

Size Reduction in PtRu Catalyst by Addition of Non-Metallic Elements

Hideo Daimon and Yukiko Kurobe

Development & Technology Division, Hitachi Maxell Ltd.,
6-20-1 Kinunodai, Yawara-mura, Tsukuba-gun, Ibaraki, 300-2496 Japan
(E-mail:hideo-daimon@maxell.co.jp)

INTRODUCTION

In fuel cell, catalytic activity and utilization efficiency of catalyst should be simultaneously improved because Pt is an expensive material and its deposits in the world are very limited and it is still the best catalyst for fuel cell application. Size reduction is effective to improve mass activity of catalyst. Carbon supports having high specific surface area have been used to obtain fine Pt and PtRu catalysts [1]-[4]. However, many micropores exist in the carbon supports. Catalysts deposited in these micropores lose their contact with fuels and solid polymer electrolyte, which results in becoming “dead catalyst”. The number of “dead catalyst” will increase even further if carbon supports having higher specific surface area are used, which deteriorates utilization efficiency of the catalyst. It seems that there is a tradeoff between improvement in catalytic activity by reducing size of catalyst with usage of carbon supports having high specific surface area and improvement in utilization efficiency of catalyst. Therefore, new technology that can simultaneously improve catalytic activity and utilization efficiency of the catalyst is strongly demanded.

It has been reported that addition of non-metallic element of P drastically reduces crystalline size of Fe single crystal in magnetic alumite films [5]. In this report, a new method to reduce size of PtRu catalyst is proposed. It is shown that addition of non-metallic element of P reduces size of PtRu catalyst and that the reduced size is retained regardless of specific surface area of carbon supports. It is demonstrated that PtRuP catalyst deposited on less porous carbon support is a candidate for improving catalytic activity and utilization efficiency of catalyst simultaneously.

EXPERIMENTAL

PtRu catalyst was synthesized by polyol process [6]-[9] using ethylene glycol as a reducer. Platinum (II) acetylacetonate ($\text{Pt}(\text{acac})_2$), ruthenium (III) acetylacetonate ($\text{Ru}(\text{acac})_3$) and carbon support were mixed in ethylene glycol and the mixture was refluxed at 473 K for 4 hours under nitrogen atmosphere. As additives of non-metallic elements, B, N, S, Si and P were selected. Precursors for these elements were dissolved in the synthetic solution and the mixture was refluxed. Morphology and dispersion of catalyst were observed by transmission electron microscope (TEM) and by scanning electron microscope (SEM). Compositional analyses of catalyst were conducted by energy dispersive x-ray spectroscopy equipped with TEM (TEM-EDX), x-ray fluorescence spectroscopy (XRF) and by x-ray photoelectron spectroscopy (XPS). Crystallographic structure of catalyst was analyzed by x-ray diffractometer (XRD). DMFC performance was measured under passive state at 298 K with fuels of 15 wt.% methanol and ambient air. Loading amount of catalyst was 5 mg/cm^2 for both anode and

cathode. For cathode, commercialized Pt catalyst (TEC10E50E, Tanaka Kikinzoku Kogyo Ltd.) was used. DuPont's Nafion 112 membrane with thickness of 50 μ m was used as solid polymer electrolyte to prepare membrane electrode assembly (MEA).

RESULTS AND DISCUSSION

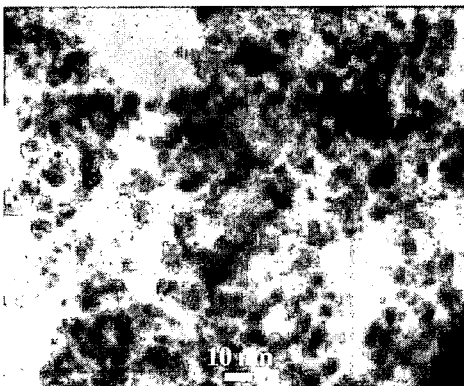
Table 1 summarizes heat of mixing with Pt of non-metallic elements [10]. Minus value in this Table indicates the mixture is energetically stabilized. Therefore, Table 1 suggests that metallic Pt-Pt bonding is cut by addition of B, P and Si and that crystalline growth of Pt is suppressed. Table 2 shows effect of the additives on size reduction in PtRu catalyst. It was found that addition of N, S and P reduces size of PtRu catalyst and that P is the most effective additive. Figure 1 shows TEM images of PtRu and PtRuP catalysts supported on Vulcan XC-72R (specific surface area:254 m²/g). It can be seen that size of PtRu catalyst is reduced in 2 nm by addition of P and that dispersion of PtRuP catalyst is greatly improved compared with that of PtRu catalyst.

Table 1 Heat of Mixing with Pt

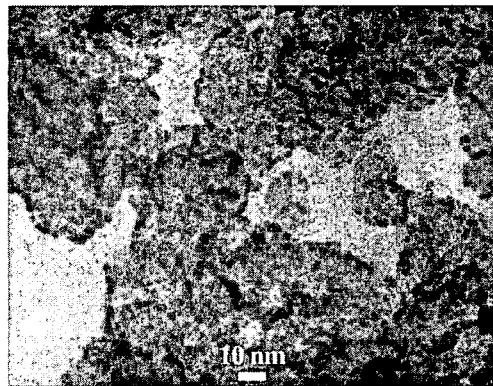
Element	Heat of Mixing (kJ/mol)
B	- 13
N	+ 103
S	—
P	- 26
Si	- 36

Table 2 Effect of Additives on Size Reduction

Additive	Size of PtRu Catalyst (nm)
Without	3.7
B	3.2
N	2.8
S	2.3
P	2.1
Si	3.3



(A) PtRu Catalyst



(B) PtRuP Catalyst

Fig.1 TEM Images of (A) PtRu and (B) PtRuP Catalysts (Carbon Support : Vulcan XC-72R).

Anode polarization characteristics of PtRu and PtRuP catalysts are shown in Fig. 2. PtRuP catalyst suppressed anode polarization by about 0.2 V at current density of 150 mA/cm², and current density increased from 35 mA/cm² to 350 mA/cm² at 0.4 V vs. NHE. Power density characteristics of DMFCs are shown in Fig. 3. Maximum power density in passive state of DMFC was improved from 38 mW/cm² to 64 mW/cm² at 298 K by using 2 nm of well dispersed PtRuP anode catalyst.

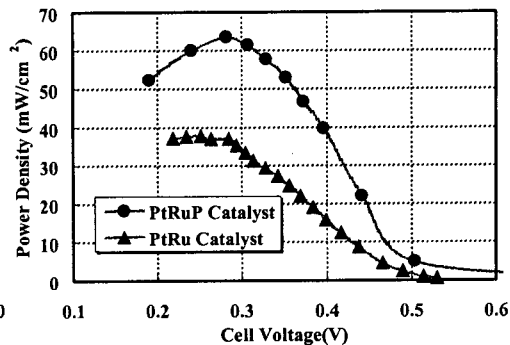
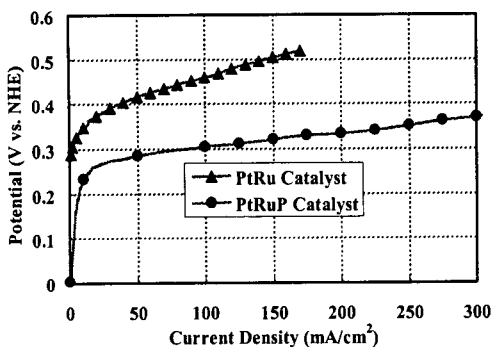


Fig. 2 Anode Polarization Characteristics. Fig. 3 Power Density Characteristics of DMFCs.

Existing state of P in PtRuP catalyst was analyzed. TEM-EDX analysis showed that none of Pt, Ru and P was detected on surface of carbon support. On the contrary, Pt, Ru and P were detected on catalyst particles. These results indicate that PtRu and P coexist. XPS analysis indicated that P in PtRuP catalyst exists as oxidized state. XPS analysis showed higher P content compared with XRF analysis, suggesting that P exists at surface of PtRu catalyst particle. In high resolution TEM observation, lattice image was observed in each PtRuP catalyst particle, implying that PtRuP catalyst exists as nearly single crystal state. XRD analysis showed that lattice distance of (111) plane of 0.224 nm changes little by addition of P, suggesting that possibility for formation of interstitial compounds such as Pt-P and Ru-P is low. Taking these analytical results into consideration, it is concluded that P exists at surface of PtRu catalyst particle as oxidized state without forming interstitial compounds.

The other feature of PtRuP catalyst is retention of its size regardless of specific surface area of carbon supports. Size of PtRuP catalyst is retained in 2 nm in case that PtRuP catalysts are loaded on carbon supports having specific surface area from 140 m²/g to 800 m²/g. Figure 4 shows TEM image of PtRuP catalyst loaded on carbon support with specific surface area of 140 m²/g (Vulvan-P). It can be seen that size of the PtRuP catalyst is retained in 2 nm and that PtRuP catalysts are well dispersed. Carbon supports with smaller specific surface area are less porous carbon supports. Usage of less porous carbon supports raises number of PtRuP catalyst existing on surface of carbon supports, which is considered to improve utilization efficiency of catalyst. Figure 5 shows SEM and TEM images of PtRuP catalyst deposited on porous carbon support of Ketjen Black EC with specific surface area of 800 m²/g. In SEM image, it is seen that 2 nm of PtRuP catalysts exist on surface of the support. In the corresponding TEM image, observed number of PtRuP catalysts is greatly raised compared with SEM image, which implies that a lot of PtRuP catalysts are buried in the micropores of the carbon support. Figure 6 shows SEM and TEM images of PtRuP catalyst deposited on less porous carbon support of Vulcan-P having specific surface area of 140 m²/g. In SEM image, it can be seen that number of 2 nm of PtRuP catalysts existing on the surface of carbon support greatly increased.

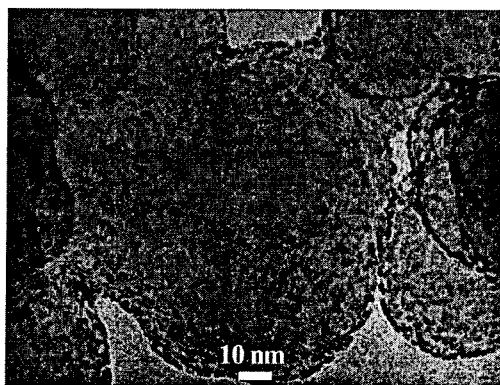


Fig. 4 PtRuP Catalyst Deposited on Less Porous Carbon Support (Carbon Support :Vulcan-P).

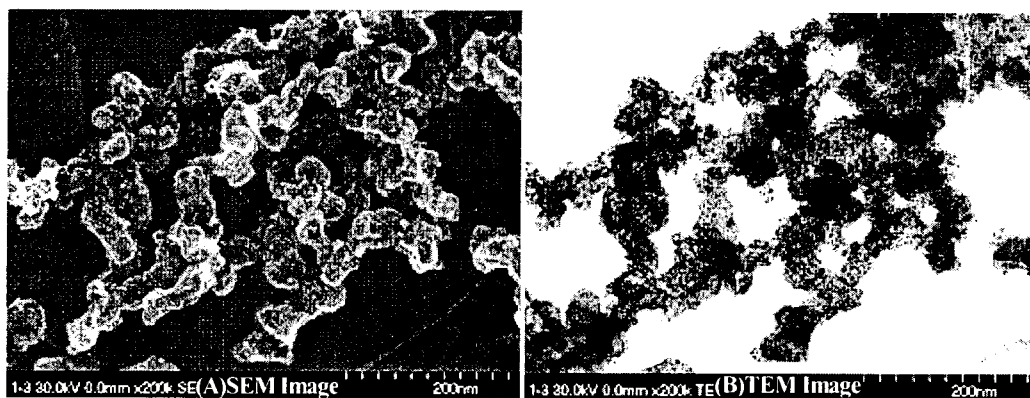


Fig. 5 SEM & TEM Images of PtRuP Catalyst Supported on Ketjen Black EC (S_{BET} :800 m^2/g).

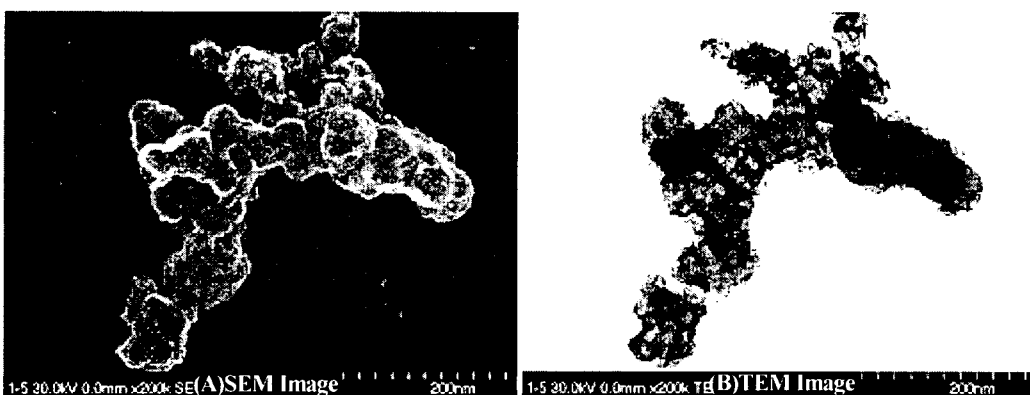


Fig. 6 SEM & TEM Images of PtRuP Catalyst Supported on Vulcan-P (S_{BET} :140 m^2/g).

Figure 7 shows power density characteristics of DMFCs using 2 nm of PtRuP anode catalyst deposited on carbon supports having specific surface area of 800 m²/g, 254 m²/g and 140 m²/g, respectively. It is clear that maximum power density of DMFCs improves with usage of carbon supports having smaller specific surface area, that is, with usage of less porous carbon supports. This is attributed to increase in number of 2 nm of PtRuP catalysts existing on surface of carbon supports by using less porous carbon supports. PtRuP catalyst, which is deposited on less porous carbon supports and retains its size in 2 nm, is a strong candidate for improving catalytic activity and utilization efficiency of catalyst simultaneously.

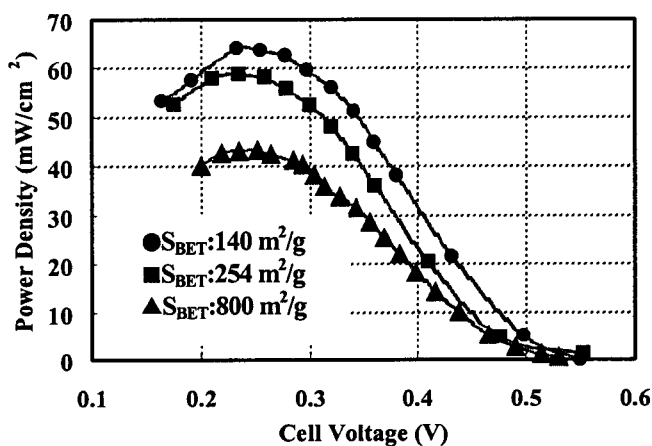


Fig. 7 Power Density Characteristics of DMFCs.

CONCLUSION

Size reduction of the PtRu catalyst by addition of non-metallic elements was examined to improve its catalytic activity. It was found that the addition of N, P and S reduces the size of the PtRu catalyst and that P is the most effective additive in size reduction. Analyses of TEM-EDX, XPS, XRF and XRD on the PtRuP catalyst showed that P exists on the surface of the PtRu catalyst particle as oxidized states without forming interstitial compounds. Maximum power density of 64 mW/cm² was achieved in passive state of DMFC at 298 K by using 2 nm of well dispersed PtRuP anode catalyst. Size of 2 nm in PtRuP catalyst was retained regardless of specific surface area of carbon supports, which made it possible to use less porous carbon supports and further raise the number of 2 nm of PtRuP catalyst existing on the surface of carbon supports, which improved utilization efficiency of the catalyst. Maximum power density of DMFC was improved from 44 mW/cm² to 64 mW/cm² by utilization of less porous carbon support having specific surface area of 140 m²/g. 2 nm of well dispersed PtRuP catalyst loaded on less porous carbon supports is a strong candidate for achieving high catalytic activity and high utilization efficiency of catalyst simultaneously.

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