Development of a micro tubular DMFC fabricated by plating technique

H. Qiao[a], T. Kasajima[a], M. Kunimatsu[b], and T. Okada[a]

[a]*National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1,Tsukuba, Ibaraki, 305-8565, Japan*
[b]*Kanagawa Industrial Technology Research Institute, kanagawa, 243-0435, Japan*

Introduction

Direct methanol fuel cells (DMFCs) are attractive as a promising candidate of the power supply for portable applications. So far, planar type air breathing DMFCs for portable applications have mostly been reported[1,2]. Despite of these researches, a new design of DMFCs utilizing tubular polymer electrolyte membranes has been successfully demonstrated for application in portable devices in AIST[3]. Now, the micro tubular DMFC single cell formed by the brushing method achieves the power density of 12 mW cm^{-2}[4]. However, the fabrication is rather time-consuming, and needs much skill to attain good contact between the catalyst layer and the membrane.

In the present work, the plating process to fabricate the catalyst layer on the micro tubular polymer electrolyte membrane is studied which is suitable for mass production.

Experimental

The Flemion® tubes (inner diameter 0.3 mm, outer diameter 0.6 mm) were used as polymer electrolyte. For preparing the tubular membrane catalysts composite, impregnation-reduction method(IR method) was carried out[5]. For cathode electrode, Pt catalyst layer was first formed by IR method. After 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 $H_2PtCl_6 \cdot 6H_2O$ and $Pb(CH_3COO) \cdot 3H_2O$. On the other hand, for anode electrode, $[Pt(NH_3)_4]Cl_2$ and $[RuCl(NH_3)_5]Cl_2$ were used as precursor, and PtRu(1:1) catalyst layer was formed on the inside surface of the tubular electrolyte membrane by IR method. The loading amount of PtRu(1:1) was optimized by using a half-cell testing.

The obtained Pt and PtRu catalyst layers were analyzed by XRD. The morphology of catalyst layers was observed by FE-SEM.

The performance of a DMFC single cell was evaluated under passive and air breathing conditions at ambient temperature and pressure.

Results and discussion

1. Characterization of tubular membrane catalysts composite

XRD patterns of Pt and PtRu membrane composites made by IR method are shown in Fig.1. For Pt catalyst layer, since the XRD pattern of Pt(fcc) crystal structure was observed, the formation of Pt particles was confirmed. For PtRu catalyst layer, the XRD pattern was similar to those of Pt. However, peaks were broadened and shifted to the large angle side compared to those of pure Pt. Meanwhile, (100) and (101) peaks of Ru(hcp) were also observed. These results suggest the existence of a mixture of PtRu solid solution and Ru metal. The surface and cross sectional images of Pt and PtRu deposited layers were observed by FE-SEM, and it is found that Pt and PtRu particles are selectively deposited near the outside and inside surface of the tubular electrolyte membrane. The obtained deposited layers are porous with the thickness of 2 μm. The size of Pt and PtRu particles was observed to be around 100 nm.

For cathode electrode, in order to control the loading amount and size of the Pt particles, electroplating was further carried out with the Pt-deposited Flemion® tube. After the electroplating process, the deposited catalyst layer increased to 12 μm in thickness with the Pt particles size of 10 nm.

2. Half cell evaluation of anode electrode

In order to optimizing the loading amount of PtRu catalyst, methanol oxidization polarization curves of anode electrodes were evaluated by using a half-cell. The loading amounts of RtRu were 1.2, 2.8 and 4.3 mg cm^{-2} corresponding to the repetition number of IR process. The methanol oxidization current density increased with increasing PtRu loading amount from 1.2 to 2.8 mg cm^{-2}. When loading amount increased to 4.3 mg cm^{-2}, opposite effect was observed. The reason is considered to be due to the spreading of PtRu particles into the membrane during the repeated IR process[5].

3. Performance of a micro tubular DMFC single cell

Based on above results, a micro tubular DMFC single cell was fabricated by plating method and the performance was evaluated under passive and air breathing conditions at ambient temperature and pressure. As shown in Fig. 2, the maximum of power density attained was 1.4 mW cm^{-2} at 10 mA cm^{-2} using 2 M methanol solution.

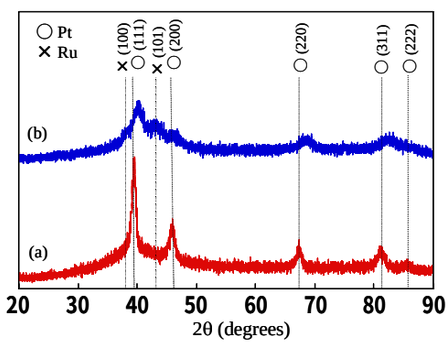

Fig.1 XRD pattern of samples prepared by the IR method. (a) Pt (b) PtRu(1:1) deposited Flemion® films.

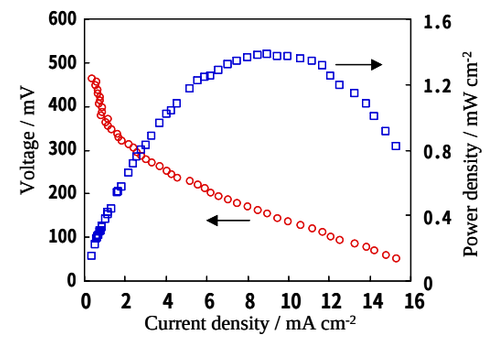

Fig.2 Performance of the micro tubular DMFC single cell (Fuel: 2 M CH_3OH; passive and air breathing).

References

[1] J. Han, E. S. Park, *J. Power sour*., **112**, 477 (2002).
[2] H. Chang, J. R. Kim, J. H. Cho, H. K. Kim, K. H. Choi, *Solid State Ionics*., **148**, 601 (2002).
[3] K.Ishida, T. Okada, M. Ishida, *Electrochemistry*, **70,** 975-979 (2002).
[4] K. Kunimatu, T. Okada, *Electrochemical and Solid-State Letters*, in press.
[5] N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazaki, *Electrochim. Acta*, **47,** 4079 (2002).