DEVELOPMENT OF A MICRO-TUBULAR DMFC
FABRICATED BY PLATING TECHNIQUE

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ABSTRACT

Plating technique has been developed for preparing catalyst layers of a micro-tubular direct methanol fuel cell. By using chemical and electroplating process, the deposited Pt cathode catalyst layer was obtained as around 12 \( \mu \)m in thickness with the Pt particles size of 10 nm. PtRu(1:1) anode catalyst layer was formed as around 2 \( \mu \)m in thickness with the PtRu particles size of 200 nm by two repetitions of the chemical plating process. The micro-tubular DMFC single cell with a 6 mg-Pt cm\(^{-2}\) cathode and a 2.8 mg-PtRu cm\(^{-2}\) anode exhibited a peak power density of 1.5 mW cm\(^{-2}\) under passive and air breathing conditions at ambient temperature and pressure.

INTRODUCTION

Among small fuel cells, direct methanol fuel cell (DMFC) with its power density potentially higher than that of lithium secondary battery is a promising candidate as the power supply for portable applications such as cell phones, PDAs and laptop computers. So far, the planar or chip type air breathing DMFCs are competitively being developed worldwide for portable applications [1-3]. At the National Institute of Advanced Industrial Science and Technology (AIST), a prototype of DMFC utilizing tubular polymer electrolyte membranes has been successfully demonstrated for application in portable devices [4]. The micro-tubular type DMFC has several advantages over the typical planar type DMFCs — large electrode surface to volume ratio, better sealing of the fuel chamber inside of the tube, and higher flexibility in shape than the planar type fuel cells. Now, the power density of the micro-tubular DMFC single cell formed by the brushing method with a hot-pressing process reaches to 12 mW cm\(^{-2}\) using 1 M methanol under passive and air breathing conditions at ambient temperature and pressure [5]. This result shows that micro-tubular DMFCs are able to perform as well as typical planar type DMFCs in terms of power density. However, the fabrication by brushing method is rather time-consuming, and needs much skill to attain good contact between the catalyst layer and the membrane.

Fabrication of catalyst layers by chemical plating process is considered to be applicable for polymer electrolyte materials with various shapes such as micro tube [6,7]. The advantage of plating method is that fabrication of the tubular membrane-catalyst composite can be accomplished through the chemical process line, which will be useful in the future mass production stage.

In the present work, a new plating process to fabricate the Pt and PtRu catalyst layers on the outside and inside surface of the micro tubular polymer electrolyte membrane...
without the hot-pressing process is developed. The performance of the micro-tubular DMFC single cell fabricated by plating technique is further evaluated.

**EXPERIMENTAL**

The polymer electrolytes were Flemion® tubes (inner diameter 0.3 mm, outer diameter 0.6 mm with an ion-exchange capacity of $1.1 \times 10^3$ eq. g$^{-1}$ in dry state, Asahi Glass Engineering). The Flemion® tubes were cleansed by successive boiling in 3 wt% H$_2$O$_2$ (30%, Wako Pure Chemical Industries, Ltd.), deionized water, 1 M H$_2$SO$_4$ (99%, Wako Pure Chemical Industries, Ltd.), and deionized water, each for 1 h.

Tubular membrane catalyst composites were prepared by plating process. For the cathode electrode, Pt catalyst layer was firstly formed by impregnation-reduction method (IR method) [6,7]. Tetraammineplatinum chloride ([Pt(NH$_3$)$_4$]Cl$_2$, Wako Pure Chemical Industries, Ltd.) was used as Pt precursor. Cation exchange was carried out by immersing the Flemion® tube in Pt complex solution at room temperature overnight. After that, the Flemion® tube was washed by deionized water to remove the excess metal species. Subsequently, the outside surface of the Flemion® tube was immersed in 0.5 mM NaBH$_4$ (90%, Wako Pure Chemical Industries, Ltd.) alkali solution at 328 K to precipitate Pt catalyst layer. Residual precursors were removed by dipping in 1 M H$_2$SO$_4$ and deionized water at 353 K. After the IR process, in order to control the loading amount and size of the Pt electrocatalyst particles, electroplating method was further carried out. The electroplating solution was 60 mM H$_2$PtCl$_6$·6H$_2$O (Wako Pure Chemical Industries, Ltd.) and 0.8 mM Pb(CH$_3$COO)$_3$·3H$_2$O (Wako Pure Chemical Industries, Ltd.). The deposition was carried out by applying a current density of 30 mA cm$^{-2}$. On the other hand, for the anode electrode, tetraammineplatinum chloride and pentaamminechlororuthenium chloride ([RuCl(NH$_3$)$_5$]Cl$_2$, Wako Pure Chemical Industries, Ltd.) were used as precursors for Pt and Ru [7]. PtRu (atomic ratio; 1:1) catalyst layer was formed on the inside surface of Flemion® tube by IR method. The PtRu ratios impregnated in the membrane and deposited on the surface were proved to be equal to those in the ion-exchange solution [7].

The obtained Pt and PtRu deposited layers were analyzed by XRD (PW1800, Philips Electronics) using the Cu-K$_\alpha$ line at 40 kV, 40 mA. The morphology of Pt and PtRu deposited layers were observed by FE-SEM (DS-720, Topcon Corp.).

Cyclic voltammogram (CV) was measured in 1 M H$_2$SO$_4$ solution and the real electrochemical surface area of Pt deposited tubular electrode was calculated from the hydrogen desorption wave capacity in the CV. For the electrochemical measurements, a new type of tubular hydrogen reference electrode was prepared by injecting the mixing paste of unsupported Pt black nanoparticles (HiSPEC-1000, Johnson-Matthey Fuel Cells) and 5 wt% Nafion® solution (Aldrich Chemical Company, Inc.) into the tubular electrolyte containing a current conducting Pt wire (Φ 0.2 mm x 100 mm, Nilaco corp.). Due to the extremely large active surface area of this electrode, it was confirmed that it can be used as both the reference and the counter electrode during the half-cell testing [8].

The activity of electrocatalytic oxidation of methanol on PtRu deposited tubular electrode was evaluated by using a half-cell testing method. Working electrode was made by injecting the mixing paste of carbon powder (Vulcan XC-72R, Cabot) and 5 wt% Nafion® solution into the PtRu deposited tubular electrolyte containing a current conducting Au wire (Φ 0.1 mm x 50 mm, Nilaco corp.). The aqueous methanol solution was fed into the tube with a syringe. Linear sweep voltammogram was measured in 1 M
H₂SO₄ solution by using a potentiogalvanostat (CV-50W, Bioanalytical Systems Inc.) at a scan rate of 5 mV s⁻¹ with IR drop compensation.

The micro-tubular DMFC single cell was fabricated to evaluate the performance of cathode electrode. The catalyst layer of the cathode was loaded by plating process. Unsupported PtRu black nanoparticles was used as anode catalyst. The anode electrode layer was made by injecting the mixing paste of catalyst and 5 wt% Nafion® solution into the Flemion® tube containing a current conducting Au wire. The loading amount of PtRu black was 6 mg cm⁻² inside the tubular electrolyte membrane. In this case, the performance of this single cell was limited by the cathode electrode. When the open-circuit potential reached a stable value, the performance was evaluated from current-voltage curves measured with a potentiogalvanostat at a scan rate of 5 mV s⁻¹.

The performance of the micro-tubular DMFC single cell prepared by plating process for both cathode and anode was also tested under passive and air breathing conditions at ambient temperature and pressure.

RESULTS AND DISCUSSION

Characterization of tubular membrane-catalyst composites

XRD patterns of Pt and PtRu(1:1) membrane composites made by IR method are shown in Fig.1. For Pt catalyst layer, since the pattern of the sample displays the (111), (200), (220), (311) and (222) reflections characteristic of Pt face centered cubic (fcc) crystal structure, the formation of Pt particles was confirmed. For PtRu(1:1) catalyst layer, the XRD pattern was similar to that of Pt. However, peaks were broadened and shifted to larger angle side compared to those of pure Pt. In addition, small (101) peak of Ru hexagonal close-packed (hcp) crystal structure was also observed. According to the phase diagram of PtRu alloy [9], only Pt (fcc) crystal structure exists at the PtRu atomic ratio of 1:1. These results suggest the existence of a mixture of PtRu solid solution and Ru metal.

The surface and cross sectional images of Pt deposited layers were observed by FE-SEM as shown in Fig. 2. It indicates that Pt particles are selectively deposited near the surface of the tubular electrolyte membrane. The obtained Pt deposited layer was porous with the thickness of 2 µm. The size of Pt particles was observed to be around 100 nm. After this IR process, the outside surface of Flemion® tube became electric conductive, and the resistance was measured to be around 40 Ω cm⁻². The average loading amount of Pt catalyst was 1.6 mg cm⁻². In order to control the loading amount and size of the Pt electrocatalyst particles, electroplating was further carried out with the Pt-deposited Flemion® tube. Figure 3 shows the surface and cross sectional FE-SEM images of the obtained sample. From these figures, it is found that the deposited Pt particles are around 10 nm in size on the surface of the tubular electrolyte membrane. The thickness of the Pt deposited layer was observed to be around 12 µm. The resistance of Flemion® tube on the surface was found to decrease to around 10 Ω cm⁻². After the electroplating process, the average loading amount of Pt catalyst on the outside surface of the tubular electrolyte membrane increased to around 6 mg cm⁻². Figure 4 shows CV of Pt deposited electrode in 1 M H₂SO₄ solution at 298 K. The electrochemical active surface area of Pt deposited tubular electrode was then calculated to be around 8.8 m² g⁻¹Pt based on the hydrogen desorption wave capacity according to the literature (210 μC/real cm² of Pt) [10].

The surface and cross sectional images of PtRu(1:1) deposited layers were observed by FE-SEM as shown in Fig. 5. It is found that PtRu particles are also selectively deposited near the surface of the tubular electrolyte membrane. The obtained PtRu deposited layer was porous with the thickness of 2 µm. The size of PtRu particles was observed to be around 100 nm. After this IR process, the outside surface of Flemion® tube became electric conductive, and the resistance was measured to be around 40 Ω cm⁻². The average loading amount of PtRu catalyst was 6 mg cm⁻². In order to control the loading amount and size of the PtRu electrocatalyst particles, electroplating was further carried out with the Pt-deposited Flemion® tube. Figure 3 shows the surface and cross sectional FE-SEM images of the obtained sample. From these figures, it is found that the deposited PtRu particles are around 10 nm in size on the surface of the tubular electrolyte membrane. The thickness of the PtRu deposited layer was observed to be around 12 µm. The resistance of Flemion® tube on the surface was found to decrease to around 10 Ω cm⁻². After the electroplating process, the average loading amount of PtRu catalyst on the outside surface of the tubular electrolyte membrane increased to around 6 mg cm⁻². Figure 4 shows CV of PtRu deposited electrode in 1 M H₂SO₄ solution at 298 K. The electrochemical active surface area of PtRu deposited tubular electrode was then calculated to be around 8.8 m² g⁻¹Pt based on the hydrogen desorption wave capacity according to the literature (210 μC/real cm² of Pt) [10].

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deposited near the inside surface of the tubular electrolyte membrane. The obtained deposited layer is porous with the thickness of 1 μm. The size of PtRu particles was observed to be around 50 nm. The average loading amount of PtRu catalyst was 1.2 mg cm⁻². In order to increase the loading amount of the PtRu electrocatalyst particles, IR process was carried out once again. The loading amounts of PtRu were around 1.2, 2.8 and 4.3 mg cm⁻² corresponding to the repetition number of the IR process. The surface and cross sectional images of PtRu(1:1) deposited layers formed by two and three repetitions of the IR process as observed by FE-SEM are shown in Fig. 6 and Fig. 7, respectively. As shown in Fig. 6, after two repetitions of IR process, the obtained deposited layer increased to 2 μm in thickness, and the size of PtRu particles was observed to be around 200 nm. When three repetitions of the IR process were carried out, the deposited layer increased to around 3 μm in thickness. In addition, the penetration of PtRu particles into the membrane was observed as shown in Fig. 7. This phenomenon can be interpreted that the reduction of the PtRu metal precursors diffusing from the inside of the tubular membrane occurs catalytically on the first PtRu deposited layer [7].

**Single cell evaluation of the cathode electrode**

The performance of the cathode electrode was evaluated by using a micro-tubular DMFC single cell shown in Fig. 8. The catalyst layer of the cathode was loaded by chemical and electroplating process. By means of brushing method, anode electrode was formed using unsupported PtRu black catalyst. As mentioned before, in this case, the performance of this single cell was limited by the cathode electrode.

As shown in Fig. 9, the maximum of power density was obtained as 2 mW cm⁻² at 250 mV using 3 M methanol solution. When 10 M methanol solution was used as fuel, the power density reduced to 1.5 mW cm⁻². The open-circuit potential for 3 M methanol solution was 650 mV while that for 10 M methanol solution was 600 mV. This result is considered to be due to the methanol crossover from the anode to the cathode side across the tubular electrolyte membrane. In short-term stability test on a single cell of micro-tubular DMFC, the power density of 1 mW cm⁻² was maintained at 300 mV for at least 6 minutes as shown in Fig. 10. After that, the power density decreased. It is considered that this decline in power density is mainly due to the exhaustion of methanol fuel in the space inside the tubular electrolyte membrane.

**Half cell evaluation of the anode electrode**

In order to optimize the loading amount of PtRu catalyst, polarization curves of methanol oxidation at the anode electrodes were evaluated by using a half-cell. Fig. 11 shows a schematic diagram of the apparatus for this half-cell testing. The loading amounts of PtRu were 1.2, 2.8 and 4.3 mg cm⁻² corresponding to the repetition number of IR process. In Fig. 12, the methanol oxidation current density increased with increasing PtRu loading amount from 1.2 to 2.8 mg cm⁻². When the loading amount increased to 4.3 mg cm⁻², the current density decreased largely. The reason would be mainly due to the spreading of PtRu particles into the membrane during the repeated IR process (see Fig. 7). PtRu deposited particles inside the membrane would result in negative effects in proton conductivity, electrical conductivity and methanol accessibility. From the above results, it indicates that the loading amount of PtRu catalyst corresponding to two repetitions of the IR process appears as optimum.
Performance of a micro-tubular DMFC single cell

Based on the above results, a micro-tubular DMFC single cell was fabricated by plating process with a 6 mg-Pt cm\(^{-2}\) cathode and a 2.8 mg-PtRu cm\(^{-2}\) anode. The performance was evaluated under passive and air breathing conditions at ambient temperature and pressure. As shown in Fig. 13, the maximum power density attained was 1.5 mW cm\(^{-2}\) at 8 mA cm\(^{-2}\) using 3 M methanol solution. In long-term stability test on a single cell of micro-tubular DMFC, the power density of 0.4 mW cm\(^{-2}\) was maintained at 200 mV as shown in Fig. 14. At the beginning stage, the power density declines rapidly due to the exhaustion of methanol fuel in the space inside the tubular electrolyte membrane. Then, the power density falls to a constant value at which the supply and exhaustion of methanol fuel reaches a steady state for at least 30 minutes. It is also plausible that insufficient removal of the cathode reaction product (water) degrades the power density in the present condition.

The performance obtained in this study did not reach the level obtained by the brushing method. This would be because the active surface area of the Pt cathode and PtRu anode prepared by the plating method was smaller than that of Pt cathode and PtRu anode formed by the brushing method using Pt black and PtRu black nanoparticles. However, the morphologies of the deposited Pt and PtRu formed by plating method might be optimized and this issue can be solved in the future work. The preparation technique reported here is also proved to be useful for applying polymer electrolyte materials with various shapes to the fuel cell system.

CONCLUSIONS

In this study, plating technique for preparing catalyst layers of a micro-tubular direct methanol fuel cell was successfully developed. The micro-tubular DMFC single cell with a 6 mg-Pt cm\(^{-2}\) cathode and a 2.8 mg-PtRu cm\(^{-2}\) anode exhibited a peak power density of 1.5 mW cm\(^{-2}\) under passive and air breathing conditions at ambient temperature and pressure. The plating technique would be useful in the practical application for manufacturing the micro-tubular DMFC in the future mass production stage.

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Fig. 1 XRD pattern of samples prepared by the impregnation-reduction method. (a) Pt; (b) PtRu(1:1) deposited Flemion® films.

Fig. 2 The surface and cross sectional FE-SEM images of Pt deposited layers prepared by the impregnation-reduction method.

Fig. 3 The surface and cross sectional FE-SEM images of Pt black prepared by the electroplating method on Pt deposited Flemion® tube.

652 Electrochemical Society Proceedings Volume 2004-21
Fig. 4 Cyclic voltammogram of Pt deposited tubular electrode in 1 M H₂SO₄ solution at 298 K.

Fig. 5 The surface and cross sectional FE-SEM images of PtRu deposited layers prepared by the impregnation-reduction method.

Fig. 6 The surface and cross sectional FE-SEM images of PtRu deposited layers prepared by two repetitions of the impregnation-reduction method.
Fig. 7 The surface and cross sectional FE-SEM images of PtRu deposited layers prepared by three repetitions of the impregnation-reduction method.

Fig. 8 A photograph of a micro-tubular DMFC single cell.

Fig. 9 Performance of a micro-tubular DMFC single cell with PtRu black anode catalyst. (Fuel: 3 M and 10 M CH₃OH; passive and air breathing.)
Fig. 10 A short-term stability test of a micro-tubular DMFC single cell with PtRu black anode catalyst under passive and air breathing conditions at room temperature in 3 M CH₃OH.

Fig. 11 A schematic diagram of the apparatus for half-cell testing.

Fig. 12 Half-cell polarization plots for PtRu deposited tubular anodic electrode with various PtRu loadings. Sweep rate: 5 mV s⁻¹; 3 M CH₃OH as fuel.
Fig. 13 Performance of a micro-tubular DMFC single cell (Fuel: 3 M CH₃OH; passive and air breathing).

Fig. 14 A long-term stability test of a micro-tubular DMFC single cell under passive and air breathing conditions at room temperature.