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Improvement of Mass Activity by Sputter-deposited Platinum Cathodes for Direct Methanol Fuel Cells

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INTRODUCTION

Direct methanol fuel cells (DMFCs) may be expected to be power sources of mobile applications instead of primary or secondary batteries, because of expected high energy density. However, the low Pt loading and improvement of catalyst utilization efficiency may be required since Pt as a catalyst is expensive. These may be realized in a sputter-deposited electrode with an only active Pt. The cathodes catalyzed by a sputtering method have been reported for the H_2/O_2 system [1, 2)], but not for DMFCs. In this study, sputter-deposited Pt electrodes were investigated electrochemically as cathodes for DMFCs and it may be clarified for the effect on the oxygen reduction reaction (ORR) behaviors.

EXPERIMENTAL

The cathodes (the apparent surface area was 2.5×2.5 cm^2) were prepared by the sputtering method on the carbon cloths with a supporting layer. The anode with Pt-Ru loading of 2.0 mg cm^{-2} was prepared by spreading the mixture, which consisted of 53.5 wt% Pt-Ru/C and 5 wt% Nafion solution, on the same carbon cloth as the cathode. The pretreated Nafion 117, the catalyzed cathode and anode were assembled by hot-pressing them under 125 ºC and 10 MPa for 2 min. The paste method was described below for the purpose of comparison. The mixture of 46.5 wt% Pt/C and Nafion was spread on the carbon cloth, corresponding to the Pt loading of 0.5 mg cm^{-2}.

All electrochemical measurements were performed at 90 ºC. Dry oxygen were supplied at 354 mL min^{-1} into the cathode and 2 mol L^{-1} methanol solution vaporized at 200 ºC were supplied at 3 mL min^{-1} into the anode. 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.

RESULTS AND DICUSSION

In order to confirm the effect of the Pt loading on the catalyst utilization efficiency for DMFCs, mass activities defined as the current per the mass of the loaded Pt were compared in Fig. 1. Mass activities of Pt loading below 0.25 mg cm^{-2} were higher than those of the cathode prepared by the paste method, suggesting that the catalyst utilization efficiency was improved. It may be affected by the thick catalyst layer prepared and a large amount of Pt loaded (0.5 mg cm^{-2}) by the paste method compared with the sputtering method. However, for sputter-deposited electrodes, the increase in Pt loading showed reducing the mass activities for the ORR at the whole range of the cathode potential. These results may indicate an increase in electrochemically inactive Pt as the Pt loading increases.

The effects of added Nafion to a catalyst layer on the polarization behaviors were shown in Fig. 2 for the purpose of improving the catalyst utilization efficiency. For the Nafion loading of 0.2 mg cm^{-2}, the maximum current density for the ORR was not affected by the added Nafion. The electrode with the Nafion loading of 0.4 mg cm^{-2} was found possible to increase the activity for the ORR. However, for the electrode with the Nafion loading of 1.2 mg cm^{-2}, the current density for the ORR decreased. This result may suggest that the oxygen diffusion was limited by the added Nafion. These results were further investigated by AC impedance measurements. The results showed that the electrode with the Nafion loading of 0.4 mg cm^{-2} showed the lowest charge transfer resistance and the largest double layer capacitance but the diffusion resistance on the electrode surface increased as the Nafion loading increased. It is considered that the optimum Nafion loading brings about the improvement of the activity for the ORR, but the excess Nafion reduce the active sites over the optimum condition.

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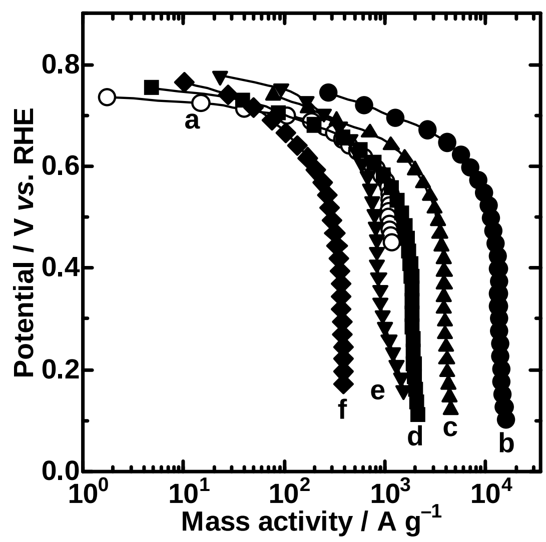

Fig.1 Mass activity for the ORR on sputter-deposited Pt electrodes. (a) paste method, (b) Pt loading of 0.04 mg cm^{-2}, (c) 0.12 mg cm^{-2}, (d) 0.25 mg cm^{-2}, (e) 0.5 mg cm^{-2}, (f) 1.0 mg cm^{-2}.

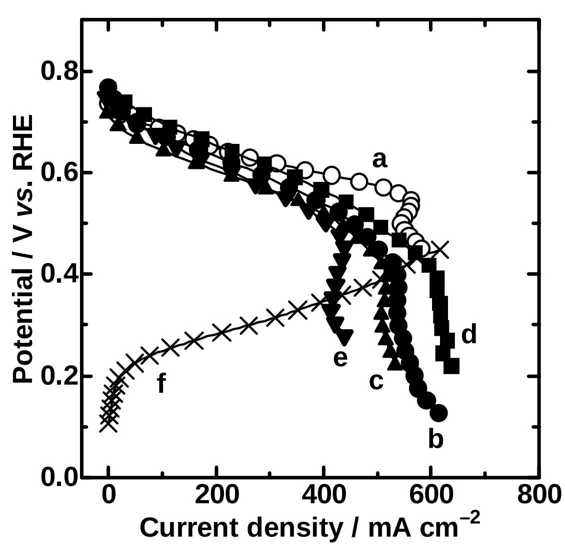

Fig.2 Cathodic polarization curves for the ORR on the sputter-deposited Pt electrodes of 0.4 mg cm^{-2} with various Nafion loadings. (a) paste method, (b) Nafion loading of 0 mg cm^{-2}, (c) 0.2 mg cm^{-2}, (d) 0.4 mg cm^{-2}, (e) 1.2 mg cm^{-2}, (f) anodic polarization for the methanol oxidation reaction.