

Ultra-Low Platinum Loading Electrodes for PEFC with High Durability Performance

Mariko Kohmoto* Kazuhide Totsuka* Shuji Hitomi*
Hideo Yasuda* Masanori Yamachi**

Abstract

The ultra-low platinum loading electrode (ULPLE) for PEFC has been found out to show high durability performance to be almost free from the essential failure mechanism losing the active surface area of platinum particle judging from the fact that the value of retention of the active surface area was 90.1% and 115% for cathode and anode respectively after 600 hours operation period at the condition of H₂/Air system at 80 °C and 200 mA cm⁻², whereas the value of that was observed 66% and 80% for the conventional electrodes, respectively. This high durability performance of ULPLE derived from the special structure that minimum loading level of platinum catalyst exist only for its active site where the surface of carbon particle contacts the proton-conductive passage of polymer electrolyte. This stability of platinum particles was also confirmed by the change in the active surface area measured by the repetitious potential-sweep method covering region of potential for dissolution-precipitation phenomenon of platinum, and its crystal structure change was recognized by cyclic voltammograms.

1 Introduction

A polymer electrolyte fuel cell (PEFC) is expected as a clean power source for automobiles as well as stationary applications because of its operation at moderate temperature below 100 °C in contrast with other types of fuel cells. There are two essential problems to be overcome for its commercialization. One is high cost and the other is low durability performance. These problems are strongly concerned with the usage of large amount of precious metal of platinum as catalyst particles

for electrodes of fuel cells. The catalyst particles tend to be aggregated and to lose its active surface area resulting in the decrease of cell performance during the continuous operation as the similar case of phosphoric acid fuel cell (PAFC).¹⁾ Therefore, the reduction of loading level of platinum catalyst particles with its high durability has been required for a long time. A lot of efforts have been made for the minimum loading level of platinum by the development of well-dispersed very small size particles with high utilization. The achieved level is not only still remained around 0.1 mg cm⁻², but also the use of small particle with nano-level diameter is obliged to accelerate the aggregation phenomenon by so called "dissolution-precipitation mechanism or sin-

*Department-E, Corporate R & D Center

**Corporate R & D Center

tering phenomenon", resulting in the low durability performance. We proposed the concept of ultra-low platinum loading electrode (ULPLE) of which platinum catalyst particle is loaded only on the active site where the surface of carbon particle contacts the proton-conductive passage of polymer electrolyte,²⁾ though the existing catalyst is further loaded on the carbon powder covered by the insulator material of rigid hydrophobic backbones of polymer electrolyte. The loading of platinum catalyst for this electrode was to be 0.01 – 0.05 mg cm⁻² without the decrease in the cell performance.

In this paper, we will focus on the other aspect of durability performance for ULPLE by the direct evaluation of change in the active surface area of platinum catalyst with its crystal structure change during the continuous cell operation test and the accelerated test by repetitious potential-sweep method to clear the feature of the catalyst of this electrode, and discuss the special feature of catalyst activity from the viewpoint of mass activity.

2 Experimental

2.1 Preparation of test electrodes

The ULPLE was prepared with the following process: the formation process of the layer composed of carbon powders (Cabot, Vulcan XC-72) coated with 35 mass% proton conductive polymer of Nafion (DuPont, 5 mass% solution); ion-exchange reaction process of proton and platinum ion in the proton conductive polymer by the immersion into 50 mmol l⁻¹ [Pt(NH₃)₄]²⁺ ion solution at 60 °C for 6 hours; washing process with deionized water; heating process at the lower temperature of 180 °C for 6 hours under the hydrogen atmosphere; rinsing process with immersion in 0.5 mol l⁻¹ H₂SO₄ at 80 °C and deionized water. The membrane electrode assembly (MEA) with 5 cm² was then prepared by the hot-pressing of the cathode catalyst layer and the anode catalyst layer on the both sides of polymer electrolyte membrane (DuPont, Nafion 115) as reported in elsewhere.²⁾ The catalyst loading level for cathode was 0.055 mg cm⁻² and 0.050 mg cm⁻² for anode. The single cell was composed of the follow-

ing serial constitution parts; anode gas flow plate / gas diffusion backing / MEA / gas diffusion backing / cathode gas flow plate. The gas diffusion backing was used of carbon paper of 0.2 mm thick treated with PTFE dispersion solution followed by sintering at 380 °C for 15 min. under nitrogen atmosphere for hydrophobic property. The existing electrode using Vulcan XC-72 carbon with Pt (Tanaka.K.K., 30 mass% Pt/C) was also prepared for comparison. The platinum loading level of cathode was 0.15 mg cm⁻² and 0.17 mg cm⁻² for anode.

2.2 Continuous operation test

The durability performance of single test cells were evaluated by the continuous operation test at 200 mA cm⁻² at 80 °C for 600 hours under the condition of hydrogen and air of humidified temperature of 80°C and 75 °C, respectively. The change in the electrochemically active surface area of platinum catalyst during the operation test was investigated by cyclic voltammograms, together with the change in the polarization curve of cells.

2.3 Accelerated evaluation test by repetitious potential-sweep method

The change in the electrochemically active surface area of platinum catalyst was investigated by repetitious potential-sweep method for accelerated test of failure mechanism losing its surface area using the wide range of potential from 0.6 V to 1.0 V vs. RHE at 25 °C covering the occurrence of dissolution-precipitation reaction of platinum for 30,000 times with sweep rate of 500 mV sec⁻¹. Argon gas flowed into working electrode and hydrogen gas for counter electrode of the test cell during the measurement. The electrochemically active surface area of platinum catalyst was calculated by columbic charge of hydrogen desorption peak on cyclic voltammogram obtained under the condition of 100 mV sec⁻¹ between 0.05 - 1.2 V vs. RHE at the appropriate intervals during the accelerated test.

3 Results and discussion

The change in the electrochemically active surface area of ULPLE after 600 hours continuous operation is summarized in Table 1. The retention

Table 1 Change in electrochemically active surface area after 600 hours continuous operation test at 200 mA cm⁻² and 80 °C.

Electrode	Pt loading level / mg cm ⁻²	Active surface area / cm ² mg ⁻¹		Retention of active surface area / %	
		Before	After		
ULPLE	Cathode	0.055	611	551	90.1
	Anode	0.050	682	782	115
Conventional electrode	Cathode	0.15	616	407	66.0
	Anode	0.17	594	477	80.0

value of electrochemically active surface area for cathode of ULPLE after 600 hours is high value of 90.1%, though the value of conventional one is drastically decreased down to 66.0%. In the case of anode for ULPLE, on the contrary, the value is increased up to 115%, whereas its value of conventional one is decreased down to 80% as the case of cathode. This tendency of change for platinum catalyst particles of ULPLE is totally different from the existing one reported so far.³⁾ In other words, the failure mechanism of aggregation phenomenon losing the electrochemically active surface area of platinum for ULPLE is drastically suppressed for cathode and rather improved for anode.

For further confirmation of this tendency, the accelerated test of failure mechanism losing the active surface area of platinum catalyst particles was conducted by repetitious potential-sweep method under the condition of the wide range of potential covering the occurrence of dissolution-precipitation reaction of platinum for 30,000 times. The change in the retention ratio of electrochemically active surface area of platinum catalyst is shown in Fig. 1. The retention value of active surface area of platinum for ULPLE is gradually decreased with repetitious cycles to show the minimum value of 80% at around 20,000 cycles and its value tends to be increased towards 30,000 cycles, whereas the value for the conventional electrode continued to be decreased down to 70%. For better analysis on these phenomena, the change in the retention ratio re-plotted in terms of logarithmic cycle number is shown in Fig. 2. The retention value of active surface area of platinum for ULPLE shows almost stable with no decrease by around 1,000 cycles as well as the case of conventional electrode. This means the platinum particles

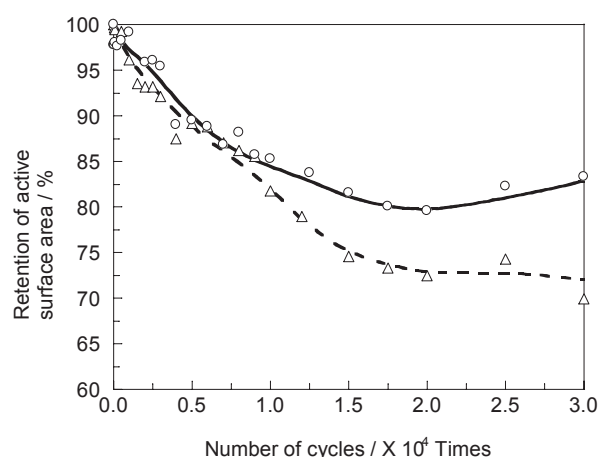


Fig. 1 Change in retention ratio of electrochemically active surface area of ultra-low platinum loading electrode (○) and conventional electrode (△) with repetitious potential-sweep cycles in the potential range of 0.6 - 1.0 V vs. RHE under argon gas at 25°C.

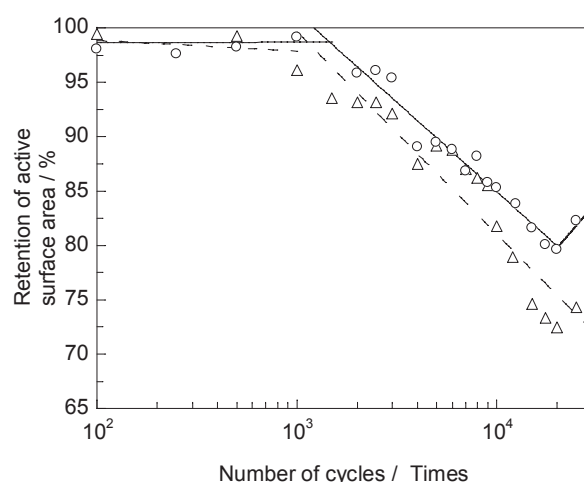


Fig. 2 Logarithmic plots of change in retention ratio of electrochemically active surface area of ultra-low platinum loading electrode (○) and conventional electrode (△) with repetitious potential-sweep cycles in the potential range of 0.6-1.0 V vs. RHE under argon gas at 25 °C.

maintain its size in this region with no change. The linear decrease in the retention value is observed beyond 1,000 cycles for both electrodes, and the increase is confirmed beyond 20,000 cycles in the case of ULPLE. This tendency is seemed to be crystallization from amorphous like platinum. The decreasing rate in electrochemically active surface area of ULPLE beyond 1,000 cycles is found out to be 4/5 of conventional electrode.

In order to consider in more detail of the above-mentioned change in the electrochemically active surface area of platinum catalyst particles, the change in potential behaviors by cyclic voltammograms of this accelerated test after 30,000 cycles is shown in Fig. 3. The desorption peak of hydrogen

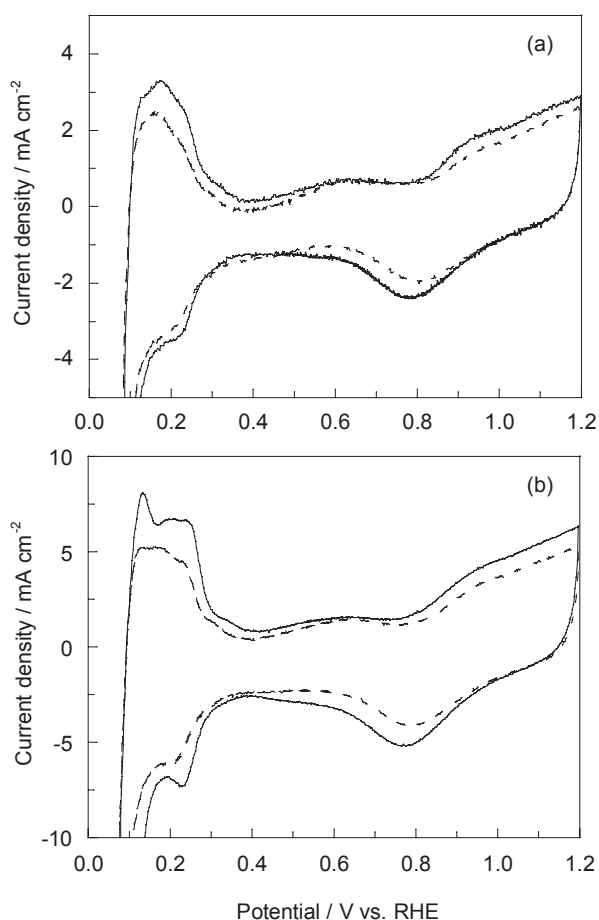


Fig. 3 Change in potential behavior of cyclic voltammograms for cathode (a) ULPLE and (b) conventional electrode after the accelerated test for 30,000 cycles between 0.6 – 1.0 V vs. RHE under the condition of H_2/Ar at 25 °C ; — initial, - - - after.

from platinum surface appeared around 0.05 – 0.4 V vs. RHE is decreased in both electrode after 30,000 cycling. However, in the case of conventional electrode, the shape of peak is found out to be the contribution of change from (111) and (110) faces to (100) face of platinum in conventional electrode.⁴⁾ On the other hand, the case of ULPLE is found out to maintain the shape indicating (111) face orientation with small platinum particle. This result clearly shows that the platinum particle in conventional electrode grows by accelerated test with potential sweep.

Furthermore, the change in potential behavior of electrodes after the continuous operation test is also shown in Fig. 4. The desorption peak of hydrogen at 0.05 V – 0.4 V vs. RHE from platinum surface becomes to be separated for both cathode and anode of ULPLE after 600 hours operation. The separated peak after operation at 0.1 V vs. RHE is characterized by (110) face, though the shape of cyclic voltammogram at the initial states shows (111) face orientation. Especially, the peak of anode becomes to be sharpened resulting in the increment of electrochemically active surface area of platinum observed in Table 1. This phenomenon is derived from the crystal structure of platinum loaded on ULPLE with the change in face orientation from indices (111) to (110) by continuous operation condition, in contrast with no appearance in accelerated test. On the other hand, the both cathode and anode peaks of conventional electrode become broad and small after the operation test resulting in the drastic decrease in electrochemically active surface area of platinum. Because this tendency has been remarkably observed in cathode side with clear appearance of shoulder peak at 0.25 V vs. RHE of which peak indicates the well known phenomenon of (100) face orientation of platinum appeared in large platinum particle more than 3.5 nm⁵⁾ with the growth of platinum particle by aggregation under the operating condition such as the case of accelerated test.

The high durability performance of platinum catalyst particle for ULPLE is able to be confirmed by the change in polarization curves of PEFC after 600 hours operation shown in Fig. 5. The cell per-

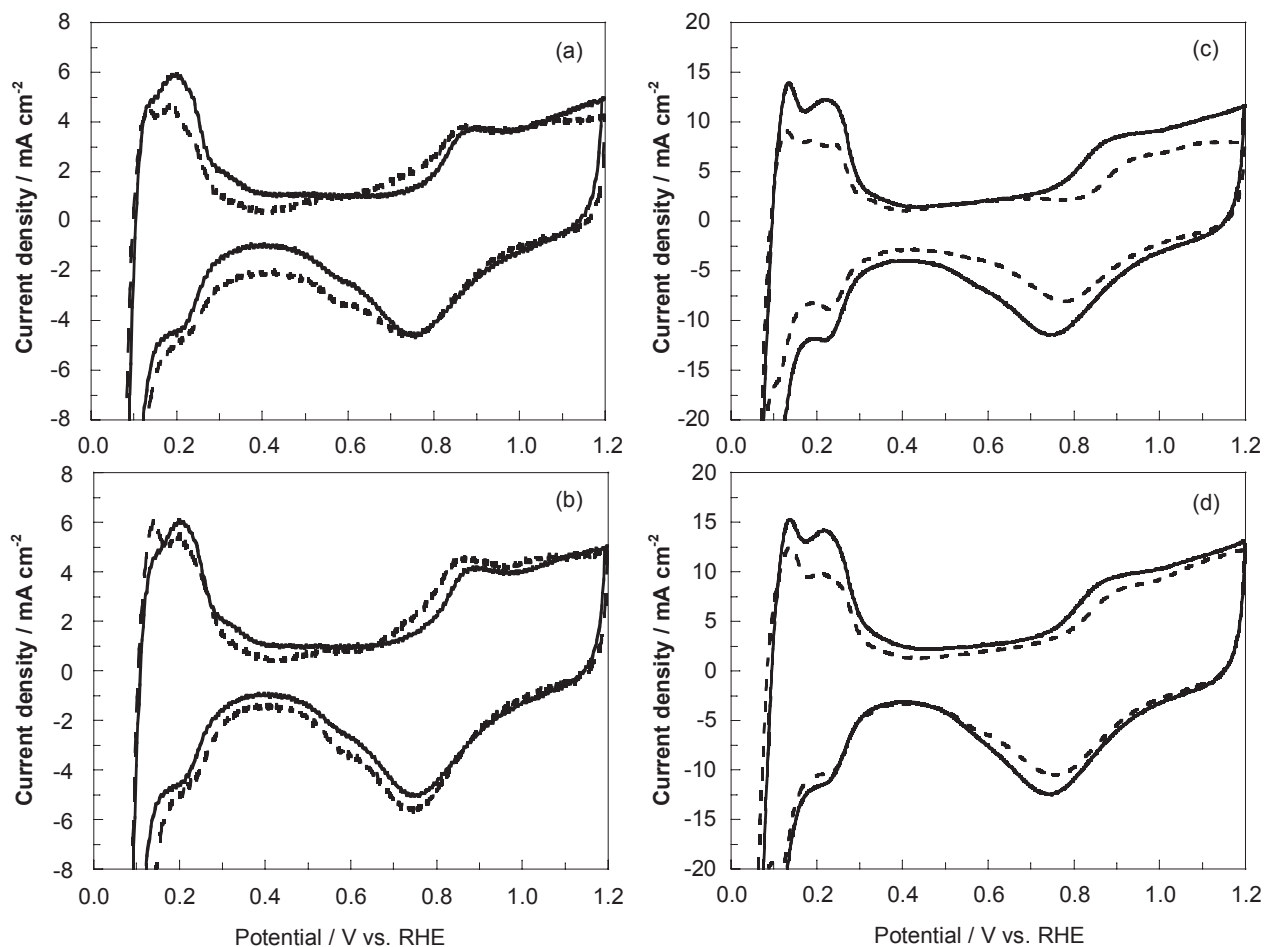


Fig. 4 Change in potential behavior of cyclic voltammograms for cathode (a), anode (b) of ULPLE and cathode (c), anode (d) of conventional electrode after the continuous operation test of 600 hours under the condition of H₂/Air at 80 °C ; — initial, - - - after.

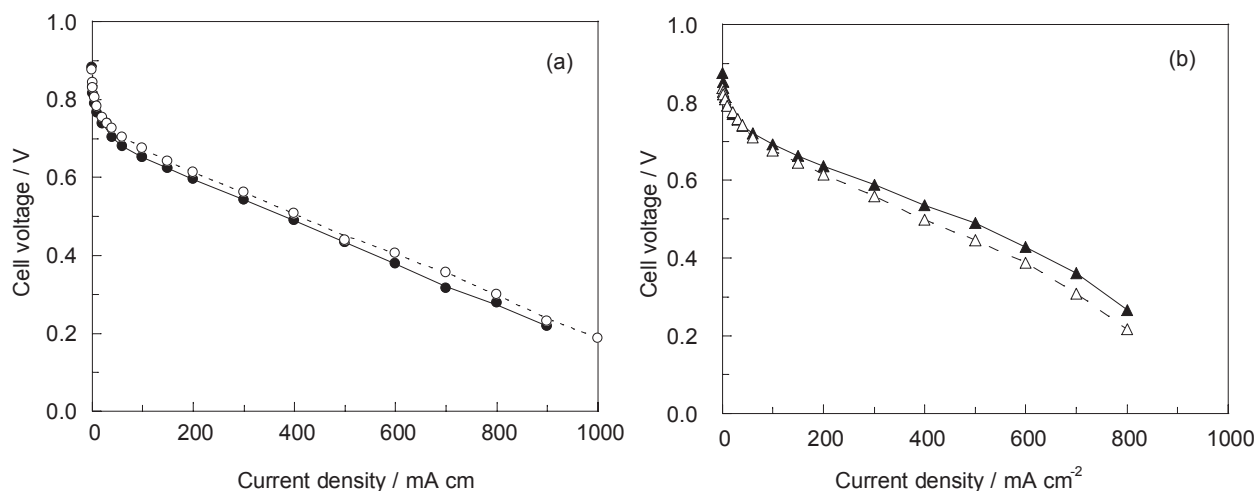


Fig. 5 Change in polarization curves of PEFC with ULPLE (a) and conventional electrode (b) after the continuous operation test of 600 hours under the condition of H₂/Air at 80 °C. ●, ▲ Initial ; ○, △ after.

formance of PEFC with ULPLE after the operation is found out to be improved by the contribution of the increment of active surface area of platinum catalyst for anode and a slight decrease of active surface area for cathode. This improvement of performance seems to be the appearance of active site of (110) face of platinum particle. On the other hand, The performance of conventional cell is also found out to be decreased by the aggregation phenomenon losing the active surface area of platinum catalyst particles for both cathode and anode electrodes.

Considering the special location of platinum catalyst particles for ULPLE, the platinum catalysts is loaded only in the proton-conductive passage in ion cluster of polymer electrolyte, wherein the nano-size platinum contacts with the surface of carbon powders. The platinum particles are formed by reduction reaction of platinum complex cation by hydrogen gas at lower temperature of 180 °C by catalytic activity of carbon. This means that the platinum catalyst particle is considered to be held in the proton-conductive passage inside the ion cluster of polymer electrolyte with the low crystallization. Therefore, the reason why ULPLE shows the drastic suppression of decrease in the active surface area of platinum catalyst particles for cathode and rather shows the increase for anode during the cell operation is considered as described below. The phenomenon losing of the electrochemically active surface area of platinum particles is mainly based on the aggregation phenomenon by dissolution-precipitation mechanism accelerated by wide range of potential change. The platinum catalyst particles of ULPLE is tightly formed inside the proton-conductive passage contacts the surface of carbon powders resulting in little occurrence of aggregation phenomenon, though its particle is very small of nano-scale size. The increase of active surface area of platinum for anode of ULPLE seems to be crystallized of the active site for hydrogen oxidation reaction at the potential region.

The change in mass activity ratio of this electrode to conventional electrode after the continuous operation test is shown in Fig.6 for the explanation of high durability performance of ULPLE. The mass

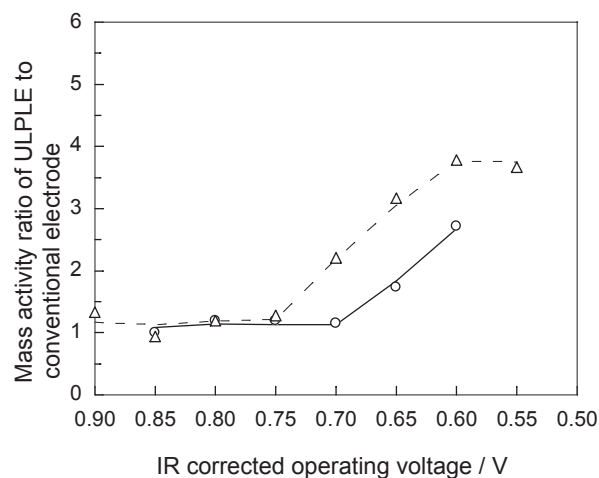


Fig. 6 Change in mass activity ratio of ULPLE to conventional electrode after the continuous operation test of 600 hours under the condition of H_2/O_2 at 80 °C. Initial ○ , after △ .

activity ratio is around 1 at the higher voltage of 0.70 V. That is to say, the active site of platinum catalyst of the conventional cell at the higher voltage of 0.70 V in the beginning is limited not only on the portion of proton-conductive passage, but also on the part of rigid hydrophobic backbone of polymer electrolyte. However, the value is increased up to 2.7 at the 0.60 V in the beginning. This suggests that the active site becomes to be almost limited to the proton-conductive passage of polymer electrolyte, but not the portion of hydrophobic backbone, considering the value of ratio is around 2.7 almost equal to the volumetric ratio of proton-conductive passage to polymer electrolyte. After 600 hours operation, the operating voltage showing the ratio of 1 shifts by higher voltage of 0.75 V and its value is increased up to 3.75 at 0.60V with lowering the operating voltage. This increase of the ratio from 2.7 to 3.7 suggests that the active site of conventional electrode is largely decreased down after operation.

4 Conclusions

The ultra-low platinum loading electrode (ULPLE) is found out drastically suppress the aggregation phenomenon losing the active surface area of platinum catalyst particles by holding the catalyst

only inside of the proton-conductive passage of polymer electrolyte in which nano-size platinum contacts with the surface of carbon powders. This feature has been clearly confirmed by change of active surface area after accelerated condition by potential sweep as well as continuous operation.

The active site of electrochemical reaction on the platinum catalyst particles shifts towards the proton-conductive passage rather than the part of hydrophobic backbone at lower voltage below 0.70 V at the beginning and 0.75 V after 600 hours operation. At the lower voltage of 0.60 V at the beginning and 0.55 V after 600 hours, the active site becomes to be limited to the proton conductive passage of polymer electrolyte, but not the portion of hydrophobic backbone, because the value of ratio at the corresponding voltage is around 2.5 equal to the ratio value of proton-conductive passage to polymer electrolyte. The high mass activity of ULPLE was indicated to be 3.7 times compared with that of conventional electrode after 600 hours operation. This phenomenon is seemed to be depended on appearance for active site of platinum of (110) face.

Therefore, ULPLE is considered to be essential technology to reach low cost and high durability performance for practical application of PEFC.

Acknowledgement

The part of this work was performed by financial support of New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

- 1) G.A.Gruver, R.F.Pascoe, and H.R.Kunz, *J. Electrochem. Soc.*, **127**, 1219 (1980).
- 2) S.Hitomi, H.Yasuda, and M.Yamachi, *40th Battery Symposium in Japan Proc.*, 167 (1999).
- 3) M.S.Wilson, F.H.Garzon, K.E.Sickafus, and S.Gottesfeld, *J. Electrochem. Soc.*, **140**, 2872 (1993).
- 4) N.Markovic, H.Gasteiger, and P.N.Ross, *J. Electrochem. Soc.*, **144**, 1591 (1997).
- 5) K.Kinoshita, *J. Electrochem. Soc.*, **137**, 847 (1990).