

DESIGN OF MULTI-LAYER SPUTTER-DEPOSITED ANODE TO REDUCE CATALYST LOADING FOR LIQUID DMFC

Hiroyuki Saito, Tsuneyoshi Nakashima, Katsuki Nakase, Masao Sudoh

Abstract:

Superior catalyst utilization of direct methanol fuel cells (DMFCs) may be obtained by localized catalyst loading on reaction sites. The objective of this work is to improve the catalyst utilization by multi-layer structure and reduction of loading catalyst. Multi-layer anode consisted of sputter-deposited Pt-Ru catalyst layer and the support layer of Nafion-carbon-Isopropanol ink (NCI). Single layer anode consisted of sputter-deposited Pt-Ru catalyst layer and the layer of carbon-glycerin ink (CG). Multi-layer (1~4 layers) and single-layer (0.04, 0.10 and 0.24 mg cm⁻²) were evaluated by using electrochemical measurement and SEM images. Three-layer anode provided 50.9 W g⁻¹, 3.4 times as mass activity of conventional paste method anode. Methanol residues stripping voltammetry revealed that electrochemical surface area (ECSA) was increased with the number of layers. Additionally, single-layer anode (0.04 mg cm⁻²) provided over 150 W g⁻¹. These results suggested that reduction of loading catalyst per unit layer and multi-layer structure enhanced catalyst utilization.

Keywords: liquid DMFC, low catalyst loading, sputter-deposition, multi-layer anode.

1. Introduction

Liquid Direct Methanol Fuel Cells (l-DMFCs) is prospective as power source for portable application because of high energy density and simple structure. However the catalyst is very expensive and it is necessary to reduce the amount of catalyst and to improve catalyst utilization. These may be realized in a sputter-deposited electrode with only active reaction sites [1]. In the previous works, sputter-deposited Pt cathode with Nafion-carbon-butyl acetate (NCB) layer showed high mass activity for oxygen reduction [2]-[4].

Mass activities could be improved by preparation of thin catalyst layer and an increase in ratio of catalyst contacted with a protonic conductor. Such a thin layer and low loaded catalyst layer could be prepared by sputtering method. In this study, multi-layer anodes and single-layer anodes with sputter-deposited Pt-Ru with NCI or CG ink were investigated electrochemically at anodes for l-DMFC to clarify effect on the mass activity and reaction sites [5].

2. Experimental

The multi-layer anodes were prepared by sputtering Pt-Ru and spreading NCI ink, which consisted of 5 wt% Nafion solution (Wako Pure Chemical Industries), carbon powder (Vulcan XC72R) and Isopropanol (Wako Pure Che-

mical Industries, > 99 %). First, NCI ink was spread on the carbon paper TGPH-90 (Toray) and drying at 333 K. Second, Pt-Ru catalyst was loaded on carbon paper TGPH-90 by sputtering method (ULVAC, RFS-200). These processes were repeated 1 to 4 times and multi-layer anodes were prepared. The total amount of Pt-Ru loading were 0.24 mg cm⁻² in all multi-layer anodes. The amount of loading catalyst in each layer of n layers anode; 0.24/n mg cm⁻². For example, the amount of loading catalyst in each layer of 3 layers anode; 0.08 mg cm⁻². The single layer anodes were prepared to investigate effects of the amount of catalyst loading by sputtering Pt-Ru and spreading CG ink, which consisted of carbon powder and glycerin (Wako Pure Chemical Industries). First, CG ink was spread on the carbon paper TGPH-90 and drying at 573 K. Second, Pt-Ru catalyst was loaded on carbon paper TGPH-90 by sputtering method. The amount of loading catalyst were 0.04, 0.10 and 0.24 mg cm⁻².

The paste method anode was prepared by spreading the mixture, which consisted of Pt-Ru/C (Tanaka Kikinzo-kogyo) and 5 wt% Nafion solution dispersed by n-butyl acetate (Wako Pure Chemical Industries, 99 %), on the carbon paper TGPH-90 and drying at 333 K. This process was repeated to achieve the Pt-Ru loading of 2.0 mg cm⁻².

The paste method cathode was prepared by spreading the mixture, which consisted of Pt/C (Tanaka Kikinzo-kogyo) and 5 wt% Nafion solution dispersed by n-butyl acetate, on the carbon cloth with support layer and drying at 333 K. This process was repeated to achieve the Pt loading of 2.0 mg cm⁻².

Nafion 117 (Du pont) used as an electrolyte membrane in DMFC was boiled in 3 wt% hydrogen peroxide (H₂O₂, Wako Pure Chemical Industries, > 30 %) solution for 1 h and rinsed in boiling deionized water for 1 h. Then it was boiled 0.5 mol L⁻¹ sulfuric acid (H₂SO₄, Wako Pure Chemical Industries, > 95 %) for 1 h and rinsed in boiling deionized water for 1 h. The pretreated membrane, the anode and cathode were assembled by hot-pressing them under 398 K and 10 MPa for 2 min to ensure good contact among the cell components.

The schematic diagram of the experimental apparatus is shown in Figure 1. All electrochemical measurements were performed at 338 K. In cell polarization curves studies, 1.0 M methanol solution was supplied at 1.25 mL min⁻¹ into the anode and dry air was supplied at 62.5 mL min⁻¹ into the cathode. In anode impedance and stripping voltammetry studies, humidified hydrogen was supplied at 30 mL min⁻¹ into the cathode that was used as reference electrode [6]. Geometrical area of electrodes were 6.25 cm².

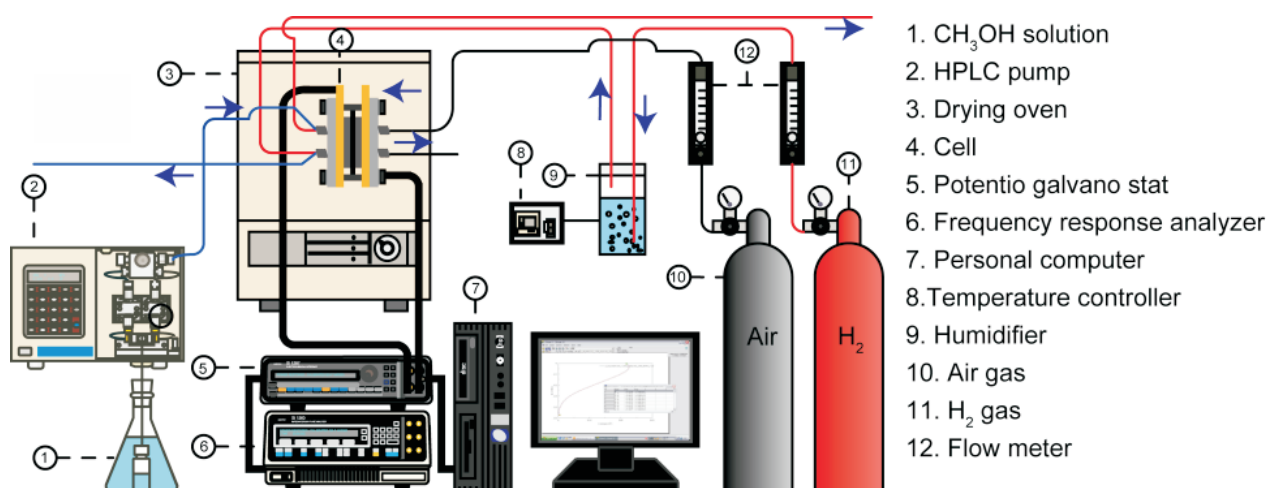


Fig. 1. Schematic diagram of the experimental apparatus.

3. Results and discussion

3.1. SEM images

The cross section of multi-layer anodes (1 layer and 3 layers) observed by SEM were given in Figure 2. Pt-Ru particles were located on white lines in Figure 2. A number of white lines were observed in cross section of 3 layers anode (Figure 2 (b)). It could be confirmed that Pt-Ru multi-layer structure was formed by repeating process of spreading NCI ink and sputtering Pt-Ru. A sputtering method was well suited to form thin catalyst layer and to deposit catalyst locally. Multi-layer structure by using sputtering method enables to build thin catalyst layer and there was a possibility that ohmic resistance and mass transfer resistance were decreased.

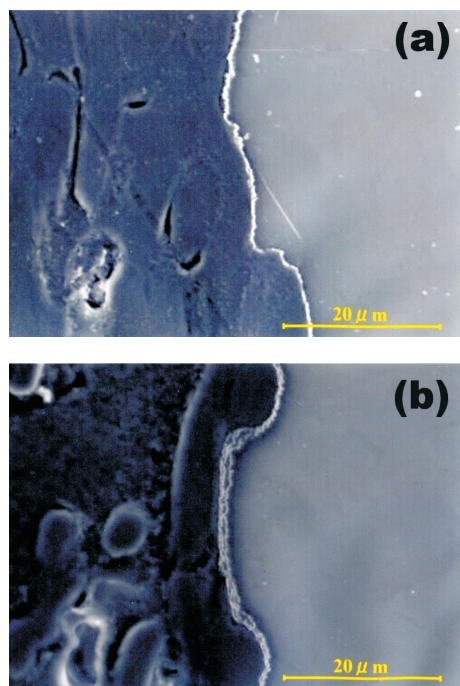


Fig. 2. SEM images of multi-layer anodes. (a) mono-layer anode, (b) three-layer anode.

3.2. Electrochemical measurements

Figure 3 shows mass activity of multi-layer anodes and paste method anode to evaluate the catalyst utilization

efficiency. In comparison of mass activity with multi-layer and paste method anode, all multi-layer anodes had higher mass activity than paste method anode. Mass activity of 3 layers anode was the highest (50.9 W g⁻¹) and it was approximately 3.4 times higher than that of paste method anode. These result may suggest that an increase in active Pt ratio in multi-layer anodes. The number of layers affected on mass activity in multi-layer anodes. Pt-Ru was only active as a catalyst when it was in contact with the electrolyte, conductive support and fuel. To increase the number of layer divided catalyst layer by Nafion as electrolyte and carbon as conductor. This may reduce inactive catalysts with an increase in amount of Pt-Ru contacted with Nafion and carbon. However, 4 layers anode had lower mass activity than 3 layers anode. There was a possibility that mass transfer was inhibited by permeating large amount of NCI ink into substance.

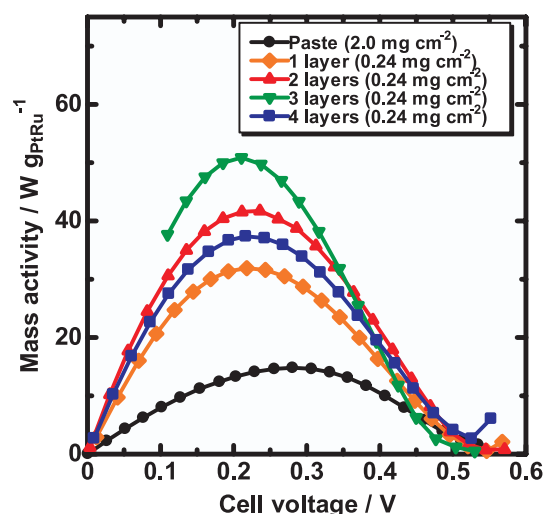


Fig. 3. Mass activity (V-W curves) for multi-layer anodes and paste method anode.

A comparison of the *in situ* stripping behavior of adsorbed methanol residues for multi-layer anodes was shown in Figure 4. The potential of the stripping peaks were almost equivalent in all multi-layer anodes. The Electrochemical surface area (ECSA) for anodic catalyst is calculated by using the following equation [7].

$$\text{ECSA (m}^2 \text{ g}^{-1}\text{)} = \frac{\text{charge area (}\mu\text{C cm}^{-2}\text{)}}{10 \times 420 (\mu\text{C cm}^{-2}) \times \text{catalyst loading (mg cm}^{-2}\text{)}} \quad (1)$$

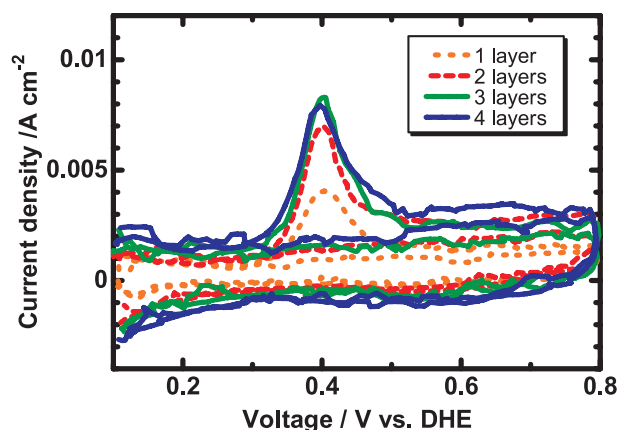


Fig. 4. In situ stripping voltammetry of methanol residues at multi-layer anodes.

The ECSA data for the multi-layer anodes calculated from Eq. 1 are summarized in Table 1. ECSA increased as the number of layers increased. In spite of same catalyst loading, 4 layers anode had ECSA about two times 1 layer anode. As a result, division of catalyst layer was effective to increase ECSA and to reduce size of Pt-Ru particle for sputtering method.

Table 1. ECSA data for multi-layer anodes.

	1 layer	2 layers	3 layers	4 layers
ECSA (m ² g ⁻¹)	9.32	15.84	18.85	20.14

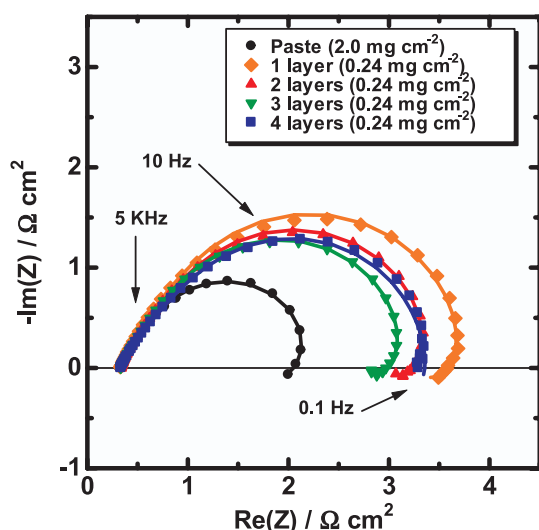


Fig. 5. Nyquist plots for multi-layer anodes and paste method anode. Plots; experimental data, lines; fitting data. Loading current density; 40 mA cm⁻².

Effects of the number of layers on anodic polarization were further investigated by AC impedance analysis at 40 mA cm⁻². Nyquist plots shown in Figure 5 were analyzed using an equivalent circuit given by Figure 6 [8] and impedance parameters were summarized in Table 2. Here,

R_m represents the resistance of membrane, and R_1 and C_1 are charge transfer resistance and double layer capacitance, respectively. R_2 and CPE_1 are related to mass transfer. L_1 is related to the adsorbed inter mediate. The fitting data well agreed with experimental data. At high and medium frequency region, the arcs of 2, 3 and 4 layers anodes were smaller than that of 1 layer anode. In Table 2, R_1 was decreased and C_1 was increased as the number of layers increased. These results showed enhancement of three phase boundary by multi-layer structured. However, mass transfer resistance R_2 of 4 layers anode was larger than other multi-layer anodes. It seems that permeating large amount of NCI ink into substance caused increase of R_2 and cell performance decreased. Figure 7 shows mass activity of single-layer anodes to evaluate the catalyst utilization efficiency. Mass activity of single layer anodes was increased with decreasing amount of loading catalyst. Mass activity of single-layer 3 (0.04 mg cm⁻²) was over 150 W g⁻¹. ECSA data for single layer anodes are summarized in Table 3. In the same manner as mass activity, ECSA was increased with decreasing the amount of loading catalyst. These results suggested that size of Pt-Ru particle was decreased and active site was increased by reduction of the amount of loading catalyst.

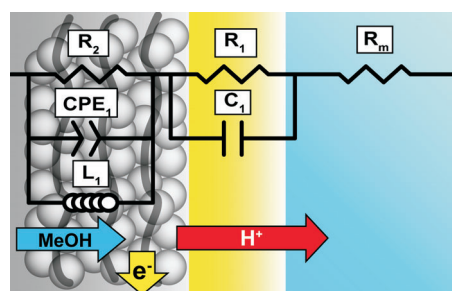


Fig. 6. Equivalent circuit of anode polarization.

Table 2. Impedance parameter of multi-layer anodes.

	1 layer	2 layers	3 layers	4 layers
R_1 (Ωcm ²)	2.977	2.674	2.488	2.275
R_2 (Ωcm ²)	0.5142	0.5193	0.4889	0.7835
C_1 (mF cm ²)	4.882	7.906	11.56	16.87

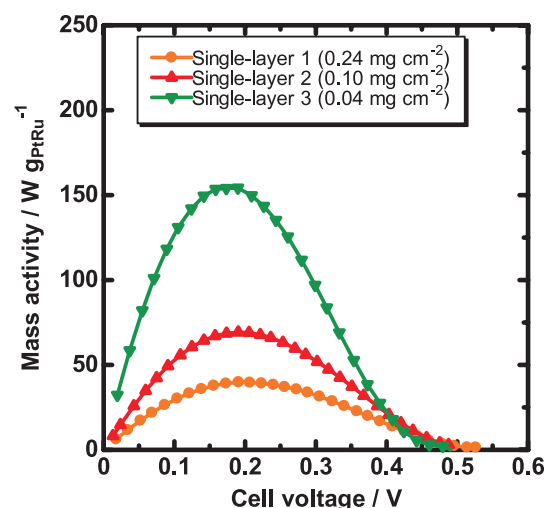


Fig. 7. Mass activity (V-W curves) for single-layer anodes.

Table 3. ECSA data for single-layer anodes.

	Single 1 layer	Single 2 layers	Single 3 layers
Loading catalyst (mg cm ⁻²)	0.24	0.10	0.04
ECSA (m ² g ⁻¹)	17.32	34.35	79.85

4. Conclusion

SEM cross section images clarified that thin multi-layer structure was formed by repeating process of spreading NCI ink and sputtering Pt-Ru. In 3 layers anode, mass activity by sputtering method was 3.4 times higher than that by paste method. ECSA increased with increasing number of layers. AC impedance analysis clarified that charge transfer resistance was reduced and double layer capacitance was increased by the increment of the number of layers. Reduction of the amount of loading catalyst per unit layer enhanced mass activity and ECSA.

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