

Nano-architecture platinum catalyst layer prepared by electrophoresis deposition for PEM fuel cells

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Abstract A Pt-loaded carbon black electrode was prepared by pulsed electrophoresis deposition in a Pt colloid solution as a plating bath to overcome the growth problem of a Pt catalyst during deposition in an electrochemical process. This method is a promising technique for preparing Pt catalyst layers at the polymer electrolyte/electrode interface. The particle size of the Pt catalyst loaded by electrophoresis deposition was the same as that of Pt nanoparticles (3–4 nm) in a colloid and the particle size was maintained even during deposition. The loading of the Pt catalyst was controlled by the pH of the Pt colloid and deposition time. The Pt nanoparticles were deposited on a carbon black electrode to a depth of 2.5 μm .

Keywords Electrophoresis deposition · Pt colloid · Catalyst · PEMFC

Introduction

The polymer electrolyte membrane fuel cell (PEMFC), which can work at low temperatures, has a great potential for use in stationary, transport and portable applications [1, 2]. One of the challenges facing PEMFC commercialization is to improve the utilization of platinum within the catalyst

layer, which should ultimately reduce the platinum loading in the electrodes [3–5]. Theoretically, all platinum in the catalyst layer should be active for hydrogen oxidation and oxygen reduction reactions. For this to be the case, the fuel and oxidant must react at the interfacial region between the polymer electrolyte (e.g., Nafion) and platinum catalyst, which is a three-phase reaction zone. Here, the electrode should be designed to allow rapid access of the reactants into this zone and the electrolyte/catalyst interface must enable the transfer of both protons and electrons [6–8]. In the conventional method, preparation of a Pt-loaded carbon black (Pt/C) electrode requires that the platinum catalyst supported on carbon black should be mixed with ionomers and the resulting colloidal ink should be sprayed onto a porous carbon support, such as carbon paper or cloth. In such cases, most of the platinum particles are not accessible to the reactants because they are deposited in the porous structure of the carbon support and some platinum particles are buried completely or partially in the ionomers [3, 6]. These problems decrease the activity of the Pt catalyst in a direct methanol fuel cell (DMFC) also [9].

On the other hand, the electrodeposition method for preparing Pt/C is advantageous in achieving greater selectivity in the placement of platinum particles into the preformed electrode [10–12] but it has also a drawback. After the initial formation of a platinum particle, further deposition continues on the same particle resulting in an increase in particle size [9, 13]. The mean particle size of electrodeposited platinum has been estimated to be 10–300 nm [9–14]. Nevertheless, the electrodeposition method appears to be the only technique through which loadings in the microgram range can be achieved.

This paper reports a new strategy for overcoming the increase in platinum particle size during electrodeposition using electrophoresis deposition, which can maintain the

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size of small platinum particles loaded on an electrode during deposition and easily control the loading. To prepare a Pt/C electrode using this electrophoresis deposition, carbon paper coated with carbon black ink (without platinum) and ionomers was used as the electrode, and a Pt colloid solution with a particle size of 3–4 nm was applied as the plating bath. This paper shows how a thin Pt catalyst layer is formed on a carbon black electrode and how the Pt catalyst loading can be controlled using the pulsed electrophoresis deposition technique. The change in the Pt nanoparticle (NP) loading was monitored by cyclic voltammetry and chemical analysis. The results show that the electrophoresis deposition has potential for the development of a highly active catalyst electrode for PEMFC.

Experimental

A 2.5 ml aqueous solution containing 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 5.8\text{H}_2\text{O}$ (Kojima Chemicals Co.) was added to 202.5 ml DI water and heated to 90 °C. Next, 45 ml of 34 mM sodium citrate was added with vigorous stirring and then kept at 90 °C for 4 h for the reduction of platinum. From this reaction, a 1 mM Pt colloid solution was synthesized. The size of the platinum NPs was 3–4 nm, and the pH of the synthesized Pt colloid was 5.

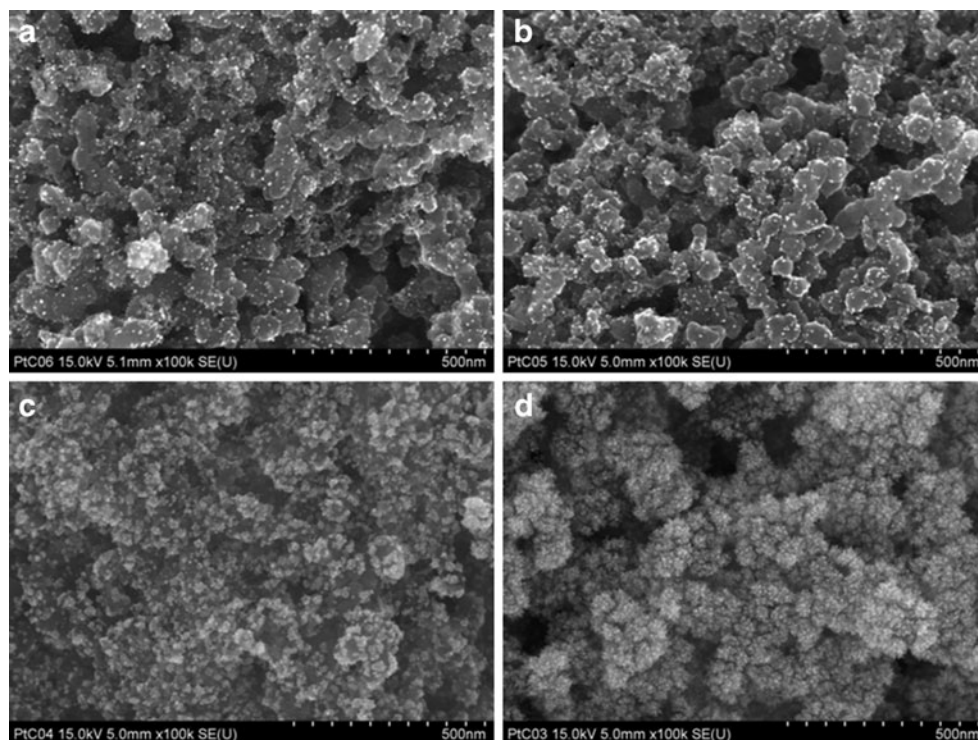
The carbon black ink was prepared by mixing 1.0 g of carbon black (Vulcan XC-72R), 2 ml isopropyl alcohol (99.5%, Showa Co.) and 3 ml of a 1 wt.% Nafion solution

(Dupont) in DI water in an ultrasonic bath for 1 h. The carbon black ink was sprayed onto carbon paper ($10 \times 10 \text{ cm}^2$, TGP-H-090; Toray Co.) and hot-pressed at 150 °C with 100 kg/cm^2 for 2 min. The carbon black-coated carbon paper was cut to pieces with a size of $1 \times 2 \text{ cm}$, and the upper half area was covered with Teflon tape after being connecting with the electrode wire. This electrode was called as carbon black electrode in this paper.

The carbon black electrode was placed in 250 ml of a 1 mM Pt colloid solution as a plating bath with a platinum plate ($2 \times 2 \text{ cm}$) as the counter electrode. The pH of the Pt colloid solution was changed from 5 to 2. Sulfuric acid (H_2SO_4 , 97%, Showa Co.) was used to decrease the pH. The electrochemical experiments were conducted on an electrochemical workstation (EG&G, 263A). Pulsed electrophoresis deposition of the Pt NPs in the colloid was performed in Galvanostatic mode to prepare the catalyst layer due to its better uniformity compared to DC electrophoresis deposition. The duty cycle $\{t_{\text{on}}/(t_{\text{on}}+t_{\text{off}})\}$ was 25%, and the $t_{\text{cycle}} (t_{\text{on}}+t_{\text{off}})$ time was fixed to 1 s.

Cyclic voltammetry experiments were performed on an electrochemical workstation (EG&G, 263A). A three-electrode electrochemical cell with Pt wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode was used for the cyclic voltammogram (CV) measurements in 1 M H_2SO_4 and 1 M CH_3OH . All tests were conducted at 25 °C at potentials ranging from -0.2 to 1.2 V at a 50 mV s^{-1} scan rate. The CV curves were generally obtained after 50 cycle scans to achieve stable current–potential behavior.

Fig. 1 FESEM images of the Pt nanoparticles loaded on a carbon black electrode by electrophoresis deposition at various pHs: **a** pH 5, **b** pH 4, **c** pH 3, **d** pH 2



For a comparison of electrophoresis deposition method with conventional spray method in the catalytic activity of Pt loaded carbon black electrode, an electrode with 0.29 mg/cm^2 of Pt was prepared by spray method using Pt/C composite powder with 40 wt.% Pt (E-tek Co.).

The morphology of the Pt NPs loaded on the carbon black support was examined by field emission scanning electron microscopy (FESEM; Hitachi, S-4800) and the deposition depth of the Pt NPs was observed by transmission electron microscopy (TEM; Hitachi, H-7650). For the TEM observations, cross-sections of the Pt loaded electrodes have been prepared by ultramicrotome (Ultracut UCT; Leica Co.). The ultramicrotomy technique consisted of embedding a small piece of the Pt loaded electrode in an epoxy resin (Epon

812, EMS) and sectioning thin slices (70 nm) of the embedded sample with a diamond knife, using ultramicrotome.

The actual Pt loading on the carbon black electrode was obtained using inductively coupled plasma spectrometry (ICPS-7500, Shimadzu Co.). To dissolve the Pt loaded on the carbon black electrode, the electrode was soaked in an aqua regia solution (3 M HCl, 1 M HNO₃) for 5 h in an ultrasonic bath.

Results and discussion

Figure 1 shows the FESEM images of the Pt NPs loaded on the carbon black electrode by pulsed electrophoresis

Fig. 2 TEM images of Pt nanoparticles loaded on a carbon black electrode by electrophoresis deposition at different depths in a carbon black layer

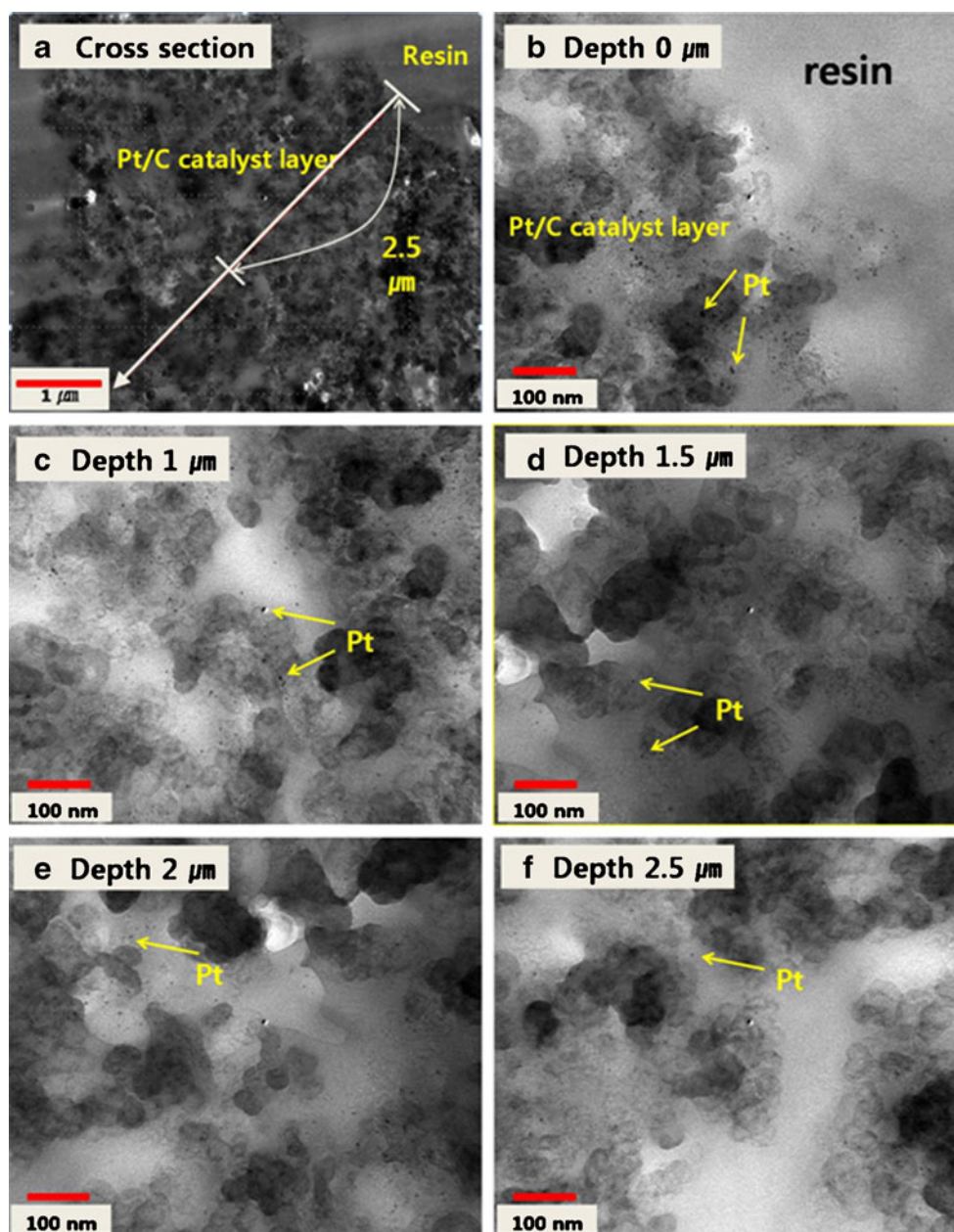


Table 1 Pt NP loading and change in current density of Pt-loaded carbon black electrode depending on the deposition times

Deposition time	5 min	10 min	15 min	20 min	E-tek Pt/C
Loading amount of Pt (mg cm^{-2})	0.12	0.16	0.27	0.59	0.29
Peak current (mA)	36.5	70.5	90.0	143.5	65.5
Mass-specific current density ($\text{mA mg}_{\text{Pt}}^{-1}$)	304.2	440.6	333.3	243.2	225.9

deposition at various pH levels. These images showed that the Pt NPs in the colloid solution were deposited on the carbon black without a change in size. The Pt NPs were isolatively dispersed on the carbon black layer when the pH of the Pt colloid solution was 5 and 4 (Fig. 1a and b). The Pt NP loading increased with decreasing pH of the Pt colloid (Fig. 1c and d). The absolute value of the zeta potential of the Pt NPs in the colloid solution decreased with decreasing pH. The zeta potentials of the Pt NPs at pH 5 and 2 were -20 and -12 mV, respectively. This suggests that the zeta potential of the Pt NPs is decreased by hydrogen ions as the pH of the Pt colloid is decreased, and the Pt NPs easily move to the carbon black electrode at low pH due to the low repulsive force between charged particles. When the pH was below 3, the deposited Pt NPs coagulated with each other like clusters, but there was no change in the particle size of the primary Pt NPs that form the cluster. As shown in Fig. 1d, the carbon black electrode was completely coated with Pt NPs.

The cross-section image of the Pt loaded carbon black electrode, which was deposited at pH 2, was observed by TEM to examine the deposition depth of Pt NPs on the carbon black electrode using electrophoresis deposition method. Figure 2 shows the TEM images of the Pt loaded carbon black electrode observed from the electrode surface to $2.5 \mu\text{m}$ in depth. Many Pt NPs were deposited within a $1 \mu\text{m}$ depth from the electrode surface, and the loading decreased sharply from $1.5 \mu\text{m}$. The deposited Pt NPs were observed to a depth of $2.5 \mu\text{m}$.

The change in Pt NP loading depending upon the deposition time was examined. Therefore, the pulsed electrophoresis deposition was carried out at pH 2 in the deposition time range from 5 to 20 min. The Pt loading increased with increasing deposition time, as shown in Table 1.

Figure 3 shows the CVs of the Pt loaded carbon black electrodes prepared by electrophoresis deposition for different deposition times in 1 M H_2SO_4 and 1 M CH_3OH . Figure 3a shows the CVs of the currents plotted for potential and Fig. 3b shows the CVs of the current values that were normalized by the actual Pt contents evaluated from ICP analysis. The peak currents and mass-specific current densities at each peak current for methanol oxidation depending on the deposition time are shown in

Table 1 with the loading amount of Pt catalyst. The peak current increased with increasing deposition time. This shows that Pt loading on the carbon black electrode increased with increasing deposition time. Therefore, the catalytic activity of the Pt NPs loaded on the carbon black electrode by electrophoresis deposition was first evaluated by a comparison with the 0.29 mg/cm^2 Pt loaded carbon black electrode prepared using the conventional spray method and an electrode which was loaded with a similar

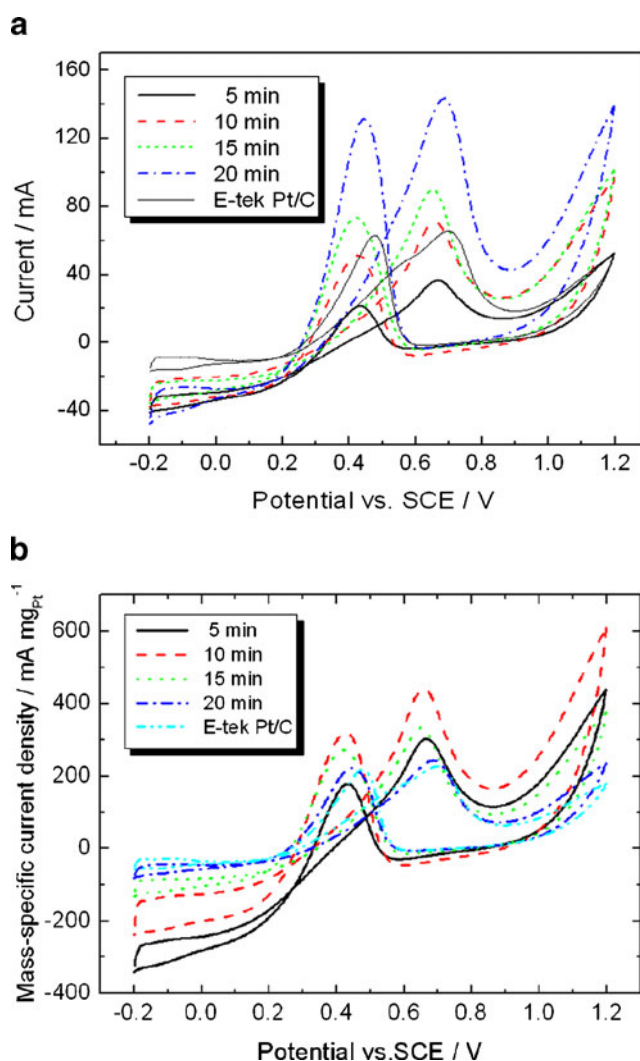


Fig. 3 CVs of Pt loaded carbon black electrodes in 1 M H_2SO_4 and 1 M CH_3OH for different deposition times: **a** current density vs. potential, **b** mass-specific current density vs. potential

amount of Pt by the electrophoresis deposition method. The peak currents of the 0.27 mg/cm² Pt loaded carbon black electrode was 90 mA, which is higher than that of the 0.29 mg/cm² Pt loaded carbon black electrode prepared using the conventional spray method. Moreover, the peak currents of the 0.16 mg/cm² Pt loaded carbon black electrode was 70.5 mA, and this electrode appears to be the highest mass-specific current density as shown in Fig. 3b. The mass-specific current density of the Pt loaded carbon black electrode at peak current showed the highest value when the deposition time was 10 min, and then decreased with increasing deposition time. This decrease in mass-specific current density was due to the coagulation of Pt NPs on the electrode. However, all mass-specific densities of the Pt-loaded carbon black electrodes using the electrophoresis deposition method was higher than that of Pt-loaded carbon black electrode using the conventional spray method. These results suggest that the catalytic activity of Pt/C electrode prepared by electrophoresis deposition was higher than that prepared by the conventional spray method because a large amount of Pt NPs existed on the surface of the carbon black electrode and were not buried in ionomers.

Conclusion

A Pt-loaded carbon black electrode was prepared by pulsed electrophoresis deposition in a Pt colloid solution as a plating bath. The particle size of the loaded Pt catalyst was the same as that of Pt NPs (3–4 nm) in the colloid, and the particle size was maintained even during deposition. Pt NP loading was controlled by the pH of the Pt colloid and deposition time. Pt NPs were deposited on a carbon black electrode to a depth

of 2.5 μm. The catalytic activity of the Pt-loaded carbon black electrode was higher than that of the Pt/C electrode prepared using the conventional spray method because a large amount of Pt NPs existed on the surface of the carbon black electrode and was not buried in the ionomers.

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References

1. Litster S, McLean G (2004) *J Power Sources* 130:61–76
2. Wee JH, Lee KY, Kim SH (2007) *J Power Sources* 165:667–677
3. Natarajan SK, Hamelin J (2007) *Electrochim Acta* 52:3751–3757
4. Ambrosio EP, Francia C, Manzoli M, Penazzi N, Spinelli P (2008) *Int J Hydrogen Energy* 33:3142–3145
5. Taniguchi A, Akita T, Yasuda K, Miyazaki Y (2008) *Int J Hydrogen Energy* 33:2323–2329
6. Hirano S, Kim J, Srinivasan S (1997) *Electrochim Acta* 42:1587–1593
7. Xiong L, Manthiram A (2005) *Electrochim Acta* 50:3200–3204
8. Chaparro AM, Gallardo B, Folgado MA, Martin AJ, Daza L (2009) *Catal Today* 143:237–241
9. Chen W, Sun G, Liang Z (2006) *J Power Source* 160:933–939
10. Lertviriyapaisan S, Tantavichet N (2010) *Int J Hydrogen Energy* 35:10464–10471
11. Rajalakshimi N, Dhathathreyan KS (2008) *Int J Hydrogen Energy* 33:5672–5677
12. Thompson SD, Jordan LR, Forsyth M (2001) *Electrochim Acta* 46:1657–1663
13. Rao CRK, Trivedi DC (2005) *Coord Chem Rev* 249:613–631
14. Wei ZD, Chan SH, Li LL, Cai HF, Xia ZT, Sun CX (2005) *Electrochim Acta* 50:2279–2287