Hydrophilic Treatment of Carbon-coated Metal by Plasma Fluorination

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Surface modification of a carbon-coated stainless steel (SUS304) was carried out by nitrogen trifluoride (NF_3) plasma irradiation. NF_3 plasma irradiation changed the surface wettability of the carbon-coated SUS304 from hydrophobic to hydrophilic.

Fuel cells are very attractive power sources owing to their high efficiency and zero-emission capability.[1] Among them, polymer electrolyte fuel cells (PEFC) have been studied as the power sources of fuel cell vehicles, portable electronic devices, and so on. In the PEFC, water generated as a by-product must be ejected rapidly from the cell. Water ejected from a gas diffusion layer passes through bipolar plates, and water flows on the surface of a bipolar plate. Hence, the surface wettability of a bipolar plate plays an important role in the ejection of water, and this is the key to solving the flooding problem.[2,3] When the surface of a bipolar plate is hydrophilic, water can flow on the liquid thin-film generated on the bipolar plate and can be ejected rapidly to the outside.

Hydrophilization of carbonaceous materials by the oxidation process has been examined. However, optimized surface oxidation of carbonaceous materials is difficult. On the other hand, hydrophilization of carbonaceous materials by fluorination was reported by Chong and Ohara.[4] In their paper, a carbon fiber was treated with fluorine gas. They pointed out that the wettability of the carbon fiber was increased because of a small amount of a semi-ionic C–F bond. However, surface fluorination has not been applied to the hydrophilization of bipolar plate materials to our knowledge. If surface fluorination can impart hydrophilicity to bipolar plate materials, the flooding problem might be overcome. Moreover, a semi-ionic C–F bond will not impair the surface conductivity of carbonaceous materials.[5] We have prepared carbon-coated metals by plasma-assisted chemical vapor deposition (plasma-assisted CVD) for metal bipolar plate materials.[6,7] Surface modification of carbon-coating is interesting so it is quite attractive to investigate the effect of surface fluorination on the wettability of carbon-coated metals. In this letter, surface fluorination of carbon-coated metals by nitrogen trifluoride (NF_3) plasma irradiation and a change of wettability are reported.

The carbon-coated metal used in this study was prepared by plasma-assisted CVD. The details of the equipment and procedure of plasma-assisted CVD were shown in our previous papers.[6–8] The substrate material is stainless steel (SUS304), 0.1-mm thick and 15-mm square. The SUS304s were polished with a waterproof abrasive paper (#2000) before the carbon-coating and placed on a ground electrode whose temperature was kept at 1053 K and the applied rf power was set at 90 W. Deposition time was 5 h. The carbon-coated SUS304 was irradiated by the NF_3 plasma. The applied rf power and the flow rate of NF_3 were 30 W and 10 $dm^3\,min^{-1}$, respectively. Plasma irradiation time was 5 min. The wettability of the carbon-coated SUS304s was examined by using a Pocket Goniometer PG-3 (FIBRO Systems AB). The interfacial contact resistance between the sample and carbon paper, which is an important property as a current collector in a PEFC stack, was measured by the method reported in previous papers.[6,7] The surface morphology and RMS (root mean square) roughness of sample were observed by an atomic force microscope (AFM; CP-II) with a tapping mode. Surface chemical analysis was carried out by X-ray photoelectron spectroscopy (XPS; ULVAC-PHI Model 5500).

Figure 1 shows charge-coupled device (CCD) camera images of a water droplet (1 µL) on the carbon-coated SUS304s. The contact angle of the sample was provided by analysis of these CCD images. The contact angle for the pristine carbon-coated SUS304(a) was about 120°, which indicated that the surface of the pristine carbon-coated SUS304 was hydrophobic. By contrast, the contact angle for the surface-modified carbon-coated SUS304(b) was below 15°, which indicated that the surface of the surface-modified carbon-coated SUS304 was hydrophilic. This result shows that the wettability of the surface of the carbon-coated SUS304 was increased by NF_3 plasma irradiation, that is, the surface of the carbon-coated SUS304 changed from hydrophobic to hydrophilic. Moreover, the value of the contact angle after NF_3 plasma irradiation was very small, which is quite an interesting property as a bipolar plate material. Next, we measured the interfacial contact resistance of samples. The interfacial contact resistance of the carbon-coated SUS304 before NF_3 plasma irradiation was 26.73 $m\Omega\,cm^2$. This value was changed to 36.74 $m\Omega\,cm^2$ after NF_3 plasma irradiation. It is considered that this increase in the interfacial contact resist-

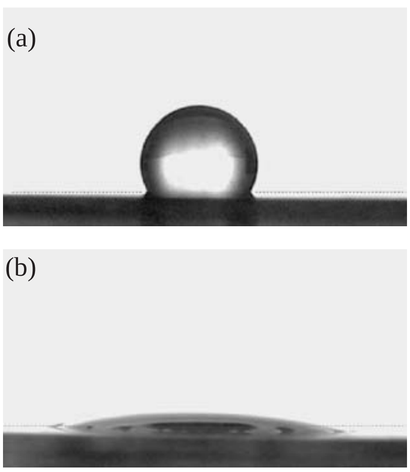

Figure 1. The CCD images of the water droplet on the (a) pristine carbon-coated SUS304 and (b) surface-modified carbon-coated SUS304. The volume of water droplet was 1 µL. The CCD images were obtained after dropping for 1 s.

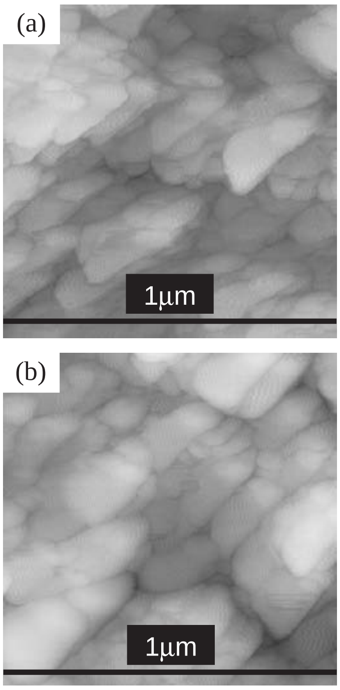

Figure 2. AFM images (1-μm square images) of carbon-coated SUS304s. (a) pristine carbon-coated SUS304 and (b) surface-modified carbon-coated SUS304.

ance is due to the decrease in the contact area with carbon paper by the plasma ablation of the carbon-coating layer.

To clarify the reason for the change of wettability of the carbon-coated SUS304, the surface morphology, RMS roughness, and surface chemical composition of the carbon-coated SUS304s were investigated. Figure 2 shows the AFM images (1-μm square images) of the carbon-coated SUS304s. There is almost no morphological difference between the pristine carbon-coated SUS304(a) and the surface-modified carbon-coated SUS304(b) from the AFM images. The values of RMS roughness calculated from the AFM images were 18.7 nm for the pristine carbon-coated SUS304 and 10.2 nm for the surface-modified carbon-coated SUS304. Because of the decrease in RMS roughness, the contact area was decreased and the interfacial contact resistance was increased. The pristine carbon-coated SUS304 showed hydrophobicity (contact angle $>90°$). If the surface RMS roughness is increased, the contact angle should be increased, considering Wenzel's formula. However, the change of surface roughness acted adversely. Hence, it is considered that the change of wettability by the surface modification was not due to the change of surface RMS roughness. So, XPS analysis was conducted to estimate the change of the surface chemical composition.

Figure 3 shows the F1s XPS spectrum of the surface-modified carbon-coated SUS304. An F1s broad peak was observed, and the binding energy was around 689 to 687 eV. This binding energy is in-between the binding energy of the covalent C–F bond and that of the ionic C–F bond, leading to the conclusion that the C–F bond on the carbon-coated SUS304 should be a semi-ionic bond. It was reported that the semi-ionic C–F bond impart the polarity to the surface of carbon.[4] Hence, the semi-ionic C–F bond in this study also enhanced the wettability. The amount of fluorine on the carbon-coated SUS304 was about 0.8 atom % after NF_3 plasma irradiation. Although it is interesting that this extremely small amount of surface fluorine imparted hydrophilicity, the reason is not clarified at this stage. The amount of oxygen on the carbon-coated SUS304 changed from about 5.2 to about 13.3 atom % after NF_3 plasma irradiation. This increased surface oxygen might influence the wettability. However, Chong and Ohara reported that the influence of surface oxidation of the carbon fiber on hydrophilicity is less than that of surface fluorination.[4] Hence, the hydrophilicity in this study is considered to be due not to the surface oxygen but to the extremely small amount of surface fluorine. The investigation of the influence of surface oxidation on the wettability is undergoing.

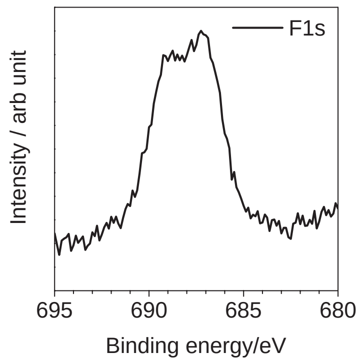

Figure 3. XPS F1s spectrum of surface-modified carbon-coated SUS304.

In conclusion, surface fluorination of carbon-coated SUS304 was achieved by NF_3 plasma irradiation. The amount of introduced fluorine was extremely small. The surface wettability of carbon-coated SUS304 changed from hydrophobic to hydrophilic. In spite of the surface hydrophilicity, the interfacial contact resistance was not so impaired. These results are quite interesting as control techniques of the wettability of bipolar plates in PEFC.

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