

Electrokinetics of Carbon Fibers Produced by a Direct Oxyfluorination

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Received: April 30, 2003; In Final Form: September 2, 2003

PAN-based carbon fibers were treated by a direct oxyfluorination method to study the chemical surface composition and electrokinetic behavior of the fibers. The physicochemical properties of the fibers were investigated by using a photoelectron spectroscopy (XPS) and zeta (ζ)-potential. As a result, the surface functional groups, including C–O, C=O, HO–C=O, and C–F_x after oxyfluorination, were formed on the carbon fiber surfaces. And the time dependence of the ζ -potential of oxyfluorinated carbon fibers reflected the surface bonding state of the obtained fiber materials, due to the dissociation of C–F_x groups. These results could be explained by the modification of chemical composition and the formation of physical bonding on the fiber surfaces, which could be attributed to the oxyfluorination.

1. Introduction

Carbon fibers are widely used as reinforcements in composites, especially in composites with epoxide matrices and of potential importance due to their real applications. They combine a high stress factor and strength with a low density, which has led to their increasing use in high-performance construction materials.^{1,2}

To improve the fiber/matrix adhesion, it is necessary to increase the surface polarity, which can be related to more sites for hydrogen bonding and the possibility for mechanical interlocking between the fiber materials and the surrounding polymeric matrix, resulting in improving good stress transfer from the matrix materials to the filling fiber materials.³

The normally used oxidative methods for the modification of such nonpolar carbon fiber surfaces include oxidation in various plasmas, oxidation in air, and electrochemical oxidation of carbon fibers used as anodes in various electrolytes or wet chemical methods, such as boiling in nitric acid. An alternative technique to increase the surface polarity of carbon is mild direct fluorination.^{4,5}

In recent years, several studies concerning fluorinated carbon fibers have been reported.^{6–8} The degree of fluorination depends on the nature of the fibers and the fluorination method used. Higher contents of intercalated fluorine can be obtained by using either better-graphitized structures or higher fluorine pressures. The reaction of fluorine and graphite at low temperature is kinetically hindered by the formation of C–F bonds at the outer surface, which prevents further migration of fluorine into the interplanar space and thus further fluorination. Therefore, a fluorination at low temperature requires the assistance of fluorides to yield fluorine-intercalated compounds or surface-fluorinated carbon fibers.⁹

When F₂ is used as an oxidizing agent, it is reduced to give the basic F[–] ion. Therefore, the presence of HF in the reaction mixture acidifies the surface and makes it kinetically more

approachable by the F₂ molecules. Although no detectable skin irritation or sensitization is found for the fully fluorinated carbon materials, the partially fluorinated variety has the potential to cause mild irritation. Neither the fully fluorinated carbons nor the partially fluorinated ones are likely to be an eye irritant in humans.^{10–12}

Therefore, in this work, different fluorination conditions are applied to modify the surface properties of carbon fibers by using direct fluorination. Especially, the O₂ gas is used to replace HF catalyst for oxyfluorination of the fibers. And the relationships between the degree of fluorination and the physicochemical properties of carbon fibers are studied by using a combination of surface analyses and electrokinetic studies.

2. Experimental Section

The carbon fibers studied in this work were untreated and unsized polyacrylonitrile (PAN)-based high-strength fibers: TZ-307 (12K) manufactured by Taekwang of Korea. The average diameter of these carbon fibers was approximately 7 μ m, and typical tensile strength and modulus were about 3.5 and 245 GPa, respectively.

Carbon fibers were subjected to oxyfluorination in different conditions. The oxyfluorination reaction was performed in a batch reactor made of nickel with an outer electric furnace, as shown in Figure 1. After evacuation, fluorine and oxygen mixtures (F₂/O₂ gases) were introduced to the reactor at room temperature, and then the reactor was heated to the treatment temperature. After the reaction, the specimens were cooled to room temperature, and then the reactive gases were purged from the reactor with nitrogen. In the case of the reaction at room temperature, the reactor was cooled and evacuated in a cooling bath prior to charging with fluorine. The reactor was removed from the cooling bath after purging fluorine with nitrogen. The fluorine pressure was 0.2 MPa and the nominal reaction time was 10 min at the treatment temperature. The experimental oxyfluorination conditions of carbon fibers studied are listed in Table 1.

The X-ray photoelectron spectroscopy (XPS) experiment was performed with a VG Scientific ESCA LAB MK-II spectrometer equipped with a Mg K α X-ray source. The base pressure in the

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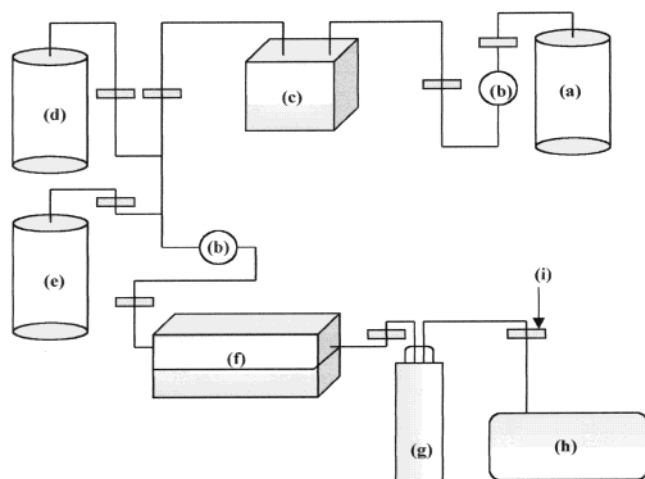


Figure 1. Schematic diagram of the fluorination reactor: (a) F₂ gas, (b) pressure gauge, (c) batch gas tank, (d) N₂ gas, (e) O₂ gas, (f) nickel reactor, (g) refrigerator, (h) vacuum pump, and (i) gas valve.

TABLE 1. Experimental Fluorinated Conditions of the PAN-Based Carbon Fibers Used

specimens	F ₂ /O ₂ mixtures (%)	fluorination temp (°C)
as-received		
CF-RT	100/0	25
CF-100		100
CFO-RT	50/50	25
CFO-100		100
CFO-300		300
CFO-400		400
CFO-70/30	70/30	100

specimen chamber was controlled in the range of 10^{-8} to 10^{-9} Torr. To avoid charging of a nonconducting specimen by the emission of photoelectrons, the specimen was neutralized by a low-energy electron beam (1–20 eV). A homogeneous charge distribution of electrons was achieved by using a nickel net attached 2 mm above the specimen leading to a better spectrometer resolution. In the survey spectrum (0–1100 eV), the XPS program package fixed the C_{1s} peak at 284.6 eV considering the neutralization. For the high-resolution C_{1s} spectra, the exact position of the C_{1s} peak was not fixed.

The ζ -potential was determined with the electrokinetic analyzer (Otsuka Electronics Co., ELS-8000) in 0.1 mol·L⁻¹ KCl electrolyte solution at 20 °C based on the streaming potential method.¹³ Thereby, the presence of acidic or basic dissociable surface functional groups can be detected, if the dissociation of the functional groups is the predominant mechanism forming the double layer. In the presence of acidic surface groups the negative ζ -potential can increase with increasing pH, due to the increased degree of dissociation of those groups until a plateau region is established by the total dissociation of these acidic groups. If basic surface functionalities are present, this process can be vice versa. Details of the ζ -potential measuring technique were reported elsewhere.¹⁴

3. Results and Discussion

Surface Properties. Wide-scan spectra in the binding energy range 0–800 eV are obtained to identify the surface elements present and carry out a quantitative analysis.¹⁵ XPS wide-scan spectra of the oxyfluorinated carbon fiber specimens are shown in Figure 2. The intensity scale factor for the oxyfluorinated carbon fibers is higher than that of the as-received carbon fiber specimen. The XPS spectra show distinct carbon, oxygen, and

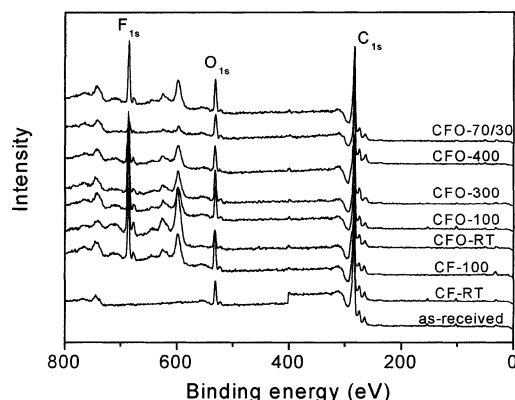


Figure 2. XPS wide-scan spectra of the oxyfluorinated carbon fibers.

TABLE 2. Composition (atom %) of Surface Oxyfluorinated Carbon Fibers Obtained by XPS Measurements

specimens	XPS			
	C _{1s}	F _{1s}	O _{1s}	O _{1s} /C _{1s}
as-received	88.38		9.59	0.109
CF-RT	81.81	10.84	6.06	0.074
CF-100	80.40	11.55	6.68	0.083
CFO-RT	74.21	13.56	10.93	0.147
CFO-100	67.72	19.50	9.27	0.154
CFO-300	79.96	10.64	8.06	0.100
CFO-400	76.93	8.91	10.13	0.132
CFO-70/30	76.25	13.31	9.24	0.121

fluorine peaks, representing the major constituents of the carbon fibers investigated. Relatively weak peaks of other major elements, such as nitrogen, are also observed. No other major elements are detected from wide-scan spectra on the surface of the carbon fibers. As expected, the fluorine peak intensity of the oxyfluorinated carbon fibers is also increased according to the fluorination temperature and oxygen content.

Quantitative peak analysis is carried out to determine the surface element concentrations. The resulting surface element concentrations of the oxyfluorinated carbon fiber specimens are listed in Table 2. It is found that the surface carbon concentrations of the as-received and CFO-100 carbon fiber specimens are 88.38 and 67.72 atom %, respectively. A lower surface carbon concentration in the CFO-100 carbon fiber specimen compared to that of the as-received specimen can be attributed to the bonding of oxygen or fluorine on the carbon surfaces produced by the oxyfluorination. The surface fluorine concentration ranges of the surface oxyfluorinated carbon fiber specimens are 8.91–19.50 atom %. The higher fluorine concentration on the CFO-100 specimen (19.50 atom %) surfaces also can be attributed to the surface oxyfluorination of the fibers. The surface concentration of oxygen in the CFO-RT specimen is relatively similar to that of the as-received carbon fiber. The broad carbon peak that is observed in the binding energy range from 281 to 293 eV is due to the several carbon-based surface functional groups which have different binding energies.^{16–19}

Therefore, it can be seen that the C–C peak both before and after the surface oxyfluorination is the major surface carbon functional component. Due to the surface oxyfluorination process in the fluorinated carbon fibers, the percentage (or intensity) of C–C is lower and the percentage of C=O is higher compared to that of the as-received carbon fibers. However, the intensity of the C–C peak in the CFO-RT specimen is relatively similar to that for the as-received carbon fiber. From these results, it can be remarked that the carbonyl content is significantly different between as-received and oxyfluorinated

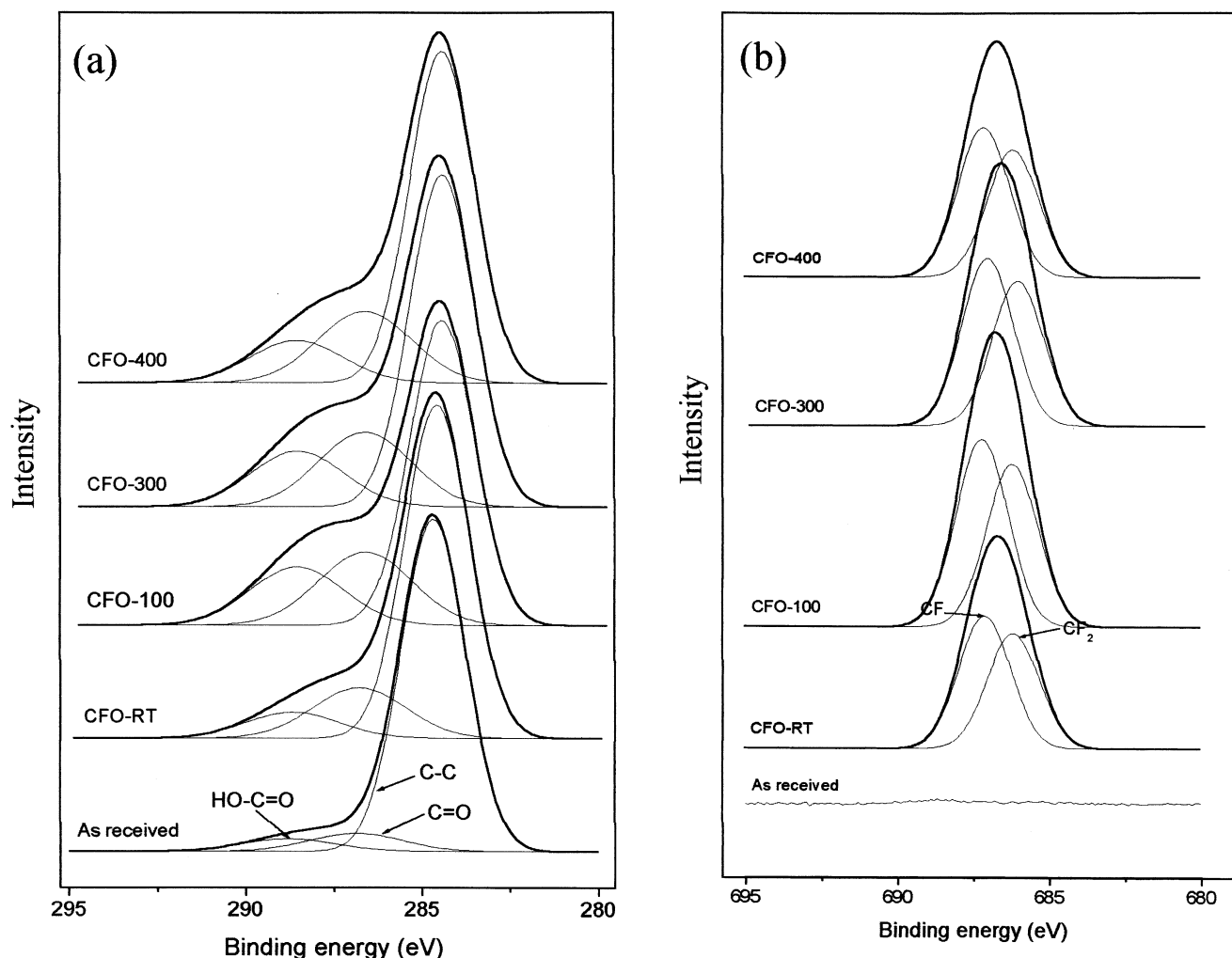


Figure 3. High-resolution curve-fitted C_{1s} and F_{1s} peaks of the oxyfluorinated carbon fibers: (a) C_{1s} spectra and (b) F_{1s} spectra.

carbon fibers at elevated temperature. In other words, the current oxyfluorination process can increase the concentration of carbonyl functional groups on carbon fiber surfaces, resulting in increasing the polarity.

In addition to the elemental composition of the surface, the bonding conditions of the elements involved are found. Different chemical environments and the bond energy shift have been developed for several functional groups. The chemical shift of the binding energy is a useful tool for the investigation of the molecular environment of an element.^{19–22} Values of relative amount are qualitative (deviation about 10%) due to the nature of the method used for the intensity determination, and moreover, the difference between the fluorine contents in the survey and C_{1s} spectra can be explained by a slight modification of the specimen surface due to the X-ray radiation. C-sec denotes a carbon atom with a carbon atom neighbor, on which fluorine is bonded and a chemical shift for this atom is detectable.²³

Typical XPS spectra of the C_{1s} peak region at 285 eV deconvoluted into surface functional group contributions of the oxyfluorinated carbon fiber specimens are shown in Figure 3a. It is found that the C_{1s} peaks of the CFO-100 specimen can be fitted to four line shapes with binding energies at 284.8, 284.7, 286.9, and 288.8 eV. These different binding energy peaks are assigned to center at 284.8 eV, C–C at 284.7 eV, –C=O at 286.9 eV, and HO–C=O at 288.8 eV. It can thus be noted that two functional components are present on the carbon fiber surfaces in addition to the C–C peak after oxyfluorination, which is located at 285.0 eV. Figure 3b shows the F_{1s} peak

deconvolution of the oxyfluorinated carbon fibers in the 687.0 eV region. In the F_{1s} spectrum the physical component occurs at $E_b = 686.7 \pm 0.05$ eV. That is, two components at 687.1 ± 0.03 (CF_1) and at 686.13 ± 0.04 (CF_2) in F_{1s} spectra are assigned to physical C–F_x ($1 < x < 2$) groups present on the surface of the fibers or at structural defects.

Also, C_{1s} and F_{1s} XPS analysis curves of oxyfluorinated carbon fibers as a function of oxygen content are given in Figure 4, parts a and b, respectively. Noticeable changes are observed with respect to the starting materials. The binding energy (E_b) of the band assigned to graphitic carbon (C–C) undergoes a slight shift (0.01–0.1 eV) toward lower E_b because of a lowering of the Fermi level (E_F) and a subsequent decrease of the energy gap between the C_{1s} core level and E_F . In the C_{1s} spectra, the component (C=O) (with $E_b = 286.83 \pm 0.06$ eV) is also connected with nonfluorinated C in the position of C–F bonds. The slight shift from (C–C) arises from the weak excess of positive charge, which is located on these atoms because of the presence of neighboring F. Since the work of Mallouk and Bartlett,²⁴ it is known that the graphene layers are associated with a physical type E_b , which lies at ca. 287.75 ± 0.06 eV (component C_{1s} HO–C=O) in C_{1s} spectra. All the C_{1s} and F_{1s} binding energies of oxyfluorinated specimens are listed in Table 3.

Consequently, with increasing the amount of oxygen and fluorine on the carbon fiber surfaces, the content of graphite-type carbon decreases, whereas the relative amounts of C–F_x increase with increasing the fluorination temperature and oxygen

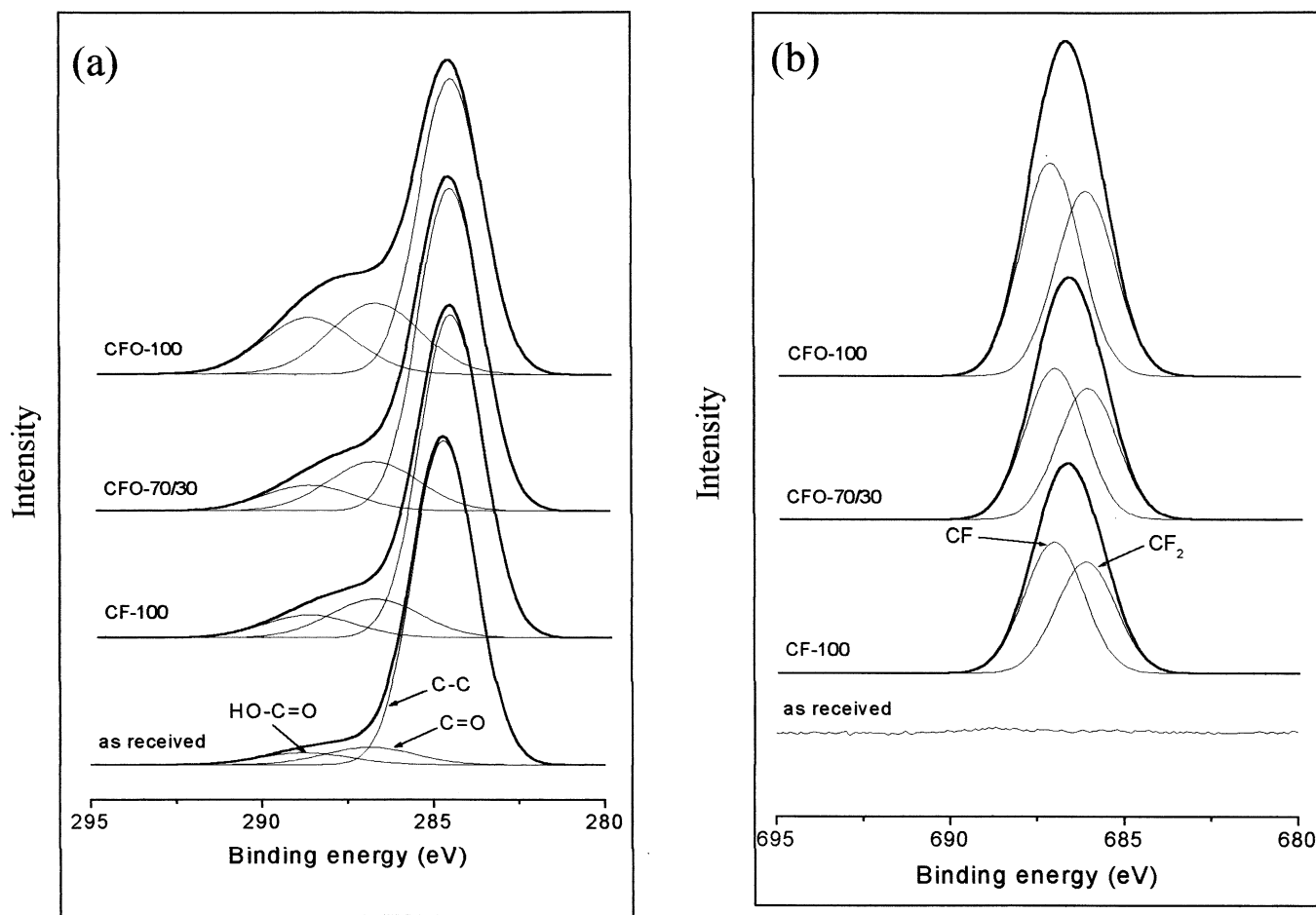


Figure 4. High-resolution curve-fitted C_{1s} and F_{1s} peaks of the oxyfluorinated carbon fibers as a function of oxygen content: (a) C_{1s} spectra and (b) F_{1s} spectra.

TABLE 3. C_{1s} and F_{1s} Binding Energies of the Oxyfluorinated Carbon Fibers

specimens	binding energy (BE, eV)						
	C_{1s}				F_{1s}		
	center	C-C	C=O	COOH	center	C-F	C-F ₂
as-received	285	284.68	286.77	287.69	687		
CF-RT	284.73	284.69	286.91	288.84	686.65	687.05	686.13
CFO-100	284.76	284.65	286.85	288.77	686.75	686.14	687.17
CFO-300	284.76	284.76	286.86	288.79	686.70	686.13	687.13
CFO-400	284.76	284.72	286.83	287.77	686.70	686.09	687.10
CFO-70/30	284.72	284.68	296.87	287.77	686.64	686.17	687.09

content, as expected, probably due to kinetic reasons, and moreover, the oxyfluorination of the bulk phase of the fiber can be considered. That is, the increase of oxygen and fluorine functional groups on the carbon fiber surfaces may be expected to promote the specific polarity of the carbon fibers as well as the interfacial binding force by establishing secondary or van der Waals forces at the interfaces between fibers and matrix, resulting in an increase in the interfacial properties of the materials.^{25–27}

Electrokinetic Properties. It is possible to acquire information from the concentration dependence of the ζ -potential about the degree of interaction between the solid surface and the ions of the electrolyte solution, based on specific or electrostatic interactions. For most fiber materials, the ζ -potential values corresponding to the Stern theory²⁸ fall in a parabolic curve like trend, which is caused by the adsorption properties of the solid for potential-determined ions as well as by specifically adsorbed ions.

Fluorine is able to form different kinds of physical bonds with graphite-like materials. With increasing the amount of fluorine onto the surfaces, the graphite-type carbon content on the surfaces is decreased. This is due to kinetic reasons, and moreover, the oxyfluorination of the bulk phase of the fibers also has to be considered. Therefore, the ζ -potential–time dependence is measured to estimate a fixed starting point for the $\zeta = (c, \text{pH})$ dependence. The time dependence of the ζ -potential closely reflects the surface composition of the obtained fiber materials, due to the dissociation of such $C-F_x$ ($x = 1-2$) groups. Fibers with a weak physical F bonding reveal the lowest negative ζ -potential, medium bonding exhibits a low negative ζ -potential, and strong bonding has the greatest negative ζ -potential value, as shown in Figure 5. This behavior coincides with the results of surface analyses.

Figure 6 shows the dependence of the ζ -potential with KCl concentration for oxyfluorinated carbon fibers as a function of oxygen content. Cl^- anions are preferentially adsorbed on all investigated carbon fibers. If water adsorption should compete with specific ion adsorption, a consequent shift of the maximal ζ -potential, ζ_{max} , must be found to lower or raise values according to the hydrophilicity and a connection between ζ_{max} and θ is obtained in the case of oxyfluorinated carbon fibers.

ζ -potential values of the fibers were determined in $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ KCl electrolyte solutions varying the pH values. The presence of acidic or basic dissociable surface functional groups can be estimated from the pH dependence of the ζ -potential. The theoretically expected ζ -potential vs pH plots are shown in Figure 7. The negative ζ -potential values become bigger with increasing pH, due to increased dissociation of acidic surface

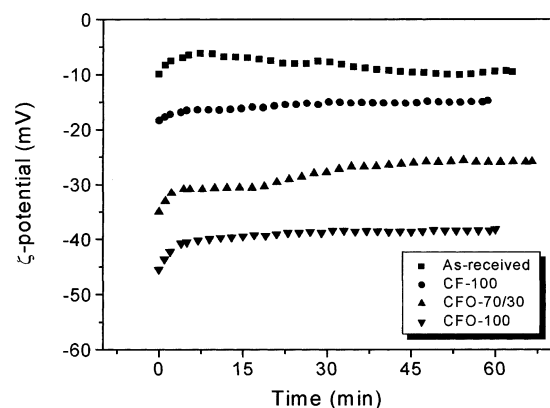


Figure 5. $\zeta = f(t)$ plots of the oxyfluorinated carbon fibers as a function of oxygen content.

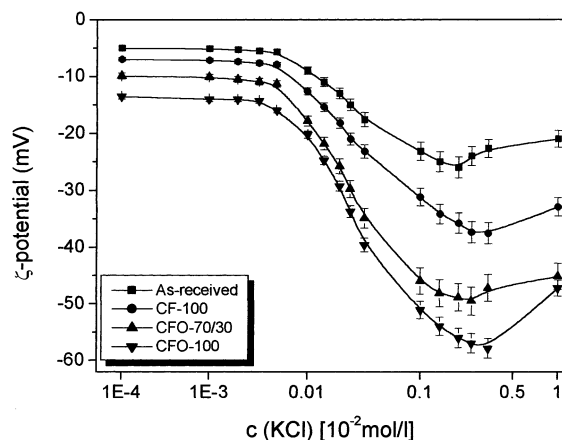


Figure 6. ζ -potential–KCl concentration plots of the oxyfluorinated carbon fibers as a function of oxygen content.

groups. If basic functions are present at the surface, the amount of positively charged groups increases with diminishing pH. Complete dissociation of surface groups causes a plateau area in the ζ -potential vs pH plot. The isoelectric point (iep) is another measure of the acidity or basicity of a solid surface, if the dissociation of surface groups is the predominate mechanism for electric double layer formation. The solid surface is acidic if the value of iep is low. If the iep value is in the alkaline range, the solid surface contains basic surface groups.²⁹

The pH dependence of the ζ -potential of the oxyfluorinated carbon fibers is determined in 10^{-3} mol·L⁻¹ KCl electrolyte solution. This makes it possible to estimate the acidic and/or basic character of a solid surface. If the investigated solid surface contains acidic functional groups, the negative ζ -potential enlarges with increasing pH, due to the increased dissociation of those groups, and remains constant from a given pH, which can be attributed to the complete dissociation of present surface functional groups. The isoelectric point is a direct measure of the acidity or basicity of a solid surface, if the dissociation of surface groups is the predominate mechanism of the information of the electric double layer. The solid surface has an acidic character if the value of the isoelectric point is low.³⁰ Measuring the ζ -pH dependence for hydrophobic solids can result in a plot without plateaus due to the absence of dissociable surface functionalities. The increase in negative and positive ζ -potential with increasing or decreasing pH is caused by the enhanced adsorption of hydroxyl ions or protons.

The pH dependence of the ζ -potential of the fluorinated carbon fibers as a function of oxygen content is shown in Figure 8. Although the oxyfluorinated carbon fibers reveal only a small

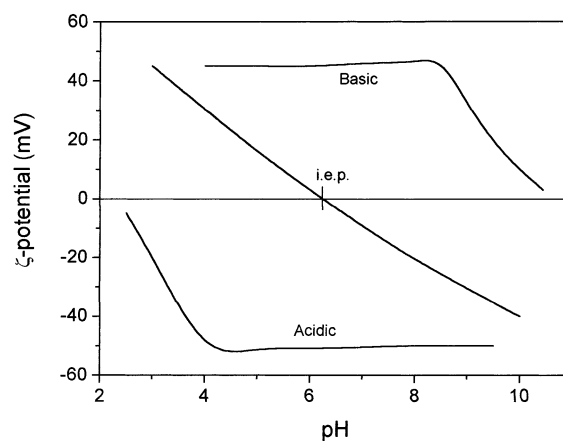


Figure 7. General pH-dependence of the ζ -potential of solids containing dissociable acidic and basic surface groups as well as hydrophobic surfaces.

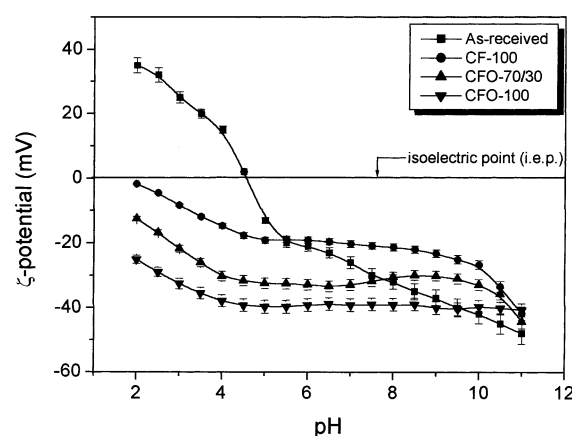


Figure 8. ζ -potential–pH plots of oxyfluorinated carbon fibers as a function of oxygen content, measured at $c(\text{KCl}) = 10^{-3}$ mol·L⁻¹.

increase in surface acidity, caused by the further oxidation after oxyfluorination, the oxyfluorinated specimens display a higher surface acidity compared to the unmodified ones.³¹ In the case of the carbon fibers fluorinated with F₂/O₂, the shift of the isoelectric point (iep) agrees with the increased amount of oxygen bonded to the surfaces.

4. Conclusions

XPS results showed that carbon, fluorine, and oxygen were the major elements on the surface of oxyfluorinated carbon fiber specimens, and the increase of oxygen-containing surface functional groups, such as C–O, HO–C=O, and the new formation of physical bonding, C–F_x, was found on the oxyfluorinated carbon fiber surfaces. ζ -potential measurements clearly followed the changes of the surface composition with oxyfluorination. The iep values shifted to lower pH values, due to the formation of more acidic surface functional groups and the increase of polarity during the oxyfluorination process. The results were dependent on the oxygen content. Consequently, a direct oxyfluorination on carbon fibers was proven to be a useful method to increase the surface polarity or to improve the oxygen functional groups on carbon fiber surfaces.

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