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Improved performance of air-cathode microbial fuel cell through additional Tween 80

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ABSTRACT

The ability of electron transfer from microbe cell to anode electrode plays a key role in microbial fuel cell (MFC). This study explores a new approach to improve the MFC performance and electron transfer rate through addition of Tween 80. Results demonstrate that, for an air-cathode MFC operating on 1 g L^{-1} glucose, when the addition of Tween 80 increases from 0 to 80 mg L^{-1}, the maximum power density increases from 21.5 to 187 W m^{-3} (0.6–5.2 W m^{-2}), the corresponding current density increases from 1.8 to 17 A m^{-2}, and the resistance of MFC decreases from 27.0 to 5.7 Ω. Electrochemical impedance spectroscopy (EIS) analysis suggests that the improvement of overall performance of the MFC can be attributed to the addition of Tween 80. The high power density achieved here may be due to the increase of permeability of cell membranes by addition of Tween 80, which reduces the electron transfer resistance through the cell membrane and increases the electron transfer rate and number, consequently enhances the current and power output. A promising way of utilizing surfactant to improve energy generation of MFC is demonstrated.

1. Introduction

MFC is a device that transforms chemical energy stored in organic matter into electricity via electrochemical reactions for energy recovery. For electricity production in an air-cathode MFC, four steps are involved: (i) electrons are produced during microbial metabolism in the anode compartment. Specifically, organic matter is oxidized to produce electrons and protons upon the catalysis of the microorganisms; (ii) electrons are transferred from the cell to the anode; (iii) subsequently, the electrons collected in the anode pass through an external load; (iv) electrons arrive at the air-cathode where they combine with protons and oxygen to form water [1].

Although the power generation from MFC has improved considerably in recent years [2–8], it is still a big challenge. The performance improvement of MFC significantly depends on the enhancement of the electron transfer rate from microbe cell to the anode. Microorganisms can transfer electrons to the anode in two ways: (i) one is using exogenous mediators. Recent studies [9–14] have demonstrated that exogenous mediators are partially beneficial for electricity generation and the use of exogenous mediators (e.g. ferricyanide, thionine or neutral red) for electron transfer to the anode is essential for power output. However, exogenous mediators have several drawbacks such as high cost, short lifetime and toxicity to the microorganisms. (ii) The other is cultivating some bacteria which can produce their own mediators or transfer electrons directly to the electrode [15–17]. In a recent study, yeast cells displayed a direct electron transfer capability and increased current generation in a mediator-less MFC. The system can be operated at a high sustained level of activity [18]. These studies suggest that it is feasible to use other mediators or some special microorganisms (e.g. *Shewanella putrefaciens*, *Geobacter sulfurreducens*, and yeast cell) to enhance electricity production in MFCs. Considering that the cell walls and membranes of bacteria contain non-conductive materials, such as lipid or peptidoglycan, it is essential to find out a new approach to further improve the electron transfer rate from cells to the anode and the power production in MFC.

It was recently reported that surfactants can change the cell membrane ultrastructure to form trans-membrane channels, which was effective for enhancing the permeability of microbial cells, reducing the resistance of membranes, expediting the transport of matters through the cell membranes, and increasing the degradation of substrates [19,20]. Accordingly, in this work, an air-cathode MFC inoculated with anaerobic microorganisms was constructed to generate electricity from glucose with Tween 80 added. This study aimed to demonstrate the feasibility of enhancing power output by adding Tween 80, and hopefully provide a new way for improving the performance of MFC. To our best knowl-

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edge, no study about increasing power production of MFC by adding Tween 80 has been reported to date.

2. Materials and methods

2.1. Air-cathode MFC configuration

An air-cathode single-chambered MFC was constructed by a Plexiglas vessel with internal dimensions of 6 cm × 6 cm × 3 cm (total volume of 108 mL, working volume of 100 mL). The cathode (6 cm × 6 cm) containing Pt catalyst (0.8 mg cm^{-2}) was prepared as Wen et al. [21], whereas the anode was carbon felt (6 cm × 6 cm). The surface areas per volume (m^3) of the anode and cathode electrodes were both 36 m^2. The two electrodes had a distance of 3 cm. The water inlet and outlet ports were set up on each side of the vessel. Two ports with an inner diameter of 1 cm were arranged for sampling and installing reference electrode. Insulated copper wires were used to connect the circuit (1000 Ω resistor unless specified otherwise) and all wire contacts were sealed with epoxy resin. The system was sealed carefully to maintain anaerobic microenvironment.

2.2. Microorganisms and medium

Bacteria from another operating MFC were used to inoculate the MFC. A glucose (1 g L^{-1}) medium (conductivity 5.06 mS cm^{-1}) was used that contained the following (per liter): KCl, 130 mg; $NaH_2PO_4{\cdot}H_2O$, 4.97 g; $Na_2HPO_4{\cdot}H_2O$, 2.75 g; and other trace elements required by microorganism growth as reported by Liu and Logan [22].

2.3. Experimental conditions

The MFC was continuously fed using peristaltic pump (BT100-1J, Baoding, China) at a flow rate of 12.5 mL h^{-1} with glucose medium at an 8 h hydraulic retention time (HRT) and a loading rate of 3 kg COD m^{-3} d^{-1}. The substrate containing Tween 80 was replaced until bacteria in the MFC colonized the electrodes and produced electricity steadily. Experiments were conducted at room temperature (24 ± 1 °C), and the pH was kept at 6.8–7.0 through dosing phosphate buffer solution throughout the experiments.

A control test was conducted with sole glucose as substrate under the same conditions. The relationship between Tween 80 concentration and electricity generation was explored by using three concentrations of Tween 80 (5, 20 and 80 mg L^{-1} in 1 g L^{-1} glucose) as substrates and the anode compartment was refilled each time with fresh medium containing 5–80 mg L^{-1} of Tween 80 (as indicated).

2.4. Electrochemical analysis

The output voltage (U) was measured across an external resistor (1000 Ω, unless stated otherwise) using a data acquisition system connected to a computer. Current was calculated according to Ohm's law as $I = U/R$, where U is voltage and R is resistance. Power (P) was calculated according to $P = IU$. Polarization curve was obtained by varying the external resistance over a range of 1–9000 Ω and data were recorded at a time interval of 10 min. Current density and power density were normalized to the MFC volume or electrode surface area (100 mL or 36 cm^{-2}). The anode and cathode potentials were measured using an Ag/AgCl electrode as the reference.

The Coulombic efficiency was calculated using the ratio of total coulombs obtained in the experiment (C_P) to the theoretical amount (C_T) available from COD removal.

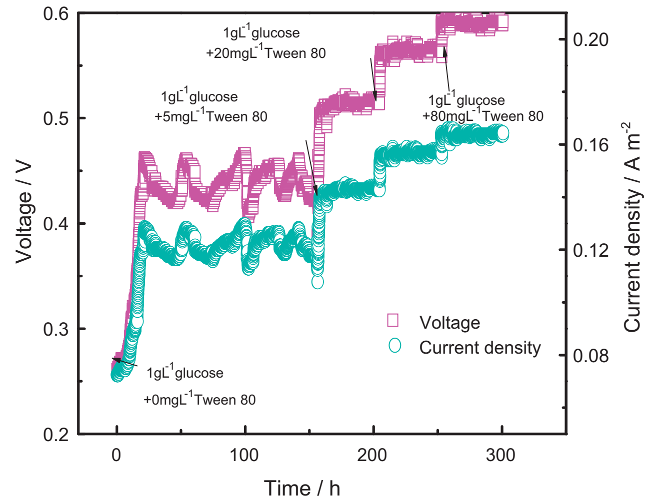

Fig. 1. Continuous voltage and current generation of MFC with different concentrations of Tween 80 at a fixed resistor of 1000 Ω.

Power density (P) was modeled as a function of Tween 80 concentration (S) using the Monod-type equation as

$$P = \frac{P_{\max} S}{K_s + S}$$

where $P_{\max}$ the maximum voltage and K_s the half-saturation constant were determined using the Origin 7.5 with non-linear curve fit.

EIS were performed over a frequency range of 0.01–10^5 Hz at open circuit condition with a perturbation signal of 5 mV using a potentiostat (CHI760C, Chenhua Instruments, Shanghai, China). Two types of measurements were carried out. One was on a two-electrode configuration with the cathode as the working electrode and the anode as the counter electrode, and the other was on a three-electrode configuration with a reference electrode (Ag/AgCl).

3. Results

3.1. Anode bacterial accumulation and power generation from the MFC

During the start-up phase, the anode in the MFC was colonized using anaerobic sludge and a glucose solution (1 g L^{-1}) in a continuous feed operational mode. As is shown in Fig. 1, the voltage gradually increased from 0.261 to 0.461 V and the corresponding current density increased from to 0.075 to 0.128 A m^{-2} at a fixed resistance of 1000 Ω. The maximum voltage stabilized at 0.460 ± 0.005 V during the next 132 h indicating exoelectrogenic biofilm formation.

After the stable power generation was achieved with 1 g L^{-1} glucose, Tween 80 was then added to anode solution of MFC. The voltage of MFC rapidly increased after addition of Tween 80 and reached to a stable value shortly. Both the voltage and current density increased with the increase of Tween 80 concentrations at a high external resistance of 1000 Ω. The voltage was 0.509, 0.561 and 0.594 V at Tween 80 concentration of 5, 20 and 80 mg L^{-1}, respectively. The corresponding current density was around 0.144, 0.158, and 0.165 A m^{-2}, respectively. The stable voltages and current densities were maintained by feeding sufficient amount of substrate directly to anode using peristaltic pump. These results demonstrated that the performance of the MFC was improved in the presence of Tween 80, and the activity of exoelectrogenic biofilm on the anode was not inhibited but improved.

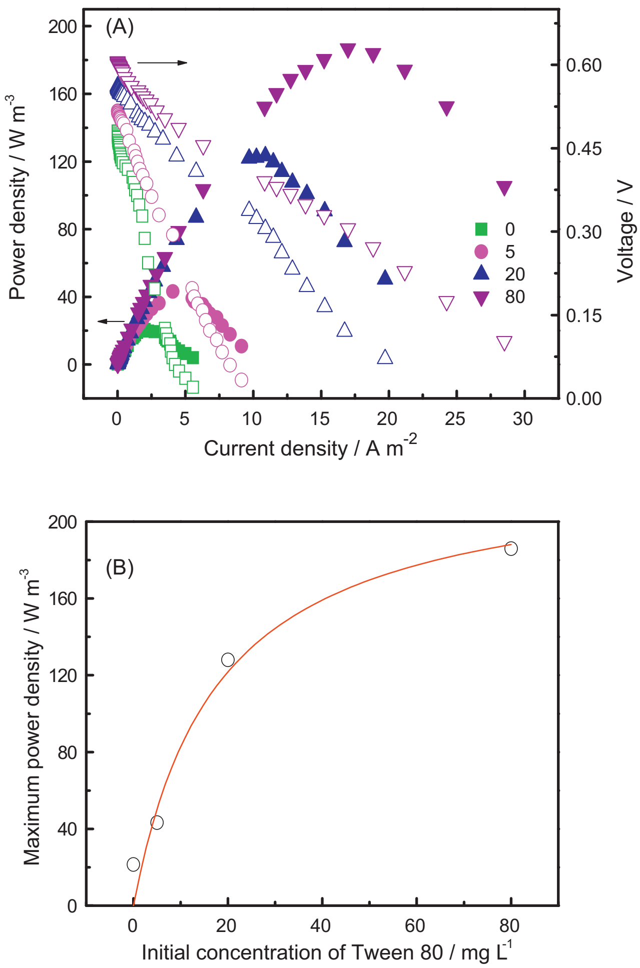

Fig. 2. Performance of MFC. (A) Polarization (hollow symbol) and power density (filled symbol) curves with different concentrations of Tween 80. (B) The maximum power density as a function of initial concentration of Tween 80 based on the simulation with the Monod-type kinetic equation.

3.2. Performance of the MFC

The effect of Tween 80 on the power output in MFC was investigated and results are shown in Fig. 2. It can be seen from Fig. 2(A) that the MFC performance was significantly improved with the increase of Tween 80 concentration. The maximum power densities increased from 21.5 to 187 W m^{-3} when the concentration of Tween 80 increased from 0 to 80 mg L^{-1}. The maximum power density of 187 W m^{-3} achieved with 80 mg L^{-1} Tween 80 at a current density of 17 A m^{-2} was nearly 9-fold that of MFC without Tween 80. When Tween 80 is added, the solution conductivity changed, which was 5.06, 5.10, 5.14 and 5.23 mS cm^{-1} at Tween 80 concentration of 0, 5, 20 and 80 mg L^{-1}, respectively. The solution conductivity increased by 3.4% as the addition of Tween 80 increased from 0 to 80 mg L^{-1}. As can be seen, there was no significant change in solution conductivity as Tween 80 added, which suggested that it was not the solution conductivity change of Tween 80 that played an important role in the improvement of power density.

The influence of Tween 80 concentration was modeled with the Monod-type kinetic equation and the results are shown in Fig. 2(B). The plot of the maximum power density against initial Tween 80 concentration indicated saturation kinetics. A maximum power density of P_{max} = 230 W m^{-3} and a half-saturation constant of K_s = 18 mg L^{-1} (R^2 = 0.968) were obtained. The small half-saturation constant implied that Tween 80 limited the process only at very low concentrations.

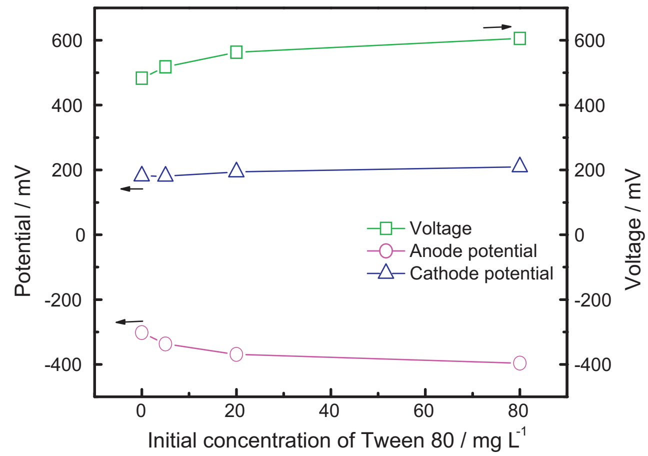

Fig. 3. Effect of Tween 80 on the open circuit voltage of MFC and the open circuit potentials of anode and cathode.

3.3. Open circuit voltage and potentials

To further examine the effect of Tween 80 on the power generation, the open circuit voltage (OCV) of MFC and open circuit potentials (OCPs) of anode and cathode with various concentrations of Tween 80 were measured. The results are shown in Fig. 3. The OCV of MFC was 483 (0 mg L^{-1}), 518 (5 mg L^{-1}), 563 (20 mg L^{-1}) and 606 mV (80 mg L^{-1}), respectively, whereas the anode OCP against the Ag/AgCl reference electrode was around −302 (0 mg L^{-1}), −337 (5 mg L^{-1}), −369 (20 mg L^{-1}) and −396 mV (80 mg L^{-1}), and the cathode OCP was 181.1 (0 mg L^{-1}), 180.7 (5 mg L^{-1}), 193.7 (20 mg L^{-1}) and 209.3 mV (80 mg L^{-1}). Lower anode potential and higher voltage were observed at higher Tween 80 concentration. The increased voltage can be primarily attributed to the decreased anode potential. The overall performance can be improved by optimizing the anode by adding Tween 80.

3.4. Electrode potential

Fig. 4 shows the relationship of anode and cathode potentials with current density of MFC operated with different Tween 80 concentrations (0, 5, 20, and 80 mg L^{-1}). At the current den-

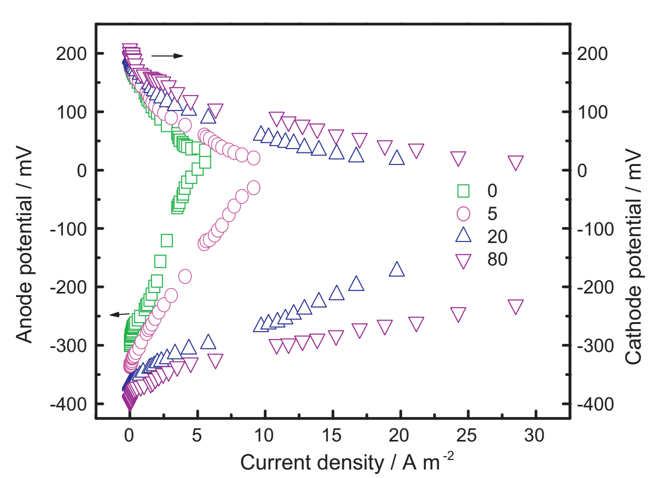

Fig. 4. The influence of Tween 80 concentration on the anode and cathode potentials at different current densities.

sity of 5.5 A m^{-2}, the anode overpotential was 315 (0 mg L^{-1}), 210 (5 mg L^{-1}), 78 (20 mg L^{-1}) and 66 mV (80 mg L^{-1}), respectively, whereas the cathode overpotentials was 143 (0 mg L^{-1}), 120 (5 mg L^{-1}), 104 (20 mg L^{-1}) and 98 mV (80 mg L^{-1}). Increasing the concentration of Tween 80 improved the anode performance (Figs. 3 and 4). Moreover, a further increase in the concentration of Tween 80 can also cause higher cathode potential, however, the cathode potential did not change significantly with the increase of current density. The effect of Tween 80 on the anode and cathode led to the enhancement in power output of MFC, meanwhile, evidence from the anode and cathode polarization curves showed that the anode was mainly responsible for the overall power output.

3.5. Electrochemical impedance spectroscopy

The improvement of MFC performance by addition of Tween 80 requires a better understanding of the distribution of internal resistance within the MFC. Quantification of the changes in individual impedances corresponding to the anode and cell with process conditions is helpful for this purpose. Therefore, changes in the anode and the whole cell impedances were measured using electrochemical impedance spectroscopy. In order to assess the impedances under Tween 80 operation conditions, the EIS analysis was conducted at different Tween 80 concentrations.

Fig. 5 shows the impedance spectra for the anode and the whole cell. The Nyquist plots without Tween 80 showed that the whole cell resistance was about 27.0 Ω, while the anode impedances were 12.6 Ω. With the addition of Tween 80, both of the impedances for the whole cell and anode were decreased. The total impedance of MFC decreased to 16.4, 7.8 and 5.7 Ω when the Tween 80 concentration increased to 5, 20 and 80 mg L^{-1}, respectively (Fig. 5(A)). The impedance associated with the anode also decreased from 8.0 to 2.5 Ω when Tween 80 concentration increased from 5 to 80 mg L^{-1}. The increase in power density might be due to the decrease in the whole cell impedance. However, it should be noted that the continued increase in Tween 80 concentration after that of 20 mg L^{-1} indicated a slow decrease in all the impedances.

3.6. Substrate utilization and Coulombic recovery

Fig. 6 indicates the Coulombic efficiency of the chemical oxygen demand (COD) removal and Coulomb production at an 8 h hydraulic retention time (HRT) with different Tween 80 concentrations. COD removal efficiency increased slowly during the experiments at different conditions (from 57 to 73%). Nevertheless, Coulomb production from 1 g COD significantly increased from 130.5 to 368.1 C g^{-1} when the Tween 80 concentration increased from 0 to 80 mg L^{-1}, thus the improvement for COD removal and especially for electricity generation in the MFC demonstrated that Tween 80 was beneficial to the metabolism of bacteria and activity of enzyme. MFC tests with Tween 80 produced much higher Coulombic efficiency than that without Tween 80 (Fig. 6). Coulombic efficiency of the MFC increased from 10.8 to 36.3% with the increase of Tween 80 concentration from 0 to 80 mg L^{-1}.

4. Discussions

4.1. Tween 80 addition to air-cathode MFC effectively improves power generation

As indicated above, the addition of Tween 80 in MFC effectively enhanced its power density. A maximum power density of 187 W m^{-3} was obtained at a Tween 80 concentration of 80 mg L^{-1}, which was 765% higher than that without Tween 80 (21.5 W m^{-3}) (Fig. 2). Liu and Logan [22] reported that an air-cathode single

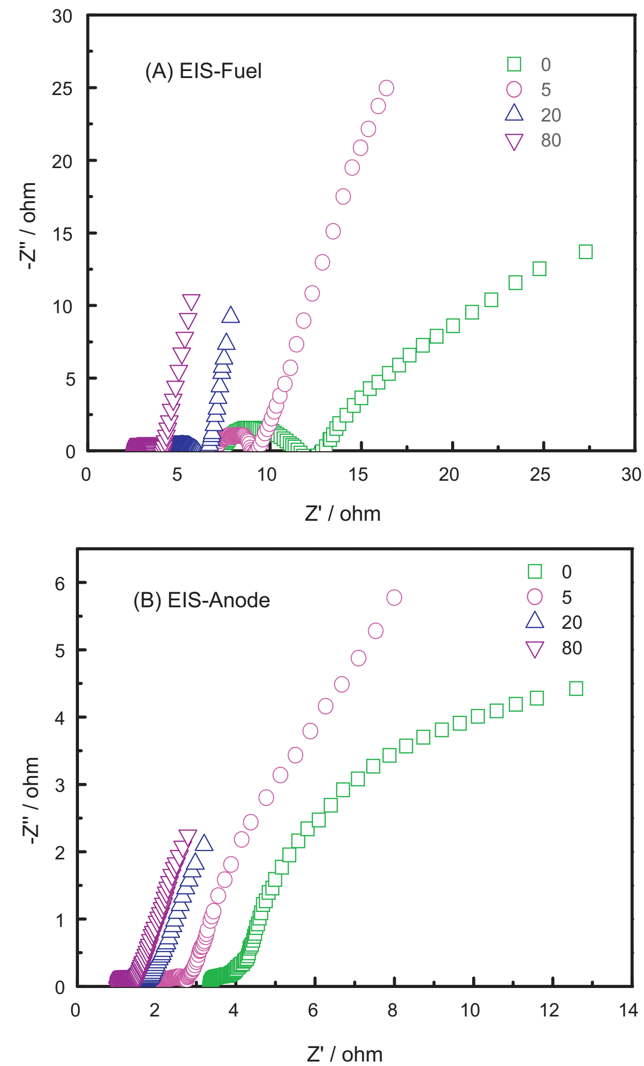

Fig. 5. Nyquist plots for the whole MFC (A) and the anode (B).

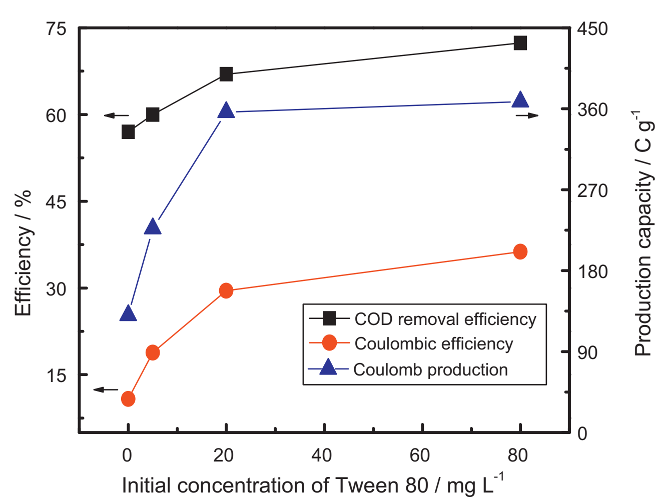

Fig. 6. Effect of Tween 80 on substrate utilization and Coulombic recovery.

chamber MFC using glucose as substrate reached a power density of 494 mW m^{-2} (12.4 W m^{-3}) at a current density of 1.3 A m^{-2}. Feng et al. [23] reported a maximum power density of 20.8 W m^{-3} for a baffled air-cathode MFC with 1 g L^{-1} glucose being fed as substrate.

According to $P_{max} = OCV^2/4R_{in}$, both the reduction in cell losses and the increase in OCVs can explain the improvement of MFC performance (Figs. 3 and 4).

As is shown in Fig. 5, the whole cell impedance decreased from 27.0 to 5.7 Ω as Tween 80 concentration increased from 0 to 80 mg L^{-1}. The changes in electrochemical impedance with Tween 80 concentrations indicated that the addition of Tween 80 could decrease the resistance of MFC, primarily resulting from the decreased electron transfer resistance through membrane and the increased quantity and activity of the exoelectrogenic biofilms on the anode.

According to the metabolic mechanism of anaerobic bacteria in the MFC, the main respiratory chain of electron transfer is in the cytoplasm. The electrons must transfer through the cell membranes to anode to generate current in the external circuit, however, the electron transfer resistance through cell membranes was determined by the composition and performance of membranes. Based on the impact of the surfactant on the microbial membranes [24–26], Tween 80 can increase the permeability of microbial membranes and reduce resistance of the electron transfer through the membranes. These can be considered as a factor leading to the low impedance and high current density. As is shown in Fig. 2(A), each current density under different external resistances with Tween 80 addition was higher than that without Tween 80, for example, at the external resistance of 1 Ω, the current density of the MFC increased from 9 to 28 A m^{-2} as Tween 80 concentrations increased from 5 to 80 mg L^{-1}. Thus, in comparison with 5.5 A m^{-2} without Tween 80 (Fig. 2(A) and Fig. 4), a 6-fold higher current density can be obtained using 80 mg L^{-1} Tween 80 in the MFC system with other experimental conditions remaining unchanged. An analysis of the electron transfer mechanism of the MFC suggests that current production mainly relies on the electron transfer between bacterial cells and electrode. Tween 80 vastly boosted the electron transfer rate from bacterial cells to anode. The ability of Tween 80 for decreasing the resistance of MFC and producing high power density indicated that MFC performance can be improved by adding Tween 80 within a certain range. Moreover, Tween 80 can promote the growth of microorganisms [19]. It has been reported that Tween 80 can be used in bacterial culture to promote passage of compounds (soluble proteins) into bacterial cells [27]. Experiments performed with Tween 80 showed the highest cell density values and maximum specific growth rate of several non-ionic surfactants [28].

On the other hand, the increase of OCV from 483 (0 mg L^{-1}) to 606 mV (80 mg L^{-1}) was mostly due to the decrease of anode OCP from −302 to −396 mV, respectively. The significant decrease in anode potential was possibly due to the improvement in bacteria growth and enzyme activity with Tween 80 addition. Moreover, Tween 80 improved the polarization of the MFC; the anode overpotential decreased from 315 to 66 mV with Tween 80 concentration increased from 0 to 80 mg L^{-1} at the current density of 5.5 A m^{-2} (Fig. 4). From the Nyquist plot of the anode (Fig. 5(B)), the low resistance of anode in the presence of Tween 80 resulted in the small anode overpotential. Since the anode potential is controlled by the kinetics of electron transfer from the microorganisms to the anode, the decrease in anode potential was tightly connected with the decrease in electron transfer resistance in the MFC. Moreover, owing to the fact that Tween 80 not only benefited anode performance but also accelerated the cathode reaction, a further increase in the concentration of Tween 80 caused a higher cathode potential with insignificant change along with the increasing current density (Fig. 4). These results implied that the performance of MFC with Tween 80 was mainly improved by anode operation.

4.2. Tween 80 improved substrate utilization Coulombic recovery

Since COD removal was increased with Tween 80 addition (Fig. 6), Tween 80 might be able to augment degradation rate of organic matter, which is favorable for electrons production in unit time, by enhancing the permeability of microbial membranes. Both the increased electrons production and increscent permeability of microbial membranes resulted in an improved ability of electron transfer, therefore brought in an increase of Coulomb production from 130.5 to 368.1 C g^{-1} (COD) and an increase in Coulombic efficiency from 10.82 to 36.29% when Tween 80 concentration increased from 0 to 80 mg L^{-1}.

5. Conclusions

The unique ability of surfactant (Tween 80) for reducing the resistance in a MFC and improving its energy production was successfully demonstrated in this study. The maximum power density of an air-cathode MFC using 1 g L^{-1} glucose as fuel increased from 21.5 to 187 Wm^{-3} with the increase of Tween 80 concentration from 0 to 80 mg L^{-1}. Tween 80 increased the permeability of microbial cells and substantially reduced the resistance of the MFC, resulting in a significant improvement in current density and power output of the MFC. This study opened up a whole new research opportunity of improving power generation of MFC.

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