

Preparation of Pt/C catalysts by electroless deposition for proton exchange membrane fuel cells

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Abstract—The aim of this research is to study the effect of different preparation conditions for making carbon supported platinum catalysts by electroless deposition on the properties and performance of proton exchange membrane fuel cells (PEMFC). The studied parameters are platinum and formaldehyde concentrations, deposition time and the method of formaldehyde addition. By a univariate approach, the optimal preparation conditions of 20 wt% Pt/C catalyst are determined as using 10 g Pt l^{-1} , two hours of deposition time and seven equally spaced additions of 0.15 M formaldehyde. SEM and TEM results indicate that the Pt/C catalyst attained has a small particle size (2–4 nm) and a good dispersion. The efficiency of the activation polarization of membrane electrode assembly (MEA) using these prepared catalysts is nearly that of commercial electrodes, but they have a significantly higher ohmic loss.

Key words: Electroless Deposition, Catalyst, Platinum, Formaldehyde, PEMFC

INTRODUCTION

The performance of proton exchange membrane fuel cells (PEMFC) is influenced by the properties of the sublayer, gas diffusion layer (GDL), catalyst, membrane, membrane electrode assembly (MEA) and the concentration of gases via effecting the activation, ohmic and concentration polarizations of fuel cells. However, the activation polarization can be reduced by suitable, typically noble metal catalysts such as platinum. The best known catalyst for electrode reactions is Pt/C [1], which can be prepared by several methods such as impregnation, reduction-impregnation, electroless and electrochemical deposition methods. The advantages and disadvantages of these techniques have been comprehensively discussed already [2–6]. For electroless deposition, the main advantages are the simple preparation process and the possibility to obtain small and uniformly deposited particles [2], whose properties depend on the preparation conditions used such as the type and concentration of the reducing agent employed, the metal ion used, the ratio of metal ion to reducing activity, the pH and the temperature. Kim et al. [5] studied the effect of reducing agents on Pt catalyst preparation and reported that the best reducing agent was the relatively strong reducing agent formaldehyde. Platinum provides a good distribution of small particle sizes, which can be decreased in size with increasing solution pH [6–8]. Kim et al. [9] demonstrated that the preparation of Pt/C for PEMFC by the alcohol-reduction method using polyvinylpyrrolidone as a stabilizer provided a highly disperse nanoparticle distribution pattern with a good size uniformity. Moreover, Pt particles prepared by electroless deposition on membranes were reported to be small and pyramidally textured [10]. Their morphology and composition were related to their preparation conditions in

terms of platinum salt concentration, electrolyte flow and surface roughness of the membrane. Beard et al. [11] deposited platinum on Rh-seed carbon support by electroless deposition using dimethylamine borane (DMAB) as a reducing agent. Rates of electroless deposition increased for pH 9–12 because activation of the DMAB reducing agent occurs over this range. At pH > 12, the thermal decomposition and adsorption of $PtCl_6^{2-}$ were inhibited. Pt particle size decreased with increasing Rh loading.

The properties of platinum catalysts depend on several parameters during the preparation process such as the type of process, concentration of platinum or other substances in the process and the conditions of operation. In this paper, the electroless deposition technique was used to prepare Pt/C catalysts for use in proton exchange membrane fuel cells (PEMFC). This technique needs a strong reducing agent to reduce the soluble platinum ion to the insoluble metal form. Several reducing agents can be used for Pt reduction, such as formaldehyde, hydrazine and sodium borohydride ($NaBH_4$), but formaldehyde was chosen as the reducing agent in this research since it has been previously reported that formaldehyde is the strongest reducing agent [5,6].

This research aimed to optimize the preparation of Pt/C catalysts by the electroless deposition technique using formaldehyde as the reducing agent. The parameter effects on catalyst properties were studied and the performance of the prepared catalysts was evaluated in PEMFC.

EXPERIMENTAL

Pt/C catalysts were prepared by electroless deposition technology with formaldehyde (HCHO) (40 wt% Carlo Erba) as the reducing agent. The studied parameters were platinum and formaldehyde concentrations, deposition time and the method of formaldehyde addition in terms of different addition frequencies but maintaining

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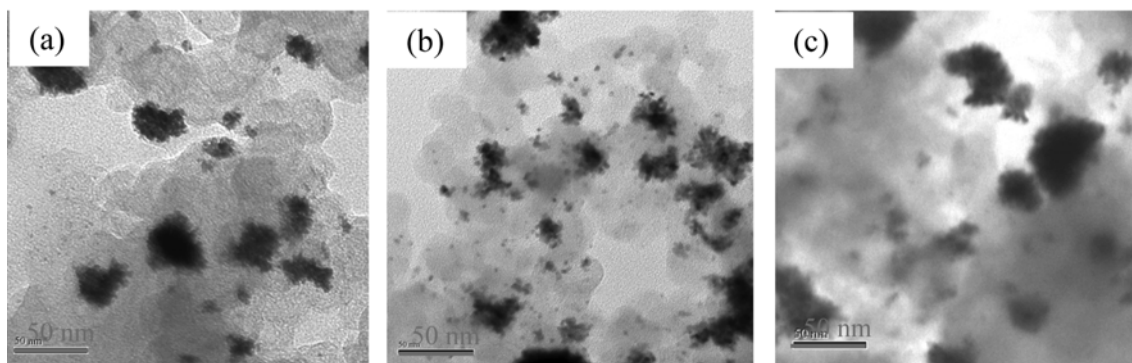


Fig. 1. Representative TEM images showing the morphologies of Pt/C catalysts prepared by electroless deposition over two hours with 0.15 M formaldehyde (single addition) and three different platinum concentrations: (a) 5 g l⁻¹, (b) 10 g l⁻¹ and (c) 15 g l⁻¹.

a constant total dose. Stock Pt solution was prepared from hexachloroplatinic acid hexahydrate H₂(PtCl₆)·6H₂O (98 wt% Fluka). For Pt/C catalyst preparation, 200 mg of carbon powder (Vulcan XC-72), 5 ml of isopropanol (Fluka) and water were mixed in an ultrasonic bath. The stock Pt solution was then added to obtain the desired final concentration of Pt (5, 10 or 15 g Pt l⁻¹) for deposition to 20 wt% Pt on carbon. The pH of the mixture was adjusted to be 8–9 by the addition of 0.5 M sodium hydroxide solution (Ajax) as required [5]. Formaldehyde at studied concentrations (0.05, 0.1, 0.15 and 0.25 M) was added as required to obtain a molar excess (respect to 4 : 1 of HCHO : Pt mole ratio). The method of formaldehyde adding was studied at different time intervals (1, 3, 6, 7 and 9 occasions over the fixed time period). The mixture was then sonicated in an ultrasonic bath at 80 °C for the stated deposition time (1, 2, 4, and 6 hours), after which the catalyst powder was filtered, washed with distilled water and dried at 110 °C in air oven for 20 hours. The distribution, size and structure of the Pt/C catalysts so obtained were analyzed by transmission electron microscopy (TEM) and X-ray diffractometry (XRD) and compared to a commercial electrode (Electrochem Co. Ltd.).

For catalyst ink preparation, 5 mg of catalyst was mixed with, in order, 1 ml isopropanol, 0.144 ml of 5 wt% Nafion solution (Fluka) and 10 µl of 60 wt% polytetrafluoroethylene (Aldrich) in an ultrasonic bath for 10, 30 and 30 minutes, respectively. The catalyst electrode was then prepared by painting catalyst ink on the gas diffusion layer (carbon paper or carbon cloth of Electrochem. Co. Ltd.) at a density of approximately 1 mg Pt cm⁻². The electrode was then dried at 80 °C for 30 minutes and the distribution of the Pt/C catalyst on the electrode was analyzed by scanning electron microscopy (SEM).

For MEA preparation, the commercial membrane (Nafion115, DuPont) was cut (25 cm²) and treated, to improve the properties of the membrane, by sequential immersion in 3 wt% H₂O₂, 0.5 M H₂SO₄ and distilled water at 80 °C for 1 hour each, respectively [12]. The treated membrane was then compressed with the 5 cm² prepared electrodes at 65 kg cm⁻², 137 °C for 5.5 minutes [13]. The MEA was composed with flow field plate and collector plate for single fuel cell. The electrochemical active surface area (EAS) was analyzed by cyclic voltammetry (CV) measurement with a potentiostat/galvanostat (Autolab Module PGSTAT30). The cell performance was analyzed in the test station by using 100 sccm of humidified

hydrogen and oxygen flow rates, and 60, 60 and 65 °C of fuel cell, cathode and anode humidifier temperatures, respectively. The performances of the prepared MEA and the commercial MEA (Electrochem Co. Ltd.) were compared to analyze the efficiency of the prepared catalyst.

RESULTS AND DISCUSSION

The results are presented as a sequential univariate approach to optimize the formation of Pt/C catalysts by the electroless deposition technique and then the analysis of the final product's functionality.

1. The Effect of Platinum Concentration

Pt/C catalysts were initially prepared using 0.15 M formaldehyde two hours of deposition time and three different concentrations of platinum solutions (5, 10 and 15 g l⁻¹). The properties of catalysts after separation and drying at 80 °C were characterized using TEM to estimate the particle sizes. Representative TEM micrographs are shown in Fig. 1, where the black particles are platinum metal on the carbon substrate. The platinum particles can be seen to be distributed on the carbon with different sizes (Fig. 2). The average particle size of the platinum metal was calculated and is summarized in

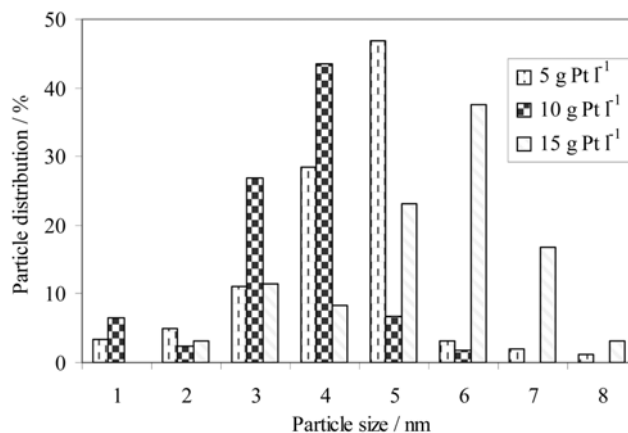


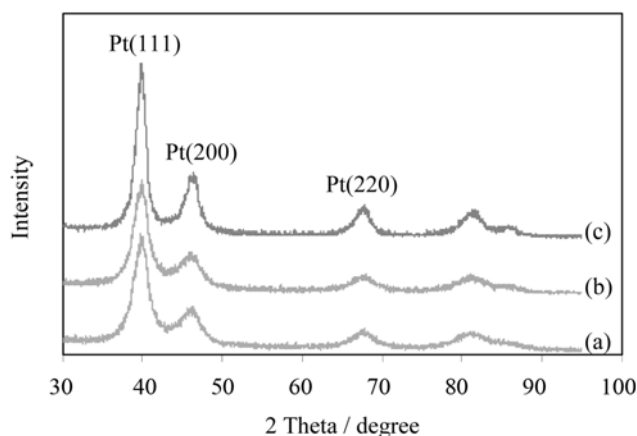
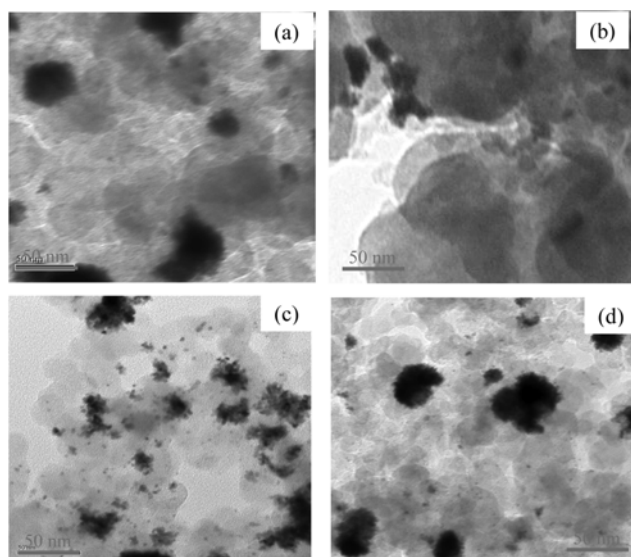
Fig. 2. Particle size distribution measured from the TEM micrographs of Pt/C catalysts prepared as outlined in Fig. 1 at three different platinum concentrations.

Table 1. Average particle size and metal surface area of platinum on Pt/C catalysts prepared from three different platinum concentrations

Concentration of Pt solution (g l^{-1})	Average particle size (nm)
5	5.0
10	4.1
15	6.1

Table 1. The average particle size was seen to vary with the Pt concentration, having the smallest average particle size, at a Pt concentration of 10 g l^{-1} . Higher (15 g l^{-1}) or lower (5 g l^{-1}) Pt concentrations gave larger average-sized platinum metal particles. This result could be explained by the formation and growth of platinum metal crystals which depend on the saturated solution and Pt to formaldehyde ratio. At low Pt concentration (5 g l^{-1}), platinum ions can be rapidly reduced by the molar excess formaldehyde forming crystals in suspension that can then agglomerate before deposition on the carbon substrate. When the Pt concentration is increased to the more optimal value (10 g l^{-1}) with the same quantity of reducing agent, sufficient Pt ions are slowly formed close to the carbon surface so as to not agglomerate. However, at higher Pt concentrations (15 g l^{-1}), additional Pt ions can be reduced on the already formed Pt metal crystals on the carbon to give large crystals, or are reduced away from the carbon surface fast enough to allow agglomeration [6]. The particle size distribution was skewed to smaller size particles in all three cases, but the catalyst prepared from a 10 g l^{-1} Pt concentration showed a clear distribution of smaller particles (2–4 nm) than those prepared using either 5 g Pt l^{-1} or 15 g Pt l^{-1} (3–5 nm and 5–7 nm, respectively) (Fig. 2).

The performance of PEMFCs is not only affected by the size and surface area of the Pt/C catalyst, but also by the structure of platinum crystals [6,11,14]. Platinum particle with (100) and (111) surface planes have been associated with more facile O_2 adsorption and dissociation into adsorbed oxygen atom. From XRD analysis of the Pt/C catalysts formed here, a clear majority of the platinum in the catalyst is in the (111) orientation, with much less in (200) and (220) orientation (Fig. 3). Indeed, the relative intensities of plati-

**Fig. 3. Representative XRD analysis of Pt/C catalysts prepared as outlined in Fig. 1 from three different platinum concentrations: (a) 5 g l^{-1} , (b) 10 g l^{-1} and (c) 15 g l^{-1} .****Fig. 4. Representative TEM analysis of 20 wt% Pt/C catalysts prepared by electroless deposition over two hours with 10 g Pt l^{-1} and a single addition of different formaldehyde concentrations at (a) 0.05 M, (b) 0.10 M, (c) 0.15 M and (d) 0.25 M.**

num orientations at (111), (200) and (220) are between 62.5–64.5%, 23.5–24.5% and 12–13%, respectively. It has been reported that the (111) Pt crystal orientation gives a higher electrocatalytic activity for oxygen reduction reaction than the others [6,15,16]. As the Pt concentration is increased, Pt crystals on the carbon are more compact in metallic form with greater relative intensities of the (111) orientation.

2. The Effect of Concentrations of Reducing Agent

Formaldehyde is a relatively strong reducing agent and well able to reduce the Pt ions [5]. As such the concentration of reducing agent relative to Pt ions could have an effect on particle size or structure of the Pt/C catalyst formed. Consequentially, we investigated the effect of formaldehyde (reducing agent) concentration on the Pt/C catalyst formed.

Fig. 4 shows representative TEM micrographs that reveal the characteristics of the platinum metal particles formed on the carbon support which were prepared from different concentrations of formaldehyde (all, however, at a molar excess with respect to 4 : 1 of $\text{HCHO} : \text{Pt}$ mole ratio) using 10 g Pt l^{-1} and two hours of deposition time. Analysis of the TEM micrographs to evaluate the average particle size of the prepared catalysts is summarized in Table 2.

The formaldehyde concentration does not show the substantial effect on the average Pt/C particle size and the distribution of plati-

Table 2. Average particle size and metal surface area of platinum on Pt/C catalyst prepared by different formaldehyde concentrations

Formaldehyde concentration (M)	Average particle size (nm)
0.05	4.4
0.10	4.2
0.15	4.1
0.25	4.4

num metal particles where the particle sizes remain in the range of 3–4 nm. The result from XRD analysis indicates that all three orientations of metallic Pt $\{(111), (200) \text{ and } (220)\}$ are seen and with essentially the same ratios in particles produced from 0.05–0.25 M formaldehyde (63.1–63.3%, 24.1–24.3% and 12.4–12.8%, respectively), which are same as the previous results (62.5–64.5%, 23.5–24.5% and 12.0–13.0%, respectively). It can be concluded that the formaldehyde concentration has no significant effect on the structure of the Pt/C catalysts because the quantities of formaldehyde used were all in excess of the Pt ion levels, so the optimum concentrations of Pt and formaldehyde are 10 g l^{-1} and 0.15 M, respectively, for two hours of deposition time. The Pt particle size obtained in this work (approximately 4 nm by TEM and 3–4 nm by XRD) is relative smaller than that obtained from Tian's research (4.2–5.8 nm) [6] because of different operating conditions.

3. The Effect of Deposition Time

The effect of the deposition time varied within the range of 1–6 hours upon the Pt/C crystals formed was evaluated using 10 g Pt l^{-1} and 0.15 M formaldehyde. Prepared catalysts were analyzed by TEM, EDX and XRD. The results from TEM show that the size of the Pt metal particles increases with increase deposition time from two to six hours (Fig. 5 and Table 3). During the deposition, Pt ions adsorb on the porous wall of carbon by chemisorptions and then are reduced

by formaldehyde [8]. When the deposition time is increased, Pt ions can be reduced on Pt particle on carbon and agglomerated to large particle. This result is similar to the study by Zhou et al. [8] who report that the Pt particle size obtained at shorter deposition time (2.6 nm for deposition time of 15 minutes) was smaller than those obtained at longer deposition time (3.2 nm and $>100 \text{ nm}$ for deposition time of 36 hours). However, if the deposition time is too short, the formaldehyde cannot completely reduce all Pt ions, so the quantity of Pt deposited on catalyst is small. Consistent with this notion is that EDX analysis confirmed that the percentage of Pt metal on the carbon at one hour of deposition time is significantly lower than those at all the other time points (Table 3). Thus, under the same assumption of independence of factor-factor interactions such univariate approaches makes, the more optimal conditions for Pt/C catalyst preparation were two hours of deposition time, 10 g l^{-1} and 0.15 M of Pt and formaldehyde, respectively.

The XRD analysis of these more optimally produced Pt/C samples again showed the same three Pt orientations, (111), (200) and (220), and a similar relative intensity of each orientation (63.1–64.3%, 23.7–24.3% and 12.0–13.1%, respectively) at different deposition times. However, when the deposition time is increased, the Pt metal particles show a more crystalline structure, presumably due to the longer time available to arrange the structure.

Since the quantities of Pt ions and reducing agent are important factors in determining the particle size of Pt/C catalysts, different addition frequencies (1, 3, 6, 7 and 9 additions/deposition time) of

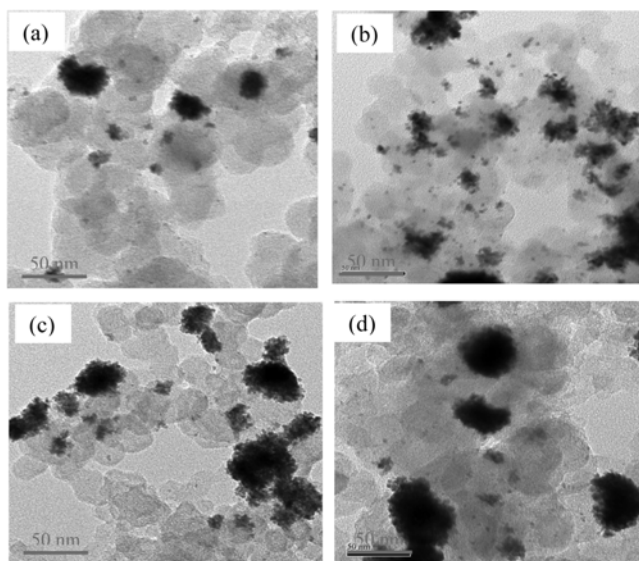


Fig. 5. Representative analysis of Pt/C catalysts prepared by electroless deposition with 10 g Pt l^{-1} and a single addition of 0.15 M formaldehyde during different deposition times: (a) 1 h, (b) 2 h, (c) 4 h, and (d) 6 h.

Table 3. Average platinum particle size and metal surface area of Pt/C catalysts prepared with different deposition times

Deposition time (hr)	Average particle size (nm)	%Pt on carbon supporter
1	4.1	12.6
2	4.1	15.1
4	5.8	16.1
6	6.5	16.5

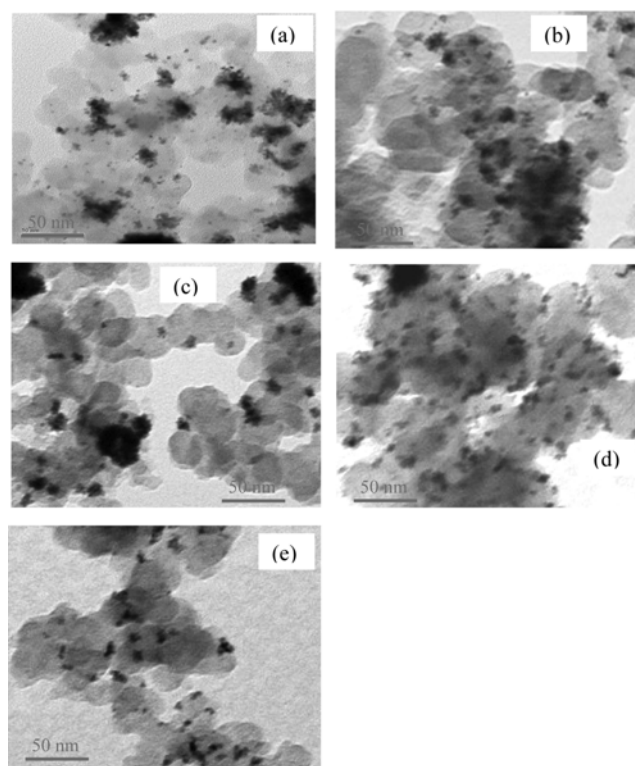


Fig. 6. Representative TEM analysis of Pt/C catalyst prepared by electroless deposition over two hours with 10 g Pt l^{-1} with different additions of 0.15 M formaldehyde: (a) single addition, (b) three additions, (c) six additions, (d) seven additions and (e) nine additions.

Table 4. Average platinum particle size and metal surface area of Pt/C catalysts prepared by different additions of 0.15 M formaldehyde

Formaldehyde frequency	Average particle size (nm)
1	4.1
3	3.2
6	3.1
7	2.9
9	3.0

formaldehyde solution during the two hours deposition time were studied. The accumulated quantity of formaldehyde for each run was kept constant at a molar excess with respect to 4 : 1 of HCHO : Pt mole ratio. TEM analysis of the resultant Pt/C products showed that the size of the Pt particles decreased when the same amount of formaldehyde was added as more frequent additions (Fig. 6 and Table 4). The concentration and quantity of formaldehyde initially added and for most of the reaction time was much lower for the higher application frequency samples, so Pt ion reduction was limited by the quantity of the now not in excess formaldehyde making it more difficult to form agglomerates of reduced Pt metal particles. The particle size of reduced Pt metal should thus be smaller in the multiple low concentration formaldehyde addition samples. The XRD analysis reveals that the Pt structure, in terms of the three orientations {(111), (200) and (220)}, does not significantly differ with the different formaldehyde dose-frequency additions (63.3-63.9%, 23.8-24.4% and 12.1-12.7%, respectively).

In conclusion, the more optimal conditions for Pt/C catalyst preparation by the electroless technique were deemed to be, accepting the untested assumptions of such a univariate approach, 10 g Pt l⁻¹, with seven additions of 0.15 M formaldehyde at a molar excess over a two hours deposition time. The Pt/C catalyst prepared under these conditions was analyzed and compared to a commercial catalyst (20 wt% Pt/C of Electrochem Co. Ltd.). The results showed that the Pt distribution and particle size of the catalyst prepared in this study were approximately the same as those of the commercial catalyst (Fig. 7 and Table 5). However, XRD analysis suggested that the Pt structure of the commercial catalyst was more amorphous than that obtained in this work (Fig. 8).

4. The Efficiency of the Pt/C Electrocatalyst in PEMFC

The prepared Pt/C catalysts were used to prepare electrodes by

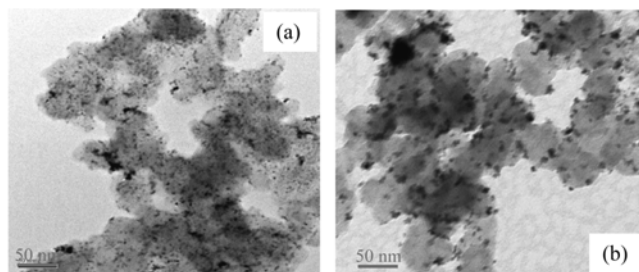


Fig. 7. Representative TEM images of Pt/C catalysts from (a) a commercial source (Electrochem Co. Ltd.), and (b) formed in this work by electroless deposition with 10 g Pt l⁻¹, seven additions of 0.15 M formaldehyde and two hours deposition period.

Table 5. Average platinum particle size and metal surface area of Pt/C catalysts used to make MEA

Type of Pt/C catalyst	Average particle size (nm)
Commercial catalyst	2.7
Catalyst in this work	2.9

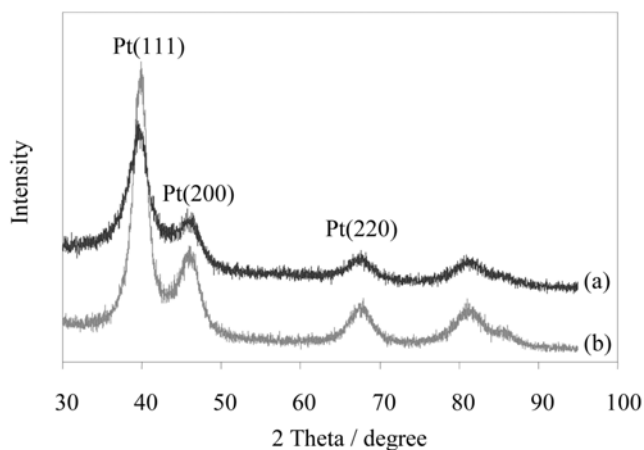


Fig. 8. Representative XRD analysis of Pt/C catalyst (a) commercial catalyst (b) this work as described in Fig. 7.

the painting method on the gas diffusion layer of carbon paper or carbon cloth at a density of ~1 mg Pt cm⁻². The characteristics of the prepared electrodes were then analyzed by SEM, and compared with the commercial electrode having the same Pt loading. Fig. 9 shows representative SEM micrographs with the Pt particles uniformly distributed on the electrode in essentially the same pattern as in the commercial electrode, except that the quantity of Pt analyzed by EDX (13.9 wt%) was found to be significantly less than

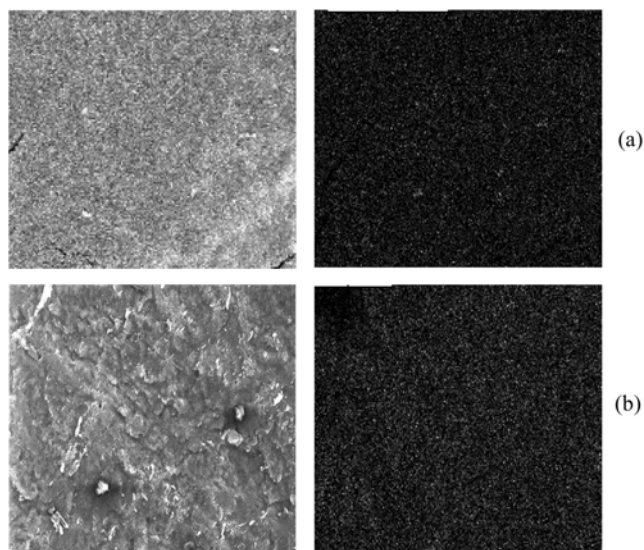


Fig. 9. SEM derived surface morphology (left) and distribution of Pt (right) on the Pt/C catalyst-electrode from (a) this work, (b) a commercial source described in Fig. 7 (all at 500× magnitude).

Table 6. Electrochemical active surface area (EAS) of electrodes prepared by different catalysts and GDLs

MEA source	GDL	EAS ($\text{m}^2 \text{g Pt}^{-1}$)
Prepared ¹	Carbon paper	9.7
Prepared ¹	Carbon cloth	10.2
Prepared ⁷	Carbon cloth	11.2
Commercial	Carbon paper	9.2
Commercial	Carbon cloth	55.2

All MEAs were comprised of 1 mg Pt cm^{-2} and were either commercially available (Commercial), from Electrochem Co. Ltd., or were prepared in house (Prepared) using 10 g Pt l^{-1} with either (¹) a single or (⁷) seven additions of 0.15 M formaldehyde during the two hours deposition time

that of the commercial electrode (17.2 wt\%). A pretreated Nafion membrane was sandwiched between two prepared electrodes and compressed by a hot pressing machine to obtain membrane electrode assemblies (MEAs), which were then analyzed for the electrochemical active surface area (EAS) by cyclic voltammetry (CV) measurement, and the performance evaluated by a polarization curve. 4-1. (A) Cyclic Voltammetry (CV) Measurement

CV measurement was used to analyze the EAS for the hydrogen oxidation reaction at the catalyst layer of the electrode. The measurement was performed at a 50 mV s^{-1} scan rate, within a $0\text{--}0.80 \text{ V}$ range, and with 100 sccm of dry hydrogen and nitrogen gas flow rates at the anode and cathode, respectively. The results, summarized in Table 6, revealed that the EAS of the prepared electrode by carbon cloth as a gas diffusion layer (GDL) was slightly higher than that by carbon paper, while the catalyst prepared with seven formaldehyde additions gave a higher EAS than that prepared with a single formaldehyde addition and the commercial electrode. However, the prepared electrode has an EAS that is significantly (~ 4.9 fold) lower than the commercial MEA from Electrochem Co. Ltd. Clearly, the process of MEA preparation in this work shows significant improvement. In this study the catalyst was not contacted with Nafion, carbon and gas (the three phase boundary) and so the EAS of the platinum was decreased. EAS affects the chemical polarization, and if the EAS is too small the rate of the electrochemical reaction will be small too, as observed and reported in the next section (performance test).

4-2. (B) Performance Testing

The performance of the prepared MEAs, and the commercial MEA as a reference, was tested based on the polarization curves. The conditions of testing were a 60°C cell temperature, 65 and 60°C anode and cathode humidifier temperatures, approximately 50 kPa gauge and 100 sccm of hydrogen and oxygen flow rates. 1 mg Pt cm^{-2} of electrodes with catalyst prepared by the above more optimal conditions (a single formaldehyde addition) were used to compare the efficiency of carbon paper and carbon cloth. The results, summarized in Fig. 10, reveal that the performance of the carbon cloth electrode is significantly better than that of the carbon paper electrode (281 and 124 mA cm^{-2} , respectively, at 0.6 V). This result corresponds with that of the higher observed EAS in the carbon cloth electrode than that of the carbon paper electrode (Table 6). Since the carbon cloth GDL is more porous than the carbon paper

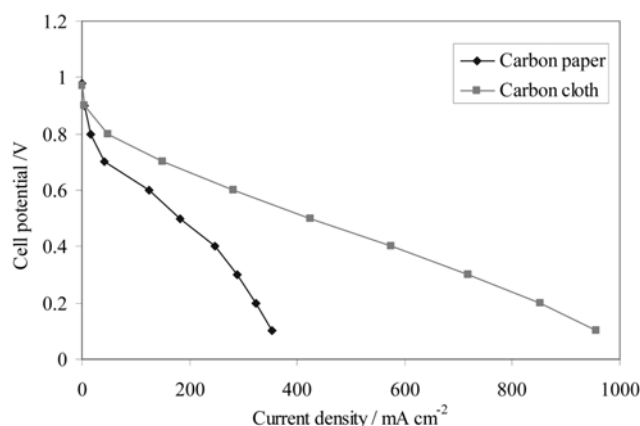


Fig. 10. Polarization curve of prepared MEA from different GDL and 1 mg Pt cm^{-2} of Pt/C catalysts prepared by electroless deposition over two hours with 10 g Pt l^{-1} and a single addition of 0.15 M formaldehyde.

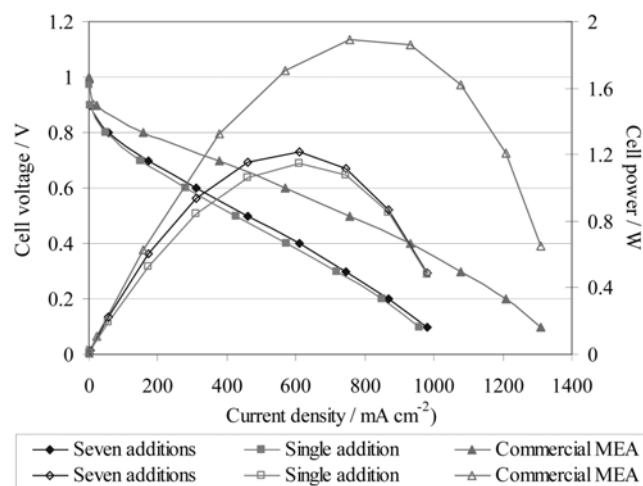


Fig. 11. Polarization curve and power of different MEAs with 1 mg Pt cm^{-2} of Pt/C catalysts prepared by electroless deposition over two hours with 10 g Pt l^{-1} and either a single or seven additions of 0.15 M formaldehyde and carbon cloth as GDL.

GDL, the carbon cloth was next used to study the performance of the catalyst. Pt/C catalyst prepared with a single formaldehyde addition was compared to that prepared with seven additions of formaldehyde and the results, summarized in Fig. 11, reveals that the catalyst prepared with seven formaldehyde additions times gave a slightly higher performance, presumably due to its smaller particle size and higher surface area (Table 4), and a larger EAS (Table 6). However, the prepared MEA has a much weaker performance than the commercial MEA used as a comparative reference, which again corresponds to the differences between these two MEA in their surface areas and EAS (Table 6). The current densities attained at 0.6 V are 295 , 366 and 570 A cm^{-2} for MEAs with catalysts prepared with one and seven additions of formaldehyde and the commercial reference MEA, respectively. The prepared MEA still has a significantly higher ohmic loss than the commercial one and clearly requires optimization. Whether this is required or attainable at the stage of MEA

preparation or the composition of MEA requires further evaluation. The maximum power densities are 230, 244 and 378 mW cm⁻² for prepared MEAs with one and seven formaldehyde additions and the commercial MEA, respectively.

CONCLUSION

The concentration of platinum and formaldehyde, and the time of deposition all have an effect on the distribution and particle size of the electroless deposition Pt/C catalyst. The more optimal preparation conditions for forming Pt/C catalysts by electroless deposition for PEMFC were determined by univariate analysis to be 10 g l⁻¹ platinum solution (as hexachloroplatinate) and seven additions of 0.15 M formaldehyde (at a molar excess with respect to Pt) evenly dispersed over two hours of deposition time. The MEA with 1 mg Pt cm⁻² of prepared catalyst can produce current and power densities of 366 mA cm⁻² and 244 mW cm⁻², respectively, at 0.6 volt. The efficiency on activation polarization of the membrane electrode assembly (MEA) using prepared catalysts was nearly that of commercial electrodes, but it had a higher ohmic loss leading to a reduced maximum power density.

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