H₂ Oxidation Activity and Tolerance to CO Poisoning of the Electrochemically Reduced Pt Oxide Catalyst

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In order to develop a novel anode catalyst for a PEFC, the Pt thin film and the Pt oxide thin film were produced by reactive sputtering, and the catalytic activity of the H₂ oxidation in the presence of CO or the tolerance to the CO poisoning was evaluated by the anodic polarization in an H₂-saturated H₂SO₄ solution or a (H₂ + CO)-saturated one. The H₂ oxidation activity of the Pt thin film remarkably deteriorated due to the CO poisoning. On the other hand, the electrochemical reduction produced a tolerance to the CO poisoning during the H₂ oxidation of the Pt oxide thin film. For the Pt oxide thin film electrochemically reduced at −0.3 V, the H₂ oxidation current in a (H₂ + 100 ppm CO)-saturated solution remained at the same level as in the H₂-saturated one. The CO stripping voltammetry also revealed that the CO coverage was only 0.15 for the electrochemically reduced Pt oxide thin film although the CO coverage on the Pt thin film was calculated to be 0.95. Therefore, the electrochemically reduced Pt oxide may be a promising anode catalyst of the PEFC having a tolerance to CO poisoning. Moreover, the XPS analysis showed that there was a distinct difference in the chemical bonding state between the Pt thin film and the electrochemically reduced Pt oxide thin film. That is, a large spectrum due to the Pt-O bond was detected for the electrochemically reduced Pt oxide thin film, while the spectrum scarcely appeared for the Pt thin film. These results suggested that the residual oxygen might improve the tolerance to the CO poisoning during the H₂ oxidation of the electrochemically reduced Pt oxide thin film.

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1. Introduction

The polymer electrolyte fuel cell (PEFC) has been expected to be used as the power source for automobiles, home appliances and portable devices because it provides an immediate response for electric generation even at low temperatures, and both the fuel cell efficiency and the power density are higher than those of other fuel cells. However, widespread use of the PEFC would require lowering the cost of the Pt-based catalyst and solving the catalyst poisoning by the CO molecule which is present in the H₂ gas as a fuel. It is a well-known fact that the performance of the PEFC is severely deteriorated by the CO poisoning on the catalyst surface. Therefore, not only the drastic reduction in the amount of the precious metals in the catalyst, but the development of a novel catalyst with a tolerance to the CO poisoning are required.

In addition, the PtRu black is widely used as the anode catalyst for the DMFC because the PtRu black is superior to the Pt black regarding CO tolerance during the methanol oxidation. The CO is an intermediate product of the methanol oxidation reaction. The bi-functional mechanism was proposed as one of the theories that explained the CO tolerance of the PtRu black catalyst. Based on this theory, the adsorbed OH is produced by the oxidation of H₂O on the Ru site at a potential which is lower than that of the Pt site. The absorbed OH is able to promote the oxidation of the absorbed CO on the Pt site contiguous to the Ru site, and readily removes the CO molecule from the Pt site. However, even the PtRu black is not sufficient as the catalyst for the H₂ oxidation in the presence of CO in order to commercialize the PEFC. For that reason, there are several different researches regarding a novel catalyst with a tolerance to the CO poisoning besides the PtRu black. Wang et al. produced a SnO₂-modified PtRu/C catalysts and evaluated the electrochemical activities by CO stripping voltammetry and single cell test. Moreover, Iori et al. and Lin et al. reported the carbon-supported Pt/MoO₃ and Pt/CeO₂ as a CO tolerant catalyst for the PEFC, respectively. However, at this point in time all we can say is that the definitive answer to a demand for developing a novel catalyst for the PEFC has not appeared yet. On the other hand, the previous study by the author et al. revealed that the electrochemically reduced Pt oxide catalyst was a promising anode catalyst for the DMFC. The catalyst might decrease the CO poisoning, which is due to the intermediate product during the methanol oxidation. Therefore, a thoroughgoing investigation on the potential of the electrochemically reduced Pt oxide as the anode catalyst for the PEFC is extremely important.

In this study, the Pt thin film and the Pt oxide thin film were produced by reactive sputtering, and the effect of the electrochemical reduction on the catalytic activity of the H₂ oxidation in the presence of CO was investigated in order to develop a novel catalyst having a tolerance to the CO poisoning. The CO stripping voltammetry and the XPS analysis were also carried out to clarify the CO coverage and the chemical bonding state of the active surface area. Based on the results of these experiments, the cause of the high catalytic activity for the electrochemically reduced Pt oxide thin film was discussed.

2. Experimental

2.1 Preparation of Pt thin film and Pt oxide thin film by reactive sputtering

The test specimens were the Pt thin film and the Pt oxide thin film, which were deposited on a Ti rod (purity: 99.5 mass%, diameter: 5.0 mm, height: 10.0 mm) by reactive sputtering without pre-heating. The surface of the Ti rod was abraded to a grid size of 1200 using waterproof emery papers and degreased with acetone. The Ti rod was placed in the vacuum chamber of a high frequency magnetron
sputtering system (JEOL, JEC-SP360R). The target was a high-purity Pt plate (purity: 99.99 mass%, diameter: 76.2 mm) and the distance between the target and the Ti rod was 60 mm. The reactive gas was fed through a mass flow controller after the pressure in the vacuum chamber had reached $2 \times 10^{-4}$ Pa or less, and the gas pressure was maintained at 2.0 Pa. The Pt thin film was obtained by sputtering of the Pt target in a 100% Ar (purity: 99.99 vol%) plasma generated at 100 W. On the other hand, the Pt oxide thin film was obtained in a 100% O$_2$ (purity: 99.99 vol%) plasma generated at 100 W. After presputtering for 300 s in order to clean the Pt target, the objective thin film was deposited on one side of the Ti rod by standard sputtering for 1.2 ks. Normally the rise in the Ti rod temperature was 10 K or less during the standard sputtering.

The chemical bonding states of the Pt thin film and the Pt oxide thin film were analyzed by X-ray photoelectron spectroscopy (KRATOSANALYTICAL, AXIS-ULTRA) with Al Kx radiation operated at a 15 kV accelerating voltage and 10 mA emission current. The photoelectron spectra of the C1s, O1s and Pt4f levels were measured. The measured spectra were analyzed by wave separation based on the Lorentz-Gauss mixed function after the charge correction of the spectra using the binding energy of the C1s level. Moreover, the O/Pt atomic ratios of the Pt thin film and the Pt oxide thin film were quantitatively analyzed by an electron micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). The intensity of the micro-probe analyzer connected to a wavelength dispersion type spectrometer (JEOL, JXA-8230). Moreover, the O/Pt atomic ratio of the Pt thin film and the Pt oxide thin film were calculated by the corrected values using the ZAF method.

### 2.2 Evaluation of H$_2$ oxidation activity by anodic polarization

The Pt thin film and the Pt oxide thin film were electrochemically reduced and their H$_2$ oxidation activities were evaluated by anodic polarization using a rotating disk electrode. The details of the anodic polarization system have been described in a previous study. The Ti rod coated with the Pt thin film or the Pt oxide thin film was attached to a brass holder and covered with an acrylic cap forming a disk electrode having a reaction area of 19.6 mm$^2$. The disk electrode was then placed on a rotating electrode system (Hokuto Denko, HR-202) as the working electrode. The counter electrode and the reference electrode were a Pt black spiral and an Ag/AgCl in 3.30 kmol·m$^{-3}$ KCl, respectively. The electrolytic solution was a 0.50 kmol·m$^{-3}$ H$_2$SO$_4$ at 303 K. The dissolved oxygen was removed from the solution by pure Ar (purity: 99.999 vol%) bubbling and then the solution was saturated with H$_2$ by pure H$_2$ (purity: 99.999 vol%) bubbling. The anodic polarization curve for the Pt thin film or the Pt oxide thin film without reduction was first measured using a potentiostat (Hokuto Denko, HR-202) in the potential range from 0 to 0.60 V vs. NHE at the scan rate of 5 mV·s$^{-1}$. The thin films were then electrochemically reduced by passing a cathodic electric charge in the range of $-0.1$ to $-1.0$ C and the same anodic polarization measurement was repeated. The anodic polarization curve was also measured in a 0.50 kmol·m$^{-3}$ H$_2$SO$_4$ saturated with CO by bubbling of a (H$_2$ + 100 ppm CO) gas in order to clarify the influence of the CO poisoning on the H$_2$ oxidation activity. Moreover, chronoamperometry was carried out in the 0.50 kmol·m$^{-3}$ H$_2$SO$_4$ solutions saturated with CO by bubbling of various (H$_2$ + CO) mixed gases. The change in the H$_2$ oxidation current at 0.05 V vs. NHE was examined for the Pt thin film or the electrochemically reduced Pt oxide thin film. After the evaluation of the H$_2$ oxidation activity by anodic polarization, the chemical bonding state and the O/Pt atomic ratio were then analyzed for the Pt thin film, the Pt oxide thin film and the electrochemically reduced Pt oxide thin film by XPS and EPMA as described in section 2.1.

### 2.3 CO stripping voltammetry

The electrochemically active surface areas of the Pt thin film and the Pt oxide thin film for CO adsorption or H desorption were determined by CO stripping voltammetry. Before and after the electrochemical reduction of the thin films by various cathodic electric charges, the CO stripping voltammetry was carried out in a 0.50 kmol·m$^{-3}$ H$_2$SO$_4$ solution at 303 K, which was previously deoxygenated by pure Ar bubbling. The working electrode was kept at 0.05 V vs. NHE for 5.4 ks in the H$_2$SO$_4$ solution saturated with CO by bubbling of a Ar-0.10 vol% CO (Taiyo Nissan) gas with the object of adsorbing the CO molecules on the electrode surface, and the dissolved CO was then removed from the solution by pure Ar (purity: 99.999 vol%) bubbling for 1.8 ks. After the CO adsorption, the linear sweep voltammetry in the potential range from 0 to 1.30 V vs. NHE was repeated twice at the sweep rate of 10 mV·s$^{-1}$. The electrochemically active surface area for CO adsorption, $S_{CO}$, was estimated by the difference in the anodic current between the first voltammogram and the second one. The electrochemically active surface area for H desorption, $S_{H}$, was also calculated from the anodic current peak in the potential range from 0.05 to 0.30 V vs. NHE, which was due to the desorption of hydrogen from the surface.

### 3. Results and Discussion

#### 3.1 Chemical bonding states of Pt thin film and Pt oxide thin film

Figure 1 shows the X-ray photoelectron spectra of the Pt thin film and the Pt oxide thin film produced by reactive sputtering. Two distinct peaks of 71.28 and 72.28 eV could be observed in the spectrum of the Pt4f$^{7/2}$ level for the Pt thin film produced in 100% Ar plasma. The former peak was attributed to the binding energy of 71.3 eV for metallic Pt and the latter was close to the binding energy of 72.3 eV for PtO. In addition, the latter intensity was considerably weaker than the former one. Therefore, it was estimated that the thin film produced in the 100% Ar plasma was primarily composed of metallic Pt. On the other hand, there were three peaks of 71.30, 71.99 and 73.89 eV in the spectrum of the Pt4f$^{7/2}$ level for the Pt oxide thin film produced in the 100% O$_2$ plasma. The peak of 71.30 eV agreed with metallic Pt but the intensity was quite low. The peaks of 73.89 and 71.99 eV were attributed to PtO and PtO$_2$, respectively. Moreover, the peak of 73.89 eV was fairly larger than that of 71.99 eV.
Consequently, the Pt oxide thin film produced in the 100% O₂ plasma was composed of PtO and PtO₂, and the PtO₂ was the core of the thin film.

3.2 Effect of electrochemical reduction on H₂ oxidation activities of Pt thin film and Pt oxide thin film

Figure 2 shows the anodic polarization curves of Pt thin film at various electrode rotation rates in 0.5 kmol·m⁻³ H₂SO₄ solutions (a) without H₂ and (b) with H₂ at 303 K. The anodic current of the Pt thin film was extremely low and independent of the rotation rate of the electrode in a 0.5 kmol·m⁻³ H₂SO₄ solution (a) without H₂. On the other hand, the anodic current sharply increased with the increasing electrode rotation rate in a 0.5 kmol·m⁻³ H₂SO₄ solution (b) with H₂. The anodic current reached the maximum value around 0.15 V vs. NHE and it took on the aspect of a diffusion limited current density at that potential or higher. From the data given in Fig. 2, it was concluded that the anodic current was due to the following H₂ oxidation:

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad (1) \]

Figure 3 shows the Levich plot of the H₂ oxidation current at 0.40 V vs. NHE for the Pt thin film and Pt oxide thin film in a 0.5 kmol·m⁻³ H₂SO₄ solution with H₂ at 303 K. The corresponding equation for the limiting current density, \( i \), developed by Levich is described as follows:\(^{17}\)

\[ i = \frac{0.62nFAD^2/3}{\bar{\nu}^{1/6}C^2_0\omega^{1/2}} \]

where \( n, F, A \) and \( D \) are the electron number of the reaction, Faraday's constant (96485 C·mol⁻¹), electrode reaction area (cm²) and diffusion constant of reactant (cm²·s⁻¹), respectively. Moreover, \( \bar{\nu}, C_0 \) and \( \omega \) are the kinematic viscosity of the solution (cm²·s⁻¹), bulk concentration of reactant (mol·cm⁻³) and angular velocity of electrode (s⁻¹), respectively. The plot of the H₂ oxidation current, \( i \), vs. the square root of the electrode rotation rate, \( \omega^{1/2} \), revealed a linear relationship, which approximately passed through the origin, for both thin films. Therefore, the rate-determining step of the H₂ oxidation could be estimated to be the diffusion of the reactant or H₂ molecule for not only the Pt thin film but also the Pt oxide thin film.

Figure 4 shows the effect of electrochemical reduction on the H₂ oxidation activity for the Pt thin film and Pt oxide thin film. The cathodic electric charge of \( -0.1 \) to \( -1.0 \) C was passed to the working electrode for the electrochemical reduction. After each electrochemical reduction of \( -0.1 \) C, the anodic polarization in the range of 0–0.6 V vs. NHE was carried out on the partially reduced thin films in order to evaluate the H₂ oxidation activity. The net current for the H₂ oxidation at 0.40 V vs. NHE could be obtained by deducting the anodic current in an Ar-saturated solution from that in an H₂-saturated solution. Consequently, the net H₂ oxidation current of the Pt thin film was slightly higher than that of the Pt oxide thin film. Moreover, the H₂ oxidation current of the Pt thin film was scarcely changed by passing the cathodic electric charge of \( -0.1 \) to \( -1.0 \) C. This figure also clearly showed that the electrochemical reduction had only a slight influence on the H₂ oxidation activity of the Pt oxide thin film. The previous study of the Pt oxide thin film\(^{8,9}\) revealed that the electrochemical reduction had a significant influence.
on the oxidation activity of methanol and ethanol. However, it was clear from Fig. 4 that the electrochemical reduction to the Pt oxide thin film had no effect on the catalytic activity of the H₂ oxidation, which occurred alone.

Figure 5 shows the influence of the CO poisoning on the H₂ oxidation current for (a) Pt thin film and (b) Pt thin film electrochemically reduced at −0.3 C. While the H₂ oxidation current of the Pt thin film was about 3 mA cm⁻² in the H₂-saturated H₂SO₄ solution, the current decreased to 1 mA cm⁻² or less in the (H₂ + 100 ppm CO)-saturated H₂SO₄ solution. The decrease in the H₂ oxidation current by changing the solution could be interpreted as the influence of CO poisoning on the Pt surface. For the Pt thin film electrochemically reduced at −0.3 C, the H₂ oxidation current was the same for the Pt thin film without reduction, or about 3 mA cm⁻² in the H₂-saturated H₂SO₄ solution. The H₂ oxidation current decreased to about 0.8 mA cm⁻² in the (H₂ + 100 ppm CO)-saturated H₂SO₄ solution. Therefore, the influence of the CO poisoning on the H₂ oxidation activity of the Pt thin film may be slightly strengthened by the electrochemical reduction.

Figure 6 shows the influence of the CO poisoning on the H₂ oxidation current for (a) Pt oxide thin film and (b) Pt oxide thin film electrochemically reduced at −0.3 C. The H₂ oxidation current of the Pt oxide thin film, which was about 2.5 mA cm⁻², was slightly lower than that of the Pt thin film shown in Fig. 5. The current peaks, which might be due to the H desorption, were also observed in the anodic
polarization curve of the Pt oxide thin film. However, the CO poisoning was confirmed even on the Pt oxide thin film because the H₂ oxidation current decreased to 1.0 mA·cm⁻² or less in the (H₂ + 100 ppm CO)-saturated H₂SO₄ solution. On the other hand, the electrochemical reduction at −0.3 C significantly reduced the influence of the CO poisoning on the Pt oxide thin film. To put it accurately, the H₂ oxidation current was maintained at a fixed level, or about 2.5 mA·cm⁻², in both the H₂-saturated and (H₂ + 100 ppm CO)-saturated H₂SO₄ solutions. Therefore, it could be concluded that the electrochemical reduction gave the Pt oxide thin film a tolerance to the CO poisoning during the H₂ oxidation, which was never observed on the Pt thin film with and without electrochemical reduction.

Figure 7 shows the influence of the CO poisoning on the fluctuations in the H₂ oxidation current at 0.05 V vs. NHE for (a) Pt thin film and (b) Pt oxide thin film electrochemically reduced at −0.3 C (303 K, 0.5 kmol·m⁻³ H₂SO₄, 900 rpm).

3.3 Active surface area and CO coverage for Pt thin film and electrochemically reduced Pt oxide thin film

Figure 8 shows CO stripping voltammograms of (a) Pt thin film and (b) Pt oxide thin film electrochemically reduced at −0.3 C in a 0.5 kmol·m⁻³ H₂SO₄ at 303 K. Each stripping voltammogram was measured twice in the potential range from 0 to 1.3 V vs. NHE. However, for the stripping voltammetry of the Pt oxide thin film electrochemically reduced at −0.3 C, the anodic polarization alone was repeated in order to prevent the additional reduction during the cathodic polarization. Since adsorbed CO molecules were on the surface, an anodic current peak was always detected around 0.6–0.9 V vs. NHE in the first voltammogram. The anodic current may be related to the oxidation of the adsorbed CO as follows:

\[
\text{Pt-CO}_{\text{ad}} + \text{Pt-OH}_{\text{ad}} \rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + e^- \quad (3)
\]

where Pt-COₐd and Pt-OHₐd are the adsorbed CO and OH on the active site of the thin films, respectively. For the Pt thin film, the anodic current peak for the CO oxidation completely disappeared and the new current peaks due to the H desorption appeared around 0.05–0.3 V vs. NHE in the second voltammogram. The voltammogram of the Pt oxide thin film electrochemically reduced at −0.3 C was fundamentally similar to that of the Pt thin film. However, there was a significant difference in the current peaks due to the CO oxidation and the H desorption between both thin films. Moreover, the setup potential of the CO oxidation for the Pt oxide thin film electrochemically reduced at −0.3 C was
0.57 V vs. NHE, which was about 60 mV lower than that for the Pt thin film. These data suggested that the CO oxidation of the Pt oxide thin film electrochemically reduced at −0.3 C could proceed easier than that of the Pt thin film. By the way, the electrochemically active surface area for the CO adsorption, $S_{CO}$ (cm$^2$), can be estimated by the following equation:14)

$$S_{CO} = \frac{Q_{CO} \text{ (mC)}}{0.42 \text{ (mC cm}$^2$)}$$  

where $Q_{CO}$ (mC) was related to the CO oxidation and can be calculated as the difference in the anodic current between the first voltammogram and the second one. The electrochemically active surface area for CO adsorption, $S_{CO}$, was 1.45 cm$^2$ for (a) the Pt thin film, while it was 7.98 cm$^2$ for (b) the Pt oxide thin film electrochemically reduced at −0.3 C. That is, the CO stripping voltammetry clarified that the $S_{CO}$ of the Pt oxide thin film electrochemically reduced at −0.3 C was 5.5 times greater than that of the Pt thin film (See Fig. 9(a)).

Moreover, the $Q_{H}$ (C) related to the H desorption was observed in the potential range of 0.05–0.30 V vs. NHE, and the electrochemically active surface area for H desorption, $S_{H}$ (cm$^2$), can be calculated by the following equation:14)

$$S_{H} = \frac{Q_{H} \text{ (mC)}}{0.21 \text{ (mC cm}$^2$)}$$  

It was also obvious that the $S_{H}$ (cm$^2$) of the second voltammogram was higher than that of the first one. The increasing of the $S_{H}$ (cm$^2$) during the second voltammogram could be explained as the result of removing the adsorbed CO from the active surface area during the first one. Therefore, the coverage of the adsorbed CO on the active surface area, $\theta$, might be approximately estimated by the following equation:

$$\theta = \frac{S_{H} \text{ at 2nd (cm}$^2$)}{S_{H} \text{ at 1st (cm}$^2$) - S_{H} \text{ at 1st (cm}$^2$)$$  

where $S_{H}$ at 1st and $S_{H}$ at 2nd were the electrochemically active surface areas for the H desorption calculated from the first voltammogram and the second one, respectively. Consequently, $\theta$ was 0.95 for the Pt thin film. The active surface area of the Pt thin film was low, or $S_{CO} = 1.45$ cm$^2$, and to make matters worse, the greater part of the active surface was covered by the poisoning CO. On the other hand, $\theta$ was 0.19 on the active surface area of the Pt oxide thin film electrochemically reduced at −0.3 C. The active surface area of the electrochemically reduced Pt oxide thin film was 5.5 times greater than that of the Pt thin film. In addition, the CO poisoning could proceed as low as 19% of the active surface area (See Fig. 9(b)). In other words, the Pt oxide thin film electrochemically reduced at −0.3 C had large regions of the active surface area on which the CO poisoning had not yet proceeded.

The chronoamperometry shown in Fig. 7 revealed that the Pt oxide thin film electrochemically reduced at −0.3 C could maintain a higher activity for the H$_2$ oxidation even in the (H$_2$ + 2000 ppm CO)-saturated H$_2$SO$_4$ solution. The higher activity can be explained by the presence of a large amount of the active surface area which was not covered with CO on the electrochemically reduced Pt oxide thin film. The decrease in the H$_2$ oxidation current by CO poisoning was slight because the Pt oxide thin film still had a sufficient active surface area to allow the H$_2$ oxidation. Therefore, the electrochemically reduced Pt oxide thin film may be a promising catalyst for the PEFC anode using a fuel containing CO.

### 3.4 Relationship between chemical bonding state and CO tolerance during H$_2$ oxidation

Figure 10 shows the X-ray photoelectron spectra of Pt4f and O1s levels on (a) the Pt thin film, (b) the Pt oxide thin film electrochemically reduced at −0.3 C and (c) the Pt oxide thin film. The spectrum of the Pt4f level of (b) the Pt oxide thin film electrochemically reduced at −0.3 C was similar to that of (a) the Pt thin film. The electrochemical reduction might change the chemical bonding state of (c) the Pt oxide from the oxide state to the new one, which was exactly similar to the metallic Pt. On the other hand, the spectrum of the O1s level$^{18,19}$ revealed that there was an essential difference between (a) Pt thin film and (b) the Pt oxide thin film electrochemically reduced at −0.3 C. Most of the spectrum was due to the Pt-O near 530.4 eV for (c) the Pt oxide, while the peak of the Pt-O did not exist in the spectrum of (a) the Pt thin film. However, there were still a large peak due to the Pt-O for (b) the Pt oxide thin film electrochemically reduced at −0.3 C. This is the factor to distinguish between the Pt thin film and the electrochemically reduced Pt oxide thin film.
Table 1 shows the O/Pt atomic ratios of the Pt thin film, the Pt oxide thin film and the Pt oxide thin film electrochemically reduced at −0.3 C, which were analyzed by EPMA. The O/Pt atomic ratios of the Pt thin film and the Pt oxide thin film without reduction were 0.01 and 1.50, respectively. These data supported the results of the XPS analysis in Figs. 1 and 10 that the former film was exactly similar to the metallic Pt and the latter one was composed of PtO₂ and PtO. On the other hand, the O/Pt atomic ratio of the Pt oxide thin film significantly decreased to be 0.11 by electrochemical reduction at −0.3 C. The O/Pt atomic ratio of 0.11 suggests that the reduction of PtO₂ and/or PtO was not completely finished yet. The suggestion is also supported by the above-mentioned XPS data that there were still a large peak due to the Pt-O for (b) the Pt oxide thin film electrochemically reduced at −0.3 C in Fig. 10.

It seems appropriate for (a) the Pt thin film that the CO molecules are strongly absorbed on the metallic Pt surfaces and not able to be removed by oxidation. On the other hand, it is highly probable that the O atom contiguous to the Pt atom affects the electron condition of the Pt. Therefore, the suppression of the CO adsorption and the promotion of the CO desorption from the surfaces of the Pt oxide thin film would have been possible by the electrochemical reduction. Moreover, the H₂ oxidation was probably inhibited by the CO poisoning because most of the Pt thin film surface was covered with CO molecules as shown in Fig. 9(b). However, the H₂ oxidation could rapidly proceed on the surface of the electrochemically reduced Pt oxide thin film, since there were a significant number of active sites, at which the CO poisoning had not occurred, or the adsorbed CO was able to be easily removed. As a result, the electrochemically reduced Pt oxide thin film might maintain the higher activity of the H₂ oxidation. Based on these results, the electrochemically reduced Pt oxide may be an excellent catalyst for the H₂ oxidation with CO-tolerance. Finally, our conclusion is that the new catalyst is a promising catalyst for not only the DMFC, but also the PEFC using H₂ containing CO as a fuel.

4. Conclusions

For the Pt thin film, the Pt oxide thin film and the electrochemically reduced Pt oxide thin film, the catalytic activity of the H₂ oxidation in the presence of CO or the tolerance to the CO poisoning was investigated. The CO stripping voltammetry and the XPS analysis were also carried out in order to clarify the cause of the higher activity for the electrochemically reduced Pt oxide thin film. Based on the results, the following conclusions are summarized:

(1) The H₂ oxidation activity of the Pt thin film significantly decreased by the CO poisoning. On the other hand, the tolerance to the CO poisoning occurred during the H₂ oxidation on the Pt oxide thin film by
electrochemical reduction. For the Pt oxide thin film electrochemically reduced at $-0.3 \, \text{C}$, the H$_2$ oxidation current in a (H$_2$ + 100 ppm CO)-saturated solution remained at the same level in an H$_2$-saturated solution. Therefore, the Pt oxide treated by electrochemical reduction may be a promising anode catalyst for the PEFC using H$_2$ containing CO as a fuel.

(2) The electrochemically reduced Pt oxide thin film had greater active surface area and showed lower CO coverage than the Pt thin film, which reflects the CO tolerance during the H$_2$ oxidation on the electrochemically reduced Pt oxide thin film.

(3) The XPS analysis revealed that a considerable amount of oxygen due to Pt-O bond was still present in the Pt oxide thin film even after the electrochemical reduction, although the spectrum of the Pt-O was scarcely detected in the Pt thin film. The results suggested that the residual oxygen might improve the tolerance to the CO poisoning during the H$_2$ oxidation of the electrochemically reduced Pt oxide thin film.

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