International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Short Communication

# **Effect of Inorganic Salt in the Culture on Microbial Fuel Cells Performance**

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Received: 28 October 2014 / Accepted: 1 December 2014 / Published: 16 December 2014

In this paper, the effect of inorganic salt in the culture on microbial fuel cells (MFCs) performance in actual wastewater treatment was studied by analyzing the output voltage, the processing time of wastewater treatment, the internal resistance and its distribution, and the electrochemical activity of anode exoelectrogens. The biogas slurry with chemical oxygen demand (COD) 1700 mg/L was as electrolyte. The results showed that the addition of inorganic salt could improve the stable output voltage by 40.21 percent and shorten the processing time of wastewater treatment by 115 hours. In addition, it could reduce the internal resistance by 27 percent. And further study showed that the effect of inorganic salt on MFC charge transfer resistance was mainly shown on the decrease of solution resistance and anode charge transfer resistance. What's more, it would enhance the electrochemical activity of anode exoelectrogens through balancing nutritive proportion.

**Keywords:** Inorganic salt; Microbial fuel cell; Power density; Internal resistance; Electrochemical activity

# **1. INTRODUCTION**

Researches on microbial fuel cells (MFCs) had got more and more achievements in recent years[1-3], since English botanist M. C. Potter proved that electrons from microbial metabolisms could be acquired with electrodes[4]. As a new environmental biotechnology, MFCs use the electron produced by the respiratory metabolism of microorganism for electricity generation [5,6]. Meanwhile, it has the function of wastewater treatment[7-9], denitrification[10], denitration[11] and hydrogen production[12,13]. All of this make it has unique technical advantages and characteristics. So far, MFCs have been an irreplaceable developing direction in the new energy field. Compared with other

systems, MFCs could extract energy from waste water, and convert into electric energy and chemical energy could be utilized by human. MFCs have superior environmental effect. And it has important significance for solving the energy crisis and the environment question[14].

Recent years, with the development of MFCs, researches related to MFCs used in treating kinds of waste water become more and more. For example, livestock wastewater, pharmaceutical wastewater, brewery wastewater and papermaking wastewater and so on, which are all regarded as substrate to be utilized by MFCs. This method not only eliminated environment pollutant but also recovered electrical energy[15,16]. However, all of the above wastewater was all need to add in inorganic salt and mineral element as follows: (Na<sub>2</sub>HPO<sub>4</sub>, 4.09g/L and N<sub>a</sub>H<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, 2.93g/L), NH<sub>4</sub>Cl (0.31g/L), KCl (0.13g/L), metal salt (12.5mL/L) and vitamin (5mL/L) solutions, in order to create create the best growth environment for exoelectrogens[17,18]. So far, researches about the effect of inorganic salt and mineral element on MFCs is relatively little. There were few reports about the research in domestic and international professional journal academic papers.

In this paper, the effect of inorganic salt and mineral element on MFCs was analyzed from the following respects, output voltage, power density, internal resistance and electrochemical activity of exoelectrogens. According to these analyzes, we expected that we could provide technical support for practical sewage treatment through MFCs.

# 2. MATERIALS AND METHODS

## 2.1 MFC reactor





Figure 1. MFC reactor construction

The diagram of the single-chamber membrane-less MFCs used in this research was shown in Figure 1. The bottom anode chamber is cylindrical with 6 cm in height and 4.2 cm in diameter and the

upper cylindrical cathode chamber exposed to air is 2 cm in height and 7.6 cm in diameter. The total empty volume of the reactor was 72 ml. 5 pieces of graphite felt was served as anode, and each one was 4cm in diameter. Meanwhile, the cathode was a piece of Pt coated  $(0.3 \text{mg/cm}^2)$  graphite felt with 3mm thick and 7.5cm in diameter. Titanium wire was used for the connection of the external circuit to the electrodes. An external resistor of 510  $\Omega$  was connected in series on the circuit, for calculating the current. A data acquisition board (AD8201H, Ruibohua Co., Beijing, China) was connected in parallel with the resistor to monitor the voltage.

#### 2.2 Experimental method

The whole experiment had two steps: (1)MFCs were fed with a medium containing 157.59 mg/L Sodium acetate in 50mM phosphate buffer solution (Na<sub>2</sub>HPO<sub>4</sub>, 4.09g/L and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, 2.93g/L), NH<sub>4</sub>Cl (0.31g/L), KCl (0.13g/L), metal salt (12.5mL/L) and vitamin (5mL/L) solutions and re-fed with 50Mm Sodium acetate every three days until the output voltage of MFCs were stabilized. (2)Feed solutions were replaced to fermentative solution the same COD concentration with above sodium acetate solution when the voltage went for a maximum remained stable. There were two groups in this step. In the first group, fermentative solution with the above 50mM phosphate buffer solution was employed as feeding. By contrast, fermentative solution without any matter was as feeding in the second groups. The two groups were marked MFC 1 and MFC 2 respectively. For the two groups, the fermentative solution were both sparged using ultra high purity nitrogen for 20 min before the operation. Mixed bacteria that screened from marine surface sediments was employed as exoelectrogenic microbes. The MFC was operated in a temperature-controlled room at 25°C in a fed batch. In order to estimate the data accurately, the experiment was repeated three times.

# 2.3 Analyses and calculations

The COD concentration of the electrolyte was determined using the standard method of potassium dichromate. The cell voltage (U) between the anode and cathode was automatically recorded by a computer-based data acquisition system (AD8201H, Ribohua Co., Ltd) every 3 min. The current (I) was calculated by Ohm's law I = V/R and the power output (P) was done by  $P = I \times U$ . And the power density was calculated by W=P/A, where A was the superficial area of anode graphite felt (in cm).

Internal resistance of MFCs was studied by using the method of polarization curve. And the components of internal resistance were measured by electrochemical impedance spectroscopy (EIS)[19]. Cyclic voltammetry (CV) and EIS were conducted using an electrochemical workstation (LK98BII, Lanlike Co., Ltd.). The specific method of internal resistance measuring was as follows: Broke the circuit when the output voltage of MFCs were maximum and stabilized. For the whole MFC electrochemical impedance spectroscopy, the anode was regarded as working electrode and counter electrode, and the cathode was considered as reference electrode. For anodic electrochemical impedance spectroscopy, the anode was regarded as working electrode was as counter electrochemical impedance spectroscopy.

electrode. The reference electrode (Ag-AgCl electrode) was inserted into the anode chamber. The scope of scanning frequency was 100 kHz~10 mHz.

The specific method of EIS was as follows: The anode of the two groups MFCs were cut into quadrate pieces (1cm\*1cm). And these anodic pieces was rinsed with deionized water. The graphite felt quadrate piece was regarded as working electrode. The platinum electrode was employed as counter electrode. Ag-AgCl electrode served as reference electrode. The electrolyte was phosphate buffer (pH 7.0, 0.2M). The scanning range was -1.2 V ~ 1.2 V, and the scanning speed was 25 mV/s.

#### **3. RESULTS AND DISCUSSION**

## 3.1. Effect of inorganic salt on output voltage and potential of anode and cathode

The voltage output of the two groups MFCs was revealed in Figure.2. As was shown in Figure.2, the stable voltage output of the two groups MFCs was about 500 mV when the sodium acetate was as feeding.



Figure 2. Voltage output of MFC 1 and MFC 2

After changed the anolyte as the biogas slurry with the same COD concentration, the voltage output were considerably smaller than the former. This was because that biogas slurry still contains large amounts of refractory organic compound. Compared with sodium acetate, microorganism required more time. On the other hand, part of the refractory organic compound might exert a depressant action on microorganism generating electricity. After replacing sodium acetate culture as biogas slurry, voltage output of MFC 1 valued peaks to 485 mV and remained relatively stable for 150

hours. Relatively, maximum of voltage output of MFC 2 was 290 mV and remained for 305 hours. With the addition of inorganic salt, the stable output voltage had risen by 40.21% and the processing time of wastewater treatment was cut by 115 hours. For MFC 2, voltage output had a small peak after changing electrolyte. It was likely to be because part of inorganic salt remained in the biogas slurry. Anolyte could provide the right environment for electricigens in a short period of time. Then nutrition proportional became imbalance as bacteria proliferate. The growth and multiplication of electricigens was affected. Accordingly, it resulted in decreased the output voltage and the organic carbon removal rate.

The output voltage of MFCs was largely determined by the cathode potential and anode potential. To make clear the causes of output voltage variety, changing curve of cathode potential and anode potential of the two MFCs were measured respectively (Figure 3). It was evident from Figure 3 that the cathode potential of MFC 1 and MFC 2 were both approximately 200 mV. However, the anode potential of two MFCs had large difference. The anode potential of MFC 1 (-240 mV) was significantly less than that of MFC 2 (-70 mV). Anode potential could be reduced greatly by adding inorganic salt. Thus, the addition of inorganic salt could increase the apparent output voltage of MFC and improve the biodegradation efficiency in some degree.



Figure 3. Cathode potential and anode potential of MFC 1 and MFC 2

As is shown in Table 1, compared with wastewater treatment by MECs published previous, the voltage output and cathode potential of MFC with inorganic salt addition were nearly high as the previous. However, the anode potential of MFC 2 without adding inorganic salt decreased significantly compared with MFC 1 and published literatures.

Substrate	V <sub>MFC</sub> (mV)	V <sub>Cathode</sub> (mV)	V <sub>Anode</sub> (mV)	Ref
Sewage wastewater	411	221	-190	20
Sewage sludge	529	129	-400	21
Glucose	500	260	-240	22
Biogas liquid(MFC 1)	485	235	-240	This study
Biogas liquid(MFC 2)	290	220	-70	-

Table 1. Performance of the MFCs reported in the literatures

### 3.2. Effect of inorganic salt on output power of MFCs

Power density of MFC 1 and MFC 2 was revealed in Figure.4. Over cycles, both the peak power density of the two MFCs increased first and then gradually declined. The maximum peak power density of MFC 1 was 292.86 mW/m<sup>2</sup>. And it was 136.24 mW/m<sup>2</sup> for MFC 2. Compared with MFC 2, a 53.48 percent increased in the maximum peak power density. Therefore, the addition of inorganic salt could improve the output power density markedly. The output power density of MFC was significantly related to internal resistance. The decrease in internal resistance could reduce the power consumption of MFC and improve the output power density to some extent. As the polarization curve shown in Figure.4, internal resistance of the two MFCs differ much. It could be calculated that internal resistance of MFC 1 was 75.69  $\Omega$ , the value was 103.78  $\Omega$  for MFC 2.

Li[26] used food waste leachate as the feed, and obtained about 410 mW/m<sup>2</sup> output power density with enough inorganic salt. Bibiana Cercado-Quezada[27] obtained 240 mW/m<sup>2</sup> output power density used food-industry waste water as feed. The power densities of both the two reports were nearly large as MFC 1. All of the values were larger markedly than MFC 2. These data met the analyzes in previous paragraph.



Figure 4. Power density and polarization curve of MFC 1 and MFC 2

## 3.3. Effect of inorganic salt on internal resistance of MFCs

The apparent internal resistance had two major components, named the ohmic resistance and non-ohmic resistance, as proposed by the literature [23]. The ohmic resistance was the resistance produced by electron transfer because of electrolyte and electrode material. And this part of resistance was due to faradic reactions. It was manifested as diffusion resistance and solution resistance[24]. The

non-ohmic resistance was the resistance due to the electrochemical reaction at the electrodes. It mainly showed the resistance caused by microbial metabolism and electrochemical reaction during transfer process. This part of resistances was collectively called charge transfer resistance[25].



Figure 5. Electrochemical impedance spectroscopy of MFC 1 and MFC 2

Electrochemical impedance spectroscopy of MFC 1 and MFC 2 were given in figure. 5. It was evident from Figure.5 that there was little difference between the two MFCs on diffusion resistance. The solution resistance of MFC 1 and MFC 2 was 15  $\Omega$  and 25  $\Omega$  respectively, and the charge transfer resistance of MFC v1 and MFC 2 was 34  $\Omega$  and 39  $\Omega$  severally. The solution resistance of MFC 1 was 40 percent lower than MFC 2. As we all knew that solution resistance mainly related to electrical conductivity of electrolyte. Obviously, inorganic salt could increase the electrical conductivity of electrolyte, and then reduce the solution resistance. To charge transfer resistance, the value of MFC 1 was slightly lower than MFC 2. The charge transfer resistance was caused by the low activating reaction rate at the surface of the electrode. The addition of inorganic salt was more conducive to the growth and metabolism of microorganism. In addition, the electrochemical performance of exoelectrogens would be improved markedly after addition of inorganic salt. Both the above two aspects could reduce the charge transfer resistance of MFCs.

In order to confirm that the change of MFC charge transfer resistance was mainly contributed to the decrease of anode charge transfer resistance, the anode electrochemical impedance spectroscopy was measured. As was shown in Figure.6, the anode charge transfer resistance of MFC 1 was 8  $\Omega$ , which was significantly less than that of MFC 2 (15 $\Omega$ ). It showed that the effect of inorganic salt on MFC charge transfer resistance was mainly shown on the decrease of anode charge transfer resistance.



Figure 6. Anode electrochemical impedance spectroscopy of MFC 1 and MFC 2

3.4. Effect of inorganic salt on electrochemical activity of anode



Figure 7. Anode cyclic voltammetry curve of MFC 1 and MFC 2

The cyclic voltammetry curves of the two MFCs were given in Figure.7. It was evident from Figure 7 that the reduction and oxidation peak currents and peak area of MFC 1 were much larger than those of MFC 2, which indicated that the electrochemical performance of MFC 1 was obviously higher than MFC 2. A couple of clearly reversible redox peaks were obtained from the cyclic voltammograms

of MFC 1. To the MFC 2, the redox peaks were not obvious. It indicated that the addition of inorganic salt improved the performance of MFC mainly through improving the electrochemical activity of anode exoelectrogens. As was described in the analysis above, the addition of inorganic salt could balance the nutritive proportion and then provide better environment for exoelectrogens growth and metabolism. These results demonstrated that adding inorganic salt would exert significant influence on anode exoelectrogens, and then enhance the electricity production performance of MFCs.

# **4. CONCLUSION**

In actual wastewater treatment by MFCs, inorganic salt had an even greater impact on the electricity production performance of MFCs as above analyzes. Its enhancement should be mainly shown in the following several aspects: improving output voltage and power density, shorten the processing time, lowering internal resistance and improving the electrochemical activity of anode exoelectrogens. With the addition of inorganic salt, the stable output voltage had risen by 40.21%, the processing time of wastewater treatment was cut by 115 hours, the internal resistance had reduced by 27% and the electrochemical activity of anode exoelectrogens had been improved obviously.

#### ACKNOWLEDGEMENTS

This work was supported by the financial support from the China Ocean Mineral Resource R&D Association (No. DY125-15-T-08) and the National Key Technology R&D Program of China (No. 2012BAB07B05). We also acknowledge the financial support from the National High Technology Research and Development Program (863 program) of China (No. 2012AA062401) and the National Natural Science Foundation of China (Nos. 21176242 and 21176026).

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