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Short communication

Wiring microbial biofilms to the electrode by osmium redox polymer for the performance enhancement of microbial fuel cells

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ABSTRACT

An osmium redox polymer, PAA–PVI–[Os(4,4′-dimethyl-2,2′-bipyridine)$_2$Cl]$^{+/2+}$ that has been used in enzymatic fuel cells and microbial sensors, was applied for the first time to the anode of single-chamber microbial fuel cells with the mixed culture inoculum aiming at enhancing performance. Functioning as a molecular wire connecting the biofilm to the anode, power density increased from 1479 mW m^{-2} without modification to 2355 mW m^{-2} after modification of the anode. Evidence from cyclic voltammetry showed that the catalytic activity of an anodic biofilm was greatly enhanced in the presence of an osmium redox polymer, indicating that electrons were more efficiently transferred to the anode via co-immobilized osmium complex tethered to wiring polymer chains at the potential range of −0.3 V–+0.1 V (vs. SCE). The optimum amount of the redox polymer was determined to be 0.163 mg cm^{-2}.

1. Introduction

In recent years, microbial fuel cells (MFCs) as a promising "green" energy source have attracted great interest among researchers. In MFCs, electricity was generated from organic or inorganic substrates with an aid of living microorganisms. One of the greatest advantages of MFCs comparing with other energy generation systems is that MFCs can utilize a diverse range of environmental fuels such as carbohydrates [1], protein [2], wastewaters [3–5] and even sunlight [6]. This enables MFCs to have great potential for a broad range of applications, particularly in the following areas: (1) power supply for small devices such as sensors, robots, space shuttles, (2) wastewater treatment and energy recovery, and (3) sustainable energy from biomass. However, the practical application of MFCs has been strongly hindered because of their low power output. One of the significant issues contributing to low performance is inefficiency of the anodic processes that involve the interaction between bacteria and the anode, an electron acceptor [7].

The anode surface modification has been demonstrated to be a useful method to improve the efficiency of extracellular electron transport and hence to improve the power output. Previous reports have shown that a number of modifiers are efficient for this purpose which include metal ions [8], mediators [9], conductive polymers [10], nano materials [11] electrospun carbon fibers [12], and flame-treated stainless steel [13]. The importance of microbial anodes is recently reviewed [14].

Another potent method to improve electron transport is to use redox polymers, which have been utilized to conduct electrons efficiently between redox centers of enzymes and the electrode surface [15]. Deeply buried redox centers prevent enzymes from electrically communicating with the outside electrode. [16,17]. With the aid of redox polymers, however, electrons can be conducted by self-exchange of electrons between metal complexes tethered to polymer networks [15]. In this way, efficient electrocatalysts for both anode and cathode have been developed. For example, glucose oxidase was wired to the anode via cross-linked osmium redox polymers [18]. Some O_2 reduction cathodes were also constructed by wiring blue copper enzymes with redox polymers. It was reported that O_2 was catalytically reduced to water under physiological conditions at much smaller overpotential than platinum [19,20]. Thus redox polymers were successfully applied for the construction of biofuel cells using enzymes as biocatalysts [21]. Recently, the concept of electrical wiring has been extended to microorganisms to prepare microbial biosensors [22,23]. Particularly noticeable is the work by Gorton et al. who showed that osmium redox polymers could find their applicability in MFCs. They successfully drew current from single strain microbes such as Gram negative [24,25], Gram positive [26], and Rhodobacter [27]. However, the application of an osmium redox polymer to an MFC with mixed cultures has not been previously reported to our best knowledge.

In this study, we utilized the wiring properties of an osmium redox polymer as a surface combined mediator to achieve high power density

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from MFCs, which is a prerequisite for the MFC to be practically adopted. The catalytic activity of a biofilm was greatly increased in the presence of the redox polymer which led to a large enhancement in power density.

2. Experimental

2.1. Osmium redox polymer and anode preparation

The copolymer of polyacrylamide (PAA) and poly(N-vinylimmidazole) (PVI) having osmium redox complex, PAA–PVI–[Os(4,4′-dimethyl-2,2′-bipyridine)$_2$Cl]$^{+/2+}$ (PAA–PVI–Os) (Schematic 1A) was prepared according to the literature [28]. The anode was prepared by the procedure shown in Schematic 1B. 1.5 mg carbon black (Vulcan XC72) was dispersed in 1 mL distilled water before 40 μL PAA–PVI–Os (6.8 mg mL^{-1}) and 30 μL poly(ethylene glycol)diglycidyl ether were added to make a mixture. The mixture was stirred at room temperature overnight. 0.1 mL Nafion was added to this mixture before modification. The final solution was brushed on carbon cloth and dried at 70 °C. Electrochemical measurements were done in a typical three-electrode electrochemical setup in 50 mM phosphate buffer at pH 7.

2.2. MFC configuration

Single-chamber MFCs with an inner volume of 10 mL were constructed as previously reported with slight modification on the anode [29]. A cylindrical MFC chamber with a length of 1.7 cm and a diameter of 3.0 cm in cathode side and 1.8 cm in anode side was made of plexiglass. The cathode surface area (7 cm^2) was made bigger than that of the anode (2.5 cm^2) in order to avoid that the performance was limited by the cathode size. The cathode was prepared from the 30% wet-proofed carbon cloth with a four layer PTFE coating. The other side of cathode was coated with Pt/C (0.5 mg cm^{-2} Pt) as an oxygen reduction catalyst layer. The anode and cathode were placed on opposite sides of the cell.

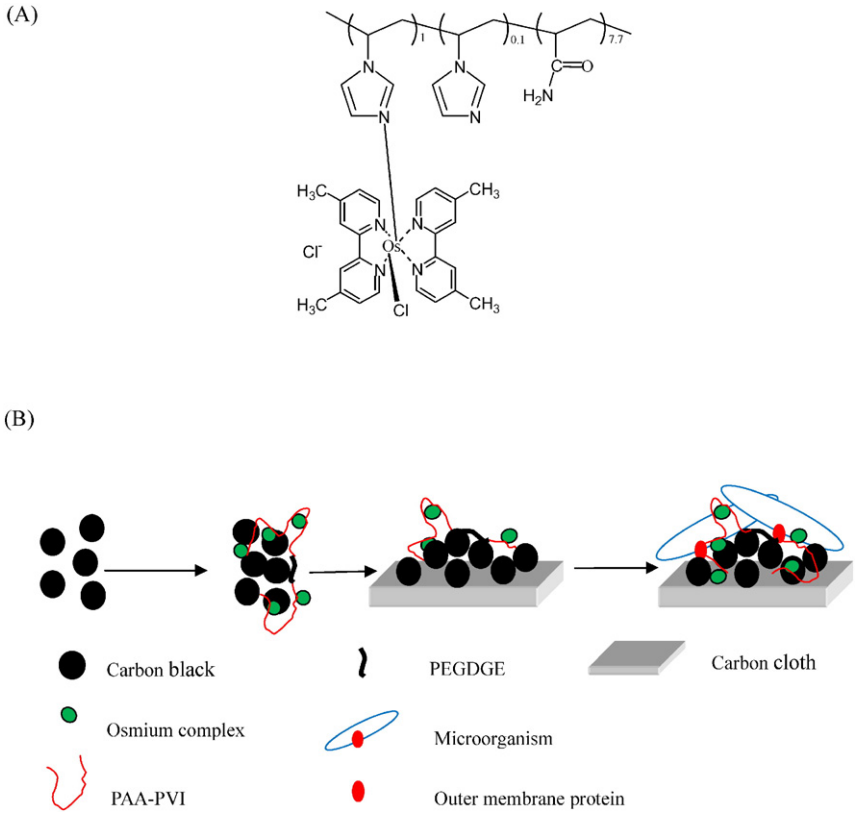
2.3. Enrichment and operation

Reactors were inoculated with 2 mL of activated sludge and 8 mL of sodium acetate (1 g L^{-1}) medium solution. After two or more solution changes with 1 kΩ external resistance loading, the feed solution was switched to a solution containing acetate medium solution only until the similar output voltage was produced over two consecutive cycles. The culture medium solution contained KH_2PO_4 (13.6 g L^{-1}), NaOH (2.32 g L^{-1}), NH_4Cl (0.31 g L^{-1}), NaCl (1.0 g L^{-1}), a vitamin stock solution (12.5 mL L^{-1}) and a mineral stock solution (12.5 mL L^{-1}) [30]. The feed solution was replaced when the voltage dropped below 50 mV, forming one complete cycle of operation. The power density was measured by varying the external resistors. All the measurements were done in triplicate and the average was taken. We found that errors were within 5%. All tests were conducted in a batch mode in a 30 °C incubator.

3. Results and discussion

3.1. Electrochemical characterization of PAA–PVI–Os immobilized on carbon cloth electrode

After the PAA–PVI–Os–carbon black composite was coated on carbon cloth, the cyclic voltammetric feature was disclosed with the scan between −0.3 V and +0.4 V (vs. SCE) (see Fig. 1). A couple of redox peak was presented on the CV with a standard potential of −0.034 V at a scan rate of 10 mV s^{-1}. It was found that the peak currents increased linearly with scan rate. Plot of peak currents vs. scan rates shown in the Fig. 1 exhibited a linear relationship for both anodic and



Schematic 1. The structure of PAA–PVI–[Os(4,4′-dimethyl-2,2′-bipyridine)$_2$Cl]$^{+/2+}$ redox polymer (A) and its modification process on the carbon cloth anode (B). PAA: polyacrylamide, PVI: poly(N-vinylimmidazole), PEGDGE: poly(ethylene glycol)diglycidyl ether.