An MFC capable of regenerating the cathodic electron acceptor under sunlight

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A renewable MFC (microbial fuel cell) cathode was used in this study because the iodide ion could react with oxygen to generate triiodide under natural sunlight. The feasibility of the regeneration of triiodide ion under natural sunlight and the effect of the regenerated triiodide ion concentration on the MFC performance were studied. The results showed that the power density of the MFC using triiodide ion as cathodic electron acceptor was significantly higher than that of using ferricyanate, and that the iodide ion can be oxidized to triiodide ion by oxygen in air at the expense of natural sunlight. In addition, it was obvious from the experimental results that the MFC performance was improved with the increase of the triiodide concentration, indicating that the concentration of triiodide ion had a critical effect on the MFC performance. The linear sweep voltammetry (LSV) curves for the electro-reduction of triiodide ion on the carbon paper were obtained and the results suggested that the diffusion process of triiodide ions to cathode was the control factor for the MFC performance.

microbial fuel cell, cathodic electron acceptor, triiodide ion

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1 Introduction

Microbial fuel cell (MFC) is a new type fuel cell using microorganism to convert the chemical energy stored in the organic matters to electricity energy. It is considered as a promising alternative power source due to its unique capability of simultaneous wastewater treatment and electricity generation and its prospect of reducing the operating fees for the wastewater treatment [1–3].

The typical structure of MFC is similar to the proton exchange membrane fuel cell (PEMFC) which usually consists of an anode and a cathode compartment separated by a proton exchange membrane (PEM). The anode and cathode compartment were full of anolyte and catholyte, respectively. In the anode compartment, microorganisms oxidize the organic matters in wastewater to produce electrons and protons. The protons migrate from the anode compartment to the cathode compartment through the PEM, while the electrons pass through the external circuit to the cathode compartment. In the cathode compartment, electron acceptors combine with protons and electrons [4].

Although the performance of MFCs has improved significantly in recently years, it is still much lower than that of chemical fuel cells. It was found that the cathodic losses, especially the cathodic activation losses, were one of the most important factors influencing the MFC performance. Hitherto, oxygen is the most widely used cathodic electron acceptor in MFCs due to its unlimited availability in the environment and high redox potential. However, the unfavorable reaction kinetics of oxygen reduction on the surface of carbon electrodes and the low mass transfer coefficient of gaseous oxygen in catholyte severely hamper its application in MFCs [5]. To overcome these disadvantages, many solu-

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ble electron acceptors with high reduction rate on carbon electrodes have been adopted in MFCs, such as hydrogen peroxide, ferricyanide, permanganate and potassium persulfate [6–9]. But all these soluble electron acceptors cannot be renewable. Rhoads et al. [10] used the redox couple MnO_2/Mn^{2+} as the mediator for electron transport from the electrode to oxygen. The manganese dioxide was reduced to Mn^{2+} on the cathode surface, and then the Mn^{2+} was biologically oxidized to MnO_2 by oxygen and deposited on the surface of the cathode. The reaction is described as follows:

$$MnO_{2} + 4H^{+} + 2e^{-} \rightarrow Mn^{2+} + 2H_{2}O \ (E^{0} = +1.28 \text{ V})$$
$$Mn^{2+} + O_{2} \xrightarrow{\text{bio-catalyst}} MnO_{2} + 2e^{-}$$

However, the MFC performance was still low due to the low reduction kinetics of MnO_2 on the carbon electrodes, as well as the slow regeneration rate of MnO_2 . In 2006, Heijne et al. [11, 12] used Fe³⁺ as cathodic electron acceptor and significantly enhanced the MFC performance. The ferric ion combined the electrons to produce ferrous ion, then the ferrous ion could be biologically (*Acidithiobacillus ferrooxidans*) oxidized to ferric iron in the presence of oxygen:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

$$4Fe^{2+} + 4H^{+} + O_2 \xrightarrow{bio-catalyst} + 4Fe^{3+} + 2H_2O$$

The MFC performance improved considerably due to its facile reaction at carbon electrodes and high standard potential. However, the hydrolysis of ferrous ion at a high pH value hinders its application in the field of MFCs.

The iodide/iodine redox couple has proved to be an effective electron mediator in dye sensitized solar cells [13]. Its practical application, however, is hampered partly because of the sluggish reaction rate of iodine reduction on carbon electrodes in organic solvents. It is known that the kinetics of iodine reduction is solvent dependent and are is facile in water. Therefore, this provides an opportunity for the utilization of iodide/iodine redox couple in the MFC cathode. In this paper, the feasibility of using triiodide ion as the cathodic electron acceptor and its regenerating capability under natural sunlight were investigated.

2 Construction of the renewable MFC cathode

The schematic depiction of the renewable MFC cathode is shown in Figure 1. As can be seen in Figure 1, iodide ions are readily oxidized to elementary iodine by oxygen under the sunlight, then the iodine combines with the iodide to form triiodide anion complex (I_3^-) . Because of the facile electrochemical reduction of I_3^- on the carbon electrode [14], it is expected that the MFC using triiodide ions will have a good cathode performance. Additionally, aqueous iodide ion solution itself offers an improved conductivity of the catholyte, hence an improved transfer rate of I_3^- and a reduced



Figure 1 Schematic of the renewable MFC cathode.

ohmic loss in the cathode compartment are achieved. Therefore, using triiodide ions as the cathodic electron acceptor for the MFC offers the advantages of ease of regeneration, high electrochemical activity and good electrode accessibility.

3 Experimental set-up and methods

3.1 Construction of H-type MFC

An H-type MFC fabricated with transparent plexiglass was used in the experiment. The MFC consisted of two equal volume (7.5 cm \times 7.5 cm \times 15 cm) chambers for the anode and the cathode separated by a proton exchange membrane with a radius of 2 cm. Both the anode and cathode electrodes were made of non-wet proof carbon paper (4.0 cm \times 4.0 cm). A copper wire was pressed on the electrode and served as the current collector. In order to minimize the contamination of Cu²⁺ in the anode and cathode compartment, all the copper wires exposed to electrolyte were sealed by epoxy glue. A resistance box was connected between the anode and cathode, and the data were recorded every 10 s by an Agilent 34970 A data acquisition unit connected to a PC.

3.2 Inoculation and MFC startup

The anaerobic sludge used in the experiments was obtained from the secondary clarifier of Banan Wastewater Treatment Plant, Chongqing, China. The fresh anaerobic sludge was purged with N₂ for 24 h to remove the dissolved O₂. For inoculation, 42 mL anaerobic sludge mixed with anolyte medium was injected into the anodic compartment of the MFC in a vacuum glove box. The anolyte medium contained CH₃COONa 2.7 g/L; Na₂HPO₄ 3 g/L; CaCl₂·2H₂O 15 mg/L; KCl 0.1 g/L; NH₄Cl 1.5 g/L; NaCl 0.1 g/L; MgCl₂·7H₂O 15 g/L and other mineral medium [15]. The medium was autoclaved before being injected into the anode compartment, and the anode compartment kept anoxic. After successful startup, the anode compartment was continuously supplied with autoclaved mineral medium and continuously stirred. The flow rate of anolyte medium was 1 mL/min.

3.3 Calculations

The current was calculated according to Ohm's law using the voltage data obtain by the Agilent 34970 A data acquisition unit:

$$I = U / R.$$

The power density (mW/m^2) was calculated as

$$PD = UI / A,$$

where A is the surface of electrode, U is the MFC voltage, and R is the external resistance. Two Ag/AgCl reference electrodes (0.196 V vs SHE) were placed in the anode and cathode compartments to independently measure the individual electrode potentials, and all the anode and cathode potentials in this paper were quoted with respect to the standard hydrogen electrode. The I_3^- concentration was determined from the absorbance of the irradiated solution, measured at 350 nm [16] using Lengguang 756mc spectrophotometer. The linear sweep voltammetry of I_3^- was tested by CHI electrochemical workstation.

4 Results and discussion

4.1 MFC performance with I_3^- as electron acceptor

After the successful startup, the performances of MFC with $I_3^{-}(2 \text{ mM})$ and $K_3[Fe(CN)_6]$ (2 mM) as the cathodic electron acceptor were respectively evaluated. The 2 mM I_3^{-} aqueous solution was prepared by 2 mM I_2 and 0.2 M KI solution. To eliminate the influence of ion strength on MFC performance, 0.2 M KCl was added to the $K_3[Fe(CN)_6]$ solution. The electrochemical reactions of the two cathodic electron acceptors were as follows

$$I_3^- + 2e^- \to 3I^-, E^0 = 0.54 \text{ V}$$
 (1)

$$[\text{Fe}(\text{CN})_6]^{3-} + e^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}, E^0 = 0.36 \text{ V}$$
 (2)

As depicted in Figure 2, the maximum power density of MFC using I_3^- was 451 mW/m², higher than that of MFC using $K_3[Fe(CN)_6]$ (326 mW/m²). It was mainly due to the combined effect of the higher onset potential, the faster reduction kinetics and the higher electron transfer number of the I_3^- reduction reaction compared with those of Fe(CN)₆³⁻. Therefore, the current of MFC with I_3^- as electron acceptor was higher and the performance was better than that of $K_3[Fe(CN)_6]$ used MFC.

4.2 Feasibility tests of regenerating I_3^- under natural sunlight

To validate the feasibility of the renewable MFC cathode,

freshly prepared KI solution (0.2 M, pH=2.0) was used as catholyte and the external resistance was set as 1000 Ω during the experiment, and then the evolutions of I_3^- concentration, cathode potential, anode potential and cell voltage under sunlight were recorded and shown in Figures 3–5.

Figure 3 shows the evolution of I_3^- concentration and cathode potential after the cathode compartment was



Figure 2 MFC performances with different electron acceptors.



Figure 3 Evolutions of cathode potential and I_3^- concentration under sunlight.



Figure 4 Evolutions of MFC voltage and cathode potential under sunlight exposure.



Figure 5 Evolutions of anode potential and MFC temperature.

exposed to the natural sunlight. As can be seen in Figure 3, the initial I_3^- concentration was 0 mM and the initial cathode potential was only 0.06 V. After the MFC cathode compartment was exposed to sunlight, the I_3^- concentration increased sharply. Accordingly, the cathode potential of the MFC increased sharply from 0.06 V to above 0.6 V during the first 15 min of sunlight exposure, and then reached a maximum value 0.653 V in the following 6.5 hours. It can be mainly attributed to the generation of I_3^- under the sunlight exposure:

$$4I^{-} + O_{2} + 4H^{+} \xrightarrow{hv} 2I_{2} + 2H_{2}O$$
(3)

$$I^- + I_2 \rightarrow I_3^- \tag{4}$$

After sunset, the cathode potential slightly decreased to 0.643 V until the cathode compartment was exposed to sunlight again. The decrease in the cathode potential resulted from a net consumption of I_3^- concentration due to the slow generation rate of iodine from potassium iodide by oxygen in the absence of sunlight. Furthermore, it implies that the accumulated I_3^- during the sunlight exposure overrides its overnight consumption. It can be also observed that the cathode potential showed a similar trend in the second and third days.

Figure 4 shows the evolutions of MFC voltage, anode and cathode potentials under the sunlight. It can be seen that the MFC voltage showed a similar trend with the cathode potential, that is, the MFC voltage increased sharply at the very beginning of sunlight irradiation and then decreased slightly after it reached the peak value gradually. It also can be seen that the range of MFC voltage decreased was higher than that of cathode potential, which can be mainly attributed to the evolution of anode potential. Figure 5 shows the evolutions of MFC temperature and anode potential. As can been in Figure 5, the MFC temperature and the anode performance of the MFC showed an opposite trend during the experiment. It was expected because the activity of microorganism improved with the increase of the temperature. Since the range of anode potential changed was smaller than that of the cathode potential, and the voltage of the MFC operating at 1000 Ω was determined by the cathode potential.

The performances of the MFC before and after sunlight exposure were shown in Figure 6. It can be seen that the MFC performance was less than 50 mW/m² before exposing to the sunlight. This may result from the slow reaction kinetics and the low concentration of the dissoved oxygen in the cathode compartment. However, after 8 h sunlight irradiation, the maximum power density of MFC increased to 450 mW/m² due to the generation and accumulation of $I_3^$ under the sunlight exposure. A further increase in the maximum power density of MFC, about 30 mW/m², was observed when the cathode compartment was areated with 25 mL/min oxygen. This is simply because of the higher $I_3^$ concentration formation rate under the areation of oxygen. It was also interesting to note that the maximum power density of the MFC after the sunlight irradiation was about 100 mW/m² when the cathode compartment was purged with N₂. This value was higher than that of the MFC before the sunlight irradiation. Jotner et al. found that I⁻ can be oxidized to I_3^- under the sunlight without oxygen, but its generation rate was much lower than that in the presence of O_2 [17]. The absence of oxygen in the cathode compartment leads to a decreased I_3^- regeneration rate, and therefore a lower I_3 concentration and a deteriorated performance. Additionally, the I_3^- concentrations in the MFC cathode compartment were also measured when the cathode compartment was purged with N₂, exposed to ambient and purged with O₂, with values of 0.04 mM, 0.55 mM and 1.80 mM, respectively. The result indicated that oxygen participated in the regeneration of I_3^- . Though the I_3^- concentration when the cathode comopartment was purged with O₂ was more than 3 times of the concentration when the cathode compartment was exposed to ambient, the improvement of the maximum power density of MFC was limited (6%). This result suggested that the supply of oxygen in MFC cathode was not the decisive factor influening MFC performance in this condition.



Figure 6 Comparision of the performances of the MFC operating with KI as cathodic electrolyte before and after sunlight exposure.

2493

4.3 Effect of mass transfer on MFC performance

Figure 7 shows the linear sweep voltammetry of I_3^- (2mM) on the carbon paper under different scan rates. It can be observed that the peak value of current density increased with the increasing scan rate. The plot inserted in Figure 7 shows that the current density is roughly proportional to the square root of the linear scan rate (V), suggesting that the diffusion process of I_3^- was a decisive step for the electrochemical reduction rate of I_3^- on carbon paper [14].

The effect of mass transfer in cathode compartment on the MFC performance operating under a fixed external resistance (400 Ω) is shown in Figure 8. It can be seen that the MFC voltage sustained at a high level when the cathode compartment was continuously stirred. When the magnetic stirring was stop, the MFC voltage began to decrease, and the decreasing rate increased with the decreasing I₃⁻ concentration, until a relatively low value was reached. Once the magnetic stirrer was turned on again, the original MFC voltage was recovered. As known, the electrochemical



Figure 7 Linear sweep voltammetry of I_3^- on carbon paper under different scan rates (2 mM I_3^- +0.2 M KI: A, 2 mV/s; B, 5 mV/s; C, 20 mV/s; D, 50 mV/s; E, 100 mV/s; F, 200 mV/s). The inset shows the relationship between the peak value of current density and the square root of linear scan rate).



Figure 8 Effect of cathodic mass transfer on the MFC performance.

reaction occurs mainly on the surface of the electrode. When the magnetic stirrer was turned on, the mass transfer mode in the cathode compartment was forced convection; hence, the I_3^- on electrode surface could be replenished in time and a high MFC performance could be sustained. However, the mass transfer mode was changed to natural diffusion when the stirring was off, and the I_3^- on electrode surface was not efficient enough to support the effective continuous reaction and hence, the MFC performance decreased. From the above results, it can be clearly seen that the concentration and the mass transfer rate of I_3^- have significant effects on the MFC performance.

4.4 Effects of I_3^- concentration on the maximum power density of the MFC

Figure 9 shows the maximum power density of the MFC as a function of I_3^- concentration. As shown in Figure 9, the maximum power density of MFC sharply increased with the increase of I_3^- concentration when the I_3^- concentration was lower than 2.0 mM, while the increasing rate began to decrease when the I_3^- concentration was higher than 2.0 mM. It was because the amount of I_3^- diffused to electrode surface was much lower than that of I_3^- consumed under a low I_3^- concentration. When the I_3^- concentration increased to 2.0 mM, the MFC performance was not limited by the mass transfer of I_3^- due to the improvement of I_3^- mass transfer rate under an I_3^- high concentration.

5 Conclusion

A renewable MFC cathode was proposed and constructed in this study. It was found that the performance of MFC using I_3^- as the cathodic electron acceptor was higher than that of MFC using K_3 [Fe(CN)₆]. It has been demonstrated that I_3^-



Figure 9 Evolution of the maximum power density of MFC against I_3 concentration.

can be regenerated by the reaction between oxygen and $I^$ under the sunlight, the I_3^- concentration and the mass transfer rate from catholyte to electrode surface were the limiting factors for the MFC performance. Additionally, it was observed that the I_3^- concentration had a significant effect on the maximum power density of MFC when I_3^- concentration was lower than 2.0 mM, while the effect began to reduce when I_3^- concentration was higher than 2.0 mM.

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