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Polyaniline Synthesis by Cyclic Voltammetry for Anodic Modification in Microbial Fuel Cells

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In this paper, PANI was electrochemically synthesized on graphite felt by cyclic voltammetry (CV), and PANI modified and unmodified graphite felts were utilized as anode of MFCs. The power generation of MFCs, electrochemical activity of graphite felts and anodic cell mass were compared. The maximum power density and the internal resistance of MFC with PANI modified anode were 4 W/m^3 and 156 Ω respectively, yet those of MFC with unmodified anode were 1.7 W/m^3 and 358 Ω. The startup time of MFC with PANI modified anode shortened and the electrochemical activity and cell mass of PANI modified graphite felt were significantly higher than that of the unmodified graphite felt. With no use of manual brushing and Nafion solution, the electrochemical synthesis of PANI by CV on graphite felt for anodic modification improved power generation and reduced the cost of MFCs.

Keywords: Polyaniline; Electrochemical synthesis; Cyclic voltammetry; Microbial fuel cells; Power enhancement

1. INTRODUCTION

Microbial fuel cells (MFCs) have drawn global attention with the property of direct conversion from chemical energy into electrical energy by exoelectrogenic bacteria attached on anode [1-3]. Thus, MFCs have provided various new opportunities for wastewater treatment and power generation. Lots of efforts have been exerted to promote the performance of MFCs in recent years [4, 5]. However, the poor power density, low electron transfer efficiency and high construction cost limit the further application of MFCs [3, 6]. In order to improve the performance of MFCs, multiple approaches for anodic modification have been employed, such as ammonia treatment [7], electrochemical treatment

[8, 9], metal oxide doping [10, 11], and polymer modification [12]. Anodic microbes degrade organic matters and release electrons to anode surface, depending on a complex system of parameters [13-15]. As a result, anodic materials and modifications as a key point influence the performance of MFCs.

With fine performance as one of promising approaches to anodic modification of MFCs, such as improving bacterial adhesion and electron transfer [12, 16], polyaniline (PANI) and polypyrrole (PPY) [17], as well as other sorts of conductive polymer, have been used widely in MFCs [18, 19]. Moreover, traditional electrode modification depends on the means of brushing catalysts manually on electrodes with activated carbon powder or carbon nanotubes doped, which is low-effective and susceptible to individuals [20, 21]. For the purpose to promote MFCs into practical application as soon as possible, any key point of MFCs assembling and electrode manufacturing should reduce the impact of artificial factors to the greatest degree. As a result, new method must be explored to replace traditional electrode modification methods. In addition, the utility of Nafion solution as the binding agent for brushing catalysts on electrodes is indispensable in traditional electrode modification [6, 22]. The high price of Nafion solution clearly contributes to further increase the construction cost of MFCs.

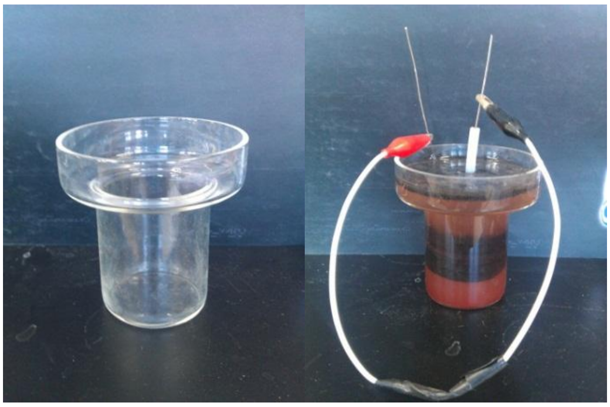
Chemical polymerization and electrochemical polymerization of aniline were the major two approaches for the PANI preparation [23, 24]. Electrochemical polymerization of conductive PANI on electrode has been widely used in previous reports with its low cost and simple operation. In this paper, cyclic voltammetry (CV) was employed for PANI synthesis on graphite felt in H_2SO_4 solution. Then the PANI modified graphite felt was used as the anode of MFCs. The power generation performance of MFCs, electrochemical activity of graphite felt and anodic bacterial morphology were studied to investigate the catalytic property of PANI on anode of MFCs. Compared with the MFCs with unmodified anode, PANI improved the anodic electrochemical activity and electron transfer and promoted the power generation of MFCs. In addition, the further promotion for the electrode modification was no use of Nafion solution and manual brushing for modification, which reduced the cost of MFCs.

2. METHOD AND MATERIALS

2.1 PANI anode preparation

Graphite felt (Sanye Carbon Co., Ltd. China) served as electrode material with the dimension of 5 mm×26.5 cm×5 cm. PANI was synthesized by CV in an upright cylindrical beaker (40 cm in height and 7 cm in diameter), with a saturated calomel electrode (SCE) as reference electrode and a fresh carbon plate (5 cm×5 cm) as counter electrode [12, 25]. CV was carried out by a electrochemical station (CHI660D, Chenhua Instrument Co., Ltd, China) with the potential ranged from 0.8 V to -0.2 V and a scanning rate of 25 mV/s (10 scanning cycles). The electrolyte contained 0.5 mL aniline (Sigma-Aldrich, USA) and 2 mol/L H_2SO_4 (purged with Argon). All graphite felts used in this paper were pretreated by heating at 400℃ for 1 hour and washed by DI water for 3 times [8].

2.2. Microbial fuel cells setup



A **B**

Figure 1. The structure of cell reactor (A) and setup diagram of MFCs.

The diagram of the single-chamber membrane-less cell reactor used was shown in Figure 1A. The bottom anode chamber is cylindrical with 6 cm in height and 4.2 cm in diameter and the upper cylindrical cathode chamber exposed to air is 2 cm in height and 7.6 cm in diameter. The graphite felt was cut into 5 pieces as anode, each 4 cm in diameter. Meanwhile, the cathode was a piece of Pd coated (0.4 mg/cm^2) graphite felt with 5 mm thick and 7.5 cm in diameter. Titanium wire was used for the connection of the external circuit to the electrodes.

MFCs were inoculated with a mixed bacterial culture from other MFCs that was originally inoculated with primary clarifier overflow from Gaobeidian Wastewater Treatment Plant in Beijing and had been running for more than two years [8]. MFCs were fed with a medium containing 0.05 mol/L Sodium acetate in 0.05 mol/L phosphate buffer solution (Na_2HPO_4, 4.09 g/L and $NaH_2PO_4 \cdot H_2O$, 2.93 g/L), NH_4Cl (0.31 g/L), KCl (0.13 g/L), metal salt (12.5 mL/L) and vitamin (5 mL/L) solutions and re-fed with 0.05 mol/L Sodium acetate every three days. MFCs were operated in fed-batch mode at a fixed external resistance of 510 Ω (except as indicated). As shown in Figure 1B, the anodes were immersed in the mixed solution as mentioned above, and one side of the cathodic graphite felt was in contact with the solution and the other side, exposed to the air. All tests were operated at 25℃.

2.3 Analyses and calculations

FTIR spectral analysis of PANI modified and unmodified graphite felt was carried out using an ALPHA Bruker FTIR Spectrophotometer. FTIR spetra of the samples were recorded between 4000 and 450 cm^{-1}. The background spectrum was automatically subtracted from the spectra of the samples.

Cell voltages were measured every 20 minutes using a data acquisition system (AD8251H, Ribohua Co., Ltd, China). The internal resistance and power density were obtained by the method of varying the external resistance (from 5000 Ω to 20 Ω). The current (I) and power density (P) of MFCs under different values of external resistance were respectively calculated by Eq. (1) and Eq. (2):

$$I = \frac{U}{R} \qquad (1)$$

$$P = \frac{U^2}{R \cdot V} \qquad (2)$$

Where, U (V) was the voltages output of MFCs, R (Ω) was the value of external resistance and V (m^3) was the volume of anode chamber. The internal resistance of MFCs was obtained by calculating the slope of polarization curves.

Electrochemical activity of anodic graphite felts was measured by Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) (CHI660D, Chenhua Instruments Co., Ltd, China). The anode with and without inoculation were cut into quadrate pieces (1 cm*1 cm). And these anodic pieces was rinsed with DI water and assembled in a three electrode electrochemical cell filled with the electrolyte (phosphate buffer, pH 7.0, 0.2 mol/L). The electrolyte was purged with Argon before the electrochemical measurements started. A saturated calomel electrode (SCE) was used as reference electrode during the tests.

Anodic cell mass was calculated by measuring bacterial protein concentration. The anodes from stable running MFCs were washed three times in 0.4 L of phosphate buffer (0.05 mol/L, pH 7.0) for 30 min. Cell lysate was extracted by alkaline treatment at 100℃ for 10 min in 1 mol/L NaOH solution and centrifugation at 10,000 g and 5℃ for 20 min [8, 26]. Protein concentration was determined with Bradford reagent at OD660.

3. RESULTS AND DISCUSSION

3.1 FT-IR studies

The graphite felt with PANI was analyzed by FT-IR to investigate the functional groups induced by cyclic voltammetric polymerization. Then the FTIR spectra of PANI modified and unmodified graphite felt was compared. As shown in Figure 2 The relative intensity of the very broad perk at around 1500 cm^{-1} associated with the characteristic absorption of polyaniline quinone diimine group and/or benzene diimine group [27]. The peak at 1272 cm^{-1} indicated the vibration absorption of C-N-C bond in PANI chains. The peak at 1108 cm^{-1} indicated the electron delocalization of PANI, which was the characteristic peak measuring the conductive ability of PANI [28]. And the peak at 1014 cm^{-1} indicated the in-plane bending vibration of C-H bond in benzene ring and the peak at 901 cm^{-1} was recognized the para-substituent absorption peak of benzene. In addition, the peaks at 630 cm^{-1} and 420 cm^{-1} confirmed the vibration absorption peak of aniline C-N and C-H bond. The result obtained by analyzing the FT-IR spectra showed the PANI on graphite felt was major in the form of emeraldine or emeraldine salt [29], which possessed superior conductivity.

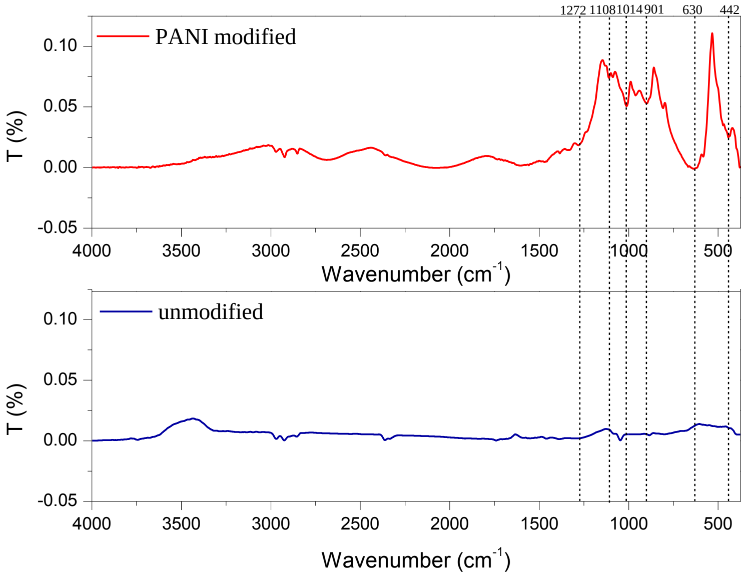
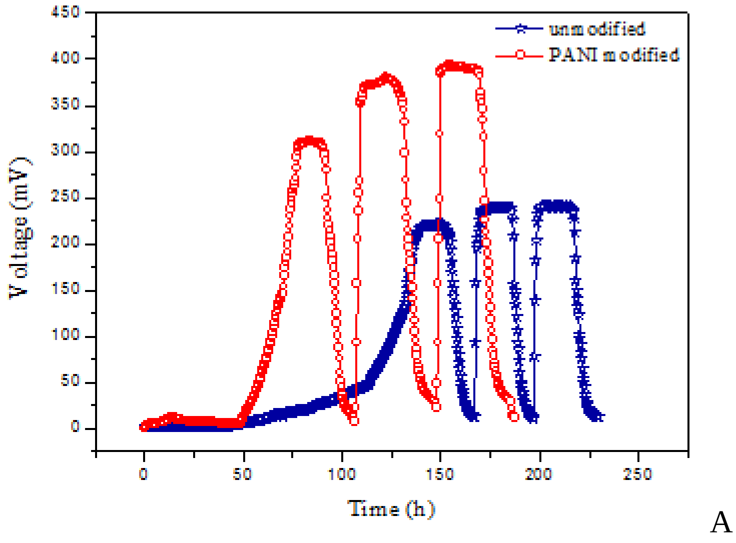


Figure 2. FTIR spectra of unmodified and PANI modified graphite felts

3.2 MFC performance

Figure 3 showed the voltage output curves (A) and power density curves (B) of MFCs with unmodified and PANI modified anode. As shown in Figure 3A, the maximum voltage output of the MFC with Fe modified anode was 392 mV, around 63% higher than the maximum voltage output of MFC with unmodified anode (240 mV). In addition, the startup time of unmodified and PANI modified MFCs was 78 and 140 hours respectively.



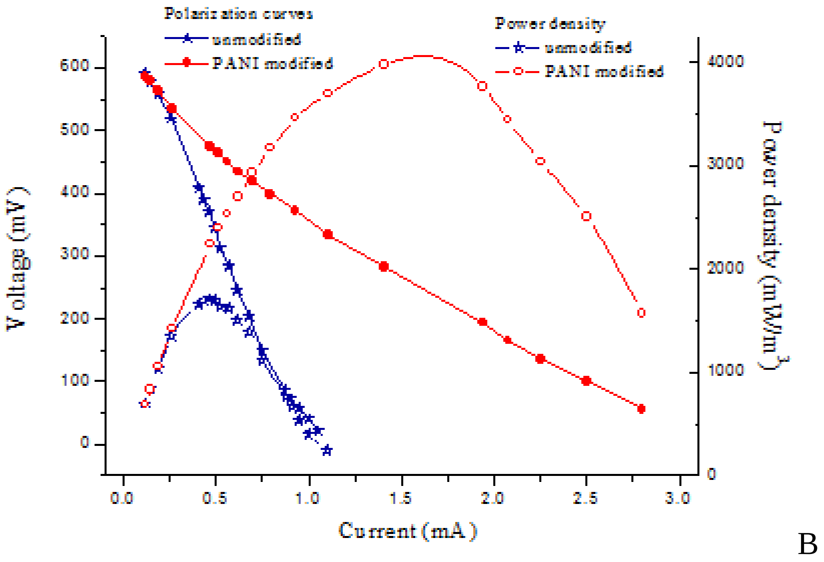


Figure 3. Voltage output curves (A), and polarization curves and power density curves (B) of MFCs

The comparative results of polarization curves and power density curves between unmodified and PANI modified MFCs was obviously distinct as shown in Figure 3B. The internal resistance of unmodified and PANI modified MFCs were 358 Ω and 156 Ω respectively by calculating the slope of polarization curves. And maximum power densities of unmodified and PANI modified MFCs obtained from curves were 1.7 W/m^3 and 4 W/m^3 respectively. The internal resistance and power density of MFC with PANI modified anode were respectively 56% lower and 135% higher than those of MFC with unmodified anode. The result demonstrated the PANI of electrochemical synthesis on graphite felt by CV significantly improved the power generation, reduced the startup time and decreased the internal resistance of MFCs, which was consistent with previous reports [12].

3.3 Electrochemical tests

Cyclic voltammetry and linear sweep voltammetry were employed to investigate electrochemical activities of unmodified and PANI modified graphite felt. In Figure 4A and Figure 4B, the peak area of PANI modified graphite felt was larger than that of the unmodified one, indicating higher electrochemical activity of PANI modified graphite felt. After inoculation, the peak area of PANI modified graphite felt significantly increased and the strong peak current of oxidation and reduction, induced by incomplete oxidation of aniline [29], confirmed much higher electrochemical activity (Figure 4B). On the contrary, the cyclic voltammogram of unmodified graphite felt changed slightly and no distinct redox activity was revealed (Figure 4A). In addition, the linear sweep voltammogram (Figure 4C) showed that the current response of PANI modified graphite felt was much more intensive compared with that of the unmodified, which indicated better conductive ability. As a result, PANI modification enhanced the anodic electrochemical activity and electron conduction.

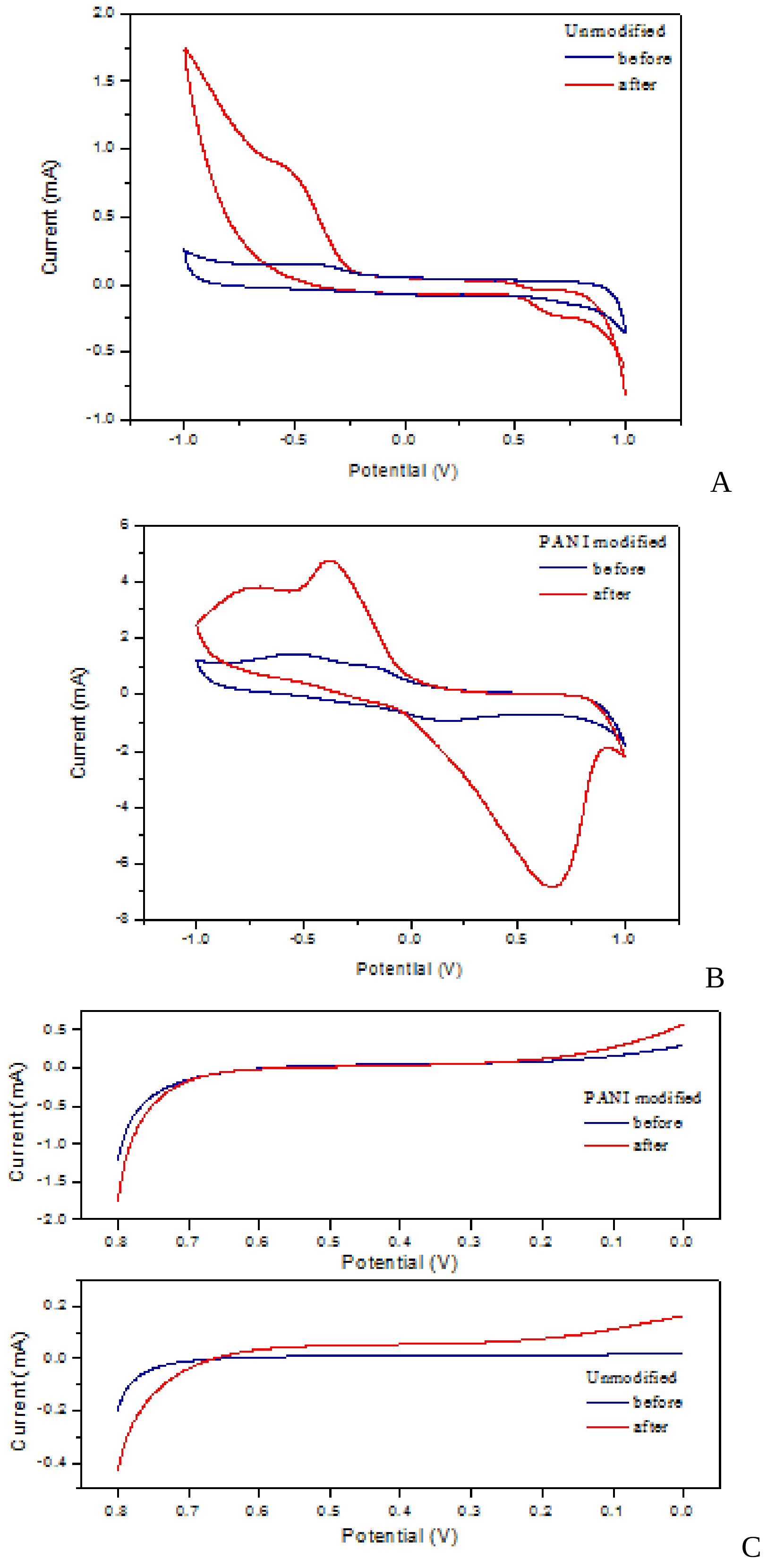


Figure 4. The cyclic voltammograms (A) (B) and linear sweep voltammogram (C) of unmodified and PANI modified graphite felt.

3.4 Anodic cell mass

The cell protein attached on anode surface was measured to investigate the effect of PANI modification on bacterial adhesion. The cell protein mass of PANI modified anode was 1589±16 μg/m^2, which was 20% higher than that of unmodified anode (1323±16 μg/m^2). The results showed that PANI modification could accelerate the interaction between microbes and anode and improve bacterial adhesion on anode, which would promote the power generation of MFCs. In addition, previous studies [12] reported that PANI affected the biofilm development and electron transfer property and promoted the bacterial adhesion and biofilm formation. The results revealed that PANI modification increased anodic bacterial adhesion and elevated the power generation of MFCs.

4. CONCLUSION

The electrochemical polymerization of aniline by cyclic voltammetry on graphite felt was employed to prepare PANI modified anode of MFCs. The MFCs performance and tests results showed the PANI on anode elevated the electrochemical activity, improved anodic bacterial adhesion, reduced the startup time and enhanced the power generation of MFCs. The method for anodic preparation of MFCs reduced the cost of construction and simplified the procedure of anodic preparation compared with previous anodic preparation.

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