

Pt catalyst configuration by a new plating process for a micro tubular DMFC cathode

H. Qiao, M. Kunimatsu¹, T. Okada*

National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1, Central 5, Tsukuba, Ibaraki 305-8565, Japan

Received 31 May 2004; received in revised form 7 July 2004; accepted 14 July 2004

Available online 17 September 2004

Abstract

A new plating process has been developed for the formation of the cathode catalyst of a micro tubular direct methanol fuel cell. By using this method, a thin porous layer of Pt electrocatalyst was firstly bonded onto a tubular polymer electrolyte membrane by chemical reduction of Pt complex impregnated in the membrane. Electroplating was further made to control the loading amount and size of the Pt catalyst particles. The deposited Pt catalyst layer is around 12 μm in thickness with the Pt particles size of 10 nm. The micro tubular DMFC with a 6 mg-Pt cm^{-2} cathode exhibited a peak power density of 2 mW cm^{-2} under passive and air breathing conditions at ambient temperature and pressure. © 2004 Elsevier B.V. All rights reserved.

Keywords: Micro tubular polymer electrolyte membrane; DMFC; Pt catalyst; Plating; Cathode; Passive and air breathing

1. Introduction

With the evolution of the information technology, power consumption of portable electronic devices such as laptop computers, cellular phones, PDAs, is increasing remarkably. Therefore, the demand for powerful power sources is becoming more and more important. Fuel cells with their potentially high power density are promising candidates of the power supply in the next generation. Among fuel cells, direct methanol fuel cells (DMFCs) are attractive as the power supply for portable applications. Because methanol is a liquid fuel at room temperature, the handling of methanol fuel is easier than that of hydrogen gas. Also, the potential of power density in DMFCs is based on the high energy density of methanol. So far, the development of planar type air breathing DMFCs for portable applications has been reported [1–5]. Despite of these researches, a prototype of DMFCs uti-

lizing tubular polymer electrolyte membranes has been successfully demonstrated for application in portable devices at the National Institute of Advanced Industrial Science and Technology (AIST) recently [6]. The advantages of tubular type DMFCs are: (1) large electrode surface to volume ratio; (2) better sealing of the fuel chamber inside the tube, and (3) higher flexibility in shape than the planar type fuel cells. Now, the micro tubular DMFC single cell where the catalyst layer is formed by the brushing method with a hot-pressing process achieves the power density of 12 mW cm^{-2} using 1 M ($\text{M} = \text{mol dm}^{-3}$) methanol solution under passive and air breathing conditions at ambient temperature and pressure [7]. However, the fabrication is rather time-consuming, and needs much skill to attain good contact between the catalyst layer and the membrane.

In this report, a new plating process to fabricate the Pt catalyst layer on the outside surface of the micro tubular polymer electrolyte membrane without the hot-pressing process is developed. The advantage of this method is that fabrication of the tubular membrane catalysts composite can be accomplished through the chemical process line, which will be useful in the future mass production stage.

* Corresponding author. Tel.: +81 29 8614464; fax: +81 29 8614678.

E-mail address: okada.t@aist.go.jp (T. Okada).

¹ resent address: Kanagawa Industrial Technology Research Institute, 705-1, Shimokoizumi, Ebina-shi, Kanagawa, 243-0435, Japan.

2. Experimental

The polymer electrolytes were Flemion[®] tubes (inner diameter 0.3 mm, outer diameter 0.6 mm with an ion-exchange capacity of $1.1 \times 10^{-3} \text{ eq. g}^{-1}$ in dry state, Asahi Glass Engineering). The Flemion[®] tubes were cleansed by successive boiling in 3 wt.% H₂O₂ (30%, Wako Pure Chemical Industries, Ltd.), deionized water, 1 M H₂SO₄ (99%, Wako Pure Chemical Industries, Ltd.), and deionized water, each for 1 h. For preparing the tubular membrane catalysts composite, chemical plating (impregnation-reduction method) was firstly carried out [8–10]. In the impregnation-reduction process, tetraammineplatinum(II) chloride ([Pt(NH₃)₄]Cl₂, Wako Pure Chemical Industries, Ltd.) was used as Pt precursor. Then, cation exchange was carried out by immersing the Flemion[®] tube in Pt complex solution at room temperature over night. 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 NaBH₄ (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 H₂SO₄ and deionized water at 353 K. After the impregnation-reduction 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 H₂PtCl₆·6H₂O (Wako Pure Chemical Industries Ltd.) and 0.8 mM Pb(CH₃COO)·3H₂O (Wako Pure Chemical Industries Ltd.). The deposition was carried out by applying a current density of 30 mA cm⁻².

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

Cyclic voltammogram (CV) was measured in 1 M H₂SO₄ solution and the real electrochemical surface area of Pt deposited tubular electrode was calculated from the hydrogen desorption wave capacity in the CV.

The micro tubular DMFC single cell was fabricated using a tubular polymer electrolyte membrane with the length of 3.5 cm. The catalysts of the cathode were loaded by plating process as mentioned above. Unsupported PtRu black nanoparticles (HiSPEC-6000, Johnson-Matthey Fuel Cells) was used as anode catalyst. The anode electrode layer was made by injecting the mixing paste of catalyst and 5 wt.% Nafion[®] solution (Aldrich Chemical Company, Inc.) into the Flemion[®] tube containing a current conducting Au wire (Φ 0.1 mm \times 80 mm, Nilaco Corp.). The loading amount of PtRu black was 6 mg cm⁻² inside the tubular electrolyte membrane.

The fabricated micro tubular DMFC single cell was tested under passive and air breathing conditions at ambient temperature and pressure. The aqueous methanol solution was fed into the tube with a syringe. When the open-circuit potential reached a stable value, the performance was evaluated from current–voltage curves measured with a

potentiostat (CV-50 W, Bioanalytical Systems Inc.) at a scan rate of 5 mV s⁻¹. In the short-term stability test, the power densities were recorded for 10 min at constant voltage.

3. Results and discussion

3.1. Characterization of tubular Flemion[®]-Pt composite

The XRD pattern of the sample made by the impregnation-reduction method is shown in Fig. 1. For comparison, the XRD pattern of the Flemion[®] film is also shown in this figure. Since the pattern of the sample displays the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections characteristic of Pt face centered cubic crystal structure, the formation of Pt particles was confirmed. Fig. 2 shows the surface and cross sectional images of Pt deposited layers observed by FE-SEM. It indicates that Pt particles are selectively deposited near the surface of the tubular electrolyte membrane. The obtained Pt deposited layer is porous with the thickness of 2 μm . The size of Pt particles was observed to be around 100 nm. After this impregnation-reduction process, the outside surface of Flemion[®] tube became electric conductive, and the resistance was measured to be around 40 $\Omega \text{ cm}^{-2}$. The average loading amount of Pt catalyst was 1.2 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. Fig. 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 . Meanwhile, the resistance of Flemion[®] tube on the surface decreased to be around 10 $\Omega \text{ cm}^{-2}$. After the electroplating process, the average loading amount of Pt catalyst on the outside surface of the tubular electrolyte membrane increased to 6 mg cm⁻².

Fig. 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_{pt}⁻¹ based on the hydrogen desorption wave capacity according to the literature (210 $\mu\text{C real cm}^{-2}$ of Pt)[11].

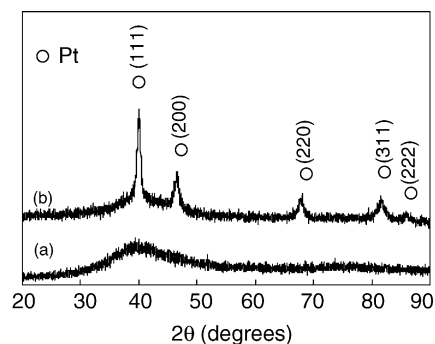


Fig. 1. XRD pattern of samples (a) Flemion[®] film, (b) Pt deposited Flemion[®] film prepared by the impregnation-reduction method.

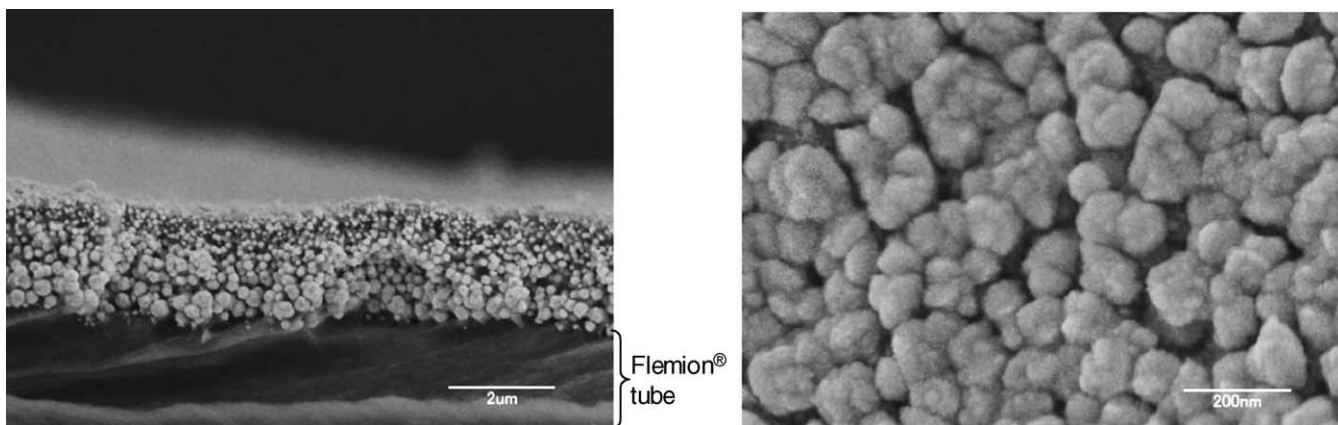


Fig. 2. The surface and cross sectional FE-SEM images of Pt deposited layers prepared by the impregnation-reduction method.

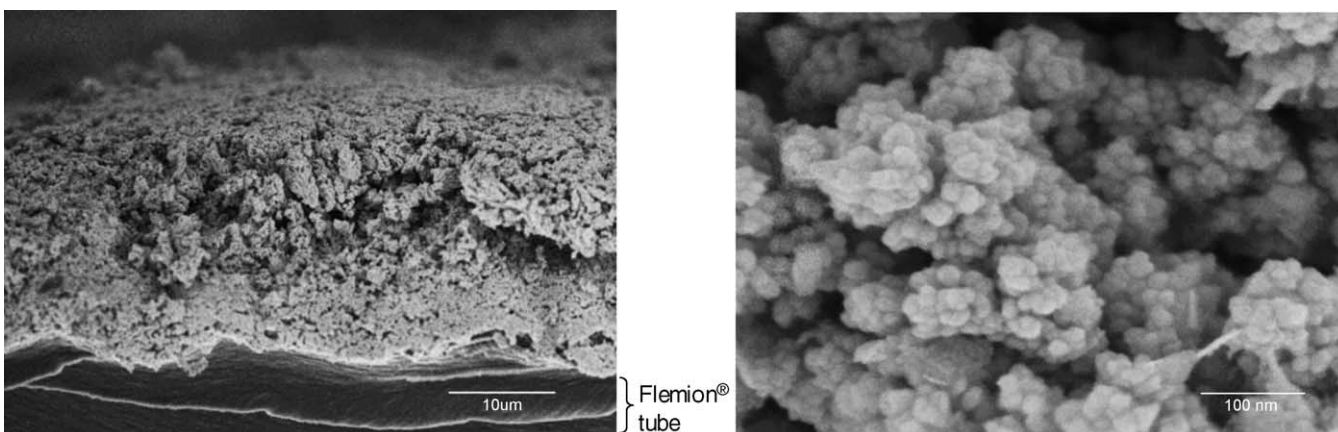


Fig. 3. The surface and cross sectional FE-SEM images of Pt black prepared by the electroplating method on Pt deposited Flemion® tube.

3.2. Performance of a micro tubular DMFC single cell

A picture of a micro tubular DMFC single cell is shown in Fig. 5, the performance of which was evaluated under

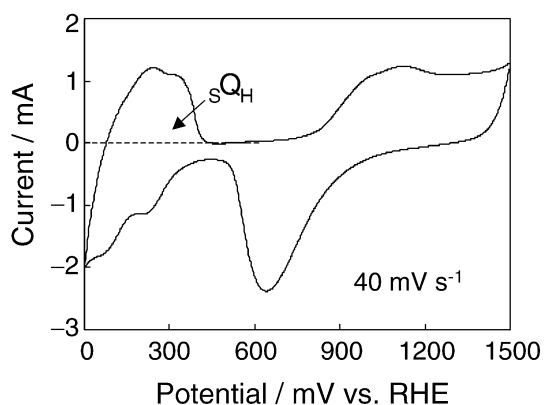


Fig. 4. Cyclic voltammogram of Pt deposited tubular electrode in 1 M H_2SO_4 solution at 298 K.

passive and air breathing conditions at ambient temperature and pressure. As shown in Fig. 6, 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 under passive and air breathing conditions at ambient temperature and pressure, the power density of 1 mW cm^{-2} was maintained at 300 mV for at least 6 min as shown in Fig. 7. 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. It is also plausible that insufficient removal of the cathode reaction product (water) degrades the power density in the present condition.

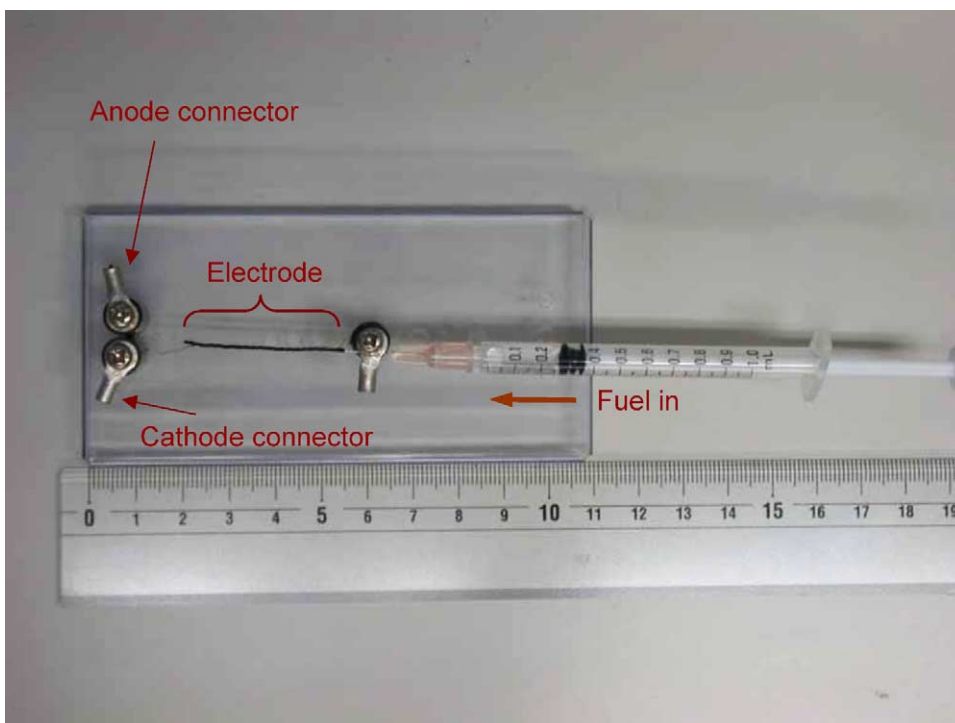


Fig. 5. A photograph of a micro tubular DMFC single cell.

The performance obtained in this study did not reach the level obtained by the brushing method [7]. This would be because the active surface area of the Pt cathode prepared by the plating method was smaller than that of Pt cathode formed by the brushing method using Pt black nanoparticles (6.5 nm, $24 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$; HiSPEC-1000, Johnson-Matthey Fuel Cells) [12]. However, the morphologies of the deposited Pt 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.

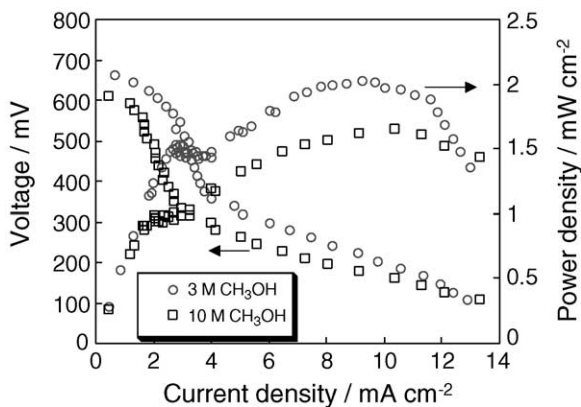


Fig. 6. Performance of a micro tubular DMFC single cell (fuel: 3 M and 10 M CH_3OH ; passive and air breathing).

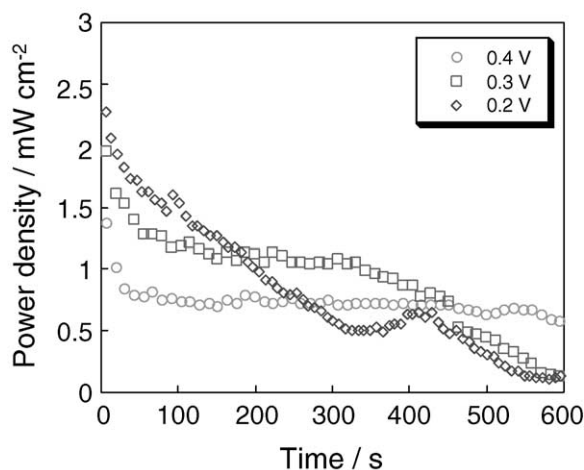


Fig. 7. A short-term stability test of a micro tubular DMFC single cell under passive and air breathing conditions at room temperature in 3 M CH_3OH .

4. Conclusions

A new plating process was successfully developed for the fabrication of a micro tubular DMFC cathode. The thin porous layer of Pt electrocatalyst was firstly selectively formed onto a tubular polymer electrolyte membrane by chemical reduction of Pt complex impregnated in the membrane. After that, electroplating was made to control the loading amount and size of the Pt catalyst particles. The

deposited Pt catalyst layer was obtained around 10 nm in particle size with the thickness of 12 μm . The performance of the micro tubular DMFC single cell with a 6 mg-Pt cm^{-2} cathode was 2 mW cm^{-2} under passive and air breathing conditions at ambient temperature and pressure. Further work aims to spread this method for preparing the micro tubular DMFC anode. The plating technique is attractive as a promising method for forming the micro tubular DMFC on a mass production.

Acknowledgement

One of the authors, M. Kunimatsu wishes to acknowledge the NEDO (New Energy and Industrial Technology Development Organization) fellowship program for its financial support.

References

- [1] J. Han, E.S. Park, *J. Power Sour.* 112 (2002) 477.
- [2] H. Chang, J.R. Kim, J.H. Cho, H.K. Kim, K.H. Choi, *Solid State Ionics.* 148 (2002) 601.
- [3] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, *J. Power Sour.* 117 (2003) 22.
- [4] C.Y. Chen, P. Yang, *J. Power Sour.* 123 (2003) 37.
- [5] D. Kim, E.A. Cho, S.A. Hong, I.H. Oh, H.Y. Ha, *J. Power Sour.* 130 (2004) 172.
- [6] K. Ishida, T. Okada, M. Ishida, *Electrochemistry* 70 (2002) 975.
- [7] K. Kunimatsu, T. Okada, *Electrochem. Solid-State Lett.* (in press).
- [8] R. Liu, W. Her, P.S. Fedkiw, *J. Electrochem. Soc.* 139 (1992) 15.
- [9] N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazaki, *Electrochim. Acta* 47 (2002) 4079.
- [10] Y-M. Kim, K-W. Park, J-H. Choi, I-S. Park, Y-E. Sung, *Electrochem. Comm.* 5 (2003) 571.
- [11] T. Toda, H. Igarashi, H. Uchida, M. Watanabe, *J. Electrochem. Soc.* 146 (10) (1999) 3750.
- [12] M.P. Hogarth, T.R. Ralph, *Platinum Met. Rev.* 46 (4) (2002) 146.