High Performance PEFCs with Sputter-Deposited Pt Layer on Low-Pt-Loading Electrode

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A small amount of platinum (Pt) electrocatalyst (0.05 mg/cm^2) was additionally deposited on the front surface of low-Pt-loading electrode ($20\% \text{ Pt/C}$, 0.4 mg/cm^2), utilizing a sputtering deposition technique. The polymer electrolyte fuel cell (PEFC), utilizing this electrode for its cathode, showed an enhanced cell performance when using air at 0.15 MPa as the oxidant gas. This enhancement in cell performance was attributed to improvement in the oxygen reduction reaction (ORR) kinetics, and lead to a 10% increase in its maximum power density, and to a 50 mV cell voltage (corresponding to a 4% increase in LHV energy conversion efficiency) over almost the entire range of operational current densities.

1 INTRODUCTION

The polymer electrolyte fuel cell (PEFC) has been considered as one of the most promising candidates for a primary power source for an electric vehicle. However, higher power density and lower platinum (Pt) electrocatalyst loading on the electrodes, without any significant performance degradation, are still needed for such automotive application to become feasible.

To obtain higher power density, generally, larger amounts of Pt are loaded onto the electrodes; this would enhance electrochemical reaction kinetics. Thus, advanced PEFCs require large amounts of Pt loading electrodes (4 mg/cm^2)^{1,2)}. However, the high Pt electrocatalyst loading is unacceptable for automotive application because of its resultant high cost; thus, low Pt loading has become a constraint for the automotive application of PEFCs. Furthermore, in automotive application, the PEFC should be operated

with air as the oxidant gas, and at lower compression pressure because high air compression pressure imposes a penalty in energy consumption. However, for its part the low air compression pressure will be unfavorable for the kinetics of the electrochemical reaction, i.e. oxygen reduction reaction (ORR).

Therefore, much effort has been directed to reduce the Pt electrocatalyst loading, without an accompanying performance degradation. One of the most effective approaches for achieving low Pt loading while maintaining ORR kinetics is to improve Pt electrocatalyst utilization in the electrode. For that reason, smaller grain size (2 to 3 nm) of Pt particles supported on carbon black particles have been used as the low-Pt-loading electrode³⁻¹³⁾. Another approach is the localization of the Pt electrocatalyst at the reaction site, i.e. the front surface of the electrode, which has been pursued by sputter-depositing Pt on the front surface of the low-Pt-loading electrode^{13,14)}. According to studies addressing such techniques, the sputter-deposited Pt layer has proven to improve ORR kinetics^{13,14)}.

The use of the sputter-deposited Pt on the low-Pt-loading electrode seems preferable for automotive application because of the benefits of higher ORR kinetics to compensate for the low compression pressure of air. In this study, the focus of the

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Table 1 Characteristics of MEAs used in the present study.

MEA#	Anode	Cathode
MEA 1	Pt/C	Pt(sp)+Pt/C
MEA 2	Pt(sp)+Pt/C	Pt(sp)+Pt/C
MEA 3	Pt/C	Pt/C

investigation was placed on the improvement of the PEFC electrode performance caused by the sputter-deposition of Pt.

2 EXPERIMENTAL

2.1 Preparation of Membrane and Electrodes Assemblies

Three types of electrodes were examined for this investigation, (i) the sputter-deposited Pt on the front surface of low-Pt-loading electrode (Pt(sp)+Pt/C), (ii) the low-Pt-loading electrode (Pt/C), and (iii) the sputter-deposited Pt on the uncatalyzed electrode (Pt(sp)). The Pt sputter-deposition was carried out in a low pressure argon environment (2.7 Pa). Sputtering conditions were 1.8 kV acceleration voltage (RF), and 80 mA plate current. The deposition rate was 0.3 $\mu\text{g}/\text{cm}^2/\text{s}$. The amount of the sputter-deposited Pt on the electrodes was 0.05 mg/cm^2 . The Pt/C and the uncatalyzed electrode were purchased from E-TEK, Inc., US. These electrodes have the same carbon cloth, amounts of carbon black loading (4 mg/cm^2), and polytetrafluoroethylene (PTFE) content (50 wt. %). The thicknesses of these electrodes were 350 μm . The amount of Pt loading of the Pt/C was 0.4 mg/cm^2 .

Three different membrane-and-electrodes assemblies (MEAs) are listed in Table 1. All MEAs used the Aciplex®-S 1004 perfluorinated sulfonic acid membrane supplied by the Asahi Chemical, Co. Ltd.; its equivalent weight was 1000, and thickness was 100 μm . All electrodes had an active geometric area of 10 cm^2 . The electrodes were impregnated with a Nafion® solution. The anode and cathode were hot pressed onto the membrane to form the MEAs. The amount of impregnated Nafion® and the hot-press condition were as given in Ref. 15.

2.2 Cell Performance Evaluation and Cyclic Voltammetry

The MEAs were positioned in a single-cell test

fixture, and reversible hydrogen electrode (RHE) was installed on the anode side, as given in Ref. 3. The cell was installed in the test station, and the cell operating conditions (temperature, pressure, and gas flow rates) were set in the test station. In all cell performance evaluations, the cell was operated at a cell temperature of 80°C, and under hydrogen and air, both at 0.15 MPa. The reactant gases were humidified via bubbling through hot water (85°C). The reactant gas flow rates were always at least three times as much as the stoichiometric levels. The electric power from the cell was connected to an electronic load box (Kikusui, Model PLZ152WA), which interfaced with a personal computer to control the current density.

Cyclic voltammetry (CV) was carried out to estimate the electrochemically active surface areas of the electrodes. CV was performed by a potentiostat (Hokuto-Denko, HA-520G), and the potential range and the sweep rate were 0.1 V to 1.1 V vs. RHE and 50 mV/s, respectively. The electrochemically active surface area was obtained from the charge required for hydrogen desorption from the Pt electrocatalyst. For the calculation of the roughness factor, the total charge of hydrogen desorption was assumed to be 210 $\mu\text{C}/\text{cm}^2$ on a smooth Pt surface.

2.3 Morphological Characterization

The dry MEAs were cut and their cross-sections

Fig. 1 Cell voltage vs. current density plots in PEFCs at 80°C, H_2/Air , 0.15 MPa; ◆ MEA 1, ▲ MEA 2, ● MEA 3.

Table 2 Comparison of cell parameters, at 80°C, with H₂/Air gas stream, at 0.15 MPa.

MEA#	E_0	b	R	Anode Voltage vs. RHE (mV)	
	(mV)	(mV/dec.)	(Ω cm ²)	@100mA/cm ²	@300mA/cm ²
MEA 1.	956	52	0.26	9	13
MEA 2	947	41	0.34	12	23
MEA 3	936	57	0.27	7	18

were exposed. Electron probe micro-analysis (EPMA) was conducted to analyze the Pt localization in the cross-sections of MEAs. The EPMA data were recorded in wavelength dispersive mode. Scanning electron microscopy (SEM) was used to examine the surface morphology of the sputter-deposited Pt layer.

3 RESULTS AND DISCUSSION

3.1 ORR Kinetics and Mass Transport Problem with Sputter-Deposited Pt Layer

Figure 1 shows plots of the cell voltage vs. current density for single cells of MEAs 1 to 3. The electrode kinetics, ohmic parameters, and anode overpotentials of these MEAs are tabulated in Table 2. These kinetics and ohmic parameters were analyzed by Equation (1), utilizing the data up to the end of the linear region of the cell potential versus current density,

as applied and shown in Ref. 3.

$$E = E_0 - b \log i - iR \quad (1)$$

It is assumed in Equation (1) that mass transport limitations and activation overpotential at the anode are negligible as compared with those at the cathode. The Tafel slope is represented by b , and R represents the resistance which causes a linear variation of the potential with current density. Using the values and the experimental cell voltage E , the IR-corrected Tafel plots were prepared by plotting $E + iR$ against $\log i$.

According to Fig. 1, the cell voltages of MEA 1 are always higher than those of MEA 3 over the entire operating current density region. The cell voltage of MEA 2, indicates almost the same cell voltage as in MEA 1 at current densities lower than 260 mA/cm². Figure 2 shows the IR-corrected Tafel plots of MEAs 1 and 3. Since the anode voltages vs. RHE of MEAs 1

Fig. 2 IR-corrected cell voltage vs. current density Tafel plots in PEFCs at 80°C; ♦ MEA 1, Δ MEA 3.

Fig. 3 Cyclic voltammograms at 60°C for electrodes; (a) Pt(sp)+Pt/C, (b) Pt/C, (c) Pt(sp).

Table 3 Roughness factors and amount of Pt loadings of electrodes.

Electrode	Amount of Pt Loading (mg/cm ²)	Roughness Factor
Pt(sp)+Pt/C	0.45	165
Pt/C	0.4	113
Pt(sp)	0.05	8

to 3 are all low at 100 mA/cm² (Table 2), the cell voltages are considered to exhibit the cathode voltages vs. RHE in the activation control region. The high cell performance of MEA 1 compared with that of MEA 3 is ascribed to the improvement of ORR kinetics by the sputter-deposited Pt layers (Fig. 2 and Table 2).

Figure 3 shows the cyclic voltammograms for the three types of electrodes: Pt(sp)+Pt/C, Pt/C, and Pt(sp). The roughness factors and the amounts of Pt loading have been tabulated in Table 3. The roughness factor of Pt(sp)+Pt/C was 1.5 times as large as that of Pt/C, although the amount of Pt loading was only 1.1 times. The difference in the roughness factors between the two electrodes was 52 – entirely attributable to the contribution of the sputter-deposited Pt layer of Pt(sp)+Pt/C. Otherwise, the roughness factor of Pt(sp) was 8. Since the amounts of carbon black and PTFE content were the same across these three electrodes, it can be assumed that the gas diffusion characteristics and ohmic resistances in the electrodes also have the same magnitudes. Thus, the difference in the roughness factors of the sputter-deposited Pt between Pt(sp)+Pt/C and Pt(sp) was assumed to be the result of the difference in the utilization of Pt electrocatalyst and/or in the cluster sizes of the sputter-deposited Pt.

According to Fig. 1, at current densities higher than 260 mA/cm², the cell voltage of MEA 2 departs from linearity and begins to drop. MEA 2 shows higher mass transport type overpotential than MEAs 1 and 3.

3.2 Cell Performance Improvement

Comparison of the cell performances among MEAs 1 to 3 are listed in Table 4. The maximum power density of MEA 1 is 1.1 times as large as that of MEA 3. The cell voltage plot of MEA 1, along with its current density, parallels that of MEA 3 (Fig. 1), and

Table 4 Comparison of cell performances.

MEA#	Max. Power Density (W/cm ²)	Energy Conversion Efficiency (LHV) (% @ 500 mA/cm ²)
MEA 1	0.43 (@ 780 mA/cm ²)	56
MEA 2	0.33 (@ 542 mA/cm ²)	52
MEA 3	0.39 (@ 720 mA/cm ²)	52

the cell voltage of MEA 1 is 50 mV higher than that of MEA 3 at the current density of 500 mA/cm². It can be deduced, then, that the energy conversion efficiency has increased 4% for the low heating value (LHV). In MEA 1, the ORR kinetic improvement, together with the lower mass transport type problem, have resulted in good cell performance.

3.3 Electrode Microstructure and Surface Morphology

Pt concentration line profiles of MEA cross-sections measured by EPMA for MEAs 2 and 3 are shown in Fig. 4. For MEA 2, the prominent Pt intensity in the immediate vicinity of the electrode and membrane interface was caused by the sputter-deposited Pt layer. The catalyzed layer of cathode consists of a 40 μ m layer of the low-Pt- loading and a thin (3 μ m) layer of high Pt content. It was considered that this feature caused the better utilization of Pt electrocatalyst as mentioned in Table 3. Figure 5 shows the SEM images of the electrode surface for Pt(sp)+Pt/C and Pt/C. Since these two images were obtained with the same acceleration voltage (20 kV), and the sample currents of these images were almost the same (10 μ A), clear and bright images of Pt(sp)+Pt/C are the result of the presence of sputter-deposited Pt layer. This feature verifies, then, that the sputter-deposited Pt layer covers the surface of the electrodes. At the current density of 300 mA/cm², the anode voltage vs. RHE of MEA 2 is higher than those of MEAs 1 and 3 (Table 2). It is assumed that hindered water transportation through the sputtered layer in the anode caused lower proton conductivity in the membrane, and also caused higher mass transport type overpotential of MEA 2 as mentioned in Section 3.1.

4 CONCLUSION

Fig. 4 Pt concentration line profiles of the MEAs cross-section measured by EPMA.

Fig. 5 SEM images of the electrode surface; (a) Pt(sp)+Pt/C, (b) Pt/C.

Through this work, it was observed the cell performance was enhanced in the PEFC with the use of the sputter-deposited Pt layer on the low-Pt-loading electrode for the cathode, and using air as the reactant gas at a pressure of 0.15 MPa. This feature would be beneficial for automotive applications, where the PEFC should be operated in air at low compression pressure. The estimated cell performance was improved by 10 % in the maximum power density, and there was a 4 %

elevation in the LHV energy conversion efficiency, when compared to the PEFC with low-Pt-loading electrodes for both the anode and the cathode. This cell performance improvement was the result of the improvement in ORR kinetics and the lower mass transport type overpotential when sputter-deposited Pt layer was applied to the cathode but not to the anode. Further investigations are needed to verify the assumption of hindered water transportation in the

sputter-deposited Pt layer.

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