

Development of Highly Durable Electrode for PEFC Using Ultra-Low Platinum Loading Carbon Powder

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Abstract

Highly durable electrode for PEFC has been developed using ultra-low platinum loading carbon powder (ULPLC®). The ULPLC® technology enables the loading level of platinum catalyst outstandingly to decrease, because the catalyst particle is located on the reactive site selectively where the carbon surface contacts the cluster of ionomer. The addition effect of tetrafluoroethylene-hexafluoropropylene copolymer (FEP) as a hydrophobic agent for the ULPLC® has been investigated to improve the durability by the suppression of flooding phenomenon. The cell voltage deterioration during continuous operation test of PEFC was found out to be strongly dependent on the content of FEP. The highest performance was obtained at 50 mass% of its content. The appearance of optimum content seems to be the feature of electrode having both appropriate hydrophobicity and high electronic conductivity maintained judging from the fact that the voltage deterioration was increased with increasing cell internal resistance beyond its content.

Key words: ULPLC; Durability performance; Hydrophobic agent; Flooding phenomenon

1 Introduction

A polymer electrolyte fuel cell (PEFC) is most promising candidate for the next generation of power sources. However, there are mainly two technical issues for its commercialization; high cost and low durability performance. For the cost reduction, ultra-low platinum loading electrode (ULPLE®) has been developed based on a new concept¹⁾ to decrease loading level of platinum catalyst. The electrode is able to be produced by using the ultra-low platinum loading carbon powder (ULPLC®). The powder is prepared by the special process of ion

exchange reaction of platinum ion and the counter ion of ionomer covering on carbon powder followed by chemical reduction of platinum ion in hydrogen. Consequently, the platinum particle is located on the reactive site selectively where the carbon surface contacts the cluster of ionomer. Therefore, ULPLE® shows high utilization of catalyst and little deterioration phenomenon losing the active surface area of platinum particles during operation time.

However, previous research on the ULPLE® has demonstrated that the performance of this electrode was affected by flooding phenomenon more sensitively compared with the conventional electrode using platinum loaded carbon, since the platinum particle was totally covered with the cluster of ionomer due

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to the special loading process.²⁾ Therefore, it is very important to suppress the occurrence of flooding for the improvement of the durability performance of this type electrode.

In this paper, we report the durability performance for the electrode for PEFC using ULPLC[®] with tetrafluoroethylene-hexafluoropropylene copolymer (FEP) as hydrophobic agent for the suppression of occurrence of flooding phenomenon.

2 Experimental

2.1 ULPLC[®]

ULPLC[®] with different FEP content were prepared by following processes: the preparation process of slurry by mixing carbon powder (Cabot, Vulcan[®] XC-72), ionomer solution (DuPont, 5 mass% solution of Nafion[®]), and dispersion of FEP as a hydrophobic agent (DuPont-Mitsui Fluorochemicals, FEP 120-J); granulation process of mixed powder using spray drying of the slurry; adsorption process of [Pt(NH₃)₄]²⁺ in the cluster of ionomer of the powder by ionexchange reaction of proton for its ion by immersing the powder into [Pt(NH₃)₄]Cl₂ solution at 80 °C for 6 h; and reduction process of the adsorbed [Pt(NH₃)₄]²⁺ ion by heating the powder in the hydrogen atmosphere at 150 °C for 6 h. In order to evaluate the effect of FEP content on the durability performance, FEP content was varied from 0 mass% to 70 mass%.

2.2 Single cell

The catalyst layer with 25 cm² was prepared by applying the mixture composed of the ULPLC[®] and NMP onto a titanium sheet. The catalyst layers were hot-pressed onto both sides of the polymer electrolyte membrane as reported in the literature.³⁾ The assembly was rinsed in 0.5 mol l⁻¹ H₂SO₄ and deionized water at 80 °C. Carbon felts were also attached on the layers to form MEA. The carbon felt as gas diffusion layer was treated with PTFE dispersion solution followed by heating at 380 °C for 15 min in the nitrogen atmosphere for hydrophobic property. The platinum loading level of cathode was 0.06 mg cm⁻². The single cell of PEFC was composed of the following serial constitution: Anode gas flow plate / MEA / cathode gas flow plate.

2.3 Continuous operation test

The single cell was operated at 300 mA cm⁻² for 300 hours. The cathode and anode were fed with air and pure hydrogen at a flow rate of 339 ml min⁻¹ (stoichiometry : 2.50) and 71.3 ml min⁻¹ (stoichiometry : 1.25), respectively. Both air and hydrogen were humidified at the temperature of 70 °C. The cell temperature was set at 70 °C. The decay rate of cell voltage was calculated from the value of change in cell operation voltage.

3 Results and discussion

3.1 Structure of ULPLC[®]

The TEM image of the cross section of ULPLC[®] containing 50 mass% FEP is shown in Fig. 1. The diameter of particle is 1.0–1.5 μm. FEP particles observed as white area are located uniformly inside of the ULPLC[®]. This means that FEP provides high hydrophobic property for not only outside but also inside of ULPLC[®] where many reactive sites exist. The Effect of FEP content on porosity of ULPLC[®] was also investigated by mercury porosimetry measurements. Volume pore size distribution curves of ULPLC[®] with various FEP contents are shown in Fig. 2. It is found out that the pores in the range of 150 – 300 nm observed at the case of free FEP dis-

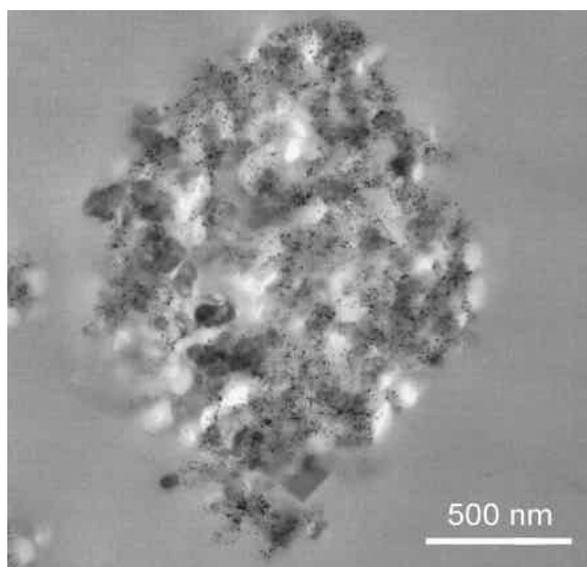


Fig. 1 TEM image of the cross section for ULPLC[®] containing 50 mass% FEP.

appear with increasing FEP content up to 50 mass%. Considering the value of ca. 150 nm for average particle diameter of FEP, this disappearance is thought to be a result of FEP located in the pores. In other words, the added FEP is located inside of the particle of ULPLC[®]. On the other hand, no change in volume pore size distributions is observed with increasing FEP content from 50 to 60 mass%. Therefore, the excessively added FEP mainly exists outside of the particle.

3.2 Effect of FEP content on durability performance

The effect of FEP content on the decay rate of cell operation voltage is shown in Fig. 3. The decay rate decreases with increasing FEP content up to 50 mass% and then increases rapidly. This means that the electrode using ULPLC with 50 mass% of FEP shows the highest durability performance. The improvement of durability performance is considered to be due to suppression of flooding phenomenon by increasing the hydrophobicity of electrode.

The effect of FEP content on cell voltage of PEFC with the ULPLC[®] at 300 mA cm⁻² before continuous operation test is shown in Fig. 4. The cell voltage is almost constant until 50 mass% FEP content and then declines. Furthermore, the internal resistance of the PEFC as shown in Fig. 5 is also kept at the constant value up to same FEP content and then tends to rise. These facts mean that the decline of cell voltage is thought to be due to decrease in electronic conductivity of the electrode by excessive addition of FEP of insulator. The electrode having low electronic conductivity is lead to current convergence at the reaction site. Therefore, the decrease in electronic conductivity means to accelerate the occurrence of flooding phenomenon. The minimum value of decay rate at 50 mass% FEP content associated with the highest durability performance is thought to be due to the competitive appearance between increase in hydrophobicity and decrease in electronic conductivity of the electrode. In other words, the suppression of flooding phenomenon seems to be derived from the property of electrode having both appropriate hydrophobicity and high electronic conductivity.

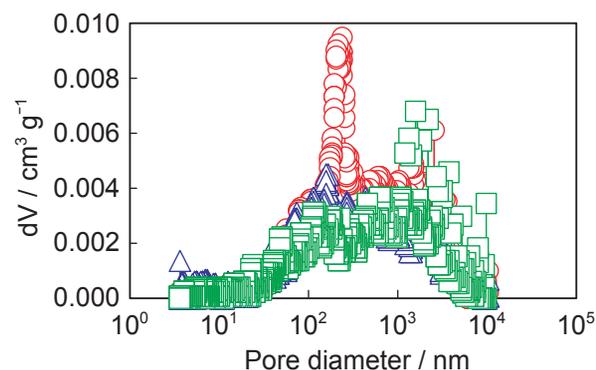


Fig. 2 Volume pore size distribution curves of UL-PLC[®] with FEP content of 0 mass% (○), 50 mass% (△), and 60 mass% (□).

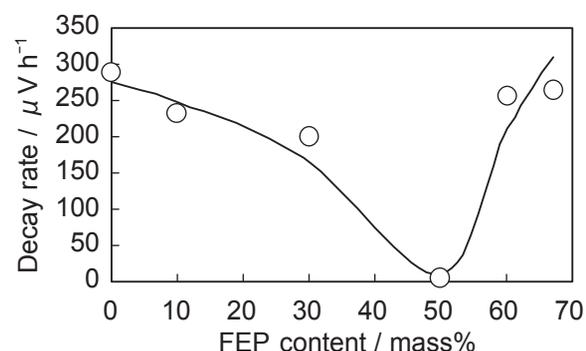


Fig. 3 Effect of FEP content on decay rate of cell voltage of PEFC with ULPLC[®] during continuous operation test at 300 mA cm⁻² for 300 hours at cell temperature of 70 °C under the condition of H₂ / air feedings with full humidification. Pt loading level : 0.06 mg cm⁻².

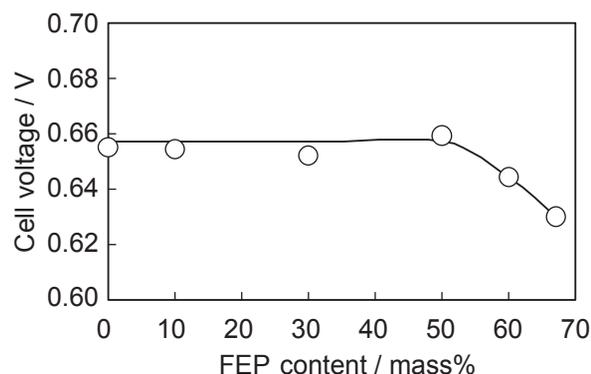


Fig. 4 Effect of FEP content on cell voltage at 300 mA cm⁻² of PEFC with ULPLC[®] before continuous operation test at cell temperature of 70 °C under the condition of H₂ / air feedings with full humidification. Pt loading level : 0.06 mg cm⁻².

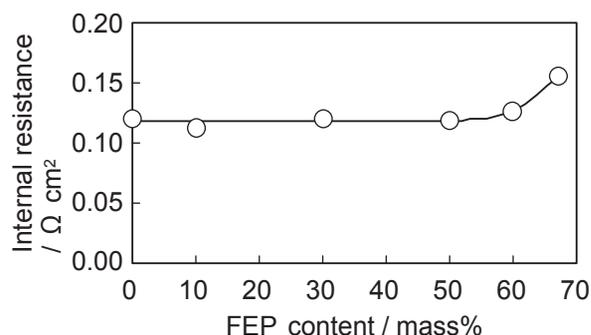


Fig. 5 Effect of FEP content on internal resistance of PEFC with ULPLC[®] before continuous operation test at cell temperature of 70 °C under the condition of H₂ / air feedings with full humidification. Pt loading level: 0.06 mg cm⁻².

4 Conclusions

Highly durable electrode for PEFC has been developed using ULPLC[®] with hydrophobic agent of FEP. The FEP particles with average diameter of 150 nm were found to be located uniformly inside of ULPLC[®] particle from both observation of cross section by TEM and analysis of pore-size distribution by mer-

cury porosimetry measurements. The minimum value of decay rate for operation voltage of PEFC was observed at 50 mass% FEP content. The improvement of durability performance is considered to be due to suppression of flooding phenomenon by the property of electrode having both appropriate hydrophobicity and high electronic conductivity.

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