Preparation of Pt/C electrocatalysts using an incipient precipitation method

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Abstract−Highly loaded and dispersed Pt/C catalysts, used as cathodic electrocatalysts in low temperature fuel cells, were prepared using a new method involving the slow addition of a Pt precursor to a solution containing dispersed carbon powder and a reducing agent. During this process, the added Pt precursor was reduced instantaneously into fine particles and adsorbed onto the carbon surface in the solution. A Pt loading of 55 wt% was obtained, which was close to the nominal amount of Pt, 60 wt%, added in the preparation step. The average particle size of Pt was about 4.2 nm, according to X-ray diffraction. The surface area of the Pt measured by cyclic voltammetry was about 61.4 m^2/(g of Pt). The activity of the prepared Pt/C, as an electrode of polymer electrolyte membrane fuel cell, was increased by 34.8% and 15.0%, according to the half- and single-cell tests, respectively, compared to the activity of one prepared using a conventional precipitation method.

Key words: Supported Electrocatalysts, Fuel Cell Electrode, Precipitation, Dispersion, Oxygen Reduction Reaction

INTRODUCTION

The performance of a polymer electrolyte membrane fuel cell (PEMFC) depends largely on the activity of the cathodic electrocatalyst because the rates of oxygen reduction are slow at low operating temperatures, typically below 80 °C. Consequently, an active catalyst with a high Pt surface area is required for the cathode. However, the preparation of highly dispersed Pt/C catalysts, especially with high Pt loading, is a challenge because the dispersed Pt particles are easily sintered due to a weak interaction between the Pt and the C.

Pt/C catalysts are commonly prepared by three methods: impregnation, colloid, and precipitation. The impregnation method, in which the metal precursor is reduced using either an aqueous reducing agent or hydrogen after the metal precursor has been introduced onto the support, is frequently used due to its simplicity. However, the method has the drawback of producing relatively large Pt particles with a broad size distribution [1-5]. As an alternative to the impregnation method, a colloidal method has been used by many researchers, in which the metal precursor is reduced chemically to form metal particles in the presence of a surfactant [6,7]. The size and distribution of metal particles can be controlled because the colloidal metals form either in the organosols or in the hydrosols. The surfactants, which are detrimental to the activity, need to be removed by washing the prepared catalyst with an appropriate solvent or by heating it at high temperatures under an inert atmosphere. However, the metal particles can agglomerate or sinter in this step, which would eventually cause them to lose their initial high dispersion. The precipitation method is similar to the colloid method except that no protective agent is used [8-11]. Precipitation requires careful control of the process parameters, such as pH and solvent concentration, to yield small Pt particles.

In this study, highly dispersed Pt/C catalysts with high Pt load-

ing were prepared using an incipient precipitation method (IPM) that mitigates the drawbacks of the conventional precipitation method (PM). Unlike the PM, in which either the precipitant or the reducing agent was added to a solution containing the metal precursor, the IPM distinguished itself by adding the Pt precursor to a solution containing the reducing agent of a controlled concentration. In this way, the added Pt precursor was allowed to reduce instantaneously into Pt nanoparticles and be adsorbed onto the carbon support dispersed in the solution. The surface characteristics and electrochemical activities of the prepared Pt/C catalysts were compared with those of the catalysts prepared using the PM.

EXPERIMENTAL

1. Preparation of Catalysts

Prior to the preparation of the Pt/C catalyst, the carbon support (Vulcan XC-72, 220 m^2/g) was heat-treated in air at 773 K for 2 h, washed with de-ionized water, and finally dried in air at 373 K for 1 h.

The Pt/C catalysts were prepared by two methods: the PM and the IPM. With the former method (PM), solution A, which contained 0.4 g of the Pt precursor (H_2PtCl_6), 35 ml of de-ionized water and a heat-treated carbon support, was introduced into a reactor and stirred at 500 rpm for 5 min. Different amounts of the carbon support were used for the purpose of adjusting the Pt loading. Another solution, B, containing 0.088 g of the reducing agent ($NaBH_4$) and 35 ml of de-ionized water was slowly added to solution A in the reactor at a rate of 1.5 ml/min, while the reactor solution was stirred at 2,500 rpm. After completion of the addition of solution B, the solution mixture was stirred at 500 rpm for 70 min before the powders were finally filtered, washed with excess de-ionized water, and dried in an oven at 373 K for 2 h.

In the latter method (IPM), the above two solutions were mixed in the opposite order, i.e., the solution containing the Pt precursor, A, was added to the solution containing the reducing agent, B. In this case, solution B contained the reducing agent ($NaBH_4$) in an

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amount ten times greater than that in the case of the PM and additionally contained the carbon support. Solution A, comprising 0.4 g of the Pt precursor and 35 ml of de-ionized water, was slowly added to solution B at a rate of 1.5 ml/min, while the latter solution was stirred at 2,500 rpm. Procedures after the completion of the addition of solution A were the same as those in the case of the PM.

2. Characterization and Testing of Catalysts

The electrochemical characteristics of the prepared catalysts were evaluated by cyclic voltammetry (CV) with a potentiostat (EG&G M263A1) connected to a three-electrode cell assembled with glassy carbon, Ag/AgCl and Pt wire as the working, reference and counter electrodes, respectively.

The electrochemical activities of the catalysts in the oxygen reduction reaction (ORR) were measured by a rotating disk electrode (RDE, PerkinElmer, Model 616) in 0.5 M sulfuric acid at room temperature. For the ORR experiments, the electrolyte was saturated with oxygen. The activity was tested for 4,000 sec at 0.9 V. The single-cell tests of the 30 wt% and 60 wt% Pt/C catalysts prepared by the two methods were made using Nafion 115 as the polymer electrolyte of the membrane-electrode assembly (MEA). The anode and cathode contained commercial 60 wt% Pt/C (E-Tek, Corp.) and the catalyst prepared in this study, respectively, and the catalyst loading was 0.3 mg/cm^2 in both the anode and cathode. The single cell, with an active area of 9 cm^2, was fed with 200 ml/min of hydrogen in the anode and with 200 ml/min of oxygen in the cathode.

The heat-treated and the pristine carbon (Vulcan XC-72) were characterized using nitrogen physisorption measurements from a Micromeritics ASAP 2010 instrument. The amounts of N_2 adsorbed on, and desorbed from, 0.1 g carbon in the adsorption cell at 77 K were calculated, and the average pore diameter and the Brunauer-Emmett-Teller (BET) surface area of the carbon were determined.

The platinum content of the prepared catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Shimadzu, ICPS-1000IV).

X-ray powder diffraction was carried out at room temperature using a D/max 2,500 V PC X-ray diffractometer (Rigaku) with monochromatized Cu Kα radiation as a source between 20 and 85° 2θ at a scan rate of 5°/min. The specimens for high resolution transmission electron microscopy (HRTEM) analysis were prepared by ultrasonically suspending the catalyst powder in de-ionized water at a catalyst/water volume ratio of 1/20. One drop of the suspension was applied to a carbon-coated Cu mesh, which was then allowed to dry in air. The samples were examined with a JEOL-3010 electron microscope operated at 200 kV.

RESULTS AND DISCUSSION

1. Effect of Carbon Burn-off

Table 1 shows the BET surface areas and the average pore dia-

Table 1. Surface area and average pore size of a carbon support measured by N_2-physisorption

	No heat treatment	500 °C in H_2	500 °C in air
Surface area [m^2/g]	220	226	303
Ave. pore dia. [nm]	6.1	5.6	4.7

meters of the carbon supports, which were treated at 500 °C in either H_2 or air. The surface area of the air-treated carbon (C_{air}) was about 38% higher than that of either the pristine carbon ($C_{pristine}$) or the H_2-treated carbon (C_{H2}). In addition, the average pore diameter of the C_{air} was smaller than that found in either the $C_{pristine}$ or the C_{H2}. The above results agree with the previous reports that air oxidation was increased in both the surface area and the surface roughness of the carbon [12].

Table 2 shows the average sizes of the Pt particles dispersed in the catalysts that were supported on either the oxidized or the pristine carbon using either the IPM or the PM. The size of the Pt particles supported on the oxidized carbon was smaller than that on the pristine carbon regardless of the preparation method, which is in accordance with the report by Ehrburger et al. [13] that the gasification of carbon promoted the dispersion of Pt on the support. They attributed the improved dispersion of the Pt to the increased surface heterogeneity of the air-treated support, i.e., the modified surface provided high energy barriers to the movement of Pt particles.

2. Characterization of Catalysts

Fig. 1 shows X-ray diffraction patterns of 30 wt% and 60 wt% Pt/C catalysts (nominal contents) prepared using the oxidized carbon by either the IPM or the PM. The average particle size of Pt was calculated from the full-width half-maximum (FWHM) value of the Pt (220) XRD peak using the Scherrer formula [3]. Table 3 summarizes the particle sizes and surface areas of Pt as estimated from XRD, and also the surface areas of Pt as estimated from the CV. The surface areas calculated from CV were smaller than those calculated from XRD, but both results showed a similar trend as catalysts were prepared under different conditions. Accordingly, it can be concluded that the catalysts prepared by the IPM contained Pt particles of smaller sizes, i.e., larger surface areas, than those prepared by the PM, regardless of the Pt loading. The HRTEM of the prepared catalysts (Fig. 2) shows that the Pt particles were uniform and well distributed in the case of 60 wt% Pt/C (IPM) but were significantly agglomerated in the case of 60 wt% Pt/C (PM).

The above results suggest that a larger number of nuclei were formed and the growth rates were slower with the IPM than with the PM. In the IPM, the Pt precursor was instantly reduced to Pt when added to solution B containing the reducing agent at high concentration. Furthermore, the growth of the Pt particles in solution B was limited because the Pt precursor was added at a slow rate, and

Table 2. Pt particle size calculated from XRD results according to preparation methods using carbon supports before and after heat treatment

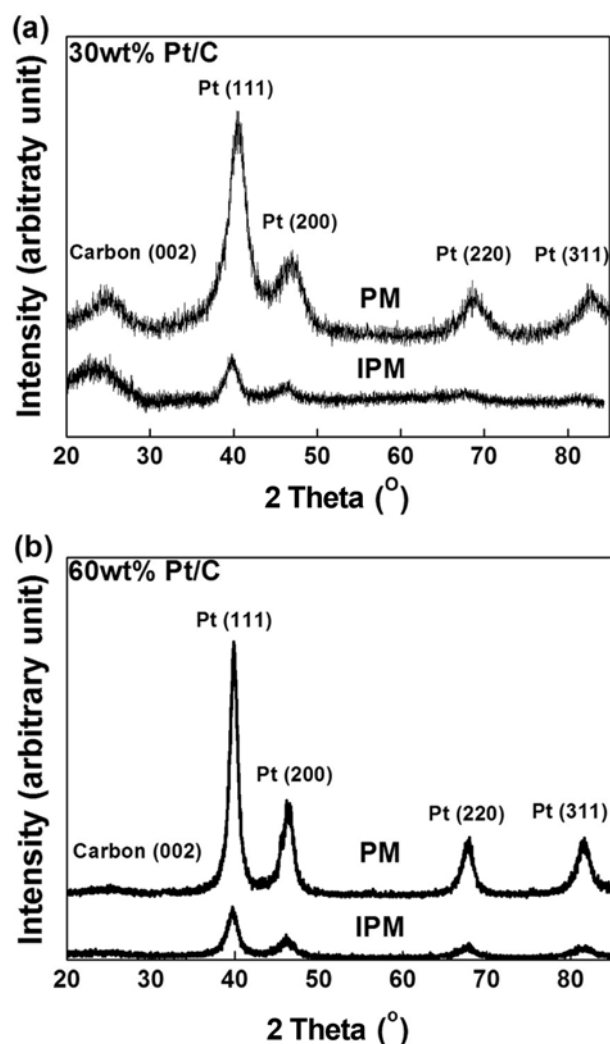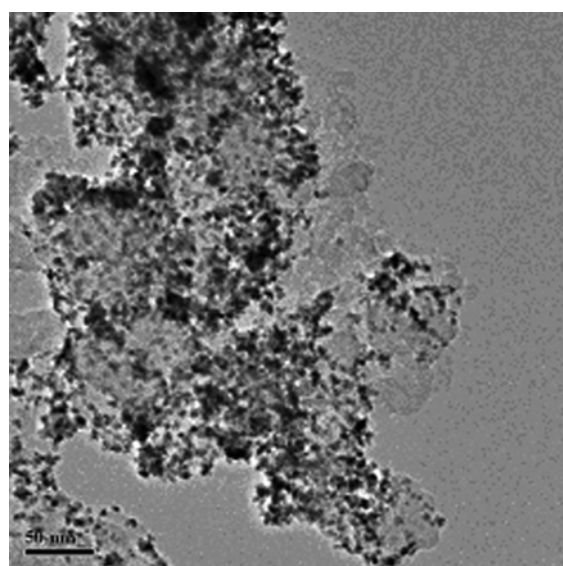| Nominal loading [wt%]	Precipitation method	Average size of Pt supported on no-treated carbon [nm]	Average size of Pt supported on air-treated carbon [nm]
60	IPM	4.7	4.2
	PM	6.4	5.3

Fig. 1. XRD pattern of Pt/C catalysts prepared by IPM and PM (a) 30 wt% (b) 60 wt%.

Fig. 2. HRTEM images of 60 wt% Pt/C catalysts prepared by (a) IPM (b) PM.
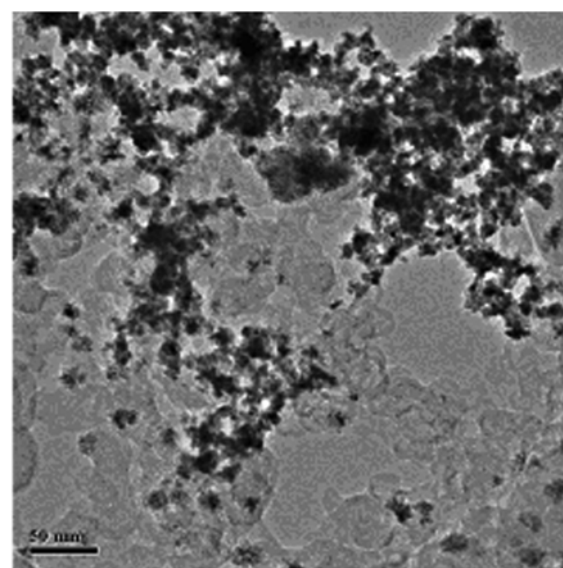
therefore solution B was very low in the concentration of the precursor. On the other hand, when the catalysts were prepared by using the PM, the Pt precursor was reduced to Pt over an extended period, being sequentially converted to Pt anions such as $PtCl_6^{2-}$ and $PtCl_4^{2-}$, because the reducing agent was added to the solution at a slow rate. The precipitated Pt particles were subject to nucleation and growth in solution A, which was already high in the concentration of the Pt precursor.

3. Electrochemical Activity

The results of the half-cell tests, shown in Fig. 3, indicate that the activity of Pt/C (IPM) was higher than that of Pt/C (PM) regard-

less of the Pt loading. The high activity of the former catalyst is attributed to its high electrochemical surface area, as mentioned above. The above trend is also observed in single-cell tests using the prepared catalysts (Fig. 4). Table 4 compares the mass activities of the prepared catalysts measured under the fixed conditions of half-cell and single-cell tests. The mass activities of the 30 wt% Pt/C catalysts

Table 3. Summary of the loading amounts of Pt, particle sizes of Pt from XRD, and surface areas of Pt calculated from XRD and CV

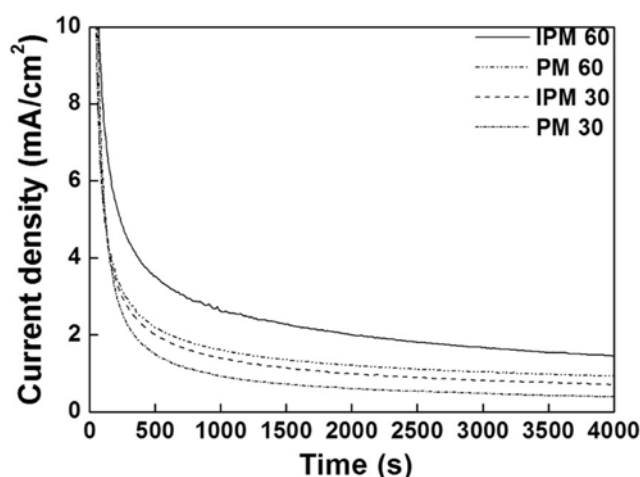| Nominal loading [wt%]	Precipitation method	Loading quantity (wt%)	Average Pt particle size based on XRD [nm]	Pt surface area based on XRD [m²/g]	Pt surface area based on CV [m²/g]
60	IPM	55.3	4.2	66.8	61.4
	PM	57	5.3	52.9	47.7
30	IPM	27.6	2.3	121.9	108.7
	PM	28.4	3.0	93.5	89.1

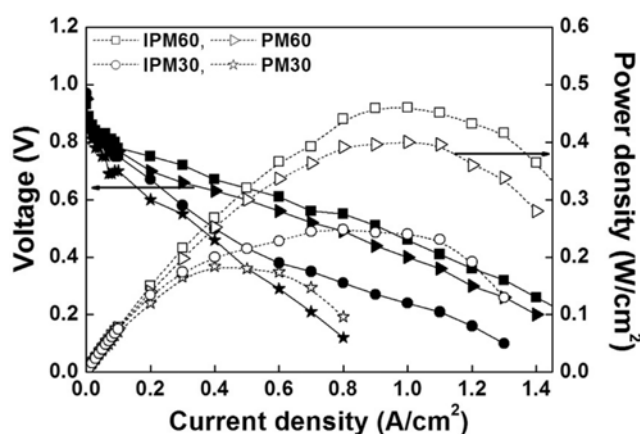**Fig. 3. The mass activity of Pt/C catalysts measured by half cell.**

Fig. 4. Single-cell performance.

were lower than those of the 60 wt% Pt/C catalysts even though the average size of the Pt particles was smaller in the former case. This was attributed to the increased mass transfer resistance of O_2 in the cathodic electrode that had a larger electrode thickness when the catalysts of lower Pt loading, 30 wt%, were used. The activity of the 30 wt% Pt/C (IPM) was similar to that of the 60 wt% Pt (PM) due to the increased resistance of O_2 diffusion, as previously mentioned. In all cases of the Pt loading and test methods, the activity of the Pt/C (IPM) was consistently higher than that of the Pt/C (PM).

The 60 wt% Pt/C (IPM) showed the best overall performance among the prepared catalysts due to the small size of the Pt particles and the thin electrode.

CONCLUSIONS

A highly dispersed 55 wt% Pt/C electrocatalyst was prepared by an incipient precipitation method (IPM), which allowed the rapid reduction of the Pt precursor to Pt nanoparticles that were eventually deposited onto the carbon support. The Pt/C catalysts prepared by the IPM showed better electrochemical performance in a polymer electrolyte fuel cell than those prepared using the conventional precipitation method (PM) with the same Pt loading.

ACKNOWLEDGMENTS

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Table 4. The ratio of Pt particle size and the activity of 30 wt% and 60 wt% Pt/C catalysts prepared by the incipient precipitation and precipitation methods

Nominal loading [wt%]	Precipitation method	Ratio of mass activity measured by half-cell test (mass activity, mA/cm²g_Pt)	Ratio of mass activity measured by unit-cell test (mass activity, W/cm²)
60	IPM	1.32 (2.71)	1.79 (0.46)
	PM	0.98 (2.01)	1.61 (0.40)
30	IPM	**1 (2.05)**	**1 (0.25)**
	PM	0.75 (1.55)	0.7 (0.17)