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Application of conductive polymers in biocathode of microbial fuel cells and microbial community

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ABSTRACT

Four kinds of conductive polymers, polyaniline (PANI) and its co-polymers poly (aniline-co-o-aminophenol) (PANOA), poly (aniline-co-2, 4-diaminophenol) (PANDAP) and poly (aniline-1, 8-diaminonaphthalene) (PANDAN) were applied to modify carbon felts as the aerobic abiotic cathodes and biocathodes in microbial fuel cells (MFC). Compare to unmodified, all the four polymers can significantly improve the power densities for both abiotic cathodes (increased by 300%) and biocathodes (increased by 180%). The co-polymers with different functional groups introduction had further special advantages in MFC performance: PANOA and PANDAP with –OH showed less sensitivity to DO and pH change in cathode; PANDAP and PANDAN with $-NH_3$ provided better attachment condition for biofilm which endowed them higher power output. With the help of conductive polymer coats, the cathode biofilm became thicker, and according to biodiversity analysis, the predominated phyla changed from β-*Proteobacteria* (unmodified) to α, γ-*Proteobacteria* (modified), which may be responsible for the superiority of the modified MFCs.

1. Introduction

Microbial fuel cell (MFC) was recognized as a promising method of wastewater treatment since they use microorganisms as the catalysts to convert the chemical energy directly into electricity power. However, the poor cathodic oxygen reduction rate, which is considered as the major limiting factor for power generation, hinders the practical application of MFC. In order to decrease the high cathodic overpotential, biocathode, which applies bacteria as the catalysts, was raised and had gained great interests for its low cost and sustainability (Clauwaert et al., 2007).

Cathode material is known to be an important factor for all sorts of cathode in MFC (Wei et al., 2011), including biocathode, since it plays a key role for the oxygen reduction and the biofilm formation. Therefore, to find superior cathode materials is a crucial problem, and is attracting more attentions.

Various materials for biocathode had been investigated. Clauwaert et al. (2007) treated the graphite felt cathode with manganese oxides to decrease the MFC startup period by 30% versus a non-treated one. You et al. (2009) used graphite fiber brush with high specific area as biocathode to increase the amount of biomass, which gained power density of 68.4 W/m^3. Zhang et al. (2011) applied graphite fiber brush together with graphite granules as biocathode, which could shorten the startup time and increase the power output comparing with the individual. Carbon nanotube/chitosan nanocomposite was used as biocompatible biocathode material by Liu et al. (2011) to improve power density by 130% compare to the unmodified cathode.

Conductive polymer polyaniline (PANI), was widely used in electronics, due to its high conductivity at room temperature and environmental stability. Some new co-polymer materials based on PANI such as poly (aniline-co-o-aminophenol) (PANOA), poly (aniline-co-2, 4-diaminophenol) (PANDAP) and poly (aniline-1, 8-diaminonaphthalene) (PANDAN) had been gradually synthesized, and these functional groups introduction can change the characteristics of primary PANI, which also endowed these co-polymers excellent performance in electrochemistry research (Mu, 2004; Li et al., 2011a).

Taking into account that PANI and its co-polymers have the ability of catalytic oxidation of oxygen and good biocompatibility (Khomenko et al., 2005), these materials seem to have the potential to improve the biocathode in MFCs.

Moreover, the biofilm on electrode is another crucial factor for the MFC performance. And the various electrode materials also influence the biofilm activities and the potential of attachment surface. However, electrode-oxidation bacteria which can catalyze cathodic reductions in cathode biofilm are rarely studied, and the information on the electron transfer mechanisms for biocathode is limited (Lovley, 2008).

In our previous study (Li et al., 2011b), conductive polymer modified anodes were prepared and their biodiversity were

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investigated. For the present work, PANI and its three co-polymers with different functional groups introduction, (PANOA with –OH, PANDAP with both –OH and $–NH_3$, PANDAP with $–NH_3$) were applied in modifying the abiotic cathodes and biocathodes, and their catalysis of oxygen reduction ability and biofilm characteristics were studied.

Therefore, the purposes of present study are to: (1) Investigate the effects of different conductive polymers modified cathodes (both abiotic cathode and biocathode) on MFC performance. (2) Discuss the relationship between the conductive polymer materials and cathode biofilm biodiversity. (3) Explore the further advantages of the functional groups on the conductive polymer modified MFC cathodes.

2. Methods

2.1. Cathode material preparation

The carbon felt with the size $4 \times 3 \times 0.3$ cm was used as basic material for cathode. Before polymerization, all the carbon electrodes were soaked into 0.1 M HCl for 24 h, and washed by purified water, and then treated by ultrasonic for 60 min in order to drive away the air in carbon felt.

Refer to the previous literature (Zhang et al., 2007), the four kinds of conductive polymer coated cathodes were prepared as:

The PANI modified cathode: carbon felt electrodes was submerged in 200 mL HCl (1 M). Aniline (0.08 mol) and ammonium persulfate (APS, 0.08 mol) were added and then stirred constantly for 8 h of polymerization by a magnetic stirrer. Washed the coated electrode by distilled water till the filtrate to colorless and then dried in ovens at 50 °C for 24 h.

The other three co-polymer modified cathodes are prepared same as above except for (respectively):

- PANOA: O-aminophenol (0.008 mol) was further added.
- PANDAP: 2, 4-diaminophenol (0.004 mol) was further added.
- PANDAN: 1, 8-diaminonaphthalene (0.004 mol) was further added.

2.2. Operation of MFC reactors

10 H-type two chamber MFC reactors were operated simultaneously in parallel. The MFC configuration is same as the previous described (Li et al., 2011b). Anode material was the primary carbon felt identical as cathodes (unmodified).

All the MFC anode chambers were inoculated by anaerobic digester sludge. The anode medium contained (per liter): KCl (0.13 g), NaH_2PO_4 (4.22 g), Na_2HPO_4 (2.75 g), $(NH_4)_2SO_4$ (0.56 g), $MgSO_4{\cdot}7H_2O$ (0.2 g), $CaCl_2$ (15 mg), $FeCl_3{\cdot}6H_2O$ (1 mg), $MnSO_4{\cdot}H_2O$ (20 mg) (You et al., 2009), and 1 g/L sodium acetate, and 1 ml/L of trace elements solution (Logan et al., 2005). The cathode medium was same as anode except for replacing the sodium acetate by 2 g/L $NaHCO_3$ (pH of both medium adjusted to 7.0 before use).

Each kind of cathode material (Four conductive polymers modified and one control) corresponded to two MFC reactors.

Group A (abiotic cathode), five MFC reactors with different cathode materials (mark as AR1, AR2, AR3, AR4 and AR5 for the unmodified, PANI, PANOA, PANDAP and PANDAN modified cathode separately), operated in abiotic cathode mode (without microorganism inoculation in cathode) for the whole experiment process.

Group B (biocathode), another five MFCs (correspondingly, marked as BR1, BR2, BR3, BR4, BR5), were inoculated by aerobic sludge in cathode after 200 h startup period.

Except for cathode material, all the MFC reactors hold the totally same operated condition at room temperature 25 °C. The external resistor was fixed at 1000 Ω, and both anode and cathode electrolyte with substrates, were replaced every 4 days (before original substrate depleted).

2.3. Electrochemical calculations and analysis

The voltage was collected by a multimeter, And the current, the power density (normalized to the cathode projected surface area, unless stated otherwise) were calculated as previous (Logan et al., 2006). Polarization curves for each MFCs were generated by changing the external resistance in the range of 10–8000 Ω.

2.4. DO and pH influence

The pH of cathode electrolyte was adjusted to 7.0, 7.4, 7.8, 8.2, 8.6 by NaOH (but retain the same conductivity with KCl), and for each pH stage, the two groups of MFCs operated for at least 8 h.

Dissolved oxygen (DO) concentration of cathode chamber was stabilized at a certain value (from 8.0 to 2.0 mg/L) by controlling aeration, each stage operated for at least 8 h.

2.5. Characterization of modified cathode

Infrared spectra of each modified cathode surface were obtained by attenuated total reflection (ATR) method. And the morphology of all cathode surfaces was observed by scanning electron microscopy (SEM) before and after biofilm attachment.

2.6. Bacterial community analysis on cathode

For Group B, at the 60th day after cathode inoculation, biofilm samples of all cathodes were scraped. PCR was performed after DNA extraction (Zhou et al., 1996), with the primers 518r and 338f (with GC-clamp) under the following conditions: 94 °C/5 min denaturation step; 30 cycles of 94 °C/40 s, 58 °C/40 s, 72 °C/55 s; and a final extension step at 72 °C/10 min. DGGE was performed as described previously (Li et al., 2011b). Some representative DGGE bands were cut for sequencing and blasted with NCBI.

3. Results and discussion

3.1. Cathode characterization

The infrared spectrum fingerprint spectrum of modified cathodes was shown in Fig. S1. For all these four conductive polymers, the peaks around 1140 and 1580 cm^{-1} showed the existence of quinoid ring. The feature which appeared at around 1450 and 1300 cm^{-1} provided the evidence of benzenoid ring. The weak peak near 1240 cm^{-1} indicated the four conductive polymers were at proton-doped state. These band positions in the spectrum were in agreement with previous literature (Karthikeyan et al., 2009). However, there were some shifts for these bands owing to the occurrence of copolymerization.

Besides molecular chain of PANI, the absorption peak around 3580 cm^{-1} confirmed that phenolic hydroxyl groups were successfully introduced to PANOA and PANDAP. On the other hand, the peak 3200–3500 cm^{-1}, which corresponds to the characteristic N–H stretching vibration, demonstrated the introduction of amino groups to PANDAP and PANDAN.

Therefore, from Fig. S1, the four kinds of materials were successfully coated on the carbon felt cathode surfaces.

In this experiment, all the conductive polymer materials were synthesized based on same amount of aniline (0.08 mol and 200 ml). It focused on the comparison of different conductive