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Graphite Felt Anode Modified by Electropolymerization of Nano-Polypyrrole to Improve Microbial Fuel Cell (MFC) Production of Bioelectricity

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Abstract

Microbial Fuel Cells (MFCs) have emerged as a potential technology for direct bioelectricity production from organic matters in wastewater streams that are otherwise unutilized. The graphite felt anode modification by nano-polypyrrole (nano-PPy) was carried out via electropolymerization reaction using cyclic voltammetry (CV). The electropolymerization trials designated PPy-1, PPy-2 and PPy-3 used 5, 10 and 20 CV cycles, respectively with a scanning voltage ranged from 0 to 0.9 V at a rate of 50 mV/s. The influences of reaction time (reflected by the number of cycles of CV) on the morphology of the polypyrrole films on the anodes and the MFC performance were investigated. The polypyrrole film thickness and particle diameter increased with reaction time. Using the PPy-2 anode, the maximum power density was 430 mW/m^2, a 15% increase compared with that of the control (i.e., MFC with an unmodified anode). Furthermore, the Coulombic efficiency and Chemical Oxygen Demand (COD) removal also increased after the anode modification.

Keywords: Microbial fuel cell; Bioenergy; Anode modification; Nano-polypyrrole; Electropolymerization; Power generation; Coulombic efficiency

Introduction

In recent years, with growing global population and prosperity in many developing countries, the energy crisis and environmental problems such as air and water pollutions have become increasingly pressing for politicians and researchers. It is desirable to harvest the energy in the chemical bonds of the organic matters during wastewater treatment. This kind of low-grade biomass is usually unutilized and often a burden to wastewater treatment facilities. Microbial Fuel Cells (MFCs) are an potential technology that uses microbial biofilms to convert the chemical energy in chemical bonds of the organic matters into bioelectricity [1,2]. Therefore, MFCs have attracted considerable attentions in recent years in the academic circle for potential applications in wastewater treatment with concomitant energy production. However, major technological breakthroughs are needed to increase the efficiency and power density before MFCs become practical [3,4].

The electrode material, especially the anode material is a key factor on MFC performance and cost [4,5]. At present, carbon-based materials such as carbon cloth and carbon paper are adopted in most MFC electrodes because of their very low costs, excellent electrical conductivity, non-corrosiveness, and good biocompatibility [4-6]. Several physical and chemical methods for anode modifications such as acid oxidation, ammonia treatment and electrochemical oxidation have been explored [7-9] and found to promote the electron transfer by the anodic biofilm to the anode, resulting in improved power densities in MFCs [10].

Conductive polymers can be used to promote the electron transfer in MFCs. Among all the conductive polymers investigated so far, nano-polypyrrole (nano-PPy) is one of the most attractive materials due to its excellent conductivity, stability and biocompatibility [11]. Zou et al. [12] used a chemical oxidation reaction to synthesize polypyrrole and found enhanced electron collection by the anode from a photosynthetic biofilm in a sun-powered MFC. Feng et al. [13] modified both the anode and the cathode to form a conductive polypyrrole (PPy)/anthraquinone-2,6-disulfonate (AQDS) film to boost MFC performance, and found the modification increased H_2O_2 generation and thus enhanced the oxidative ability of the electro-Fenton process. PPy could be synthesized by either conventional chemical oxidation or electropolymerization [14]. Compared with the chemical oxidation method, electropolymerization is simple, low-cost and quantifiable, making it a convenient and effective method for electrode modification.

In this work, graphite felt anodes were modified by nano-polypyrrole through an electricpolymerization reaction using cyclic voltammetry (CV). The effects of reaction time (indicated by the number of CV cycles) on the morphology of polypyrrole and on the MFC performance were investigated.

Experimental Methods

Modification of anodes

Graphite felt (Jilin Carbon Plant, China) was used to make the anodes. It was soaked in acetone overnight and rinsed with water before being used as the "unmodified" or the "control" anode material.

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Electropolymerization was carried out through CV scan in a three-electrode system with unmodified anode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite rod as the counter electrode and at 5°C in an anaerobic chamber. The electrolyte solution was a mixture of pyrrole, high chlorine acid lithium, soluble starch and phosphate buffer. The scanning voltage ranged from 0 to 0.9 V at a rate of 50 mV/s. The graphite felt was modified by nano-PPy through the electropolymerization reaction using CV with 5, 10, 20 cycles resulting in anodes designated as PPy-1, PPy-2 and PPy-3 anodes, respectively. All modified anodes were cleaned with distilled water three times before being used in MFCs. All MFCs were operated under the same operating conditions.

MFC reactor operation

Single-chamber MFCs with an air-cathode were constructed as described by Cheng et al. [15]. They were operated in batch mode. Each reactor had an anolyte volume of 14 mL. The distance between the anode and the cathode was 2 cm. Four MFCs with different anodes (unmodified, PPy-1, PPy-2, PPy-3) and identical cathodes of carbon cloth containing 0.35 mg/m^2 Pt catalyst were operated simultaneously. Each MFC was inoculated with a small amount of an anaerobic sludge (20% anolyte volume) from The TEDA Sewage Treatment Plant (Tianjin, China). The initial anolyte was a 50 mM phosphate buffered nutrient solution (NH_4Cl 0.31 g/L, KCl 0.13 g/L, $NaH_2PO_4{\cdot}2H_2O$ 3.32 g/L, $Na_2HPO_4{\cdot}12H_2O$ 10.36 g/L; trace minerals and vitamins) containing 1.0 g/L glucose as substrate. The reactor underwent a start-up period and the voltage output exhibited the typical cyclic behavior while climbing as observed by Zhou et al. [10] in their MFC operations. When two cycles were completed after the voltage started to take off, the MFC operation was considered stable. At this time, the anolyte was emptied and replaced with a new culture medium containing 1.0 g/L glucose and 50 mM PBS. This medium replacement usually took place roughly 150 hours after inoculation. The external load of each MFC was fixed at 1000 Ω and the initial pH of the feed was adjusted to 6.9-7.0. The feed solution was replaced by a new one when the MFC voltage dropped below 50 mV. All the reactors were operated in an incubator at a temperature of 30 ± 0.5°C.

Measurements and calculations

A data acquisition system (PISO-813, ICP DAS Co., Ltd., Taiwan) was used to sample cell voltage every minute. Polarization curves were obtained by varying external resistances (R_{ex}) from 1000 to 50 Ω when the MFC operation became stable. Power and current densities were calculated using the effective anode surface area [5]. The Coulombic efficiency (C_E) was calculated from the equation below [16],

$$C_E = \frac{\sum_{i=1}^{n} U_i t_i}{R_{ex} Fb(\Delta COD)V} \times M \qquad (1)$$

in which U_i is the output voltage (V) at time t_i, F is Faraday's constant (96,485 C/mol), b the number of electrons exchanged per mole of oxygen (=4), ΔCOD the removal of Chemical Oxygen Demand (COD) in mg/L, V the wastewater volume in L, and M the molecular weight of oxygen, respectively. COD was measured using a commercial COD detector (HACH, DRB 200, DR/890 Colorimeter, USA).

CV was performed on an electrochemical station (CHI600D, Shanghai Chenghua, Shanghai, China) in a standard three-electrode system at a rate of 50 mV/s ranged between -0.4 and 1.2 V. The anode to be used in MFCs served as the working electrode, the counter electrode served as the cathode and the reference electrode was an SCE. A 0.5 M H_2SO_4 solution was used as the electrolyte at room temperature for all the tests. Pure oxygen was passed through the solution for 20 min before redox measurements to make the solution oxygen saturated. A Field Emission Scanning Electron Microscope (FESEM, S-4700, Hitachi, Japan) was used to examine surface morphologies of the anodes before incubation.

The Electrochemical Impedance Spectroscope (EIS) was also conducted for the MFC systems on the electrochemical station. The MFC anode served as the working electrode and the cathode served as both the counter electrode and the reference electrode. The value of external bias voltage was the anode potential of MFC, usually ranging between -0.5 and -0.4 V. The impedance measurement was done in the range of 10^5-0.01Hz with amplitude of 0.06V.

Results and Discussion

Anode characterizations

The SEM images of the graphite felt anodes are presented in figure 1. Compared with the bare surface of the unmodified anode, PPy films on the modified anodes are clearly seen. The PPy particles appeared to be rather uniform in particle diameter for each case. Particles aggregated together to form large grains. With a longer reaction time (i.e., more CV cycles), the particle diameter and film thickness both increased.

Figure 2 shows the CV (A) and the EIS (B) plots of the four anodes, respectively. Figure 2A exhibits much higher redox currents on the modified anodes. This means that the modified anodes possessed much better electron-transfer abilities than the control. Figure 2B indicates that the ohmic resistance of Ppy-1 and Ppy-3 films were both 50 Ω. The PPy-2 film had the minimum ohmic resistance (24 Ω), which was lower than the control (26 Ω). This indicated that the polypyrrole film deposited on the anode by the electropolymerization reaction using 10 cycles CV cycles was most effective for promotion of electron transfer. The difference in ohmic resistance was likely related to the thinness of

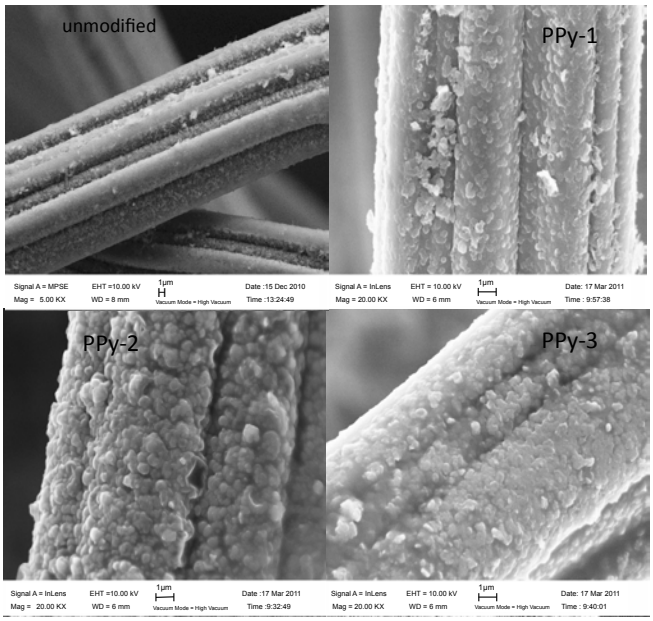

Figure 1: SEM images of the unmodified and modified anodes.

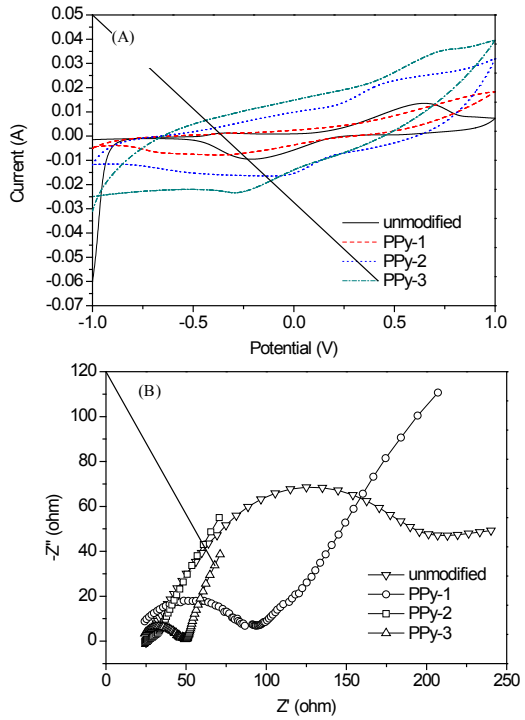

Figure 2: CV (A) and EIS (B) plots of four anodes.

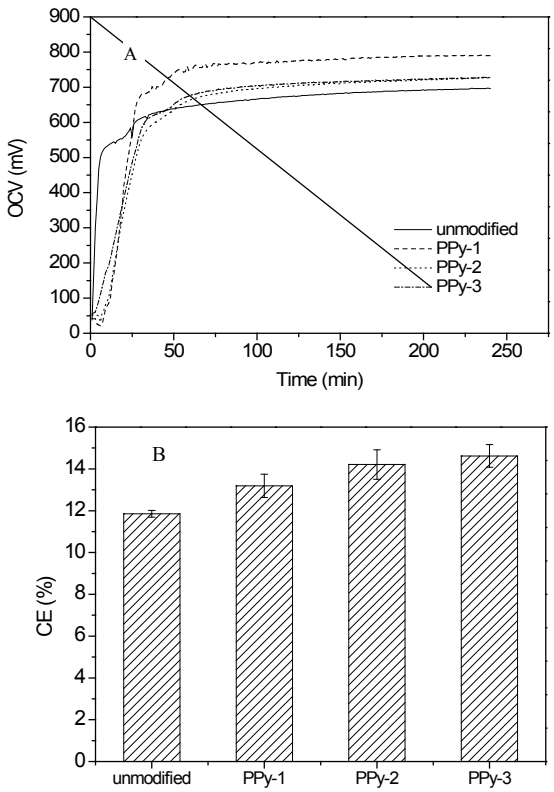

Figure 3: Open-circuit voltage (A) and Coulombic efficiency (B) of the four MFCs after the anolyte replacement (glucose 1 g/L, external load 1000 Ω, initial pH 7).

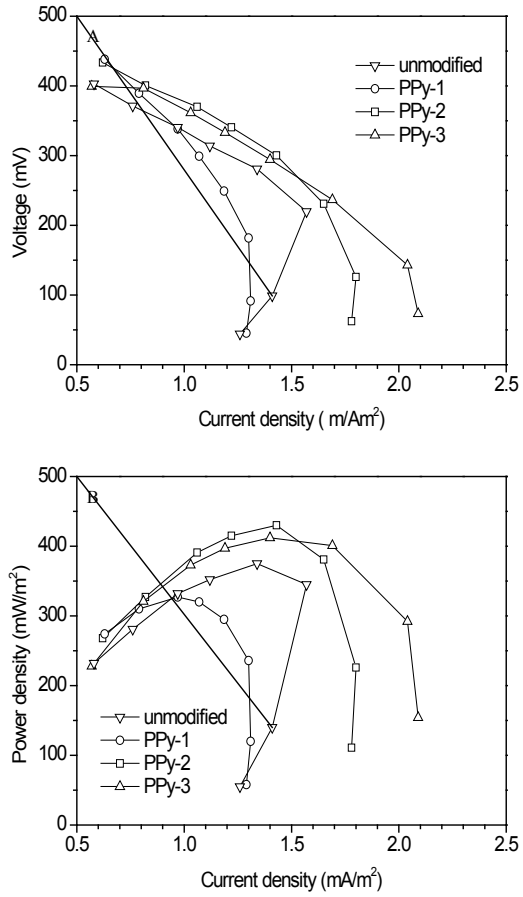

Figure 4: Polarization curves (A) and power density curves (B) as a function of current density for four MFCs.

the film, which was dependent on the number of CV cycles used during electropolymerization.

Measurement of MFC performance

Figure 3A clearly demonstrates that the open-circuit voltages (OCVs) were higher than the control after the anode modification. Among the modified MFCs, the PPy-1 achieved the highest OCV of 790 mV at about 60 min, which was 100 mV larger than that for the control (690 mV). Electron recovery by the external circuit is a major indicator of MFC performance during substrate degradation, which is reflected by the Coulombic efficiency (Figure 3B). The Coulombic efficiency of the unmodified MFC was 11.9%, and of its values for the three modified MFCs were 13.2% (PPy-1), 14.2% (PPy-2) and 14.6% (PPy-3), respectively. Thus, the anode modification improved the MFC performance.

Figure 4 shows the polarization curves (A) and power density curves (B) for the four MFCs using steady discharging method [15]. The anode modification increased the maximum output voltages of PPy-1 and PPy-2 MFCs to 438 mV and 434 mV, 8.7% and 7.7% higher than that for the control (403 mV), respectively. The maximum output voltage of the PPy-3 MFC was 399 mV, slightly lower than that for the control. Although the maximum output voltage of PPy-1 MFC was the highest at the beginning, the voltage dropped quickly with the change of the resistance. The power density of PPy-2 peaked at 430 mW/m^2, which was 15% higher than the control (375 mW/m^2).

MFC	COD removal efficiency (%)				
Initial COD (mg/L)	1010	1019	1023	1045	average
unmodified	57.9	60.5	57.8	57.7	58.5
PPy-1	62.3	64.5	71.8	64.0	65.6
PPy-2	59.9	59.7	68.9	57.8	62.6
PPy-3	61.9	61.5	69.6	64.0	64.3

Table 1: COD removal efficiencies of four MFCs.

Table 1 summarizes COD removal efficiencies before and after the anode modification. The average COD removal efficiencies after the anode modification were 65.6%, 61.6% and 64.3%, all higher than that for the control (58.5%).

Conclusions

This work showed that the electropolymerization method was an effective method to modify MFC anodes for improved MFC performance in terms of power generation and wastewater treatment (COD removal) efficiency. It was found that: (1) The graphite felt was successfully modified by nano-polypyrrole through electropolymerization and the reaction time increases led to thicker films, (2) the maximum output voltages of PPy-1 and PPy-2 MFCs were increased to 438 mV and 434 mV, respectively compared with the 403 mV for the control, and maximum power density of the PPy-2 MFC was 430 mW/m^2, a 15% increase compared with the control (375 mW/m^2), (3) the CV analysis showed that much higher redox currents on the PPy-2 and PPy-3 anodes, (4) the EIS analysis indicated that the ohmic resistance of the PPy-2 MFC was the lowest (24 Ω).

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