Waterproofing of Carbon Paper by Plasma Polymerization

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ABSTRACT: Waterproof treatment by plasma polymerization was applied to the porous material of proton exchange membrane fuel cells (PEMFCs). Carbon paper used for PEMFCs was waterproofed by the gas plasma of hexafluoropropylene (HFP) prior to binding to the polymer electrolyte membrane, Nafion®. A plasma-polymerized HFP thin film on the surface of the carbon fiber increased the contact angle of the carbon paper. The inner surface of the carbon paper was also waterproofed as well as its outer surface. It was found from the fuel cell performance test that this waterproofing method of the carbon paper was effective in the high-current density region where the condensed water product tends to accumulate. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1748–1753, 2006

Key words: plasma polymerization; waterproofing; fuel cell; surfaces; fluoropolymers

INTRODUCTION

Recently, environmentally clean power generation has been needed around the world. Proton exchange membrane fuel cells (PEMFCs), which electrochemically convert the chemical energy of a fuel directly into electrical energy, have been brought into focus as promising candidate power sources for electrically powered vehicles, small scale stationary power generations, and portable electronics devices in the near future.[1–4] Some vacuum processes are beginning to be studied for manufacturing parts of the micro-PEM fuel cells.[5–7] Recently, a reliable production process with a high reproducibility is becoming an important issue from the viewpoint of commercialization.[8–10]

A PEMFC consists of a polymer electrolyte membrane, two electrodes (catalyst layers), two gas-diffusion backings, and two sets of flow channels for the reactants, as seen in Figure 1. Hydration of the membrane is required to maintain proton conductivity during high performance of the PEMFC. Water is fed to each side of the membrane by a humidified gas stream and it is transported through the gas-diffusion backing and electrode to the membrane by either diffusion or convection. Water is produced at the cathode by the fuel cell reaction. Also, water is transported from the anode to the cathode by the movement of protons, i.e., electro-osmotic drag. The water at the cathode may be transported through the gas-diffusion backing into the flow channel and exhausted at the outlet.[11,12] An electrically conductive highly porous material, carbon paper or carbon cloth made of carbon fibers, are used as the gas-diffusion backing (or sometimes called diffusion layer, gas diffuser, or current collector). Carbon paper or carbon cloth is present between the catalyst layer and gas flow channel, and plays an important role in the fuel cell electrode performance. The carbon fibers direct the electric current, and the pores allow for transport of the reactants to the electrodes and removal of water vapor product to the flow channels. To maintain a good gas diffusion property at high-current densities, the current collector is waterproofed usually by an impregnation process with a PTFE water dispersion following thermal sintering.[13–15] When used without waterproofing, the pores of the current collector tend to flood with water and hinder the supply of gaseous reactants to the electrodes. However, a uniform distribution of PTFE throughout a sheet of carbon paper with high reproducibility is not easy by a conventional impregnation process with the PTFE water dispersion. In addition to this nonuniformity, sintered PTFE often blocks the pores between the carbon fibers in this process.[13,14]

It is known that plasma treatments uniformly modify the surface properties of materials without modifying the bulk properties such as electrical conductivity. Plasma polymerization is a rapid and simple process carried at room temperature for thin polymer film deposition without using a solvent.[16–18] Plasma-polymerized ultrathin films are also known to be thermally and chemically stable because of their highly crosslinked structure. Good adhesion to various substrates is also a characteristic of the plasma-polymerized thin films. It has been shown by several groups

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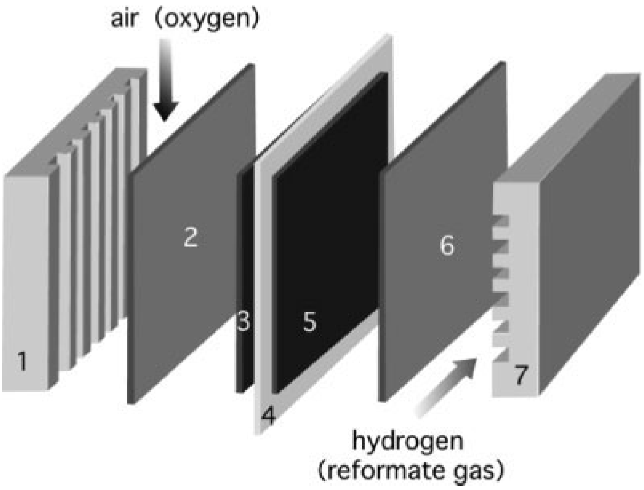

Figure 1 Schematic drawing showing a cell unit of the PEFC. 1: bipolar plate, 2: gas diffusion backing (carbon paper), 3: air electrode (catalyst layer), 4: polymer electrolyte membrane, 5: fuel electrode (catalyst layer), 6: gas-diffusion backing (carbon paper), and 7: bipolar plate.

that plasma polymerization can be used for the waterproofing of hydrophilic surfaces.[19–21] On the other hand, plasma coating of the inner surface of a complex structure is an important problem in plasma technology. The permeation of the plasma coating into porous materials has been reported by some researchers.[22–24] Krentsel et al. investigated the depth and possible mechanism of the penetration of the surface modification into sheets of nonwoven fabrics of poly(ethylene terephthalate), using a low-temperature cascade arc torch.[22] Mukhopadhyay et al. studied the treatment of filter paper using plasma created in a wave reactor having parallel plate electrodes.[23,24] The results of their works are encouraging, showing the possibility of applying this technology to the treatment of high-porosity materials such as filter paper and woven fibers. In this report, waterproofing of the carbon paper was carried out by plasma polymerization of hexafluoropropylene (HFP) as a novel waterproofing method for electrochemical porous materials, such as the electrodes for PEMFCs.

EXPERIMENTAL

The plasma polymerization was carried out using a vacuum glow discharge apparatus with a 13.56 MHz power supply, as seen in Figure 2. Carbon papers having a typical thickness of 0.2 mm (provided by Toray, Tokyo, Japan, under the designation TGP-H-060) and area of 10 cm^2 were used and placed on the downer earth electrode. After the chamber was evacuated to below 1.0 Pa, hexafluoropropylene (HFP) as a monomer gas was introduced into the glass reactor at 30 cm^3 min^{-1} and the pressure was adjusted to 13.3 Pa. A radio-frequency power of 3 W was then applied. For investigation of the permeation of the plasma coating into the carbon paper, the stack of five carbon papers was taped together at the sides to prevent any plasma penetration through the edges according to the method of other researchers.[22–24] Figure 3 shows this arrangement. The outer surface is the top surface of the first layer (1) and the bottom surface of the fifth layer (5). The other surfaces are internal surfaces accessible only through the porosity of the outer papers. A surface analysis of the treated carbon paper was carried out by XPS (ESCA 3400, Shimadzu, Kyoto, Japan). The water repellency was examined by measuring the contact angle for an ultrapure water drop with a contact-angle meter (CA-DT, Kyowa Interface Science, Saitama, Japan). A magnified image of the carbon paper was observed with a field emission scanning electron microscope (JSM-6700FA, JEOL, Tokyo, Japan).

The contact resistance of the treated carbon paper was evaluated by measuring the through-plane electrical resistance of the carbon paper between copper plates. The sample was sandwiched between two copper electrodes with a 55 mm diameter circular surface, and the electrical resistance was measured under various applied pressures using an impedance meter (Loaded Impedance Meter SPEC 40026S, Kikusui, Yokohoma, Japan) after verifying the constancy of the short-circuit resistance of the copper electrodes (without a sample between them). The measured resistance includes contributions from the bulk carbon paper and the two contact resistances between the carbon paper and copper electrode.

Fuel cell electrodes were prepared from a 20 wt % carbon black supported platinum (Pt/C) electrocatalyst (Johnson Matthey, London, UK) and a Nafion®

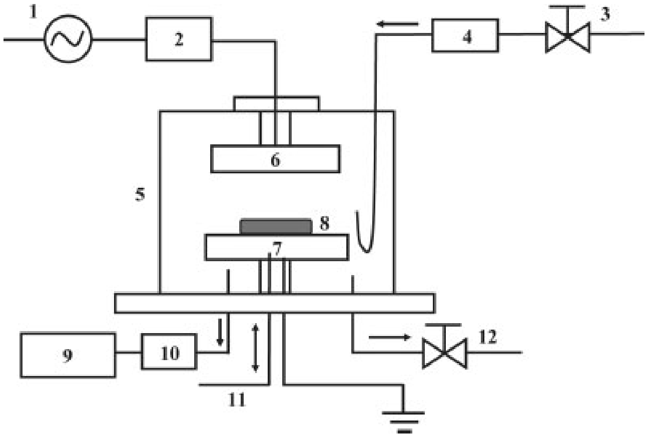

Figure 2 Schematic diagram of plasma polymerization apparatus. 1: RF power generator, 2: impedance matching box, 3: monomer gas inlet, 4: flow meter, 5: glass reactor, 6: RF electrodes, 7: earth electrodes, 8: substrate, 9: rotary pump, 10: cold trap, 11: cooling water, and 12: leak valve.

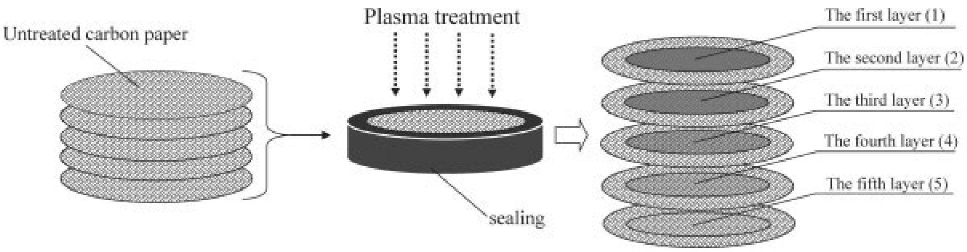

Figure 3 Schematic drawing of the stack arrangement of five carbon papers taped together on the sides to prevent any plasma penetration through the edges.

solution (5 wt % solution, E.I. Du Pont de Nemours and Company, Wilmington, DE). The catalyst slurry was prepared by adding the Nafion solution to the electrocatalyst powder, and the resulting slurry was applied on the PTFE sheet and transferred to the proton exchange membrane (PEM), Nafion® 117 (E.I. Du Pont de Nemours and Company) by hot-pressing to manufacture an assembly of electrodes and the polymer electrolyte membrane. The waterproofed carbon paper was then hot-pressed to the assembly. Fuel (hydrogen) and oxidant (oxygen) gases were humidified and fed to each electrode at 0.10 MPa for evaluating the cell performance. The cell performance was measured at 80°C. The performance was galvanostatically evaluated using an electronic load (Loaded Impedance Meter SPEC 40026S, Kikusui).

RESULTS AND DISCUSSION

To investigate the permeation of the plasma coating into the carbon paper, a stack of five carbon papers was also used as the substrate. The stack was taped together at the sides to prevent any plasma penetration through the edges. This method was used for studying the plasma permeation into porous media by Krentsel[22] and Mukhopadhyay.[23,24] The contact angles measured for the treated samples are shown as a function of position in Figure 4(a,b). The contact angles were measured at three points on each carbon paper. Since no significant difference was observed between the bottom sides of an individual carbon paper and the contacted top side, i.e., the upper side, of the next carbon paper, the data shown are for the analysis performed only on the top surface of each carbon paper. The contact angle of the untreated carbon paper, 130°, could be increased up to 148° by this treatment. This figure showed that the effect of the treatment is not limited to the top surface of the carbon paper. This fact indicates that a small amount of polymer-forming active species created in the glow discharge plasma penetrated into the carbon paper and reached the internal surfaces of the carbon paper through the porosity of the outer papers during the plasma polymerization. The longer the treatment time, the further the active species migrated into the carbon paper and the contact angle of the internal surfaces increased.

The surface of the treated carbon paper was analyzed by XPS. The measured C1s XPS spectrum of the upper surface of each carbon paper layer plasma-treated for 5 min are shown in Figure 5. Figure 5(a) shows the spectrum for the outer surface, i.e., the top surface of the first layer (1), of the carbon paper stack. It can be seen that the plasma polymer is composed of highly hydrophobic —CF_3 and —CF_2— species. The appearance of the —CF— and —C—CF_n components

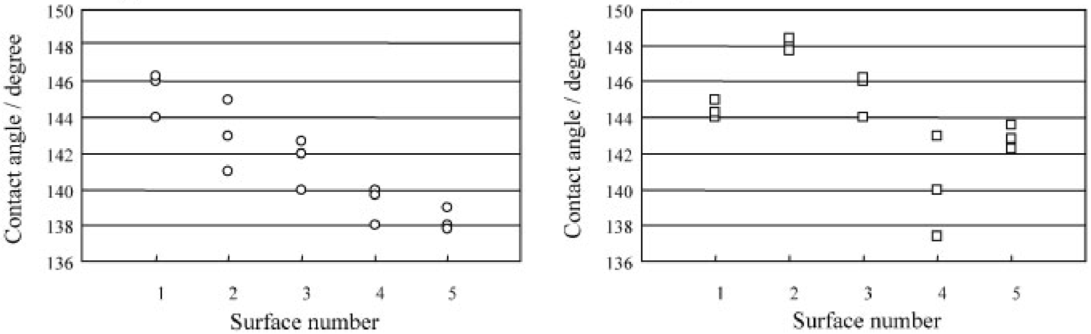

Figure 4 The dependence of the contact angle measured on the top surface of carbon papers treated by plasma polymerization on the sample position: (a) plasma waterproofing for 10 s; (b) plasma waterproofing for 5 min.

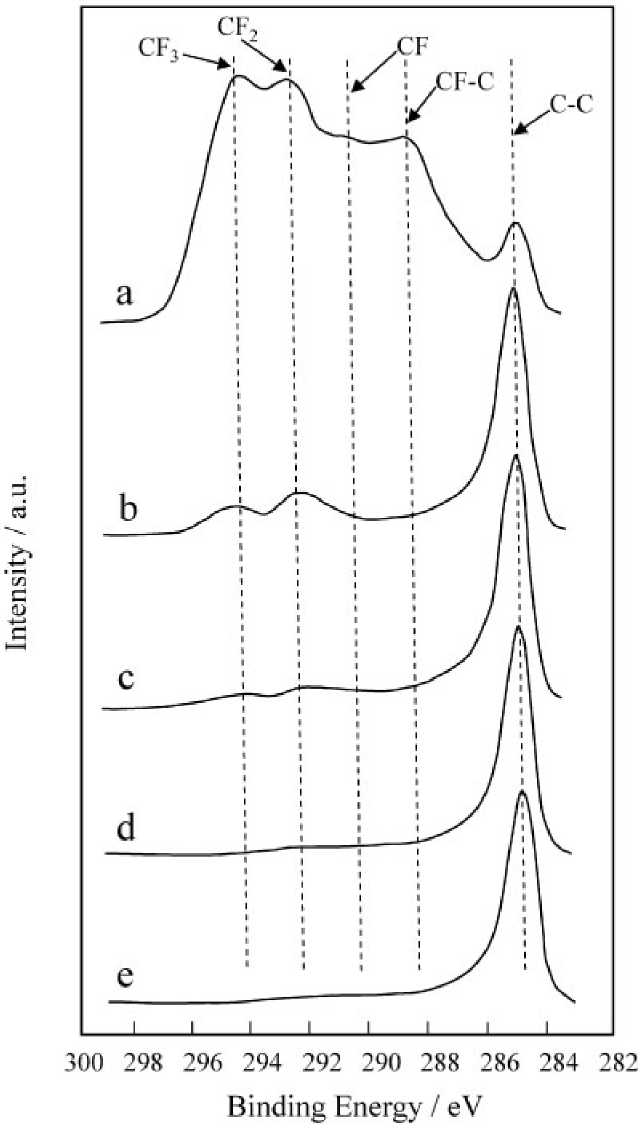

Figure 5 C1s XPS spectra of the top surface of carbon paper treated by plasma polymerization for 5 min. (a) The first layer; (b) the second layer; (c) the third layer; (d) the fourth layer; and (c) the fifth layer.

indicates the highly branched and crosslinked structure of the plasma polymer. Figure 5(b) shows the spectrum for the top surface of the second layer (2) of the plasma-treated carbon paper stack. Besides the large peak for graphite of the carbon fiber at 285 eV, a small peak for the species —CF$_3$ and —CF$_2$— were seen. Although these peaks became smaller in the spectrum for the lower layers of carbon paper stack, they were detected even in the spectrum for the upper surface of the bottom layer (5). It is considered from these results that a very thin hydrophobic film on the surface of carbon fiber can produce a high water contact angle, and the contact angle depends on the surface ratio of highly hydrophobic group, —CF$_3$. On the other hand, it is also considered that surface coverage of plasma polymer decreases on lower layer of the carbon paper stack, and the contact angle depends on the surface coverage. We think that it is not needed to coat over entire inner surface for such waterproof treatment.

Single carbon papers were plasma treated for evaluation of the electrical and gas distributor characteristics for fuel cells. The scanning electron microscope image of the untreated carbon paper was almost the same as the image of the plasma-treated carbon paper. The carbon paper has a structure with a pore size between 0.020 and 0.050 mm, according to the SEM image. The plasma polymerized film is so thin that it affects neither the porosity nor the pore size distribution of the carbon paper. The surface of the treated carbon paper showed a high water-repellency, and a water droplet dropped onto it rolled down when the carbon paper was angled.

Figure 6 shows the through-plane electrical resistance of carbon paper sandwiched between two copper electrodes. The electrical resistance depends on the applied compression pressure. This figure shows that the interfacial resistance of the treated carbon paper increased with the increasing treatment time. The increase in the treatment time negatively affected the contact resistance, probably due to an increase in the thickness of the insulating surface-hydrophobic layer with treatment time.

The performances of the cells with the plasma-treated and untreated carbon paper were compared in Figure 7. The top surface, upper side, of the plasma-treated carbon paper was bound to the catalyst layer. It is evident from the figure that the cells using carbon paper treated by the plasma polymerization have a

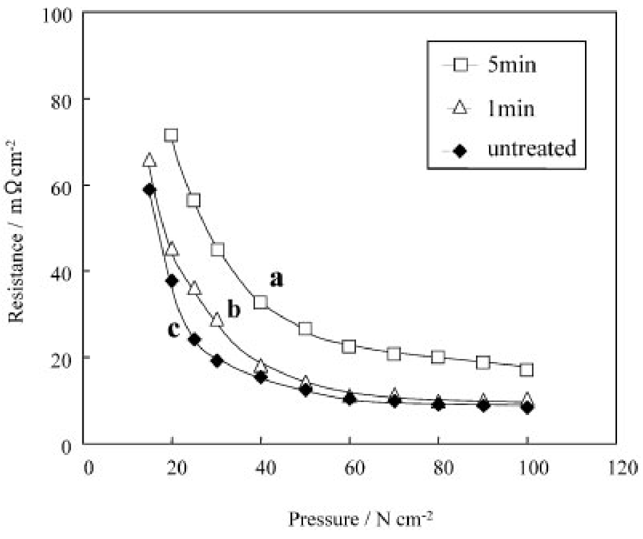

Figure 6 The through-plane electrical resistance of carbon paper sandwiched between two copper electrodes measured at various pressure. (a) Plasma waterproofing for 5 min; (b) plasma waterproofing for 1 min; and (c) untreated.

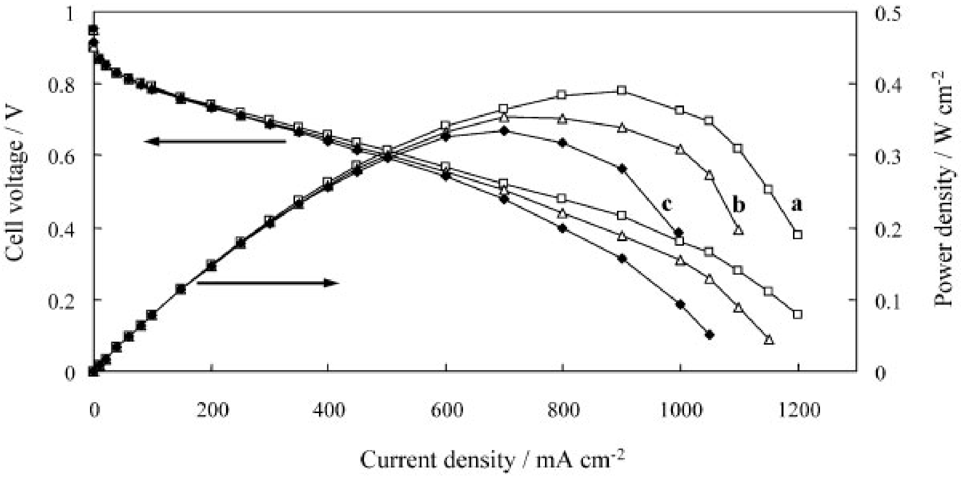

Figure 7 The current-voltage characteristics of the PEFC cells. (a) Plasma waterproofing for 5 min; (b) plasma waterproofing for 1 min; and (c) untreated.

better performance than the cells using the untreated carbon paper. This result can be attributed to the better gas-permeation character of the waterproofed carbon paper treated by plasma polymerization. The carbon paper treated for 5 min exhibited a better performance than that for 1 min, in spite of the increase in the contact resistance as shown in Figure 7. This result can be attributed to the higher hydrophobic property of the carbon paper treated for 5 min as already described. Plasma polymerization of the HFP was found to be effective for the PEMFC as a waterproofing method from this result.

In this study, the catalyst layer of the fuel cell was fabricated on a PTFE blank sheet followed by a transfer process onto the Nafion membrane: the so-called indirect decal method.[8,10,25] On the other hand, the catalyst layer is directly painted as sprayed onto carbon paper in another fabrication method, i.e., the gas diffusion layer (GDL)-based method. The GDL-based method has the advantage that the catalyst loading

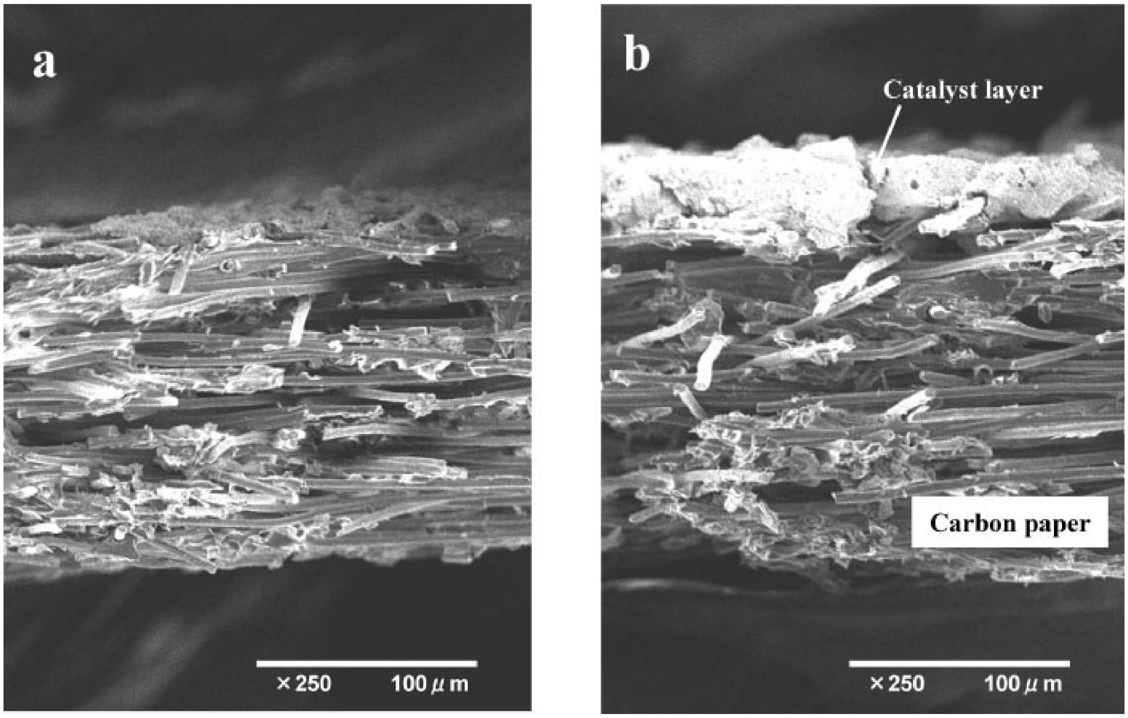

Figure 8 Scanning electron micrograph of a cross section of the Toray carbon paper directly coated with a catalyst slurry in the GDL-based method. (a) Untreated; and (b) plasma waterproofing for 5 min.

can be very precisely adjusted.[10] In the fabrication process of this GDL-based method, however, leaking of the catalyst slurry into the carbon paper occurs and thereby decreasing the catalyst utilization and increasing the tendency of electrode flooding. Figure 8 shows scanning electron micrographs of a cross section of the carbon paper directly coated with a catalyst slurry. These micrographs were obtained by SEM observation of the samples after the drying process. When using carbon paper without the water-proof coating, the catalyst slurry penetrates into the carbon paper after applying the slurry on it, and the catalyst layer could not be fabricated on the carbon paper surface as seen in Figure 8(a). On the other hand, the plasma-treated surface of the carbon paper reduced the penetration of the catalysts into the carbon paper, and the catalyst layer was successfully deposited on the surface of the carbon paper as shown in Figure 8(b). This result shows the effective surface hydrophobicity of the plasma-treated carbon paper. It was reported that the content of the waterproofing agent in the carbon paper should be optimized, since too little causes flooding and too much disturbs the gas diffusion.[26] However, the top surface of the carbon paper should be highly waterproofed to disturb the penetration of the catalyst slurry. Consequently, the plasma treatment technology, which enables a high waterproof coating especially near the top surface of the carbon paper by adjusting the plasma conditions, is also expected in this point.

CONCLUSIONS

PEMFC carbon papers were waterproofed by plasma polymerization. The effect of the treatment was not limited to the top surface of the carbon paper and reached the internal surfaces of carbon paper through to porosity during the plasma polymerization. There seemed to be an increase in the PEMFC performance in the higher current density region above 600 mA cm^{-2} because of this plasma treatment. Plasma polymerization is expected to be a novel, effective, and highly reproducible technique for waterproofing the gas-diffusion backing for PEMFCs and for studying the waterproofing effect on the performance of PEMFC.

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