



Short communication

Polypyrrole/carbon black composite as a novel oxygen reduction catalyst for microbial fuel cells

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ABSTRACT

A polypyrrole/carbon black (Ppy/C) composite has been employed as an electrocatalyst for the oxygen reduction reaction (ORR) in an air-cathode microbial fuel cell (MFC). The electrocatalytic activity of the Ppy/C is evaluated toward the oxygen reduction using cyclic voltammogram and linear sweep voltammogram methods. In comparison with that at the carbon black electrode, the peak potential of the ORR at the Ppy/C electrode shifts by approximate 260 mV towards positive potential, demonstrating the electrocatalytic activity of Ppy toward ORR. Additionally, the results of the MFC experiments show that the Ppy/C is well suitable to fully substitute the traditional cathode materials in MFCs. The maximum power density of 401.8 mW m^{-2} obtained from the MFC with a Ppy/C cathode is higher than that of 90.9 mW m^{-2} with a carbon black cathode and 336.6 mW m^{-2} with a non-pyrolysed FePc cathode. Although the power output with a Ppy/C cathode is lower than that with a commercial Pt cathode, the power per cost of a Ppy/C cathode is 15 times greater than that of a Pt cathode. Thus, the Ppy/C can be a good alternative to Pt in MFCs due to the economic advantage.

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1. Introduction

Microbial fuel cells (MFCs) are devices that convert organic substrates into electricity with the aid of microorganisms as catalysts. Since they can generate electricity even from various wastewaters while treating them, increasing interests have been paid to their development and improvement in recent years [1–3]. However, the commercial MFC applications have been severely hindered due to the high cost of the materials used in MFCs, especially the cathode catalyst. It should be noted that the cost of cathode accounts for more than half of the total cost of a lab-scale MFC due to the use of noble metal platinum. So far, most efforts have been focused on the development of new inexpensive, non-noble metal electrocatalysts to replace the platinum. Phthalocyanines and porphyrins were firstly examined as alternatives to Pt in MFCs [4]. Thereafter, other metal complexes and metal dioxides have also been considered, such as Fe-EDTA [5], MnO_2 [6] and PbO_2 [7]. However, the long-term instability of the phthalocyanines and transition metal macrocycles and the toxicity of metal dioxides make them impractical.

Conductive polymer, such as polypyrrole (Ppy) has attracted great interests since being electrochemically synthesized for the first time more than two decades ago. Due to its interesting prop-

erties, such as environmental stability, ease of synthesis and high conductivity at room temperature, conductive polymer shows great potential for application in the preparation of actuators, chemical sensors, biosensors and electronic devices [8,9]. Previously, Khomenko et al. revealed the catalytic activity of Ppy toward ORR and proposed the possible mechanism based on the quantum-chemical calculations of the electronic structure of Ppy [10]. However, this material has not been systematically studied and its potential application as electrocatalysts in fuel cells has not been noticed. The aim of this work is to study the possibility of using the Ppy as an oxygen reduction catalyst to replace the conventional noble metal Pt in an MFC. Electrochemical analyses were conducted to investigate the capability of Ppy toward ORR in a defined system. Air-cathode single-chamber MFCs were constructed with various cathode oxygen catalysts including carbon black alone, Ppy/C, non-pyrolysed FePc, and Pt. The costs with various cathode materials were compared based on the MFC power outputs.

2. Experimentals

2.1. Preparation of cathodes

The water proof layer of cathodes was operated according to the procedures described previously [11]. The catalytic layer was produced as follows: 7 mg Ppy/C (Sigma-Aldrich, 20 wt% Ppy content, doped with proprietary organic sulfonic acid) was firstly dispersed in 1 mL ethanol by sonicating for 10 min to form a Ppy/C ink.

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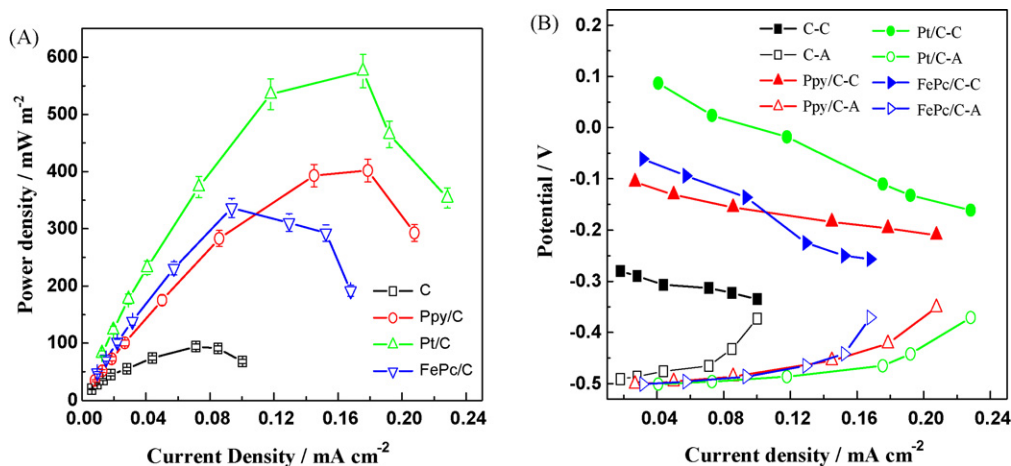


Fig. 1. Power density versus current density curves with various cathodes (A) and electrode potentials (vs. SCE) as a function of different cathodes (B); carbon-cathode (C-C), carbon-anode (C-A).

Then, 0.25 mL Nafion solution was added before the resulted ink was coated on 30% wet-proofed carbon cloth (type B, E-Tek) on whose side gas diffusion layer coating was not made, resulting in 1 mg cm⁻² Ppy/C (0.2 mg cm⁻² Ppy) loading. To make an iron phthalocyanine (FePc)/C cathode, 7 mg carbon black (Vulcan XC72) and 7 mg FePc were mixed and dispersed in 1 mL ethanol, then sonicated for 30 min after adding 0.25 mL Nafion solution. The resulted ink was coated on carbon cloth cathode as well. Pt/C cathode was produced using the same method with 0.5 mg cm⁻² Pt loading. All electrodes were dried at 70 °C in an oven for at least 2 h before use.

2.2. MFC configuration

Air-cathode single-chamber MFCs with an inner volume of 12 mL were constructed as reported previously [12]. A cylindrical MFC chamber with a length of 1.7 cm and a diameter of 3.0 cm was made of plexiglass. Both anode and cathode surface area were 7 cm². Non-wet proofing carbon cloth (type A) was used as an anode without further treatment. The anode and cathode was placed on opposite sides with the oxygen catalyst coating layer facing to the anode and the polytetrafluoroethylene (PTFE) coated gas diffusion layer facing to air.

2.3. Electrochemical measurements

In order to investigate the ORR characterization of Ppy/C, cyclic voltammograms (CVs) and linear sweep voltammograms (LSV) were performed with the conventional three-electrode system. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The working electrodes were prepared as follows: 2.5 mg Ppy/C or carbon black, 1.0 mL ethanol and 0.1 mL of 5 wt% Nafion solution were blended in an ultrasonic bath, and then 2 μL of this ink was dropped onto the cleaned glassy carbon (GC) electrode (3.0 mm diameter). All electrochemical measurements were conducted at a scan rate of 50 mV s⁻¹ and with 50 mM phosphate buffer as the electrolyte.

2.4. Enrichment and operation

Reactors were inoculated with 2 mL activated sludge and 10 mL glucose (1000 mg L⁻¹) culture media solution. The culture media solution contained: KH₂PO₄ (13.6 g L⁻¹), NaOH (2.32 g L⁻¹), NH₄Cl (0.31 g L⁻¹), NaCl (1.0 g L⁻¹), a vitamin stock solution (12.5 mL L⁻¹) and a mineral stock solution (12.5 mL L⁻¹) [13]. The power density was measured by varying the external resistance in the MFC circuit

from 98 to 7600 Ω. All tests were conducted in batch mode in a 30 °C incubator. The power was normalized by the projected surface area of the cathode.

3. Results and discussion

3.1. Cathode performance

In previous studies, polypyrrole has been considered as useful matrices for the immobilization of the ORR catalysts such as metal oxides and complexes in fuel cells due to its good electronic conductivity [14–16]. Negligible attention has been paid to the electrocatalytic activity of Ppy alone toward the electroreduction of molecular oxygen and its applications to fuel cells. In this study, Ppy was solely used as a catalyst for ORR in MFCs. Although the conductivity of Ppy was rather high, the conductive and the electroactivity of the polymer would be further improved when it was composited with high conductive materials such as carbon black according to previous report by Wu et al. [17], which would benefit the fuel cell performances. Therefore, the composite instead of the polymer alone was applied in the present study.

The electricity generation with a Ppy/C cathode, together with carbon black, FePc, and Pt as controls, was examined. The power density versus current density curves were presented in Fig. 1. The maximum power density achieved from an MFC with the Ppy/C cathode was 401.8 mW m⁻², which was higher than that from an MFC with the carbon black alone cathode, 93.9 mW m⁻². This result strongly suggests that Ppy contributes to the power increase due to its catalytic activity to ORR. It was also worth noting that the energy output from an MFC with the Ppy cathode was higher than that from a MFC with the FePc cathode. Previous studies showed that FePc was a good alternative to Pt in a MFC [18]. The electricity generation capability of FePc cathode was similar to that of a Pt cathode when the FePc was pyrolysed. In this study, the FePc was used as received without any pyrolysis. Therefore, a relatively low power output was obtained. Fig. 2 shows the curves of the individual cathode or anode potential versus current density. The anode potentials of various MFCs were almost consistent while the cathode potentials varied. Due to the presence of Ppy, an obvious increased cathode potential under all currents was obtained compared with that with the carbon black cathode, indicating that the difference on the MFC performances resulted from the difference of the catalytic activity of the catalysts in cathodes. In order to further confirm the catalytic activity of Ppy to oxygen reduction, CV and LSV were conducted in a conventional three-electrode system. Fig. 3A

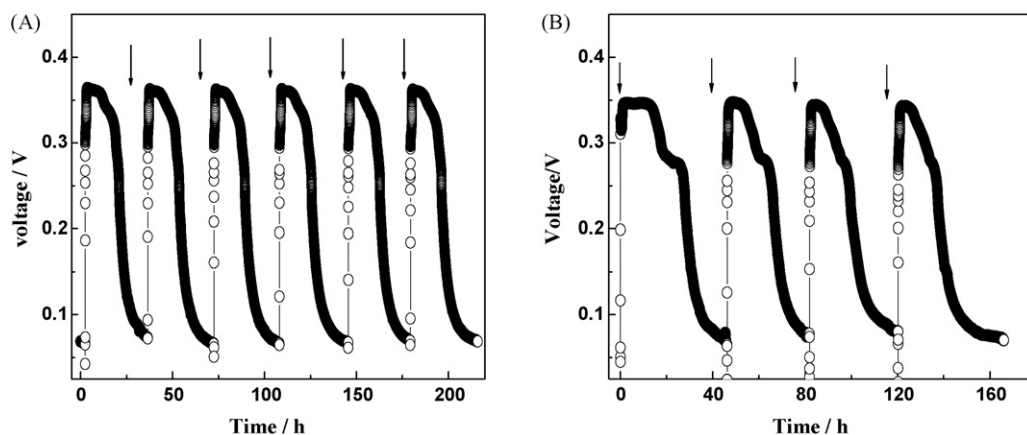


Fig. 2. Voltage output with Ppy cathode under $1000\ \Omega$ loading (arrow indicates the replacement of substrate) (A) and voltage output from a new Ppy cathode that replaced an old one in a well operation MFC (B).

shows the CVs of the carbon black and Ppy/C modified electrodes both in the presence and absence of oxygen. An obvious oxygen reduction peak appeared on the CV of carbon black at the potential of approximate -0.60 V . On the CV of Ppy in the absence of oxygen, a couple of redox peaks appeared at around -0.458 and -0.604 V . Since no such peaks were verified on the CV of carbon black, it was concluded that this pair of peaks were characteristics of the Ppy redox. When the Ppy/C electrode was scanned in the presence of oxygen, a new peak at the potential of -0.34 V was acquired. This potential was more positive than that obtained from a carbon black electrode (-0.60 V), and the peak current was almost twice greater than that of carbon black electrode, suggesting that the shifted peak potential and increased peak current result from the Ppy. The same phenomenon also occurred on the LSV curves (Fig. 3B). According to the previous report by Khomenko et al. [10], the main mechanism of ORR by Ppy was that the carbon atoms on pyrrole ring could supply an active site for oxygen chemical adsorption, which could weaken the O–O bond of oxygen and lower the activation energy for reduction.

3.2. Effect of cathode biofilm formed upon Ppy/C on MFC performance

It is well known that a biofilm would form on the cathode surface after long period of operation in a single-chamber air-cathode MFC. In order to evaluate the effect of cathode biofilm on the MFC performance, the voltage output versus time curves were recorded in

two cases. The first one was performed when the well operated MFC was renewed with fresh glucose medium over 200 h. As shown in Fig. 2A, very stable voltage output cycles were obtained. The other case was conducted when the well operated MFC with the Ppy cathode was replaced by a new Ppy/C cathode, and the voltage output curve was presented in Fig. 2B. The voltage output was almost the same in both cases. The only difference came from the first two cycles in which the voltage duration was gradually reduced, presenting a gradual decrease on coulombic efficiency. It was probably because that a biofilm was formed on the new cathode, and the substrate (glucose) was consumed by both the anode and the cathode biofilm, resulting in a fast consumption of glucose. On the other hand, many recent studies have shown that the cathode biofilm may work as a biocatalyst to some terminal electron acceptors such as oxygen or carbon dioxide, which was named as the biocathode. However, in the present study the voltage was generated immediately after a new Ppy/C cathode was assembled to the MFC, indicating that the Ppy/C rather than the biofilm contributes to the oxygen catalytic reduction and the electricity generation.

3.3. Effect of Ppy loading on MFC performance

In order to optimize the cathode operation condition in an air-cathode single-chamber MFC, the effect of Ppy loading on the power output was evaluated. The highest power density was obtained with 0.2 mg cm^{-2} Ppy loading (1.0 mg cm^{-2} Ppy/C) at the cathode (Fig. 4). Contrary to our expectation, the higher amount of

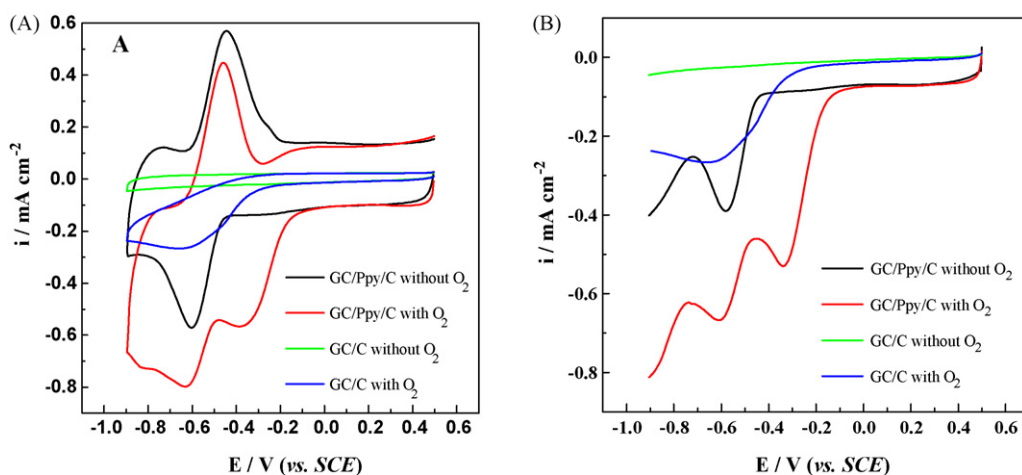


Fig. 3. CV (A) and LSV (B) of various materials for the oxygen reduction.

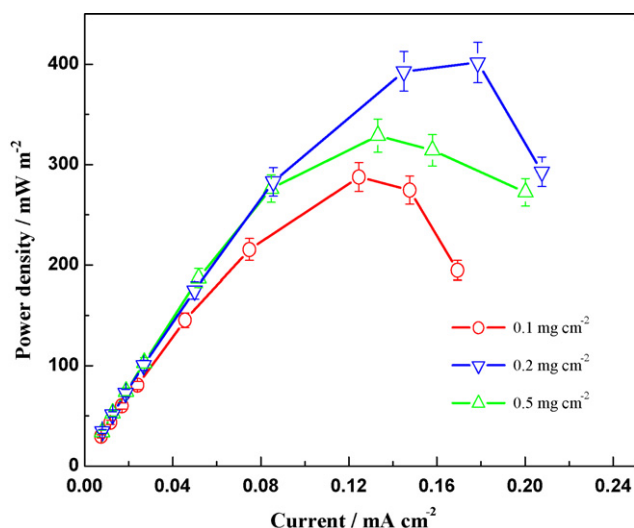


Fig. 4. Effect of Ppy loadings on the power output.

Table 1

Comparison of the cost of cathode materials.

Cathode material	Price(g ⁻¹) ^a	Power density (mW m ⁻²)	Power per cost of cathode material (mW \$ ⁻¹)
Polypyrrole/C	3.39	401.8	8.29
Pt/C	29.38	575.6	0.55
FePc/C	7.42	336.6	3.17

^aNormalized to cathode materials.

Ppy resulted in the lower power density. This might be due to a decrease in oxygen diffusion rate on highly packed surface, which then led to an increase in the diffusion resistance of the cathode [19].

3.4. Cost of cathode materials

As mentioned above, the high cost of MFCs is limiting its practical applications. Thus, it is critical to replace the noble Pt by other cheap and efficient oxygen reduction catalysts. Ppy/C could be one of those good candidates. The comparison of the cathode costs was listed in Table 1. The Ppy/C cathode produced the most power per dollar, which was followed by FePc/C and Pt/C. The power per cost of Ppy/C (8.29 mW \$⁻¹) was 15 times greater than that of Pt/C

(0.55 mW \$⁻¹). Due to this huge economic advantage, the Ppy/C could be a good alternative to Pt in MFCs. Besides, the studies using the Ppy/C composite with various Ppy weight ratios are underway. In order to further improve the Ppy/C performance for ORR, several pretreatment processes for the composite are also being tested based on the improvement of its conductivity and electroactivity.

4. Conclusions

The aim of this study was to lower the cost of cathodes in MFCs, using a cheap conductive polymer/C composite (Ppy/C) to replace the noble metal Pt. In view of the MFC power outputs, the Ppy/C cathode is even better than a FePC cathode in which the FePc was not pyrolysed. Although the energy output from the MFC with a Ppy/C cathode was a little lower than that with a Pt cathode, the power per cost of Ppy/C is 15 times higher than that of Pt. Therefore, Ppy/C offered a good alternative to Pt in MFC practical applications.

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