



Anthraquinone-2-sulfonate immobilized to conductive polypyrrole hydrogel as a bioanode to enhance power production in microbial fuel cell



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ABSTRACT

In this study, anthraquinone-2-sulfonate (AQS), a redox mediator, was covalently bound to conductive polypyrrole hydrogel (CPH) via electrochemical reduction of the *in-situ*-generated AQS diazonium salts. The porous structure and hydrophilic surface of this CPH/AQS anode enhanced biofilm formation while the AQS bound on the CPH/AQS anode worked as a redox mediator. The CPH/AQS bioanode reduced the charge transfer resistance from 28.3 Ω to 4.1 Ω while increased the maximum power density from 762 \pm 37 mW/m² to 1919 \pm 69 mW/m², compared with the bare anode. These results demonstrated that the facile synthesis of the CPH/AQS anode provided an efficient route to enhance the power production of microbial fuel cell (MFC).

1. Introduction

Microbial fuel cell (MFC) is a novel electrochemical device that directly converts chemical energy from organic matters into electrical energy via the catalysis of electrochemically active microorganisms. This technology has showed a promising potential for various applications, such as wastewater treatment, power production, environmental monitoring, chemical synthesis and bioremediation (Oliveira et al., 2013). The practical applications of MFCs, however, are restricted because of the rather low power production, due to the slow oxygen reduction at the cathode, the low ionic conductivity of the solution and the lack of electroactive biofilm formation on anode.

Anode plays an important role in the power production of MFCs. It serves as the electrochemically active biofilm carrier and consequently affects the biofilm formation. Up to now, a variety of carbon materials, such as carbon cloth, carbon fiber, carbon paper and graphite felt, have been intensively employed in MFCs due to their high conductivity, high specific surface area and strong stability. These materials, however, display quite low biocatalytic activities in MFCs (Lai et al., 2011). Accordingly, preparation of anode with high biocatalytic activity is expected to improve the power production of MFCs.

Recently, there is a growing interest in conducting polymer anodes in MFCs because of the enhanced electrochemically active bacteria loading (Lai et al., 2011). Typically, these materials possess porous structure that allows more microorganisms to be attached on the anode surface (Lai et al., 2011). These conducting polymers, however, are physically adsorbed on the anode surface via weak force which can

easily be desorbed or coated on the anode by binders such as polytetrafluoroethylene and Nafion, which are prohibitively expensive (Lai et al., 2011). Conducting polymer hydrogel, having the properties of both hydrogels and conducting polymer, showed excellent catalytic activity in electrochemical devices (Pan et al., 2012). However, conducting polymer hydrogels for improved MFC anode performance have rarely been reported.

Redox mediators have been physically immobilized on the anode surface to boost the power production of MFCs by improving mediated electron transfer rate (Lowy et al., 2006). However, the current output decreases over time because the mediators can easily be desorbed under regular experimental circumstances. Covalently grafting redox mediators onto the anode surface can solve this problem and ensure the long-term stability of the modified electrodes (Tang et al., 2014).

In this work, a facile and scalable method was employed to prepare conductive polypyrrole hydrogels (CPH). Furthermore, anthraquinone-2-sulfonate (AQS), a redox mediator, was covalently immobilized onto CPH via electrochemical reduction of the *in-situ*-generated aryl diazonium cations (Allongue et al., 1997). The biofilm formation, anodic electron transfer and electricity production of the CPH/AQS used as a bioanode in MFC were investigated.

2. Materials and methods

2.1. Preparation of the CPH/AQS anode

CPH was synthesized via the commonly used ammonium persulfate

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oxidation using phytic acid as the crosslinker and dopant (Liu et al., 2013). In particular, 0.084 mL pyrrole monomer and 0.184 mL phytic acid solution (50%, wt% in water, Sigma Aldrich) were firstly mixed with 2 mL of isopropanol alcohol to produce solution A. Then 0.274 g ammonium persulfate (98%, Sigma Aldrich) was dissolved into 2 mL of DI water to prepare solution B. Both solutions were then rapidly iced to 0 °C, mixed and sonicated for 5 min to form a CPH liquid. Subsequently, a piece of graphite felt (Sanye Carbon Co., Ltd) was dipped into the CPH liquid and then the CPH-coated graphite felt was dried in a vacuum oven. The dried CPH-coated graphite felt was then immersed in DI water and isopropanol alcohol solution to remove the excess inorganics salts and phytic acid.

The next step was to covalently immobilize AQS onto the CPH anode *via* the electrochemical reduction of the *in-situ*-generated AQS diazonium cations. First, AQS diazonium cations were generated by diazotation of 1- aminoanthraquinone-2-sulfonate (10 mM) with NaNO₂ (15 mM) in HCl (0.5 M) solution (Allongue et al., 1997). Then, AQS grafting onto the CPH anode was conducted *via* electrochemical reduction of the *in-situ*-generated AQS diazonium cations by immersing the CPH anode in AQS diazonium cations solution and polarizing at –0.5 V (vs Standard Hydrogen Electrode) for 1 h. Finally, the CPH/AQS anode was sequentially sonicated in acetonitrile and DI water for 10 min each with the purpose of thoroughly removing the physically adsorbed species.

2.2. Characterization of anodes

Surface morphology of the CPH and anodes was imaged by field emission scanning electron microscopy (FESEM) (JSM-6701F, JEOL). The chemical structure of the CPH was analyzed by Fourier transform infrared spectroscopy (FT-IR). Specific surface area was tested by multiple point BET method (ASAP, Micromeritics). Contact angles were measured by goniometer (Rame-Hart 100-00, USA).

Cyclic voltammetry (CV) was conducted in a three-electrode system (CHI660D, Chenhua Instrument Co., China) to study the activity of AQS grafted on CPH surface in an oxygen free phosphate buffer solution (50 mM, pH 7.0) at a scan rate of 50 mV/s. The CPH/AQS anode was the working electrode, whereas a Pt foil electrode was utilized as the counter electrode and a saturated calomel electrode (SCE) was employed as the reference electrode. The CV tests were carried out at a potential range from –0.9 V to 0.1 V (vs. SCE) at room temperature.

Electrochemical impedance spectroscopy (EIS) was performed to determine the anodic resistance of the MFCs under working condition. The test was carried out over a frequency between 100 kHz and 0.1 Hz at the working potential with a perturbation signal of 10 mV when the MFCs were stably running over an external resistance of 50 Ω. The MFC anode was used as the working electrode, whereas the cathode worked as the counter electrode and an SCE placed in the anode chamber was the reference electrode. For comparison, bare anode and CPH anode were also studied for all the characterization tests.

2.3. MFC construction and operation

Dual chamber MFC was fabricated as previous report using proton exchange membrane (Nafion 117, 4 cm × 4 cm) as the separator (Tang et al., 2014). The total volume of each chamber (4 cm × 2 cm × 4 cm) was 32 mL. The CPH/AQS anode and Pt/C cathode (0.5 mg Pt/cm², 4 cm × 0.3 cm × 4 cm) were placed in the anode chamber and cathode chamber, respectively. MFCs using bare graphite felt anode and CPH anode were also constructed exactly the same as the experimental MFC.

Each MFC was inoculated with 10 mL of anodic effluent from another stably running MFC in the laboratory, which was originally started up with primary clarifier overflow from a wastewater treatment plant. Anolyte and catholyte were prepared as previously reported (Tang et al., 2014). The anode chamber was kept under anaerobic condition and the cathode chamber was purged with sterile air (10 mL/

min). The MFCs were operated at 30 °C in a fed batch mode across an external resistance of 200 Ω. The feeding solutions were replaced when the voltage fell below 30 mV. All the tests were conducted in triplicate.

2.4. Analyses and calculations

Voltage output (V) was recorded by a data acquisition system. Polarization and power density plots were acquired by varying the external resistance (R). Current (I) was calculated by $I = V/R$, and power density (P) was normalized to the projected area of the anode surface (S), calculated as $P = V \times I/S$.

Biofilm formation on anodes in stably running MFCs was imaged by FESEM. In order to investigate the bacterial loading more accurately, biomass on the anode surface was quantified by measuring bacterial protein using Bradford protein assay at 595 nm. In order to remove the biofilm and adsorbed species, the anode was treated with 1 M NaOH for 10 min at 100 °C and then was ultrasonicated for 20 min.

3. Results and discussion

3.1. FT-IR and morphology characterization of the modified anode

The absorption peak at 1551 cm⁻¹ from the FT-IR spectra of the CPH was attributable to the stretching vibration of C=C bonds in the polypyrrole rings. The peaks at 1044 cm⁻¹ and 1307 cm⁻¹ were owing to the C–H in-plane vibration. The peak at 1189 cm⁻¹ was due to the C–N stretching vibration in polypyrrole. These characteristic peaks validated that polypyrrole hydrogels were produced *via* ammonium persulfate oxidation (Shi et al., 2014).

SEM images of the as-synthesized CPH revealed that this material displayed a porous structure. The CPH demonstrated micrometer- and nanometer-sized pores (average pore size of 30 nm). The porous structure could offer higher specific surface area for electroactive bacteria to form the biofilm and enhance the mass transfer in the anode. The specific surface area of the bare graphite felt and CPH was about 0.5 m²/g and 37.3 m²/g, respectively. Phytic acid, as both the crosslinker and dopant, played a significant role in the synthesis of the porous structured CPH (Pan et al., 2012). By protonating the nitrogen of polypyrrole, phytic acid could crosslink the polymer chains to form a highly interconnected structure. There was an excess of phosphorous groups in each phytic acid molecule, which indicated that the CPH was hydrophilic (the water contact angle was less than 10° for CPH while it was 130° for graphite felt). It was reported that a hydrophilic surface could enhance the electroactive biofilm formation (Guo et al., 2013). As a result, the porous structure and hydrophilic property of the CPH/AQS was anticipated to have excellent biocompatibility.

3.2. Electrochemical characterization of the CPH/AQS anode

CV was carried out to study the electrochemical properties of the anodes (Fig. 1A). There was no redox peaks for bare or CPH anode. The CPH/AQS anode, however, exhibited an obvious pair of redox peaks. The midpoint redox potential was approximately –0.239 V (vs. NHE), which was very close to the standard redox potential of AQS (–0.225 V vs. NHE). The peak current was linearly dependent on potential scan rate. These CV tests proved that the anode surface area was greatly increased and the AQS was covalently grafted onto the anode surface *via* electrochemical reduction of the *in-situ*-generated AQS diazonium cation.

The AQS density on the anode surface was 1.33–1.75 × 10⁻⁸ mol/cm², calculated from the CV by the previously used method (Seinberg et al., 2008). Compared to anode with anthraquinone (surface concentration of 2.0–5.4 × 10⁻⁹ mol/cm²) adsorbed physically on carbon surface, this covalently bound AQS had a much higher AQS density (Abdelwahab et al., 2009).

EIS is a powerful tool for examining the electrode resistances in

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