OPTIMIZED CO TOLERANT ELECTROCATALYSTS FOR POLYMER ELECTROLYTE FUEL CELLS

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ABSTRACT

Ten different kinds of Pt-based alloy electrocatalysts (Pt-Ru, Pt-Ir, Pt-V, Pt-Rh, Pt-Cr, Pt-Co, Pt-Ni, Pt-Fe, Pt-Mn and Pt-Pd) were studied as potential CO tolerant electrocatalysts for anodes in Polymer Electrolyte Fuel Cells (PEFCs). Of the above, the electrocatalyst made of Pt-Ru showed the highest tolerance to CO. The alloy ratio and the thickness of the active layer have been optimized for the Pt-Ru electrocatalyst. As a result, fuel cell performance equivalent to that of pure hydrogen fuel has been attained, even with a CO concentration of 100 ppm.

INTRODUCTION

Fuel cells have received increasing attention as an energy power source gentle to the earth's environment. Polymer electrolyte fuel cells (PEFCs) in particular are seen as a potential energy source for electric vehicles, because of their high energy conversion efficiency and high power density. In the application of PEFCs to automobiles, hydrogen (H₂) generated from methanol by steam reforming process is a viable fuel source, as it is known that methanol can be stored more easily on vehicles than hydrogen. However, in addition to H₂, methanol reformate gas can contains as much as 25% carbon dioxide (CO₂), along with a small amount of carbon monoxide (CO). It has been proven that PEFC performance drops with a CO concentration of only several ppm (1-5). This is due to the strong chemisorption force of CO onto the Pt generally used as the anode electrocatalyst in PEFCs. CO concentration can be reduced by installing a CO selective oxidization unit to the reformer. It is, however, extremely difficult to suppress the CO concentration below 10 ppm.
ppm continuously and stably. Moreover, it has been determined that a PEFC must be capable of tolerating a CO concentration of at least 100 ppm in order to reduce the size of the reformer unit.

There are two methods to avoid the effect of CO on PEFC performance. The first method is to reduce CO poisoning the electrocatalyst by blowing 2% of air (O₂) into the anode, as reported by M. S. Wilson et al. (2). This method, however, makes the structure and control of the PEFC system complex. The second method is to enhance the CO tolerance of the electrocatalyst by alloying the Pt with a second element. This method has been studied recently at a number of research institutes (4-6) since it was discovered that it could be used to operate a PEFC system with reformate gas containing CO. No report has been published to indicate that adequate CO tolerance can be obtained with this method.

This paper reports an alloy electrocatalyst with high CO tolerance for anodes of PEFCs, developed by conducting studies on Pt-based alloy electrocatalysts.

**EXPERIMENTAL**

Pt-based alloy electrocatalysts made of Pt-Ru, Pt-Ir, Pt-V, Pt-Rh, Pt-Cr, Pt-Co, Pt-Ni, Pt-Fe, Pt-Mn and Pt-Pd respectively were studied as anode electrocatalysts. All of them were made of 20wt% alloy on carbon (Vulcan XC72R) with the Pt loading rate of 0.4 mg Pt/cm². Cathode electrocatalysts were made of 20wt% Pt/C (Vulcan XC72R) with 0.4 mg Pt/cm². After mixing the Pt/C or the alloy electrocatalyst on carbon with 5wt% Nafion solution (Aldrich), the mixture was applied onto the uncatalyzed carbon backing (geometric area of electrode: 10 cm²). Such an anode and cathode were hot-pressed into a membrane of Nafion® 115 to form a membrane and electrode assembly (MEA).

The cell performance was evaluated with single cell testing. The MEA was set into a holder, while pure H₂ or 100 ppm CO/H₂ was supplied to the anode using a gas cylinder. Air was also supplied to the cathode using a gas cylinder. Pressure was set at 0.15 MPa for both of the gases, while the cell temperature was set at 80°C. The MEA was humidified by bubbling. The cell performance was measured using an electronic load application device (EUL300 a B made by FUJITSU DENSO LTD.) and a power supply (PK46 made by KIKUSUI ELECTRONICS CORP.).
RESULTS AND DISCUSSION

Alloy Electrocatalysts

Pt-based alloy electrocatalysts - Pt-Ru, Pt-Ir, Pt-V, Pt-Rh, Pt-Cr, Pt-Co, Pt-Ni, Pt-Fe, Pt-Mn and Pt-Pd - were compared as anode electrocatalysts in terms of CO tolerance. It was verified with X-ray diffraction (XRD) that all of those electrocatalysts were properly alloyed. Figure 1 shows the CO tolerance where Pt-Ru, Pt-Ir, Pt-V, Pt-Rh, Pt-Cr, Pt-Co and Pt-Ni were used respectively as anode electrocatalysts. Their cell voltages at 0.4 A/cm² are shown in the figure, where the CO concentration was set at 100 ppm. The Pt-Ru electrocatalyst was found to be the only alloy having a higher CO tolerance than the Pt electrocatalyst. The CO tolerances of Pt-Fe, Pt-Mn and Pt-Pd were also evaluated, but none of them showed higher CO tolerance than Pt-Ru.

The mechanism that enhances CO tolerance was studied using the Pt-Ru electrocatalyst. Table 1 shows the analytical results of gases at the anode inlet and the outlet, where the 500 ppm CO/H₂ gas was supplied at the rate of 100 ml/min. The anode electrocatalyst used for the analysis was 20wt % Pt/C (0.4 mg Pt/cm²) with the current density of 0.3 A/cm². At the anode gas outlet, CO₂ was detected together with CO. The sum of the molar quantity of CO and CO₂ at the anode gas outlet agrees roughly with the molar quantity at the gas inlet. It was deduced from the results that part of the CO absorbed onto the Pt was oxidized and became CO₂, then desorbed from the Pt and exhausted out of the cell. It was also deduced that the oxidizing reagent for the CO was the steam supplied for the humidification of electrolytic membrane. Therefore, it is presumed that the oxidization from CO to CO₂ takes place by the reactions that would occur in the following two stages.

$$\text{CO} + \text{Pt} \rightarrow \text{CO-Pt} \tag{1}$$

$$\text{CO-Pt} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{Pt} + 2\text{H}^+ + 2\text{e} \tag{2}$$

where reaction [1] is the process of absorbing CO onto Pt, while reaction [2] is the process of the absorbed CO oxidizing into CO₂ with H₂O.

Figure 2 shows the measured results of CO oxidization potentials of a Pt electrocatalyst and a Pt-Ru electrocatalyst. Cyclic voltammograms measured with the bipolar method using the anode as the working electrode, while using the cathode as the counter/reference electrode, are shown here. 1000 ppm CO/N₂ gas was fed into the anode, while H₂ gas was
fed into the cathode. The cell temperature was 40°C and the gas pressure was 0.10 MPa. Voltage was applied to the cell at the scanning speed of 20 mV/sec. In the case of Pt-Ru, the CO oxidization peak shifted toward the lower potential side by 200 mV, compared to that of Pt. The affinity of Ru for H₂O is stronger than that of Pt (that is, water absorption occurs at a lower potential for Ru). Hence the CO absorbed onto Pt should be oxidized into CO₂ with a lower potential.

Figure 3 shows the CO tolerances of an electrocatalyst in which Pt and Ru are alloyed, and another electrocatalyst in which Pt and Ru are not alloyed but mixed. The latter is a Pt-Ru without heat treatment for alloying. The figure indicates that alloying is necessary in order to obtain high CO tolerance. The oxidization of CO occurs by the interaction between Pt and Ru as expressed in Equation [3]. Therefore, it is confirmed that the Pt atom and Ru atom must be adjacent to each other.

\[
\text{Pt-CO} + \text{Ru-OH} \rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + \text{H}^+ + e^- \tag{3}
\]

**Pt/Ru Alloy Ratio**

It was necessary to optimize the Pt/Ru ratio for the enhancement of the Pt-Ru electrocatalyst's CO tolerance. The atomic ratio of Pt/Ru was hence varied in the range of 100:0 to 0:100. All of those electrocatalysts were made of 20wt % alloy on carbon with the Pt loading rate of 0.4 mg Pt/cm² (except for an electrocatalyst made of 100 % Ru with the loading rate of 0.4 mg Ru/cm²). It was verified by means of XRD that these electrocatalysts, thus prepared, had the crystal structures expected for their alloy compositions (7). Figure 4 shows the cell voltages at a CO concentration of 100 ppm (0.3 A/cm²). The figure indicates that high cell voltages can be obtained only where the Pt:Ru ratio is 50:50, for both pure hydrogen and 100 ppm CO/H₂. In the case of pure hydrogen, practically the same performance was obtained when the Ru rate was 0 to 50 %, while the Pt loading rate was kept constant at 0.4 mg/cm². Performance dropped when the Ru rate was 50 to 100 %, as the active layer became thicker. CO tolerance increased as the Ru rate became higher, up to 50 %. However, when the Ru rate was over 50%, the power was reduced as the electrode performance (in pure hydrogen) was reduced.

It can be seen in the phase diagram shown in Figure 5 that CO tolerance is ensured over a wide range of Pt/Ru ratios (85:15 to 15:85). This is true regardless of the crystal structure of the electrocatalyst, though the crystal structure changes around the Pt/Ru ratio of 30:70. This indicates that proper CO tolerance can be obtained as long as an Ru atom exists in either one of adjacent atoms to a given Pt atom.
Active Layer Thickness

The active layer thickness can be reduced by increasing the weight percentage of electrocatalyst supported in the carbon powder, without changing the amount of electrocatalyst per unit area of electrode. The CO tolerance was measured using three kinds of electrocatalysts of 20, 30 and 40wt % Pt-Ru supported on carbon, where the Pt rate in each electrocatalyst was kept constant at 0.4 mg/cm². Figure 6 shows their cell voltages (0.6 A/cm²) in the CO concentration of 100 ppm. It is seen that the electrocatalyst of 40wt % Pt-Ru on carbon has the highest CO tolerance. Table 2 shows the active layer thickness of each electrocatalyst determined by SEM, and the Pt surface area that can contribute to the electrode reaction determined by the cyclic voltammogram. It was confirmed that the higher the weight percentage of Pt-Ru on carbon, the thinner the active layer becomes and the greater the Pt surface area that can contribute to the reaction.

It was reported in a study conducted by S. Srinivasan et al. (8) that the fuel cell electrode reaction actually occurred in a small area of less than 10 μm from the surface of the active layer. Where the active layer was thicker than the above, the presence of Pt was limited to the region of shallow depth from the surface of the active layer. An electrocatalyst located at a deeper region (on the membrane side) did not contribute to the reaction of the active layer. By increasing the weight percentage of Pt-Ru on carbon, it was possible to concentrate electrocatalysts in the active region without changing the amount of electrocatalysts per unit geometric area of electrode. As a result, the cell performance was enhanced by increasing the number of Pt particles that could contribute to the reaction.

CO Tolerance of Pt-Ru Electrocatalyst

A membrane and electrode assembly (MEA) was prepared according to the results/findings described above, using a Pt-Ru electrocatalyst (0.4 mgPt/cm²) with the Pt/Ru ratio of 50:50 and the weight percentage of 40 % on carbon as the anode electrocatalyst. The cell performance using this MEA operated in 100 ppm CO/H₂ is shown in Figure 7. Operated with pure hydrogen, better cell performance was recorded using the optimized Pt-Ru electrocatalyst than that obtained using Pt as the anode electrocatalyst. Moreover, performance equivalent to the Pt electrocatalyst operated with pure hydrogen was attained with the Pt-Ru operated with in a CO concentration of 100 ppm.
SUMMARY

Results of the study done on Pt-based alloy electrocatalyst, identified the Pt-Ru electrocatalyst as having excellent CO tolerance.

It was deduced that the Ru in the Pt-Ru electrocatalyst absorbs H\textsubscript{2}O and facilitates the oxidization of CO.

Although, adequate CO tolerance can be obtained over a wide Ru range of 15 to 85 %, the optimum ratio of Pt/Ru was determined to be around 50:50.

By using an electrocatalyst having a high weight percentage of Pt-Ru on carbon, the number of Pt particles that can contribute to the reaction is increased and CO tolerance is also increased without changing the amount of electrocatalyst per unit area.

By optimizing the Pt-Ru electrocatalyst, cell performance equivalent to that of pure hydrogen can be attained with a CO concentration as high as 100 ppm.

It is expected that the improvement in CO tolerance indicated by the above described electrocatalyst will allow PEFCs to be operated stably, even under the condition where the CO concentration in the reformer generated gas is high, such as at the time of system start up.

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Table 1. Molar quantity CO and CO$_2$ at anode inlet and outlet. Anode electrocatalyst: 20wt%Pt/C, 0.4 mg Pt/cm$^2$. Current density: 0.3 A/cm$^2$. Anode gas: 500 ppm CO/H$_2$(100 ml/min). Pressure: 0.10MPa.

|          | Molar quantity in CO | Molar quantity in CO$_2$ | Molar quantity in CO+CO$_2$ |
|----------|----------------------|--------------------------|-----------------------------|
| Anode inlet | $1.73 \times 10^{-6}$ mol | 0 mol                     | --                          |
| Anode outlet | $1.26 \times 10^{-6}$ mol | $0.42 \times 10^{-6}$ mol | $1.68 \times 10^{-6}$ mol   |

Table 2. The active layer thickness of 20, 30, 40wt% Pt-Ru/C with the Pt loading rate of 0.4 mg Pt/cm$^2$ determined by SEM and the Pt surface area that can contribute to the electrode reaction determined by the cyclic voltammogram.

| Pt-Ru wt % on carbon | 20% | 30% | 40% |
|----------------------|-----|-----|-----|
| Active layer thickness (μm) | 41  | 24  | 8   |
| Pt surface area contributable to electrode reaction (m$^2$) | 0.10 | 0.12 | 0.14 |
Figure 1. Cell voltages of alloy electrocatalysts in hydrogen or 100 ppm CO/H2. All alloy electrocatalysts for anodes are made of 20wt % alloy/C (Vulcan XC72R) with Pt loading rate of 0.4 mg Pt/cm2. All alloy electrocatalysts for cathodes are made of 20wt % Pt/C (Vulcan XC72R) with Pt loading rate of 0.4 mg Pt/cm2. Cell temperature: 80°C, pressure: 0.15 MPa.

Figure 2. Bipolar cyclic voltammograms using each anode as the working electrode and cathode as the counter/reference electrode. Pt: 20wt % Pt/C, 0.4 mg Pt/cm2. Pt-Ru: 20wt % Pt-Ru/C, 0.4 mg Pt/cm2. Anode gas: 1000 ppm CO/N2. Cathode gas: H2. Scanning speed: 20 mV/sec. Cell temperature: 40°C. Pressure: 0.10 MPa.
Figure 3. CO tolerances of Pt-Ru alloy and mixed Pt-Ru. Pt-Ru alloy: 20wt % Pt-Ru/C (Pt/Ru = 50:50), 0.4 mg Pt/cm². Mixed Pt-Ru: 13.2wt % Pt/6.8wt % Ru/C, 0.4 mg Pt/cm² (without heat treatment for alloying). CO concentration: 100 ppm. Cell temperature: 80°C. Pressure: 0.15 MPa.

Figure 4. Cell voltage plotted against Ru atomic ratio in Pt-Ru alloy in hydrogen or 100 ppm CO/H₂ (0.3 A/cm²). All anode Pt-Ru electrocatalysts were made of 20wt % Pt-Ru/C (Vulcan XC72R) with Pt loading rate of 0.4 mg Pt/cm². Cell temperature: 80°C. Pressure: 0.15 MPa.
Figure 5. Phase diagram of Pt-Ru alloy (7)

Figure 6. Relationship between Pt-Ru alloy/carbon ratio and cell voltage. Anode Pt loading rate: 0.4 mg Pt/cm². Cathode electrocatalyst: 20wt% Pt/C (Vulcan XC72R) with Pt loading rate of 0.4 mg Pt/cm². Cell temperature: 80°C. Pressure: 0.15 MPa.

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Figure 7. Cell voltage plotted against current density in hydrogen or 100 ppm CO/H$_2$. Anode Pt electrocatalyst: 20wt % Pt/C with 0.4 mg Pt/cm$^2$. Pt-Ru electrocatalyst: 40wt % Pt-Ru/C (Pt/Ru ratio = 50:50) with 0.4 mg Pt/cm$^2$. Cathode: 20wt % Pt/C with 0.4 mg Pt/cm$^2$. Cell temperature: 80°C. Pressure: 0.15 MPa.