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Stimulated electron transfer inside electroactive biofilm by magnetite for increased performance microbial fuel cell

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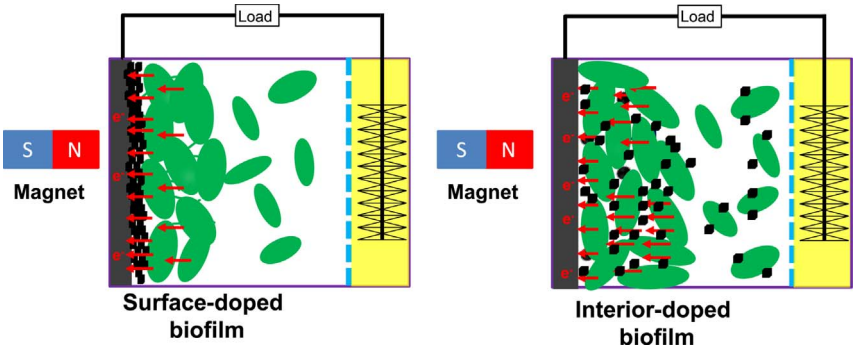
HIGHLIGHTS

- Electroactive biofilm was doped with magnetite interiorly.
- The MFC's power density improved 47% with the magnetite interior-doped biofilm.
- Electron transfer efficiency was improved in interior-doped biofilm.
- Charge transfer resistance reduced by 32% in interior-doped biofilm.

GRAPHICAL ABSTRACT



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ABSTRACT

Inefficient extracellular electron transfer within bioanode leads to low current production by microbial fuel cell (MFC). In this study, magnetite was sprinkled in electroactive biofilm with the aid of magnet field. Magnetite located inside biofilm (interior-doped biofilm) facilitated the electron delivery of electroactive bacteria far away from electrode surface. Electron transfer efficiency was improved by 12% and 37% compared with that of biofilms with magnetite located at the interface of biofilm/electrode (surface-doped biofilm) and that without any magnetite (control biofilm) respectively. The output power density of MFC with interior-doped biofilm ($764 \pm 32\,mW\,m^{-2}$) was greatly increased compared with that of MFCs with surface-doped biofilm ($604 \pm 22\,mW\,m^{-2}$) and control biofilm ($475 \pm 12\,mW\,m^{-2}$). SEM images showed that magnetite evenly distributed inside the interior-doped biofilm and penetrated the electroactive biofilm, which would facilitate extracellular electron transfer across electroactive biofilms and thus improving the bioelectricity production.

1. Introduction

Microbial fuel cells (MFCs) use bacteria as catalyst to convert chemical energy in organic matters into electricity energy, and are considered as a green, efficient and sustainable technology to recovery electricity from wastewater treatment [1–4]. Although MFCs have been used for many fields, such as wastewater treatment and soil remediation, and biosensors, the low power output of MFCs has limited their application [5–8]. It is of great interest that to improve the power extraction by enhancing extracellular electron transfer in MFCs [3,9]. The electroactive bacteria in the anode chamber deliver electrons to electrode surface via multiple extracellular electron transfer (EET) ways [2,10,11]. The electron transfer pathways are spatially and mechanistically heterogeneous for electroactive bacteria in different locations from electrode surface. Electroactive bacteria in close contact with electrode directly deliver the electrons using outer membrane

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cytochromes [12], while for electroactive bacteria far away from electrode surface, electrons transfer mostly relies on conductive nanowire or immobile compounds including riboflavin and quinones [10,13]. Various electrode materials have been applied to improve the electrode physicochemical properties such as surface functionality, stability and electric conductivity, which works to stimulate the interface electron transfer between electroactive bacteria and electrode [14–17]. But as electroactive biofilm grows, most electroactive bacteria are forced away from electrode surface and electron transfer becomes inefficient across the biofilm thickness, and then the current production will be limited again [10].

Highly conductive biofilm can facilitate electrons transfer of electroactive bacteria that are positioned away from electrode surface [18], as it provides intensive electron shuttles and abundance of nanowires, which allow electroactive bacteria to overcome the electron transfer limitation across the biofilm thickness [13,19–21]. Highly conductive biofilms could be obtained by introducing the specific genes and then inducing more electron transfer relative proteins or molecules production through applying genetic switches and related tools [22–24]. For example, heterologously expressing the PilA gene in *Geobacter sulfurreducens* yielded highly conducive biofilms and thus the electricity output was greatly improved [23]. However, operating genetic switches it too complicated for practical bioelectrochemical reactors. Nano-materials such as reduced graphene oxide (rGO), hematite and carbon nanotube (CNT) powders could be served as additional conductive networks and electroactive biofilms doped with these materials exhibited high electron transfer efficiency [25–27]. The doping process mainly relied on the capture of rGO/CNT by the bacteria and the electrode. But the weak force between the material and electroactive bacteria/electrode led a low doping efficiency. Moreover, the doping was inefficient for mix-culture bioelectrochemical system, in which non electroactive bacteria would also adsorb doping material and most of doping materials would be waste.

Magnetite, a good conductive iron oxide, had been used to enhance EET in anaerobic digestion where high methane production efficiency was obtained as the elevated conductance of co-aggregations [28]. Bioelectrochemical reactors fertilized with magnetite could produce a higher current production and more hydrogen [29]. Considering the electron transport within electroactive biofilm was similar to that in *Geobacter* rich co-aggregations [30,31], hence, electroactive biofilm was proposed to be doped with magnetite. A magnetic field was employed in the doping process as the magnetite would migrate fast in the magnetic field and was easily captured by the electrode. Then electroactive biofilm could be doped with magnetite conveniently and efficiently. According to the different locations of magnetite in the electroactive biofilm, three types of biofilms were obtained and referred to surface-doped biofilm, interior-doped biofilm and control biofilm. The electron transfer efficiency of these three types of biofilms was compared and as well as the bioelectricity output of MFCs assembled with the three biofilms.

2. Materials and methods

2.1. Preparation of the magnetite nanoparticle

To prepare uniform magnetite (Fe_3O_4) nanoparticles, the following experiments were performed [32]. Firstly, 0.85 mL of 12.1 mol L^{-1} HCl was mixed with 25 mL of ultrapure, deoxygenated water (18.2 MΩ in resistance and bubbled with nitrogen gas for 30 min). Then 5.2 g of $FeCl_3$ and 2.0 g of $FeCl_2$ were successively dissolved in the prepared solution with mechanical stirring. NaOH solution (250 mL, 1.5 M) was added in the solution dropwise under vigorous stirring. A magnet was placed near the result black precipitate to collect magnetite in situ and the supernatant was removed. The collected precipitate was rewashed with deoxygenated water and the supernatant was carefully decanted after centrifugation at 4000 rpm for 10 min. This procedure was repeated for three times to purify the magnetite. A Hitachi-600 transmission electron microscope (Hitachi Corp., Tokyo, Japan) was used to observe magnetite nanoparticles and calculate the size. Fig. S1 shows a TEM image of Fe_3O_4 particles.

2.2. MFCs setup and operation

A dual chamber MFC was constructed with two equal rectangular polymethyl methacrylate structure (each with a net volume of 21 mL), separated by a flat cation exchange membrane (Ultrex CMI7000, Membrane International Inc.). The graphite plate (front side with a diameter of 3 cm) was used as the anode and carbon brush as the cathode. The anode substrate contained acetate (1.64 g L^{-1}), plus NH_4Cl (0.31 g L^{-1}), 20 mmol L^{-1} phosphate buffered solution (PBS), $CaCl_2$ (0.1 g L^{-1}), $MgCl_2{\cdot}6H_2O$ (0.1 g L^{-1}), KCl (0.13 g L^{-1}), trace minerals (12.5 mL L^{-1}) and vitamins (5 mL L^{-1}). The catholyte contained 20 mM potassium ferricyanide and 20 mM PBS. Duplicate MFCs were carried out as the parallel experiments. Two biofilms with the magnetite were prepared as follows. In order to obtain surface-doped biofilm, 5 mL of magnetite suspension (6 mM L^{-1}) was added in the anode chamber before inoculum and a magnet was placed near the anode (the magnet field density was about 1180 mT) to attract the magnetite thoroughly. To obtain the interior-doped biofilm, the magnetite suspension (1 mL, 6 mM L^{-1}) was added to the anode every three days after inoculum and the same magnet was also placed near the anode in the whole startup process. When the control group was conducted, the same magnet was also placed near the anode chamber but without magnetite. All MFCs were inoculated with 10 mL of anode effluent collected from a MFC stably operated for a year, and started up with an external load resistor of 1000 Ω. After all MFCs startup, all magnets were removed and the external load resistor was changed to 300 Ω for the comparison of MFCs discharge performance.

Cell voltages across the external resistance were recorded every 30 min using a data acquisition system (AD8201H, Ribohua Co., Ltd). Polarization and power density curves of tested MFCs were obtained by varying the external resistance (R) from 100 Ω to 8000 Ω. Before the measurement, all MFCs were operated at open circuit for 24 h. A saturated calomel electrode (SCE, 242 mV versus the standard hydrogen electrode, Leici Co., Ltd., Shanghai, China) was inserted to MFC anode chamber to measure the anode potential. For each tested external resistance, at least 10 min was remained to obtain a stable voltage output. The cathode potential was determined by subtracting anode potential from total cell potential. Current (I) was calculated by $I = U/R$, where U and R represent cell voltages and external resistance, respectively. Power density (P) was normalized to the projected area of anode surface, and calculated as $P = UI/A$, where A is the projected area of anode surface.

2.3. Electrochemical properties of electroactive biofilms

The electrochemical properties of different electroactive biofilm was characterized with cyclic voltammetry (CV) in a conventional three electrode system, in which the anode served as working electrode, a SCE as reference electrode and the cathode as counter electrode. The CV tests were performed under the turnover condition in which sodium acetate was sufficient. For non-turnover condition, CV tests were performed in the absence of metabolic substrates. Prior to non-turnover CVs measurements, a fixed potential (+0.2 V vs. SCE) was applied to promote the compete oxidation of the acetic in the anolyte. All CV tests were carried out at a potential range from −0.8 V to 0 V (vs. SCE) at room temperature. The electrochemical impedance spectroscopy (EIS) analysis was carried out in three electrode system and at a frequency range from 10 mHz to 1 Hz with perturbation amplitude of 5 mV. All electrochemical tests were performed by using an Autolab potentiostat (PGSTAT 128N, Metrohm Autolab, Netherlands).