EVALUATION OF OXYGEN ELECTROREDUCTION ON METAL OXIDE-SUPPORTED PLATINUM CATALYSTS

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ABSTRACT

Polymer electrolyte Fuel Cells (PEFCs) have been expected to apply the electric vehicles and stationary power sources. However, a large cathode overpotential should be solved to obtain a higher efficiency. In this study, the catalytic activity for oxygen reduction reaction of platinum sputtered on metal oxides (WO₃, V₂O₅, SnO₂ and Cr₂O₃) and glassy carbon was evaluated in the solid-state cell with polymer exchange membrane. The highest specific activity was observed for Pt/V₂O₅/GC over 1 μg cm⁻² Pt loading. The oxygen reduction current at Pt/V₂O₅/GC at 0.9V was 1.5 times larger than that of Pt/GC. The high activity Pt catalyst showed less quantity of Pt oxide. These results indicated that when metal oxides decrease oxide on platinum surface, it could improve the activity of platinum for oxygen reduction reaction.

INTRODUCTION

Before PEFC is widely used as the electric vehicle and stationary power sources, one must resolve a number of issues, including those related to economy and technology. The development of high activity cathode electrocatalysts is one of the key technology issues, affecting the overall performance of PEFC. Highly dispersed platinum on carbon powder is used as a commercial cathode catalyst at present. Though platinum is generally used as a catalyst in many industrial fields, its electrocatalytic activity for oxygen reduction reaction (ORR) is not enough to obtain a sufficient efficiency (1). Pt alloys with transition metals (Co, Cr, Ni, Fe, etc.) have shown the enhancement of electrocatalytic activity for ORR in comparison with Pt (2, 3). Mukerjee et al. have reported that the best catalyst, Pt-Cr/C, furnished current densities about three to four times the currents provided by Pt/C cathodes. However, transition metals dissolve in acid electrolyte, so that the stability of alloy catalysts becomes a problem for practical operation. The dissolution rate of metal oxide (MO) is generally slower than just transition metals in cathode condition of PEFCs. Some MOs (WO₃, TiO₂, etc.) has been reported as the material can enhance the catalytic activity of platinum for ORR (4, 5). In light of these facts, the system Pt-MO might be a high activity cathode electrocatalyst in practical PEFC.
Pt-MO electrocatalysts have usually been investigated as a carbon supported catalyst (Pt-MO/C) in fuel cells (4, 5). However, the addition of MO results not only to improve the activity of Pt but also to reduce the electric conductivity of the electrode because of the electric and contact resistance of MOs. We cannot separate the increase of activity and influence of resistance by the cell test. Also, the position of MO added to Pt particles supported on carbon particle is important. The synthesis of an ideal Pt-MO/C electrocatalyst cannot readily be done for various MOs by the conventional technique. In the present work, we attempted to develop a two-dimensional model electrode, which consists of Pt particles supported on MO thin films by a radio frequency (RF) sputtering apparatus. It could separate the increase of activity and influence of electric resistance by adjustment of MO film thickness.

As a first stage, the main objective of this study is to investigate the electrocatalyst of system Pt-MO that has high activity for ORR in cathode condition of PEFCs. In this paper, we have investigated about the electrochemical behavior between Pt and MO sputtered on glassy carbon, and evaluated the catalytic activity of Pt on MO support (Cr$_2$O$_3$, SnO$_2$, V$_2$O$_5$ and WO$_3$) and grassy carbon (GC) support for ORR on polymer electrolyte membrane.

**EXPERIMENTAL**

**Sample preparation**

The MOs were deposited onto a miller polished GC rods (Tokai Carbon, f 6.0mm and 10mm length) by Radio Frequency (RF) sputtering apparatus (ULVAC MUE-ECO-EV). Pt catalyst was also deposited onto the MO film on the GC rod or the GC rod without the MO film. The sintered WO$_3$, V$_2$O$_5$, SnO$_2$, and Cr$_2$O$_3$ targets (purity 99.9%, Furuuchi chemical co.) were used. The sputtering was carried out in Ar atmosphere. The sputtering pressure in the chamber was 1x10$^{-1}$ Pa. The deposited amounts of the oxide and the Pt were measured by a quartz crystal microbalance. The average thickness of a MO film was around 1nm. Pt loadings were in the range from 0.6 to 2.1µg cm$^{-2}$.

**Electrochemical measurement**

The characteristics and the electrocatalytic activity of the ORR were investigated by electrochemical measurements. The electrochemical measurements were carried out at 30°C in the solid-state cell with Nafion®117 as shown in Fig. 1 (7). The sputter-deposited Pt/MO/GC or Pt/GC sample was used as the working electrode. The electrolyte membrane was sandwiched between the working electrode and the counter electrode. The counter electrode was platinum foil with Pt black. The reference electrode was the reversible hydrogen electrode (RHE). The contact pressure of the working electrode on the polymer electrolyte was controlled at 2.4kg cm$^{-2}$ by a strain control screw using a strain gauge. Humid oxygen or nitrogen gas fed into the cell. They were humidified with a bubbler at 50 ºC in order to attain a saturated humidity.

The electrochemical stability for Pt/MO/GC, MO/GC, and Pt/GC electrodes was estimated by the 50-cycles of cyclic voltammograms (CVs) in the range from 0.05 to 1.2V vs. RHE with 50mV s$^{-1}$ of the sweep rate. The catalytic activity for ORR current density of Pt/MO/GC and Pt/GC electrodes was evaluated by 3-cycles of the slow sweep voltammetry in the potential range from 0.4 to 1.2V with 5mV s$^{-2}$ of the sweep rate in O$_2$.
and N₂ atmosphere. The ORR current was estimated by the difference of the 3rd cycle current in O₂ and N₂ atmosphere.

RESULTS AND DISCUSSION

Electrochemical stability

Figure 2 shows CVs of MO/GC and GC electrodes measured on Nafion®117 at sweep rate of 50mVs⁻¹ for 2nd, 10th, and 50th cycle. At the initial cycle, oxidation and reduction current was observed for the all MO/GC at the lower and higher potential, respectively. In the case of SnO₂/GC, since only oxidation current was observed, SnO₂ would be oxidized to higher oxidation phase than the prepared by RF sputtering. As the cyclic, all MO/GC electrodes became stable profile up to the 50th cycle (steady-state). The steady-state voltammograms of MO/GC were larger than that of GC electrode because of their double layer capacitance. The steady-state voltammogram of Cr₂O₃/GC showed redox current by a hydrate reaction of Cr₂O₃ around 1.0V vs. RHE.

Figure 3 shows the steady-state CVs of Pt/MO/GC electrodes measured on Nafion®117 at the sweep rate of 50mVs⁻¹ with the Pt/GC. All voltammograms showed the similar profile to typical polycrystalline platinum. The specific redox current peak was observed for Pt/SnO₂/GC (Fig. 3 (c)) and Pt/WO₃/GC (Fig. 3 (d)). The redox current of Pt/SnO₂/GC at 0.6-0.8V vs. RHE in Fig. 3 (c) was not observed for SnO₂/GC in Fig. 2 (c). The redox current is likely to be associated with redox coupling of Pt°/Pt²⁺ or Pt²⁺/Pt⁴⁺ (8). In Fig. 3 (d), the redox current of tungsten bronze would be observed at 0.2-0.5V vs. RHE, which was not observed for WO₃ in Fig. 2 (d). These results might indicate that Pt interacted with SnO₂ and WO₃.

Figure 4 shows the change of the CVs from 2nd to 50th cycle for (a) Pt/GC, (b) Pt/SnO₂/GC and (c) Pt/WO₃/GC electrocatalysts. At the initial cycle, H-adsorption/desorption and Pt oxidation/reduction current were smaller and broader than that of later cycle (Fig. 4(a)). The H-adsorption/desorption and Pt oxidation/reduction current increased and H-adsorption/desorption peak became sharp with the cycles. This result suggested that the Pt particles sputtered on grassy carbon which are small and amorphous would grow up to stable particle size of polycrystalline by the continuous potential sweep. In Fig. 4 (b), (c), the peculiar redox current peaks for Pt/SnO₂ of 0.6-0.8V and Pt/WO₃ of 0.2-0.5V also increased more clearly.

Figure 5 shows the reduction peak potential of Pt oxide in Fig. 3 as a function of Pt loading for each Pt/MO/GC and Pt/GC. The reduction peak potential of Pt oxide might be representative of the shift of Pt oxide reduction wave. The reduction peak potential for every catalyst tended to increase with Pt loading. This trend is believed to be due to the change of Pt size on these electrodes as reported by S. Mukerjee (11).

Pt loading has relation to the size of Pt particle on the electrode, and the size decreased with decreasing loading. The peak potentials for the kinds of electrode differ. At 2.1µg cm⁻² of Pt loading, the peak potential of Pt/WO₃/GC and Pt/V₂O₅/GC were higher than that of Pt/GC, whereas, at 0.6µg cm⁻² of Pt loading, the potential were lower than that of Pt/GC. In the case of Pt/Cr₂O₃/GC, the peak potential were lower than that of Pt/GC at every Pt loading. The peak potential of Pt/SnO₂/GC was lower than that of

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Pt/GC at 2.1μg cm\(^{-2}\) of Pt loading, however, didn’t change much with Pt loading. MOs change might be able to change the oxidation condition on Pt surface similar to Pt particle size (11).

Electrocatalytic activity for Oxygen reduction

Figure 6 shows the Tafel plots of specific ORR current, which is the current per real surface area of the platinum, the cathodic sweep at sweep rate of 5mV s\(^{-1}\) on Pt/MO/GC and Pt/GC electrodes (Pt loadings is 2.1μg cm\(^{-2}\)) on Nafion\(^{®}\)117. At the sweep rate of 5mV s\(^{-1}\). The ORR current density was estimated from the difference of the current under O\(_2\) and N\(_2\) atmosphere, because the current of the cathodic sweep in O\(_2\) or N\(_2\) atmosphere includes the discharge current of the double layer and the reduction current of platinum oxides at the sweep rate of 5mV s\(^{-1}\). The real surface area was determined coulometrically of the hydrogen desorption of the potential range from 0.05 to 0.4V vs. RHE by the CV (Fig. 3). The quantity of the coulometrically by the hydrogen desorption per 1cm\(^2\) of real Pt surface was assumed 210μC (9). Tafel slopes of these electrodes were in the range of 55-59mV dec\(^{-1}\), and no difference among the Pt/MO/GC and the Pt/GC electrodes was observed. The oxygen reduction current density in the Tafel region for the Pt/MO/GC electrodes was the same or larger than that for Pt/GC electrodes. This result should shows the oxygen reduction reaction was activated by the MO supports, especially on V\(_2\)O\(_5\).

Figures 7 and 8 show the specific activity: \(i_s\) and the mass activity: \(i_m\) as a function of Pt loading at 0.9V vs. RHE, respectively. The activity of Pt/GC at Pt loading 21μg cm\(^{-2}\) is also shown in the same figure. The specific activity of Pt/V\(_2\)O\(_5\)/GC at 2.1μg cm\(^{-2}\) showed the highest activity in these electrodes that included 21μg cm\(^{-2}\) Pt loaded Pt/GC electrode. In the case of Pt particle electrocatalyst, it is known that the specific activity for ORR decreases with the Pt size decreasing (particle size effect) (10, 11). However the highest specific activity of Pt/V\(_2\)O\(_5\)/GC isn’t due to the particle size effect, since the Pt particles of Pt/GC at 21μg cm\(^{-2}\) should be the largest in these catalysts. The mass activity of Pt/V\(_2\)O\(_5\)/GC at 2.1μg cm\(^{-2}\) also showed the highest of these catalysts, too. From these results, the existence of V\(_2\)O\(_5\) would improve the oxygen reduction activity.

In Fig. 7, the specific activity of each electrode lightly changed at the loading of 1-2μg cm\(^{-2}\). However, below the loading less than 1μg cm\(^{-2}\), the activity remarkably decreased for Pt/V\(_2\)O\(_5\), WO\(_3\), and Cr\(_2\)O\(_3\)/GC. On the contrary, the specific activity of Pt/SnO\(_2\)/GC slightly decreased, and it was higher activity than Pt/GC at low Pt loading. The mass activity of Pt/SnO\(_2\)/GC at 1μg cm\(^{-2}\) is high following the result of Pt/V\(_2\)O\(_5\)/GC at 2.1μg cm\(^{-2}\). In this research, the specific activity of Pt/WO\(_3\)/GC was not so much high as like reported (5).

To analyze the relationship between ORR activity and the reduction of platinum oxide, we evaluated the quantity of electricity of platinum oxide and the reduction peak potential of platinum oxide (Fig. 9). The reduction peak potential increased with the quantity of electricity decrease.

Figure 10 shows the relationship between the reduction peak potential of platinum oxide (Fig. 5) and the specific activity for ORR (Fig. 7). The specific activity for ORR increased with the reduction potential of platinum oxide for these Pt/MOs/GC and Pt/GC. Oxygen reduction reaction is occurred on Pt surface. Therefore, this result might indicate
that if metallic platinum surface remains at higher potential, the oxygen reduction current would be increase. As indicated from the result of Fig. 5 and 9, MOs addition could change the quantity of Pt oxide. When metal oxide is added in order for the Pt oxide to decrease, Pt activity for ORR is improved.

CONCLUSION

The effects of metal oxide supports (WO3, V2O5, SnO2 and Cr2O3) to Pt activity for oxygen reduction have investigated by the two-dimensional electrode in the solid-state cell. The highest specific activity was observed for Pt/V2O5/GC over 1 μg cm−2 Pt loading. The oxygen reduction current at Pt/V2O5/GC at 0.9V was 1.5 times larger than that of Pt/GC. It is considered that V2O5 is a material which improves the Pt activity for ORR. However, the activity of Pt/MO/GC (except for SnO2) at 0.6μg cm−2 was very low. The results of reduction peak potential of platinum oxide on these electrodes indicated that MO addition influences the quantity of Pt oxides. When metal oxide is added in order for the Pt oxide to decrease, Pt activity for ORR is improved.

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Fig. 2. Cyclic voltammograms for MO/GC and GC electrodes on Nafion®, 50mV s⁻¹, 30 °C. (a) V₂O₅; (b) Cr₂O₃; (c) SnO₂; (d) WO₃; (e) GC.
Fig. 3. Steady-state cyclic voltammograms for Pt/MO/GC and Pt/GC electrodes on Nafion®117, 50mV s⁻¹, 30 °C. (a) V₂O₅; (b) Cr₂O₃; (c) SnO₂; (d) WO₃; (e) GC.  
------: Pt/MO/GC, -------: Pt/GC.

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Fig. 4. Cyclic voltammograms for Pt/MO/GC and Pt/GC electrodes on Nafion®117, 50mV s⁻¹, 30 °C. (a) GC (b) SnO₂; (c) WO₃.
Fig. 5. Reduction peak potential of platinum oxide for Pt/MO/GC and Pt/GC electrodes on Nafion®117, 50mV s⁻¹, 30 °C.

Fig. 6. Tafel plots for oxygen reduction reaction current on Pt/MO/GC and Pt/GC electrodes on Nafion®117, 5mV s⁻¹, 30 °C. Pt loadings is 2.1 μg cm⁻². The current density is the current per real surface area of platinum.
Fig. 7. Relationship between Pt loading and specific activity calculated from the cathodic sweep ORR density at 0.9V (vs. RHE) for Pt/MO/GC and Pt/GC electrodes on Nafion®117, 5mV s⁻¹, 30°C.

Fig. 8. Relationship between Pt loading and mass activity calculated from the cathodic sweep ORR density at 0.9V (vs. RHE) for Pt/MO/GC and Pt/GC electrodes on Nafion®117, 5mV s⁻¹, 30°C.
Reduction peak potential of platinum oxide / V vs. RHE

Fig. 9. Relationship between the reduction peak potential and the quantity of electricity of platinum oxide. Pt loadings is 2.1 μg·cm⁻².

Log (iₜ / mA cm⁻² Pt)

Reducation peak potential of platinum oxide / V vs. RHE

Fig. 10. Relationship between the reduction peak potential of platinum oxide and specific activity for ORR.