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Enhanced *Shewanella oneidensis* MR-1 anode performance by adding fumarate in microbial fuel cell

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HIGHLIGHTS

- Fumarate addition enhanced the electricity generation of *Shewanella* cells.
- Fumarate could promote the bacteria propagation and the anode biofilm formation.
- The riboflavin secretion of *Shewanella* cells was impaired with fumarate addition.

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ABSTRACT

The anode biofilm plays an important role in the microbial fuel cell (MFC) performance, which relies on the catalytic function of the anodic biofilm to transform the chemical energy into electricity energy. In this study, fumarate, as a kind of electron acceptor, is added into the anode system of MFC to figure out its effect on the biofilm formation of *S. oneidensis* MR-1. With fumarate addition, more bacteria are observed on the anode surface, and the power density has been promoted by 2.41 times than that without fumarate. Mechanism analysis shows that the fumarate addition could impair the secretion of riboflavin and inhibit the indirect electron transfer process, by finishing the respiration process with fumarate as electron acceptor, which promoted the bacteria proliferation and the anode biofilm formation.

1. Introduction

Microbial fuel cell (MFC), an emerging technology for simultaneously treating wastewater and recovering electricity energy, has drawn lots of attentions in recent years [1–4]. MFCs are able to generate electricity by oxidizing a variety of organic substrates, including cellulose [5], organic acids [6–8] and pollutants [2,9]. In MFCs, electrons are transferred to anode by bacteria, which possess certain electron transfer pathways that electrically connect intracellular catabolic reactions with extracellular electron acceptors [10,11]. In general, the electricity-generating bacteria could form a layer of biofilm on the anode, which could determine the electricity generation performance of MFC technology.

In MFCs, *Shewanella* species, one of the most widely studied exoelectrogens, have all the known bacterial extracellular electron transfer strategies, i.e. indirect electron transfer (IET) via self-secreted electron mediators and direct electron transfer (DET) via outer membrane cytochrome *c* and nanowire [12,13]. The performance of *Shewanella* biofilm could be affected by many diverse factors [14], including pH, dissolved oxygen concentration, temperature and electrode material [15,16]. *Shewanella,* as facultative exoelectrogens, can propagate and generate electricity under both anoxic and aerobic situations [17–19]. *S. oneidensis* MR-1 is an extensively investigated strain of *Shewanella* species [20]. This bacterium could respire using a wide variety of substrates as electron acceptor, including oxygen, fumarate, nitrate, nitrite, thiosulfate, Fe(III), Cr(VI), dimethyl sulphoxide (DMSO) and trimethylamino oxide (TMAO) [21–23]. Even though as a competing electron acceptor to electrode, oxygen is reported to be able to promote the biofilm formation of *S. putrefaciens* CN32 [14]. For *S. oneidensis* MR-1, oxygen could also increase the biomass proliferation, resulting in an overall increase in electricity generation [15]. A possible reason has been affirmed that, oxygen could promote the bacteria growth and therefore increase the bacteria attachment on anode. Moreover, further research pointed out that oxygen exposure always promotes biomass growth and impedes per-cell extracellular electron transfer (EET) rate. Thus, when the increase of

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biomass overcome the decrease of per-cell EET ability at a certain level of oxygen concentration, higher current generation could be achieved.

Fumarate is another kind of electron acceptor for *Shewanella* bacteria. The electrons, derived from the substrate metabolism inside of the cell, are transferred to the periplasmic fumarate reductase FccA, where fumarate was reduced to succinate [24]. It was reported that fumarate respiration could induce permeability of *S. decolorationis* S12 cell membranes, which could be repaired by switching fumarate-respiration to electrode-respiration [25]. The current output and overall performance of a *S. oneidensis* MR-1 MFC could be modulating the lactate and fumarate concentration, tipping the balance between cells inside and outside the electrode environment [26]. Thus, as another competitive electron acceptor to electrode, fumarate may also promote the *Shewanella* biofilm formation on the anode by increasing the biomass proliferation. However, it was rarely reported the current generation performance of MFCs with pure cultures in the present of fumarate as electron acceptor. In this study, we added fumarate in the anode chamber with *S. oneidensis* MR-1 as exoelectrogen to figure out whether the existence of fumarate would facilitate anode bacteria attachment and promote electricity generation. A two-chamber MFC system has been setup, and the electricity generation and electrochemical performance of the reactors with and without fumarate addition were compared.

2. Experiments

2.1. MFC operation and bacteria culture

Two-chamber MFCs, with volume of 300 mL for each chamber, was separated by proton exchange membrane (Nafion 117 PEM, from Hesen, Shanghai) and used in this experiment (Fig. 1). Carbon cloth (WOS1002, CeTech Co., Ltd) with a size of 1 * 2 cm and a size of 2 * 4 cm were used as anode and cathode, respectively. The anode and cathode were connected to the external circuit via titanium wire.

All MFCs were operated under batch mode with a consistent resistance of 1000 Ω. For the control experiment, the anode medium was 18 mM sodium lactate dissolved in 50 mM phosphate buffer solution (PBS) ($Na_2HPO_4{\cdot}12H_2O$, 10.32 g/L; $NaH_2PO_4{\cdot}2H_2O$, 3.32 g/L; NH_4Cl, 0.31 g/L; KCl, 0.13 g/L; trace minerals and vitamins). For the experimental groups, despite the same ingredient as the control one, 9 mM fumarate was also added into the anode electrolyte. The cathode solution was 50 mM $K_3[Fe(CN)_6]$ dissolved in the PBS solution. All the tests were operated in triplicates. *S. oneidensis* was cultured at 30 °C in LB medium (25 g/L) with shaking at 150 rpm for the chemostat until the optical density at 600 nm (OD_{600}) reached about 1.5 [27,28]. The cells were collected by centrifugation (5000 rpm, 10 min) and washed with PBS for three times. Then, the cells were re-suspended with electrolyte (95% PBS and 5% LB, 18 mM lactate) to desired concentration (OD_{600} = 1) [27]. And 10 mL of the electrolyte were inoculated in the anode chamber of MFC. After a batch operation ended, both the anode and cathode solution were refreshed to start the next batch operation. After the start-up, all the MFC were refreshed with anolyte without fumarate.

2.2. Electrochemical measurements

The voltage of the external resistance connected to the MFCs was recorded at 30 min intervals by a data acquisition system (PISO-813, ICP DAS Co., Ltd.) connected to a computer. Current density (I) was calculated as $I = V$ (voltage)/R (external resistance)/A (anode surface area), and the power density was calculated as $P = V * I$ [29]. Power density and polarization curves were obtained using an electrochemical working station (Metrohm, Autolab, B.V) by varying the applied voltage. Cyclic voltammetry (CV) was conducted by an electrochemical workstation (Metrohm, Autolab, B.V.) with Ag/AgCl electrode and Pt wire as the reference electrode and counter electrode, respectively. The CVs were tested at a scan rate of 1 mV/s and a potential window of −0.6 V to 0.2 V at turnover condition. The Columbic efficiency (CE) of the MFC was calculated as $E = (C_p/C_T) \times 100\%$, where C_p is the total coulombs calculated by integrating the current over the time for lactate consumption, and C_T is the theoretical amount of coulombs that can be produced from the metabolism of lactate, calculated as

$$C_T = bF(\mathrm{mol}_{\mathrm{lactate}}) \quad (1)$$

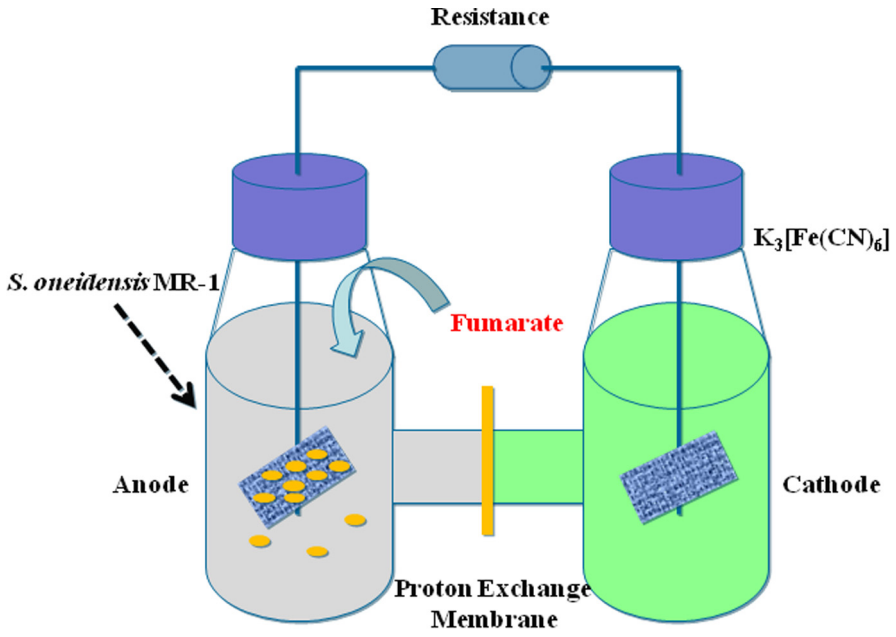

Fig. 1. The schematic picture of the two-chamber MFC used in this experiment.