Development of platinum supported on single-walled carbon nanotubes by deposition-precipitation for microbial fuel cells

P. Pusomjit, O. Chailapakul, H. Y. Ng and N. Thepsuparungsikul

ABSTRACT

Microbial fuel cells (MFCs) are an ecologically friendly technology that can recover electricity and simultaneously treat wastewater. Among all the influential factors, cathode material and catalyst play a crucial role in electricity production and oxygen reduction. In this study, Pt nanocatalysts deposited on single-walled carbon nanotubes (Pt/SWCNTs) were synthesized by the deposition-precipitation (DP) method under optimal conditions. The results show that DP might be a promising method for the preparation of Pt/SWCNTs due to its simple, cost-effective and time-saving procedure, in addition to being highly efficient at creating small Pt particles (0.9 nm) that were very uniformly distributed. The synthesized Pt/SWCNTs suspension was spray-coated on to carbon cloth and then used as a cathode for MFCs. The electricity generation of MFCs equipped with a Pt/SWCNTs cathode was evaluated in terms of open circuit voltage (0.6954 V), internal resistance (63.3 Ωm²) and maximum power density (2,022 mW/m²). The chemical oxygen demand removal, biological oxygen demand removal, total dissolved solids removal, total suspended solids removal and silver recovery was satisfactory at 84.5%, 74.0%, 45.7%, 60.0% and 99.0%, respectively. Therefore, Pt/SWCNTs from the DP method was identified as a potential candidate to replace commercial Pt-carbon cloth for MFC cathodes.

Key words | cathode, deposition-precipitation, microbial fuel cell, platinum, single-walled carbon nanotubes

INTRODUCTION

Microbial fuel cells (MFCs) are an ecologically friendly method that can treat wastewater and simultaneously recover electrical energy directly from a variety of organic matter. MFCs use bacteria in wastewater as catalysts to directly convert organic matter to carbon dioxide, water and energy (Logan et al. 2006). Another potential application of MFCs is to remove and recover metals from wastewater. At the cathode, the metal is reduced to its metallic form and deposited on the cathode surface. At the anode, electrical energy can be obtained from the oxidation of organic matter (Ter Heijne et al. 2010; Tao et al. 2012).

Among the factors that influence MFC performance, both cathode and catalyst play integral roles in electricity generation, organic removal efficiency and metal removal efficiency. At the cathode, oxygen is the most suitable electron acceptor. However, the oxygen reduction reaction (ORR) is slow, leading to high reduction overpotential. Therefore, a catalyst is generally required to decrease the activation energy of ORR (Rismani-Yazdi et al. 2008). It is known that a catalyst support affects the stability and performance of the catalyst due to the interaction between the catalyst and support (Shen et al. 2008). The specific requirements for catalyst supports include high specific surface area, high conductivity, corrosion resistance and the capability to create anchoring sites with the catalyst (Timur et al. 2007). At present, carbon nanotubes (CNTs) are attractive candidates as both catalyst support and cathode material due to their excellent structural, physical and chemical properties (Qiao et al. 2007; Timur et al. 2007).

Platinum (Pt) is currently the most popular metal catalyst for ORR in MFCs due to its excellent catalytic ability. However, the commercial feasibility of Pt is limited because of its high cost and possible toxicity (He & Angenent 2006). Therefore, the Pt load could be reduced or alternative
catalysts might be investigated. To reduce the Pt load while still maintaining high catalytic ability, a suitable catalyst loading method and a catalyst support with a high specific surface area are the important factors. Various decoration methods of Pt catalysts have been reported for a variety of supporting materials. However, little research has been conducted on CNT supports.

An extensive review of studies conducted on the preparation of Pt decorated CNTs as the cathode material for MFCs is summarized in Table 1. The decoration methods include chemical reduction (Yang et al. 2011; Ghasemi et al. 2013; Halakoo et al. 2015) and electrodeposition (Xie et al. 2011; Yen et al. 2015; Quan et al. 2015). However, the electrodeposition method requires specific and expensive equipment. Also, the chemical reduction method from some studies provided large Pt catalysts with low uniformity on the supports. Alternatively, the deposition-precipitation (DP) method is characterized by the precipitation of the active phase precursor on the surface of the supports, followed by crystallographic deposition. Typically, DP is a simple, cost-effective, time-saving and efficient decoration method for Au on SiO2 or TiO2 supports (Phonthammachai et al. 2008; Sandoval et al. 2011; Ruiz et al. 2013), but it has scarcely been used to prepare supported Pt catalysts. To date, no known research studies on DP for Pt on CNT supports have been reported. Therefore, the decoration of Pt catalysts on CNT supports by DP needs to be further investigated in order to obtain small particles of Pt catalyst that are very uniformly dispersed, resulting in improvement of catalytic ability.

In this study, Pt nanocatalysts supported on single-walled CNTs (Pt/SWCNTs) were synthesized by DP. The properties of synthesized Pt/SWCNTs were evaluated based on morphology, composition and size distribution. The Pt/SWCNTs were sprayed onto carbon cloth and used as a cathode. The performance of MFCs equipped with Pt/SWCNTs spray-coated onto carbon cloth was evaluated in terms of electricity generation, organic removal efficiency and metal recovery. In addition, the performance of these MFCs, using Pt/SWCNTs spray-coated onto carbon cloth as cathodes, was compared with SWCNTs spray-coated onto carbon cloth, commercial Pt-carbon cloth and plain carbon cloth. In addition, PTFE membrane replaced Nafion membrane and used as the electrolyte for reasons of cost.

**MATERIALS AND METHODS**

**Preparation of Pt/SWCNTs-COOH**

Pt catalysts on SWCNTs-COOH were prepared by DP. Single-walled CNTs with carboxyl functional groups (SWCNTs-COOH; Carbon Solutions Inc., USA) were ultrasonically dispersed in deionized water for 60 min. The SWCNTs-COOH suspension was mixed with 1.5 mM chloroplatinic acid hexahydrate solution (H2PtCl6·6H2O; Sigma-Aldrich, USA), followed by adjustment of pH to 7. The suspension was then vigorously stirred at a reaction temperature of 80 °C for 60 min to produce the Pt/SWCNTs-COOH.

**Cathode preparation**

The synthesized Pt/SWCNTs-COOH and SWCNTs-COOH were coated onto a carbon cloth (non-wet-proofed, type B, E-TEK, USA). For this purpose, 1% (v/v) Nafion 117 (Sigma-Aldrich, USA) was added to the CNTs suspension and ultrasonically dispersed for 60 min. Then, the suspension was spray-coated onto carbon cloth at a Pt loading of 0.2 mg/cm² by air-brush and dried on a hotplate. In addition, carbon cloth (non-wet proofed, type B, E-TEK, USA) and commercial Pt-carbon cloth (0.2 mg/cm², Fuel Cells Etc, USA) were used for comparison with SWCNTs-COOH-based cathode.

### Table 1 | Literature review of MFCs equipped with Pt/CNT-based cathodes from various decoration methods

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>Supporting material</th>
<th>Catalyst</th>
<th>Decoration method</th>
<th>Pmax (mW/m²)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon paper</td>
<td>CNTs</td>
<td>Pt</td>
<td>Chemical reduction</td>
<td>147</td>
<td>Halakoo et al. (2015)</td>
</tr>
<tr>
<td>Carbon paper</td>
<td>MWCNTs</td>
<td>Pt-Pd</td>
<td>Electrodeposition</td>
<td>762</td>
<td>Quan et al. (2015)</td>
</tr>
<tr>
<td>Carbon paper</td>
<td>CNTs</td>
<td>Pt</td>
<td>Chemical reduction</td>
<td>169</td>
<td>Ghasemi et al. (2015)</td>
</tr>
<tr>
<td>Carbon cloth</td>
<td>MWCNTs</td>
<td>Pt</td>
<td>Electrodeposition</td>
<td>59</td>
<td>Yen et al. (2015)</td>
</tr>
<tr>
<td>Carbon paper</td>
<td>Polyamidoamine-DENs</td>
<td>Pt</td>
<td>Chemical reduction</td>
<td>630</td>
<td>Yang et al. (2011)</td>
</tr>
<tr>
<td>Textile</td>
<td>SWCNTs</td>
<td>Pt</td>
<td>Electrodeposition</td>
<td>837</td>
<td>Xie et al. (2011)</td>
</tr>
<tr>
<td>Carbon cloth</td>
<td>SWCNTs-COOH</td>
<td>Pt</td>
<td>Deposition-precipitation</td>
<td>In this work</td>
<td></td>
</tr>
</tbody>
</table>
Cathode characterization

The morphology and size distribution of the synthesized Pt/SWCNTs-COOH were characterized by a transmission electron microscope (TEM, JEOL, JEM-2100, Japan) operating at 200 kV. The samples were prepared by placing a drop of suspension onto a formvar carbon-coated copper grid (FCF300-Cu, Electron Microscopy Sciences, USA) and dried at room temperature.

The crystalline structures of the synthesized Pt/SWCNTs-COOH were measured with an X-ray powder diffractometer (XRD, XRD-6000, Shimadzu, Japan). Cu Kα-ray operating at 40 kV and 50 mA was used as the X-ray source. The reflections in powder XRD were obtained in the 2θ range between 10–85°.

The structure and composition of the cathodes were determined by a field emission scanning electron microscope-energy dispersive X-ray spectroscope (FESEM-EDX, JEOL, JSM7610F, Japan). The samples were mounted onto an aluminum stub prior to measurement.

MFC construction and operation

H-shaped dual-chamber MFC reactors, each with an electrode chamber holding a volume of 600 mL were constructed. The chambers were separated with polytetrafluoroethylene (PTFE) membrane (0.45-μm pore-sized, Sartorius Stedim Biotech, Germany). In this study, the PTFE membrane replaced Nafton membrane, which is generally used as proton exchange membrane (PEM). From an economic point of view, PTFE membrane was found to be a cost-effective (US$4.03/reactor), which was 4.41 times lower than Nafton (US$17.79/reactor). The apparent anode and cathode surface areas were similar at 25 cm² each. Nichrome wires were used to connect each electrode to the external circuit. Four different types of MFC reactors were constructed (Table 2).

Canteen wastewater collected from the septic tank of the Srakaew canteen at Silpakorn University, Thailand, was used as the inoculum and substrate. The canteen wastewater had a chemical oxygen demand (COD) ranging from 720–1,200 mg O₂/L, biological oxygen demand (BOD) ranging from 290–390 mg O₂/L, total dissolved solids (TDS) ranging from 1,200–1,600 mg/L and total suspended solids (TSS) ranging from 50–120 mg/L. The cathode chamber was filled with a mixture of NaCl and NaHCO₃ and aerated to provide O₂ as the electron acceptor. For the metal recovery study, 100 ppm of AgNO₃ solution (Chemisches Laboratorium, Germany) was placed in the cathode chamber and used as the electron acceptor. N₂ gas was used to purge the chamber for 15 min. All the reactors were operated in batch reactor mode at room temperature (30 ± 2 °C).

Analysis of MFC performances

The MFC reactors were evaluated including electricity production, organic removal efficiency and metal recovery. The voltage (V) of the MFC was continuously measured every 30 min by a data logger with a computerized data acquisition system (GL220, Graphtec, Japan). The power density (P, mW/m²) was calculated from P = IV/A, where I is the current, V is the voltage and A is the surface area of cathode. Polarization curves were drawn by changing the external resistance from 900,000 to 10 Ω and then used to determine the open circuit voltage (OCV), the internal resistance (Rint) and the maximum power density (Pmax) (Logan et al. 2006).

The COD and BOD concentrations of the influents and effluents were measured according to the American Public Health Association’s Standard Methods (APHA 2012) to calculate %COD removal and %BOD removal. TDS and TSS concentrations of the influents and effluents were measured by gravimetric analysis according to the American Society for Testing and Materials’ Standard Test Methods (ASTM 2013) to calculate %TDS removal and %TSS removal. The silver ion concentrations before and after operation of MFCs were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent, 710, USA) at 328.068 nm to calculate silver recovery.

RESULTS AND DISCUSSION

Catalyst characterization

Morphology and size distribution of catalyst

As shown in Figure 1(a), the SWCNTs-COOH dispersed in deionized water (DI) water presented a well-defined tube

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Detailed list of electrodes for each MFC set-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Cathode</td>
</tr>
<tr>
<td>MFC-1</td>
<td>Carbon cloth</td>
</tr>
<tr>
<td>MFC-2</td>
<td>Carbon cloth</td>
</tr>
<tr>
<td>MFC-3</td>
<td>SWCNTs-COOH on carbon cloth</td>
</tr>
<tr>
<td>MFC-4</td>
<td>PT/SWCNTs-COOH on carbon cloth</td>
</tr>
<tr>
<td>MFC-5</td>
<td>Carbon cloth</td>
</tr>
<tr>
<td>MFC-6</td>
<td>Commercial Pt-carbon cloth</td>
</tr>
</tbody>
</table>
structure with outer diameter ranging from 5 to 15 nm. In order to improve catalytic ability, Pt nanocatalysts were prepared by the DP method. The spherical-shaped Pt nanocatalysts on the SWCNT surfaces are shown in Figure 1(b). At optimal DP conditions, Pt nanocatalysts are small in size and uniformly distributed on the SWCNTs-COOH. The particle size of Pt nanocatalysts was in the range of 0.4 to 1.6 nm and demonstrated the highest distribution at 0.9 nm. It is worth noting that this was the first study which demonstrates the achievement of small and highly active Pt nanocatalysts on SWCNTs-COOH using the simple, cost-effective and time-saving DP method. In addition, the average size of Pt nanocatalysts (0.9 nm) in this study was competitive when compared to those from chemical reduction (Yang et al. 2011; Ghasemi et al. 2011; Halakoo et al. 2015) and electrodeposition (Xie et al. 2011; Yen et al. 2013; Quan et al. 2015).

**Cathode characterization**

The surface morphological images of all types of cathodes, as observed by FESEM, are shown in Figure 4. The smooth and straight fibres from plain carbon cloth are shown in Figure 4(a). Both CNT-based cathodes clearly show a uniform distribution of highly entangled three-dimensional CNT networks (Figure 4(c) and 4(d)) which might assist the deposition of nanocatalyst and serve as nanowires to support electron transfer (Wang et al. 2011; Zhang et al. 2011). This structure might improve the transition catalytic ability due to its impact on the three-phase ORR (Lefebvre et al. 2012). In addition, the results from EDX element mappings (Figure 5) indicated that Pt from Pt/SWCNTs-COOH provided a higher distribution than that from commercial Pt-carbon cloth.

**MFC performance**

The average electrical performance of MFCs equipped with a variety of cathodes is summarized in Table 3. In
comparison to cathodes without a catalyst, cathodes with Pt catalysts displayed high electrical performance. This excellent performance could be directly related to the catalyst deposited on supporting materials which decreased the activation energy barrier and improved the kinetics of ORR at the cathode surfaces (Rismani-Yazdi et al. 2008). Among MFCs equipped with a non-catalyst cathode, the MFC with SWCNTs-COOH/carbon cloth exhibited higher OCV and $P_{\text{max}}$ (0.5022 V and 1,698 mW/m$^2$) than the MFC with carbon cloth (0.4657 V and 1,632 mW/m$^2$) (Figure 6). This could be due to the excellent conductivity, high specific surface area and three-dimensional network structure of SWCNTs-COOH, which enhanced active spaces for ORR and improved electron transfer capability (Wang et al. 2011; Thepsuparungsikul et al. 2014). MFCs equipped with cathodes coated with Pt catalysts displayed high OCV and high $P_{\text{max}}$, which is in the highest tier in MFC research. The $P_{\text{max}}$ values obtained from Pt/SWCNTs-COOH/carbon cloth (2,022 mW/m$^2$) and commercial Pt-carbon cloth (3,055 mW/m$^2$) were higher than those reported in literature (Table 1). Comparable results of OCV were obtained at $p > 0.05$ by analysis of variance (ANOVA) indicating no significant differences among cathode materials with Pt catalyst. In addition, the %RSD obtained from MFCs with different cathode materials was less than 5% ($n = 3$), demonstrating high precision in terms of MFC electrical performance. In conclusion, high catalytic ability from small and uniform dispersion of Pt nanocatalysts from DP together with excellent properties of SWCNTs-COOH resulted in improvement...
of MFC performance. From an economic point of view, Pt/SWCNTs-COOH/carbon cloth proved cost-effective, being 15% lower in cost compared to commercial Pt-carbon cloth. Therefore, Pt/SWCNTs from DP was identified as a potential candidate to replace commercial Pt-carbon cloth for MFC cathodes.

Figure 4 | FESEM images of cathodes (50,000x magnification): (a) carbon cloth; (b) commercial Pt-carbon cloth; (c) SWCNTs-COOH on carbon cloth; and (d) Pt/SWCNTs-COOH on carbon cloth.

Figure 5 | EDX element mappings of Pt from cathodes: (a) commercial Pt-carbon cloth; and (b) Pt/SWCNTs-COOH on carbon cloth.
The COD, BOD, TDS and TSS removal efficiencies are summarized in Table 4. From MFCs with all types of cathodes, COD removal efficiencies were over 80%, while BOD removal efficiencies ranged from 69.5 to 74.5%. TDS and TSS removal efficiencies ranged from 43.7 to 46.4% and from 57.1 to 68.5%, respectively. From Table 4, the %RSD of all MFCs was less than 10% (\(n = 3\)), demonstrating good precision in terms of organic removal efficiencies. Results showed that no significant differences at a 95% confidence level in organic removal efficiencies were observed regardless of the presence of Pt and types of supporting materials used at the cathode. In addition, the organic removal efficiencies of SWCNT-based cathode MFCs in this study were competitive when compared to the published literature with commercial Pt-carbon cloth cathodes (Lorenzo et al. 2010) and with CNT-based cathodes (Tsai 2010).

### Table 3 | MFC electrical performance using various cathodes

<table>
<thead>
<tr>
<th>MFC</th>
<th>OCV (V)</th>
<th>Internal resistance ((\Omega \cdot \text{m}^2))</th>
<th>Maximum power density ((\text{mW/m}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon cloth</td>
<td>0.4657 ± 0.0084</td>
<td>29.4 ± 1.1</td>
<td>1,632 ± 23</td>
</tr>
<tr>
<td>SWCNTs-COOH on carbon cloth</td>
<td>0.5022 ± 0.0097</td>
<td>43.5 ± 2.2</td>
<td>1,698 ± 27</td>
</tr>
<tr>
<td>Pt/SWCNTs-COOH on carbon cloth</td>
<td>0.6954 ± 0.0071</td>
<td>63.3 ± 2.6</td>
<td>2,022 ± 24</td>
</tr>
<tr>
<td>Commercial Pt-carbon cloth</td>
<td>0.7095 ± 0.0074</td>
<td>47.6 ± 1.4</td>
<td>3,055 ± 44</td>
</tr>
</tbody>
</table>

### Table 4 | Organic removal efficiencies and % Ag recovery achieved by MFCs using various cathodes

<table>
<thead>
<tr>
<th>MFC</th>
<th>COD removal (%)</th>
<th>BOD removal (%)</th>
<th>TDS removal (%)</th>
<th>TSS removal (%)</th>
<th>% Ag recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon cloth</td>
<td>85.9 ± 2.9</td>
<td>69.3 ± 3.9</td>
<td>43.9 ± 2.6</td>
<td>57.1 ± 2.2</td>
<td>46.0 ± 3.5</td>
</tr>
<tr>
<td>SWCNTs-COOH on carbon cloth</td>
<td>84.9 ± 3.6</td>
<td>74.5 ± 4.5</td>
<td>43.7 ± 3.9</td>
<td>68.5 ± 3.4</td>
<td>49.4 ± 3.9</td>
</tr>
<tr>
<td>Pt/SWCNTs-COOH on carbon cloth</td>
<td>84.5 ± 3.2</td>
<td>74.0 ± 4.2</td>
<td>45.7 ± 3.5</td>
<td>60.0 ± 3.5</td>
<td>99.0 ± 2.8</td>
</tr>
<tr>
<td>Commercial Pt-carbon cloth</td>
<td>82.9 ± 3.0</td>
<td>71.0 ± 4.3</td>
<td>46.4 ± 4.7</td>
<td>58.4 ± 4.2</td>
<td>74.1 ± 3.0</td>
</tr>
</tbody>
</table>

**Figure 6** | (a) Polarization curves and (b) power density curves obtained with MFCs equipped with different types of cathodes.
et al. 2009; Lu et al. 2011). For the silver recovery study, the shiny rods of silver on the cathode surfaces were visibly observed in all MFCs. The MFC equipped with Pt/SWCNTs-COOH on the carbon-cloth cathode achieved the highest silver recovery of 99% and showed a significant difference ($p < 0.0001$) to other cathode materials. Overall, all results indicated the potential of MFCs to recover and remove silver from wastewater.

**CONCLUSION**

Pt/SWCNTs-COOH coated onto carbon cloth was identified as a potential material to replace commercial Pt-carbon cloth for MFC cathodes. Pt/SWCNTs-based cathodes from the DP method displayed an improvement of MFC performance and reduction of cathode cost due to small particles of Pt that are very uniformly distributed, together with supporting material from SWCNTs. Moreover, the DP method was a simple, cost-effective and time-saving procedure. Pt/SWCNTs-COOH/carbon cloth as a cathode and carbon cloth as an anode greatly increased the OCV (0.6954 V) of the MFC system and generated $P_{\text{max}}$ 1.2-fold higher than plain carbon cloth. In addition, the COD removal efficiency and silver recovery were very satisfactory at 84.5% and 99.0%, respectively.

**ACKNOWLEDGEMENT**

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**REFERENCES**


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