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Catalysis Today 87 (2003) 237–245
CATALYSIS TODAY
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Preparation of platinum-based electrode catalysts for low temperature fuel cell

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Abstract

We have studied systematically the effects of synthesis parameters in both precipitation and colloidal methods to obtain highly dispersed Pt/carbon catalyst and compared the characteristics of prepared catalysts with commercial ones. The average Pt particle size at optimum condition for 10–60 wt.% Pt/carbon was in the range 1.7–3.8 nm which was about 70–80% of the commercial catalysts at the same Pt loading. The Pt surface area was also 20–40% higher than those of the commercial catalysts. The activities of prepared catalysts, measured by a single cell unit, were comparable with those of commercial ones.

Keywords: Platinum; Electrode catalyst; Fuel cell; Particle size

1. Introduction

Fuel cell is getting more attentions with growing interest to the energy and environmental issues since it is an electrochemical power plant which directly converts chemical energy into electrical energy resulting in high energy conversion efficiency and high environmental affinity. There are several types of fuel cell systems working at different temperature. PEMFC (polymer electrolyte membrane fuel cell) and DMFC (direct methanol fuel cell) operating at low temperature have great potential to be commercialized for portable and automobile application. PEMFC and DMFC are also called LTFC (low temperature fuel cell).

The major hurdle for the commercialization of LTFC is the high cost of MEA (membrane electrode assembly). The price of proton conductive membrane and bipolar plate can be reduced through the mass production. However, the price of electrode catalysts will not be affected because the electrode catalyst for the LTFC mainly consists of precious metals, such as Pt and Ru. Pt is the only catalyst known to be active for hydrogen oxidation, methanol oxidation, and oxygen reduction at low temperature. Although there have been several attempts to find non-precious metal electrode catalysts such as Chevreal-phase type ($MoO_4Ru_2Se_8$) [1], transition metal sulfide ($Mo_xRu_yS_z$ and $Mo_xRh_yS_z$) and chalcogenide ($(Ru_{1-x}Mo_x)SeO_z$) [2], none showed promising results.

The typical Pt loading used for PEMFC has been between 20 and 40 wt.% Pt/carbon. However, 60 or 70 wt.% Pt loading [3] will be favorable if sufficient Pt surface area is obtained because high Pt loading reduces relative amount of supporting carbon resulting in promotion of internal mass transfer of reactants in an electrode. Unfortunately, it is difficult to gain the high Pt loading and dispersion at the same time. Therefore, enhancement of Pt dispersion at high loading is an important research issue in preparing electrode catalysts.

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doi:10.1016/j.cattod.2003.10.016

Two methods frequently used for preparation of Pt/carbon catalyst are the precipitation method using pH adjustment followed by liquid-phase reduction [4,5] and the colloidal method using PtO_2 colloid [6]. Other noble methods have also been proposed. Bönnemann et al. [7] suggested NR^{4+}-stabilized metal colloid route, Sung and co-workers [8] suggested the usage of water-incompatible organic solvent in nitrogen atmosphere to form nano-sized particles of colloidal Pt, and Zhou et al. [9] suggested polyol process. However, their methods have disadvantages of using special Pt precursor and/or organic solvents, which make the commercial production less feasible.

Unfortunately, we could hardly find systematic studies on the function of preparation parameters of the most frequently used methods such as precipitation and colloidal methods in open literatures. We therefore investigated key synthesis parameters to control the Pt particle size and Pt dispersion. Through adjustment of important synthesis parameters optimum conditions were extracted. The prepared catalysts were compared with commercial ones in the Pt dispersion and electrochemical activity.

2. Experimental

2.1. Preparation of catalysts by precipitation

The carbon slurry was prepared by mixing carbon black (Vulcan XC72R, Cabot) vigorously with the 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 $NaHCO_3$. The chloroplatinic acid (CPA) solution, prepared by dissolving CPA (H_2PtCl_6, Strem) 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/carbon slurry was filtered, washed, and then dried at 80 °C in a vacuum oven.

2.2. Preparation of catalysts by colloidal method

Both the PSA (platinum sulfite acid) method and the CPA method developed by Petrow and Allen [6] were used for the preparation of Pt/carbon catalysts. In the PSA method, PtO_2 colloids were obtained by oxidizing PSA by H_2O_2 and deposited onto the carbon support. In the CPA method, CPA was used as the starting material. By adding $NaHSO_3$ to CPA, PSA could be obtained. Once PSA formed, the next procedure was the same as in the PSA method. The PtO_2/carbon catalysts were reduced at room temperature in 50% H_2/50% N_2 flow.

2.3. Characterizations of Pt/carbon catalysts

The phase compositions of the prepared catalysts were determined by XRD (X-ray powder diffraction, Rigaku, Geigerflex D/max-IIIC). The average size of Pt particle was calculated using Scherrer equation using Pt (1 1 1) peak [10]. The instrumental line broadening was not taken into consideration since the width of Pt (1 1 1) peak in our samples was very wide due to the small particle size. In order to confirm the validity, the Pt dispersion on carbon and Pt particle size were also checked using TEM (transmission electron microscope, Philips, TECNAI 20-S). The values determined from both XRD and TEM images were in good agreement with a deviation less than 0.5 nm. The Pt metal loading after preparation of Pt/carbon was determined by ICP (inductively coupled plasmaspectrometer, GBC, Integra XMP).

The catalyst prepared by PSA contained 2.6 wt.% sulfur (determined by scanning electron microscope with energy dispersive spectrometer analysis) which was originated from the Pt precursor while the amount of sulfur in Pt/carbon supplied by E-Tek was also 2.3 wt.%. However, the residual sulfur detected in the tested catalysts did not seem to affect the performance of fuel cell in the experimental conditions of the present study.

2.4. Single cell test

The MEA was prepared by coating the prepared Pt/carbon on both sides of membrane (Nafion®), covering with carbon paper, and hot-pressing those. The Pt loading was maintained at about 0.5 mg/cm^2. The MEA was mounted into a single cell unit. The single cell performance was evaluated in the H_2/air operation mode.

3. Results and discussion

3.1. Precipitation

Precipitation of a metal precursor on the support is a widely used method for the catalyst preparation because the procedure is relatively easy and simple. However, various synthesis parameters can affect the size and dispersion of the precipitated metal on the support. Table 1 shows the effect of synthesis temperature and reducing agent on the Pt particle size in 20 wt.% Pt/carbon prepared by precipitation described in Section 2. The pH adjustment, Pt solution introduction, and, liquid-phase reduction are carried out at a fixed temperature which could influence Pt precipitation and reduction rate. As synthesis temperature increases from 75 to 90 °C, the Pt particle size decreases from 3.5 to 2.0 nm. The Pt loading efficiency on the catalyst prepared at 75 °C was around 90%, which was lower than the others. One may expect that as the temperature in precipitation increases, collisions between Pt precursor complex increase, resulting in bigger Pt particles. However, in the presence of the high surface area support, such effect may be inhibited. Instead, as the synthesis temperature increases, the carbon support with a very low density may reach an ideal colloidal state in water, which is favorable for the higher Pt dispersion. Synthesis of Pt/carbon at temperatures higher than 90 °C did not improve Pt dispersion.

The reducing agent also influences the Pt particle size as shown in Table 1. Formaldehyde and $NaBH_4$ result smaller Pt particles than *iso*-propyl alcohol and ethyl alcohol. The agent with a higher reducing power leads to higher dispersion of Pt resulting in smaller particles. Similar results for Rh particles were reported by Busser et al. [11]. They found that alcohols did not induce good dispersion while hydrogen, a strong reductant, resulted in the small particles. Among the reductants tested in this study, formaldehyde is shown to be the best reductant to obtain the highly dispersed Pt on carbon.

Table 1
Dependence of Pt particle size on synthesis temperature and reductant material for 20 wt.% Pt/VXC72R[a]

Synthesis temperature (°C)	Reducing agent	Average particle size (nm)[b]
75	HCHO	3.5
85	HCHO	2.3
90	HCHO	2.0
90	$NaBH_4$	2.2
90	*i*-PrOH	2.4
90	EtOH	2.7

[a] The pH is maintained between 8.5 and 9.
[b] Determined by XRD peak analysis (Scherrer formula based on half width of Pt (1 1 1) peak).

The effect of pH value during precipitation on Pt particle size is depicted in Fig. 1. Compared to the effect of the synthesis temperature and reducing agent, the influence of pH value on Pt particle size is more profound. The average size of Pt particles synthesized at pH 7 is 9.5 ± 0.5 nm. As the pH value increases further, the size decreases very steeply. It was difficult to obtain reproducible data in the average Pt particle size in the pH range between 7 and 8. At the pH values higher than 8 the average particle size around 2 nm was obtained with good reproducibility. Precipitation rate may be slow at around pH 7 where Pt precursor starts to precipitate, which could cause Pt agglomeration before its deposition on carbon. However, at higher pH values than 7, as soon as Pt precursor precipitates Pt complex will deposit on carbon, inducing small Pt particles. The same trend has been reported for Au precipitation. Wolf and Schüth [12] studied the synthesis of Au particles on several metal oxides via deposition–precipitation. Their XRD results clearly showed that the higher pH value during the precipitation led to smaller Au particles. The average Pt size did not change too much as the pH value further increases from 8 up to 12.

In Fig. 2, dependence of Pt particle size on the ratio of the amount of solvent (ml) to Pt weight (g) is shown. As the amount of solvent increases, the average particle size of Pt increases very slightly indicating that there is no positive effect of diluting Pt precursor on reducing Pt particle size in the case of precipitation method. This could be a favorable aspect for mass production of Pt/carbon, compared with the one of colloidal methods (will be mentioned in Fig. 4a) in which a large reactor volume is needed since Pt size and Pt loading can be controlled by significant dilution.

We have also investigated the effect of mixing time and sonication of the slurry of carbon and water, the amount of reductant, and the point of pH adjustment.

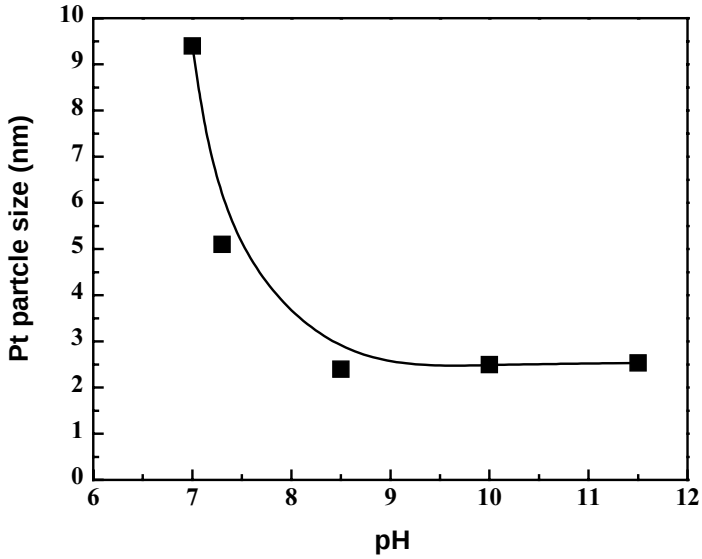

Fig. 1. Dependence of Pt particle size on pH for 20 wt.% Pt/VXC72R catalysts prepared by precipitation method.

However, any significant difference in Pt particle size was not observed.

3.2. Colloidal method

Colloidal method for Pt/carbon was developed originally by Petrow and Allen [6]. They prepared 10 wt.% Pt/carbon catalyst using PSA as Pt precursor according to the following equation:

$$H_3Pt(SO_3)_2OH + 3H_2O_2 \rightarrow 2H_2SO_4 + PtO_2 + 3H_2O \quad (1)$$

The key idea is slow oxidation of PSA to PtO_2 colloids. The slow oxidation of PSA prevents PtO_2 colloid from agglomeration and also creates a large number of PtO_2 colloids in a time. The preparation route starting from PSA complex gives not only a narrow particle size distribution but also a good dispersion of Pt particle.

In this study, the effects of PSA concentration and pH on the Pt particle size and the yield of Pt loading were examined. Fig. 3a shows that PSA concentration does not affect both the average Pt particle size and the yield of Pt loading significantly. That is, the rate of formation of PtO_2 colloid is independent of the PSA concentration. In the case of pH adjustment (Fig. 3b), an increase of Pt size at pH 8 is due to the fast oxidation reaction. The presence of OH^- ion accelerates the oxidation of PSA by H_2O_2 [13], which attributes to large Pt size. Below pH 7, Pt size is almost constant. pH adjustment is not an important factor for the yield of Pt loading.

Since the expensive PSA is one disadvantage of this preparation method, Petrow and Allen developed

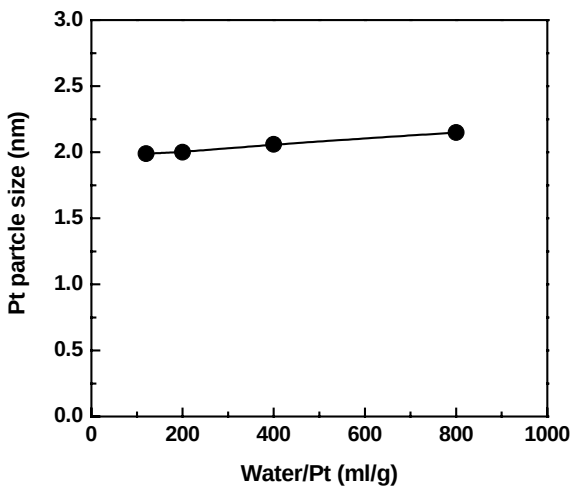

Fig. 2. Dependence of Pt particle size on the amount of solvent for 20 wt.% Pt/VXC72R catalysts prepared by precipitation method.

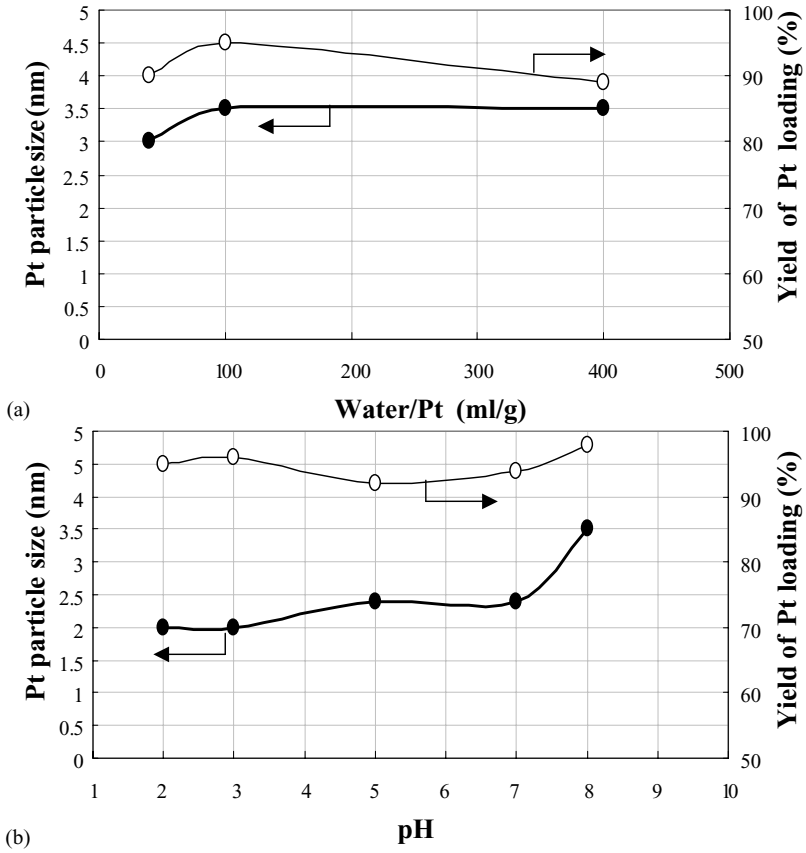

Fig. 3. Dependence of Pt particle size and yield of Pt loading on PSA concentration (a) and pH (b) for 20 wt.% Pt/VXC72 catalysts prepared by the PSA method.

another process using cheap CPA according to the following equation:

$$H_2PtCl_6 + 3NaHSO_3 + 2H_2O \rightarrow H_3Pt(SO_3)_2OH + Na_2SO_4 + NaCl + 5HCl \quad (2)$$

For use of CPA, it needs one more step to change CPA to PSA as shown in reaction (2) before oxidation (1). However, there is also a weak point in the CPA method as shown by the following equation:

$$H_3Pt(SO_3)_2OH + HCl + H_2O_2 \rightarrow H_2PtCl_6 + \text{etc.} \quad \text{unwanted reaction} \quad (3)$$

The presence of Cl^- and H^+ accelerates reaction (3), which results lower yield of Pt loading in the CPA method than in the PSA method.

For the CPA method, the effects of CPA concentration and pH were examined (Fig. 4). The concentration of CPA is critical to the yield of Pt loading. The lower CPA concentration results in the higher yield of Pt loading due to suppression of the reaction (3) by dilution effect. When the pH value is increased, the yield of Pt loading and Pt size increase simultaneously. It means that it is difficult to find the best condition for both high Pt yield and small Pt size in the case of the CPA process. The increase of Pt yield comes from suppression of reaction (3) and the increase of Pt size is due to the high loading and fast oxidation. In order to obtain satisfying Pt/carbon catalysts via the CPA

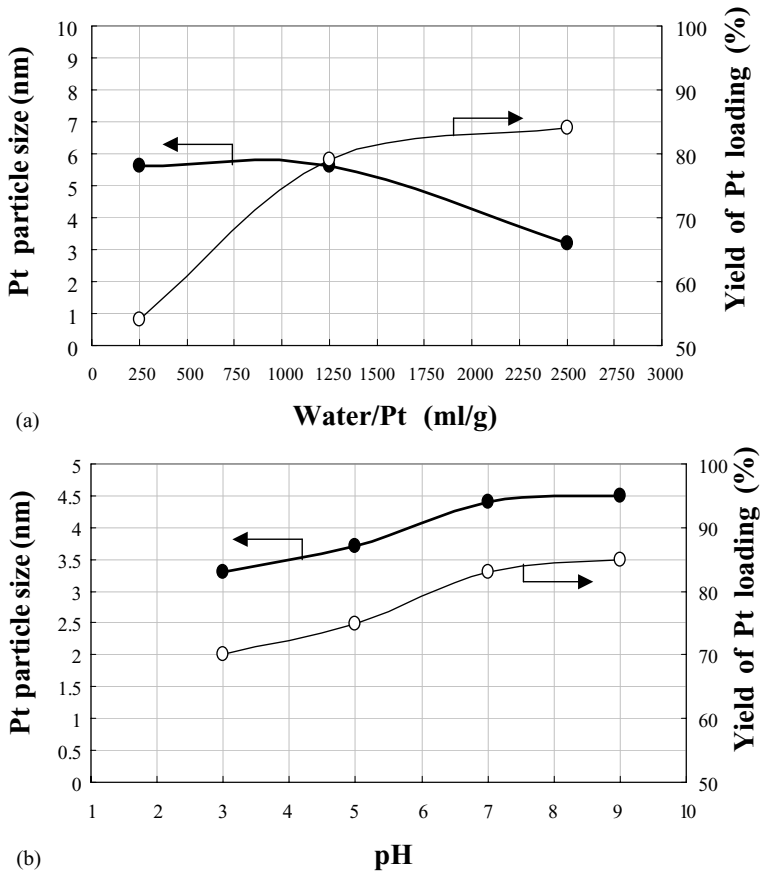

Fig. 4. Dependence of Pt particle size and yield of Pt loading on CPA concentration (a) and pH (b) for 20 wt.% Pt/VXC72 catalysts prepared by the CPA method.

method it is desirable to dilute the CPA solution and keep optimum pH around 5.

3.3. Characterization of Pt/carbon catalysts

Fig. 5 shows TEM images of 20 wt.% Pt/carbon catalysts prepared by precipitation method and PSA method as well as the commercial E-Tek catalyst for comparison. Carbon black (Vulcan XC72R for precipitation and Vulcan XC72 for PSA) with 20–30 nm particle diameter used as the support is clearly seen in TEM images. All the catalysts show well-dispersed Pt particle of around 2–3 nm in size on carbon. However, small islands of Pt particles on carbon surface can be found in the catalyst prepared by precipitation and E-Tek catalyst, while they are hardly seen in the catalyst prepared by the PSA method. A uniform Pt size and even distribution of Pt particles on carbon surface for the catalyst prepared by the PSA method could be attributed to the PtO_2 colloid formation. The slow PtO_2 colloid formation gives uniform colloid size and the formed PtO_2 colloid keeps constant distance each other to minimize electronic repulsion.

The average sizes of Pt particles of the prepared catalysts and commercial ones are shown in Table 2. They were determined using the characteristic XRD peak as described in Section 2. The average Pt particle size increases with increasing Pt loading. For E-Tek catalyst made through PSA method [14] the Pt particle size drastically increases when the Pt loading increases from 40 to 60 wt.%. However, our Pt/carbon catalysts

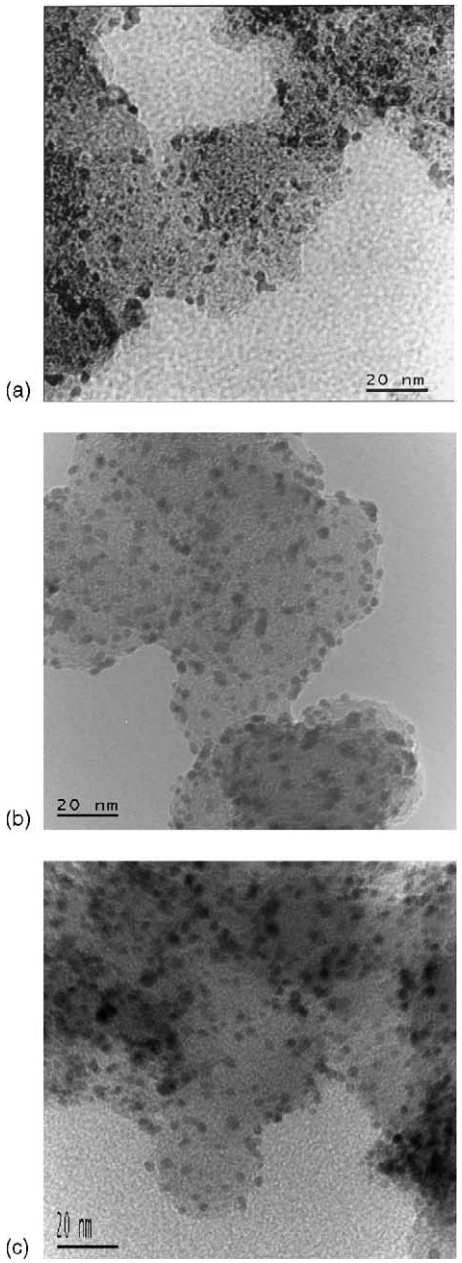

Fig. 5. TEM images of prepared catalysts by precipitation (a) and PSA method (b), and E-Tek catalyst (c). Pt loading amount on carbon is 20 wt.% for all catalysts.

prepared at optimum conditions have much smaller Pt particle size. The yield of Pt loading on the carbon support did not decrease with increasing Pt loading up to 60 wt.% as shown in the table. The Pt loading of 90 wt.% would be required for the complete coverage of carbon having the BET surface area of 250 m^2/g with the 3 nm platinum particles.

Table 2
Pt particle size[a] of prepared catalysts and commercial catalysts

Pt wt.%	Precipitation	PSA method	E-Tek	Johnson–Matthey
10	1.8 (92.7)	1.7 (93.0)	2.0	2.3
20	2.0 (95.5)	2.0 (96.0)	2.5	2.6
40	2.9 (96.3)	2.6 (95.0)	3.9	3.5
50	–	–	–	3.7
60	3.8 (97.7)	3.9 (96.7)	8.8	–

[a] Pt particle size (nm) is determined by XRD peak analysis. The number in the parenthesis is the yield of Pt loading measured by ICP.

3.4. Electrochemical reactivity of Pt/carbon catalysts

The electrocatalytic activity of prepared catalyst was tested using a single cell and is shown in Fig. 6. The commercial E-Tek catalyst was also tested for comparison. The Pt loading amount is 40 wt.% for both catalysts. Fig. 6a is a cyclic voltammogram obtained in a single cell unit by setting the anode as a reference electrode and the cathode as a working electrode. In the range of the voltage between 0.1 and 0.2 V sharp peaks for hydrogen oxidation and reduction are clearly shown for both the prepared catalyst in this study and commercial one. The peak area for the hydrogen oxidation region of voltammogram is proportional to electrochemical Pt surface area [15]. Therefore, Fig. 6a indicates that the catalyst prepared by precipitation method in this study has larger electrochemical Pt surface area than commercial one, which agrees well with the results shown in Table 2. However, the result of single cell test (Fig. 6b) shows that prepared catalyst exhibits only slightly higher electrocatalytic activity than commercial one containing the residual sulfur. Since the data obtained in the single cell test include ohmic resistance of the fuel cell components and mass transfer resistance due to the reactant depletion at the reaction zone, the increment that comes from catalytic enhancement may not be reflected clearly. This may be the reason of the difference between the results of cyclic voltammogram and single cell test.

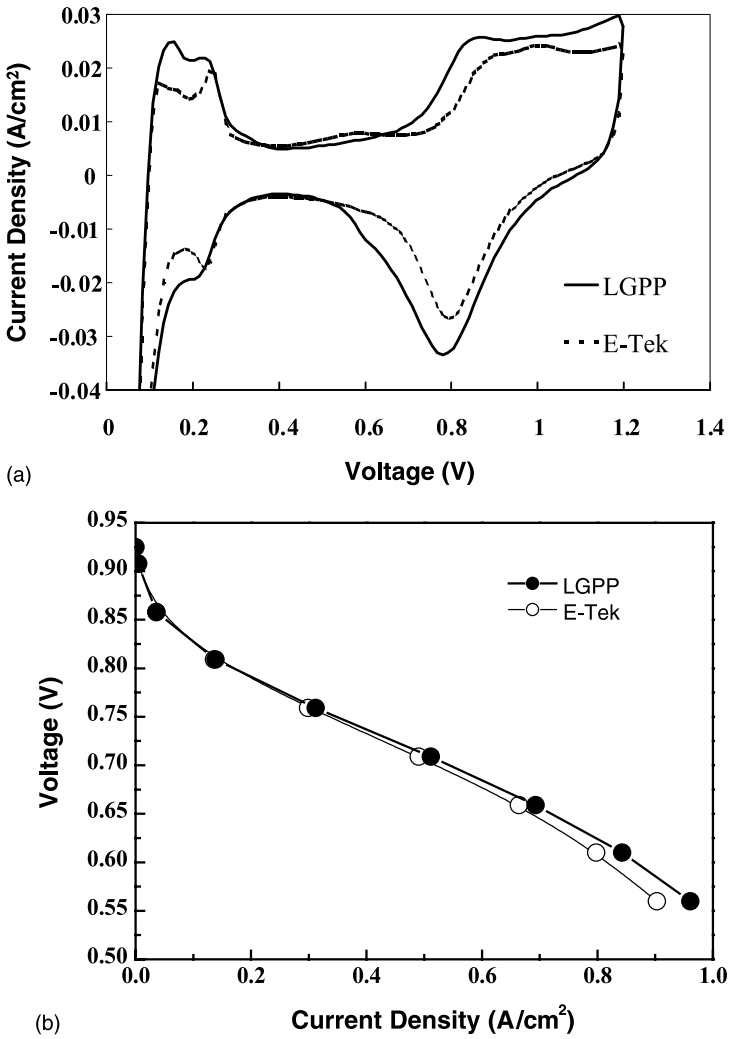

Fig. 6. Cyclic voltammogram (a) and potential–current density curves (b) for electrodes with 40 wt.% Pt/VXC72R prepared by precipitation method and E-Tek 40 wt.% Pt/carbon catalyst (operation temperature: 70 °C, anode: 1 atm H_2, cathode: 1 atm air, Pt loading amount: 0.5–0.55 mg/cm^2).

4. Conclusions

Precipitation and colloidal methods for Pt/carbon were systematically investigated. The Pt particle size was found to be sensitive to synthesis parameters such as pH value, Pt precursor concentration, synthesis temperature, and reducing condition.

Through optimization of precipitation and colloidal methods, high Pt dispersion and high Pt loading were obtained. In a single cell test, our prepared catalysts showed comparable fuel cell performance to commercial catalysts. More investigations on the dependence of fuel cell performance on Pt dispersion will be followed.

Acknowledgements

We thank Dr. Hachull Chung, Mr. Kyoungil Park, and Mr. Seongmin Song for preparing the MEA and

doing single cell performance test. We also thank Mr. Hyoshik Kil for the ICP analysis.

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