Effect of PFSA Polymer Content in Catalyst Layer on PEFC Performance under Several Humidity Conditions

Katsuhiro UNO^{a,*}, Mika EGUCHI^b, Taku SUZUKI^b and Yasuyuki TSUTSUMI^c

^aGraduate school of Science and Engineering, Ibaraki University(4-12-1, Nakanarusawa, Hitachi, Ibaraki 316-8511)

^bFaculty of Engineering, Ibaraki University(4-12-1, Nakanarusawa, Hitachi, Ibaraki 316-8511)

^cFC Development CO.,Ltd.(4-12-1, Nakanarusawa, Hitachi, Ibaraki 316-8511)

The effects on cell performance of Nafion[®] content in 1 mg/cm² Pt with a Pt and carbon mixture containing 50 wt.% Pt (50 wt.%Pt/C-1 mgPt/cm²) catalyst layers were studied under several humidified operating conditions at 80 °C and 1 atm. The optimum Nafion[®] content for these conditions was 28–32 wt.% (0.76–0.95 mg/cm²). The value obtained using the 50 wt.%Pt/C catalyst was compared with reported values obtained using 20 wt.%Pt/C or 20 wt.%PtCr/C catalyst. The catalyst layer's activation polarization with insufficient Nafion[®] decreases concomitantly with increased humidity, but that of a layer with excessive Nafion[®] increases with increased humidity.

Keywords : Fuel Cell, PEFC, PFSA, Catalyst Layer, Humidity

1. Introduction

The PFSA(perfluorosulfonic acid)polymer content in the catalyst layer is an important parameter for obtaining a high performance PEFC(polymer electrolyte fuel cell). Nafion[®] is a typical PFSA polymer. Several researchers have investigated it under various test conditions. P. Staiti et al.¹⁾ used 20 wt.%Pt/C-0.5 mgPt/cm² catalyst layers. Their catalyst layers are composed of catalyst particles bonded with PTFE and impregnated with Nafion[®] dispersed liquid. The 20 wt.%Pt/C means a carbon supported Pt catalyst having Pt of 20 wt.% and carbon of 80 wt.%. The 0.5 mgPt/cm² means loaded Pt weight of 0.5 mg per electrode area of 1 cm². Their optimum Nafion[®] content was 47 wt.% at 200 mA/cm². J. Xie et al.²⁾ used 20 wt.%PtCr/C-0.2 mgPt/cm² catalyst layers manufactured by the Decal method³⁾, and their optimum Nafion[®] content was 28 wt.% at 1–1.5 A/cm², 80 °C, 2.04 atm, at dewpoints of 105 °C (H₂)/80 °C (air). Z. Qi et al.⁴⁾ used 20 wt.%Pt/C-0.12 mgPt/cm² catalyst layers applied onto the gas diffusion layer, and their optimum Nafion[®] content was 30 wt.% at 600 mA/cm², 35 °C, 1 atm, at dewpoints of 45 °C (H₂)/45 °C (air). A 50 wt.%Pt/C catalyst has recently been used instead of a 20 wt.%Pt/C catalyst. This paper reports the effects of the Nafion[®] content in 50 wt.%Pt/C-1 mgPt/cm² catalyst layers on the cell performance at 80 °C, 1 atm, under several humidified operating conditions.

The amount of an optimal ionomer changes depending on various factors like the structural materials of the catalyst layer, the ingredient ratio of them, and the operating conditions of the cell, etc. It is now difficult to discuss which factors influence determination of the optimal ionomer. Therefore, we cannot discuss the source of the difference but only explain the result under the certain circumstances. This paper discussed the influence of the Nafion[®] content in the catalyst layer of 50 wt.%Pt/C-1 mg/cm² into the cell performance under the conditions of 80 °C and 1 atm, and humidity as a parameter. These parameters were

selected after consideration of recent trends of the cell structural material and test methods. It has been reported that the surface area per 1 g of Pt decreases with an increase of Pt wt.% in the catalyst⁵⁾. However, the increment of Pt wt.% is preferable for PEFC under high current density and high power density operation, because the catalyst layer becomes thin so that the gas easily pass through the layer. As shown in previous report¹⁾, there were a few examples of experiments using 20 wt.%Pt/C catalyst layer in 1990s. The catalyst with 40–70 wt.%Pt/C was examined recently⁶⁾ and the 50 wt.%Pt/C catalyst has been widely used in the fuel cell application study by NEDO(New Energy and Industrial Technology Development Organization). However, this report may be the first report about an optimal ionomer content of 50 wt.%Pt/C catalyst.

2. Experimental

2. 1 Test specimens

The 50 wt.%Pt/C catalyst(N.E.CHEMCAT Corp., SA50BK)of 1 mgPt/cm² was used in both electrodes, which means that 2 mg/cm² of catalyst was used. Carbon particles of the catalyst include many pores having different pore diameter. The pore volume in the 1 g carbon particles within a range of pore diameter from 1 nm to 400 nm was 0.95 ml. A 5 wt.% Nafion[®] dispersed liquid (Aldrich Corp.) was used for the PFSA polymer solution. Nafion[®] 112(DuPont Corp.) was used for the electrolyte membrane. The 3-layer MEAs(membrane electrode assemblies) were manufactured using the Decal method. The catalyst ink for spray coating included the catalyst, Nafion[®] dispersed liquid and water, but did not include any other additives. **Fig. 1** is a SEM photograph of the catalyst layer, which shows a porous configuration made from catalyst particles coated by the PFSA polymer. The electrode area was 25 cm². Five kinds of catalyst layer were prepared for the tests. The Nafion[®] in the cathode catalyst layer was 0.76 mg/cm²(standard, corresponding to 28 wt.% of the catalyst layer), 0.38 mg/cm²(50% of the standard, 16 wt.% of the catalyst layer), 0.57 mg/cm²(75 % of the standard, 22 wt.% of the catalyst layer), 0.95 mg/cm²(125 % of the standard, 32 wt.% of the catalyst layer

* E-mail: k-uno@mx.ibaraki.ac.jp

), and 1.14 mg/cm^2 (150 % of the standard, 36 wt.% of the catalyst layer). The Nafion® in the anode catalyst layer was constant and was 0.76 mg/cm^2 (28 wt.% of the catalyst layer). The thickness of the catalyst layer was measured with a dial gauge (Mitutoyo Corp., ID-F125), while a surface pressure of 20 kPa was applied to a disc-like measuring terminal of 1 cm in diameter. The cathode gas diffusion layer was prepared by loading the MPL (micro porous layer) of 60 wt.% PTFE-bonded Vulcan XC-72R (Cabot Corp.) onto carbon paper (TORAY Co. Ltd., TGP-H-060). A gas diffusion layer without the MPL was used for the anode.

2. 2 Test conditions for the PEFC performance

The gas humidity has a great influence on the PEFC performance, because water promotes the proton conductivity of the electrolyte and hinders gas diffusion. The cell performance was measured at 80°C cell temperature, at 80°C of hydrogen gas humidifying temperature, and at 60°C , 70°C , and 80°C of air humidifying temperature. In order to prevent steam condensation, the temperature of the inlet gas supplying pipe lines was maintained at 110°C . The gas flow rate was constant while the cell performance was evaluated. The flow rate was adjusted to correspond to 70 % hydrogen utilization and 40 % air utilization at 500 mA/cm^2 .

3. Results and Discussion

3. 1 Effect of MPL (micro porous layer) on the cell performance

Before the tests for the catalyst layers, the effect of a MPL applied on the cathode gas diffusion layer on the cell performance was studied. Fig. 2 shows that a gas diffusion layer with 2 mgC/cm^2 MPL has a greater gas diffusion ability than that with 0 or 4 mgC/cm^2 , where the standard 3-layer MEAs (50 wt.%Pt/C, Nafion® content 28 wt.% for both electrodes) as described in 2.1 were used, but the catalyst loading of the cathode was 0.5 mgPt/cm^2 which was half that of the standard. In order to evaluate the gas diffusion ability of the gas diffusion layer, thin catalyst layers having a high gas diffusion ability were used. The test conditions for Fig. 2 were 80°C cell temperature, 80°C of H_2 humidifying temperature, 60°C of air humidifying temperature, and the flow rate was adjusted to correspond to 70 % hydrogen utilization and 40 % air utilization at 500 mA/cm^2 as described in 2.2. In the catalyst layer without MPL (0 mg/cm^2), the performance deterioration would come from defective gas diffusion with the stag-

nated water generated by cathode reaction. On the other hand, it was thought that the performance decreased due to decrease of gas diffusion caused by the thickness of the catalyst layer in thick MPL (4 mg/cm^2). Therefore, the gas diffusion layers with 2 mgC/cm^2 MPL were used here after, and the performance lower than ● in Fig. 2 was considered due to performance decay caused by the cathode catalyst layer and not performance decay caused by the gas diffusion layer.

3. 2 Thickness of the catalyst layer

Though the catalyst layer thickness has hardly been reported in other literature sources, it may be an important factor for optimum PFSA polymer content, because a bulky layer having a low volume ratio of the PFSA polymer has difficulty in providing ionic channels through the layer. Fig. 3 shows the measured thickness of the catalyst layer. It is seen that the catalyst layer thickness was hardly influenced by the amount of the PFSA polymer within the range of the measurements, though it increased in proportion to the Pt loading. This independency may be under-

Fig. 2 Effects of micro porous layer of cathode gas diffusion layer on cell performance. The 3-layer membrane electrode assembly was composed of two catalyst layers with 0.5 mgPt/cm^2 of 50 wt.%Pt/C and an electrolyte membrane of Nafion® 112. The cell was operated at 80°C cell temperature, and $80^\circ\text{C}/60^\circ\text{C}$ of H_2 /Air humidifying temperature, with 0.7/0.4 of fuel/air utilization at 500 mA/cm^2 .

Fig. 1 SEM photograph of catalyst layer composed of 1 mgPt/cm^2 of catalyst (50 wt.%Pt/C) and 0.76 mg/cm^2 of Nafion® content.

Fig. 3 Thickness of catalyst layer composed of 50 wt.%Pt/C and PFSA polymer. PFSA-1 (○) means the standard weight ratio of PFSA polymer to catalyst of 0.76/2 and 28 wt.% PFSA polymer content in the catalyst layer. PFSA-0.5 (●) and PFSA-1.5 (●) means the weight ratio of PFSA polymer to the catalyst of $0.76 \times 0.5/2$ and $0.76 \times 1.5/2$, respectively.

stood that the PFSA fills up the vacant spaces between carbon particles of Pt catalyst. The volume ratio of the PFSA polymer in the catalyst layer is calculated to be 13 vol.% for the standard PFSA polymer content of 0.76 mg/cm².

3. 3 Effect of air humidifying temperature on the cell performance and its dependency on the catalyst layer thickness

The cell performances at 60, 70 and 80 °C of air humidifying temperature are shown in Fig. 4 and Fig. 5. The catalyst loadings are 0.5 mg Pt/cm² in Fig. 4 and 1.0 mgPt/cm² in Fig. 5, which correspond to the thickness of the catalyst layer of about 15 μm and about 30 μm, respectively, as shown in Fig. 3. Both catalyst layers contained the standard Nafion® ratio, 0.76 mg/cm² per 1 mgPt/cm², which are denoted as "PFSA1.0" in the figures. The cell voltage at comparatively low current density up to 600 mA/cm² or 450 mA/cm² decreased with the decrease in air humidifying temperature as shown in Fig. 4 or Fig. 5. The decrease in humidity at low current density is considered to decrease the ionic conductivity of the PFSA polymer and decrease the cell voltage. However, the bending around 300–400 mA/cm² shown in the data of 60 °C in Fig. 4 and 5 is not observed in the data of Fig. 2 acquired with different equipment at different time. It suggests that this phenomenon does not appear reproducibly. On the

Fig. 4 Effects of humidifying temperature on cell performance. The cathode catalyst layer contained 0.5 mgPt/cm² of 50 wt.%Pt/C and 0.38 mg/cm² of Nafion® and its thickness was 15 μm.

Fig. 5 Effects of humidifying temperature on cell performance. The cathode catalyst layer contained 1.0 mgPt/cm² of 50 wt.%Pt/C and 0.76 mg/cm² of Nafion® and its thickness was 30 μm.

contrary, the voltage at high current density above 600 mA/cm² or 450 mA/cm² decreased with the increase in the air humidifying temperature as shown in Fig. 4 or Fig. 5. Because the amount of water production in the cathode catalyst layer increases with the increase in current density, a high air humidity in the cathode gas will fill the catalyst layer with water and inhibit gas diffusion. The cell voltage then drops more rapidly with an increase in gas humidity. The cell voltage of the 0.5 mgPt/cm² and 1.0 mgPt/cm² loaded cells drops rapidly from 650 mA/cm² and 500 mA/cm². Gas diffusion seems to be difficult with a thick catalyst layer.

3. 4 Performance of catalyst layer including insufficient Nafion®

Figure 6 and Fig. 7 show the performance of the cell using insufficient Nafion® (0.5 and 0.75 times of the standard, respectively) for the cathode catalyst layer, which are denoted as "PFSA0.5" and "PFSA0.75" in the figures. The cell voltage at low current density decreased with the decrease in Nafion® content. A cell voltage decrease of this type is regarded as an increase in activation polarization⁷⁾ and suggests a decrease in Pt utilization. Insufficient Nafion® is considered to cause an increase

Fig. 6 Performance of the cell using insufficient PFSA polymer (0.5 times) in the cathode catalyst layer operated at 80 °C of cell temperature, 80 °C/60 °C (△, ○), 80 °C/70 °C (●), or 80 °C/80 °C (●) of H₂/air humidifying temperature, with 0.7/0.4 of fuel/air utilization at 500 mA/cm². The PFSA polymer content was 16 wt.%.

Fig. 7 Performance of the cell using insufficient PFSA polymer (0.75 times) in the cathode catalyst layer operated at 80 °C cell temperature, 80 °C/60 °C (△, ○), 80 °C/70 °C (●), or 80 °C/80 °C (●) of H₂/air humidifying temperature, with 0.7/0.4 of fuel/air utilization at 500 mA/cm². The PFSA polymer content was 22 wt.%.

in ineffective platinum having no ionic contact with the membrane. The cell performance using insufficient Nafion® increased with increase in humidity.

3. 5 Performance of catalyst layer including excessive Nafion®

Figure 8 and Fig. 9 show the performances of the cells using excessive Nafion® (1.25 and 1.5 times of the standard, respectively) for the cathode catalyst layer, which are denoted as

Fig. 8 Performance of the cell using excessive PFSA polymer (1.25 times) in the cathode catalyst layer operated at 80 °C cell temperature, 80 °C/60 °C ($\triangle$, $\circ$), 80 °C/70 °C ($\bullet$), or 80 °C/80 °C ($\bullet$) of H₂/air humidifying temperature, with 0.7/0.4 of fuel/air utilization at 500 mA/cm². The PFSA polymer content was 32 wt.%.

Fig. 9 Performance of the cell using excessive PFSA polymer (1.5 times) in the cathode catalyst layer operated at 80 °C cell temperature, 80 °C/60 °C ($\triangle$, $\circ$), 80 °C/70 °C ($\bullet$), or 80 °C/80 °C ($\bullet$) of H₂/air humidifying temperature, with 0.7/0.4 of fuel/air utilization at 500 mA/cm². The PFSA polymer content was 36 wt.%.

“PFSA1.25” and “PFSA1.5” in the figures. A steep cell voltage decrease at high current density is observed in Fig. 9, which used 1.5 times excessive Nafion®, but the performance of the cell using 1.25 times excessive Nafion® was almost equal to that using the standard Nafion® content as shown in Fig. 8. The cell voltage decrease as shown in Fig. 9 is regarded as an increase in concentration polarization⁷⁾ and suggests a decrease in gas diffusion ability. In the catalyst layer of PSFA1.25, it is thought that the performance degradation was almost never observed because it has not arrived at defective gas diffusion yet. The excessive Nafion® is considered to prevent gas diffusion by filling the gas channels in the catalyst layer.

The concentration polarization of the catalyst layer including excessive Nafion® increased with the increase in humidity.

4. Conclusions

In the previous works, the researches about the Nafion® optimum amount in some different operating conditions were reported by using 20 wt.%Pt/C. However, the report about the optimal amount of Nafion® using 50 wt.%Pt/C, which was a recent main current have not been performed yet. Our research may be the first one that reported on the relation between Nafion® amount and the humidifying condition when 50 wt.%Pt/C was used. The optimum Nafion® content was 28 - 32 wt.%(0.76 mg/cm² - 0.95 mg/cm²) for these conditions. The value was almost equal to that reported by J. Xie et al.²⁾ and Z. Qi et al.⁴⁾ but lower than that reported by P. Staiti et al.¹⁾. Activation polarization of the catalyst layer including insufficient Nafion® decreases with the increase in humidity. On the other hand, the concentration polarization of the catalyst layer including excessive Nafion® increases with the increase in humidity.

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