



Short communication

## Microbial fuel cell cathode with dendrimer encapsulated Pt nanoparticles as catalyst

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### ABSTRACT

In this paper, we investigated the use of polyamidoamine (PAMAM) dendrimer-encapsulated platinum nanoparticles (Pt-DENs) as a promising type of cathode catalyst for air-cathode single chamber microbial fuel cells (SCMFCs). The Pt-DENs, prepared via template synthesis method, have uniform diameter distribution with size range of 3–5 nm. The Pt-DENs then loaded on to a carbon substrate. For comparison, we also electrodeposited Pt on carbon substrate. The calculation shows that the loading amount of Pt-DENs on carbon substrate is about  $0.1 \text{ mg cm}^{-2}$ , which is three times lower than that of the electrodeposited Pt ( $0.3 \text{ mg cm}^{-2}$ ). By measuring batch experiments, the results show that Pt-DENs in air-cathode SCMFCs have a power density of  $630 \pm 5 \text{ mW m}^{-2}$  and a current density of  $5200 \pm 10 \text{ mA m}^{-2}$  (based on the projected anodic surface area), which is significantly better than electrodeposited Pt cathodes (power density:  $275 \pm 5 \text{ mW m}^{-2}$  and current density:  $2050 \pm 10 \text{ mA m}^{-2}$ ). Additionally, Pt-DENs-based cathodes resulted in a higher power production with 129.1% as compared to cathode with electrodeposited Pt. This finding suggests that Pt-DENs in MFC cathodes is a better catalyst and has a lower loading amount than electrodeposited Pt, and may serve as a novel and alternative catalyst to previously used noble metals in MFC applications.

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### 1. Introduction

Microbial fuel cells (MFCs), a type of biological fuel cells, are devices that transform chemical energy from organic materials directly into electrical energy through electrochemical reactions [1–4]. MFCs are known as environmental-friendly bio-technology as they utilize renewable resources for energy generation. Although the concept of MFCs was put forward 100 years ago, it has not progressed rapidly until recent years owing to the constant decline in the supply of fossil fuels and the intensification of environmental problems. In recent years, MFCs have gained worldwide interest and the power output has been enhanced; however it is still far from utilizing it in practical applications [5]. Major drawbacks in the development of the MFCs include the instability, inefficiency, low output and high cost [6,7].

The overall performance of MFCs is affected by many factors, namely the reactor configuration [8–10], microbial activity, chemical substrates [11], pH and temperature [12], electrode material [13–16], type of proton exchange membrane [17], and electron

acceptor. Among them, the cathode material is an important factor [18], due to the limited kinetics of oxygen reduction in the medium [19]. David et al. [20] estimated oxygen reduction kinetics, indicating that the high overpotentials of cathodic reactions in oxygen-based microbial fuel cells can significantly affect the MFC performance. In addition, several other methods to improve the cathode performance include lowering the internal resistance of the cathode material [21], using more effective electron acceptors such as ferricyanide, potassium permanganate, manganese oxide in place of oxygen [22–25], and using a catalyst that efficiently enhances cathodic reactions at room temperature [26].

Pt is commonly used as MFCs cathode catalyst owing to its effectiveness in lowering the activation energy of cathodic reactions and in improving the reaction kinetics at the cathode. Despite the efforts made to explore alternative catalysts, Pt is still one of the most effective catalysts currently in use. However the high cost of Pt drives the need for reduced the Pt loading amount and improved catalytic activity. The effect of loading amount on power generation has been examined. [26], results indicate that the Pt loading amount in air-cathode MFCs ranging from 0.1 to  $2 \text{ mg cm}^{-2}$  has no obvious influence on power density. Yamamoto et al. [27] presented a spherical macromolecular templated synthesis for ultrafine sub-nanometer platinum clusters with diameters of 2–5 nm on carbon

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supports. The resulted clusters exhibited very high catalytic activity for the four-electron reduction of oxygen molecules.

In recent years, dendrimer–metal nanocomposites have been intensively investigated and characterized in terms of catalytic properties and multilayer formation using poly(amidoamine) (PAMAM) dendrimers [28]. Partially quarternized PAMAM dendrimers with both quaternary ammonium groups and primary amines can be used as a polymeric template reservoir to prepare stable dendrimer-encapsulated platinum nanoparticles with well-defined composition, structure and size. [29,30]. The dendrimer–metal complex is advantageous due to its ease of separation from products and recyclability, in addition to its unique catalytic properties, including high activity, selectivity and stability [31,32]. Crooks et al. [33] prepared a type of Pt dendrimer encapsulated nanoparticles, with an average diameter of 1.4 nm, which showed excellent catalytic activity for oxygen reduction reaction. In our recent research, much effort has been devoted to integrate the Pt-DENs nanocomposites into air-cathode MFCs, with the goal to decrease the Pt loading and improve the performance of MFCs.

In this work, Pt-DENs were produced with uniform diameters and used as catalyst in the cathodes of air-cathode SCMFCs. The performances of Pt-DENs/carbon paper cathode and electrodeposited Pt were compared in terms of voltage values and power densities over several circular tests in MFCs systems. Electrochemical tests were conducted to examine the cathodic performance with two types of Pt catalyst.

## 2. Materials and methods

### 2.1. Cathode preparation and fabrication

The preparation of Pt-DENs was carried out in accordance with previous report. Briefly, 1 mL of a 1 mM poly(amidoamine) dendrimer aqueous solution was added to 10 mL of water. Subsequently, 0.25 mL of a 0.1 M  $K_2PtCl_4$  aqueous solution was added. After stirring for 48 h, 1.67 mL of a 0.3 M  $NaBH_4$  aqueous solution was added. The resulting dark brown solution was purified by dialysis against water for 24 h to produce Pt-DENs. The Pt-DENs/carbon paper cathode was made by adding the Pt-DENs solution to the heated carbon paper drop by drop to ensure that the loading amount of Pt-DENs on carbon support was adjustable. Finally, Pt-DENs/carbon paper and proton exchange membrane (PEM) were hot pressed together by heating to 140 °C at 1780 kPa for 3 min.

Electrodeposition of Pt on carbon paper was performed in a three-electrode system with a deposition potential of  $-0.3$  V, a sweep rate of  $50$   $mV s^{-1}$  and an operation time of 15 min.  $H_2SO_4$  at  $0.5$   $mol L^{-1}$  and  $H_2PtCl_6 \cdot 6H_2O$  at  $1$   $mmol L^{-1}$  were used as electrolytes. Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The as-prepared Pt-DENs/carbon paper was used as the working electrode. The electrodeposited Pt/carbon paper cathode was prepared the same way as the Pt-DENs/carbon paper cathode.

### 2.2. Construction of the air-cathode SCMFC

The anode and the cathode of SCMFC were placed on opposite sides of a plastic (Plexiglas) cylindrical chamber of 3.5 cm long by 3 cm in diameter. The empty bed volume was 24.5 mL; and the anode surface area was  $7$   $cm^2$  (Fig. 1). Graphite plate anode with electrogenic bacterial strain *Shewanella putrefaciens* (CICC 22940) was used to generate electrons from organic substrate. The PEM (Nafion 117) was sequentially boiled in  $H_2O_2$  (30%), deionized water,  $0.5$  M  $H_2SO_4$ , and deionized water for 1 h in each medium. Electrodes were connected through an external circuit.

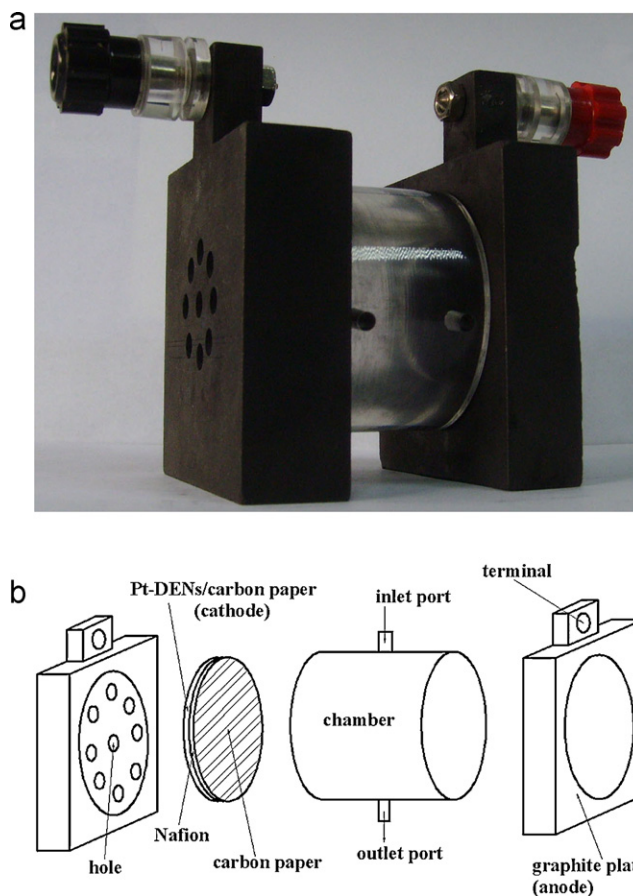


Fig. 1. (a) Schematic and (b) laboratory-scale of SCMFC used to generate electricity from acetate.

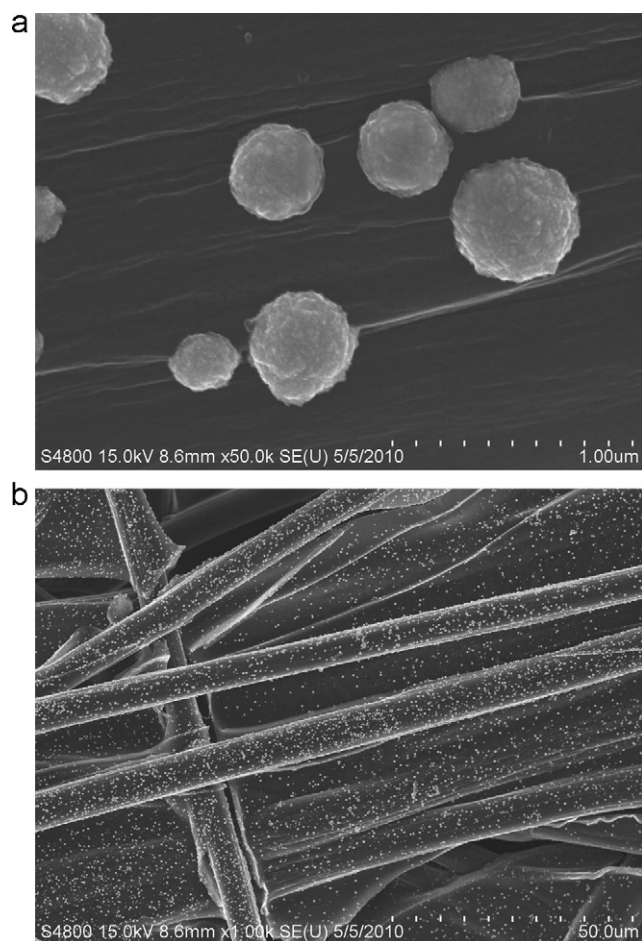
### 2.3. SCMFC operation

The reactor was inoculated with *S. putrefaciens* coated graphite particles, and operated in batch mode for approximately 1 week each time. Acetate was injected as fuel at concentration of  $1$   $g L^{-1}$  once a day. The cathode was exposed to air on one side and water on the other side. No precautions were taken to remove dissolved oxygen from the medium or to maintain anaerobic conditions in the anode chamber. All experiments were performed at room temperature.

### 2.4. Air-cathode SCMFC performance analyses

The patterns of Pt particles on the carbon paper were examined using scanning electron microscope (JSM-6360LV) and transmission electron microscope (JEOL-2100) while the loading amount of Pt on the carbon paper was examined by using an Inductively Coupled Plasma–Optical Emission Spectrometry (Vanand 710, IRIS). Voltage ( $V$ ) between the two electrodes was recorded by Data Acquisition Card (Hytek, U1208LOG), with the data automatically recorded on a personal computer. Power density ( $P = IV/A$ ) was measured by a SourceMeter (2400 Keithly, Cleveland, OH) according to the measured voltage ( $V$ ), current ( $I = V/R$ ), and surface area of the anode electrode ( $A$ ). The maximum power output was determined by the polarization curves.

Linear sweep voltammetry (LSV) was used to measure the electrochemical performance of Pt-coated cathode materials. Electrochemical measurements were carried out with CHI 660C workstation (CH Instruments, Chenhua, Shanghai, China) connected to a personal computer. A three-electrode set-up was used



**Fig. 2.** (a) SEM image of Pt electrodeposited on carbon paper and (b) magnification SEM image of the Pt nanoparticles.

in this experiment. This set-up consists of either a piece of Pt-DENSs/carbon paper or an electrodeposited Pt/carbon paper (a circle with 3 cm in diameter) serving as the working electrode; Ag/AgCl (3 M KCl) as the reference electrode; and platinum wire as the counter electrode. The scan rate was  $1 \text{ mV s}^{-1}$ , and the potential was scanned from +0.5 to 0 V versus standard hydrogen electrode.

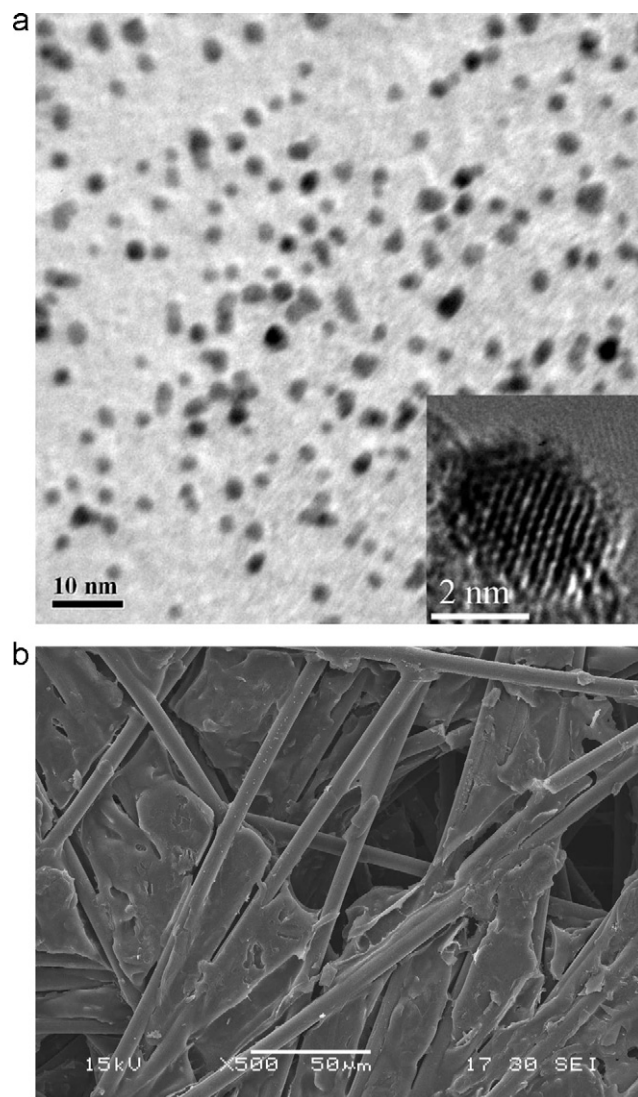
### 3. Results and discussion

#### 3.1. Surface topography of Pt particles on carbon paper

The electrodeposited Pt particles have been investigated by SEM. As clearly illustrated in Fig. 2a, Pt nanoparticles were deposited and dispersed uniformly on the whole surface of the carbon paper. The corresponding high-magnification SEM image showed that Pt nanoparticles have a wide diameter distribution ranging from 200 to 400 nm (Fig. 2b).

The resulting Pt-DENSs were examined by using HRTEM. As illustrated in Fig. 3a, well-defined and almost spherical Pt nanoparticles were obtained using the dendrimer as template. The mean size of the nanoparticles was about 4 nm. Moreover, the dendrimer-encapsulated Pt nanoparticles are dispersed uniformly and densely on the carbon paper, as shown in the SEM image in Fig. 3b.

Also, Inductively Coupled Plasma-Optical Emission Spectrometry was used to examine the loading amounts of Pt on carbon paper. The results showed that the electrodeposited Pt and Pt-DENSs have the loading amount about 0.3 and  $0.1 \text{ mg cm}^{-2}$ , respectively

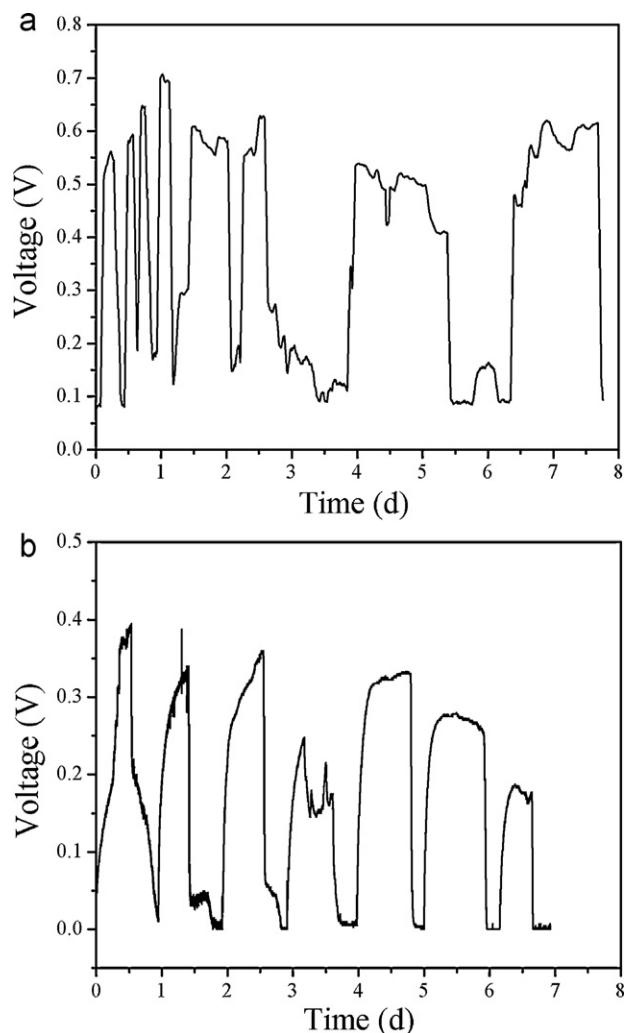


**Fig. 3.** (a) HRTEM image of Pt-DENSs. The inset shows a crystal lattice of the single Pt nanoparticle. The well defined, almost spherical particle with a diameter of 4 nm is clearly seen, (b) SEM image of Pt-DENSs dispersed uniformly and densely on the whole surface of carbon paper.

#### 3.2. Performance of electrodeposited Pt cathode in SCMFC compared with Pt-DENSs cathode

Experiments were conducted under the same conditions and repeated 2–3 times to evaluate the performance of SCMFC with two types of Pt catalysts. SCMFC with electrodeposited Pt or Pt-DENSs in cathodes rapidly produced voltage after inoculation, and generated stable voltages at a certain resistance. After addition of acetate to the anode, it was observed that the voltage of the Pt-DENSs increased to a maximum value of 700 mV (Fig. 4a), the maximum voltage was stable for 6 h and then gradually decreased to the minimum value of 100 mV in a week. Correspondingly, the electrodeposited Pt in MFCs cathodes achieved a maximum voltage value of 400 mV and a minimum of 10 mV, as shown in Fig. 4b. Obviously, the cathodes with Pt-DENSs produced higher voltages than the cathodes with electrodeposited Pt. This indicates that the Pt-DENSs have better performance than electrodeposited Pt in lowering the activation energy of the cathode and in improving the reaction kinetics at the cathode.

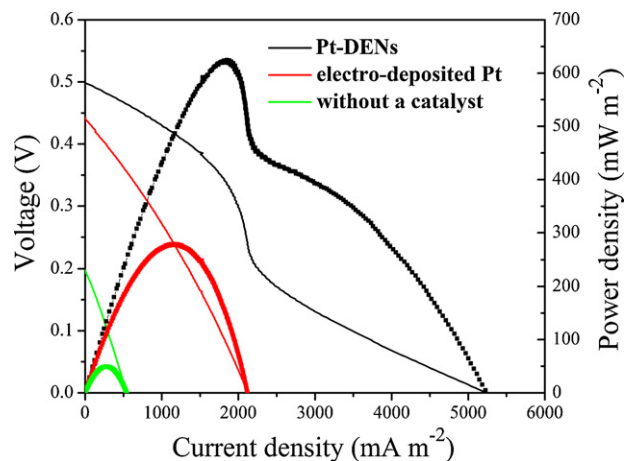
In some circumstances, MFCs was observed to lose its systematic stability at higher current density due to limitation in kinetics or



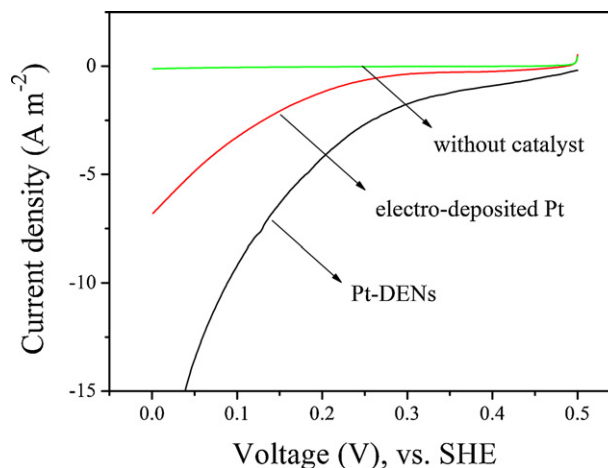
**Fig. 4.** Voltage generated using catalyst of Pt-DENS and electrodeposited Pt in SCMFC cathodes, with  $1 \text{ g L}^{-1}$  sodium acetate.

mass-transfer, and this may lead to a substantially unstable voltage output, as shown in the voltage curve of Fig. 4.

Major differences in power production were observed in the study of polarization and power density. As shown in Fig. 5,



**Fig. 5.** Polarization curve and power density curve of SCMFCs with catalyst of Pt-DENS and electrodeposited Pt in cathodes, and without catalyst (normalized to anodic surface area).



**Fig. 6.** LSV of cathode with Pt-DENS or electrodeposited Pt, and without catalyst. The scan rate was  $1 \text{ mV s}^{-1}$ , and the potential was scanned from +0.5 to 0 V versus standard hydrogen electrode.

the open circuit voltage for Pt-DENS was  $0.5 \pm 0.05 \text{ V}$ . This is significantly better than both the electrodeposited Pt cathode ( $0.43 \pm 0.05 \text{ V}$ ) and the cathode without catalyst ( $0.2 \pm 0.05 \text{ V}$ ). Moreover, the cathode with Pt-DENS displayed better cell voltage stability and a higher current density than in the other cases. These results suggest that the cathode material consisting of Pt-DENS/carbon paper had a lower ohmic resistance than the other composite cathode materials used in the experiment. The largest power density obtained using Pt-DENS as cathodic catalyst reached  $630 \pm 5 \text{ mW m}^{-2}$  whereas the electrodeposited Pt in cathode only reached a power density of  $275 \pm 5 \text{ mW m}^{-2}$ . Furthermore, the current density of the Pt-DENS ( $5200 \pm 10 \text{ mA m}^{-2}$ ), was more than twice the current density observed for the electrodeposited Pt ( $2050 \pm 10 \text{ mA m}^{-2}$ ). The cathode without catalyst exhibits inferior performance with the maximum power density of  $50 \text{ mW m}^{-2}$  and the highest current density of  $500 \text{ mA m}^{-2}$ . These results suggest that, when the cathode is under kinetic control, meaning that the mass transfer is not a limiting factor, the oxygen reduction reaction can be effectively and more efficiently catalyzed by smaller Pt constituents (Pt-DENS) deposited throughout the electrode as opposed to Pt deposited on the surface of the cathode.

### 3.3. Electrochemical characterization of electrodeposited Pt and Pt-DENS

LSV tests were conducted to evaluate the electrochemical performance of the cathodes in the absence of bacteria. As shown in Fig. 6, Pt-DENS as cathode catalyst had a significant catalytic current, readout while the cathode without catalyst hardly had any response. Clearly, the cathodic catalyst is essential for enhanced overall performance of MFCs. Compared to electrodeposited Pt-based cathode, the Pt DENS/carbon paper cathode showed better electrochemical performance with a higher current response. These results illustrated that Pt-DENS/carbon paper cathode have excellent catalytic activity for the oxygen reduction reaction in the cathode.

## 4. Conclusions

In this work, Pt-DENS used as cathode catalyst in air-cathode SCMFC was investigated. A current density as high as  $5200 \text{ mA cm}^{-2}$  was achieved in the resulted MFC, which indicates that the Pt-DENS has good catalytic efficiency to ensure desirable performance. Although the loading amount of Pt in the form of Pt-DENS

( $0.1 \text{ mg cm}^{-2}$ ) is lower than electrodeposited Pt ( $0.3 \text{ mg cm}^{-2}$ ), a better overall performance was obtained. Moreover, we found that the SCMFC with Pt-DENs had a higher power density in comparison with electrodeposited Pt. Therefore, this performance of lower loading amount and higher power efficiency illustrated the excellent potential of the Pt-DENs for MFCs. As a renewable and environmentally friendly bio-technology, the MFCs need to be further studied for the development of new applications. Building upon this work, we will attempt to construct a microbial photo-electrochemical cell.

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