Electrochemical preparation and application of PANI/MWNT and PPy/MWNT composite anodes for anaerobic fluidized bed microbial fuel cell

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Abstract

Polyaniline (PANI)/multi-walled carbon nanotubes (MWNT) and polypyrrole (PPy)/MWNT composite anodes were first prepared using electrochemical cyclic voltammetry (CV) method. FTIR and SEM spectra proved that PPy/MWNT and PANI/MWNT were successfully modified on graphite rods, meanwhile, the modified mechanism was also investigated. EIS tests indicated that the R_{ct} values for unmodified anode, PANI/MWNT anode and PPy/MWNT anode were 226.20, 87.93 and 34.95 Ω , respectively, which meant that PPy/MWNT composite anode possessed best electrical conductivity compared with PANI/MWNT anode and unmodified anode. By using PPy/MWNT and PANI/MWNT modified anodes in AFBMFC, the maximum output power density improved by 65.13% and 45.59% compared to that of PPy anode and PANI anode, respectively. Meanwhile, the COD removal rates for the three anodes followed as PPy/MWNT anode > PANI/MWNT anode > PPy anode > PANI anode > unmodified anode.

Keywords Microbial fuel cell · PPy/MWNT · PANI/MWNT · Power density

Introduction

Microbial fuel cell (MFC) is a device of green bio-electricity generation that combines the traditional biodegradation and electrochemical technologies. The chemical energy contained in organic or inorganic pollutants can be directly converted into electrical energy by means of the catalysis of living microorganisms (Logan et al. 2006; Rulkens 2008; Li et al. 2018). As the demand for energy and wastewater treatment constantly increases, more and more attention has been paid to MFC for solving the energy crisis and huge environment pressure.

Recently, a lot of improvements have been made in the technology of MFC. However, inefficient power production is one of the main bottlenecks hindering MFC from being more feasible (Fan et al. 2008; Kong et al. 2011; Kumar et al. 2013). As the carrier for microorganisms, the anode

can influence the amount of attached microorganisms and the efficiency in electron transfer (Qiao et al. 2007). Therefore, it is essential to select potential materials with excellent performance for the modification of anodes which will be helpful to expand the application of MFC.

Some polymers, such as polyaniline (PANI) and polypyrrole (PPy) are outstanding engineering materials with good conductivity, low cost and unique morphology which are also environment-friendly. These materials have been investigated for the improvement of MFC as anode modifiers. Hou et al. (2013) prepared a novel MFC anode by electrochemically reducing graphene oxide and coating PANI nanofibers on the surface of carbon cloth. They found the modified anode can greatly increase the bacterial biofilm loading and the charge transfer efficiency. Zhang et al. (2017a, b) applied carbon cloth with brush-like polyaniline nanowire arrays anode in MFC and the power output improved by 58.1% compared to that of plain cloth. Yuan et al. (2016) synthesized hierarchical multi-walled MnO_2 /polypyrrole/ MnO_2 nanotubes anode by a hydrothermal method and applied the modified anode in MFC. The results showed that the modified anode possessed a large specific surface area and good biocompatibility which could facilitate biofilm growth and promote extracellular electrode transfer between

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the bacteria and the electrode. Carbon nanotubes (CNTs) are superior materials with specific gap structures, outstanding electrochemical character and strong conductivity (Liu et al. 2006; Forrest and Alexander 2007; Mehdinia et al. 2014). The modification of CNTs on the anode of MFC has been widely investigated which can increase the specific surface area of the electrode and reduce the internal resistance with better biocompatibility on the anode surface and faster electron transfer (Liu et al. 2014; Filip and Tkac 2014; Zhang et al. 2017a, b). It also has been proved that multi-walled carbon nanotubes (MWNT) can be easily chemically functionalized by carboxylic groups and possess larger specific areas than CNTs (Thepsuparungsikul et al. 2014; Fan et al. 2017).

In this paper, PANI/MWNT and PPy/MWNT composite anodes were first synthesized by electrochemical cyclic voltammetry (CV) method. The modified anodes were tested by FTIR and SEM tests, and the polymerization mechanism was also investigated. Then the modified anodes were applied in the anaerobic fluidized bed microbial fuel cell (AFBMFC) to examine the production of electricity and the efficiency of wastewater treatment.

Experiment

Materials and apparatus

The anodes are five graphite rods (5 cm, diameter 2 mm) connected with the outer circuit wire by tin welding. The cathode is made of a carbon cloth (3.14 cm², 0.35 mg cm⁻² Pt, 30% wet-proofing). The PPy/MWNT and PANI/MWNT composite anodes were prepared in our laboratory by CHI660C (Shanghai CH Instrument Company, China) and characterized by FTIR (Nicolet 6700, USA) and SEM (JSM-6700F, Japan) tests. Other chemicals used in the experiments were purchased from commercial suppliers.

AFBMFC construction and setup

The schematic diagram of single-chamber AFBMFC is showed in Fig. 1. The anode chamber is a cylindrical plexiglass anaerobic fluidized bed reactor which is 45 mm in diameter and 400 mm in height. 50 g of activated carbon with an average diameter of particle size 0.45–0.9 mm is added into the anode chamber as the carrier media for bio-film. The distributor, a porous glass plate (2 mm thick with a pore size of 2 mm and a fractional perforated area of 20%) is set under the bottom of the chamber. A peristaltic pump (BT600-01, Baoding Qili Constant-flow Pump co., Ltd) is used to send water into the anode cell and then flew water back into the water storage tank from the upper exit of the anode cell to finish a cycle. The speed of water flowing is set at 59 r min⁻¹ and the outer wire is connected to a ZX21

Fig. 1 Schematic diagram of AFBMFC

adjustable resistor. The output voltage is collected by a data acquisition card (USB-1608FS, American measurement) and showed on a computer.

The AFBMFC is inoculated with 50 mL of anaerobic sludge collected from the Wastewater Treatment Plant, Qingdao and was fed with the nutrient buffer solution containing the following: saccharose 1.00 g L⁻¹, NH₄Cl 0.23 g L⁻¹, CaCl₂ 0.123 g L⁻¹, NaCl 0.31 g L⁻¹, KCl 0.33 g L⁻¹, MgCl₂ 0.315 g L⁻¹, K₂HPO₄ 1.30 g L⁻¹, KH₂PO₄ 0.42 g L⁻¹, yeast powder 1.00 g L⁻¹ (Wu et al. 2016). The pH of the solution in anode chamber is initially adjusted to around 7.0. A water storage tank (B-260, Shanghai) is used for maintaining the solution at the temperature of 30 °C. During the investigations, the feed solution was replaced when the voltage dropped below 20 mV, representing one complete cycle of operation.

PPy/MWNT and PANI/MWNT anodes preparation

Before modification, the graphite rods were ultrasonically washed successively in H₂SO₄ solution (1.0 mol L⁻¹), anhydrous ethanol and deionized water to remove impurities. The MWNT (95%, 8–15 nm) was treated with nitric acid during the purification process and then filtered, rinsed with distilled water and dried. The three-electrode system included a working electrode (graphite rod), a counter electrode (Pt electrode) and a reference electrode (saturated calomel electrode). 0.01 mol K₂SO₄, and 0.001 mol pyrrole or aniline and 5% wt MWNT were ultrasonically dissolved in 100 mL distilled water for preparing PPy/MWNT and PANI/MWNT anodes. The graphite rods were coated with PPy/MWNT or PANI/MWNT using the electrochemical cyclic voltammetry (CV) method on CHI660C. The scanning speed was 50 mV s⁻¹, and

the scanning cycle was 16. The composite anodes were washed with deionized water, and then dried in the drying oven.

Electrochemical measurements and calculations

Electrochemical impedance spectroscopy (EIS) measurements were performed and the EIS measurement was conducted in the phosphate buffer solution (0.1 mol L^{-1} , $\text{pH} = 7$). A frequency range of $100 \text{ k} \sim 0.01 \text{ Hz}$ was utilized.

Polarization curves describe the relationship between the voltage and the current. The polarization curve of AFBMFC is measured using the steady state discharge method, during which the voltage is measured after adjusting the resistance. The output voltage is collected by the voltage data acquisition card. The power density can be calculated using the following Eq. (1):

$$P = \frac{UI}{A} = \frac{U^2}{RA} \quad (1)$$

where P (mW m^{-2}) indicates power density, U (mV) is voltage, I (A) indicates current, A (m^2) indicates the size of the anodes, R (Ω) is the external resistance.

The internal resistance r (Ω) of the AMBMFC is calculated by the polarization slope method (Wang et al. 2014). The measurement of the removing rate of organic matter is indicated by the varying COD values of the solution. COD value in the wastewater is measured by the potassium dichromate standard method. The removing rate of COD is calculated as Eq. (2):

$$\text{COD}_{\text{cr}} = \frac{\text{COD}_0 - \text{COD}_i}{\text{COD}_0} \times 100\% \quad (2)$$

where COD_0 represents the initial COD concentration in the feed and COD_i represents the COD concentration as a function of time, COD_{cr} is the removing rate of COD.

Results and discussion

Anode electropolymerization by CV method

The polymerization curves of PANI/MWNT and PPy/MWNT are showed in Fig. 2. As shown in Fig. 2a, obvious redox peaks appeared during the polymerization of PANI/MWNT, which gives an evidence that the PANI/MWNT was polymerized onto the graphite rod. Furthermore, the current values of the redox peaks corresponding to PANI/MWNT polymerization increases with the increase of cycle numbers. This is due to that polyaniline possesses a certain catalytic effect on the polymerization of aniline monomers which enabled the continuous polymerization of aniline to the electrode surface (Wang et al. 2007). In the process of aniline polymerization, the positive charges of the polymerization system need to be balanced, and carbon nanotubes with carboxyl functional groups were modified together onto the graphite rod. As shown in Fig. 2b, reduction and oxidation occur during the PPy/MWNT polymerization process. The peak values of oxidation and reduction are about 0.29 V and 0.48 V, respectively, indicating that the quasi-reversible redox behavior occurs during the polymerization process.

FTIR spectra and electropolymerization mechanism

The FTIR spectra of PANI/MWNT and PPy/MWNT films are showed in Fig. 3. The results indicate that for PANI/MWNT films, the Ar-H adsorption peaks appear at 1038 and 1178 cm^{-1} . The 1300 cm^{-1} peak is assigned to the

Fig. 2 Polymerization curves of **a** PANI/MWNT and **b** PPy/MWNT

Fig. 3 FTIR spectra of PANI/MWNT and PPy/MWNT composites

characteristic adsorption vibration of N-Ar-N structure. The out-of-plane bending wagging of the benzene ring appears at 819 cm^{-1} (Rodrigues et al. 2002). Peaks at 3407 and

1688 cm^{-1} belongs to C=O and -OH groups in acidification MWNT, respectively, and the peaks occur at 1530 cm^{-1} may be due to the -O-N structure between PANI and MWNT (Shen et al. 2012). For PPy/MWNT films, the ring functional group vibration of PPy occurs at 1578 cm^{-1} , and the C-H plane vibration and C-N stretching vibration of pyrrole ring appear at 1305 and 1148 cm^{-1} , respectively. The peak occurs at 3400 cm^{-1} is assigned to the stretching vibration of C=O group. (Zou et al. 2008; Tabaciaraova et al. 2015; Cetiner et al. 2010). These characteristic peaks indicate the formation of PANI/MWNT and PPy/MWNT composite membranes.

Based on the relevant literatures (Wang et al. 2007; Shen et al. 2012; Huang et al. 2016; Iroh and Wood 1997; Zhou and Heinze 1999) and the analyses mentioned, possible electropolymerization mechanisms of PANI/MWNT and PPy/MWNT compounds are shown in Fig. 4. The oxidation of aniline or pyrrole to PANI or PPy is performed by a mediated electron transfer process which can be described as a sequence of adsorption of anilinium and anion on pernigraniline sites. The pyrrole or aniline monomer is oxidized to lose electrons and become free radicals, then protons are

Fig. 4 Electropolymerization mechanism of PANI/MWNT and PPy/MWNT composites

released causing free radical–radical coupling until the chain growth is terminated. In the process of polymerization, the charge of the system needs to be balanced. As the acidification carbon nanotubes possess $-\text{COOH}$ groups, the initiation step is followed by a complexation step, where the radical ion associates with the counterion. Then the free radicals carried the carbon nanotubes onto the graphite rod together.

SEM results

The morphologies of the three anodes are tested by SEM and showed in Fig. 5. As shown in Fig. 5a, the unmodified graphite rod is smoothness which possesses small specific surface and less active sites for microorganism to adhere to. Figure 5b is the SEM image of PANI/MWNT composite anode which presents a loose and porous three-dimensional network structure. This kind of structure possesses large specific surface area and could provide more sites for microbial adhesion. During the polymerization of PPy/MWNT,

pyrrole polymerized with MWNT as the polymerization core, pyrrole radical ions grew around the core and arranged closely. It can be seen from Fig. 5c, the microstructure of PPy/MWNT composite membrane is showed as cauliflowers and the polymerized film has higher density. The structure may increase the attachment sites of the anode for microorganisms to adhere to.

Electrochemical impedance spectra analysis

EIS measurements have been widely applied in resistance assessment mainly including ohmic resistance (R_s) and charge transfer resistance (R_{ct}) (Amin et al. 2007; Quraishi and Rawat 2002). Figure 6 shows the Nyquist impedance plot and equivalent circuit diagram fitting by impedance diagram. The equivalent circuit diagram consists of circuit by R_s , electrode solution interface double layer capacitance (CPE), R_{ct} and weber impedance (W) of charge diffusing through a barrier (Hassan et al. 2007). As shown in Fig. 6,

Fig. 5 SEM images of **a** unmodified anode, **b** PANI/MWNT composite anode and **c** PPy/MWNT composite anode

Fig. 6 EIS of unmodified anode, PANI/MWNT and PPy/MWNT composite anodes

the semi-circles represents the process of electric charge transfer, and the diameters of the semi-circles (R_{ct}) indicating the resistance of charge transfer.

The R_{ct} values for unmodified anode, PANI/MWNT and PPy/MWNT composite anodes are 226.20, 87.93 and 34.95 Ω , respectively, indicating that the composite anodes are more conducive for charge transfer than unmodified anode. Meanwhile, the R_{ct} value of PPy/MWNT composite anode is the smallest which meant best electrical conductivity. These results may be caused by the following rationales. Firstly, as a new type of nano material, MWNT possesses orderly molecule pattern, high specific surface area and low resistance. These features can enhance the dispersion and conductivity of composite anode, thus the R_{ct} values of the modified anodes are much lower than those of the unmodified anode. Secondly, as the tube walls of MWNT possess

highly delocalized π bonds, PPy or PANI with conjugated π bonds can form π - π non-covalent bonds with the exterior walls of MWNT. Then the polymer can provide more free electrons and the moving area of electrons also expands to make the path of electrons and their transfer smoother. Thirdly, the morphologies of PANI/MWNT and PPy/MWNT films are very different, and PPy/MWNT polymerized film has higher density than the three-dimensional network structure of PANI/MWNT which might be better for charge transfer.

Analysis of the production of electricity of MFC

Figure 7 and Table 1 show the polarization and power density curves of AFBMFC equipped with the different anodes. The open circuit voltage of the unmodified anode, PANI anode, PPy anode, PANI/MWNT anode and PPy/MWNT anode are 556.93, 705.52, 725.50, 824.8 and 827.39 mV, respectively. As shown in Fig. 7b, the typical relationship between power density and the current is that the current increases first until the output power reaches the largest and then fall until it reaches the electrode over-potential spot with the ohmic loss. The curves indicate that the largest AFBMFC power density of unmodified anode, PANI anode, PPy anode, PANI/MWNT anode and PPy/MWNT anode are 37.76, 97.46, 122.03, 177.66 and 201.51 mW m^{-2} , respectively. AFBMFC achieves best performance by using PPy/MWNT composite anode. According to the results of EIS measurements, better transfer efficiency of PPy/MWNT composite anode may lead to higher power density and open circuit voltage of AFBMFC. Furthermore, the internal resistance of AFBMFC follows the order as: unmodified anode > PANI anode > PPy anode > PANI/MWNT anode > PPy/MWNT anode. As internal resistance of AFBMFC is one of the main factors affecting the power

Fig. 7 Polarization curves (a) and power density curves (b) of MFC with three anodes

Table 1 Parameters for the performance of AFBMFC

Anode	Fitting equation	r/Ω	U/mV	P/mW m ⁻²
Unmodified	$U = -1790.09I + 556.93$	1790.09	556.93	37.76
PANI	$U = -1315.61I + 688.49$	1315.61	688.49	97.46
PPy	$U = -1121.25I + 703.91$	1121.25	703.91	122.03
PANI/MWNT modified	$U = -1038.05I + 824.8$	1038.05	824.80	177.66
PPy/MWNT modified	$U = -869.09I + 827.39$	869.09	827.39	201.51

generation and power output, the PPy/MWNT composite anode is more suitable for AFBMFC than unmodified anode, PANI anode, PPy anode and PANI/MWNT anode.

Wastewater treatment performance of AFBMFC

The purifying effect of water samples for AFBMFC with different anodes was measured by examining COD. The water samples are simulate wastewater with initial concentration of COD at 2010 mg L⁻¹. Figure 8 shows that the removing of COD is generally fast for all anodes at first but then slows down as time passed by. This process removes organic carbon compounds, depending on a combination of adsorption and biodegradation. The biomass growth was promoted by the biodegradable matter in the water. Adsorption of nutrients, which leads to retention of them on the carbon surfaces, extends contact time between the contaminant and the biomass. This process promotes biodegradation and improves the removal of COD. After analysis, mixed electricity-generating bacteria consume some organic matter. Moreover, some anaerobic bacteria reduce the concentration of organic matter in the wastewater as they produced methane after nitration. When the concentration reduces to a certain amount, mixed bacteria declined accordingly and the removing rate of COD is kept at a low level. The removing rates of COD of the unmodified electrode, PANI anode, PPy anode, PANI/MWNT and PPy/MWNT composite anode after the AFBMFC performed for eight days are 66.89%, 67.43%, 69.92%, 71.79% and 89.92%, respectively.

The results indicates that the treatment effect of modified anodes is better than that of unmodified anode. Modified anodes make organisms stick to them more easily and thus accelerate the consumption of organic matter in the water samples.

Conclusion

PANI/MWNT and PPy/MWNT composite anodes were first synthesized using CV method and applied in the AFBMFC. Then the electricity production and wastewater treatment ability of the composite anodes in AFBMFC were examined. The following conclusions are drawn from the experiments:

- (1) CV electrochemical polymerization is a rapid and effective method for the modification of PANI/MWNT and PPy/MWNT composite anodes, which can not only reduce the consumption of catalyst, but also simplify the synthesis process.
- (2) The PANI/MWNT and PPy/MWNT composite anodes significantly reduce the R_{ct} values and increase the conductivity of graphite rod. Furthermore, PPy/MWNT anode shows better conductivity than PANI/MWNT anode.
- (3) PPy/MWNT anode achieves the best performance in the AFBMFC. The open circuit voltage, internal resistance and the largest power density are 827.39 mV, 869.00 Ω and 201.51 mW m⁻², respectively. And the removing rate of COD is 94.51% after one cycle.

Fig. 8 Curve of COD versus operation time in AFBMFC (a unmodified anode, b PANI anode, c PPy anode, d PANI/MWNT composite anode and e PPy/MWNT composite anode)

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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