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Novel PEMFC Cathodes Prepared by Pulse Deposition

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A pulse electrodeposition method of preparing thin platinum catalyst layers for polymer electrolyte membrane fuel cell (PEMFC) cathodes has been developed through surface activation of the gas diffusion layer (GDL) by a wetting agent. The performance of the catalyst layer was optimized by wetting agent type, immersion time in the wetting agent, and pulse deposition parameters such as total charge density, peak current density, and duty cycle ratio. The \( T_{on} \) time played a more important role than the \( T_{off} \) time in determining the electrode characteristics such as high concentration of Pt, smaller particle size, and loading. Pt cathodes prepared using a peak current density of 400 mA/cm\(^2\) with a duty cycle of 10.7% and total charge density of 6 C/cm\(^2\) resulted in a thin platinum catalyst layer (1.92 \( \mu \)m) and uniformly distributed platinum nanoparticles (3–4 nm) on the GDL surface. Novel cathodes with Pt loading of 0.33 mg/cm\(^2\) prepared in the present study exhibited 746 mA/cm\(^2\) at 0.7 V.

The polymer electrolyte membrane fuel cell (PEMFC) offers many advantages in portable devices and in the automotive industry. Platinum and its alloys have been employed for fuel oxidation and oxygen reduction due to their good catalytic activity and stability during fuel cell operation.\(^1\)\(^-\)\(^3\) Enormous research work has been carried out to explore the possibility to minimize the Pt loading by reducing the particle size and by increasing the catalyst utilization.\(^4\) The fabrication of membrane electrode assemblies (MEAs) falls mainly into two approaches, namely, (i) electrocatalyst powder or powder type and (ii) in situ electrocatalyst formation or non-powder type. The former method includes a conventional method of solution precipitation which involves preparation of ink/paste with electrocatalysts, carbon powder, solvent, and binder. However, this method suffers from low platinum utilization coupled with higher production cost, Also, the ratio of Pt/C cannot be increased beyond 30–40%.\(^5\)\(^,\)\(^6\) In the latter method, the electrocatalyst is formed directly on the surface of the gas diffusion layer (GDL) or on the membrane. Hence, this method has an advantage of improved platinum utilization with the low loading of platinum, thereby reducing the cost of MEA fabrication. The formation of electrocatalysts primarily includes impregnation and deposition methods. Among these, deposition has been very attractive due to the formation of high-purity platinum and ease of control of catalyst loading. In addition, it involves simple operation during MEA fabrication and low-cost requirement without sacrificing its performance in the fuel cell. The deposition method includes physical vapor deposition, chemical vapor deposition, sputter deposition, and electrodeposition.\(^7\)\(^-\)\(^9\)

Among these deposition techniques, electrodeposition has been widely used because of its ease of operation, ease of control over the experimental conditions, and low cost requirement. Choi et al.\(^10\) studied the effect of pulse parameters on the fuel cell performance using dc and pulse electrodeposition methods. Taylor et al.\(^11\) developed a nonpowder process through an electrochemical catalysis technique in which the platinum ions are diffused through a thin Nafion layer and electrodeposited only in the regions of ionic and electronic conductivity. Antoine and Durand\(^12\) performed the deposition directly on a Nafion active layer, associating both the impregnation and in situ electrochemical reduction steps. Wei et al.\(^13\) performed direct deposition of platinum onto a Nafion-bonded carbon electrode from an aqueous solution consisting of hydrochloric acid and hexachloroplatanic acid.

The electrodeposition process includes dc deposition and pulse current (PC) deposition. Comparatively, PC deposition offers more advantages over particle size control, uniform distribution, and strong adhesion.\(^14\) PC deposition has three independent variables, namely, on time \( T_{on} \), off time \( T_{off} \), and peak current density \( i_p \). The duty cycle variable is defined as follows

\[
duty \text{ cycle} \left( \% \right) = \frac{T_{on}}{T_{on} + T_{off}} \times 100
\]

[1]

Previously, our research group described a pulse deposition process which required introduction of a new hydrophilic layer over the hydrophobic GDL using a carbon ink which was applied by tapping.\(^15\)\(^,\)\(^16\) Pulse deposition provides close contact between the submicrometer particles of platinum and the membrane. In addition, it helps to generate lower grain size and a thin catalyst layer of Pt at the membrane electrode interface. Pulse electrodeposition was performed over the hydrophilic carbon surface followed by the removal of organic additives such as glycerol and isopropanol alcohol, which introduced hydrophilic nature, by heat-treatment. Since the formation and removal of the hydrophilic layer is very difficult to scale up for industry, the present work was aimed at substituting the introduction of the new hydrophilic layer with a new surface activation process.

In the present study, an attempt was made to activate the hydrophobic carbon support using a wetting agent followed by pulse electrodeposition to prepare a thin Pt catalyst layer on the surface-activated GDL. The present approach will help in achieving the goals of cost reduction, increased platinum utilization, and uniform catalyst distribution.

**Experimental**

**Surface activation of GDL.**— Commercial GDL (LT 1400-W, E-TEK) cut to 4 × 3 cm size and 5 cm\(^2\) area was exposed by masking the edges using adhesive tape. Commercially available organic compounds with an alcohol (−OH) functional group were used as wetting agents. Prior to pulse electrodeposition, the exposed area of the GDL was activated using wetting agents for various activation times to introduce hydrophilicity only at the surface.

**Pulse electrodeposition.**— The electrodeposition of platinum was carried out on the surface-activated GDL using a platinum plating bath consisting of hexachloroplatatin acid (H\(_2\)PtCl\(_6\), 10 g/L) and HCl (60 g/L) at room temperature. Platinum-coated titanium mesh was used as the anode. A pulse generator (WSa Series, TecNu, Inc.) was used for the deposition, and pulse parameters such as total charge, peak current density, and duty cycle were varied in order to obtain thin Pt catalyst layer over the GDL surface.

**Post-treatment and MEA fabrication.**— After pulse electrodeposition, the prepared cathodes were thoroughly washed with distilled water and dried followed by heat-treatment at 300°C for 2 h in hydrogen atmosphere. After the heat-treatment, Nafion solution
(5 wt % solution from Aldrich) was sprayed on the catalyst surface to achieve a dry Nafion loading of 0.8 mg/cm². The electrode purchased from E-TEK (20 wt % Pt/C, 0.2 mg/cm²) was used as the anode with a dry Nafion loading of 1.2 mg/cm². Nafion 112 membrane was used as the electrolyte. The anode, electrolyte membrane, and pulse deposited cathode were bonded to form MEA by hot pressing at 130°C for 3 min at 140 atm pressure. The MEA was then tested in the fuel cell test station (Fuel Cell Technologies) under ambient pressure with 1.5:2 stoics of H₂ and O₂.

**Characterization of the electrode.**—The hydrophilic nature of the GDLs before and after platinum deposition was characterized by surface contact-angle measurement (SCAM) using a sessile-drop method. Measurements were performed using a Ramé-Hart contact angle standard goniometer, provided with DROP image standard software. The particle size of the platinum electrocatalyst was determined by transmission electron microscopy (Hitachi, model H-8000). Scanning electron microscopy (SEM) and backscattered SEM (FEI Quanta 200) were used to observe the surface morphology of the electrode and to measure the thickness of the electrocatalyst layer. The platinum particle size was measured by transmission electron microscopy (TEM, Hitachi H-8000). The Pt plated carbon particles were scrapped from the GDL and dispersed in ethanol. The amount of platinum electrodeposited on the GDL was estimated by using atomic absorption spectroscopy (AAS, Perkin Elmer 3300), and it was compared with weight difference by weighing the GDL before and after platinum deposition. Electron microprobe analysis (EMPA, Cameca Instrument SX50) was used to observe the distribution of Pt at the membrane electrode interface.

**Results and Discussion**

*Effect of wetting agents on fuel cell performance.*—Because the commercial GDL is essentially hydrophobic in nature due to the presence of Teflon, it has very low affinity for high-polar solvents such as water. Therefore, during electrodeposition, Pt ions present in the aqueous electrolyte do not have sufficient contact with the carbon particles present in the hydrophobic GDL surface. Hence, it is necessary to make the GDL surface hydrophilic to obtain a desired Pt particle size without any agglomerates. Once the GDL surface becomes hydrophilic, the plating bath with Pt ions can penetrate into the interior of the porous carbon layer, leading to a more uniform distribution throughout the carbon particles. During electrodeposition, the thickness of the catalyst layer is controlled by the electrolyte penetration into the porous carbon layer of the GDL. This phenomenon depends on the hydrophilicity and surface energy of the GDL. Thus, the optimum hydrophilic property of the GDL would lead to a desired Pt particle size while reducing the catalyst layer thickness. In order to introduce the hydrophilic character on the GDL surface, in the present study, three different kinds of the wetting agents were used and their physical properties are shown in Table I. Figure 1 compares the polarization curves of MEAs prepared using cathodes made by applying different types of wetting agents. The Pt pulse electrodeposition on the GDL treated with different wetting agents was performed under the following conditions: (i) peak current density = 400 mA/cm², (ii) duty cycle = 2.91%, (iii) total charge density = 6 C/cm². As shown in the figure, wetting agents 2 and 3 exhibited 0.36 and 0.15 A/cm² at 0.7 V, respectively, and wetting agent 1 delivered the highest current density of 0.63 A/cm² at 0.7 V. This indicates that the fuel cell performance of pulse-deposited Pt catalyst is greatly influenced by the properties of the wetting agents.

**Contact angle measurement.**—The contact angle of water with (i) as-received, (ii) activated, and (iii) Pt-deposited GDL were measured and given in Table II. The GDL is made of high-surface-area carbon particles together with Teflon which is used as a binder and provides a hydrophobic nature to the GDL. The contact angle of water with the as-received GDL was measured to be 142.48°, which indicates high hydrophobicity that is needed during fuel cell operation. The GDL surface was made hydrophilic with contact angles 26.33° and 42.81°, respectively, after activation with wetting agents 1 and 2, while wetting agent 3 did not introduce enough hydrophilic character (θ = 119.56°). After pulse deposition, the GDL attained its hydrophobic nature back when using wetting agents 1 and 2, as evidenced from the higher contact angles of 127.63° and 128.47°, respectively. This confirms that after pulse deposition, the wetting agent has been removed completely from the GDL surface to make it hydrophobic in nature, which is necessary during fuel cell operation.

Figure 2 shows the backscattered electron microscopic images of the cross section of MEA consisting of an E-TEK anode and pulse-deposited cathode prepared using different wetting agents. The thickness of the Pt catalyst layer formed is similar when using wetting agents 1 and 2, whereas wetting agent 3 does not provide a sufficient platinum catalyst layer on the GDL surface. The AAS analysis showed ~0.1 mg/cm² Pt loading in the case of wetting

**Table I. Physical properties of different wetting agents.**

<table>
<thead>
<tr>
<th>Wetting agent</th>
<th>Boiling point (°C)</th>
<th>Surface tension (dynes/cm²)</th>
<th>Solubility (g/100 g H₂O)</th>
<th>Dipole moment (D)</th>
<th>Sp. gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>82.5</td>
<td>23.78</td>
<td>∞</td>
<td>1.66</td>
<td>0.786</td>
</tr>
<tr>
<td>2</td>
<td>64.5</td>
<td>22.65</td>
<td>∞</td>
<td>2.87</td>
<td>0.800</td>
</tr>
<tr>
<td>3</td>
<td>195</td>
<td>25.75</td>
<td>0.05</td>
<td>2.88</td>
<td>0.830</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td>73</td>
<td>—</td>
<td>1.85</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table II. Results of water contact angle measurement.**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received GDL</td>
<td>142.48</td>
</tr>
<tr>
<td>Activated GDL</td>
<td></td>
</tr>
<tr>
<td>Wetting agent 1</td>
<td>26.33</td>
</tr>
<tr>
<td>Wetting agent 2</td>
<td>42.81</td>
</tr>
<tr>
<td>Wetting agent 3</td>
<td>119.56</td>
</tr>
<tr>
<td>Pulse-deposited</td>
<td></td>
</tr>
<tr>
<td>electrode</td>
<td></td>
</tr>
<tr>
<td>Wetting agent 1</td>
<td>127.63</td>
</tr>
<tr>
<td>Wetting agent 2</td>
<td>116.40</td>
</tr>
<tr>
<td>Wetting agent 3</td>
<td>118.62</td>
</tr>
</tbody>
</table>
agent 3 and almost identical loading for wetting agents 1 and 2 (0.33 and 0.32 mg/cm², respectively). The low platinum amount deposited while using wetting agent 3 can be related to its solubility in water. As shown in Table I, wetting agent 3 exhibits high surface tension and low solubility in water so that it may not have introduced adequate hydrophilic nature on the GDL surface. The surface tension is considered in terms of components, each due to a particular kind of intermolecular force. Such surface tension components, although not thermodynamically defined, are regarded as unique physical properties of the material.19,20 Therefore, at a water-Teflon interface, because only dispersion forces are present in Teflon, the large polar and hydrogen-bonding forces in water do not act across the interface to affect the interfacial tension directly.20 The wetting agents or surfactants absorb preferentially on the surface of a water droplet and reduce its surface energy. Then the water droplet can spread out and wet the GDL. As can be seen from Table I, wetting agents 1 and 2 have lower surface tension when compared to wet-
The high surface tension and low solubility of wetting agent 3 resulted in poor wetting of the GDL surface when compared to wetting agents 1 and 2. Even though the wetting characteristics of wetting agents 1 and 2 are similar, wetting agent 2 did not result in better fuel cell performance when compared to wetting agent 1. This can be explained as follows. When platinum was deposited with wetting agents 1 and 2, a secondary reaction, i.e., formation of hydrogen bubbles, was observed on the GDL surface. The hydrogen evolution was higher in the case of wetting agent 1 than in wetting agent 2. Also, these hydrogen bubbles were not observed with wetting agent 3 and without wetting agent. This reveals that wetting agents 1 and 2 accelerate the chemical reduction of $\text{PtCl}_6^{2-}$ to Pt, which can act as a reducing agent as well as a wetting agent. It has been reported in the literature that the size of the platinum particle is greatly influenced by the kind of wetting agent because the reduction rate of $\text{PtCl}_6^{2-}$ to Pt is affected by the type of wetting agents. Even though the platinum catalyst layer thickness is similar when employing wetting agents 1 and 2, the difference in the fuel cell performances is related to the particle size of platinum in each catalyst layer. Figure 3 exhibits the SEM images of Pt-electrodeposited electrodes: (a) no activation, (b) 10 s, (c) 30 s, and (d) 60 s.
sulted in agglomeration of platinum particles on the GDL surface. This behavior can be explained by the difference in boiling points of the wetting agents. It has been reported that the reduction of \([\text{PtCl}_6]^{2-}\) by the wetting agent with higher boiling point produces more platinum nuclei and suppresses the growth of platinum particles. Based on the results of contact angle measurement and fuel cell performance, the rest of the pulse deposition studies were carried out with wetting agent 1, which has higher boiling point than wetting agent 2, and produced uniformly distributed platinum catalyst on the GDL.

**Optimization of surface activation time.**— Figure 4 compares the polarization curves of MEAs employing cathodes prepared at different activation times in wetting agent 1. The polarization curve of the MEA with cathode prepared without surface activation is also shown in the figure for comparison. The pulse electrodeposition was carried under the following conditions: (i) peak current density = 400 mA/cm², (ii) on-time \(T_{\text{on}} = 3\) ms, (iii) off-time \(T_{\text{off}} = 100\) ms, and (iv) total charge density = 6 C/cm². As shown in the figure, the fuel cell performance was greatly improved when the wetting agent was used to activate the GDL and the fuel cell performance increased with decreasing activation time. However, no increase in performance was observed when the activation time was decreased to less than 10 s. In this study, the fuel cell performance was related to both size and distribution of Pt particles. When the immersion time was increased from 5 to 60 s, the agglomeration of Pt particles increased, resulting in a decrement of three-phase boundary which reduced the fuel cell performance. The best catalyst performance was observed for 10 s immersion time, which resulted in an optimum Pt particle size and distribution.

Figure 5 shows the SEM images of Pt-deposited electrodes prepared using as-received GDL and GDL with different surface activation agent 1. It can be seen that the platinum particles formed large agglomerates when no wetting agent was used. This is because a strong hydrophobic nature of the as-received GDL did not allow the Pt ions to penetrate into the porous structure of the carbon layer and consequently, nonuniform platinum deposition occurred on the GDL surface. In the case of surface-activated GDL with wetting agent 1, smaller platinum particles are observed at the surface with the uniform distribution. Pt deposition occurred on the GDL surface. In the case of surface-activated GDL with wetting agent 1, smaller platinum particles are observed at the surface with the uniform distribution. It appears that the chemical reduction of \([\text{PtCl}_6]^{2-}\) to Pt by the wetting agent 1 produced more platinum nuclei in the same pulse period and inhibited the growth of platinum particles. However, with increase in the surface activation time, more platinum particles were deposited on the GDL and agglomerates were formed.

Figures 6a-c show the backscattered electron microscopic images of the cross section of MEA consisting of an E-TEK anode and pulse-deposited cathode. The bright portions between the membrane and the GDL indicate the Pt catalyst layer. The thickness of the Pt catalyst layer increased with increasing surface activation time. As can be seen from the figure, the thickness of the catalyst layer increased from 5 to 12 μm when the activation time was increased from 10 to 60 s. It is envisaged that the fuel cell performance can be related to the thickness of the electrodeposited Pt catalyst layer. Generally, thicker catalyst layer results in lower catalyst utilization efficiency due to transport limitations of dissolved oxygen and protons in the ionomer. Based on the fuel cell performance and thickness measurements, the activation time of GDL with wetting agent was optimized at 10 s and followed for further studies.

**Effect of pulse parameters on fuel cell performance.**— The effect of pulse parameters on the fuel cell performance was systematically studied by varying (i) total charge density, (ii) peak current density, (iii) \(T_{\text{on}}\), and (iv) \(T_{\text{off}}\). The optimized surface activation time of 10 s with the wetting agent 1 was used for these studies.

Figure 7 shows the polarization curves of the cathodes prepared at different total charge densities. Pulse deposition was performed under the following conditions: (i) peak current density 400 mA/cm², (ii) \(T_{\text{on}} = 3\) ms, and (iii) \(T_{\text{off}} = 100\) ms. As shown in the figure, the fuel cell performance increased with increase in the total charge density from 2 to 6 C/cm². For total charge densities higher than 6 C/cm², the fuel cell performance decreased. Consequently, the platinum loading and thickness increased from

![Figure 6](image-url)
0.18 to 1.12 mg/cm$^2$ and from 3 to 4.4 μm, respectively, when the total charge density was varied from 2 to 8 C/cm$^2$ as shown in Fig. 8. It is observed that if the total charge density is low, the amount of platinum deposited is too low to catalyze the oxygen reduction reaction at the cathode. Conversely, when the total charge density is high, thick catalyst layers are obtained which result in transport limitations during fuel cell operation. Based on these results, the total charge density was optimized at 6 C/cm$^2$ and used for further studies.

The effect of peak current density on the performance of the cathode in the fuel cell was studied by keeping constant total charge (6 C) and duty cycle (2.91%). The peak current density was varied between 200 and 800 mA/cm$^2$ for the cathode preparation. Figure 9 shows the polarization curves obtained from the fuel cells, employing cathodes prepared using different peak current densities. It can be seen that the fuel cell performance increased when the peak current density was changed from 200 to 400 mA/cm$^2$. The fuel cell performance decreased for the cathode prepared at higher peak current densities. Based on the results of fuel cell performance, the peak current density was optimized to be 400 mA/cm$^2$. However, the platinum loading obtained under optimized total charge density and peak current density is still higher (0.8 mg/cm$^2$) than that in commercial electrode (0.4 mg/cm$^2$). Therefore it is necessary to prepare cathodes with reduced catalyst loading while maintaining good fuel cell performance. It has been reported that a gas-evolving electrochemical process is necessary in parallel with platinum electrodeposition for obtaining low loading and smaller particle size of platinum.24 During pulse deposition, the superficial concentration of adsorbed [PtCl$_4$]$^{2-}$ species decreases due to particle growth. At the same time, the platinum surface area on which hydrogen evolution takes place increases, and this competitive reaction becomes overwhelmingly preponderant and acts as a limiting factor on the platinum particle size and loading.22 Therefore, at high overvoltage, the rate of hydrogen evolution increases that in turn inhibits the secondary nucleation.25 It is realized that the deposition should be performed at higher average current density by varying $T_{on}$ or $T_{off}$ in order to increase the rate of hydrogen evolution reaction, thereby decreasing the catalyst loading and particle size.

Figure 7. Effect of total charge density on the fuel cell performance of the cathodes.

Figure 8. Variations of the Pt loading and thickness with the total charge density.

Figure 9. Effect of the peak current density on the fuel cell performance of the cathodes.

Figure 10. Effect of the $T_{on}$ time on the fuel cell performance of the cathodes.
The effect of \( T_{\text{on}} \) time on the fuel cell performance of the cathodes was studied by varying the \( T_{\text{on}} \) time from 3 to 24 ms while keeping constant \( T_{\text{off}} \) time (100 ms), peak current density (400 mA/cm\(^2\)), and total charge (6 C) for the electrode preparation. Figure 10 shows the polarization curves of different cathodes prepared at different \( T_{\text{on}} \) times. It is seen that the fuel cell performance at 0.7 V increased from 0.565 to 0.737 A/cm\(^2\) when \( T_{\text{on}} \) time was increased from 3 to 12 ms, and the electrode prepared at \( T_{\text{on}} = 6 \) ms showed higher current density (0.74 A/cm\(^2\)) at 0.7 V than other electrodes. However, if the fuel cell performance is normalized with respect to the Pt loading, then the pulse deposition with \( T_{\text{on}} = 12 \) ms leads to the best fuel cell performance over the entire operating potential ranges. However, the fuel cell performance decreased when the \( T_{\text{on}} \) time was increased beyond 12 ms due to very low Pt loading (0.20 mg/cm\(^2\)). Figure 11 presents SEM images of electrodes prepared with different \( T_{\text{on}} \) times. It is observed that the grain size and agglomeration of Pt decreased with increasing \( T_{\text{on}} \). This phenomenon indicates that at high overpotential (due to increase in \( T_{\text{on}} \)), the hydrogen evolution reaction, which becomes the main electrochemical reaction on the already-formed Pt particles, helps in the formation of smaller particles.

Similarly, the effect of \( T_{\text{off}} \) time was studied by varying the \( T_{\text{off}} \) time from 3 to 24 ms while keeping constant \( T_{\text{on}} \) time (100 ms), peak current density (400 mA/cm\(^2\)), and total charge (6 C) for the electrode preparation. Figure 12 shows the polarization curves of different cathodes prepared at different \( T_{\text{off}} \) times. It is seen that the fuel cell performance at 0.7 V increased from 0.565 to 0.737 A/cm\(^2\) when \( T_{\text{off}} \) time was increased from 3 to 12 ms, and the electrode prepared at \( T_{\text{off}} = 6 \) ms showed higher current density (0.74 A/cm\(^2\)) at 0.7 V than other electrodes. However, if the fuel cell performance is normalized with respect to the Pt loading, then the pulse deposition with \( T_{\text{off}} = 12 \) ms leads to the best fuel cell performance over the entire operating potential ranges. However, the fuel cell performance decreased when the \( T_{\text{off}} \) time was increased beyond 12 ms due to very low Pt loading (0.20 mg/cm\(^2\)). Figure 11 presents SEM images of electrodes prepared with different \( T_{\text{off}} \) times. It is observed that the grain size and agglomeration of Pt decreased with increasing \( T_{\text{off}} \). This phenomenon indicates that at high overpotential (due to increase in \( T_{\text{off}} \)), the hydrogen evolution reaction, which becomes the main electrochemical reaction on the already-formed Pt particles, helps in the formation of smaller particles.

![Figure 11. SEM images of pulse-deposited Pt electrodes prepared at different \( T_{\text{on}} \) times: (a) 3, (b) 6, (c) 12, and (d) 24 ms.](image)

![Figure 12. Effect of \( T_{\text{off}} \) on the fuel cell performance of the cathodes.](image)
time from 100 to 12.5 ms while keeping other pulse parameters constant. That is, total charge density 6 C/cm², \( T_{\text{on}} = 3 \) ms, and peak current density 400 mA/cm² was kept constant during the electrode preparation. Figure 12 shows the polarization curves of the cathodes prepared at different \( T_{\text{off}} \) time. Table III summarizes the fuel cell performance and properties of the pulse deposited cathodes prepared at different \( T_{\text{off}} \) time. It is seen that by varying the \( T_{\text{off}} \) time, the fuel cell performance of the cathode was altered and maximum fuel cell performance was obtained for the cathode prepared at 25 ms \( T_{\text{off}} \) time (10.7% duty cycle) with a catalyst layer thickness of 1.92 \( \mu \)m. The platinum loading of this electrode was determined to be 0.33 mg/cm², which was considerably lower than that in commercial electrode (0.40 mg/cm²). Figure 13 represents backscattered electron images of the cross section of the MEA consisting of

<table>
<thead>
<tr>
<th>( T_{\text{off}} ) (ms)</th>
<th>Current density at 0.7 V (A/cm²)</th>
<th>Thickness of catalyst layer (( \mu )m)</th>
<th>Volumetric current density at 0.7 V (A/cm³)</th>
<th>Pt loading (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.613</td>
<td>3.56</td>
<td>1721.91</td>
<td>0.72</td>
</tr>
<tr>
<td>50</td>
<td>0.374</td>
<td>3.49</td>
<td>1071.63</td>
<td>0.61</td>
</tr>
<tr>
<td>25</td>
<td>0.746</td>
<td>1.92</td>
<td>3885.41</td>
<td>0.33</td>
</tr>
<tr>
<td>12.5</td>
<td>0.486</td>
<td>1.69</td>
<td>2875.73</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**Figure 13.** Backscattered electron images of the cross section of different MEAs. The MEAs were fabricated using cathodes prepared at different \( T_{\text{off}} \) times: (a) 100, (b) 50, (c) 25, and (d) 12.5 ms.
E-TEK anode and pulse-deposited cathode prepared with different $T_{\text{on}}$ times. As shown in the figure, the thickness of the Pt catalyst layer increased with increase in the $T_{\text{off}}$ time due to increase in the platinum loading. The increase in platinum catalyst layer thickness can be explained as follows. During longer $T_{\text{off}}$ time, desorption of hydrogen from the existing Pt particle activates the growth centers and results in grain growth, which leads to increased catalyst layer thickness. In addition, platinum adatoms at longer $T_{\text{off}}$ time have more time to migrate over the already-deposited platinum particles and enhance the grain growth process. Similar grain growth behavior has been reported in the literature for pulse deposition of Zn.27

The Pt concentration profiles obtained from electron probe microanalysis (EPMA) across the MEA are shown in Fig. 14. Platinum cathodes prepared at different $T_{\text{off}}$ times were used for the MEA fabrication. As can be seen from the Pt line scan, the pulse-deposited cathodes exhibited high concentration at the membrane electrode interface within $\pm 2 \mu$m thick catalyst layer, while the E-TEK electrode showed less Pt concentration distributed over $\pm 12 \mu$m thick catalyst layer. It is to be mentioned here that high concentration of platinum catalyst particles at the membrane/electrode interface results in high catalyst utilization. Figure 15 shows the TEM image of the catalyst prepared using pulse parameters optimized in the present study. The dark spots indicate Pt particles and the gray background is the carbon support. It is seen that the Pt particles of 3–4 nm are uniformly distributed over the carbon support. TEM study confirmed that nanosized Pt particles can be obtained by the surface activating the commercial GDL with wetting agent followed by pulse electrodeposition.

Table IV summarizes the fuel cell performance and properties of the pulse-deposited cathodes prepared using selected $T_{\text{on}}$ and $T_{\text{off}}$ times. As can be seen from the table, the cathode prepared at 25 ms $T_{\text{off}}$ time showed better performance (0.746 A/cm$^2$ at 0.7 V) with lower loading of Pt (0.33 mg/cm$^2$) than the one prepared at 12 ms $T_{\text{off}}$ time (0.704 A/cm$^2$ at 0.7 V, 0.42 mg/cm$^2$). This indicates that the duration of pulse off time ($T_{\text{off}}$) plays an important role during deposition to obtain high concentration of Pt, smaller particle size, and low loading. It has been reported in the literature that $T_{\text{on}}$ and $T_{\text{off}}$ do not have the same influence on the structure of the final deposit because each system may react differently during the electrocrystallization/nucleation process.

Comparison with dc-deposited Pt catalyst.— When compared to dc deposition, pulse electrodeposition offers high cathode current density at the electrode interface due to the higher concentration of metal ions at the surface of the electrode. According to the theoretical model analysis, the limiting current density of pulse electrodeposition is always higher than that of dc electrodeposition. Moreover, the pulse electrodeposition can be carried out at higher current density by varying the pulse period or duty cycle to obtain a finer crystal grain size, which further enhances the fuel cell performance.15,16 Figure 16 shows the polarization curves of the PEMFC prepared by dc and pulse electrodeposition methods. The pulse-electrodeposited electrode was prepared under the optimized conditions mentioned in the previous section. For dc electrodeposition, constant current density of 42.86 mA/cm$^2$ was applied continuously. This is the average current density that was calculated based on the peak current density used for the optimized pulse conditions mentioned above. Total charge density was fixed at 6 C/cm$^2$ in both the cases. As seen in the figure, both dc and pulse-deposited electrodes exhibited $-0.75$ A/cm$^2$ at 0.7 V with only a small difference in performance. In our previous study, the former showed much better fuel cell performance than the latter due to the difference in the Pt particle size. However, in the present study, the observed small variation in the fuel cell performance between the PC and dc deposited electrodes can be attributed to similar Pt particle size, as shown in Fig. 17. As can be seen from the figure, the grain size and distribution of the Pt for both PC and dc deposition techniques are similar. TEM results (not shown) also revealed that the particle size in both cases was in the range from 3 to 4 nm. As mentioned earlier, the chemical reduction of $[\text{PtCl}_6]^{2-}$ to Pt by the wetting agent produces more platinum nuclei in the same pulse period and inhibits the growth of platinum particles.21 Because a wetting agent was used for the deposition process in both cases, it can be concluded that the chemical reduction of $[\text{PtCl}_6]^{2-}$ to Pt by the wetting agent resulted in similar particle size. The open-circuit voltage of all the fuel cells tested in the present investigation was in the range between 0.95 and...

![Figure 14. Pt profiles along the cross section of the MEAs. The MEAs were fabricated with cathodes prepared at different $T_{\text{off}}$ times.](image)

![Figure 15. TEM image of Pt supported on carbon prepared by pulse electrodeposition (magnification $\times 300,000$).](image)
However, the exchange current density values calculated for different gas diffusion electrodes by using the Tafel equation indicated only a small difference in the current density values among the electrodes.

Comparison studies with commercial Pt catalyst.— The fuel cell performance and the electrode properties of the pulse-deposited electrodes (USC) and electrodes prepared using commercial Pt catalysts (E-TEK) are compared in Table V. The pulse deposition was performed under the following conditions: peak current density 400 mA/cm$^2$, $T_{\text{on}} = 3$ ms, $T_{\text{off}} = 25$ ms, and total charge density 6 C/cm$^2$. Significant difference in the performance of the electrodes was observed. That is, the pulse-electrodeposited electrode exhibited 0.746 A/cm$^2$ at 0.7 V, whereas the E-TEK electrode delivered a current density of 0.62 A/cm$^2$ at 0.7 V. The volumetric current density is also higher for the USC electrode when compared to the E-TEK electrode (Table V). An important feature is that the pulse-deposited electrode has less platinum loading (0.33 mg/cm$^2$) and very thin catalyst layer (1.92 $\mu$m) when compared to the E-TEK electrode, which has 0.4 mg/cm$^2$ loading and six times higher catalyst layer thickness (~12 $\mu$m). According to literature, the best fuel cell performance has been achieved with catalyst thicknesses less than 10 $\mu$m. In our study, the observed difference in fuel cell performance when compared to commercial E-TEK catalyst results from thinner catalyst layers and better Pt nanoparticle distribution due to pulse deposition.

**Figure 16.** Fuel cell performance of PC- and dc-electrodeposited electrodes.

**Figure 17.** SEM images of Pt-electrodeposited electrodes: (a) 42.8 mA/cm$^2$ of dc electrodeposition, (b) 400 mA/cm$^2$ of peak current density, 3 ms $T_{\text{on}}$ and 25 ms $T_{\text{off}}$. The total charge density is fixed at 6 C/cm$^2$ in both cases.
Table V. Comparison of fuel cell performance and electrode properties of commercial and pulse-deposited electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Current density at 0.7 V (A/cm²)</th>
<th>Thickness of catalyst layer (μm)</th>
<th>Volumetric current density at 0.7 V (A/cm³)</th>
<th>Pt loading (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USC</td>
<td>0.746</td>
<td>1.92</td>
<td>3885.41</td>
<td>0.33</td>
</tr>
<tr>
<td>E-TEK</td>
<td>0.620</td>
<td>12</td>
<td>413.33–516.66</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Conclusion

An attempt was made to introduce a hydrophilic property on the GDL surface by using commercially available organic liquids as wetting agents. By varying wetting agent type, immersion time, and pulse parameters, it was possible to decrease the catalyst layer thickness, Pt loading, and maintain higher Pt concentration at the membrane-electrode interface. The presence of a wetting agent controlled the initial platinum nuclei size and distribution on the GDL. The $T_{\text{cell}}$ time played a more important role than the $T_{\text{on}}$ time in determining important electrode characteristics such as high concentration of Pt, smaller particle size, and loading. Similar fuel cell performance was observed while using PC- and de-deposited electrodes due to the presence of similar particle size. The optimized pulse-deposited cathode with low Pt loading (0.33 mg/cm²) and low catalyst layer thickness (1.92 μm) resulted in better fuel cell performance of 746 mA/cm² at 0.7 V than commercial E-TEK electrode.

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