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Preparation of PEM fuel cell electrodes using pulse electrodeposition

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Abstract

A new approach based on pulse electrodeposition is demonstrated to be an attractive technique to replace conventional powder type membrane electrode assembly (MEA) preparation methods. The performance of the catalyst layer is optimized by controlling the pulse deposition parameters such as the peak current density, duty cycle and the total charge density. The peak current density and the pulse duty cycle are found to control the nucleation rate and decrease the catalyst dendric growth. The amount of platinum loading is controlled by the total charge density. Preparing the electrode using a peak current density of $400 \, \text{mA/cm}^2$, a duty cycle of 2.9% and a total charge density of $8 \, \text{C/cm}^2$ results in a high catalyst performance of $380 \, \text{mA/cm}^2$ at 0.8 V.
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1. Introduction

Polymer electrolyte membrane (PEM) fuel cells offer low weight and high power density and are being considered for automotive and stationary power applications [1–4]. Current approaches for preparing a membrane electrode assembly (MEA) for PEM fuel cells can be broadly divided into two different categories—powder type and non-powder type. The powder type involves the process of catalyzation on a high surface area of carbon. The prepared carbon supported catalyst is mixed with binder and then applied to the membrane followed by gas diffusion layer (GDL) addition or to the GDL followed by membrane addition. Ulchida et al. [5] prepared a colloid mixture containing Pt/C powder, perfluorosulfonate ionomers (PFSI, such as Nafion) and solvent using ultrasonic treatment. This paste was then spread over the wet-proofed gas diffusion layer of carbon paper. The electrodes with the paste on it were hot-pressed to both sides of a membrane to fabricate an MEA. The observed increase in MEA performance was attributed to the increase in contact area between the PFSI and the Pt particles. Wilson and Gottesfeld developed a catalyst decaling process in order to produce a dense and thin catalyst layer [6,7]. The first step in this process is preparing ink containing Pt/C powder, Nafion

solution and solvent. This ink is then applied to a Teflon blank and heated until dry. More layers of Pt/C/Nafion ink are added until the desired catalyst loading is achieved. The catalyst coated Teflon blanks are hot pressed to the Nafion membrane. Then, the Teflon blank is peeled away from the membrane, resulting in the MEA.

The catalyst layer in powder type MAE has a uniform concentration profile of the catalyst, since the Pt/C powder is thoroughly mixed with the binder before being applied to the membrane or GDL. A high content of Pt in the Pt/C powder allows reducing the thickness of the catalyst layer without sacrificing the catalyst loading per area of electrode. However, it is difficult to control the particle size of the catalyst when the Pt to carbon ratio increases more than 40 wt.%.

In order to overcome this limitation, several non-powder type processes were developed. These processes create the catalyst directly on the surface of carbon electrode or membrane. Fedkiw and Her [8] describe a two-step impregnation-reduction method in which the Nafion membrane first undergoes an ion exchange reaction with a metal salt, then the impregnated membrane is exposed to a reducing agent to form a catalyst layer directly on the membrane. Another method is evaporative deposition, in which, as described by Foster et al. [9], a Pt salt is evaporated and deposited on a membrane. A third MEA preparation technique is sputtering. Hirano et al. [10] show that a very thin layer of sputter deposited platinum on a wet-proofed GDL performs very similarly to a standard E-TEK electrode.

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However, this technique is not a volume production method. It requires expensive vacuum equipment and cannot be used for fabrication of large structures with complex shapes.

A non-powder type electrodeposition technique has attracted attention due to its ease of preparation and low cost requirement. Taylor et al. [11] developed an electrochemical catalyzation (ECC) technique to improve the utilization of Pt catalyst. In this technique, platinum ions are diffused through a thin Nafion layer and electrodeposited only in regions of ionic and electronic conductivity. This post-catalyzation process can avert the loss of active Pt site by PTFE binder coverage. However, this process is strongly limited by diffusion of Pt complex ion across the Nafion layer. To avoid this limitation, Antoine and Durand [12] impregnated carbon with H_2PtCl_6 and applied an electrochemical pulsed current to deposit Pt in the Nafion active layer. This process guarantees a smaller active layer thickness and high platinum mass fraction up to 40 wt.%. However, in terms of Pt concentration distribution, it has a profile like that of a powder type process, and Cl^- ions produced from electrodeposition of Pt from H_2PtCl_6 remain in the active layer. The Cl^- ions are known to poison platinum and reduce the catalytic activity of platinum [13].

A new approach to prepare MEAs based on pulse electrodeposition was described in our previous paper [14]. Using a novel pulse plating technique, it was possible to increase the Pt/C ratio up to 75 wt.% near the surface of the electrode, resulting in a ~6 μm thick catalyst layer. The results indicated that pulse deposition may be an attractive technique to replace conventional powder type MEA preparation methods and help achieve industry goals of reducing the cost and increasing the efficiency of polymer electrode membrane fuel cells.

The objective of this study was to optimize the performance of the catalyst layer by controlling the pulse deposition parameters.

2. Experimental

2.1. Uncatalyzed carbon electrode

The experimental procedure to prepare the carbon blank electrode have been described in detail previously [14]. The blank carbon electrode consists of two different carbon layers—hydrophobic and hydrophilic. In order to prepare the hydrophobic carbon layer, a carbon black (Vulcan XC-72 from Cabot) with well-defined masses of PTFE solution (60 wt.%) and isopropyl alcohol were thoroughly mixed in a supersonic bath. The prepared paste is applied and rolled onto a hydrophobic carbon cloth and annealed at 300 °C in air. The resulting substrate has a strong hydrophobic nature. Subsequently, an organic solvent is added to the above mixture, which is then homogenized using ultrasound for 30 min. This ink is applied on the hydrophobic carbon layer prepared in the first step. The resulting blank carbon

electrode has a hydrophilic surface due to the addition of the organic solvent.

2.2. Electrodeposition

The electrodeposition of platinum was performed on the carbon blank electrode using a Pt plating bath containing 10 g/L of H_2PtCl_6 and 60 g/L of HCl at room temperature. The blank carbon electrode was loaded on the sample holder coupled with a copper plate as a current collector. The electrodeposited size of the electrode was varied from 5 to 25 cm^2 by adjusting the window size of the sample holder exposed to the electrolyte. Platinum gauze was used as an anode. A pulse generator controlled both the pulse wave and the deposition current density. The current densities, the duty cycle and the charge density were changed to optimize the deposition rate.

2.3. MEA fabrication

After electrodeposition, the electrodes were heated at 300 °C in air to remove the solvent contained in the hydrophilic carbon layer. In the second step, the electrodes were heat treated in H_2 at 300 °C for 2 h. After the heat treatment, the electro-catalyzed electrode was impregnated with 5 wt.% of Nafion solution by spraying and then dried at 80 °C for 2 h. The amount of Nafion loading was controlled to 0.8 mg/cm^2. The commercial ETEK electrode (20 wt.% Pt/C, 0.4 mg/cm^2) was used as the anode for all tests in order to eliminate experimental error originating from anode preparation. A total of 1.2 mg/cm^2 Nafion solution was applied to E-TEK anode electrodes by brushing and spraying. The Nafion-impregnated electrodes and the membrane (Nafion 112) were bonded to form a MEA by hot pressing at 130 °C for 3 min at a pressure of 140 atm. The reaction gases were supplied through a humidifier and a mass flow controller from hydrogen and oxygen tanks. The reactant gases flowed according to the cell performance (1.5/2 stoics for H_2 and O_2). The cell was operated under ambient pressure.

2.4. Characterization of the electrode

Cyclic voltammetry was used to determine the Pt effective surface area. The experiment was performed in 0.5 M H_2SO_4 at 25 °C saturated with nitrogen using a conventional three-electrode cell. Saturated Hg/Hg_2SO_4 equilibrium served as a reference electrode. Electron probe microanalysis (EPMA, Cameca instrument incorporated, model MBX) was used to measure the thickness of the electrocatalyst layer across the cross-sectioned MEA. The particle size of the Pt prepared by pulse electrodeposition was determined using transmission electron microscopy (TEM, Hitachi H-8000 model). Energy dispersive analysis by X-ray (EDAX) coupled with environment scanning electron microscopy (ESEM) was used to obtain the surface

morphology of the electrode and to determine the Pt/C ratio on the surface of the carbon electrode. The amount of platinum electrodeposited on the electrode was estimated by using ICP-AES (Perkin-Elmer 400) analysis.

3. Results and discussion

In an electroplating process, metal ions are transferred to the cathode and adatoms are formed by the charge transfer reaction and finally incorporated into the crystal lattice. This phenomenon occurs by building up existing crystals (growth of crystals) or creating new ones (nucleation). These two steps are in competition and can be influenced by the surface diffusion rate of adatom and the rate of charge transfer reaction. High surface diffusion rates, low population of adatoms caused by slow charge transfer reaction and low overpotential lead to the growth of crystals; conversely, low surface diffusion rates, high population of adatoms, and high overpotential increase the rate of nucleation [15]. The nucleation rate [16] is given by

$$J = K_1 \exp\left[\frac{-bs\varepsilon^2}{zekT\eta}\right] \tag{1}$$

where K_1 is the rate constant; b, the geometric factor depending on the shape of the 2D cluster ($b = P^2/4S$, where P is the perimeter and S, the surface area); s, the area occupied by one atom on the surface of the nucleus, ε, the edge energy; k, the Boltzmann constant; z, the electronic charge of the ion; e, the charge of the electron and; T, the temperature. The overpotential, η, is given by the Tafel expression,
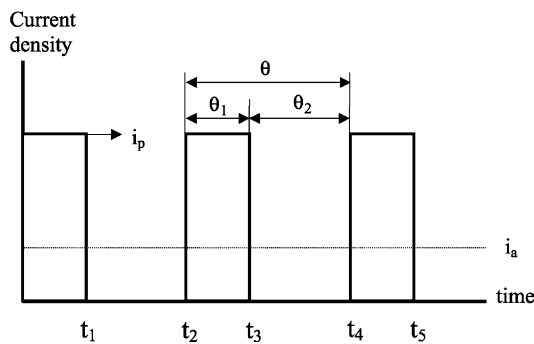
$$\eta = \alpha + \beta \log i \tag{2}$$

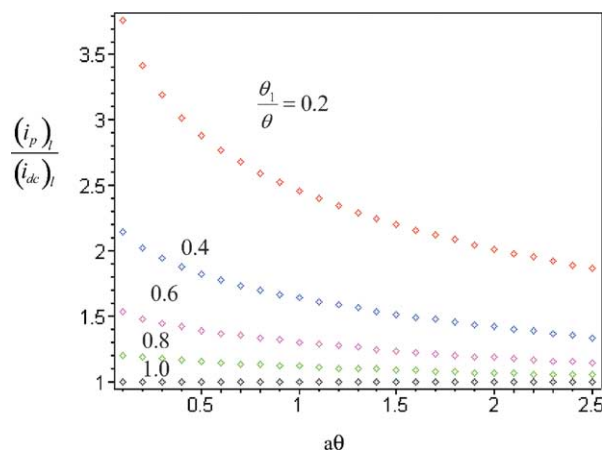Fig. 1. Current waveform and pulse deposition parameters.

Fig. 2. The ratio of limiting current density between pulse electrodeposition and direct current electrodeposition with respect to pulse period and duty cycle.
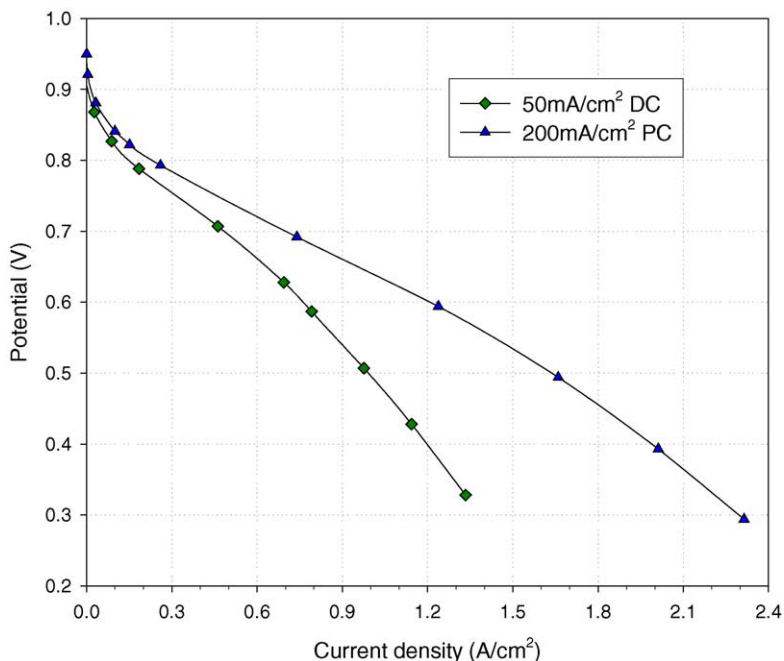

Fig. 3. Polarization curves of MEAs prepared by direct current and pulse electrodeposition.
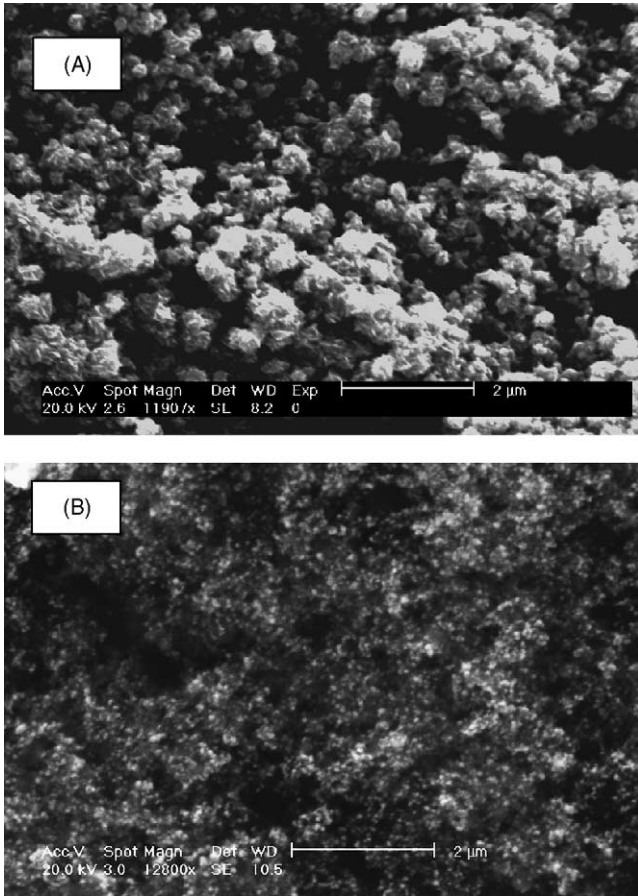
Fig. 4. SEM images of Pt electrodeposited electrodes: (A) 50 mA/cm^2 of DC electrodeposition; (B) 200 mA/cm^2 of peak current density, 5.2 ms on time and 70 ms off time. The total charge is fixed at 6 C/cm^2 in both cases.

where α and β are the constants, and i is the current density. From the above equations, it can be seen that as the applied current density increases the overpotential increases, which in turn according to Eq. (1) increases the nucleation rate.

When compared to direct current (dc) deposition, pulse electrodeposition enables higher cathodic current density to be applied at the electrode interface due to the higher concentration of metal ions at the surface of electrode. A simple diffusion model was suggested in earlier research to interpret theoretically the pulse and DC deposition processes [17,18]. The current wave form of pulse deposition is shown in Fig. 1. Pulse electrodeposition has three independent variables, namely, on time (θ_1), off time (θ_2) and peak current density (i_p). The duty cycle is defined as follows.

$$\text{duty cycle (\%)} = \frac{\theta_1}{\theta_1 + \theta_2} \times 100 \tag{3}$$

The ratio of the limiting current density in pulse electrodeposition $(i_p)_l$ and DC plating $(i_{dc})_l$ was determined by Cheh [17] and is given below.

$$\frac{(i_p)_l}{(i_{dc})_l}$$

$$= \frac{1}{1 - 8/\pi^2 \sum_{j=1}^{\infty} 1/(2j-1)^2((\exp[(2j-1)^2 a\theta_2] - 1)/ (\exp[(2j-1)^2 a\theta] - 1))} \tag{4}$$

where $a = \pi^2 D/4\delta^2$ (s^{-1}) is the diffusion parameter. This ratio for various values of $a\theta$ (pulse period) and θ_1/θ (duty cycle) is plotted in Fig. 2. The result shows that the limiting
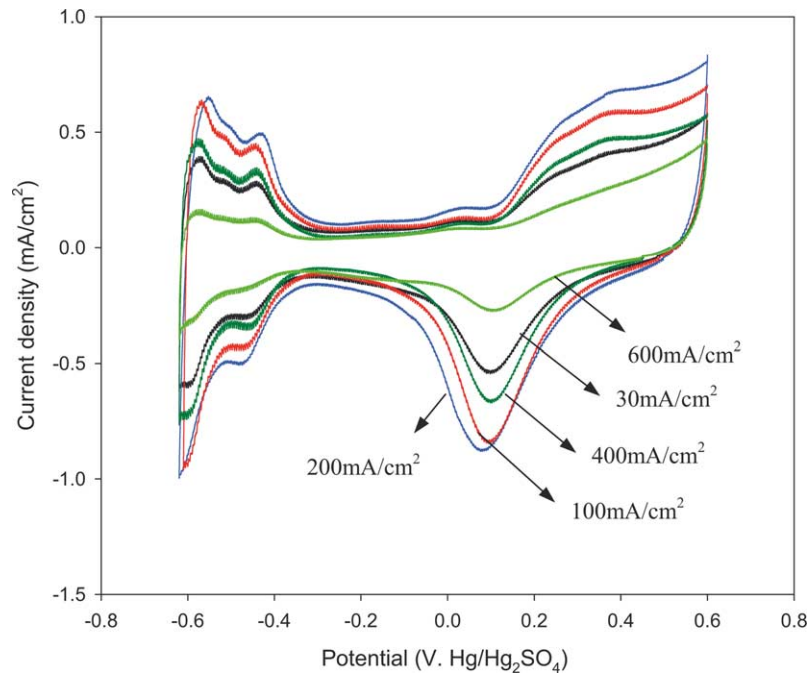

Fig. 5. Cyclic voltammograms of the electrodes prepared at different peak current densities in pulse electrodeposition. Total charge density is fixed at 6 C/cm^2.

Table 1
Summary of effective surface area and Pt wt.% estimated for different deposition conditions[a]

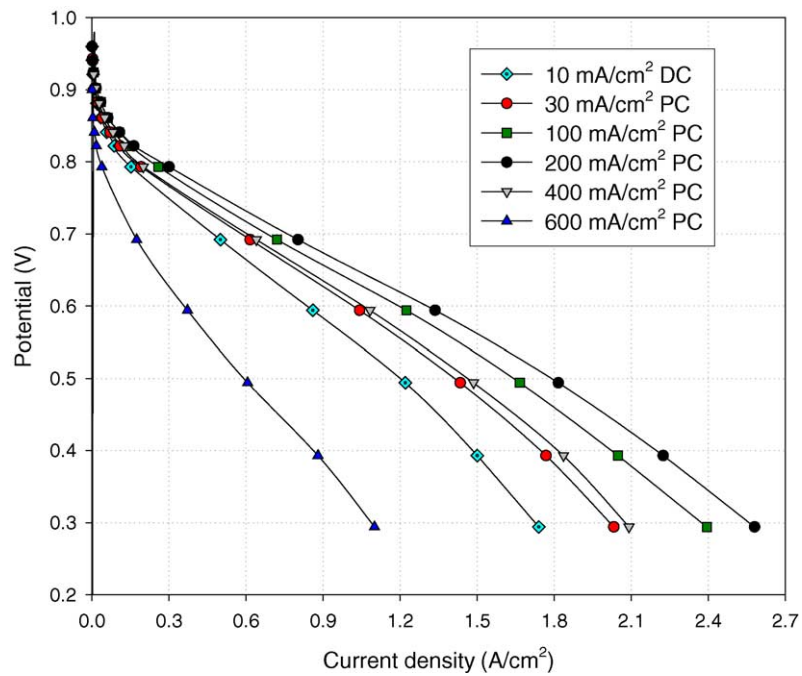| Peak current density (mA/cm^2)	On time (ms)	Off time (ms)	Duty cycle (%)	Effective surface area (cm^2)	Pt wt.%
10 DC	–	–	–	223	40
30 PC	34.7	73.3	32.1	252	36
100 PC	10.4	97.6	9.6	380	46
200 PC	5.2	102.8	4.8	423	52
400 PC	2.6	105.4	2.4	319	55
600 PC	1.7	106.3	1.6	85	26

[a] Total charge density is fixed at 6 C/cm^2.

Fig. 6. Effect of the peak current density of pulse electrodeposition on the performance of the PEM fuel cell.
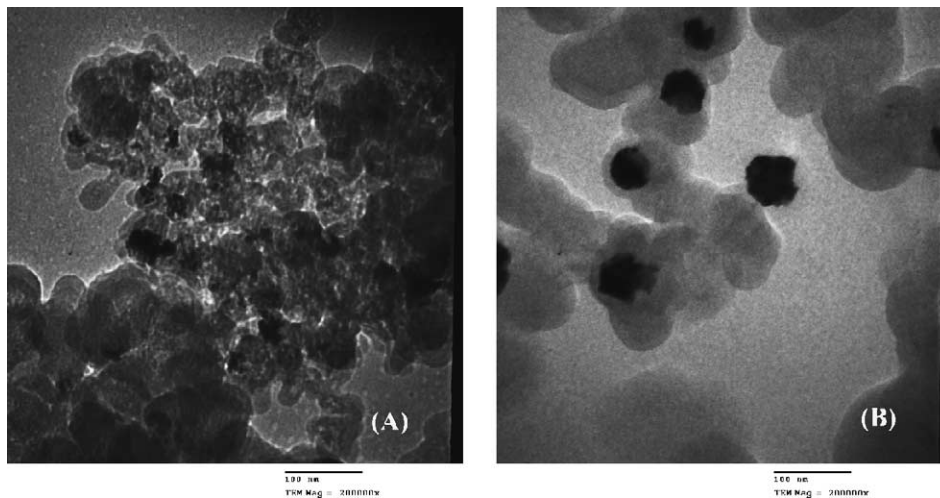

Fig. 7. TEM images of Pt deposited on carbon under different electrodeposition conditions: (A) 200 mA/cm^2 of PC; (B) 10 mA/cm^2 of DC.

Table 2
Effective surface area and Pt loading estimated for different duty cycles

Off time (ms)	Peak current density (mA/cm^2)	On time (ms)	Duty cycle (%)	Effective surface area (cm^2)	Pt loading (mg/cm^2)
30	200	5.2	14.7	161	0.68
70	200	5.2	6.9	338	0.24
140	200	5.2	3.5	157	0.15

current density of pulse electrodeposition is always higher than that of dc electrodeposition. Moreover, the electrodeposition can be carried out at a higher current density by decreasing the pulse periods or by decreasing the duty cycle. According to Eq. (2), the larger the current density, the higher the overpotential. Thus, the nucleation rate increases, resulting in a finer crystal grain.

Fig. 3 shows the polarization curves of the PEM fuel cell prepared by dc and pulse current (PC) electrodeposition of Pt. The pulse electrodeposited electrode was prepared under the conditions of 200 mA/cm^2 of peak current density, 5.2 ms on time and 70 ms off time. The current density of 50 mA/cm^2 was applied continuously for dc electrodeposition. Total charge density was fixed at 6 C/cm^2 in both cases. The results clearly show the advantage of pulse electrodeposition. The MEA prepared by pulse electrodeposition at higher current density exhibits better performance than the MEA prepared by direct current deposition at lower current density. The observed difference in the MEA performance can be explained by taking into account different Pt particle sizes of the electrodes prepared by using DC and PC deposition techniques.

Fig. 4 presents SEM images of electrodes prepared using DC and PC deposition techniques. The grain size of the Pt

deposited at 50 mA/cm^2 by DC deposition is larger than that of the Pt prepared at 200 mA/cm^2 by PC deposition. By increasing the current density for pulse electrodeposition, the deposition overpotential is also increased, resulting in an increase in the rate of nucleus formation. In the case of PC deposition, metal ions diffuse into the surface of the electrode during the off time so that it is possible for the electrodeposition to be performed at higher peak current density. DC deposition continuously consumes metal ions without any relaxation time. Consequently, the current density reaches the point where the concentration of the metal ions is insufficient even at lower current density and enormous growth of platinum occurs, decreasing the effective surface area of Pt, which explains the observed decrease in the MEA performance.

The effect of peak current density in PC mode on Pt electrodeposition was studied by supplying a constant number of Pt atoms to the carbon surface. In this experiment, the peak current density was varied while keeping both the average current density and the number of coulombs per pulse constant [15]. Fig. 5 shows cyclic voltammograms of electrodeposited electrodes prepared at different peak current densities. The CVs were performed in 0.5 M H$_2$SO$_4$ saturated with N$_2$ at scan rate of 5 mV/s. The effective surface
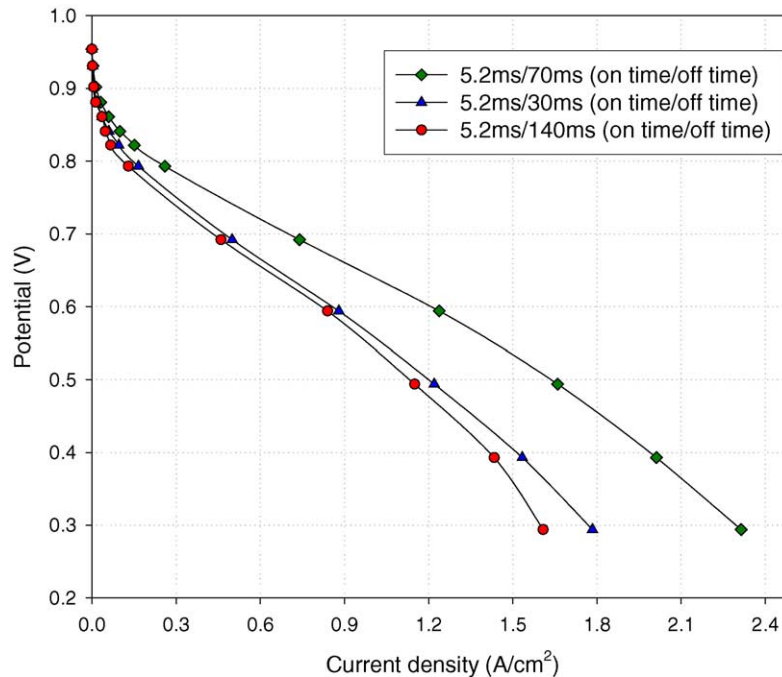

Fig. 8. Polarization curves of MEA prepared at different duty cycles.

area of Pt was calculated from the area of hydrogen desorption peak between -0.62 and -0.25 V versus Hg/Hg_2SO_4 after subtracting the contribution of the double layer charge. This area is converted into the effective active surface area of Pt using the factor of $210\,\mu C/cm^2$ [19].

The pulse condition, specific surface area and wt.% of Pt on the surface of the electrode, measured by EDX, are summarized in Table 1. It is clear from this data that the peak current density does affect the active surface area of the Pt due to changes in Pt grain size. With increase in peak current density, the effective surface area of Pt also increases, indicating that smaller particles of Pt are deposited. However, the effective surface area shows a dramatic decrease when a peak current density of $600\,mA/cm^2$ is used to deposit Pt. At this high current density, hydrogen evolution reaction occurs at a very high rate and destroys the surface of the electrode. As a result, the Pt wt.%, measured by EDX, decreases from 55 to 26 wt.%.

The polarization curves for MEAs prepared by using different current densities are shown in Fig. 6. The electrodes prepared at peak current density of $200\,mA/cm^2$ show better performance than those deposited at lower current density in both DC and PC mode. The increase in performance is contributed to the increase in both, the active surface area of platinum and platinum loading in the catalyst layer. As expected, the electrode prepared using very high current density ($600\,mA/cm^2$) has the lowest performance, which accords with the observation made from cyclic voltammetry.

The TEM images presented in Fig. 7 show the effect of current density on Pt particle size. When the current density $10\,mA/cm^2$ is used for deposition, the particles aggregate, resulting in formation of large particles. When the peak current density is increased to $200\,mA/cm^2$, the particle size of the deposit becomes smaller, indicating that the nucleation rate has increased.

Fig. 8 shows the polarization curves of the electrodes prepared at different duty cycles. The duty cycle was changed by increasing the off time while the peak current density, on time and total charge density were fixed at $200\,mA/cm^2$, $5.2\,ms$ and $6\,C/cm^2$, respectively. The estimated active surface area and the Pt loadings are summarized in Table 2. The results indicate that the duration of the off time plays an important role in the deposition since the recovery of concentration of the electroactive species on the surface electrode occurs in this period. As shown in Fig. 9A, with a decrease of the off time (30 ms), a large increase of the particle size of the deposit is observed. The results can be explained by taking into account that the limiting current density decreases with an increase of the duty cycle (a decrease of the off time) [20]. Since the limiting current density is below the applied peak current density ($200\,mA/cm^2$), the deposition results in a formation of larger particle sizes. The deposition efficiency also increases with a decrease of the off time because the platinum deposition overpotential on the surface of platinum is lower than that on the carbon surface [21]. When the off time is too long, the limiting current density becomes
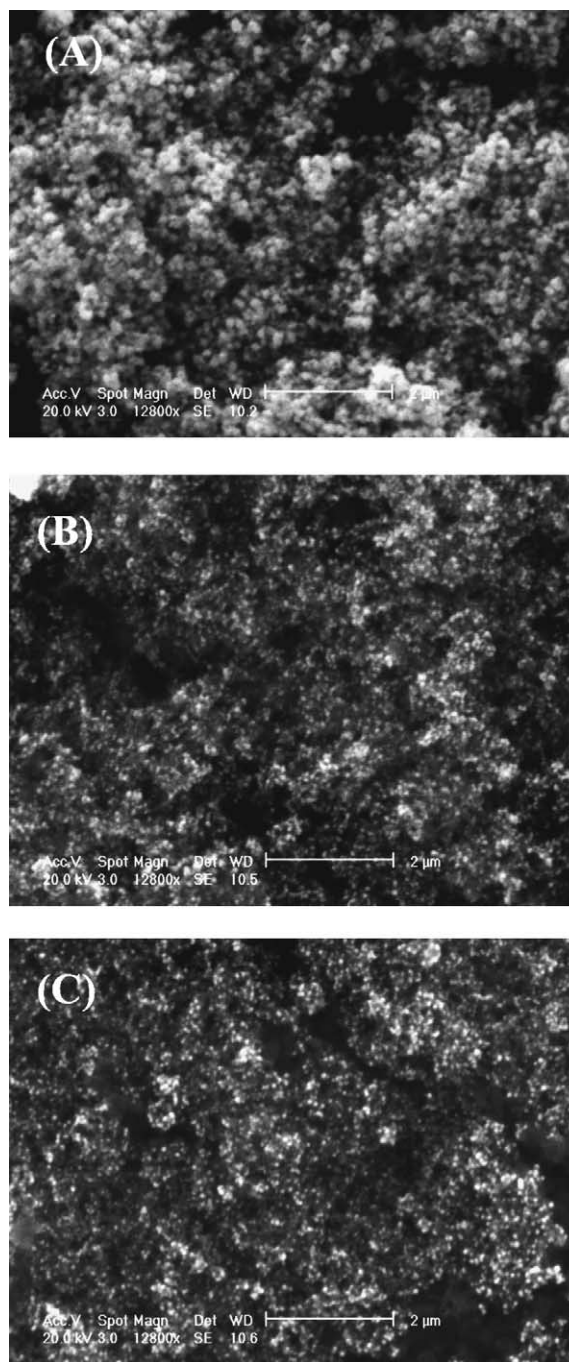

Fig. 9. S.E.M. images of pulse electrodeposited electrode with different duty cycles: (A) 5.2 ms on time/30 ms off time; (B) 5.2 ms on time/70 ms off time; (C) 5.2 ms on time/140 ms off time.

higher than the applied current density. In this case a longer deposition time is necessary in order to achieve the same platinum loading. This is a similar situation as in the case when a low peak current density is applied to the system. As discussed above, low peak current densities decrease the nucleation rate of the deposit. Thus, the off time should be optimized in order to decrease the catalyst particle size and to increase the MEA performance.
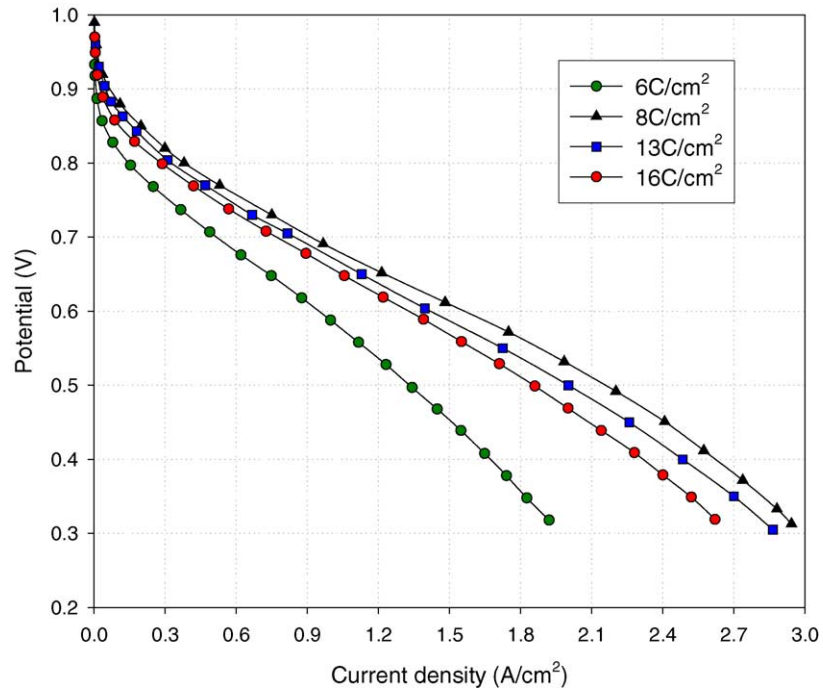
Fig. 10. Effect of charge density on the performance of the PEM fuel cell.

In pulse electrodeposition, by varying the total charge applied for electrodeposition the amount of Pt loading can be controlled. In order to study the effect of this parameter, the total charge density was varied in the range between 6 and $20 \, C/cm^2$ while the peak current density and the duty cycle were fixed at $400 \, mA/cm^2$ and 2.9% (3 ms on time, 100 ms off time), respectively. The duration of electrodeposition time was between 8.5 and 28.6 min. Fig. 10

shows the polarization curves of the MEAs prepared using different charge densities. As shown in Fig. 10, the MEA performance increases with the increase in the total charge density from 6 to $8 \, C/cm^2$. For charges higher than $8 \, C/cm^2$, the MEA performance decreases.

The effect of charge density on the active surface area of platinum was studied more extensively by using cyclic voltammetry. From the CVs, the active surface area of
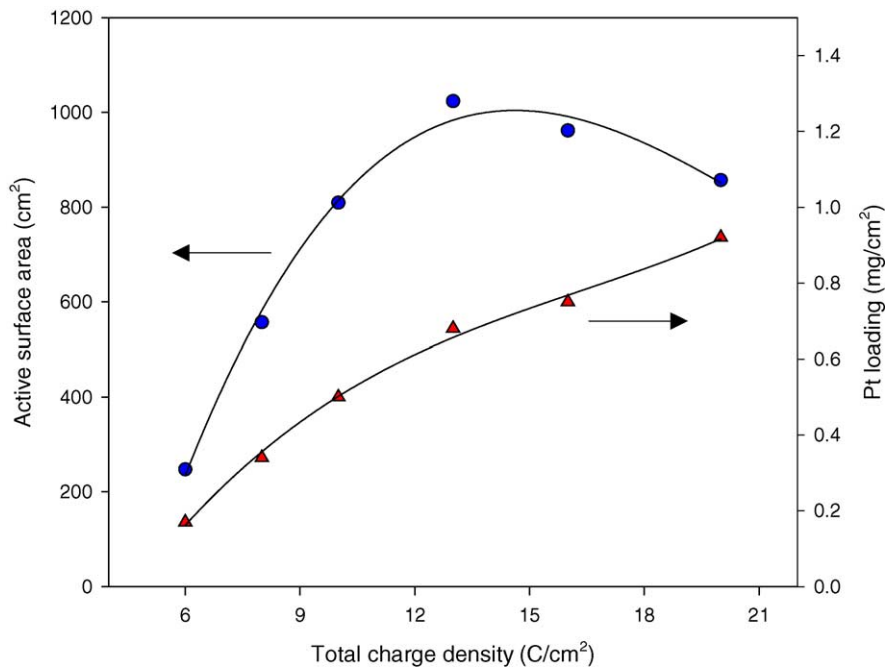

Fig. 11. Effective surface area and Pt loading with respect to the charge density.
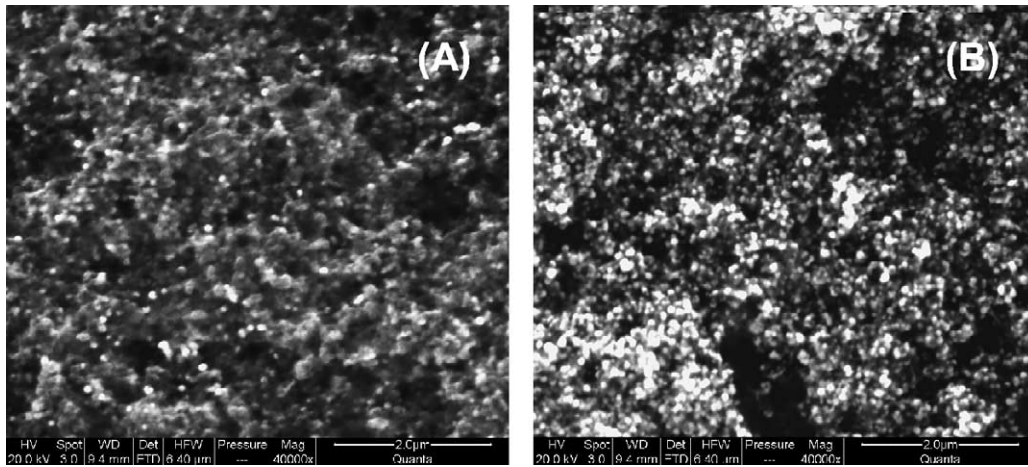
Fig. 12. SEM images of pulse electrodeposited electrode with different charge densities: (A) 6; (B) 13 C/cm^2.

platinum was estimated for each charge density used to deposit platinum on carbon. The platinum loading was measured using ICP-AES. The effective surface area and Pt loading as a function of charge density are presented in Fig. 11. As shown in this figure, the Pt loading increases from 0.17 to 0.92 mg/cm^2 with the increase in the total charge. These results are in agreement with the SEM images shown in Fig. 12. The white spots in Fig. 12, corresponding to platinum deposit increase in number and cover the entire surface of the carbon electrode when the charge density is increased. The active surface area shows a maximum of approximately 13 C/cm^2. The results can be explained by taking into account the fact that the carbon surface area is insufficient to accommodate any new nucleation at high total charge densities, which results in deposition of large particle sizes of the catalyst. The estimated specific active surface decreased from 33 to 19 m^2/g when the charge den-

sity was increased above 13 C/cm^2. The other possible explanation for the observed decrease in MEA performance is the increase of the thickness of the catalyst layer when the Pt loading was increased. When the deposition time increases, the amount of platinum deposited inside the electrode also increases thus, increasing the thickness of the catalyst layer.

Both experimental and modeling studies of membrane electrodes indicate that active layers thicker than 10 μm result in low catalyst utilization due to transport limitations of dissolved oxygen and protons in the ionomer [22]. To estimate the thickness of the catalyst, a Pt line scan in the cross-section of MEA was performed using EPMA. Fig. 13 compares the Pt line scan image in the cross-section of two MEAs constructed with different Pt loadings, namely 8 and 20 C/cm^2. According to this analysis, the Pt content in the catalyst layer in both cases shows the highest level at the surface of electrode and decays with increasing distance from
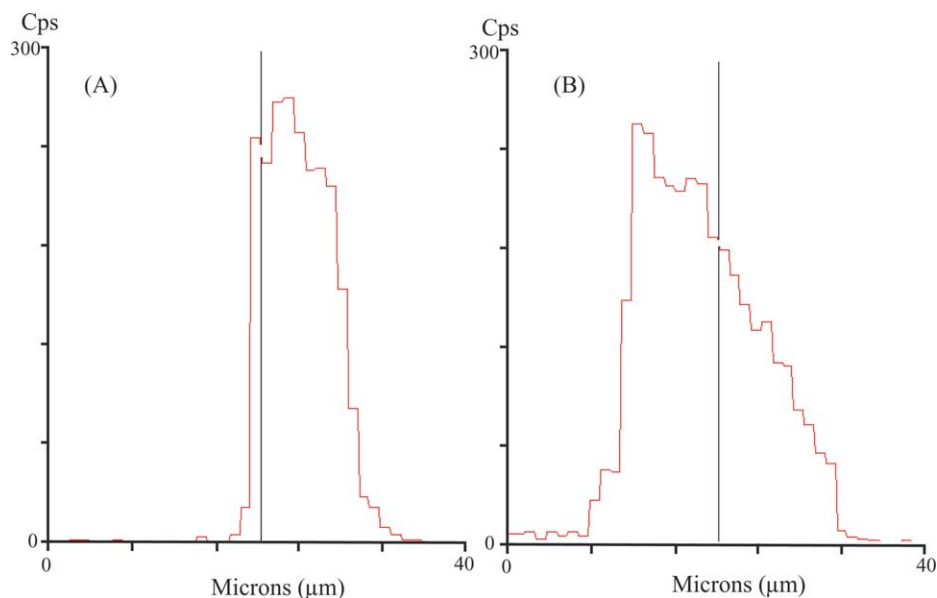

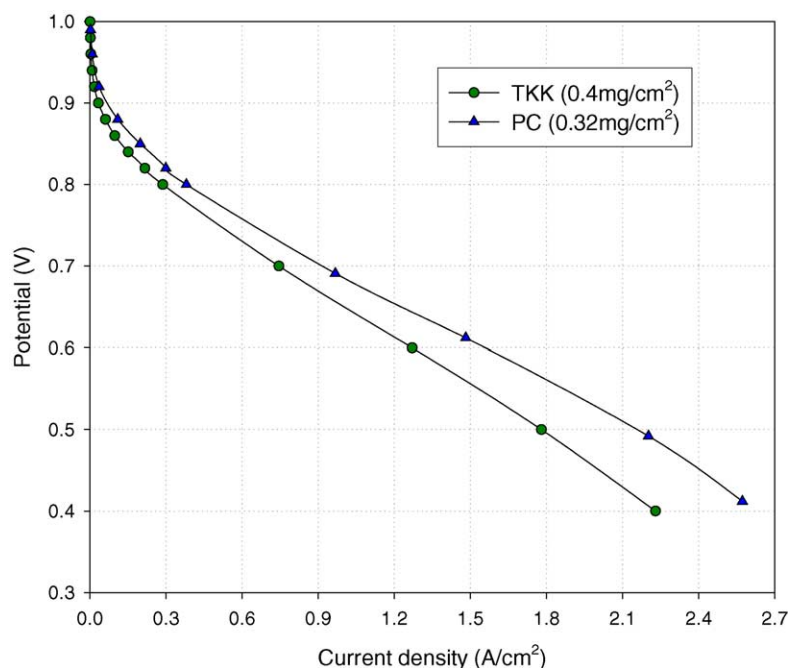Fig. 13. Comparison of Pt line scan image in the cross-section of the MEA between: (A) 8 and; (B) 20 C/cm^2.

Fig. 14. Comparison of MEA performance between pulse electrodeposited electrode and TKK electrode, H_2/O_2, 75 °C, 1 atm.

the membrane to the GDL. This is a typical phenomenon observed in the pulse electrodeposition method, since the electrodeposition is controlled by the diffusion of electrolytes in the porous electrode. When comparing the thickness of the catalyst layer, a much thicker layer is detected in the electrode prepared at higher total charge density. Fig. 14 shows the comparison of performance between the pulse electrodeposited electrode and one prepared by using TKK Pt/C powder (46 wt.%). The TKK electrode was prepared by spraying a mixture of TKK Pt/C and Nafion solution onto the E-TEK gas diffusion layer. The Pt loading of TKK electrode was 0.4 mg/cm². The result indicated that the pulse electrodeposited electrode has higher current densities at a given potential under the same operating conditions with less amount of Pt loading of 0.32 mg/cm².

4. Conclusion

The pulse electrodeposition technique has been developed as a new method of fabricating MEA. By localizing platinum on the surface of a blank carbon electrode, it is possible to decrease the thickness of the catalyst layer and increase the efficiency of platinum usage. By increasing the peak current density, the particle size of platinum was decreased and the performance of MEA increased.

The results indicate that the duration of the pulse off time plays an important role in the deposition. When the off time is too long, a longer deposition time is required to achieve the same platinum loading, while the overall overpotential of the platinum reduction decreases due to a decrease in the mass transfer overpotential. Consequently, a longer off time

results in a decrease in the nucleation rate. By varying the total charge applied for electrodeposition, the amount of Pt loading in the catalyst layer can be controlled. Any increase in charge density beyond 8 C/cm² increases the Pt loading and the thickness of the catalyst layer without increasing the catalyst efficiency. MEA performance strongly depends on the pulse plating deposition parameter, which can be optimized following the guidelines outlined in this paper.

Acknowledgements

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