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Short communication

Performance of sputter-deposited platinum cathodes with Nafion and carbon loading for direct methanol fuel cells

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Abstract

One of the difficulties for a direct methanol fuel cell (DMFC) is low catalyst utilization efficiency because a certain amount of Pt loading is inactive as the catalyst. Sputter-deposited Pt electrodes are expected to improve mass activities for oxygen reduction reaction (ORR) compared with those prepared by a conventional method. Meanwhile, mass activities of sputter-deposited Pt cathodes for the ORR decreased with an increase in amount of Pt loading. In this study, the loading of protonic and electronic conductors to improve mass activities of sputter-deposited Pt electrode were investigated as cathodes for DMFCs.

Cathodes prepared by spreading the mixture of Nafion, carbon and butyl acetate (NCB) solution on sputter-deposited Pt showed an increase in current densities and mass activities for the ORR. These may suggest an increase in catalyst active sites. Moreover, results of AC impedance analysis showed a decrease in charge transfer resistance and an increase in double layer capacitance for a sputter-deposited Pt cathode with NCB spread. Consequently, effects of NCB on cathodic polarization were explained by supplying protonic and electronic conduction paths to electrochemically inactive Pt with the oxygen diffusion path maintained. Mass activities were found about fifteen times higher than a Pt/C cathode prepared by a conventional method.

Keywords: Direct methanol fuel cell; Sputter-deposition; Mass activities

1. Introduction

Direct methanol fuel cells (DMFCs) are expected to be alternative power sources to secondary batteries because of high energy density and low environmental loading. DMFCs are required to be low cost for popularization. This may be realized by low catalyst loading and an improvement of mass activities of the catalyst for electrode reactions. For electrodes prepared by a conventional method, which is the preparation by the paste consisted of carbon-supported platinum and ionic conductor such as Nafion, catalyst particles were highly dispersed and catalyst layers were three-dimensionalized. Meanwhile, these electrodes are known as low mass activities because loaded Pt is partially inactive as the catalyst. This may be related to form insufficient reaction sites consisted of supplied gas, proton and electron. Consequently, mass activities could be improved by preparation of thin catalyst layer and an increase in ratio of the catalyst contacted with a protonic conductor. Such a thin and a low loaded catalyst layer could be prepared by a sputtering method.

Several researchers have studied improvements of catalyst utilization efficiency. These included the premixing of ionomer before the loading of the catalyst layer [2–6], Pt loading onto the carbon particles [7,8] and the reduction of Pt particle size by electrodeposition [9–14] and sputter-deposition [1,15–18] onto the membrane and the carbon substrate were reported. Mass activities were, however, insufficiently obtained although these trials were attempted.

The catalyst loading by a sputtering method seems to be an effective method due to easy way of Pt loading control, possibility of ultra-low level loading and possibility of a simple catalyzed process. Although the studies on cathodes as membrane electrode assemblies (MEAs) for proton exchange membrane fuel cells (PEMFCs) [1,16,17] and anodes for DMFCs in sulfuric acid [15,18] catalyzed by a sputtering method were reported, characteristics as cathodes for DMFCs were not clarified in detail.

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In this study, sputter-deposited Pt electrodes were evaluated as cathodes in MEAs for DMFCs. Moreover, the electrodes with ionic and electronic conductors spread on sputter-deposited Pt to obtain high mass activities of the catalyst were compared with an electrode prepared by a conventional method.

2. Experimental

2.1. Preparation of membrane electrode assemblies (MEAs)

The catalyzed Pt cathodes were prepared by a sputtering method (EIKO, IB-3) on the carbon cloths with a supporting layer (E-TEK). The amounts of Pt loading were controlled by various sputtering times. Moreover, the other sputter-deposited Pt cathodes were prepared by spreading the mixture (NCB) solution, which consisted of 5 wt% Nafion solution dispersed by *n*-butyl acetate (Wako Pure Chemical Industries, >99%), carbon powders (Vulcan XC-72) and *n*-butyl acetate (Wako Pure Chemical Industries, >99%). The catalyzed Pt-Ru/C anodes were prepared by spreading the mixture, which consisted of 53.5 wt% Pt-Ru/C (Tanaka Kikinzoku Kogyo) and 5 wt% Nafion solution dispersed by *n*-butyl acetate (Wako Pure Chemical Industries, >99%), on the same carbon cloth as the cathode and then dried at 60 °C. This process was repeated to achieve the Pt-Ru loading of 2.0 mg cm^{-2}. Nafion 117 (Du pont) used as an electrolyte in DMFC cells was boiled in 3 wt% hydrogen peroxide (H_2O_2, Wako Pure Chemical Industries, >30%) solution for 1 h and rinsed in boiling deionized water for 1 h. Then it was boiled in 0.5 mol L^{-1} sulfuric acid (H_2SO_4, Wako Pure Chemical Industries, >95%) for 1 h and rinsed in boiling deionized water for 1 h. The pretreated membrane, the catalyzed cathode and anode were assembled by hot-pressing them under 125 °C and 10 MPa for 2 min to ensure good contact among the cell components.

A paste method, which was the conventional method, was described below for the purpose of comparison with a sputtering method. In this method, the cathode was prepared similarly to the anode described above. The powder of 46.5% Pt/C (Tanaka Kikinzoku Kogyo) was added to Nafion solution dispersed by *n*-butyl acetate at 2:1 in wt%, and dispersed by a supersonic treatment. The mixture was repeatedly spread on the carbon cloth with a supporting layer and dried at 60 °C up to achieving the Pt loading of 0.5 mg cm^{-2}.

2.2. Electrochemical measurements

All electrochemical measurements were performed at 90 °C. Dry oxygen were supplied at 500 mL min^{-1} into the cathode and 2 mol L^{-1} methanol solution vaporized at 200 °C were supplied at 3 mL min^{-1} into the anode. The outlet pressures of the cathode and the anode were regulated at 0.2 and 0.1 MPa, respectively. The reference electrode consisted of a platinum wire which humidified hydrogen was supplied to at 30 mL min^{-1} and 0.1 MPa, which was placed close to the cathode. Geometrical area of all cathodes and anodes prepared by a sputtering method or a paste method were defined to 6.25 cm^2.

The electrochemical properties were amperometrically and galvanostatically measured by the electrochemically measuring system (Scribner Associates Inc, series 890B, Solartron SI 1250, Hokuto Denko HZ-3000 and Solartron SI1287/SI1260).

The surfaces of sputtered-deposited Pt cathodes were observed using Scanning Electron Microscopy (SEM, JEOL, JSM-5600).

3. Results and discussion

3.1. Effects of amount of NCB

Since an increase in Pt loading reduced mass activities [19], Nafion and carbon were added to catalyst layer to enhance more mass activities. This may increase mass activities with an increase in amounts of Pt contacted with Nafion. On the other hand, excess Nafion and carbon may prevent oxygen diffusion, so it is important to investigate optimum amounts of Nafion, carbon and *n*-butyl acetate (NCB) solution loading. Effects of NCB loading on cathodic polarization were compared in Fig. 1. Polarization curves were not influenced by amounts of NCB loading. NCB loading 0.4 mg cm^{-2}, which was used in following experimental data, to Pt loading of 0.04 mg cm^{-2} was found enough to increase current densities.

3.2. Effects of Nafion or carbon

NCB was found possible to increase current densities, but effects of Nafion or carbon on polarization curves might be unclear. Comparison among sputter-deposited Pt electrodes with Nafion and/or carbon are shown in Fig. 2. A sputter-deposited Pt electrode with both of Nafion and carbon was found possible to obtain large current densities compared with a one without

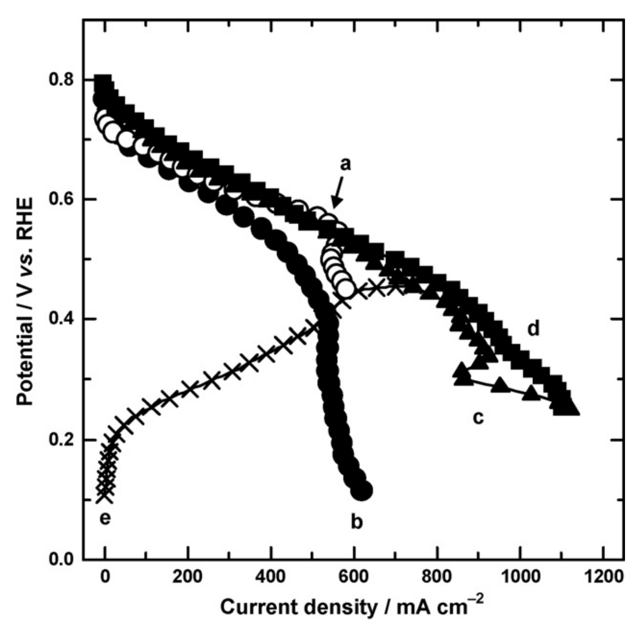

Fig. 1. Cathodic polarization curves for the oxygen reduction reaction on sputter-deposited Pt cathodes with NCB. (a) Paste-loaded Pt electrode of 0.5 mg cm^{-2} (Pt:Nafion:carbon:butyl acetate = 1:2:1:1 in weight), NCB (Nafion:carbon:butyl acetate = 1:1:1 in weight) loading of (b) 0 mg cm^{-2}, (c) 0.8 mg cm^{-2}, (d) 0.4 mg cm^{-2}, (e) anodic polarization for the methanol oxidation reaction.

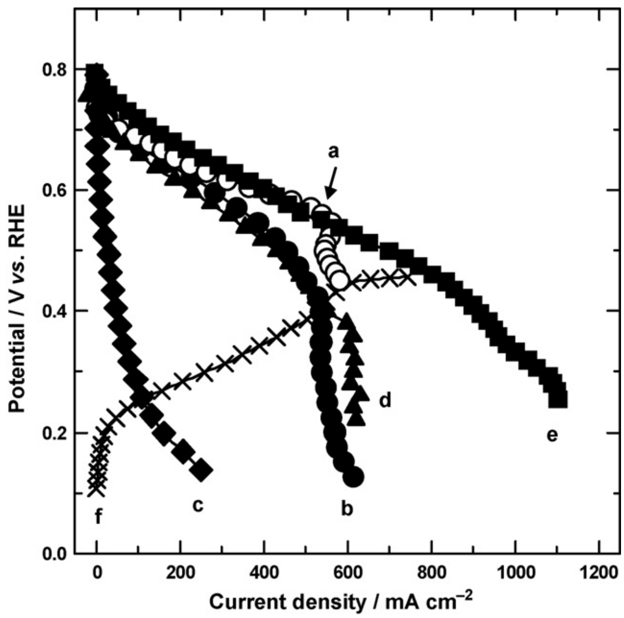

Fig. 2. Cathodic polarization curves for the oxygen reduction reaction on sputter-deposited Pt cathodes (0.04 mg cm^{-2}) with or without Nafion and carbon. (a) Paste-loaded Pt electrode of 0.5 mg cm^{-2} (Pt:Nafion:carbon:butyl acetate = 1:2:1:1 in weight), (b) only sputter-deposited Pt of 0.04 mg cm^{-2}, (c) carbon loading of 0.2 mg cm^{-2}, (d) Nafion loading of 0.2 mg cm^{-2}, (e) carbon and Nafion loading of 0.2 mg cm^{-2}, respectively, (f) anodic polarization for the methanol oxidation reaction.

Nafion and carbon. Meanwhile, a sputter-deposited Pt electrode with only carbon hardly appeared the current densities and a one with only Nafion showed almost same behavior as a one without Nafion and carbon. These results may suggest improvement of protonic and electronic conductivities by added Nafion and carbon.

3.3. *Effects of amounts of Nafion on cathodic polarization*

Effects of NCB with various amounts of Nafion loading to constant carbon loading (0.2 mg cm^{-2}) on cathodic polarization are compared in Fig. 3 in order to optimize [Nafion]/[carbon] (=r) ratio. Various NCB solutions were prepared by changing amounts of Nafion contents with a ratio of carbon and n-butyl acetate fixed. All loadings of sputter-deposited Pt with NCB spread were 0.04 mg cm^{-2}. For $r = 0$, current densities for the ORR hardly appeared because carbon between membrane and sputter-deposited Pt prevented protonic conduction from Nafion membrane. However, current densities increased with an increase in r at range of 0–1. NCB was found possible to increase current densities. These results may suggest that all sputter-deposited Pt were unavailable catalyst even at the low loading of 0.04 mg cm^{-2}. Probably, the surface of the supporting layer used as a substrate in case of preparation of sputter-deposited Pt was not flat, so that a part of sputter-deposited Pt might be separated from Nafion membrane. Meanwhile. for $r = 2$ current densities decreased, suggesting the existence of optimum r. Oxygen diffusion from a backing may be limited by excess Nafion.

Mass activities of catalysts are investigated in Fig. 4 to evaluate the catalyst utilization efficiency. The mass activity is defined

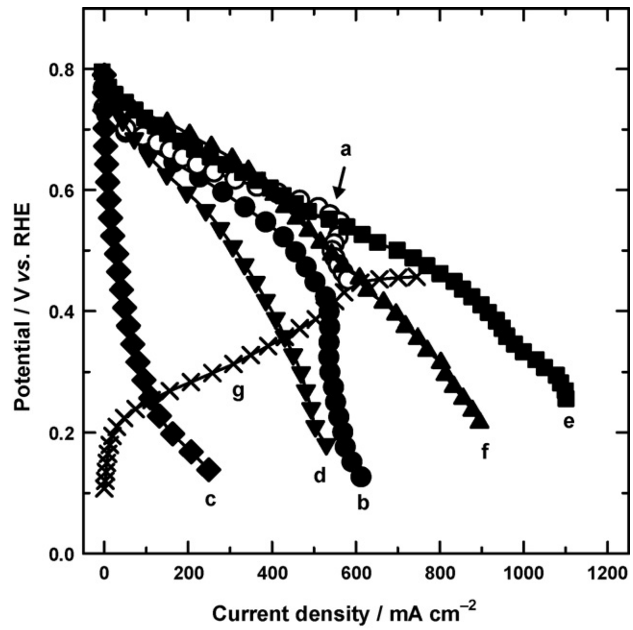

Fig. 3. Cathodic polarization curves for the oxygen reduction reaction on sputter-deposited Pt electrodes with NCB spread of 0.04 mg cm^{-2}. (a) Paste-loaded Pt electrode of 0.5 mg cm^{-2}, $r = 2$, (b) without NCB spread, (c) $r = 0$, (d) $r = 0.5$, (e) $r = 1$, (f) $r = 2$, (g) anodic polarization for the methanol oxidation reaction.

as the current per the mass of the loaded Pt. Mass activities of a sputter-deposited Pt electrode were 10 times higher than those of a paste-spread electrode. Moreover, mass activities at $r = 1$ increased by approximately 1.5 times, suggesting that the catalyst utilization efficiency was improved. The highest mass activity was obtained at Pt loading of 0.01 mg cm^{-2} by Cha and Lee [1] and a maximum power density at that of 0.02 mg cm^{-2} by

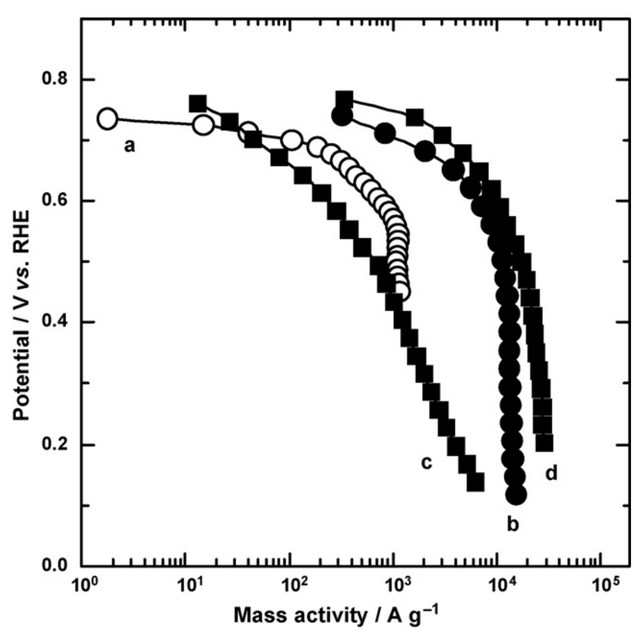

Fig. 4. Mass activity curves for the oxygen reduction reaction on sputter-deposited Pt electrodes. (a) Paste-loaded Pt electrode of 0.5 mg cm^{-2}, $r = 2$, (b) without NCB spread, (c) $r = 0$, (d) $r = 1$.

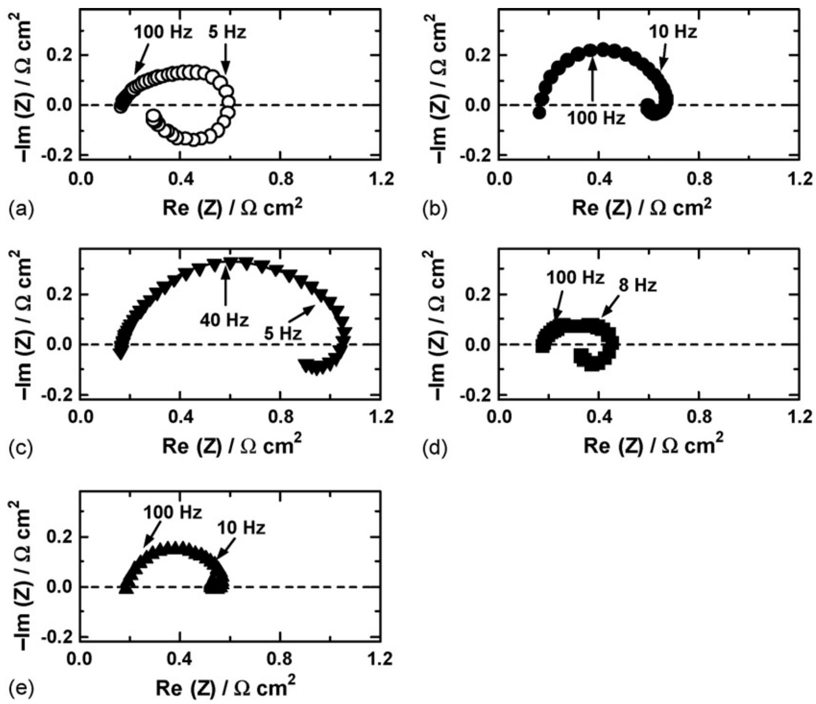

Fig. 5. Impedance plots of sputter-deposited Pt electrodes loaded 0.04 mg cm^{-2} with NCB spread for the oxygen reduction reaction at 200 mA cm^{-2}. Paste-loaded Pt electrode of 0.5 mg cm^{-2} (a) $r=2$, (b) $r=0$, (c) $r=0.5$, (d) $r=1$, (e) $r=2$.

Prinz et al. [17], evaluated as the cathodes consisted of sputter-deposited Pt directly on Nafion membrane for PEMFCs. These disagreements with the highest current density and mass activities obtained at 0.04 mg cm^{-2} in this study may be explained by the difference in substrates for sputter-deposited Pt. Since Nafion surface used as substrates is more smooth than one of a supporting layer on carbon cloths used in this study, small effective surface area in case of Nafion membrane may reduce of cathode performance with an increase in Pt loading. Therefore, substrates with more roughness surface may be suitable due to the formation of Pt layer without agglomerated particles. Taking account of these considerations, NCB may activate sputter-deposited Pt without contact with Nafion membrane, which partially exist in Pt loading of 0.04 mg cm^{-2} on a carbon cloth.

3.4. AC impedance analysis

Effects of amounts of Nafion on cathodic polarization are further investigated by AC impedance analysis at 200 mA cm^{-2}. Cole–Cole plots shown in Fig. 5 are analyzed using an equivalent

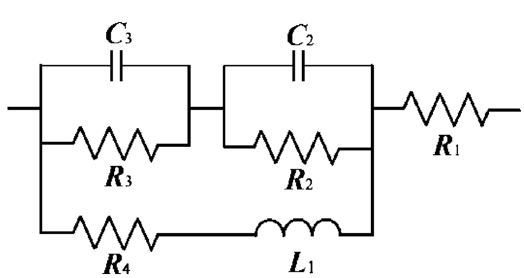

Fig. 6. Equivalent circuit of cathodic polarization at 200 mA cm^{-2}.

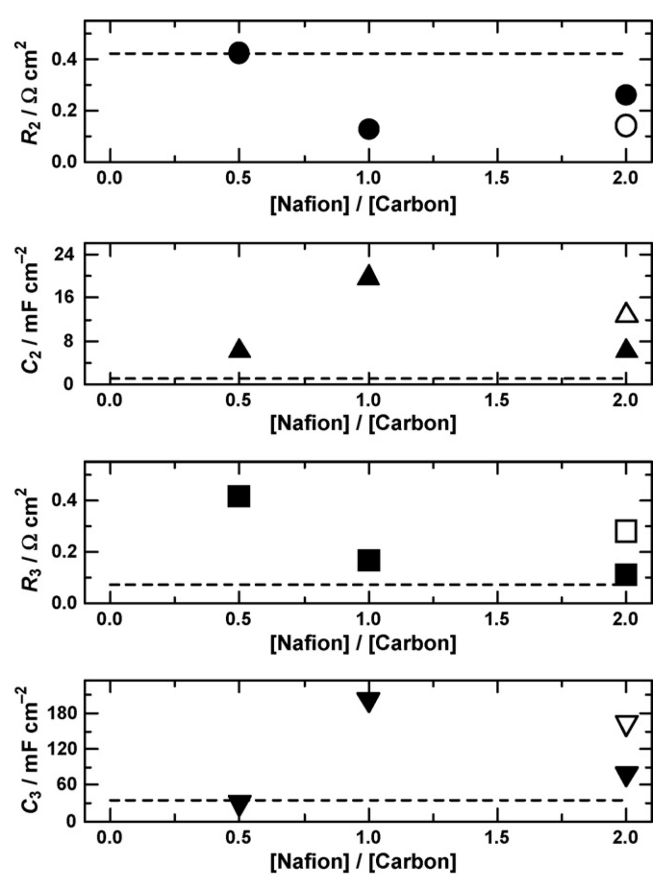

Fig. 7. Impedance parameters of sputter-deposited Pt cathodes with NCB spread compared with a paste-loaded Pt cathode.

circuit given in Fig. 6 [4,20–22] and then impedance parameters are summarized in Fig. 7. Here, R_1 represents an ohmic resistance. R_2 and C_2 are charge transfer resistance and double layer capacitance, and R_3 and C_3 are the diffusion resistance and capacitance related to the adsorbed oxygen. The inductive L_1 and the resistance R_4 are relevant to the adsorbed intermediate. The fitted data well agreed with experimental data. All sputter-deposited Pt electrodes with and without NCB spread and a paste-spread Pt electrode showed two capacitive semicircles at high and medium frequency region. Moreover, an inductive circle appeared at low frequency region. This inductive behavior may suggest that oxygen reduction process involves the adsorbed intermediate [6,9,10]. In the comparison between a sputter-deposited Pt electrode without NCB spread and a paste-spread Pt electrode, sputter-deposited Pt electrodes showed larger R_2 and smaller C_2 than a paste-spread Pt electrode, respectively. Since in general C_2 depends on the surface area and the surface concentrations of the involved species of the electrode reaction [1], the surface area of sputter-deposited Pt contacted with Nafion might be small compared with that of paste-spread Pt. At range of $r = 0.5–1$, R_2 decreased and C_2 of sputter-deposited Pt electrodes with NCB spread increased with an increase in amounts of Nafion. These results of AC impedance measurements agreed with those of cathodic polarization.

4. Conclusion

A cathode prepared by spreading the mixture of Nafion, carbon and butyl acetate solution (NCB) on sputter-deposited Pt increased current densities and mass activities for the ORR. Meanwhile, the excess Nafion over the optimum condition reduced the active sites. Mass activities of the electrode with NCB ($r = 1$) spreaded on sputtered-Pt layer were fifteen times higher than ones of a paste-spread Pt electrode.

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