removed.

The sample detreated in this manner was exposed to the atmosphere for 24 h and then analyzed by XPS to determine if the heat treatment had rendered the fiber surface more prone to air oxidation (as is sometimes the case). Analysis revealed no change in the surface chemistry of the detreated fibers, indicating that the procedure has not adversely altered the nature of the fiber.

3.5. Electrochemical Oxidation of Detreated Fibers. The surface chemistry of the detreated fibers has been shown to be very similar to that seen in the graphitic fibers without sizing.[27,39,52] Therefore, we expect that the detreated samples will also behave in the same manner as untreated fibers when subjected to electrochemical treatment. To study this, samples of commercially treated fibers were detreated in the manner described previously. These samples were then potentiostatically oxidized in the same way as the commercially treated fibers and were analyzed using XPS. The spectra for these samples is given in Figure 8.

3.5.1. Overall Spectra. Figure 8(I) shows all spectra of samples from (a) to (e). All survey spectra show an

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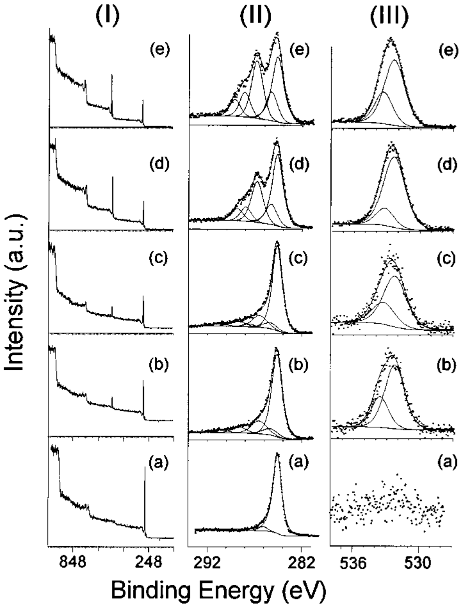

Figure 8. XPS spectra of the detreated IM7 carbon fibers and the same fibers electrochemically oxidized in 1 M HNO_3 in potentiostatic mode for 20 min. (I) survey, (II) C 1s, and (III) O 1s.The labels (a)−(e) are described in Table 1.

Table 4. Chemical Shift (CS, eV), fwhm (eV), and Relative Area (%) of C 1s XPS of IM7 Carbon Fibers Detreated in Vacuum and Electrochemically Treated in 1 M HNO_3 in Potentiostatic Mode for 20 min

		as-detreated (a)	0.5 V (b)	1.0 V (c)	1.5 V (d)	2.0 V (e)
peak 1 (C−C)	CS	0	0	0	0	0
	fwhm	1.07	1.30	1.26	1.37	1.46
	area	97.7	68.7	70.5	45.8	36.9
peak 2 (β-C)	CS		0.70	0.73	0.65	0.65
	fwhm		1.91	1.82	1.48	1.43
	area		7.2	6.8	12.9	14.5
peak 3 (C−OH)	CS	1.43				
	fwhm	1.05				
	area	2.3				
peak 4 (HBS)	CS		1.90	1.88	2.15	2.2
	fwhm		1.91	1.82	1.48	1.43
	area		14.3	13.5	25.8	29.0
peak 5 (C=O)	CS			3.03	3.35	3.5
	fwhm			1.43	1.34	1.34
	area			2.7	8.2	11.6
peak 6 (COOH)	CS		4.00	4.23	4.3	4.55
	fwhm		1.72	1.91	1.43	1.34
	area		6.1	6.5	7.3	7.9
area ratio	C_{ox}/C_{tot}	2.3	20.4	22.7	41.3	48.5

intense C 1s peak at a binding energy of 284.6 eV with a low-intensity C(KVV) Auger peak at 993 eV. They also show a O 1s peak and an O(KVV) Auger peak at 531 and 743 eV, respectively. The relative intensity of the O 1s peak and O(KVV) Auger peak increase as the level of electrochemical treatment increases. Also, we observe a very low intensity N 1s signal at 401 eV in all samples arising from residual nitrogen on these PAN-based fibers.

3.5.2. C1s Spectra. Figure 8(II) shows the C 1s core level region spectra fitted according to the positions of oxidized carbon species describedpreviously. For the detreated fibers, the oxygen present is mainly due to adsorbed water (this has a chemical shift that is similar to that of C−OH). For the fibers subjected to electrochemical oxidation, five peaks can be distinguished as shown in Table 4. In general, the chemically shifted peaks due to oxidized carbon increased in relative intensity with an increase in the polarizing potential.

Table 5. Binding Energy (BE, eV), fwhm (eV), and Relative Area (%) of O 1s XPS of IM7 Carbon Fibers Detreated in Vacuum and Electrochemically Treated in 1 M HNO_3 in Potentiostatic Mode for 20 min

		as-detreated (a)	0.5 V (b)	1.0 V (c)	1.5 V (d)	2.0 V (e)
peak 1 (C−O)	BE		533.6	533.2	533.2	533.3
	fwhm	0	1.82	2.43	1.91	1.91
	area		29.4	30.3	16.9	29.6
peak 2 (C=O)	BE		532.2	532.2	532.2	532.3
	fwhm	0	2.10	2.45	2.34	2.20
	area		70.6	69.7	83.1	70.4

The as-detreated fibers have a very high graphitic order, where the graphitic carbon ratio on the surface is over 97%, as shown in Table 4. The C 1s spectrum can be fitted to a single C 1s peak corresponding to graphitic carbon with the expected exponential tail. In the oxidation process at 0.5 V, all forms of oxidized carbon on the carbon fiber surface increased in intensity and the peak area ratio of the oxide (C_{oxide}/C_{total}) rose from 13.9% to 20.4% for a 20-min treatment and to 22.7% at 1.0 V for a 20-min treatment. The fwhm of the graphite carbon peak became wider from 1.00 to 1.30 eV in the oxidation process, suggesting that disordering of the carbon lattice might result from the oxidation process. This is because the C 1s peak increases in width as the form of carbon becomes more disordered.[38] It is very interesting to note that, after oxidization in the potentiostatic mode for detreated fibers, the hydroxide group is not present on the carbon fibers, which shows that this functional group is not stable under these electrochemical oxidation conditions and is probably converted into HBS groups.

There is a substantial change in the C 1s spectra between the sample treated at 1.0 V and the sample treated at 1.5 V, compatible with the cyclic voltammetric results. The sample treated at 1.5 V has about twice the amount of oxidized carbon species; thus, the HBS peak increases from 13.5% to 25.8% of the total carbon content. The total oxidized carbon concentration almost doubles from 22.7% to 41.3%. The width of the graphitic carbon shows little change, though there is a narrowing in the widths of the HBS, C=O, and COOH peaks. For the oxidation at 2.0 V, the oxidation products increase to 48.5%. These changes are compatible with the very substantial increase in current between 1.0 and 1.5 V in the cyclic voltammetric measurement.

3.5.3. O 1s Region and N 1s Region. Column III in Figure 8 shows the O 1s region spectra fitted to two peaks for different carbon fibers. This region has been fitted in a manner consistent with our previous studies of surface-treated carbon fibers[27] without the chemisorbed oxygen signal. Consistent with the results of fitting the C 1s region and recognizing that the O 1s and C 1s regions probe different depths into the surface, the peaks can be assigned as peak 1 (~533.0 eV) and peak 2 (~532.0 eV), corresponding to C−OH and C=O groups, respectively. Relative peak areas are shown in Table 5.

N1s spectra are presented in Figure 9 (I). The shape and position of the peak changes slightly, although it

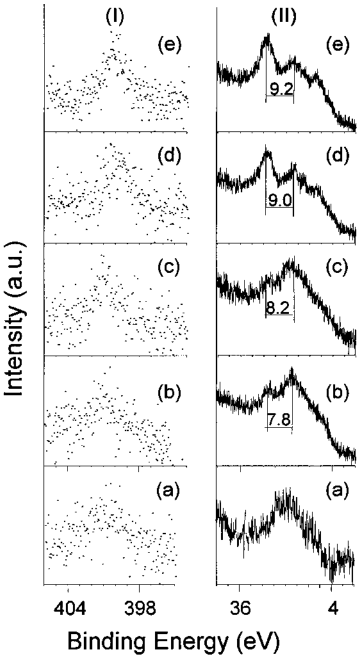

Figure 9. XPS N 1s (I) and valence band (II) spectra of the detreated IM7 fibers and the same fibers electrochemically oxidized in 1 M HNO_3 in potentiostatic mode for 20 min. The labels (a)−(e) are described in Table 1.

is narrower and more intense in the case of high potential polarization. It is difficult to predict the change of the oxide on the fiber surface from the N 1s spectra.

3.5.4. Valence Band Spectra. The valence band spectra could supply some evidence of chemistry that core level spectra cannot provide. As shown in Figure 9(II), there is only a C2s peak at about 20 eV and no oxygen signal in the valence band of the detreated IM7 fibers. The changes in the valence band with oxidation are consistent with previous results reported for oxidized fibers.[50] The separations between C 2s and O 2s are shown in Figure 9(II). This separation became larger as the oxidation time increased, increasing from 7.8 to 9.2 eV when the oxidation potential increased from 0.5 to 2.0 V. This is compatible with the formation of increasing amounts of the HBS structure as discussed previously.

The detreated fibers behave in a manner similar to that of untreated fibers subjected to electrochemical oxidation and reported previously by our group. We thus conclude that the detreatment of the commercial fibers is very successful in removing surface oxidation and restoring the carbon fiber surface.

4. Conclusions

It was found that carbon fibers that were previously surface-treated by the manufacturer can be further treated to change the surface chemistry by electrochemical polarization. However, electrochemical treatment of previously surface-treated fibers leads to a *different* surface chemistry than the surface chemistry that results when untreated fibers are subjected to electrochemical treatment. The prior commercial treatment influences the subsequent surface treatment that can be applied, making the final surface chemistry dependent upon this prior treatment. The resulting surface chemistry typically has a greater diversity of functional groups, making such further treated fibers potentially less useful than fibers that are treated in one step. For example, the predominant HBS feature formed on untreated fibers is no longer the predominant feature on the commercially treated fibers subjected to further electrochemical polarization. These further treated fibers are less likely to be of value in situations where specific chemical interaction with a matrix material is sought. The previously applied commercial treatment can be removed by heating in a vacuum, allowing the detreated fibers to be electrochemically oxidized to provide surface chemistries similar to untreated carbon fibers. This work demonstrates the importance of having an untreated surface as a starting material in the preparation of surface-treated fibers used in the construction of carbon fiber composites.

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