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Optimization of the sputter-deposited platinum cathode for a direct methanol fuel cell

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Abstract

The electrodes prepared by a sputtering method were evaluated as the cathodes for direct methanol fuel cells (DMFCs). Pt loading below 0.25 mg cm^{-2} achieved higher mass activities than that of 0.5 mg cm^{-2} prepared by the paste method, which was general conventional method. However, an increase in Pt loading reduced the catalyst activity for the oxygen reduction reaction (ORR). This result may suggest an increase in only electrochemically inactive Pt. Pt utilization efficiency can be found about ten times higher at Pt loading of 0.04 mg cm^{-2}. Moreover, addition of Nafion to sputter-deposited Pt cathodes is found possible to improve the catalyst activity for the ORR, but the excess Nafion over the optimum condition reduces the active sites.

Keywords: Direct methanol fuel cell; Sputtering method; Mass activity; Sputter-deposited cathode; Catalyst utilization efficiency

1. Introduction

Direct methanol fuel cells (DMFCs) may be expected to be alternative power sources instead of secondary batteries, because methanol as fuel is directly oxidized on an electrode and have large electrochemical equivalence. However, low amounts of Pt loading and improvement of mass activities are required since Pt used as a catalyst is expensive. A cathode prepared by a paste method which is general conventional method showed low mass activities because of partially inactive catalysts [1–5]. Therefore, optimized preparation of a catalyst layer may be required, improving mass activities without reduction of the catalyst activity. These may be realized by a sputtering method for depositing catalysts due to ease of catalyst loading control, possibility of ultra-low levels loading and possibility of simplification in a catalyzed process. The cathodes catalyzed by sputtering methods have been reported for the H_2/O_2 system [1–3] and the anodes for DMFCs [4,5] by several researchers, but not cathodes for DMFCs. Sputter-deposited Pt cathodes for the H_2/O_2 system indicated that the catalyst utilization efficiency was improved but the performance was low compared with a conventional method (paste method) by spreading the paste consisted of the carbon-supported catalyst and Nafion ionomer. Consequently, improvement of mass activities with sputter-deposited Pt cathodes may not be compatible with the catalyst activity with ones prepared by a paste method.

In this study, oxygen reduction reaction on sputter-deposited Pt electrodes was electrochemically evaluated as cathodes for DMFCs and compared with a cathode prepared by a paste method [6–8]. Moreover, sputter-deposited Pt cathodes optimized for addition of Nafion to catalyst layers were investigated and may be clarified for the effect on the oxygen reduction reaction (ORR) behaviors.

2. Experimental

2.1. Preparation of membrane electrode assemblies (MEAs)

The cathodes were prepared by the sputtering method (EIKO, IB-3) on the carbon cloths with a supporting layer

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(E-TEK). The extents of Pt loading were controlled by various sputtering times. Moreover, the other sputter-deposited cathodes were prepared by spray-treatment of Nafion. The anode was prepared by spreading the mixture, which consists 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) 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) 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.

The paste method, which was the conventional method, was described below for the purpose of comparison. 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 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 pressures at outlet in 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 cathodes and anodes prepared by the sputtering method and the paste method were defined to 6.25 cm^2.

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

The surface of the sputtered-deposited cathodes was observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. The surface investigation of sputter-deposited Pt

The surfaces of sputter-deposited cathode on the carbon cloths observed by SEM were given in Fig. 1. The Pt particles became large from several nanometers at 0.4 mg cm^{-2} to about 1 μm at 1.0 mg cm^{-2} as amounts of Pt loading increased. Since the surfaces of substrates used by the sputtering method were more rough than ones of the flat and smooth Nafion membrane [2,3], it seemed that the sputter-deposited Pt layer also maintained porosity even at Pt loading of 1.0 mg cm^{-2}.

3.2. Effects of amounts of Pt loading on cathodic polarization

In order to confirm the effects of amounts of Pt loading on the oxygen reduction reaction (ORR) for DMFCs, relationship between the potential (versus RHE) and current density (based on apparent geometrical area) were compared in Fig. 2. The potentials for the sputter-deposited electrodes

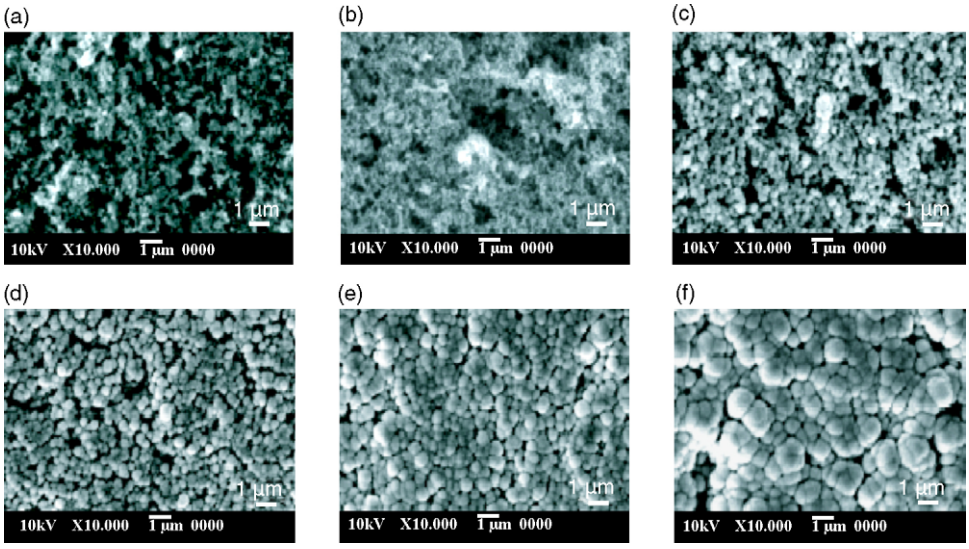

Fig. 1. SEM images of sputter-deposited Pt surface on the carbon cloth with a supporting layer at 10,000 times magnification. (a) No Pt loading (carbon cloth); Pt loading of: (b) 0.04 mg cm^{-2}, (c) 0.12 mg cm^{-2}, (d) 0.25 mg cm^{-2}, (e) 0.5 mg cm^{-2} and (f) 1.0 mg cm^{-2}.