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Highly water-proof coating of gas flow channels by plasma polymerization for PEM fuel cells

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Abstract

Gas flow channels of proton exchange membrane fuel cell were highly water-proofed by plasma polymerization. Pretreatment by sand-blasting was efficient for increasing water-contact angle of the coated surface. With a very low water wettability of gas flow channels, peak power of the fuel cell increased in the condition where the condensed product water tends to accumulate.

Keywords: Plasma polymerization; Water-proofing; Fuel cell; Bipolar plate

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) which electrochemically convert the chemical energy of a fuel directly into electrical energy are emerging as promising power sources for electrically powered vehicles and distributed power generation in the near future [1–3]. Small-sized PEMFCs (micro-fuel cells) have been also developing for powering portable electronic equipment such as laptop computers, cellular telephones and so on [4]. Some vacuum processes begin to be studied for manufacturing parts of micro-PEM fuel cells [5,6].

In the case of stack, conductive flow field plates 'bipolar plates (separators)' are positioned between adjacent electrochemical cells. In this type of fuel cell, the both reactants were usually fed to the fuel cell in fully humidified condition for humidification of polymer electrolyte membrane. Water converges at cathode via three processes, that is, transport by the humidified reactants, water generation at the cathode reaction, and transport via the electro-osmotic drag associated with proton transport across the polymer electrolyte membrane.

Although these bipolar separator plates are typically made from graphitic carbon now, metallic conductors, such as titanium and stainless steel, are expected for cost down [7,8]. Since the gas flow channels in metal bipolar plates have hydrophilic nature, the channels may flood with water and hinder the supply of gaseous reactants to the electrodes. Therefore, the surfaces of gas flow channels are preferably hydrophobic to prevent liquid product water from condensing on the surface of gas flow channels. In this work, the hydrophobic thin film was deposited on the surface of the gas flow channels by plasma polymerization of hexafluoropropylene in order to make the channels hydrophobic. Plasma polymerization is rapid, simple and low temperature process without using solvent [9–11]. As an accurate dimension is needed for uniform distribution of gas and heats in gas flow channel of fuel cells, uniform thin film coating technique is desired. Plasma-polymerized thin film is also known as the character of highly cross-linked structure and pinhole free. Water-repellent plasma-polymerized thin film prevents the attachment of water droplet on the surface of gas flow channels. In addition, the water-repellent plasma-polymer coating

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will prevent the penetration of liquid water into the coating, which will also aid in preventing corrosion of the metal substrate.

2. Experimental

Plasma-polymer coating was carried out using a vacuum glow discharge apparatus with 13.56 MHz power supply as shown in Fig. 1. Cleaned titanium and stainless steel plates were used as substrates for measurement of water-contact angle and they were cleaned ultrasonically in acetone for 10 min. Sand-blasting, as a pretreatment of substrates for surface roughening, was carried out. After cleaning, they were placed on the downer earth electrode. After the chamber was evacuated to below 0.8 Pa, hexafluoropropylene (HFP) as a monomer gas was introduced into the glass reactor at 30 cc min^{-1} and the pressure was adjusted to 13.3 Pa. RF power of 3 W was then applied for 5 min.

Water-repellency was examined by measuring the contact angle for water drop with a contact-angle meter (CA-DT, Kyowa Interface Science). A sand-blasting and plasma-polymer coating of gas flow channels of the cell made from titanium were conducted as shown schematically in Fig. 2. The parts of a cell where the cell contacts with an electrode were masked with masking tape (Scotch® Brand Tape, 3 M) before processing and were not water-proofed for avoiding increase of electrically contact resistance. The masked cell was placed on the downer earth electrode in the plasma reactor after sufficient cleaning following sand-blasting, and then surface-treated by the same procedure described above.

Fuel cell electrodes were prepared by a 40 wt.% carbon black (Vulcan® XC-72) supported platinum electrocatalyst (Johnson Matthey). Catalyst slurry was prepared by mixing electrocatalyst powder with Nafion® solution (5 wt.% solution, E.I.DuPont de Nemours and Company). The resulted slurry was stirred and applied on the PTFE sheet, and then transferred to proton exchange membrane, Nafion® 117 (DuPont), by hot-pressing in order to manufacture a membrane electrode assembly, MEA. Wet-proofed carbon paper (TGP-H-060, Toray) was used as gas diffusion backing.

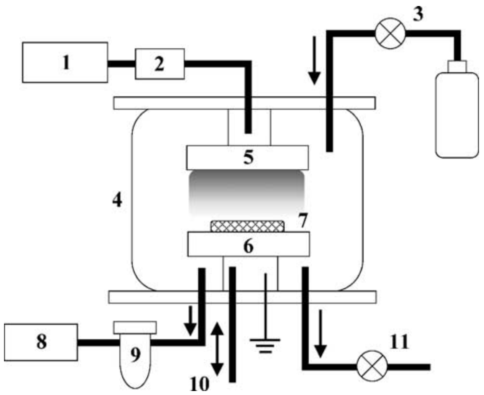

Fig. 1. Schematic diagram of plasma polymerization apparatus. (1) RF power generator, (2) impedance matching box, (3) monomer gas inlet, (4) glass reactor, (5) RF electrodes, (6) earth electrodes, (7) substrate, (8) rotary pump, (9) cold trap, (10) cooling water, (11) leak valve.

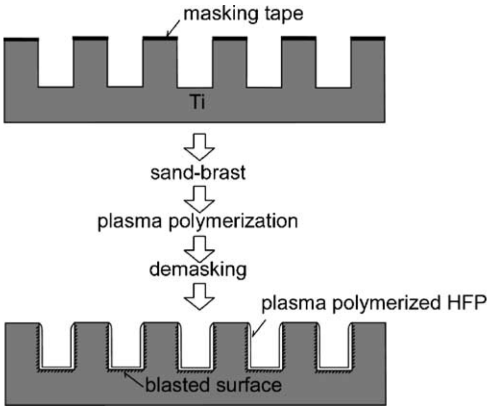

Fig. 2. Scheme of water-proofing of gas flow channels.

Single cell tests were carried out using a cell with 10 cm^2 active area at cell temperature 80 °C. Fuel (hydrogen) and oxidant (oxygen) gases as reactants were humidified and fed to each electrode for evaluating the cell performance. The performance was evaluated galvanostatically through electronic load (SPEC40026, Kikusui).

3. Results and discussion

The measured water-contact angle for each untreated and treated substrate materials are summarized in Fig. 3. As substrate materials, titanium is used as bipolar plate not only for PEMFCs but also unitized regenerative fuel cells using PEMFC technology developed in our group [12,13]. Plasma polymerization of HFP increased water-contact angle of substrates. Although plasma-polymer coating has a lot of advantage as described above, water-contact angle was lower than that of commercially available PTFE sheet. This could be explained by a structure of plasma polymer containing $-CF-$, $-C-CF_n$ species as can be seen in XPS C 1s spectrum of the deposited plasma polymer (Fig. 4), resulting in lower contact angle than PTFE sheet, which is composed of $-CF_2-$ structure [11]. Pretreatment by sand-blasting offered the significant improvement in water-repellency of the coated surface as expected, shown in Fig. 3. It is known that combining surfaces of low surface energy with appropriate surface roughness realizes high contact angles [14]. Surface roughening by sand-blasting was found effective for bipolar plate metals. On the other hand, plasma-etching pretreatment by oxygen plasma in the same reactor (at 100 W and 6.7 Pa for 10 min) had almost no effect, showing almost the same contact angle as the one without pretreatment.

Fig. 5(a and b) are photographs of cross-sectional view of gas flow channel hollowed from the cell without and with plasma polymerization after sand-blast pretreatment. The change of water drops in gas flow channels resulted from

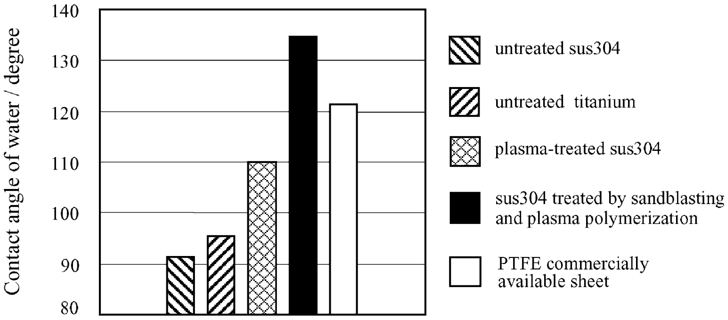

Fig. 3. Effects of pretreatment by plasma, sand-blasting, and plasma polymerization of HFP on the water-contact angle of metal plate.

this process are seen in this figure. It is clear from these figures that the gas flow channel treated by this process has high water-contact angle and prevents the attachment of water droplets. On the other hand, the gas flow channel without plasma polymerization has low contact angle and got wet easily.

Fig. 6 illustrates a comparison of the performance of the cell with untreated and treated gas channel in the condition of oxygen flow rate of 50 cc min^{-1}. The cell performances of the two cells are about equal in the low and middle current density region. There are differences on cell voltage and power density under high current density region where the effect of diffusion limit of oxygen (concentration overvoltage) appears [1,15]. The difference began to appear clearly in the current region where oxygen utilization was over about 40%. Although cell internal resistance increased as the current drawn from the fuel cell, the differences were not seen between these two cells as shown in Fig. 7. From these facts, the difference of cell performance can be attributed to the concentration overvoltage at electrode. Rapid voltage decay suggests a ‘flooding’ condition, which may result from water trapping in gas channel or gas diffusion pore in the electrode. A blocking of gas channel by water droplet causes a blocking of gas diffusion pore in the electrode by accumulated water secondarily. As a result, the maximum power of fuel cell was improved from 0.37 to 0.41 W cm^{-2} by this water-repelling treatment in such condition where the condensed product water tended to accumulate water drops in gas flow channels. A water droplet in the gas flow channels treated by this water-proofing process can be swept away more easily by gas stream than that without the treatment because of low wettability of water-proofed gas flow channels. Fig. 8 shows the comparison in the condition of oxygen flow rate of 100 cc min^{-1}. It can be seen that the effect of water-proofing decreased in this condition. The oxygen utilization is below 40% all over the current density region shown in this figure. This fact indicates that a water droplet in the gas flow channels can be swept away more easily by gas stream in the high flow rate condition without water-proofing. In other words, the water-proofed cell can exhibits high performance even at low flow rate condition. This character is important for improvement of fuel cell system efficiency, because high flow rate results in low oxidant utilization and large power consumption for driving air compressor or blower to supply air to the fuel cell in case of using air as an oxidant [16]. In the practical fuel cell stack with large electrode area, blocking of gas flow channel by condensed liquid water tends to occur and results in serious degradation as electrode area, reactant utilization and hu-

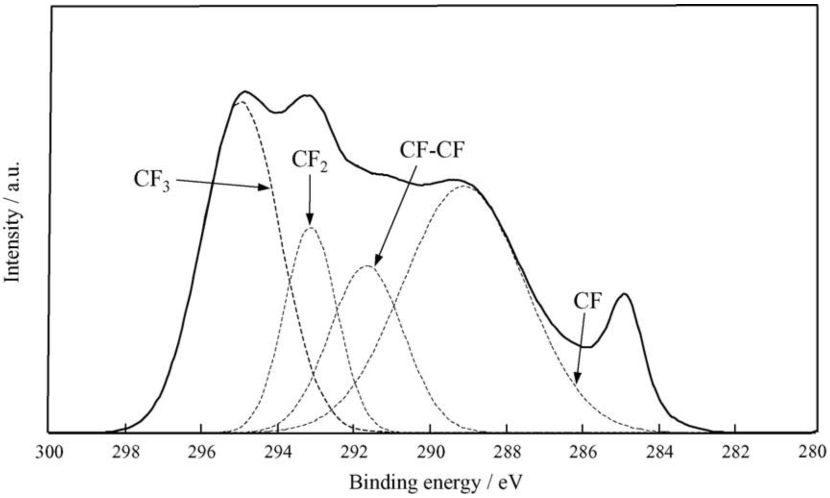

Fig. 4. A XPS C 1s spectrum of the deposited plasma-polymerized hexafluoropropylene.

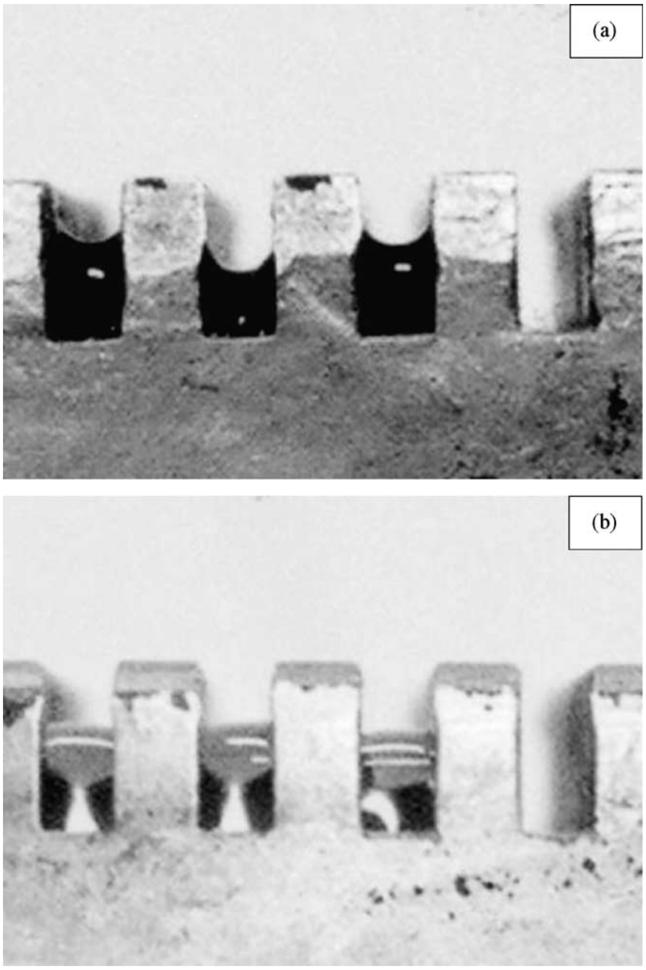

Fig. 5. Photographs of water drops in gas flow channels of PEMFC: (a) without and (b) with sand blasting followed by plasma polymerization.

midifying temperature increases. This process is potentially applicable for overcoming such water management problems in PEMFCs. As long as the authors know, this is the first paper showing the effects of water-repelling coating of the gas flow channels of PEMFC and the application of plasma polymerization for this purpose. Thinner surface treatment is our next stage for this process without using masking tape for avoiding increase of electrically contact resistance.

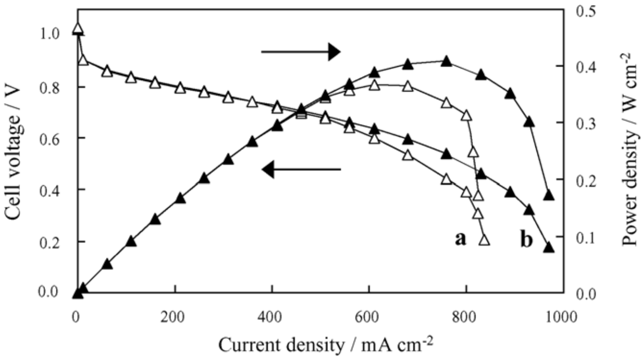

Fig. 6. Current–voltage and current–power density performance of PEMFC with (a) untreated and (b) plasma-treated gas channel at the oxygen flow rate of 50 cc min^{-1}.

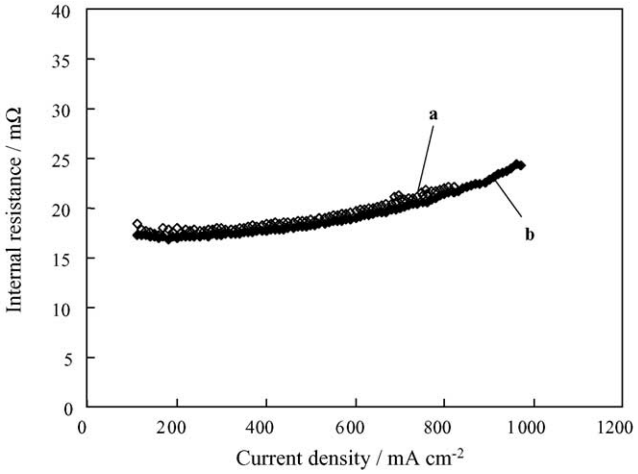

Fig. 7. Cell internal resistance of PEMFC with (a) untreated and (b) plasma-treated gas channel at the oxygen flow rate of 50 cc min^{-1}.

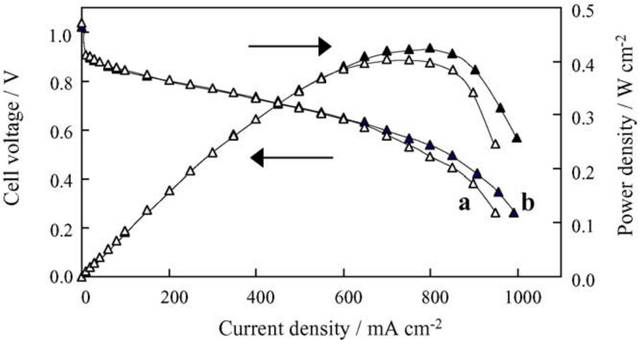

Fig. 8. Current–voltage and current–power density performance of PEMFC with (a) untreated and (b) plasma-treated gas channel at the oxygen flow rate of 100 cc min^{-1}.

4. Conclusion

Gas flow channels of PEMFC were water-proofed by plasma polymerization. Water-contact angle of the substrate surface treated by the combined process of plasma polymerization and sand-blast pretreatment was increased in comparison with that treated by plasma polymerization without sand-blast pretreatment. There seemed the improvement of peak power in the PEMFC with gas flow channels, which were surface treated by sand-blast pretreatment and the following plasma polymerization. The water-proofing was effective in the condition of lower oxidant flow rate.

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References

[1] R.A. Lemons, J. Power Sources 29 (1990) 251.

[2] P. Costamagna, S. Srinivasan, J. Power Sources 102 (2001) 253.

[3] F. Preli, Fuel Cells 2 (2002) 5.

[4] C.K. Dyer, J. Power Sources 106 (2002) 31.

[5] H.L. Maynard, J.P. Meyers, J. Vac. Sci. Tech. B 20 (2002) 1287.

[6] S.J. Lee, A. Chang-Chien, S.W. Cha, R. O’Hayre, Y.I. Park, Y. Saito, F.B. Prinz, J. Power Sources 112 (2002) 410.

[7] R.L. Borup, N.E. Vanderborgh, Mater. Res. Soc. Symp. Proc. 393 (1995) 151.

[8] H. Wang, M.A. Sweikart, J.A. Turner, J. Power Sources 115 (2003) 243.

[9] H. Yasuda, Plasma Polymerization, Academic Press, New York, 1985.

[10] G.H. Yang, Y. Zang, E.T. Kang, K.G. Neoh, A.C.H. Huan, D.M.Y. Lai, J. Mater. Chem. 12 (2002) 426.

[11] K. Yasuda, Y. Uchimoto, Z. Ogumi, Z-i. Takehara, J. Electrochem. Soc. 141 (1994) 2350.

[12] T. Ioroi, N. Kitazawa, K. Yasuda, Y. Yamamoto, H. Takenaka, J. Electrochem. Soc. 147 (2000) 2018.

[13] T. Ioroi, K. Yasuda, Z. Siroma, N. Fujiwara, Y. Miyazaki, J. Power Sources 112 (2002) 583.

[14] A. Nakajima, K. Hashimoto, T. Watanabe, Monatshefte fur Chemie. 132 (2001) 31.

[15] D.M. Bernardi, M.W. Verbrugge, J. Electrochem. Soc. 139 (1992) 2477.

[16] C.E. Borroni-Bird, J. Power Sources 61 (1996) 33.