

Controlling Factors in Durability Performance for PEFC with Ultra-Low Platinum Loading Carbon Powder

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Abstract

For improvement of durability, the controlling factors of PEFC performance was investigated with ultra-low platinum loading carbon powder (ULPLC[®]). The ULPLC tested was composed of platinum particles, carbon powder, ionomer, and tetrafluoroethylene-hexafluoropropylene copolymer (FEP) as hydrophobic resin and it was aimed to apply as cathode catalyst layer. The ULPLC powder gave almost the same durability performance and V-I characteristic for the PEFC using only the one third or less of the platinum loading level comparing to the existing Pt/C catalyst. The performance was also found out to be independent of additional porosity of the cathode catalyst layer by pore-formation process which seems to be caused by the high water repellency of FEP in the powder. Moreover, the voltage decay rate observed at the first 300 hours operation was remarkably lower than that of existing Pt/C at the same condition of platinum loading level. This is considered to be derived from its larger active surface area of platinum resulting in the decrease of current density on the reaction site leading to suppression of flooding phenomenon.

Key words: ULPLC[®]; FEP; Voltage decay rate; Platinum loading level

1 Introduction

Polymer electrolyte fuel cells (PEFC) have recently drawn much attention as a promising candidate for clean power source for both stationary and mobile applications. However, two technical issues of further cost reduction and durability improvement still remain for its commercial success. We have recently developed ULPLC[®] composed of platinum particles, carbon powder, ionomer, and hydrophobic resin.¹⁾ The utilization of platinum in ULPLC[®] is very high, and the aggregation of platinum catalyst during

continuous operation of the PEFC is drastically suppressed²⁾ resulting in the solution of above mentioned technical issues, since the platinum particle is selectively loaded on the interface between hydrophilic cluster of ionomer and carbon powder by the special process of ion-exchange reaction of platinum ion and the counter ion of ionomer existing on the surface of carbon followed by chemical reduction of its platinum ion under hydrogen gas atmosphere.³⁾ Therefore, the investigation on controlling factors in performance of new PEFC using ULPLC[®] with hydrophobic property is strongly requested for its practical application especially to cathode catalyst layer for the further improvement of durability performance of PEFC.

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This paper describes the key factors of porosity and platinum loading level of cathode catalyst layer on basic characteristics and durability performance for this type PEFC focusing on the difference from the existing one.

2 Experimental

2.1 ULPLC[®]

ULPLC[®] was prepared by following procedure: preparation process of slurry by mixing carbon powder (Cabot, Vulcan XC-72R), ionomer solution, and dispersion of FEP (Dupont-Mitsui Fluorochemicals, FEP 120-J) as a hydrophobic agent; granulation process of mixed powder using spray drying of the slurry; adsorption process of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ in the cluster of ionomer on the powder by ion-exchange reaction of proton for its ion by immersing the powder into $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution at 80 °C for 6 h; and reduction process of the adsorbed $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ion under hydrogen atmosphere at 150 °C for 6 h. The content of FEP was 50 mass% to the total of FFP and carbon.

2.2 Cathode catalyst layer

The cathode catalyst layer with 25 cm² was prepared by applying the mixture composed of the ULPLC[®] and N-methyl-2-pyrrolidone (NMP) onto a polymer film and dried at 80 °C for 30 min. In order to evaluate the effect of porosity of the layer on PEFC performance, catalyst layer was pore-formed by adding pore-forming agent of CaCO₃ into the mixture. The performance using ULPLC[®] was compared with the case of commercially available platinum loaded carbon (Pt/C, Pt: 50 mass%). The latter catalyst layer was prepared by applying the mixture of the Pt/C, ionomer solution, FEP dispersion, CaCO₃, and N, N-dimethylformamide (DMF). The surfactant in FEP dispersion was removed by drying the layer at 150 °C for 30 min. under reduced pressure.

2.3 Anode catalyst layer

The anode catalyst layer with 25 cm² was prepared by applying the mixture of the platinum-ruthenium loaded carbon (Pt: 29.7 mass%, Ru: 23.7 mass%), ionomer solution, FEP dispersion, CaCO₃ as pore-forming agent, DMF, and 2-propanol onto a substrate and then dried at 80 °C for 30 min. The surfactant in

FEP dispersion was removed by drying the layer at 150 °C for 30 min. under the reduced pressure. The content of FEP is 30 mass% to the total of FFP and carbon.

2.4 Single test cell

The cathode and anode catalyst layers were hot-pressed onto both sides of polymer electrolyte membrane at 150 °C for 5 min. The assembly was rinsed first by 0.5 mol l⁻¹ HNO₃ to remove CaCO₃, then 0.5 mol l⁻¹ H₂SO₄ at 80 °C for 30 min., and finally deionized water at 80 °C for 30 min. The single test cell was composed of the following serial constitution: anode gas flow plate / gas diffusion layer (GDL) / the assembly / GDL / cathode gas flow plate, where the GDL was composed of macro and micro porous carbon layers.

2.5 Performance evaluation procedure for single test cell

2.5.1 V-I characteristic

The cell voltage as a function of current density was measured under the condition: cell temperature of 70 °C; fully humidified reactant gases of air and pure H₂; and the corresponding stoichiometry number of 2.5 and 1.25, respectively.

2.5.2 Continuous operation test

The durability performance of single test cells was evaluated by the continuous operation test of 300 mA cm⁻² under the same condition described in section 2.5.1. The voltage decay rate was calculated from the change in operation voltage for the first 300 hours.

3 Results and discussion

The value of porosity for the cathode catalyst layer with ULPLC[®] or Pt/C using pore-formation is listed in Table 1. The V-I characteristics for PEFC single test cells with the layer are shown in Fig. 1. The characteristics for PEFC with ULPLC[®] is found

Table 1 Porosity of cathode catalyst layer.

Catalyst	Pore-formation process for cathode catalyst	Porosity / %
ULPLC	Without	54
ULPLC	With	78
Pt/C	With	78

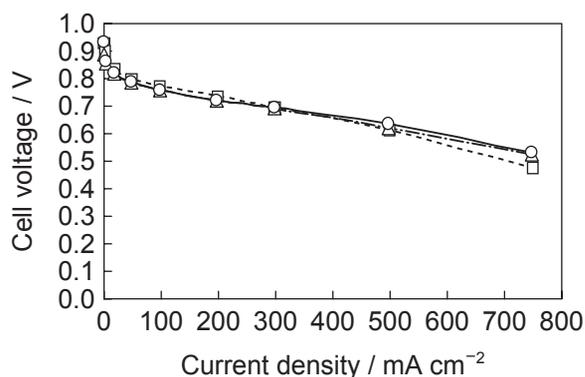


Fig. 1 V-I characteristics for PEFC with ULPLC[®] (○), using additional cathode catalyst layer pore-formation process (△), and existing Pt/C using the process (□) under the condition of cell temperature of 70 °C, fully humidified reactant gases of H₂ / air, and the corresponding stoichiometry number of 1.25 and 2.5, respectively.

Pt loading level: ○ 0.10 mg cm⁻²; △ 0.10 mg cm⁻²;
□ 0.30 mg cm⁻².

Porosity: ○ 54%, △ 78%, □ 78%.

out to be almost same as the case of Pt/C with 3 times loading level of platinum. This shows that the utilization of platinum for this powder is much higher than that of Pt/C. Furthermore, the characteristics are almost same level with or without pore-formation in the case of ULPLC[®]. The previous paper reported that the mass activity of platinum in ULPLC[®] not containing FEP remarkably declined with the decrease of the porosity of the catalyst layer according to the appearance of flooding phenomenon caused by special location of platinum particles loaded on carbon in contact with cluster of ionomer.⁴⁾ This means that the hydrophobic ULPLC[®] containing FEP keeps high mass activity of its platinum even under the low porosity, namely without pore-formation process of the catalyst layer.

The change in cell voltages at 300 mA cm⁻² obtained from the V-I characteristics as a function of the loading level is shown in Fig. 2. Cell voltages for ULPLC[®] with and without pore-formation are found out to be almost same at the range of 0.06 to 0.20 mg cm⁻² of the platinum loading level. Moreover, each cell voltage is also found out to increase with the platinum loading level and reach to a constant value above 0.12 mg cm⁻² for ULPLC[®] and 0.32 mg cm⁻² for Pt/C, respectively. In order to examine this

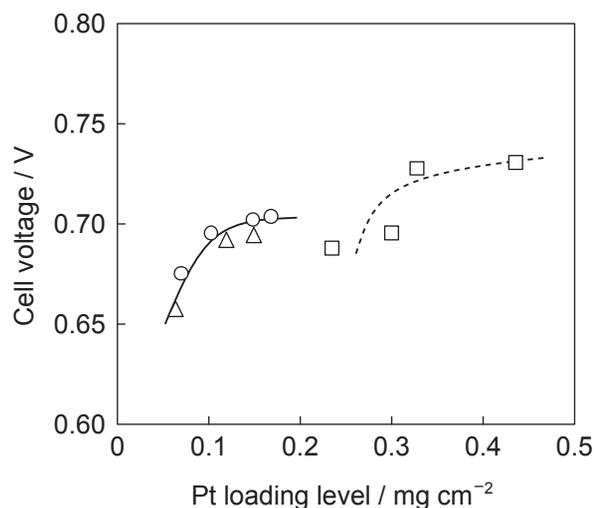


Fig. 2 Effect of Pt loading level on cell voltage at 300 mA cm⁻² for PEFC with ULPLC[®] (○), using additional cathode catalyst layer pore-formation process (△), and existing Pt/C using the pore-formation process (□) under the condition of cell temperature of 70 °C, fully humidified reactant gases of H₂ / air, and the corresponding stoichiometry number of 1.25 and 2.5, respectively.

phenomenon in detail, the value of O₂ gain concerned with gas diffusibility of electrode is shown as a function of the platinum loading level in Fig. 3. The value has a minimum at around 0.12 mg cm⁻² and 0.32 mg cm⁻² for ULPLC[®] and Pt/C, respectively and tend to increase beyond the point. Each point coincides with the loading level at which the cell voltage reaches to the constant value. The phenomenon is considered to be derived from the fact that the thickness of catalyst layer increased with the platinum loading level resulting in the decrease of the diffusibility of O₂ in cathode catalyst layer. The typical durability performance of ULPLC[®] with hydrophobic property is shown in Fig. 4. The operation cell voltage is found to be stable beyond 300 hours, and the average voltage decay rate was 5 μV h⁻¹ during total 5000 hours. The decay rate of the first 300 hours period is shown in Fig. 5 as a function of the platinum loading level. The decay rate of ULPLC[®] is found to be almost same regardless of the pore-formation process of catalyst layer. This is attributed to the high hydrophobic property of FEP resulting in the suppression of the flooding phenomenon in the cathode catalyst layer. The decay rate is also found to be remarkably

lower than that of existing Pt/C at the same condition of platinum loading level. Further, the decay rate turns out to decrease with the platinum loading level for both cases of ULPLC[®] and Pt/C. The first decay rate for the single cell with 0.1 mg cm⁻¹ platinum loading level in cathode is plotted in Fig. 6 as a function of current density. The decay rate is found

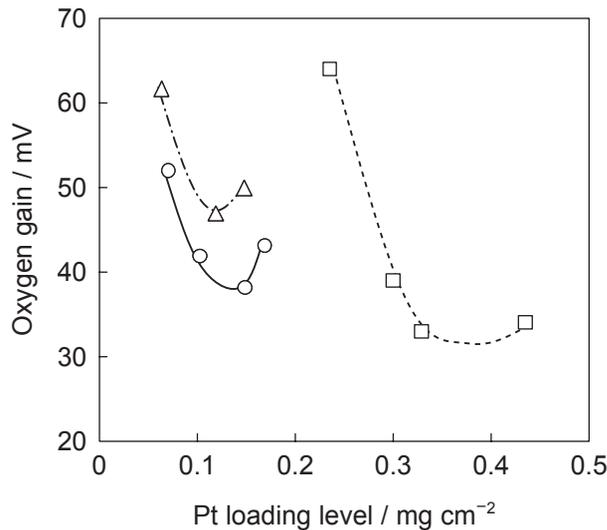


Fig. 3 Effect of Pt loading level on oxygen gain at 300 mA cm⁻² for PEFC with ULPLC[®] (○), using additional cathode catalyst layer pore-formation process (△), and existing Pt/C using the pore-formation process (□) under the condition of cell temperature of 70 °C, fully humidified reactant gases of H₂ / O₂ and H₂ / air, and the corresponding stoichiometry number of 1.25 and 2.5, respectively.

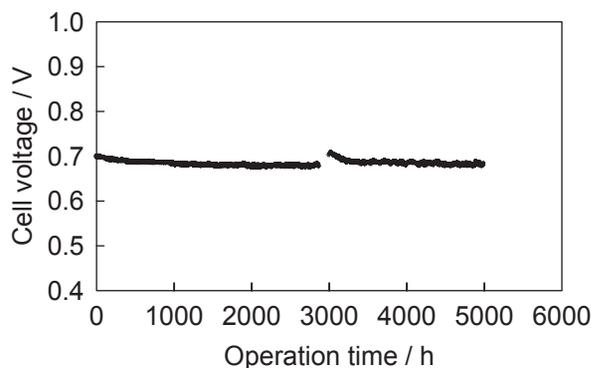


Fig. 4 Durability performance for PEFC with ULPLC[®] at 300 mA cm⁻² under the condition of cell temperature of 70 °C, fully humidified reactant gases of H₂ / air, and the corresponding stoichiometry number of 1.25 and 2.5, respectively. Pt loading level : 0.17 mg cm⁻².

out to increase significantly with the increase of the current density. This means in other words that the flooding phenomenon is suppressed by the decrease of current density. Both the lower decay rate of UL-

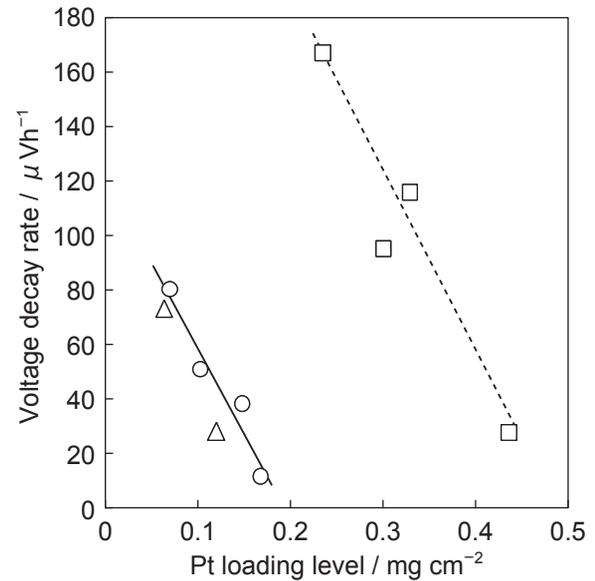


Fig. 5 Effect of Pt loading level on the first 300 hour decay rate of cell voltage at 300 mA cm⁻² for PEFC with ULPLC[®] (○), using additional cathode catalyst layer pore-formation process (△), and existing Pt/C using the pore-formation process (□) under the condition of cell temperature of 70 °C, fully humidified reactant gases of H₂ / air, and the corresponding stoichiometry number of 1.25 and 2.5, respectively.

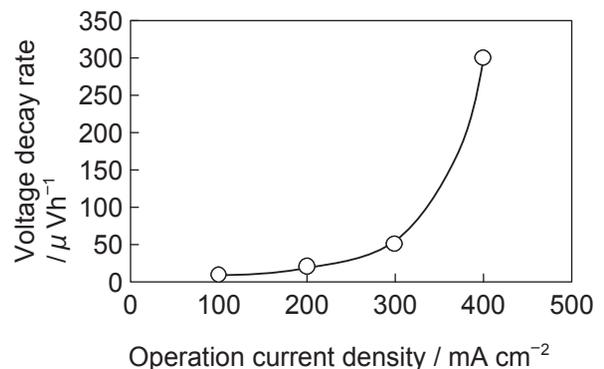


Fig. 6 Voltage decay rate during the first 300 hours continuous operation as a function of current density for PEFC with ULPLC[®] not using pore-formation process of cathode catalyst layer under the condition of cell temperature of 70 °C, humidified reactant gases of H₂ / air, and the corresponding stoichiometry number of 1.25 and 2.5, respectively.

PLC[®] and the drastic decrease of its rate with platinum loading level are considered to be derived from the fact that the active surface area of platinum of ULPLC[®] is so much larger that the increase of the area with platinum loading level effectively contributes to decrease the current density on the reaction site resulting in the suppression of the flooding phenomenon.

4 Conclusions

The results of this paper are summarized as described below.

- (1) The values of cell voltage and its decay rate were found out to be independent of additional porosity of catalyst layer by pore-formation process for hydrophobic ULPLC[®].
- (2) V-I characteristic and durability performance for PEFC with the ULPLC[®] were improved with the increase in platinum loading of which level was one third or lower than that of existing catalyst of Pt/C.

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