Methanol Oxidation Activities of Pt Oxide Thin Films Prepared by Reactive Sputtering

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Methanol oxidation is the anodic reaction in a direct methanol fuel cell (DMFC). The development of a new catalyst, which can efficiently promote the anode reaction, is very important. In this study, a Pt thin film and two kinds of Pt oxide thin films prepared by reactive sputtering were characterized by XRD, XPS and EPMA, then their methanol oxidation activities were investigated using the rotating disk electrode method in a ($\text{H}_2\text{SO}_4 + \text{CH}_3\text{OH}$) solution. The Pt, PtO and PtO₂ thin films were obtained by sputtering a Pt target in 100% Ar, Ar - 50% O₂ and 100% O₂ plasma, respectively. Neither PtO nor PtO₂ had an excellent activity when the thin films were used as-received. However, an apparent catalytic activity of methanol oxidation was observed in the partially reduced Pt oxide thin films, whose ratios of O/Pt were significantly decreased by passing a cathodic current. On the other hand, the methanol oxidation activity of the Pt thin film was hardly changed by the electrochemical reduction. The methanol oxidation current showed that the electrocatalytic activity of the partially reduced Pt oxide thin films was about hundred times higher than that of the Pt thin film. Therefore, the partially reduced Pt oxide is a material with a significant potential for use as a catalyst for not only the DMFC, but also a fuel cell using the carbon compound as the fuel.

Key Words : Methanol oxidation, Pt oxide, Anode catalyst, Fuel cell

1. INTRODUCTION

The direct methanol fuel cell (DMFC), in which methanol is directly supplied to the anode, has been expected as a new power source for portable computers and mobile phones^{[1][2]}. However, the DMFC has several technical problems. One of the major obstacles to the practical use of the DMFC is the lack of an efficient anode catalyst, which causes a poor power density in the cell. The adsorbed carbon monoxide, which is an intermediate product of the methanol oxidation, restricts the anode reaction rate that lowers the performance of the DMFC^{[3][4]}. At present, minute Pt-Ru particles are the preferred catalyst for the DMFC anode. However, the anode catalyst does not always maintain its original state. The surface composition of the catalyst may change and the chemical binding of the catalyst may change from the metallic to oxide state during operation. Therefore, an understanding of the composition and the surface properties of the catalyst when operating is essential in order to develop an efficient anode catalyst.

The purpose of this study is to clarify the relationship between the oxygen/noble metal ratio of the noble metal oxides as the anode catalyst of the DMFC and their electrocatalytic activities. To specifically explain the idea, the objective is to demonstrate the influence of the O/Pt ratio on the electrocatalytic activity of the Pt oxides. Therefore, a Pt thin film and two kinds of Pt oxide thin films with different compositions were prepared by reactive sputtering^[2] for characterization by XRD, XPS and EPMA. Their methanol

oxidation activities were also measured using a rotating disk electrode in a ($\text{H}_2\text{SO}_4 + \text{CH}_3\text{OH}$) solution.

2. EXPERIMENTAL

2.1 Preparation of sample film

The Pt thin film and two kinds of Pt oxide thin films were prepared on a titanium rod (purity : 99.9 mass%, diameter : 5.0 mm, height : 10.0 mm) by a high frequency magnetron sputtering system (JEOL, JEC-SP360R) in order to investigate their methanol oxidation catalytic activity. The surface of the titanium rod was abraded to a grid size of 1000 using water-resistant emery papers and degreased with acetone in an ultrasonic cleaner. The rod was then placed in a stainless holder in the vacuum chamber of the sputtering system along with a high purity platinum target (purity : 99.99 mass%, diameter : 7.62 mm). The distance between the titanium rod and the platinum target was 60 mm. The reactive sputtering was started after the pressure in the chamber reached 2×10^{-4} Pa. The reactive gas was fed through a mass flow controller and the gas pressure of the chamber was maintained at 2.0 Pa during the sputtering. The Pt thin film was obtained by sputtering of the platinum target in a 100% Ar plasma generated at 100 W. On the other hand, two kinds of Pt oxide thin films with different O/Pt ratios were deposited in a 100% O₂ plasma or 50% Ar - 50% O₂ plasma.

The sputtering products were analyzed by x-ray diffractometer (JEOL, JDX-3530) with Cu K α . The accelerating voltage and the

emission current of the XRD were 40 kV and 40 mA, respectively. The spectra of the products were also measured using x-ray photoelectron spectroscopy (JEOL, JPS9000SX) with Mg K α radiation in order to analyze the chemical binding. The accelerating voltage and the emission current of the XPS were 10 kV and 20 mA, respectively. EPMA (JEOL, JSM-5900LV) using an electron beam of 20 kV was then used to analyze the O/Pt atomic ratio of the products.

2.2 Measurement of methanol oxidation current

Figure 1 shows the rotating disk electrode used for measuring the methanol oxidation current. The titanium rod with the sputtered product was attached to this electrode, and the electrode was attached to a rotating electrode system (Hokuto Denko, HR-200) as shown in Figure 2. The counter electrode and the reference electrode were a Pt spiral and an Ag/AgCl electrode in 3.30 kmol m⁻³ KCl, respectively. A salt bridge was used in order to avoid the bad influence of chloride ions on the working electrode, and all measured potentials were quoted with respect to the normal hydrogen electrode (NHE). The electrolyte solution was 1.0 kmol m⁻³ CH₃OH with 0.5 kmol m⁻³ H₂SO₄, which was deoxidized by bubbl-

ing of a high purity argon. The temperature of the solution was changed from 298 to 323 K, but the rotation rate of the working electrode was fixed at 900 rpm. The anodic polarization curve was measured using a potentiostat (Hokuto Denko, HZ-5000) in the potential range from 0.42 to 1.22 V vs. NHE.

3. RESULTS AND DISCUSSION

3.1 Properties of Pt and Pt oxide thin films

Figure 3 shows photographs of (a) Pt, (b) Pt oxide and (c) Pt oxide thin films prepared by sputtering a Pt target in 100% Ar, Ar-50% O₂ and 100% O₂ plasma, respectively. The color of (a) the Pt thin film was shiny silver-grey, while (b) the Pt oxide thin film prepared by sputtering in Ar-50% O₂ was a dull grey. On the other hand, the color of (c) the Pt oxide thin film changed to a dark brown when the reaction gas was 100% O₂. The composition of the Pt oxide thin film prepared by sputtering in Ar-50% O₂ was determined to be approximately PtO_{0.9}, and that in 100% O₂ was PtO_{2.2} by chemical analysis using EPMA.

Figure 4 shows the x-ray photoelectron spectra of Pt and Pt oxide thin films prepared by sputtering. The spectrum of the Pt

Figure 1 Rotating disk electrode.

Figure 2 Measuring system of methanol oxidation activity.

Figure 3 Photographs of (a) Pt, (b) Pt oxide and (c) Pt oxide thin films prepared by sputtering Pt target in 100% Ar, Ar-50% O₂ and 100% O₂ plasma, respectively.

Figure 4 X-ray photoelectron spectra of Pt and Pt oxide thin films prepared by sputtering.

thin film, whose peak was at the binding energy of 71.4 eV, was smaller than those of the Pt oxide thin films. The binding energy of the spectrum peak for the Pt thin film approximately corresponds to 71.3 eV, the binding energy of metallic Pt^[5]. On the other hand, the spectrum peaks of the Pt oxide thin films prepared by sputtering in Ar-50% O₂ and 100% O₂ were 72.1 and 74.6 eV, respectively. The former corresponds to approximately the binding energy of 72.3 eV for PtO and the latter can be assigned to that of 74.4 eV for PtO₂, which were reported by Abe et al.^[6] It is concluded from the EPMA and XPS analysis results that we can prepare the metallic Pt and two kinds of Pt oxide thin films, PtO and PtO₂, by changing the composition of the reactive gas.

3.2 Activities of Pt and Pt oxide thin films as DMFC anode catalysts

Figure 5 shows the first anodic polarization curves of Pt thin film prepared using 100% Ar. The current density of the Pt thin film obviously increased with the increasing temperature in 0.5 kmol m⁻³ H₂SO₄ + 1.0 kmol m⁻³ CH₃OH. The current density was also very low in the solution without CH₃OH. Therefore, it can be confirmed that the anodic current peaks around 0.9 V vs. NHE are caused by the oxidation of CH₃OH.

Figure 6 shows the second anodic polarization curves of the Pt oxide thin film prepared using Ar-50% O₂, which was identified as PtO by both the XPS and EPMA analysis, in 0.5 kmol m⁻³ H₂SO₄ + 1.0 kmol m⁻³ CH₃OH at 298-323 K. There is a significant difference in the activity of the methanol oxidation current between the Pt thin film in Figure 5 and the Pt oxide thin film in Figure 6. That is to say, the peak current density of the Pt oxide thin film is about 600 mA cm⁻², which is 200 times greater than that of the Pt thin film at 323 K. The current density of the Pt oxide increased and the potential at the peak current shifted to the more positive direction with the increasing temperature.

Figure 5 Anodic polarization curves of Pt thin film prepared using 100% Ar in 0.5 kmol m⁻³ H₂SO₄ + 1.0 kmol m⁻³ CH₃OH at 298 - 323 K.

3.3 Influence of polarization on methanol oxidation activity of Pt oxide thin films

Figure 7 shows the influence of the cycle number of the anodic polarization measurement on the maximum current density of the methanol oxidation for the Pt oxide thin film prepared using Ar-50% O₂ at 298 - 323 K. Although the Pt oxide thin film had only a slight activity for the methanol oxidation during the first polarization, the second or third repetition of the polarization measurement did abruptly increase the methanol oxidation current. However, the current density was tending downward by the fourth repetition or more.

Figure 8 shows the x-ray diffraction patterns of the Pt oxide

Figure 6 Anodic polarization curves of Pt thin film prepared using Ar-50% O₂ in 0.5 kmol m⁻³ H₂SO₄ + 1.0 kmol m⁻³ CH₃OH at 298 - 323 K.

Figure 7 Influence of cyclic number of anodic polarization measurement on maximum current density of methanol oxidation for Pt oxide thin film prepared using Ar-50% O₂ at 298 - 323 K.

thin films prepared on the Ti substrate after the third anodic polarization measurement, where the oxide thin films had the highest current density for the methanol oxidation at 298–313 K. It is noteworthy that there are several peaks from Pt, and not the Pt oxides in the XRD patterns. This result suggests that the Pt oxide thin films were partially reduced to a composition close to the Pt metal. In fact, the EPMA analysis showed that the O/Pt ratios of the Pt oxide thin films prepared using Ar-50% O₂ and 100% O₂ were reduced by repeating the anodic polarization to be 0.14 and 0.37, respectively. These reductions can take place at the beginning of the anodic polarization, where a small cathodic current was observed at the potential of 0.5 V vs. NHE or lower.

Figure 8 X-ray diffraction patterns of Pt oxide thin films prepared on Ti substrate after the third anodic polarization measurement.

Figure 9 Influence of quantity of electricity passed for cathodic reduction on methanol oxidation activity of Pt thin film.

3.4 Influence of cathodic reduction on methanol oxidation activity of Pt oxide thin films

The methanol oxidation of Pt oxide thin films may be activated by passing a cathodic current during the polarization measurement. In the secondary stage, the Pt thin film and two kinds of Pt oxide thin films were electrochemically reduced to investigate the activity of the methanol oxidation.

Figure 9 shows the influence of the quantity of electricity passed for the cathodic reduction on the methanol oxidation activity of the Pt thin film. After the cathodic reduction of -1.0 mA for 100 s intervals, the polarization measurement was repeated in the potential range between 0.62 to 1.2 V vs. NHE to avoid pass-

Figure 10 Influence of quantity of electricity passed for cathodic reduction on methanol oxidation activity of Pt oxide thin film prepared using Ar-50% O₂.

Figure 11 Influence of quantity of electricity passed for cathodic reduction on methanol oxidation activity of Pt oxide thin film prepared using 100% O₂.

ing a useless cathodic current to the sample electrode. The peak current density of the methanol oxidation for the Pt thin film was no more than 1.6 mA cm^{-2} , regardless of the quantity of electricity passed for the cathodic reduction. On the other hand, the methanol oxidation for the two kinds of Pt oxide thin films was significantly activated by the cathodic reduction (See Figure 10 and Figure 11). The peak current density of the Pt oxide thin film prepared in the Ar-50% O₂ plasma increased with the increasing quantity of the cathodic electricity to about 140 mA cm^{-2} at -0.7 C . The current density of about 160 mA cm^{-2} was also observed for the Pt oxide thin film prepared in the 100% O₂ plasma. These current densities of the Pt oxide thin films are nearly 100 times greater than the Pt thin film.

Figure 12 shows the relationship between the cathodic electricity and the peak current densities of the Pt and Pt oxide thin films. It is quite obvious that the cathodic reduction for the Pt thin film hardly influenced the activity of the methanol oxidation. However, the current densities of the methanol oxidation for the Pt oxide thin films were increased with the increasing cathodic electricity up to -0.7 C . By passing the cathodic electricity over -0.7 C , the current densities decreased with the increasing electricity. Based on the SEM observations, the decrease in the current density may be related to the peeling off the specimen film from the Ti substrate.

The total reaction of methanol oxidation can be represented by Equation (1). And the adsorbed CO on the Pt catalyst, which was produced by Equations (2) - (5), acts as a depressor of the methanol oxidation or a catalyst poison^[7]:

Figure 12 Relationship between cathodic electricity and peak current densities of Pt and the Pt oxide thin films.

The surface analysis and the anodic polarization suggest that the electrocatalytic activity of the methanol oxidation is deeply related to the residual oxygen in the partially reduced Pt oxide thin films, because the Pt thin film without oxygen could not efficiently allow the anode reaction. Although neither PtO nor PtO₂ before the partial reduction had an excellent activity, these Pt oxide thin films may have a resistance to the catalyst poison by CO as well as a high activity for the methanol oxidation after the reduction treatment. Therefore, the partially reduced Pt oxide is a significantly active material as a catalyst for not only the DMFC, but also the fuel cell using the carbon compound as the fuel.

4. CONCLUSION

The development of a new catalyst, which can efficiently allow the methanol oxidation, is very important for the practical use of the DMFC. In this study, Pt, PtO and PtO₂ thin films were prepared by sputtering a Pt target in 100% Ar, Ar-50% O₂ and 100% O₂ plasma, respectively. Although neither PtO nor PtO₂ had an excellent activity for the methanol oxidation when the films were as-received, an apparent catalytic activity was observed in the partially reduced Pt oxide thin films. The current density of the methanol oxidation for the Pt thin film was no more than 1.6 mA cm^{-2} , regardless of the cathodic reduction. On the other hand, these current densities of the PtO and the PtO₂ thin films increased to $140\text{-}160 \text{ mA cm}^{-2}$ by the partial reduction of the cathodic current. Moreover, a surface analysis suggests that passing cathodic current decreases the O/Pt ratio in the Pt oxide thin films and the residual oxygen in the thin film plays an important role in the activation for the methanol oxidation.

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