

Improved photographic production of Pt nano-particles for fuel cell electrodes

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Received 18 June 2007; received in revised form 25 July 2007; accepted 26 July 2007

Available online 11 August 2007

Abstract

An improved photographic Pt printing process has been developed, which is called the print-out process (POP). No developer is required in this process and the deposition efficiency was significantly improved by more than 6 times on carbon paper (CP) and 22 times on carbon-black-coated carbon paper (CB/CP) over the previously reported develop-out process (DOP) [1]. The Pt particle size can be easily controlled by varying the moisture content in the substrate and was reduced to 5 nm on blank CP by adding a stabilizing agent, ethylene glycol (EG), to the photo-emulsion. Due to the hydrophobic nature of CB/CP, both Nafion ionomer solution and ethylene glycol (EG) were mixed with the emulsion during the printing. SEM revealed that on this substrate Pt was distributed as ~25 nm clusters consisting of 5 nm particles on the carbon-black. The mass specific catalytic activity for methanol oxidation of Pt printed on CB/CP by POP was increased five times compared to that of Pt printed by the previous DOP. The performance of the POP Pt in a H₂ PEM single fuel cell (5 cm²) was also evaluated. A peak power density of 288 mW cm⁻² was achieved with an anode POP Pt catalyst loading of 0.16 mg cm⁻² at 70 °C and 0.9 mg cm⁻² JM Pt at the cathode. Compared to the DOP Pt catalyst at about the same loading, peak power density was improved more than four times by using the POP Pt.

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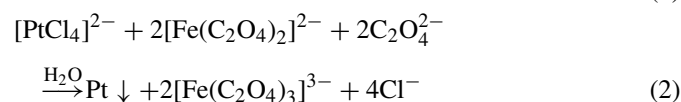
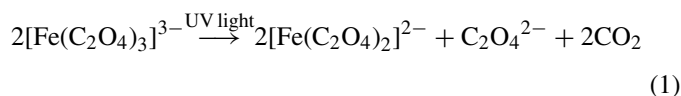
Keywords: Photographic printing; Pt deposition; Nano-particle; Catalyst; Fuel cell

1. Introduction

In order to improve the deposition efficiency and the retention of Pt particles on the substrate surface, a “new” print-out photographic Pt-printing process (POP) has been developed for the production of Pt catalysts directly on substrates. The previous wet-development Pt printing process [1,2] is called a develop-out process (DOP), in which a developer solution was used and the metal particles were formed during the wet-development step. The new process does not require a developer and the metal catalysts are formed directly during exposure. In photography this process is also known as the Ware/Malde method [3,4], which actually stems from the old photographic Pt printing work of Pizzighelli and Hübl [5,6].

Even though the developer solution is not necessary for the new process, a metal catalyst, e.g. Pt, will not form on the

fully dehydrated substrate even though the UV sensitizer is photo-excited. A certain level of moisture content is required to confer a limited mobility to the sensitizer ions on the substrate and allow the redox reaction to take place there. Because the solubility of iron(II) oxalate used in the DOP is so low, ammonium-based chemicals are used in the new POP. Good results have been achieved with ferric ammonium oxalate (NH₄)₃[Fe(C₂O₄)₃] as the sensitizer, and ammonium tetrachloroplatinate(II) (NH₄)₂[PtCl₄] as the metal precursor salt for Pt printing. The reactions taking place are [4]:



In addition to the hygroscopic action of the ammonium salts to provide moisture, it is a common photographic practice to control the moisture content of the sensitized paper by allowing it to equilibrate with the vapor above a saturated aqueous solu-

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tion of an inorganic salt (e.g. saturated CuSO_4 solution) within an enclosure. This saturated solution provided a known constant relative humidity. However, it was found that equilibrating with saturated aqueous solutions was not an efficient way to increase the water content of hydrophobic substrates such as carbon paper (CP). We determined that “steaming” the sensitized CP with water at different temperature for different durations was the simplest and most efficient hydration method for substrates like CP. The control of the substrate moisture content was found to be so important in POP that it governed not only the deposition efficiency, but also the particle size. On more hydrophobic and higher surface area substrates, such as carbon-black-coated carbon paper (CB/CP), Nafion ionomer solution was added to the photo-emulsion as a surfactant to obtain a uniform coating.

In order to further prevent nano-particle agglomeration, ethylene glycol (EG) was used as a stabilizing agent in the modified POP. It is known that ethylene glycol can work as a stabilizing agent in metal nano-particle synthesis [7,8]. In Wang's work [8], metal nano-particles were synthesized in an ethylene glycol solution without the addition of other stabilizer molecules. It was suggested that the colloids were stabilized by the “dielectric” properties of the ethylene glycol solvent. In a similar synthesis of PtRu nano-particle in ethylene glycol solution at high pH, Bock et al. [7] found that the reaction mechanism involved the oxidation of ethylene glycol and that the oxidation product, glycolate, acted as the stabilizer. Regardless of which mechanism controls the process, when ethylene glycol was used as the stabilizer, the surface catalytic sites of the metal nano-particles were easily freed-up [7]. Therefore, ethylene glycol was chosen in our new photographic Pt printing process to prevent particle agglomeration. It also provided the additional benefit of increasing the viscosity of the photo-emulsion. Therefore, in the future the photo-emulsion may be applied onto substrates by spin-coating, which makes the process more compatible with Si-based electronic device manufacturing and could serve to enable the easy incorporation of micro fuel cell fabrication into the production of electronic devices.

The major benefit of allowing Pt to be formed by this new print-out process (POP) is that no chemicals are lost when Pt is reduced as is the case of the wet-development step in the DOP. Therefore the deposition efficiency of Pt can be significantly increased. Compared to the Pt catalyst deposited by the previous DOP [1,2], preliminary experimental results showed that both the deposition efficiency and the mass specific catalytic activities were dramatically improved due to the better control of particle size achieved with the new POP process.

2. Materials and methods

2.1. Photographic deposition process

For POP, the Pt precursor salt $(\text{NH}_4)_2[\text{PtCl}_4]$, and the UV sensitizer $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ were purchased from Alfa Aesar (Ward Hill, MA). The Pt precursor solution was $0.67 \text{ mol l}^{-1} (\text{NH}_4)_2[\text{PtCl}_4]$ dissolved in millipore

water (Millipore, Bedford, MA), which was made at least 24 h before use. The photo-emulsion was made by mixing equal volumes of the Pt precursor solution and $1.4 \text{ mol l}^{-1} (\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$. This photo-emulsion was rested at room temperature in a closed container for at least 2 h. The two printing substrates used included (1) Toray carbon paper (TGPH-060, thickness = 0.17 mm, E-TEK Inc., Somerset, NJ), and (2) carbon-black ink painted Toray carbon paper (TGPH-060) with a carbon-black loading of 1.0 mg cm^{-2} . The carbon-black ink was prepared by adding 400 mg carbon-black (stock # 39723, Alfa Aesar, Ward Hill, MA) and 0.8 ml 5 wt% Nafion ionomer solution (Aldrich, Milwaukee, WI) to 15 ml of methanol. This carbon-black ink was stirred vigorously for at least 12 h before air-sprayed to the carbon paper. Depending on the desired Pt loading, a measured amount of the emulsion was applied to the surface. Then the samples were hydrated by steaming with water at different temperature for different lengths of time. The coated substrate was then exposed to a mercury lamp UV light source with an exposure intensity of 11.5 mW cm^{-2} and primary exposure wavelength of 350–500 nm for 2 min. After exposure, the Pt-coated substrate was washed with 500 ml slightly agitated 9 wt% EDTA (ethylenediamine tetraacetic acid, Bostick & Sullivan, Santa Fe, NM) aqueous solution for 30 min followed by 3 cycles of wash with 500 ml millipore water for 30 min each. When printed onto CB/CP, due to the hydrophobic nature of the carbon-black layer and in order to achieve a uniform coating of the photo-emulsion on the substrate, a 5 wt% Nafion ionomer solution (5 wt% in lower aliphatic alcohols/ H_2O mix) was mixed with the photo-emulsion to a volume content of 10 vol%. Then the samples were printed in the same way as on the blank CP. The prepared samples were air-dried and stored in a desiccator.

In the modified POP involving the use of a stabilizer, ethylene glycol (Fisher, Fairlawn, NJ) was added to the photo-emulsion to the concentration of 20 vol%. After coating with the photo-emulsion, the CP was then baked on a hot plate at 170°C for 10 s, followed by an immediate hydration. The hydration was performed by resting the sample at 2 cm above the surface of room temperature water for 30 s, with the coated surface facing towards the water. Then the sample was exposed to the UV light for 2 min. Finally the sample was washed with EDTA and millipore water. For CB/CP, the Nafion ionomer solution was mixed with EG and the emulsion to improve the uniformity of the emulsion coating. In this case, the photo-emulsion contained 18 vol% EG and 10 vol% Nafion ionomer.

The DOP Pt for comparison was printed onto the Nafion membrane as described before [1].

2.2. SEM and ICP analyses

Scanning electron microscope (SEM) images were taken with a Hitachi S4500 field emission SEM (Hitachi, Tokyo, Japan). The mass of Pt was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Optima 3300XL, Perkin-Elmer, Wilton, CT) after dissolving the Pt from the substrates of known size in aqua regia.

2.3. Electrochemical studies of the catalytic activity of Pt nano-particles for the methanol oxidation reaction

A three-electrode electrochemical cell (Voltalab[®] C145/170, Hach Company, Loveland, CO) was used with a SCE reference electrode and a Pt disk counter electrode. For methanol oxidation measurements, cyclic voltammetry (CV) scans (from -0.25 V to 1.25 V versus SCE, with a 20 mV s⁻¹ scan rate at ambient temperature) in a solution of 0.5 M H₂SO₄/1 M CH₃OH were performed on each sample. The working electrode held a disk sample with a silicone rubber washer to define the actual exposed area to be 0.5 cm². A graphite disk was placed at the back of the carbon paper to prevent the solution from permeating through the carbon paper and reaching the stainless steel current collector on the backside [1].

2.4. H₂ PEMFC performance test for Pt-printed electrodes

The performance of the Pt-coated CB/CP in a full fuel cell arrangement was evaluated with a Scribner 890C load system controlled by fuel cell for Windows[™] software (Scribner Associates, Inc., Southern Pines, NC). A single cell (Electrochem Inc., Wobum, MA) with 5 cm² active area was used.

The gas diffusion layer (GDL) was CB/CP with a carbon-black loading of 1.0 mg cm⁻², which was the same as used in the Pt printing. The control gas diffusion electrode (GDE) was made by air-spraying Johnson Matthey (JM) Pt catalyst (HiS-PEC 1000, Alfa Aesar, Ward Hill, MA) onto a GDL. The JM Pt ink for spraying was prepared by adding 300 mg JM Pt catalyst and 1.21 ml Nafion ionomer solution into a mixture of 7 ml methanol and 7 ml isopropanol. The actual loading of sprayed Pt catalyst on the control GDE was 0.9 mg cm⁻² (ICP-OES confirmed).

For the other GDEs tested, the Pt catalyst was photographically deposited onto the same GDLs. Pt was deposited by the modified POP with both Nafion ionomer solution and EG added to the photo-emulsion. The photo-emulsion contained equal volumes of Pt precursor and the iron-containing UV sensitizer solutions, and 10 vol% Nafion ionomer solution and 18 vol% EG, as described in Section 2.1.

Nafion 117 membrane (Nuvant System Inc., Chicago, IL) was used as the polymer electrolyte. Before use, the Nafion membrane was cleaned in turn in 90 °C 3% H₂O₂, 90 °C 1 M H₂SO₄ and 90 °C millipore water (Millipore, Bedford, MA) for 1 h each. This cleaning cycle was repeated at least three times and the cleaned Nafion membrane was stored in millipore water. The MEAs were hot-pressed at 150 °C under 1000 lb in.⁻² pressure for 2 min. Prior to the polarization tests, all MEAs were pre-humidified overnight at 40 °C with 100% relative humidity (RH) H₂ purged on both anode and cathode sides. All cells were operated with pure H₂ and pure O₂ at the same flow rates of 0.1 l min⁻¹ on both sides. The gases were fully humidified to 100% RH and preheated to the cell temperature prior to entering the cell. Both anode and cathode were at ambient pressures.

Four types of MEAs were prepared (Fig. 1). The first type was the control MEA, which had air-sprayed Johnson Matthey (JM) Pt black on CB/CP as both the anode and the cathode. The ICP Pt loadings on both sides were the same, which was 0.9 mg cm⁻². The second type of MEA had POP Pt as the anode catalyst, with an ICP Pt loading of 0.16 mg cm⁻². Pt was photographically deposited by the modified POP onto the same CB/CP as used in the control GDE. The cathode of this MEA was identical to the control MEA with JM Pt as the catalyst. The third type of MEA had POP Pt as the cathode catalyst, with an ICP Pt loading of 0.16 mg cm⁻². The anode was identical to the control MEA. In the fourth MEA, POP Pt was used as the catalyst on both anode and cathode sides. The Pt loading on both sides was 0.16 mg cm⁻².

The DOP Pt layer for comparison was printed on the Nafion membrane on the anode side and hot-pressed to a control CB/CP GDL [1].

3. Results and discussion

3.1. SEM imaging

3.1.1. POP Pt without stabilizer

SEM images in Fig. 2 compare the morphologies of the printed-out (POP) Pt particles on CP and CB/CP with those

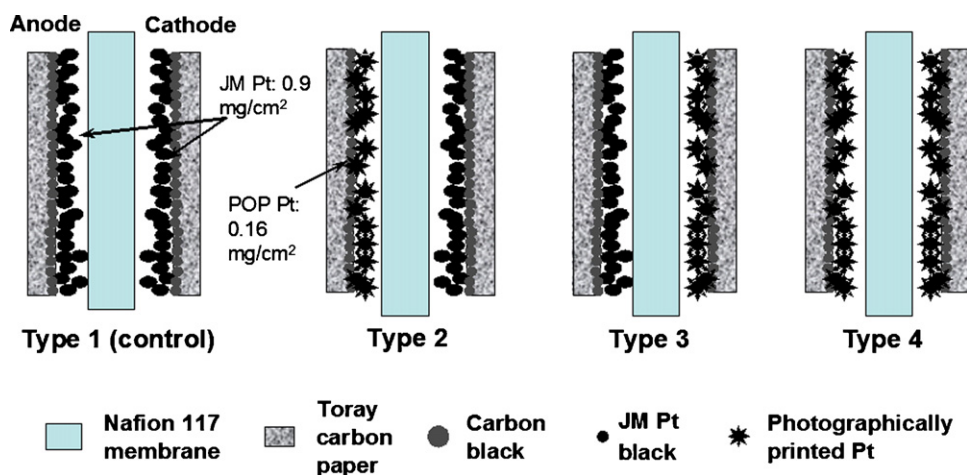


Fig. 1. Configurations of the four types of MEAs tested.

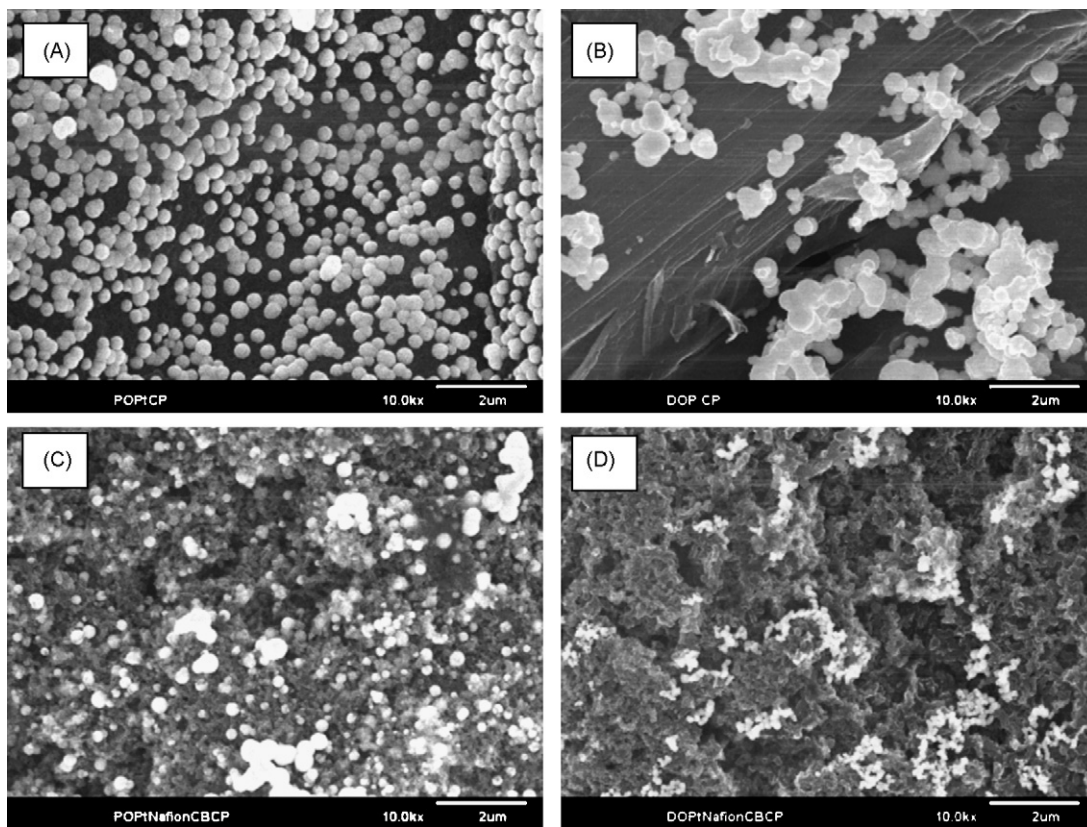


Fig. 2. SEM images of printed-out Pt on (A) CP and on (C) CB/CP, and of developed-out Pt on (B) CP and on (D) CB/CP.

of the developed-out (DOP) Pt on the same substrates. Samples A and C were made by POP on blank CP and CB/CP, respectively. Samples B and D were made by DOP, exposed under UV for 5 min and developed with ammonium citrate [1]. Samples A and C were steamed with 90 °C water for 30 s and exposed under the UV light for 1 min. The difference is that for sample C, 10 vol% Nafion ionomer solution was mixed with the photosensitive emulsion since the substrate was CB/CP. From the images, it can be clearly seen that the deposition efficiencies on both substrates were dramatically improved by the POP. It was confirmed by the ICP-OES Pt loading analysis (Table 1) that on CP, the deposition efficiency (ICP measured Pt on the substrate of known surface area divided by Pt amount applied to that substrate during printing) was increased from 2.6% to 13.4%; while on CB/CP, from 0.49% to 11.3%. The images also clearly show that the printed-out Pt particles appeared to be more dispersed and of more uniform size. On blank CP, POP generated Pt particles were about 245 ± 60 nm in diameter. On CB/CP, a smaller particle size of 175 nm was obtained, but with a larger standard deviation of 160 nm.

Table 1
ICP-OES analysis of Pt contents for samples A–D shown in Fig. 1

Sample ID	Substrate	Printing process	Theoretical Pt loading (mg cm^{-2})	Actual ICP Pt loading (mg cm^{-2})	Deposition efficiency (%)
A	CP	POP	0.5	0.067	13.4
B	CP	DOP	1.5	0.032	2.6
C	CB/CP	POP	1.0	0.113	11.3
D	CB/CP	DOP	1.0	0.0049	0.49

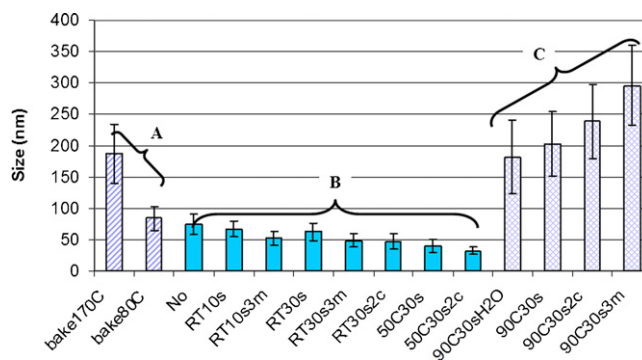


Fig. 3. The dependence of Pt particle size on the hydration conditions.

On blank CP, we further studied the particle size control mechanism. Table 2 and the chart in Fig. 3 summarize the results of Pt particle sizes produced under different hydration conditions and reaction temperatures to establish the primary size control mechanism: reaction kinetics or diffusion. The SEM

Table 2
Process conditions and sizes of Pt particles for the samples showing in the chart (Fig. 3)

Sample #	Sample ID	Process conditions	Average particle size (nm)	Standard deviation (nm)
A				
1	Bake170C	Baked sample for 10 s at 170 °C	187.4	47.3
2	Bake80C	Baked sample for 10 s at 80 °C	83.9	18.4
B				
3	No	No hydration and baking	74.6	16.7
4	RT10s	Hydrated with room temperature water for 10 s	66.7	12.4
5	RT10s3m	Hydrated with room temperature water for 10 s and exposed for 3 min	52.3	11.6
6	RT30s	Hydrated with room temperature water for 30 s	62.9	14.0
7	RT30s3m	Hydrated with room temperature water for 30 s and exposed for 3 min	48.9	11.2
8	RT30s2c	Hydrated with room temperature water for 30 s and repeated the hydration-exposure cycle twice	46.7	12.4
9	50C30s	Hydrated with 50 °C water for 30 s	40.6	10.1
10	50C30s2c	Hydrated with 50 °C water for 30 s and repeated the hydration-exposure cycle twice	31.9	5.9
C				
14	90C30sH ₂ O	Hydrated with 90 °C water for 30 s, finally washing with water instead of EDTA	181.3	58.7
11	90C30s	Hydrated with 90 °C water for 30 s	202.5	50.8
12	90C30s2c	Hydrated with 90 °C water for 30 s and repeated the hydration-exposure cycle twice	238.6	59.0
13	90C30s3m	Hydrated with 90 °C water for 30 s and exposed for 3 min	295.8	64.1

images of four representative samples with different particles sizes are shown in Fig. 4.

When samples were hydrated with 90 °C water (group C samples in Fig. 3), visible water droplets were formed on the carbon paper. In this case, the Pt formation redox reaction took place in a large volume of liquid phase as evidenced by the visible presence of the condensed water and the nuclei grew to larger particles because of the high mobility of the ions in the liquid phase. This paralleled the process environment of the developer solution in the DOP process, where particles of a similar size were obtained. However, when hydrated with water at or below 50 °C (group B samples), the water vapor was absorbed by the hygroscopic ammonium-based salts and the Pt producing redox reaction was restricted to small regions due to the lower mobility of the ions. Therefore, particles of 50 nm or smaller were formed. When samples were baked and UV exposed hot (group A samples), the redox reaction rate and the diffusion of ions were both enhanced. However, the moisture content of the substrate was low in this case, therefore particle sizes in the intermediate range (80–180 nm) were observed. In conclusion, small particles were formed when no condensed water was present on the substrate and reaction temperatures were low. The representative SEM images in Fig. 4 show that POP not only improved the dispersion of the Pt particles and narrowed their size distribution, but also demonstrated that Pt particles of different sizes can be formed by controlling the process conditions.

3.1.2. POP Pt with EG stabilizer-modified POP

In order to prevent agglomeration, EG was mixed with the photo-emulsion to stabilize the particles. It was found that after the substrate was coated with the emulsion and then baked

at 170 °C for 10 s before hydration and UV exposure, 5 nm well-dispersed Pt particles were obtained (see Fig. 5A). When compared to air-sprayed Johnson Matthey (JM) Pt catalysts (Fig. 5B), it was observed that the particle sizes for both cases are about the same (estimated from FESEM images at 500k \times , average size for printed Pt is 4.9 ± 0.9 nm, and for JM Pt is 5.8 ± 1.2 nm). However, JM Pt particles tend to form agglomerates after applied to the substrate by air spraying, which is a common problem usually associated with ink-based catalysts.

When printed on CB/CP, both Nafion ionomer and EG were mixed with the photo-emulsion. When only EG was added to the emulsion, the coating was not uniform. Areas with no particles were found on the substrate. Conversely, if only Nafion ionomer solution was added to the photo-emulsion, a more uniform coating was obtained; however, the Pt particles formed 175 nm clusters (Fig. 2C). Therefore, samples were produced from emulsions containing both EG and the Nafion ionomer (Fig. 5C1 and C2). In this case, Pt particles of less than 5 nm were formed. Although the particles formed clusters on CB/CP, the cluster size was reduced to less than 25 nm as compared to air-sprayed JM Pt black on CB/CP with the cluster sizes up to 2 μ m while the individual particle size remained comparable. It could be expected that when the surfactant and the stabilizer (Nafion ionomer and EG) are at optimal compositions, the best-dispersed distribution of Pt particles can be achieved. According to ICP studies, we found that on blank CP, the deposition efficiency decreased from 13.4% to 3.2% when EG was used as the stabilizing agent (Table 3) and only a monolayer of Pt particles was deposited (Fig. 5A). On a substrate such as CB/CP with a larger surface area, the deposition efficiency improved to 6.3%.

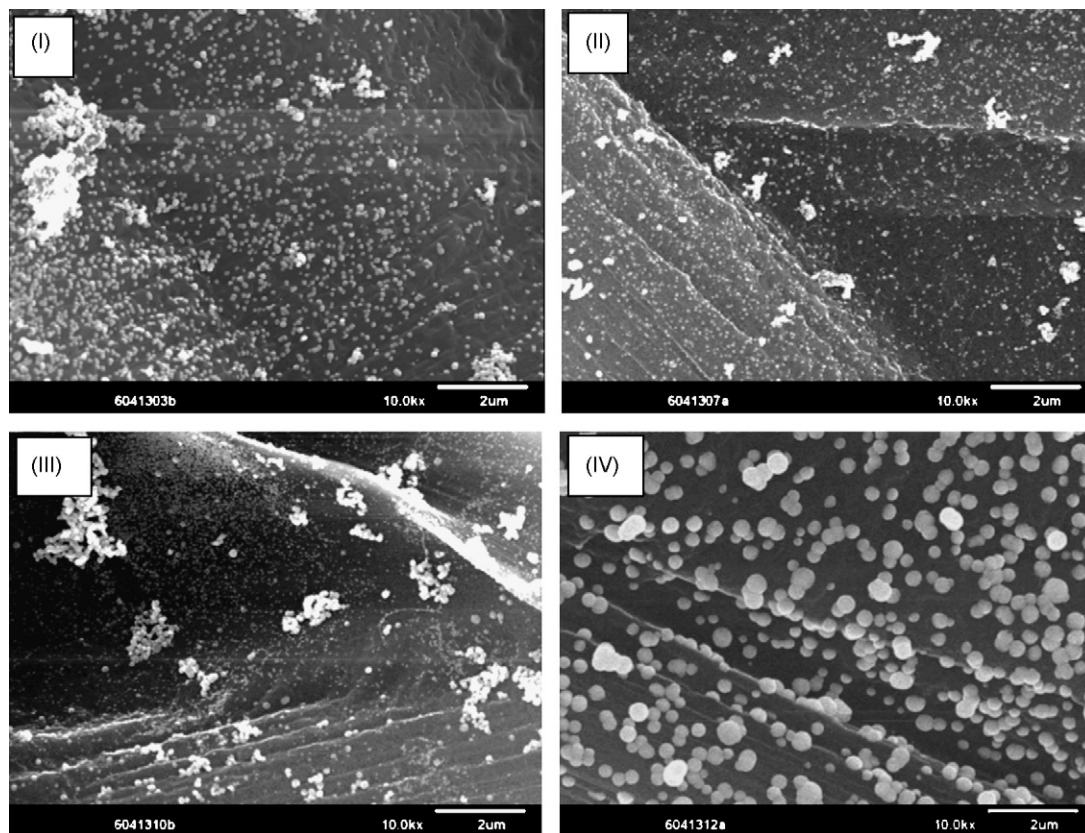


Fig. 4. Representative SEM images of POP Pt particles produced on CP under different hydration conditions. The average particle sizes for these samples are (I) 74.6 nm (sample 3); (II) 48.9 nm (sample 7); (III) 31.9 nm (sample 10); and (IV) 238.6 nm (sample 12).

3.2. CV investigation of Pt catalyst activity for the MeOH oxidation reaction

Results of CV measurements in 0.5 M H₂SO₄ + 1 M methanol of the samples printed on different substrates with or without EG/Nafion ionomer solution at the same hydration and exposure conditions (hydrated with room temperature water for 30 s and exposed for 2 min) are shown in Fig. 6 and compared to the DOP Pt and JM Pt catalyst by plotting the mass specific methanol oxidation currents versus applied potential. The curves in Fig. 6 show typical methanol oxidation peaks in the forward scans for all of the samples. The deposition conditions,

Pt real loadings, deposition efficiencies, particle sizes (cluster sizes), and mass specific methanol oxidation currents of all the samples are summarized in Table 3. Except for JM Pt catalyst, the cluster sizes are listed for photo-printed Pt catalysts which usually consist of particles of about 5 nm size. For JM Pt catalyst after air-sprayed onto the GDL, the aggregate size could be up to 2 μm.

Compared to the DOP Pt (sample F) and JM Pt catalyst (sample A), the maximum mass specific oxidation current density of the POP Pt with Nafion and EG (sample E) is about five times higher. This specific current density is also about 1.4 times higher than when printed on blank CP (sample C) as a result of

Table 3

Comparison of the effect of Pt deposition conditions on deposition efficiency and mass specific MeOH oxidation current

Sample ID	Pt deposition conditions	Theoretical Pt loading (mg cm ⁻²)	Actual ICP Pt loading (mg cm ⁻²)	Deposition efficiency (%)	Particle size (nm)	MeOH oxidation peak height (mA mg ⁻¹)
A	Air-sprayed JM Pt black on CB/CP	0.98	0.690	70.4	5.8 ± 1.2	45.8
B	POP Pt, on CP	0.50	0.067	13.4	55.3 ± 11.9	34.5
C	POP Pt, 20% EG on CP	0.50	0.016	3.2	4.9 ± 0.9	145.0
D	POP Pt, 10% Nafion on CB/CP	0.50	0.0575	11.5	175 ± 83	48.1
E	POP Pt, 10% Nafion + 18% EG on CB/CP	0.50	0.0316	6.3	25 ± 6.7	205.2
F	DOP Pt, on Nafion	1.25	0.2	16.0	286 ± 51	55

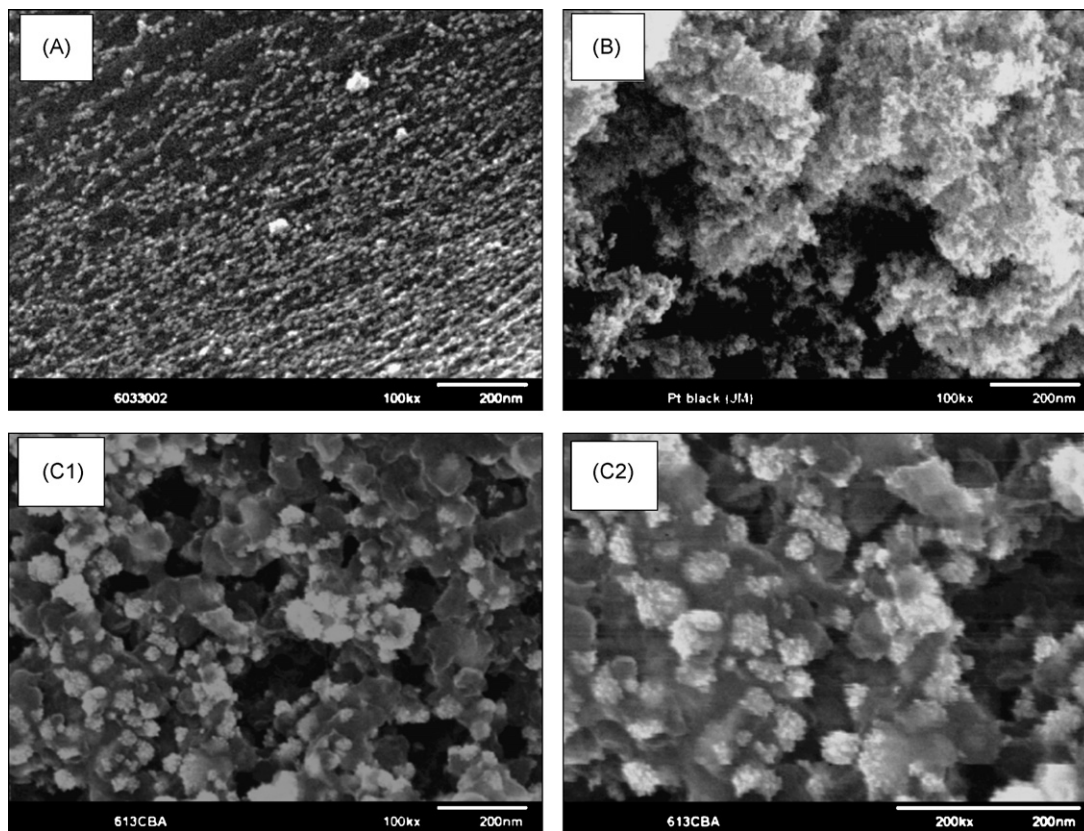


Fig. 5. FESEM images of (A) Pt particles printed on CP with ethylene glycol mixed with the emulsion and (B) air-sprayed JM Pt particles on carbon paper. (C1, C2) Pt printed on CB/CP with 10 vol% Nafion ionomer and 18 vol% EG mixed with the emulsion. All images are at the magnifications of 100k \times except (C2) at 200k \times to show the individual particles in the clusters.

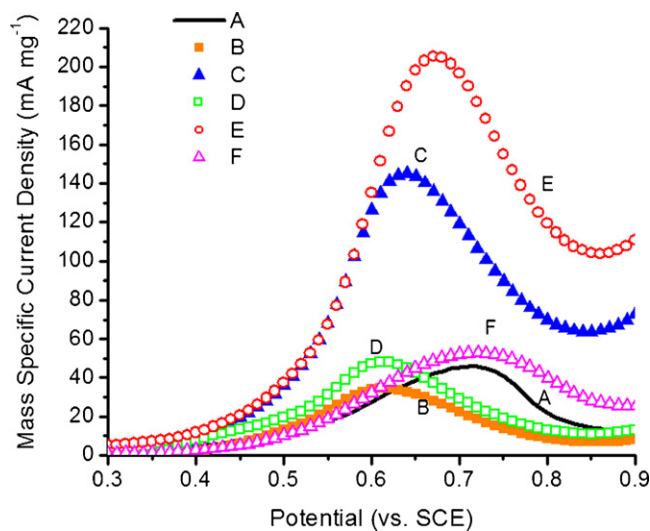


Fig. 6. CV measurements of samples (A) JM Pt on CB/CP; (B) POP Pt on CP without EG; (C) POP Pt on CP with EG; (D) POP Pt on CB/CP, with Nafion ionomer; (E) POP Pt on CB/CP with Nafion ionomer and EG; (F) DOP Pt on Nafion 117 membrane. All scans were performed in 0.5 M H₂SO₄ + 1 M methanol at a 20 mV s⁻¹ scan rate. The curves plotted are the 20th forward scans for all of the samples.

the higher substrate surface area, and the enhanced deposition efficiency.

3.3. Study of POP Pt catalyst performance in a single H₂ PEM fuel cell

Pt has been deposited on 5 cm² CB/CP electrodes by the modified POP printing process. The photo-emulsion consisted of 18 vol% EG and 10 vol% Nafion ionomer. The amount of the emulsion put on the substrate resulted in a real Pt loading of 0.16 mg cm⁻² (ICP confirmed) with a deposition efficiency of 6.4%, which was consistent with the average deposition efficiency listed in Table 3. These Pt printed CB/CP electrodes were placed in a H₂ PEM single fuel cell as the anode or the cathode or both, and the catalytic activities were evaluated by a Scribner fuel cell testing system (Scribner Associates, Inc., Southern Pines, NC).

Fig. 7 compares the performance of the four types of MEAs at different cell temperatures from 50 °C to 80 °C. These four types of MEAs have been described in detail in Section 2.4 and also illustrated in Fig. 1.

We can see that when the JM Pt on the anode side was replaced with our POP Pt at only 18% of the loading, similar power densities were achieved at lower cell temperatures and POP Pt outperformed the JM Pt at temperatures above 70 °C, Fig. 7C and D. When the JM Pt on the cathode side was replaced with

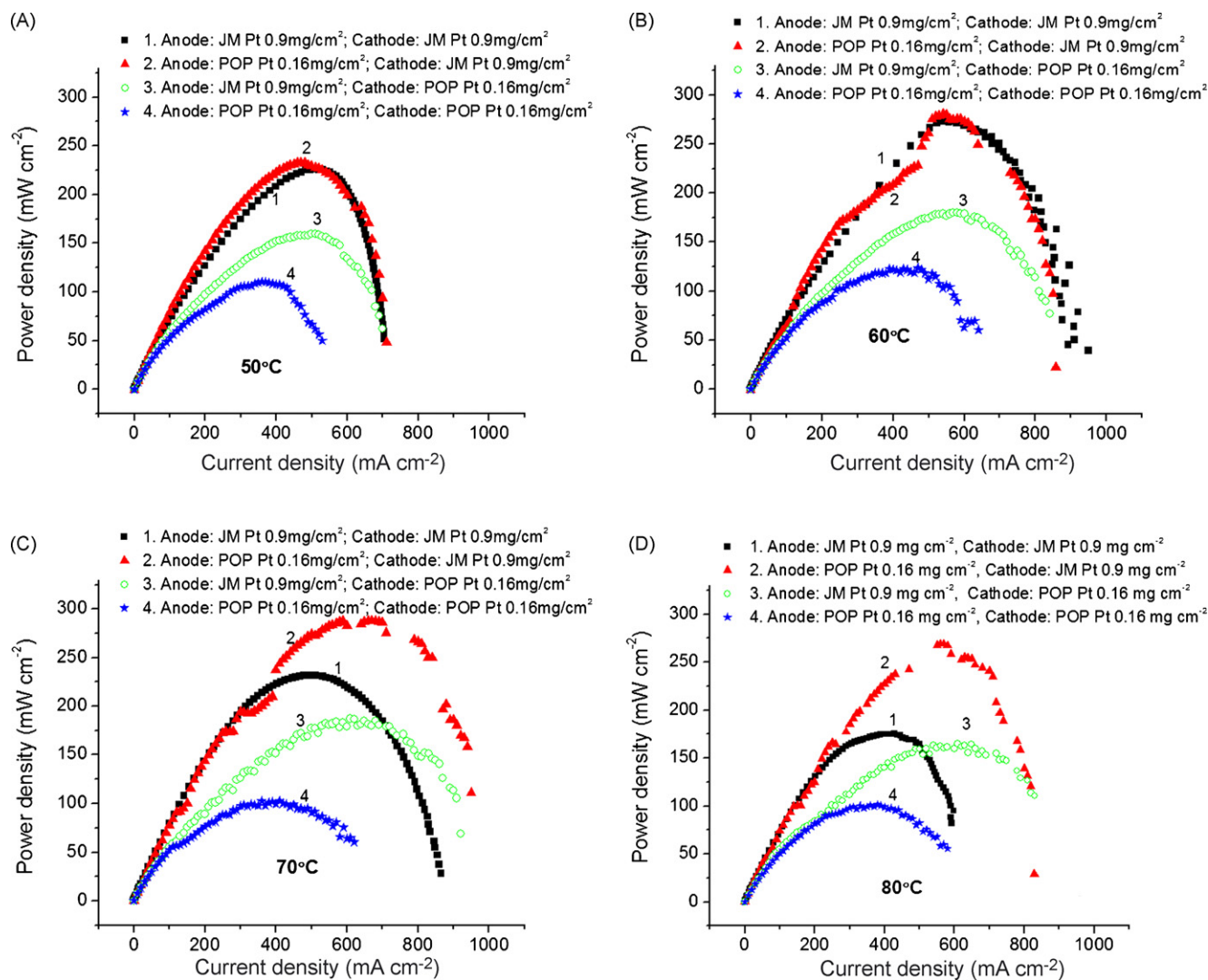


Fig. 7. The H_2 PEMFC performance of the four MEAs at the cell temperatures of (A) 50°C , (B) 60°C , (C) 70°C , and (D) 80°C . The active area of the single cell was 5 cm^2 . All tests were run at 100% RH and ambient pressure. Pure H_2 and pure O_2 were used as the anode and cathode fuel, respectively. The flow rates were 0.11 min^{-1} for both H_2 and O_2 .

our POP Pt, the maximum power density decreased because the oxygen reduction reaction is so kinetically sluggish compared to the hydrogen oxidation reaction that a higher catalyst loading is required to attain a good performance. In this study the Pt loading was reduced from 0.9 mg cm^{-2} to 0.16 mg cm^{-2} when the catalyst was changed from JM Pt to our POP Pt and therefore, the drop of the performance is reasonable. For the fourth type of MEA, both anode and cathode had POP Pt as the catalysts at a loading of 0.16 mg cm^{-2} . The performance was further decreased because of the very low catalyst loadings on both sides, but primarily controlled by the cathode reaction. As the cell temperature was increased, the performance gaps between the control MEA and the third and fourth MEAs became smaller due to the enhancement of the reaction kinetics at high temperatures.

It is noticed that our control MEA with JM Pt catalyst had a lower performance than what we expected, which requires further investigation. The loading of JM Pt was much higher than POP Pt due to the difficulty to prepare uniform catalyst

layer at low loadings by our current air-spray method. In the mean time, POP Pt tends to stay as a monolayer of particles or clusters at certain printing conditions, which makes it inefficient to increase the Pt concentration in our photo-emulsion during the printing. Much higher performances than our control MEA by using Pt catalysts prepared by conventional methods or advanced techniques at very low Pt loadings have been reported [9–13]. However, due to the difference of electrolyte membrane, or gas diffusion layer, or operating conditions, a direct comparison to our POP Pt is not available. Therefore the performance of POP Pt has been compared to our previous DOP Pt to further demonstrate the improvement of this printing technique.

In the previous DOP printing, due to the extremely low deposition efficiency on CP, Pt was deposited onto the Nafion membrane in order to make a workable MEA [1]. With the same control JM Pt GDE on the cathode side, we compared the performance of POP Pt on the anode side which deposited on the CB/CP GDL by the modified POP with the DOP Pt deposited on the Nafion membrane at the anode side, and the

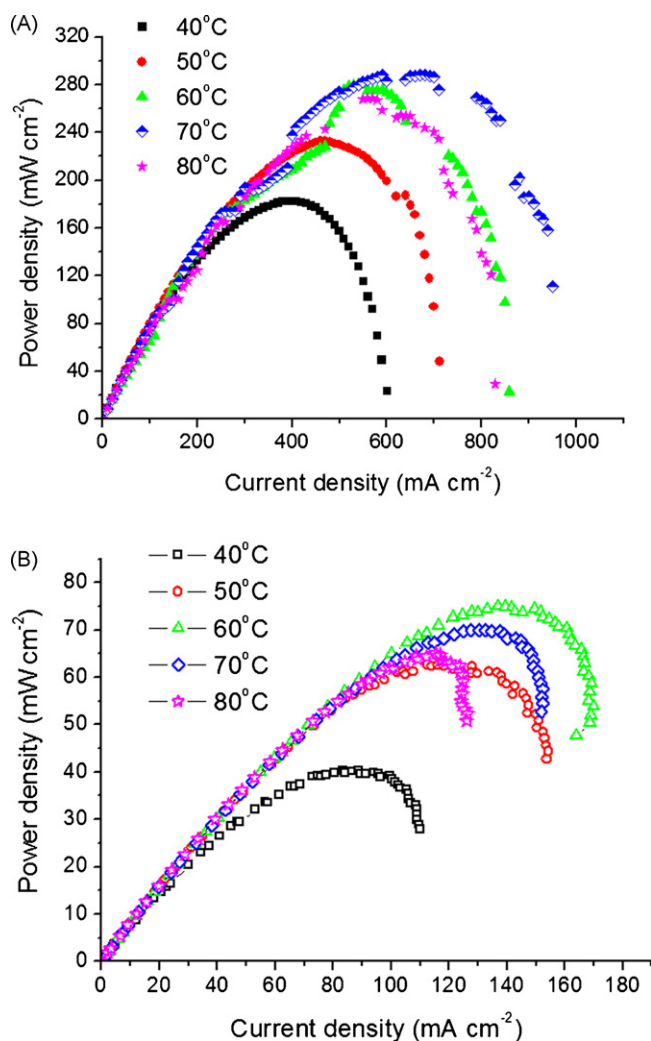


Fig. 8. The H₂ PEMFC performance of MEA (A) POP Pt on the anode side with Pt loading of 0.16 mg cm⁻² and MEA (B) DOP Pt on the anode side with Pt loading of 0.12 mg cm⁻², at different cell temperatures. The cathodes for both MEAs were the same control JM Pt GDEs. The active area of the single cell was 5 cm². All tests were run at 100% RH and ambient pressure. Pure H₂ and O₂ were used as the anode and cathode fuel, respectively. The flow rates were 0.1 l min⁻¹ for both H₂ and O₂.

results were shown in Fig. 8. In Fig. 8, the anode POP Pt loading was 0.16 mg cm⁻²; while the anode DOP Pt loading was 0.12 mg cm⁻². With the similar Pt loadings on the anode side, the performance was improved by a factor of 4 in the cell temperature range from 50 °C to 80 °C. This enhancement is not only due to the reduction of particle agglomeration but also due to the elimination of the deposition inside the Nafion membrane, which dramatically increased the accessible active catalyst surface area.

4. Summary

POP Pt printing significantly increased the deposition efficiency by more than 6 times on CP and 22 times on CB/CP over the DOP, thereby making CP or CB/CP suitable substrates for this catalyst production method. Results of the studies indicated that the final particle sizes were determined by the diffusion

volume of the nucleation/growth region, and that the hydration conditions prior to the UV exposure controlled the Pt particle sizes. Steaming was a very practical and efficient hydration method for hydrophobic substrates like CP. It allowed the control of the particle size simply by varying the steaming water temperature and the steaming time. The particle size could be reduced from 250 nm to about 30 nm if no condensed water was visible on the substrates prior to the UV exposure. In addition, particle size could be further reduced by using ethylene glycol as a stabilizing agent. Dispersed Pt particles of 5 nm were formed by this modified POP.

When printed on high surface area but hydrophobic substrates, such as CB/CP, both a surfactant, e.g. Nafion ionomer, and a stabilizing agent, e.g. EG, were needed to achieve a uniform printing of smaller dispersed Pt particles on the substrate. In this study, with Nafion ionomer and EG concentrations of 10 vol% and 18 vol%, respectively, 25 nm clusters consisting of Pt particles of less than 5 nm were formed on the surface and gave a mass specific methanol oxidation current five times greater than the previous DOP Pt. The catalytic activity of the modified POP Pt on CB/CP was also evaluated using a single H₂ PEM fuel cell. When cell temperature was in the range from 50 °C to 80 °C, the performance was increased more than four times compared to the DOP Pt. This enhancement was due to the improved dispersion of Pt particles on a high surface area substrate and the increased accessible Pt active surface area. So far, the concentrations of the Nafion ionomer and EG in the emulsion have been kept constant, but they can be optimized to achieve smaller particle sizes, more dispersed distribution of Pt particles, and further improved catalyst performance.

Acknowledgements

The research described herein was supported by the Indiana 21st Century Research and Technology Fund (contract number 910010465) and the U.S. Army CECOM RDEC through Agreement DAAB07-03-3-K414. Such support does not constitute endorsement by the U.S. Army of the views expressed in this publication. The authors are grateful for the valuable discussion with Prof. Davide Hill and the lab assistance from Timothy Hall and Loukas Tsagalas. The authors also want to thank the Center for Environmental Science and Technology for the use of ICP-OES.

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