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Short communication

The preparation of Pt/C catalysts using various carbon materials for the cathode of PEMFC

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Abstract

Various 60 wt% Pt/C catalysts were prepared using LG precipitation method with Vulcan XC-72, Ketjen black EC 300J, and Ketjen black EC 600JD. The average Pt particle size decreases with increasing the surface area of carbon black supports. The 60 wt% Pt/C catalyst with 1.6 nm of Pt particle size and good dispersion could be prepared using Ultra high Surface Area Carbon (USAC, Ketjen black EC 600JD). In single cell test, the activity of electrode catalysts was enhanced with Pt surface area increase above 0.6 V but the correlation between activity of catalysts and Pt surface area was not clear below 0.6 V. Pt catalyst supported on USAC showed good oxygen reduction activity in all voltage regions and also showed stable voltage of 0.6 V at 900 mA cm^{-2} without degradation over 180 h of durability test.

Keywords: Fuel cell; Catalysts; Pt/carbon; Precipitation; Carbon black; Cathode

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is an attractive power source for various applications such as backup power systems, stationary power systems, electrically powered vehicles, and distributed power generations, since it is an electrochemical power plant that directly converts chemical energy into electrical energy efficiently without air pollution. The depletion of crude oil and the increment of oil consumption by BRICs will continuously threaten stable energy supply. To reduce the consumption of crude oil and air pollution, the development of renewable energy source, such as fuel cell, photovoltaic cell, wind power generation, geothermal energy, and so on, is encouraged in many countries. All kinds of renewable energy can be used for the generation of electricity. For the automobile application, however, PEMFC is the most appropriate energy source because it could be operated at any time with the supply of fuel.

One of the significant obstacles for the commercialization of PEMFC is the high cost of MEA, especially the high cost of noble metals used as electrode catalysts such as Pt and Ru [1] since the cost of these noble metals could not be reduced by the mass production. Pt is the only catalyst known to be active for hydrogen oxidation, methanol oxidation, and oxygen reduction at low temperature [2]. The first progress of Pt catalyst was the development of the carbon supported Pt catalysts to replace Pt black catalysts used in Phosphoric Acid Fuel Cell (PAFC) by United Technologies Corporation (UTC) in the 1970s, which reduced the required Pt amount from 5 to 1 mg cm^{-2} [3].

Most commonly used carbon support is Vulcan XC-72 with BET specific surface area of 250 $m^2\,g^{-1}$ that was developed for PAFC catalysts but also good as a PEMFC catalysts so far. The carbon support is important to obtain sufficient active Pt surface area by helping the dispersion of small Pt particle. Also, carbon support materials have an excellent combination of electron conductivity, corrosion resistance, surface properties, and low cost for the commercialization of fuel cell [4]. Therefore, many research groups have studied various carbon support materials such as carbon nanotube [5], graphitic carbon nanofiber [6], carbon nanohorn [7], carbon nanocoil [8], ordered uniform porous carbon networks [9], and so on, in order to replace commonly used Vulcan XC-72. However, the promising carbon support that could replace Vulcan XC-72 is not discovered yet.

Herein, we synthesized Pt catalysts (60 wt% Pt/C) on carbon black with various surface areas. We found that the average Pt

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particle size decreases with increasing the surface area of supports by the same Pt/C fabrication method. We measured the oxygen reduction activities of catalysts using single cell test apparatus. LG3 catalyst, the catalyst using Ultra high Surface Area Carbon (USAC, BET S.A. = 1500 $m^2 g^{-1}$), showed the best electro-catalytic activity compared with other LG Pt/C catalysts using the lower surface area carbon black and the best commercial Pt/C catalysts. LG3 catalyst also showed stable activity for more than 180 h on durability test.

2. Experimental

2.1. Preparation of catalysts by precipitation

Modified precipitation method was used to prepare Pt/C with high loading and good dispersion on the carbon surface. The following describes simple and short procedure that is well explained in our previous paper [10]. The carbon slurry was prepared by vigorous mixing of carbon black with distilled water. Then the slurry was heated up to a desired temperature around 90 °C. The pH of the slurry was adjusted to the basic using Na_2CO_3. The chloroplatinic acid solution, prepared by dissolving chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, Heesung Engelhard) into the distilled water, was added to the carbon slurry and the pH of the slurry was again adjusted to the basic. Reducing agent was then introduced into the slurry for *in situ* liquid-phase reduction. The Pt/C slurry was filtered, washed, and then dried at 80 °C in an oven.

2.2. Characterizations of Pt/C catalysts

The crystal structure of prepared catalysts was determined by X-ray powder diffraction (XRD, Bruker, D4 Endeavor). The average size of Pt particle was calculated by Debye-Scherrer equation using Pt(1 1 1) peak while the instrumental line broadening was not taken into consideration [11]. Pt dispersion on carbon and Pt particle size were also checked using Transmission Electron Microscope (TEM, Philips, TECNAI 20-S). The Pt metal loading after preparation of Pt/C was determined by Inductively-Coupled Plasmaspectrometer (ICP, GBC, Integra XMP). For the ICP analysis**,** the Pt/C catalysts were dissolved in aqua regia.

2.3. Preparation of MEA

Pt/C catalysts (60 wt%) were prepared for the fabrication of a membrane electrode assembly (MEA). Various catalyst inks containing Nafion® ionomer (Dupont, 5 wt% solution), Pt/C powder, and isopropyl alcohol were applied on carbon paper substrates (SGL 10BC) with 0.2 mg Pt cm^{-2} loading on the cathode and 0.4 mg Pt cm^{-2} (Johnson Matthey; HiSPEC® 9100) loading on the anode. The active area of MEA was 6.25 cm^2 (2.5 cm × 2.5 cm). Catalysts on the cathode are LG series catalysts or commercial catalysts as a reference. Nafion® 112 (thickness 50 μm, Dupont) membrane was inserted between anode and cathode layers by hot pressing. MEA was hot pressed at 140 °C for 2 min under a pressure of 1 tonne.

The active area of MEA for the durability test was 25 cm^2 (5 cm × 5 cm) and 0.4 mg Pt cm^{-2} was loaded on the cathode. The other conditions were same as above.

2.4. Single cell test

The electrochemical activity of Pt/C in the cathode catalysts was evaluated using pure hydrogen as a fuel and air as an oxidant at 70 °C cell temperature. The hydrogen flow rate was 200 ml min^{-1} and the air flow rate was 1000 ml min^{-1}. Anode and cathode were fully humidified. Single cell tests were carried out in 6.25 cm^2 single cell with one-channel serpentine flow field for anode and cathode side. A method to measure the MEA performance was as follows. First, single cell was operated at 0.6 V to activate the MEA and a stable current density was obtained after 4 h. Then, the polarization curves were obtained.

The durability of MEA was tested using large MEA in constant current mode at 900 mA cm^{-2} for more than 180 h. The hydrogen flow rate was 300 ml min^{-1} and the air flow rate was 1200 ml min^{-1}. The MEA was aged in constant voltage operation at 0.6 V for 1 day. The durability test was performed after aging.

3. Results and discussion

3.1. Preparation of catalysts by precipitation

Precipitation of a metal precursor on the support is a common method in the preparation of electrode catalyst because the procedure is relatively easy and simple comparing with colloidal method [12]. However, various synthesis parameters can affect the size and dispersion of the precipitated metal on the support. Usually Pt loading of Pt/C catalysts is between 20 and 60 wt%. The lower the Pt loading, the thickness of electrode catalyst layer is increased to meet the same Pt loading amount on electrode. As a result, the mass transfer of fuel and air in electrode is prohibited. Therefore, it is important to use catalyst with high loading of Pt to enhance the mass transfer of reactant. However, the preparation of catalyst becomes more difficult by the increase of Pt loading on support because the Pt particle starts to agglomerate at high Pt loading.

Though the PEMFC system market is not open yet, the initial market of PEMFC is already exist and there are several companies that commercially produce electrode catalysts. In market, the first generation of supported Pt catalysts used Vulcan XC-72 as a support for long time but the second generation of supported Pt catalysts, used high surface area carbon black (HSAC, BET S.A. = 700–800 $m^2 g^{-1}$) to increase the active Pt surface area by making smaller Pt particle, has been developed recently [13,14]. The maximum Pt loading was around 60 wt% with Vulcan XC-72 but now it could be reach up to 80 wt% using HSAC according to Johnson Matthey [15].

We prepared catalysts with 60 wt% Pt loading using different carbon blacks. The BET specific surface area of carbon blacks are 242 (Vulcan XC-72), 780 (Ketjen black EC 300J), 1475 $m^2 g^{-1}$ (Ketjen black EC 600JD), respectively. The TEM images of prepared catalysts show that the Pt particles are well

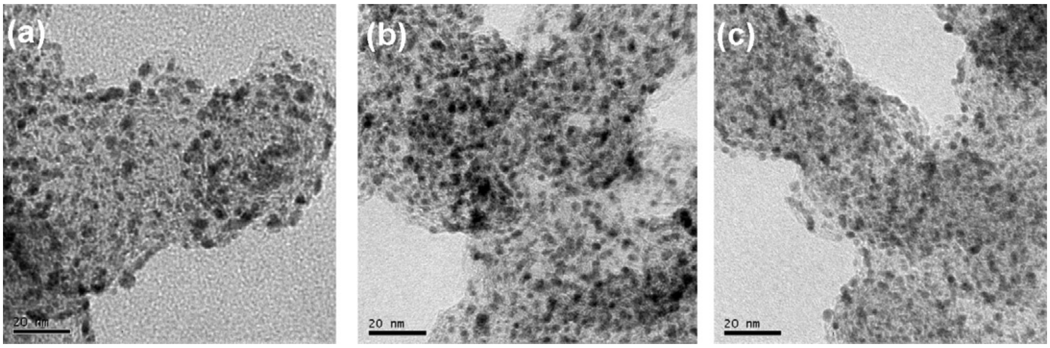

Fig. 1. The TEM images of (a) LG1, (b) LG2, and (c) LG3.

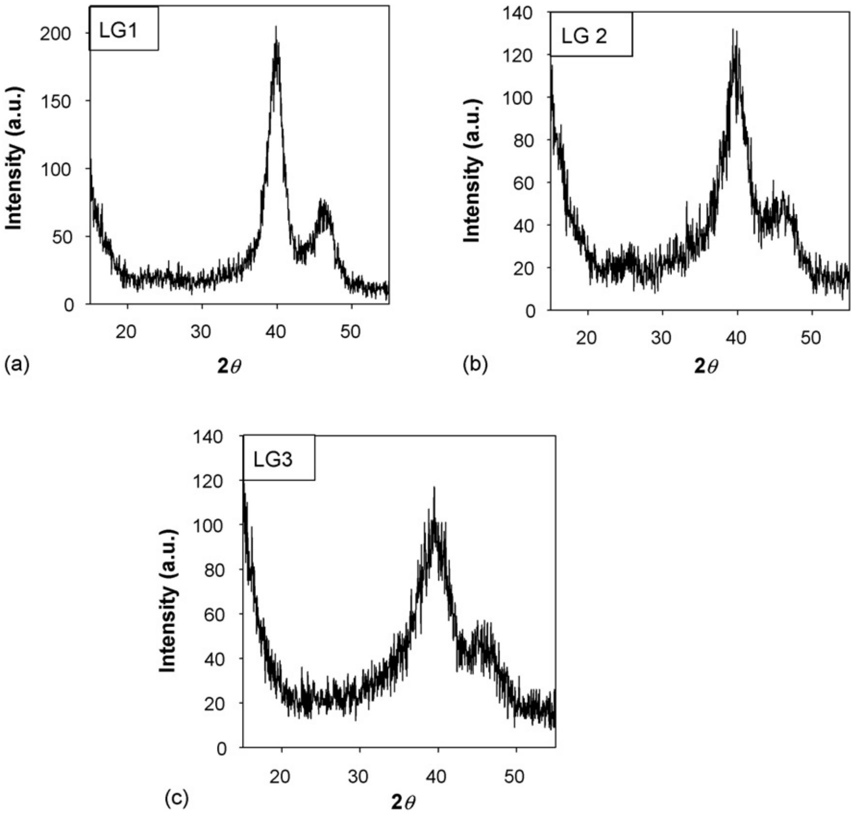

Fig. 2. The XRD spectra of (a) LG1, (b) LG2, and (c) LG3.

dispersed on the carbon surface (Fig. 1). Fig. 2 shows the XRD spectra of LG catalysts. The width of Pt(1 1 1) peak around 40° clearly shows the change of Pt particle size by the change of carbon support materials.

The calculated Pt particle size and the yield of Pt are summarized in Table 1, which shows the effect of the surface area of carbon black on the Pt particle size. As the surface area of carbon support materials increases, the average particle size of Pt decreases. The preparation of catalysts was performed with same conditions except carbon materials. The ICP analysis result shows that the yield of Pt on the carbon black is over 90%. All of the LG catalysts show 93% Pt yield that could be improved over 95% by the further optimization of preparation parameters. The physical properties of commercial catalysts are also shown in Table 1. The Pt particle size of LG3 catalyst is 1.6 nm that is smaller than those of commercial catalysts. This small particle size increases the active surface area of Pt on support and also increases the mass activity of catalyst. The preparation of catalyst with more than 60 wt% loading of Pt on the USAC will be studied in next step.

Table 1
The physical properties of LG 60 Pt/C catalysts and commercial 60 Pt/C catalysts

Catalysts	BET S.A. of carbon support ($m^2 g^{-1}$)	Pt particle size by XRD (nm)	ICP yield (%)
LG1	242	3.4	93
LG2	780	2.3	93
LG3	1475	1.6	93
Company A	800	2.1	n.a.
Company B	740	1.9	n.a.

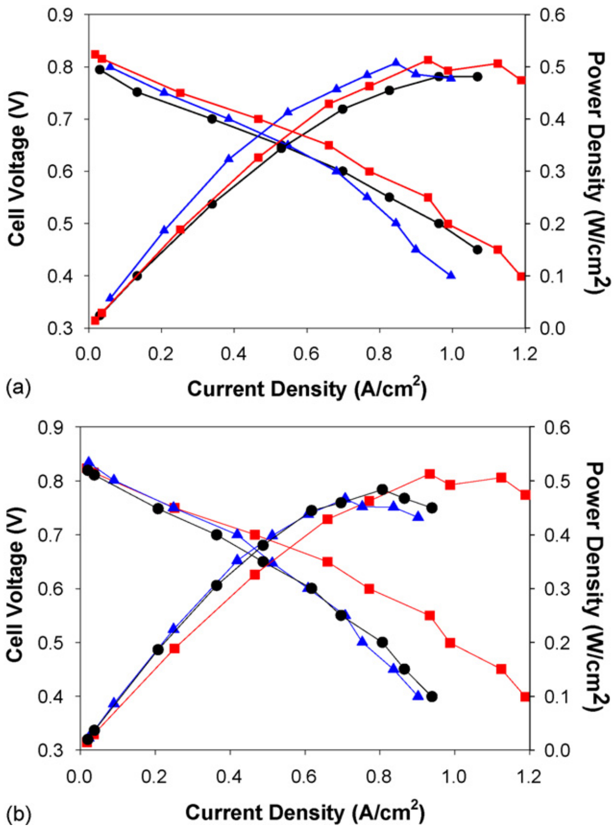

Fig. 3. (a) The polarization curves of LG1 (●), LG2 (▲), and LG3 (■), and (b) the polarization curves of LG3 (■), Company A (▲), and Company B (●) (H_2/air = 200/1000 sccm, anode/cell/cathode = 85/70/80 °C).

3.2. *Electrochemical reactivity of Pt/C catalysts*

The electro-catalytic activity of prepared catalyst and commercial catalysts were tested using a single cell and the polarization curves are shown in Fig. 3. LG Pt/C catalysts and commercial catalysts have the same Pt loading (60 wt% Pt) with different carbon support materials. The oxygen reduction reaction is known as rate-determining step in PEMFC system since exchange-current density of the oxygen reduction reaction (10^{-9} A $\mathrm{cm_{Pt}^{-2}}$) is six orders of magnitude lower than the hydrogen electro-oxidation reaction (10^{-3} A $\mathrm{cm_{Pt}^{-2}}$) [16]. Therefore, we examined the oxygen reduction activities of LG catalysts with fixed anode condition. Pt amount on cathode is generally 0.5 mg Pt cm^{-2} that is enough amounts to avoid MEA degradation by the deactivation of catalyst. We chose 0.2 mg Pt cm^{-2} for cathode because it is difficult to compare the activity of catalysts with regular amount of Pt on cathode. Fig. 3a shows the polarization curves of a single cell unit using LG catalysts as the cathode. The operating cell temperature was 70 °C and anode and cathode were fully humidified. At 0.6 V (Fig. 3a), the current density of LG3 catalyst is 780 mA cm^{-2} that is higher than that of LG1 and LG2. Above 0.6 V, the order of activity is LG1 < LG2 < LG3 and it is same as expectation. Below 0.6 V, LG2 catalyst showed fast voltage drop comparing with LG1 and it is also same as expectation. LG3, however, showed very different behavior below 0.6 V. We expected faster voltage drop comparing with LG2 but LG3 showed higher voltage than LG1. This implies that Pt particle size is not the only factor to affect the activity of electrode catalyst. LG3 catalyst could be used even in mass transfer limitation region in spite of thicker electrode layer than other catalysts. It might be attributed to the intrinsic properties of LG3 support and the preparation method of electrode catalyst. In our experiment, the activity of catalyst is mainly related with the available Pt surface area in high voltage region and the activity of catalyst is not directly related with the available Pt surface area in low voltage region.

In addition, Fig. 3b shows that the current density of LG3 is much higher than that of the commercial ones in all voltage regions even though Pt particle size is similar comparing LG3 catalyst with commercial catalysts. In our experiments, the excellent performance of LG3 catalyst is attributed to the high active surface area of Pt and the preparation method of LG electrode catalyst. Tada reported that the mass activities of electrode catalysts improved as the surface area of carbon support increased because of the increasing Pt surface area [17]. He studied carbon supports with surface area from 60 to 800 m^2 g^{-1} and he found almost linear increase of mass activities with the surface area of carbon support. Our result partially coincides with the result of Tada. The main factor for the excellent performance of LG3 electrode catalyst is under investigation.

The cyclic voltammograms of LG catalysts are shown in Fig. 4. The oxidation peak of hydrogen occurs around 0.2 V and this peak area could be used to determine the active Pt surface area by electrochemical method. The order of active surface area was LG1 < LG2 < LG3. These results are well correlated with the activity data over 0.6 V (Fig. 3).

The operating cell voltage of PEMFC is usually between 0.6 and 0.8 V, preferably 0.65 and 0.75 V because the stack efficiency and fuel utilization can be maximized in this voltage range. It is generally known that the performance of carbon support with high surface area is not good in mass transfer limitation region but this mass transfer limitation region is not an operating window in practical system. LG3 catalyst showed good performance in this practical operating condition and also in mass transfer limitation region. This implies that LG3 catalyst is more flexible in different humidification condition and also more robust to flooding in electrode. We expect LG3 catalyst

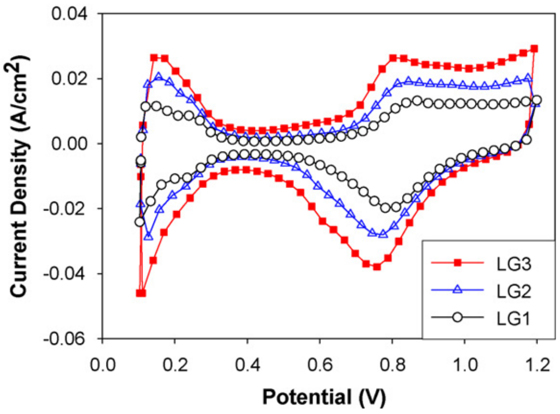

Fig. 4. The cyclic voltammogram curves of LG1 (●), LG2 (▲), and LG3 (■).

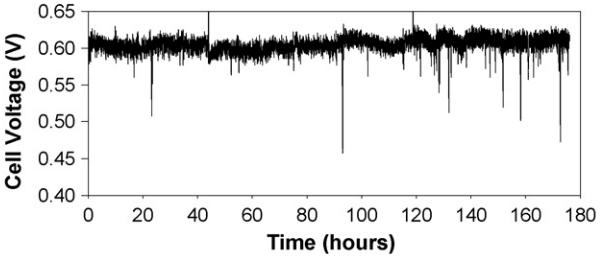

Fig. 5. The durability test of MEA using LG3 at 900 mA cm^{-2} (H_2/air = 300/1200 sccm, anode/cell/cathode = 85/70/75 °C).

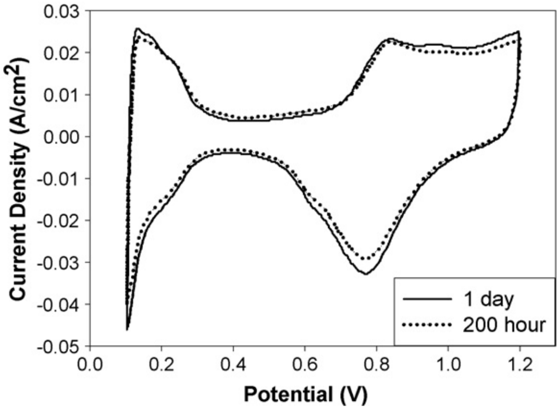

Fig. 6. The cyclic voltammogram curves of LG3 after 1 day and 200 h operation.

could be further improved by the increment of Pt loading higher than 60 wt% and it is under investigation.

3.3. Durability of Pt/C catalyst

The major hurdles for the commercialization of PEMFC are cost, performance, and durability. The durability is most difficult to measure because it takes thousands of hours of operation time and the factors affects durability are too many. For example, humidification condition, flow rate, cell temperature, channel design, gas diffusion layer, method of MEA manufacturing, mode of operation, and so on. The deactivation of catalysts shows slow decrease of MEA activity and the degradation of membrane also shows slow decrease of MEA activity. However, the abrupt failure of MEA happens when the pinhole is developed in membrane [18]. We performed primary durability test using LG3 at constant current of 900 mA cm^{-2}. According to report from Gore, the degradation rate of Gore MEA is 6 μV h^{-1} to 11,000 h at 800 mA cm^{-2} [19]. It is generally required less than 10 μV h^{-1} of MEA degradation rate for PEMFC application. The cell voltage was about 0.6 V at 900 mA cm^{-2} and the degradation of MEA was not observed after 180 h of operation (Fig. 5). The cyclic voltammograms of LG3 are shown in Fig. 6. There was no decrease of active Pt surface area after 200 h comparing with after 1 day of operation.

4. Conclusions

The effect of the surface area according to carbon support materials on Pt/C fabrication was investigated. The average Pt particle size decreases with increasing the surface area of carbon supports. The 60 wt% Pt/C catalyst with 1.6 nm of Pt particle size and good dispersion could be obtained using LG precipitation method. In single cell test, the activity of electrode catalysts was enhanced with Pt surface area increase above 0.6 V but the correlation between activity of catalysts and Pt surface area was not clear below 0.6 V. Pt catalyst supported on USAC showed good oxygen reduction activity comparing with catalysts using lower surface area supports and commercial catalysts in all voltage regions. The USAC supported catalyst also showed no deactivation over 180 h of durability test.

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