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Pt Alloy Catalysts for Use with PEFC Cathodes Research Report Takahiko Asaoka, Kazutaka Hiroshima, Yu Morimoto PEFCカソード用Pt合金触媒

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Abstract

Various Pt alloy catalysts have been prepared, and their electrochemical activities have been evaluated. Alloys of Ti, Cr, Mn, Fe, Co, Ni and Ru with Pt have exhibit higher specific activities than pure Pt. Their mass activities, however, are not increased because of the aggregation of the alloy particles during the heat-treatment process.

A novel preparation process is proposed, achieving the inhibition of the aggregation of the alloy catalysts through the use of a chelating agent. An iron-platinum alloy, prepared with this process, has a smaller particle size and, thus, a high mass activity was obtained.

Polymer electrolyte fuel cell, Oxygen reduction, Catalyst, Alloy, Platinum, Activity Keywords

要

固体高分子形燃料電池 (PEFC) の空気極用電極 触媒としては、一般にカーボンブラックに担持さ れたPt (Pt/C) が用いられている。しかし、さらな る高エネルギ効率化、あるいはPt使用量低減のた めには、触媒のより高活性化が望まれる。

本論では、Pt表面積あたりの酸素還元活性を向 上させることを目的として、Ptに遷移金属を固溶 させた合金触媒について検討した。

Ti, Cr, Mn, Fe, Co, Ni, Ru などの遷移金属との合 金化で、Pt触媒はPtサイトあたりの触媒活性を向

旨

上できることを示した。しかし、これらの触媒は、 不活性ガス中での熱処理によって合金化するが, 同時に粒子の凝集により表面積の低下を引き起こ し、合金化で得られる活性向上効果を相殺してし まう。

我々が新たに提案した,キレート剤を用いる合 金触媒担持法は,従来法に比べ,巨大粒子の生成 を抑制する効果があることが分かった。この方法 は、より高分散で、かつ高活性なPt合金触媒を得 るためのひとつの方向を示すものである。

1. Introduction

Fuel cell powered vehicles have been developed by several automakers, and have now been leased to national and local governments and energy-related companies. As this example shows, the polymer electrolyte fuel cell (PEFC) is expected to be on alternative to the internal combustion engine as a vehicle power source.

The main feature of the PEFC is its high energy conversion efficiency. When hydrogen is used as fuel, reactions that occur in the fuel cell are as follows.

Cathode: $1/2 O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Overall: $H_2 + 1/2O_2 \rightarrow H_2O$

The theoretical energy conversion efficiency of these electrochemical reactions, which is calculated by dividing the Gibbs energy change by the heat of combustion of hydrogen, is as high as 83% at 25°C. However, as shown in **Fig. 1**, in a typical voltagecurrent density characteristic, the actual voltage, (the primary factor of the efficiency), is significantly lower. The causes of the voltage loss are classified into three elements: electrocatalytic activity, ohmic resistance and supply of the reactants to the electrode surface. Above all, the insufficiency of the activity of the cathode catalyst causes a significant loss (cathode loss) over the whole current density range.

Increasing the surface area of the electrocatalyst is a strategy to increase the apparent activity. After the work by R. J. Allen, who used carbon-supported

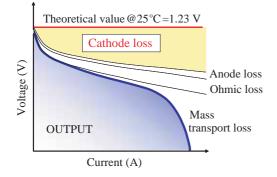


Fig. 1 Schematic illustration of Current-Voltage characteristic of PEFCs.

platinum as the catalyst,¹⁾ several efforts have been made to increase the platinum content (defined as the platinum weight divided by the total weight of platinum and carbon) and to decrease the particle size of platinum in order to increase the catalyst surface area.²⁻⁵⁾ At present, the state-of-the-art Pt/C catalyst has a Pt content of more than 60wt% and a particle size of less than 2nm. There would seem to be little room left for improvement in the catalyst surface area.

Another strategy is to increase the intrinsic activity by modifying the catalyst. A few studies of this have been reported,⁶⁻⁸⁾ but adequate increase has not yet been observed.

In this study, various Pt alloy catalysts were prepared by precipitation, and their electrochemical activities were evaluated. Furthermore, an ironplatinum alloy catalyst was prepared using a chelating agent to decrease the size of the alloy particles.

2. Experimental

2.1 Catalyst preparation

2.1.1 Platinum catalyst

Three Pt/C catalysts with different carbons and different Pt content were prepared according to the literature.¹⁾ First, Pt was deposited as a fine oxide colloid on a furnace black (Vulcan XC-72R, Cabot Corp.) or an acetylene black (DENKA BLACK, DENKI KAGAKU KOGYO KABUSHIKI KAISHA). The colloidal platinum oxide/carbon catalyst was reduced at 200°C in H₂ for 2 hours. The Pt content was 20 or 40wt% for the furnace black and 40wt% for the acetylene black.

2.1.2 Alloy catalysts

Nine different alloy catalysts with Ti, Cr, Mn, Fe, Co, Ni, Ru, Rh and Ir were prepared using the Pt/C of the acetylene black. Nitrates of the alloying metals were separately dissolved in the slurries containing the Pt/C. Then, the pH of the solutions was controlled to 10 by adding 28% NH₃(aq) solution in order to deposit the metals as hydroxides. The slurries were filtered and then dried at 80°C overnight. The catalysts were heat-treated to form alloys at 1000°C in N₂ for 2 hours. Henceforth, these alloy catalysts are denoted as MPt/C, where M is the dopant metal employed. Furthermore, FePt/C, MnPt/C and CoPt/C were also prepared using the 40wt% Pt/C with the furnace black employing heattreatment at 350, 500, 700 and 900°C. The undoped Pt/C catalyst was also heat treated at the same temperatures for comparison. The atomic ratio of M to Pt was 1 : 3 for all the alloy catalysts.

2.1.3 Alloy catalyst using a chelating agent

Another preparation method, using a chelating agent, was utilised in the preparation of an ironplatinum alloy catalyst in order to avoid the aggregation of Pt particles during the heat-treatment. Ethylenediamine-N,N,N',N'-tetraacetic acid, iron(III) complex (Fe(III)-EDTA) sodium salt trihydrate (DOJINDO LABORATORIES) was added to the slurry of the 40wt% Pt/C with the furnace black. The mixture was first evaporated under vacuum conditions at 45°C and then vacuum-dried at 80°C overnight. Then the product was heat-treated at 900°C in N₂. The atomic ratio of Fe to Pt was 1 : 3. This catalyst is denoted as EDTA-FePt/C.

2.2 Characterization

In order to estimate the particle size of the catalyst, an XRD analysis was carried out using a RINT-2000 (Rigaku) diffractrometer. A TEM observation was also conducted using a JEOL-2000EX (JEOL) electron microscope.

2.3 Fabrication of membrane electrode assemblies (MEAs)

Membrane electrode assemblies were fabricated from Nafion 112 membranes (E. I. du Pont Nemours and Co., Inc.) and ELAT gas diffusion layers (E-TEK Div. of De Nora N. A., Inc.). Catalyst slurries containing Nafion (Aldrich, 5wt% Nafion solution) and the catalyst (0.3mgPt/cm²) were applied onto the gas diffusion layer. Then, the gas diffusion layer was hot-pressed on the Nafion membrane for 20 minutes at 120°C and 50kgf/cm². A 20wt% Pt/C with the furnace black was used as the anode in all cases. The apparent electrode area was 13cm².

2.4 Cyclic voltammetry

Cyclic voltamemetry was applied to the cathode to estimate the electroactive surface area of the catalyst. Water vapor-saturated-N₂ and water vaporsaturated-H₂ were supplied to respectively the cathode and anode compartments at 40°C and ambient pressure, and the anode was used as the both counter and reference electrode. The potential was cycled between 50mV and 1300mV vs. RHE at 50mV/s.

2.5 Single cell test

Current-voltage curves were obtained at a cell temperature 80° C in order to evaluate the catalytic activity. Hydrogen (fuel) and oxygen (oxidant) were each humidified and fed to the anode and cathode, respectively, at a high stoichiometric flow rate.

3. Results and discussion

3.1 Catalyst characterization

The interplanar spacing (*d*) of the catalyst microcrystals, estimated from the diffraction peaks (111) of Pt, is shown in **Fig. 2** as a function of the heat-treatment temperature. For FePt/C, *d* decreases with increasing heat-treatment temperature and approaches that for the Pt₃Fe intermetalic compound, whilst the *d* value of CoPt/C already attains that of Pt₃Co at 350°C. These results indicate that alloy formation is promoted by heat-treatment. It was noted that Mn differs from Fe or Co as *d* value with Mn is close to that of pure Pt even at 900°C.

The size of the alloy particles evaluated from their XRD peak widths⁹⁾ are shown in **Fig. 3**. All alloys exhibit particle sizes more than 5 times larger than the particles on Pt/C without heat-treatment. This implies that the aggregation of Pt particles occurs during the alloying process. The aggregation is

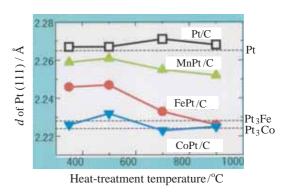


Fig. 2 Spacing of Pt(111) plane, d, of heat-treated catalysts: FePt/C (●), MnPt/C (▲), CoPt/C (▼) and Pt/C (□). Specifications of all catalysts are as follows.
Weight ratio of platinum/carbon = 40/60 Atomic ratio of second metal/platinum = 1/3 Carbon support : furnace black (Vulcan XC-72R)

promoted at the heat-treatment temperature as shown in **Fig. 4**, where the large particle sizes of the alloys indicated that the aggregation is also promoted by alloying.

TEM images of Pt/C, FePt/C and EDTA-FePt/C are presented in **Fig. 5**, and the particle size distributions obtained from these images are shown in **Fig. 6**. Furthermore, **Table 1** shows the average

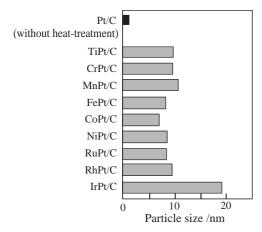
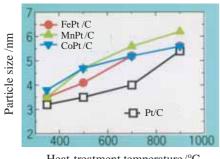


Fig. 3 Particle sizes of catalysts estimated from XRD peak width.

Weight ratio of platinum/carbon = 40/60 Atomic ratio of second metal/platinum = 1/3 Carbon support : acetylene black (DENKA BLACK) Temperature of heat-treatment : 1000 °C (except Pt/C)



Heat-treatment temperature/ ^{o}C

Fig. 4 Particle sizes of the heat-treated catalysts:
FePt/C(●), MnPt/C(▲), CoPt/C(▼) and
Pt/C(□). Particle size is estimated from XRD peak width. Specifications of all catalysts are as follows.

Weight ratio of platinum/carbon = 40/60 Atomic ratio of second metal/platinum = 1/3 Carbon support : furnace black (Vulcan XC-72R) particle sizes obtained from the XRD peak width and the TEM images. The particle sizes of the two alloy catalysts are increased by the heat-treatment.

3.2 Determination of the real surface area

Figure 7 shows an example of the cyclic voltammogram for an alloy catalyst. The surface areas of electrochemically active platinum (ECA) were determined from the charge associated with hydrogen desorption (Q_H) according to literature¹⁰ and are shown in **Fig. 8**.

3.3 Electrocatalytic activity

Figure 9 shows the current-voltage characteristics of the alloy catalysts. The IR-compensated voltage,

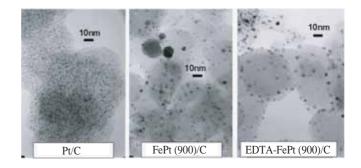


Fig. 5 TEM images of the catalysts. Tow alloy catalysts were heat-treated at 900 °C and Pt/C was not heat-treated. Other specifications are as follows.

Weight ratio of platinum/carbon = 10/90 Atomic ratio of second metal/platinum = 1/3 Carbon support : furnace black (Vulcan XC-72R)

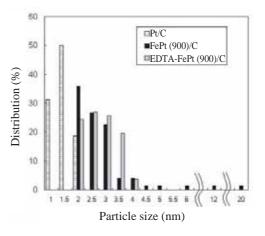


Fig. 6 Particle size distribution of Pt/C, FePt(900)/C and EDTA-FePt(900)/C estimated from TEM image.

which eliminates the ohmic loss from the terminal voltage, is almost the same as, or lower than, that of Pt/C. The current-voltage characteristics with the

Table 1 Characteristics of prepared catalysts.

	Particle size by XRD (nm)	Particle size by TEM (nm)
Pt/C (without heat-treatment)	0.8	1.5
FePt(900)/C	2.9	3.2
EDTA-FePt(900)/C	2.7	2.8

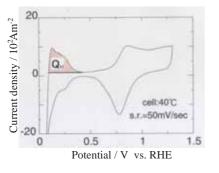


Fig. 7 An example of cyclic voltammogram of Pt alloy catalysts. Q_H is the amount of the electric charge for desorption of absorbed hydrogen on Pt surface.

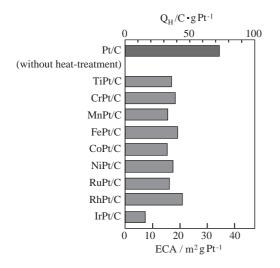


Fig. 8 The surface areas of electrochemically active platinum (ECA) determined by the charge of hydrogen desorption (Q_H) of catalysts presented in Fig. 3.

current density normalized to ECA are shown in **Fig. 10**. All alloy catalysts, except IrPt/C and RhPt/C, have higher activities than Pt/C.

Figure 11 shows the apparent current density at the IR compensated voltage of 0.85V and the specific surface area estimated from the TEM images as a function of the heat-treatment temperature. For both Pt/C and FePt/C, the surface area decreases with increasing heat-treatment temperature. The current density, however, increases with temperature for FePt/C, whilst it decreases for Pt/C.

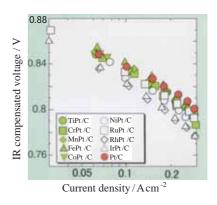


Fig. 9 Current-Voltage characteristics of Pt alloy catalysts presented in Fig. 3. The condition of the fuel cell test is as follows.
Cell temperature: 80°C
Anode gas: H₂, 0.1MPa, dew point 85°C
Cathode gas: O₂, 0.1MPa, dew point 75°C
Voltage is compensated with ohmic loss (=IR drop).

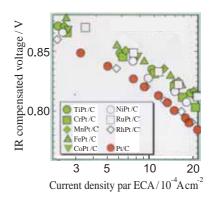


Fig. 10 Current-Voltage characteristics of Pt alloy catalysts presented in Fig. 3. Current density is normalized by ECA. Figure 12 shows the current density normalized to the real surface area vs. heat-treatment temperature. The FePt/C catalyst shows higher specific electrocatalytic activity than Pt/C at the heattreatment temperatures higher than 600° C, where Fe is mostly solved into Pt to form Pt₃Fe. Therefore, forming an alloy phase, not just a bi-metallic mixture, is essential to impart a higher specific activity to FePt/C.

3.4 Iron-platinum alloy catalyst prepared using a chelating agent

As shown in Fig. 5 and Fig. 6, large particles having a diameter more than 5 nm are observed in FePt/C, but not in EDTA-FePt/C. This indicates that particle aggregation does not occur in the catalysts

prepared using the chelating agent complex. A possible explanation for this difference is as follows. In the case of the conventional method, the iron source would be deposited as large hydroxide particles. Particle aggregation is likely to occur during the heat-treatment because the large iron hydroxide particles are likely to become correspondingly large iron metallic particles. In contrast, each iron atom in EDTA-Fe(III) is separated by an organic ligand, which can prevent the iron metal aggregation.

Figure 13 shows the current-voltage characteristics for Pt/C, FePt/C and EDTA-FePt/C. The current density is normalized to the weight of Pt in order to compare their mass activities. Both the

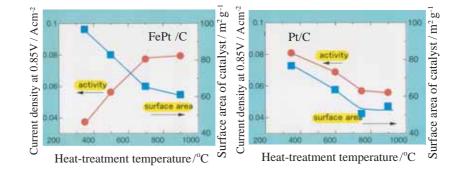


Fig. 11 Apparent current density at 0.85V on the fuel cell test and surface area of the catalysts estimated from TEM image vs. heat-treatment temperature. Condition of fuel cell test is equal to Fig. 9 and specifications of catalysts are same to Fig. 4.

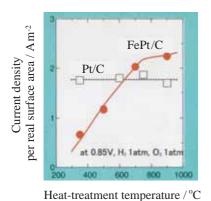


Fig. 12 Current density normalized by the catalyst surface area vs. heat-treatment temperature. Condition of fuel cell test is equal to Fig. 9 and specifications of catalysts are same to Fig. 4.

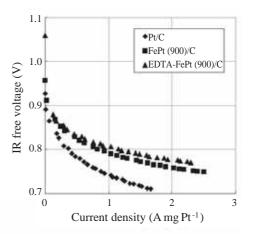


Fig. 13 Current-Voltage (IR compensated) characteristics of Pt/C (♠), FePt(900)/C (■) and EDTA-FePt (900)/C (▲) catalyst. Operating condition was the same with Fig. 9.

alloy catalysts show higher mass activities than Pt/C over the whole range of current densities. The EDTA-FePt/C catalyst shows a higher mass activity than FePt/C because of the smaller size of the catalyst particles.

4. Conclusion

Carbon-supported alloy catalysts of Ti, Cr, Mn, Fe, Co, Ni or Ru with Pt show higher specific activity Pt/C. The formation of an alloying phase, not just a bi-metallic mixture, is necessary to increase the specific activity. Their mass activities were, however, not enhanced because of the aggregation of the alloy particles during heat-treatment process.

A novel preparation procedure using a chelating agent was proposed and an alloy catalyst having a smaller particle size was obtained. With this method, alloy catalysts having both a high specific activity and a high surface area can be developed.

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