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Correlation of C_{1s} chemical state intensities with the O_{1s} intensity in the XPS analysis of anodically oxidized glass-like carbon samples

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An XPS study of anodic oxidized glass-like carbon (GC) was conducted in order to investigate the inconsistency between O_{1s}/C_{1s} and oxygen concentration (Ocal.) calculated from the curve fitting results of the C_{1s} spectrum. Consideration of the asymmetric peak shape of the C_{1s} spectrum is normally done in order to obtain precise curve fitting results. However, it was found that the 2nd-carbon peak should also be taken into consideration in the curve fitting process in addition to the effect of asymmetric peak shape of carbon to obtain a consistent value of O_{1s}/C_{1s}. The 2nd graphitic peak is normally located $+0.7$–$+0.8$ eV away from the original C_{1s} spectrum. The ratio of the 2nd graphitic peak area in the C_{1s} spectrum increased as the electrical charge increased. However, the peak shapes of C_{1s} spectra of anodic oxidized GC after heat treatment at 1500 °C in argon atmosphere were almost the same as the C_{1s} of untreated GC. Although the origin of the 2nd graphitic peak is not well understood, it may be related to the amount of oxygen on the GC surface.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is one of the most useful techniques for surface analysis in order to obtain chemical information. Therefore, it is often used for evaluation of the surface oxygen concentration and surface functional groups on carbon fiber surfaces in order to study the effect of surface treatment on the interfacial shear strength of the composite. Many researchers have performed surface analysis of carbon fiber surfaces before and after surface treatment, producing various data [1–5]. However, there seems to have been a serious problem, i.e., inconsistency between the O_{1s}/C_{1s} value and the oxygen concentration obtained from the curve fitting results of C_{1s} spectrum (O cal.). Originally, both values must be equal. Such inconsistency may generate a suspicion against XPS analysis as a valuable technique for evaluation of the surface chemistry. Therefore the value of each functional group has been used for comparative study against various surface treatment conditions. For example, the author carried out the anodic oxidation of pitch based-carbon fiber and PAN based-carbon fiber. The results showed a good relationship between the O_{1s}/C_{1s} values and the O cal. (oxygen concentration calculated from the C_{1s} curve fitting results). The values of oxygen concentration calculated from the C_{1s} curve fitting were much larger than the values obtained from O_{1s}/C_{1s} [6, 7].

The asymmetric peak shape of the C_{1s} spectrum of graphite is already well recognized [8]. Some researchers have suggested that the asymmetric peak shape of the C_{1s} spectrum should be taken into consideration when the curve fitting of the C_{1s} spectrum is done. Ishitani *et al.* suggested the use of the difference spectrum technique for the curve fitting of the C_{1s} spectrum [9]. Proctor *et al.* suggested the use of non-linear background subtracted spectra as the best approach to the curve fitting [10]. The difficulty of C_{1s} curve fitting caused by the asymmetric peak shape of C_{1s} is already well recognized and various techniques have been suggested to overcome this problem, however, the inconsistency of O_{1s}/C_{1s} and the O cal. obtained from C_{1s} curve fittings has not been sufficiently considered yet.

In this study, anodic oxidation of glass-like carbon with NaOH solution was carried out in order to investigate the inconsistency of these two kinds of oxygen values. The asymmetric peak shape of the C_{1s} spectrum was taken into consideration in the curve fitting by using the original C_{1s} peak of each surface treated specimen. They were measured after heat treatment at 1500 °C under Ar atmosphere. The effect of the adsorbed water and impurities were also removed by using infrared heating under vacuum conditions.

2. Experimental

2.1. Materials

Specimens with dimensions of 30 (L) × 15 (W) × 1.2 mm (T) were cut out from a GC plate by using a wire discharged cutting machine DWC-90H manufactured by Mitsubishi Electric Ltd. After cutting, the surface of each specimen was polished with 3 μm diamond slurry, because the surface becomes oxidized due to the high temperature when the specimens are cut out. Furthermore, each specimen was heat-treated at 1500 °C under Ar atmosphere before anodic oxidation, in order to remove oxygen from the surface of each specimen. Each specimen was kept in an oven under Ar atmosphere until the temperature had come down to the room temperature in order to prevent further oxidation of the specimen. In addition, after taking out from the oven, specimens were also kept in a desiccator until the surface treatment was carried out in order to eliminate the possibility of the adsorption of water and other impurities on the surface.

2.2. Surface treatment

The equipment for anodic oxidation is shown in Fig. 1. The specimen was connected to the anode using a platinum wire with silver paste and the cross section of the specimen was covered using epoxy resin in order to prevent oxidation. It was immersed in the NaOH solution up to a depth of 20 mm keeping equal distance from the cathode in each end of the vessel. This should give the same level of surface treatment conditions on each side of the specimen.

0.05 mol/ℓ NaOH solution was used for this anodic oxidation of GC. The electric current was kept at 10 mA throughout the treatment by using a galvanostat HA-310 and the amount of electricity was measured by a bi-polar coulomb meter HF-202D manufactured by Hokuto Denko, Ltd. The amount of electricity was varied from 1.0×10^{-4} to 2.0×10^{-2} C/mm^2. After the anodic oxidation, treated specimens were immersed in 0.1 mol/ℓ HCl solution, rinsed with freshly distilled water several times then dried at 70 °C under vacuum conditions for 3 h.

2.3. XPS analysis

An Ulvac ϕ 5400 series X-ray photoelectron spectrometer with monochromated AlK_α-X-ray source was used in order to evaluate the treated and untreated specimens. The detection angle was 65° and the pass energy was 89.45 eV for survey and 35.75 for high resolution measurement. The scanning condition for survey measurement was 100 ms/step, 0.1 eV/step and 7 sweep. In the case of high resolution measurement, the scanning condition was as follows; 100 ms/step, 0.1–0.05 eV/step and 8 sweep.

In order to remove the influence of adsorbed water or other impurities, each specimen was rinsed with acetone for 1 min then heated by infrared heater for 10 min under vacuum (1.3×10^{-4} Pa). The temperature of the surface of the specimen was increased to around 100 °C due to the infrared heating. This treatment was carried out in a sub-chamber of the XPS analyzer. Therefore the specimen was not exposed to air after heating at all.

The development of this pretreatment technique to remove oxygen and impurities has been reported elsewhere, using highly oriented pyrolytic graphite (HOPG) [11]. Based on this study, it was confirmed that Ar ion sputtering was not a suitable method to remove the adsorbed water, because the peak shapes of C_{1s} spectrum were changed after sputtering. On the other hand, the heat treatment by infrared was effective and did not alter the peak shape of C_{1s} spectrum. The oxygen concentration O_{1s}/C_{1s} was decreased from 3.32 to 1.82%. Although it was not possible to remove all of the oxygen atoms from the surface of the specimen, it was obvious that this pre-treatment method was effective in order to minimize the effect of oxygen on the scattering of the data of surface analysis. Therefore, infrared heating in the sub-chamber of the XPS equipment was conducted for all specimens.

3. Results

3.1. XPS analysis of untreated GC

A survey spectrum of untreated GC is shown in Fig. 2 and a high resolution spectrum is shown in Fig. 3.

It was evaluated that approximately 2.0% of oxygen still remained on the surface of a specimen. As mentioned above, every sample was heat-treated at 1500 °C under Ar atmosphere and kept in a desiccator before

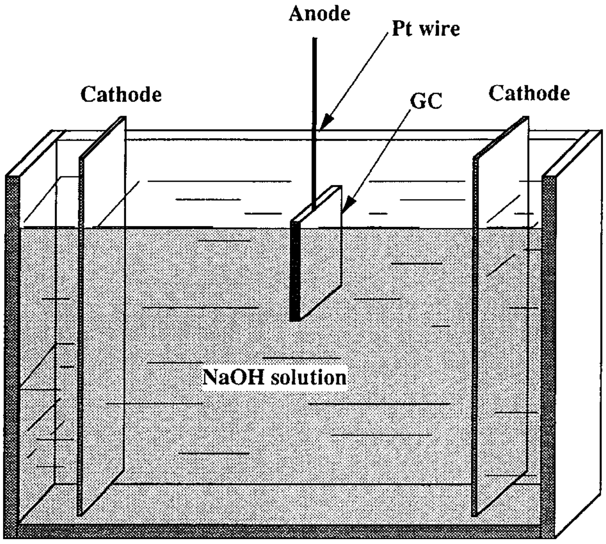

Figure 1 Apparatus for anodic oxidation.

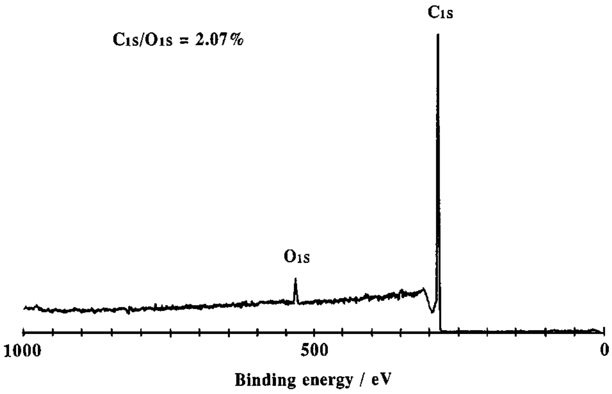

Figure 2 Survey spectrum of untreated glass-like carbon after infrared heating.

XPS analysis. Furthermore, each specimen was heat treated again by infrared heater in a sub-chamber of XPS under vacuum condition. Therefore, oxygen on the surface should be eliminated completely. Regarding this remaining oxygen, the adsorption of water could be considered, presumably moisture in the air. The effect of adsorbed water has already been confirmed by XPS analysis of a cleaved high oriented-pyrolytic graphite (HOPG). The results have also been reported elsewhere [11].

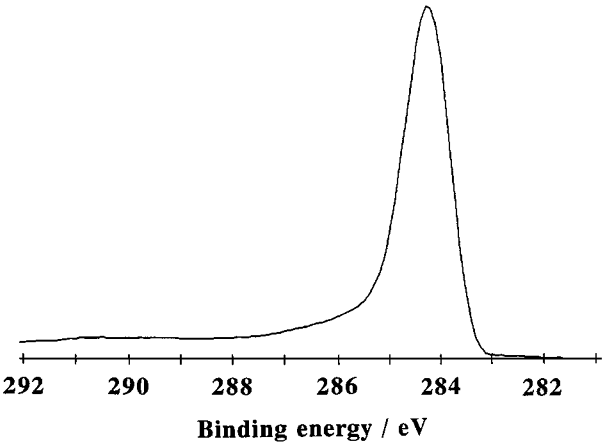

Figure 3 C_{1s} spectrum of untreated glass-like carbon.

The C_{1s} peak of untreated GC was fairly sharp and its full width at half maximum (FWHM) was 0.96 eV.

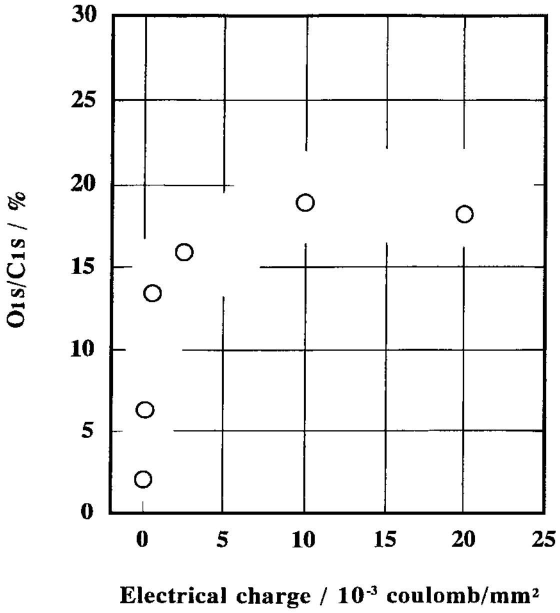

Figure 5 Effect of electrical charge on oxygen concentration of glass-like carbon.

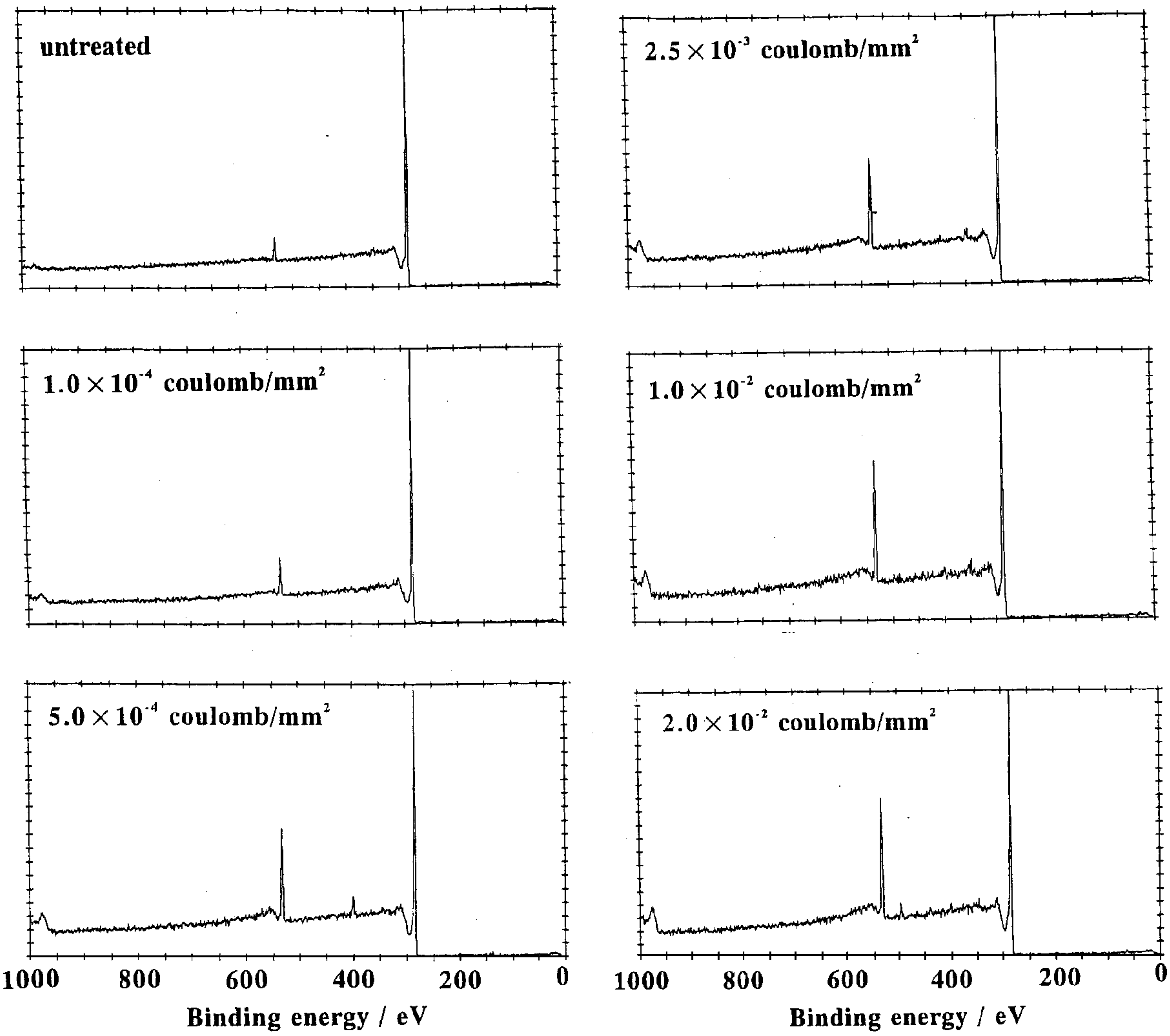

Figure 4 Survey spectra of untreated and treated glass-like carbon at various electrical charges.

In addition, no outstanding chemical shifts could be detected in the C_{1s} peak. It was confirmed that the specimen was prepared very well for the precise experimental work.

3.2. Anodic oxidation of GC

Fig. 4 shows the survey spectra of untreated and treated GC at various electrical charges. Fig. 5 shows the O_{1s}/C_{1s} of GC anodic oxidized in NaOH solution at various electrical charges. O_{1s}/C_{1s} values increased rapidly as the electrical charge increased. However, over the range of 2.5×10^{-3} C/mm^2, the O_{1s}/C_{1s} values reached a plateau. A similar tendency regarding the O_{1s}/C_{1s} values was also reported in the study of anodic oxidation of carbon fiber. It infers that the anodic oxidation of GC might be conducted properly [12, 13].

The changes in the C_{1s} spectrum are shown in Fig. 6. Obviously, one or two shoulders which have higher binding energies in comparison with the graphitic C_{1s} peak could be observed. For example, a $+1.5$–$+1.8$ eV chemically shifted shoulder could be observed in the C_{1s} spectra of GC treated at 1.0×10^{-4} C/mm^2. It can be considered to be due to a hydroxyl group. Further surface treatments have given different chemical shifts. At 5.0×10^{-4} C/mm^2, at least two chemical shifts could be confirmed. One peak showed approximately $+2.2$–$+2.4$ eV chemical shift and the other showed around $+3.9$–$+4.1$ eV and it seemed that the chemical shift became higher gradually with increasing of the amount of electrical charge. It could be considered that the former shifts showed the existence of a carbonyl group and the latter showed the formation of a carboxyl group. These results clearly showed that the species of the functional groups was changed with the progress of the degree of the oxidation.

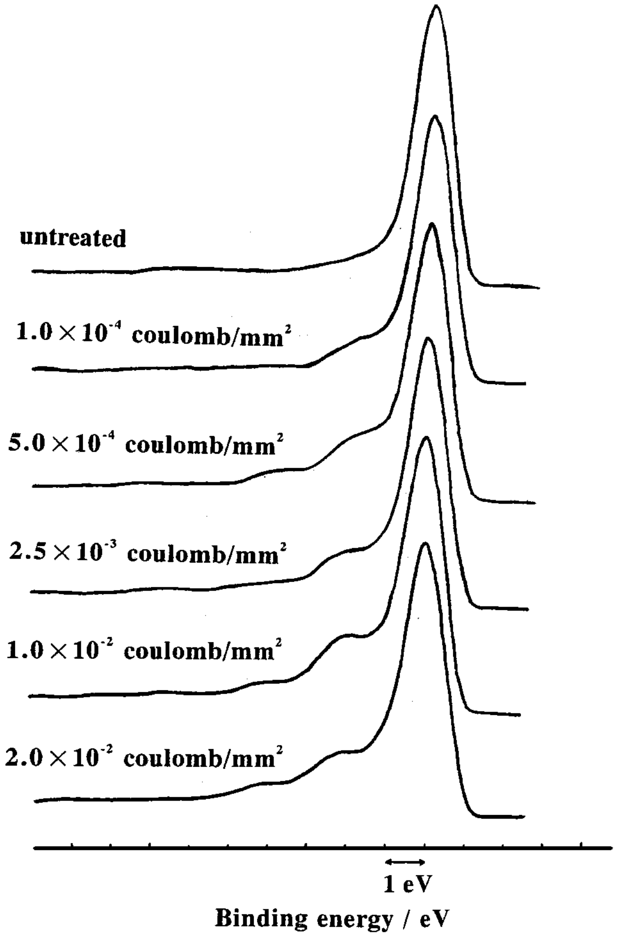

Figure 6 C_{1s} spectra of untreated and treated glass-like carbon at various electrical charges.

TABLE I Peak area ratio of each functional group of each sample evaluated by the curve fitting technique with the Gaussian distribution

	Peak area ratio (%)		
Sample	C–OH	C=O	COOH
Untreated	14.01	2.57	—
Treated at 1.0×10^{-4} C/mm^2	16.76	3.89	2.50
Treated at 5.0×10^{-4} C/mm^2	20.63	8.29	5.77
Treated at 2.5×10^{-3} C/mm^2	19.09	7.80	5.53
Treated at 1.0×10^{-2} C/mm^2	23.78	5.16	5.95
Treated at 2.0×10^{-2} C/mm^2	18.48	9.39	7.29

3.3. Curve fitting of C_{1s} spectrum

Curve fitting of C_{1s} spectra of each anodic oxidized GC was performed by using the Gaussian distribution. The binding energy of C–C and C–H were normally assigned at 284.5–285.0 eV. Chemical shifts of $+1.5$, $+2.5$ and $+4.0$ eV are usually used for each functional group, such as C–OH, C=O and COOH [5, 9]. However, in practice, it is very difficult to fix their chemical shifts from the C_{1s} peak precisely as mentioned elsewhere [14]. It should be considered that the values of chemical shifts of each functional group from the C_{1s} peak should have some distributions, e.g., $+1.3$–$+1.7$ eV for C–O, $+2.5$–$+3.0$ eV for C=O and $+4.0$–$+4.5$ eV for COOH [1, 14–16]. Therefore, the peaks in these ranges should be assigned as C–O, C=O and COOH respectively.

C_{1s} spectra after the curve fitting mentioned above are shown in Fig. 7 and the values of each functional group evaluated from these curve-fitted spectra are shown in Table I. The value of oxygen concentration (O cal.) was calculated using the following equation by using the values shown in Table I.

$$\text{O cal. [\%]} = A_{\text{C-OH}} + A_{\text{C=O}} + 2 \times A_{\text{COOH}} \qquad (1)$$

where $A_{\text{C-OH}}$, $A_{\text{C=O}}$ and A_{COOH} show the ratio of each peak area in the C_{1s} spectrum. The values of O cal. against O_{1s}/C_{1s} are shown in Fig. 8 as a symbol mark of "□". Although these two values should be consistent in principle, the result shows that there are considerable differences between O cal. and O_{1s}/C_{1s} values.

4. Discussion

In this discussion, the reason for the inconsistency between O cal. and O_{1s}/C_{1s} will be focused on.

4.1. Asymmetric curve fitting of C_{1s} spectra

To take an asymmetric peak shape of C_{1s} into consideration for the curve fitting has been commonly used. In

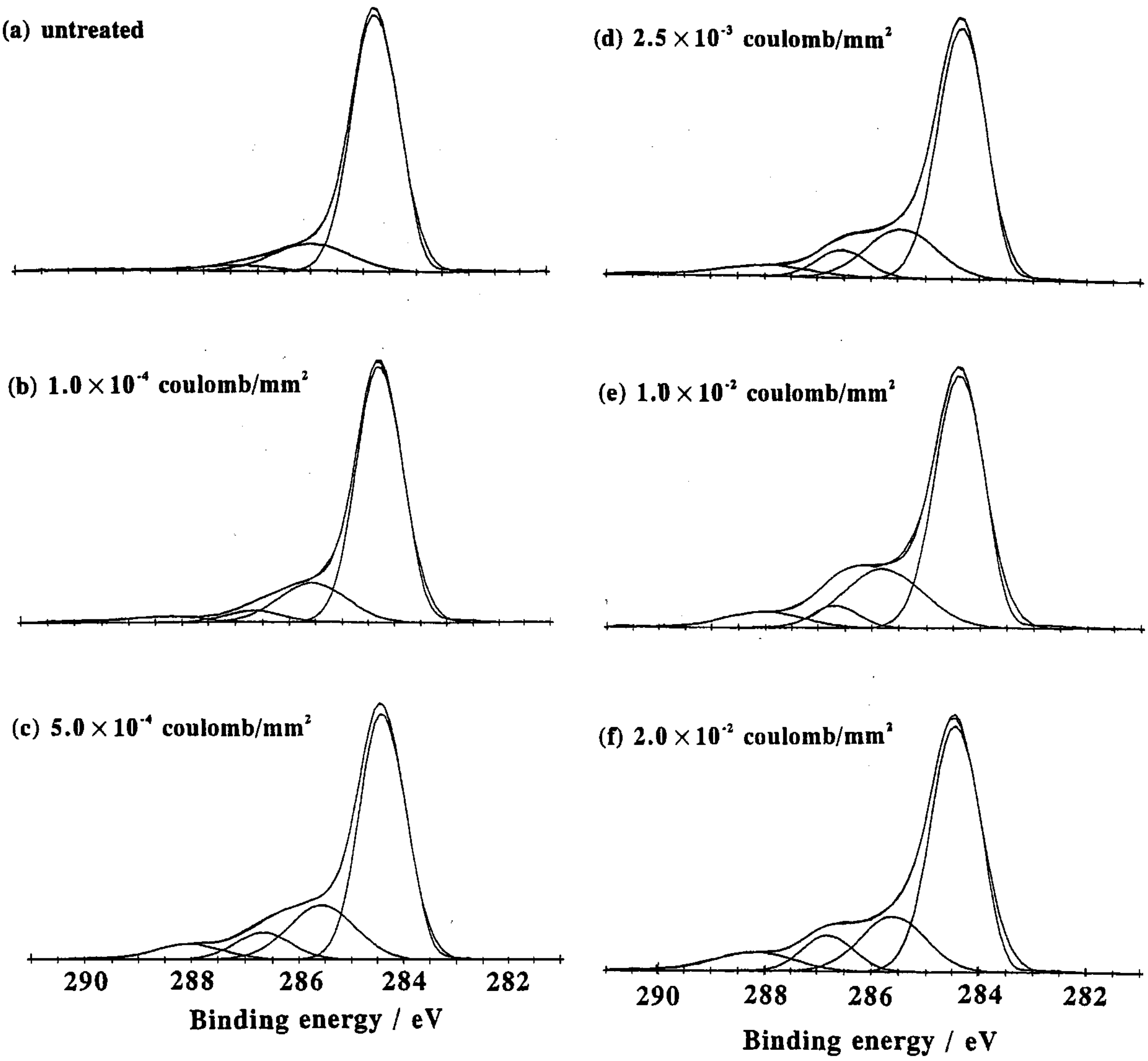

Figure 7 Curve fitting of C_{1s} spectra of untreated and treated glass-like carbon by using the Gaussian distribution.

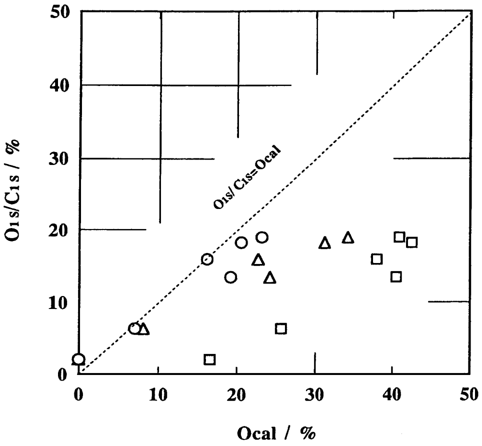

Figure 8 Comparison between O_{1s}/C_{1s} and C cal. calculated by various curve fitting techniques: □, Gaussian distribution; ○, Asymmetric (2nd graphitic peak); △, Asymmetric (assumed that 2nd graphitic peak shows a functional group).

TABLE II FWHM, tail parameter and scale parameter of each sample after heat treatment at 1500 °C under Ar atmosphere

Sample	FWHM (eV)	Tail	Scale
Untreated	0.96	15.2	0.41
Treated at 1.0×10^{-4} C/mm^2	0.95	14.9	0.38
Treated at 5.0×10^{-4} C/mm^2	0.96	13.9	0.46
Treated at 2.5×10^{-3} C/mm^2	0.96	14.8	0.38
Treated at 1.0×10^{-2} C/mm^2	0.94	15.0	0.38
Treated at 2.0×10^{-2} C/mm^2	0.96	15.0	0.37

this study, in order to take the asymmetric peak shape of C_{1s} spectra into consideration in the curve fitting technique, C_{1s} spectra of each surface treated specimen were measured after the heat treatment at 1500 °C under Ar atmosphere. Each C_{1s} spectra is shown in Fig. 9. Each C_{1s} spectra was analyzed by using the "Asymmetric Gaussian-Lorentzian Formula" program of an Ulvac ϕ 5400 series X-ray photoelectron spectrometer. FWHM, tail parameter and scale parameter of each C_{1s} spectrum are shown in Table II. These values were used in order to describe exactly the same graphitic peak shape when the curve fitting was carried out below.

Fig. 10 shows the curve fitting result of C_{1s} spectra of GC treated at 1.0×10^{-2} C/mm^2 by using the

TABLE III Peak area ratio of each functional group of each sample evaluated by the asymmetric curve fitting technique with 2nd graphitic peak

	Peak area ratio (%)		
Sample	C–OH	C=O	COOH
Untreated	—	—	—
Treated at 1.0×10^{-4} C/mm^2	6.99	—	—
Treated at 5.0×10^{-4} C/mm^2	11.95	—	3.61
Treated at 2.5×10^{-3} C/mm^2	—	11.06	2.56
Treated at 1.0×10^{-2} C/mm^2	—	16.14	3.49
Treated at 2.0×10^{-2} C/mm^2	—	12.14	4.19

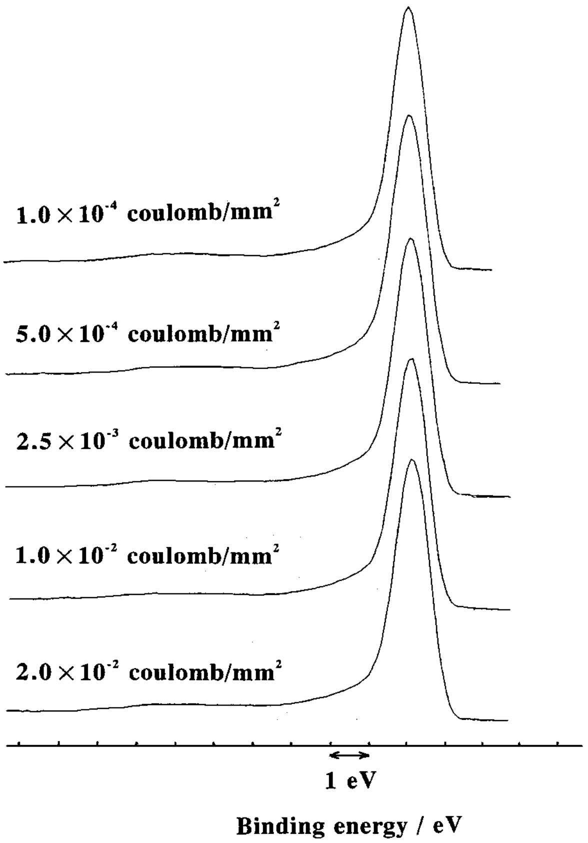

Figure 9 C_{1s} spectra of heat treated glass-like carbon at 1500 °C under Ar atmosphere.

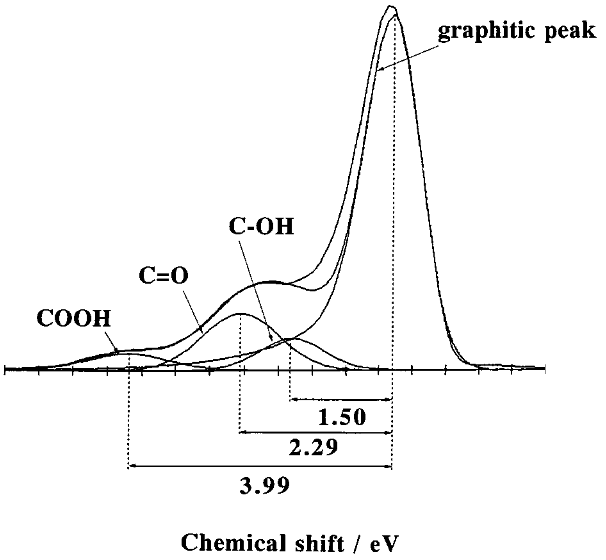

Figure 10 Asymmetric curve fitting of C_{1s} spectrum of glass-like carbon treated at 1.0×10^{-2} C/mm^2.

asymmetric graphitic peak, which is shown in Fig. 9 and chemical shifts previously reported [5, 9]. This result shows that there is still a big gap between the original C_{1s} curve and the curve fitting result. Furthermore, this result also indicates that another peak which has +0.7–+0.9 eV chemical shift and 1.0–1.3 FWHM should be necessary for obtaining a better curve fitted result as shown in Fig. 11e. If the existence of the additional peak which has +0.7–+0.9 eV chemical shift was used, better curve fitted results could be obtained for all specimens as shown in Fig. 11 and Table III.

4.2. 2nd graphitic peak

In the above discussion, it was suggested that it was useful to take a peak with +0.7–+0.9 eV chemical shift into consideration in order to obtain better curve fitting results. However, it is not clear why the peaks with +0.7–+0.9 eV chemical shift were generated.

Regarding this, two possibilities might be considered. One is due to a functional group such as a phenolic group. However, concerning this, it seemed to be difficult to regard the peaks with +0.7–+0.9 eV chemical shift as a functional group such as a phenolic group, because the chemical shift is so small for this functional group. It would be difficult to find another functional group which has +0.7–+0.9 eV chemical shifts from the graphitic peak. In addition, if the peak with +0.7–+0.9 eV chemical shift was assumed as a functional group containing an oxygen, O cal. values including this peak should be larger as shown in Fig. 8 with "△" symbol mark.

The other possibility is to assume the existence of a 2nd graphitic peak which may be affected by the carbons bonded with oxygen. Fig. 12 shows the relationship between O_{1s}/C_{1s} and the 2nd graphitic peak area. It can be recognized that the peak area increased rapidly with increasing O_{1s}/C_{1s} value. This result should be recognized circumstantial evidence for the existence of a 2nd graphitic peak. In addition, O cal. values without this peak and the O_{1s}/C_{1s} values showed good consistency as shown in Fig. 8 with "○" symbol mark.

Based on the above discussion, it should be concluded that the peak which has +0.7–+0.9 eV chemical shift and 1.0–1.3 FWHM was caused by a 2nd graphitic peak (i.e. carbons bonded to oxidized carbons), and is not due to the existence of some other functional group. This result is very similar to those from Sherwood *et al.* [1] and Lindberg [17]. The result also suggested that to take the asymmetric peak shape of the graphitic peak into consideration was not sufficient in order to obtain a well fitted curve fitting result. It is also necessary to use the 2nd carbon peak when the curve fitting of C_{1s} spectrum is carried out.

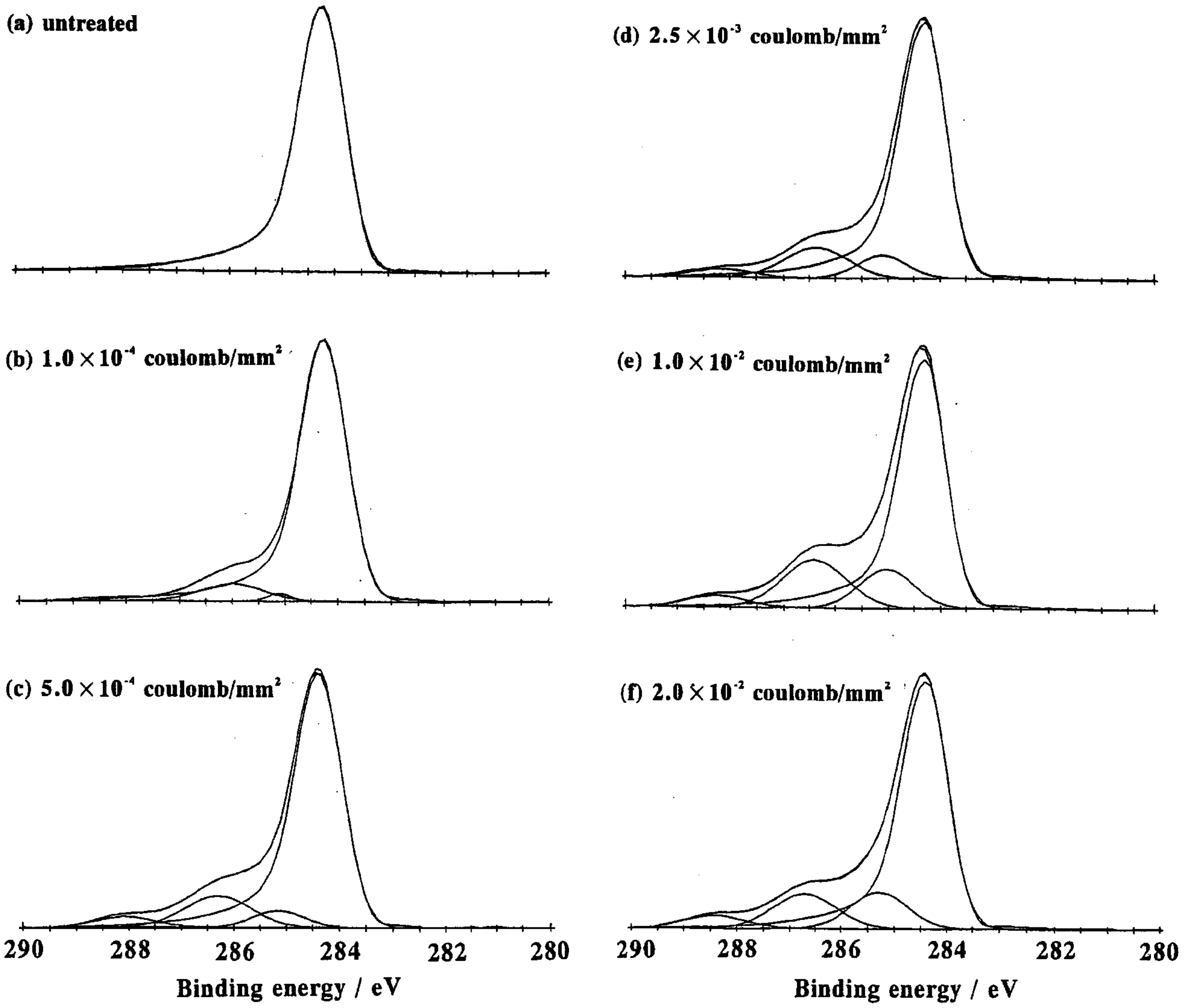

Figure 11 Asymmetric curve fitting of C_{1s} spectra of untreated and treated glass-like carbon with 2nd graphitic peak.

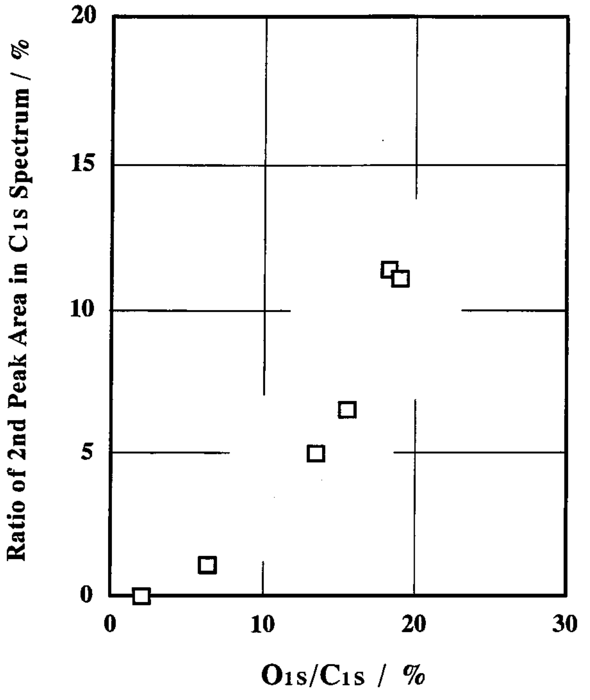

Figure 12 Relationship between O_{1s}/C_{1s} and the ratio of 2nd graphitic peak.

5. Conclusion

Anodic oxidation of GC was performed with NaOH solution. The O_{1s}/C_{1s} value was increased with increasing electrical charge and it was confirmed that the functional groups such as C–OH, C=O and COOH were formed after the treatment. However, the values of O_{1s}/C_{1s} and oxygen concentration calculated by using the values of each functional group (O cal.) were not equal. To consider the asymmetric peak shape of C_{1s} spectra was not enough to interpret this inconsistency. The extra peak with +0.7–+0.9 eV chemical shift and 1.0–1.3 FWHM should be considered for good curve fitting results and in this case O cal. showed fairly good consistency with O_{1s}/C_{1s} values measured by XPS. The amount of the 2nd graphitic peak was influenced by the amount of oxygen. This might show that the 2nd graphitic peak correspond to the carbon which bonded with oxidized carbon.

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