



Effect of Electrolyte Conductivity and Aeration on Performance of Sediment Microbial Fuel Cell

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ABSTRACT

Sediment microbial fuel cells (SMFCs) are a promising technology for a viable source of energy. This technology is faced with many challenges, such as limited mass transfer and low electricity generation. The aim of this research was to investigate the effect of electrolyte conductivity and aeration effect on power generation from SMFCs. Electrical conductivity was adjusted at 6 different levels by adding several concentrations of NaCl and KCl, which are abundant and economic salts. By adding NaCl, the performance of SMFCs improved about 3.25 fold. Maximum generated power and current density of 32.76 mW/m² and 330.14 mA/m² are obtained, respectively after NaCl addition. Also, with aeration dissolved oxygen level increased as an electron acceptor in cathode portion, thereby power density enhanced from 16.36 mW/m² to 38.31 mW/m² which was a 234% increase compared to the situation before aeration.

1. INTRODUCTION

Microbial fuel cell (MFC) is a device that is able to convert chemical energy existing in organic/inorganic matters to bioelectricity by active bacterial oxidation [1-7]. Sediment microbial fuel cell (SMFC) is a simple configuration of MFC, which generates electricity from aquatic environment [8-12]. SMFC involves an embedded anode in anoxic sediment and a located cathode in the overlying oxic water. Microorganisms naturally present in the sediment degrade organic/inorganic matters contained in the sediment and produce electrons and protons [13]. The electrons transfer via external circuit and protons pass from sediment to cathode surface, react with dissolved oxygen to form water [14, 15]. In these systems, the membranes commonly used in MFCs are eliminated, because natural gradient in sediment begets anaerobic environment, thus sediment plays the role of membrane and there is no need for it. Furthermore, due to the existence of bacteria, like Geobacteraceae family, which are capable of transferring electrons directly to electron acceptor (anode), mediators, which are toxic and have negative effects on environment, are not used [16]. In addition, continuous replacement of organic matter into

sediment by the above liquid column helps this device to be used as viable power supplier [17].

Based on the related literature, it has been proved that SMFC has several benefits, such as viable power source to powering low electricity device, enhance anaerobic degradation of organic pollutants in soil or sediment and production of algal biomass [18-22]. Therefore, SMFCs receive significant attention. In general, SMFCs, due to scanty content of organic matter and mass transfer limitation in sediment, generate low electricity which is too low for application [19]. In spite of the fact that they generate low electricity, some researchers have successfully used this technology for electrification of low power equipments [23]. Donovan *et al.* have used SMFC to power wireless sensor [10] and Tender *et al.* also used it in meteorological buoy [19]. Several factors have been investigated and many efforts have been made to improve power generation [16, 24-30]. Rezaei *et al.* illustrated that with addition of chitin and cellulose as substrate, mass transfer limitation can be overcome [13]. Zhen *et al.* used rotating cathode to increase the power generation in SMFC [31]. Research in this field of fuel cell must be continued to improve SMFC performances.

Dominant ohmic losses in catholyte of SMFC can be reduced by enhancing the electrical conductivity resulting a higher output power from marine environment compared to freshwater environment. The objective of this study is investigating the effect of

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electrolyte conductivity on power generation. To increase electrolyte conductivity, NaCl and KCl with several concentrations were selected as a cheap, abundant and easy available substance to increase electrolyte conductivity. Also, oxygen is used as an electron acceptor for the cathodic reaction in the SMFCs; when dissolved oxygen level increases in cathode portion, the electrons on the electrode remove faster and next electron has sufficient space to flow cathode surface; as a result the current and power generation improve. Accordingly, we increased dissolved oxygen level in the catholyte to enhance power generation from SMFC by air pump. Since the power generated by SMFCs are low to run the low power equipments, these attempts were made to study if we can enhance the performance of SMFC to run an electric devise in the Mahmudabad river?

2. MATERIALS AND METHODS

2.1. Sediment sampling Sandy sediment (0-15 cm below the sediment/water interface) and associated water were gathered from Mahmudabad River estuary located in Mahmudabad in the north of Iran. Samples were carried to laboratory in plastic containers and mixed mechanically for two hours to ensure that composition of sediment became homogeneous. Moreover, samples were used without any pre-treatments.

2.2. SMFC'S setup and operation The cylindrical shape SMFCs were made of polycarbonate with an inner diameter of 8cm and height of 15cm Figure 1. Graphite plates were used as electrode for both the anode (3cm* 3cm*0.5cm) and cathode (3cm*3cm*0.5cm) and applied with no catalysts on it. Each container was filled with 600ml wet sediment. The anode embedded 8cm below the sediment/water interface. After that, SMFC was filled with 200ml water and cathode placed 2cm above sediment/water interface. SMFCs were assembled as soon as samples arrived. Electrodes were conjuncted to data logger by electrically insulated copper wire connected to computer subsequently. In addition, the circuit was open and no external resistor was included. During the experiment, SMFCs were operated at ambient temperature (8-17°C); the temperature was not controlled throughout the operation. Lost water by evaporation was manually replenished with distilled water to constant level of dissolved oxygen concentration, electrical conductivity, pH and salinity identical to the nature environment. The cells were operated in duplicate to ensure that the results are trustworthy.

2.3. Instrumentation and analyses The open circuit voltage (OCV), current and power generated by

SMFC were measured via a homemade 16-channel collection instrument. Power and current were calculated based on the following equations:

$$P=I*E \quad (1)$$

$$I=(E/R_{ext}) \quad (2)$$

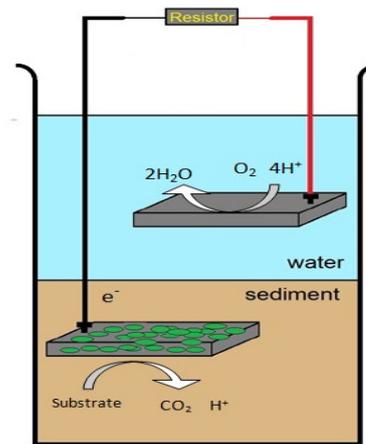


Figure 1. Schematic diagram of lab-scale SMFC

where P is the generated power, E the measured cell voltage, R_{ext} the external resistance and I the produced current. Polarization (I–V) and power curves of the probed SMFCs were measured by changing resistances ranging from 65M Ω to 1 Ω . As known to measure the polarization and power curve resistance of circuit must change from a value about open to close resistance. When the system reached steady state condition, polarization curve was taken from SMFCs. In order to calculate power and current density, these values were normalized with surface area of the anode also the internal resistance obtained by determining slope of polarization curve [1]. Ion conductivity of catholyte increased by addition of NaCl and KCl. All chemicals used for the experiments were supplied by Merck (Darmstadt, Germany). Electrical conductivity and dissolved oxygen measured with conductivity meter (Mettler Toledo FiveGo, Switzerland) and DO meter (Mettler Toledo, CH-8603, Switzerland), respectively. The aquarium pump (Boyu, Sc7500 - China) was used for the sake of aerating the water.

3. RESULT AND DISCUSSION

3.1. Effect of conductivity increment The river SMFC was operated at ambient temperature. In any power supply, the main important goal is to increase output power and then to acquire the highest current density under this situation of the maximum power density. In this aim, electrical conductivity was increased during 6 levels (10.95, 20.96, 25.8, 30.3, 35, 40 and 44 mS/cm) by NaCl addition (0.2, 0.4, 0.6, 0.8, 1, 1.2 and 1.4 M). The experiments began 2 days After SMFC running, when the bacteria colonized on the

surface of anode electrode and the cell reached to a high voltage.

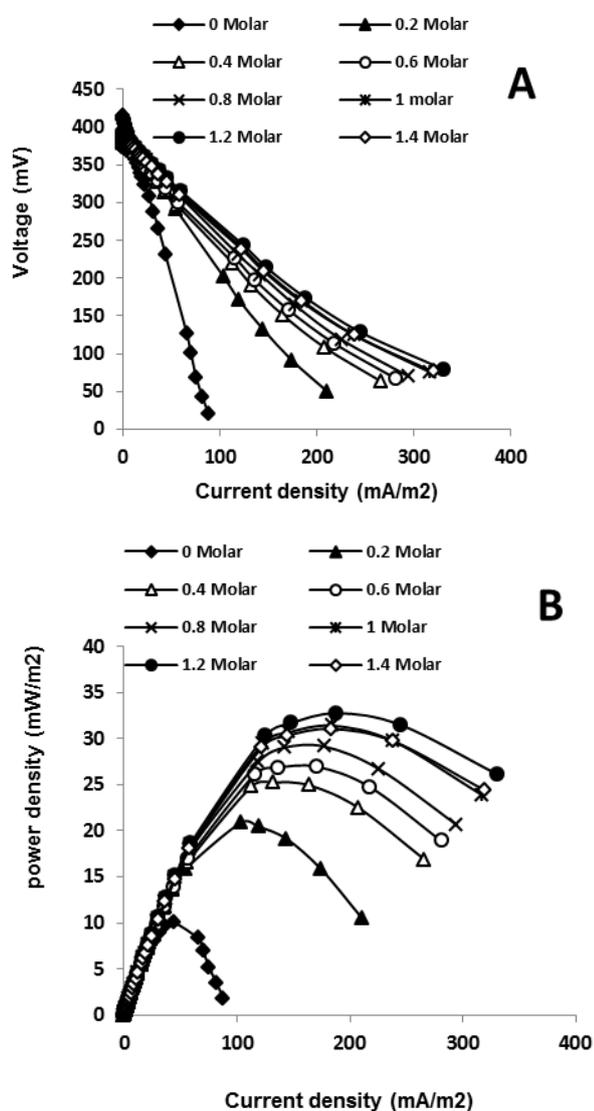


Figure 2. Generated polarization (A) and power density (B) curves at different concentration of NaCl in the cathode compartment

At first, when the polarization test was taken from cell before adding NaCl, the maximum power and current density of 10.08 mW/m^2 and 87 mA/m^2 , respectively obtained at water conductivity of 1.053 mS/cm . In the following, electrical conductivity increased during 6 levels with adding NaCl. The test conducted when the voltage stabled after adding salt. As shown in Figure 2. it is clear that the power improved, with respect to increase of conductivity. Polarization curve slope shows the internal resistance such that as slope descents the internal resistance decreases. (Figure 2.A) demonstrates

that with the increase of conductivity the internal resistance decreases and power density improves.

When catholyte solution was prepared with concentration of 0.2 M NaCl , internal resistance decreased intensively from 445Ω to 177Ω (Table 1). As a result, the power generation significantly increased from 10.08 mW/m^2 to 20.90 mW/m^2 (Figure 2.B).

TABLE 1. Maximum generated power and current density, and internal resistance obtained from this study at several concentrations of NaCl

Molarity (M)	Conductivity (mS/cm)	Maximum current density (mA/m ²)	Maximum power density (mW/m ²)	Internal resistance (Ω)
0	1.053	87	10.08	445
0.2	10.95	210.20	20.90	177
0.4	20.96	266.56	25.25	130
0.6	25.8	281.01	26.94	120
0.8	30.3	294.68	29.13	115
1	35	316.42	31.41	110
1.2	40	330.14	32.76	101
1.4	44	319.08	31.05	106

The maximum power and current density at each concentration of NaCl is summarized in table 1. This table indicates that the conductivity of cathode solution is an important parameter in SMFC. With NaCl addition, which is a cheap and economic substance, the performance of SMFC improved. In addition, table 1 indicates NaCl with concentration of 1.2 M has the best ability of transferring produced protons to cathode surface. This concentration of NaCl in aerobic cathode compartment increased produced power more than 3.25 times greater than when NaCl is not used in SMFC. Furthermore, NaCl addition to 1.2 M caused decrease of internal resistance and increase of power density; but after that with increasing the concentration of NaCl, internal resistance increased and power density decreased. Catholyte conductivity cannot increase more than 1 M KCl because bacteria's growth influenced significantly[32].

The results of experiments with KCl addition were similar to NaCl (Figure 3.). At first, with adding KCl the internal resistance rapidly decreased and power generation increased, same as the previous experiments, but with more KCl the varying intensity in the internal resistance and power generation decreased. This trend continued until the concentration of 1 M KCl , after that by adding the salt, internal resistance and power generation slightly increased. The maximum power and current density obtained in 0.8 M KCl , 28.79 mW/m^2

and 234.16 mA/m², respectively, which are 5.8 and 3.79 fold greater than before the use of KCl.

The maximum power and current density at each concentration of KCl is summarized in table 2. Also the minimum resistance was observed in 0.8 M.

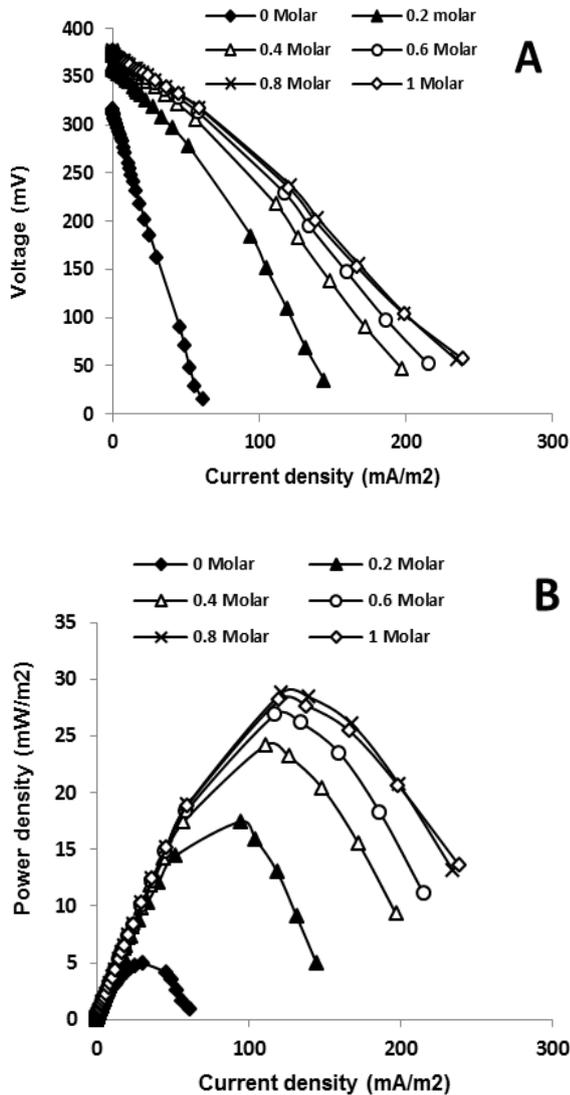


Figure 3. Generated polarization(A) and power density(B) curves at different concentration of KCl in cathode compartment.

Effects of solution chemistry and architecture (for example electrode spacing) on performance of bio electrochemical devices are usually calculated in terms of internal resistance, R_{int} [33]. There are several important parameters related to the internal resistance, include contribution of solution ohmic resistance as well as the polarization behavior of the anode and cathode [1]. In some bio electrochemical devices, electrolyte ohmic resistance accounts for a major portion of the total internal resistance [3]. The ohmic resistance will

be decreased by increasing the electrolyte conductivity, and it has been shown that power density can be substantially increased by adding salt to the solution [34, 35]. Further increases of salt concentration, however, reduce power production by inhibiting bacterial growth [36].

TABLE 2 : Maximum generated power and current density, and internal resistance obtained from this study at several concentrations of KCl

Molarity (M)	Conductivity (mS/cm)	Maximum current density (mA/m ²)	Maximum power density (mW/m ²)	Internal resistance (Ω)
0	1.037	61.65	4.93	490
0.2	8.59	144.24	17.46	211
0.4	14	197.24	24.23	158
0.6	18.92	215.08	26.88	147
0.8	25.1	234.16	28.79	129
1	31	238.63	28.20	130

Salt (NaCl and KCl) addition consistently decreases the overall R_{int} of the SMFCs. R_{int} can be separated into electrolyte, anode, and cathode resistances. Electrolyte resistance is directly related to the solution conductivity, and decreases when adding salt (please see Table 1 and 2). Anode resistance arises from the bio-electrochemical reaction at anode, and thus the activity of the electricity-generating bacteria. Salt addition did not produce appreciable changes in anode potentials except at the very highest salt concentration (Figures 2. and 3.).

3.2. Effect of aeration Final electron acceptor shortage in the cathode portion is one of the limiting factors to produce power from SMFC. Concentration of electron acceptor affects directly on output power [1]. In general, oxygen is used as an electron acceptor in cathodic reaction in most fuel cells [1]. When cathode is in the atmospheric condition, DO is the main limiting factor. This affection is resulted by two important roles of oxygen in cathode portion, which are electron acceptance at cathode surface and restriction of anaerobic bacteria on anode. Furthermore, a myriad DO level causes permeate of oxygen into anode portion and growth of heterotrophic microorganisms, which contest with generation of electron bacteria and decrease cell performance.

Nevertheless, oxygen is the most utilized electron acceptor in catholyte due to its availability and non-toxicity. In this study, we used aquarium to increase DO

level of catholyte. OCV was recorded in one-hour intervals during 7 days of experiments (Figure 4.).

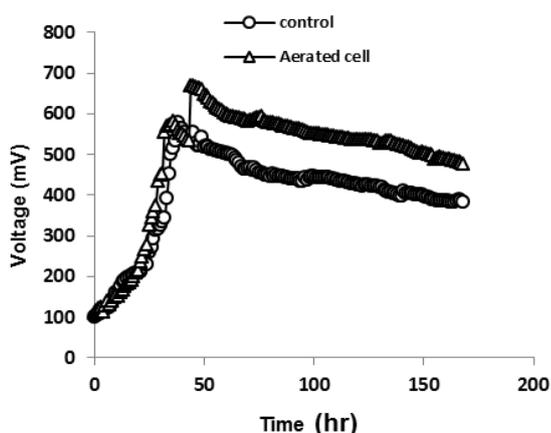


Figure 4. OCV of aerated and controlled SMFC

Initially, the voltage increased rapidly and after 45 hours maximum voltage gained. Then air pump switched on and penetrated air to catholyte with 3l/min flow rate. As a result, DO increased from 6.35mg/l to 8.19mg/l, also OCV quickly enhanced (580mV to 670mV). Over the next hours, the organic/inorganic matters contained in sediment was consumed by the organism. As a result, the OCV of aerated cell and control decreased with similar patterns.

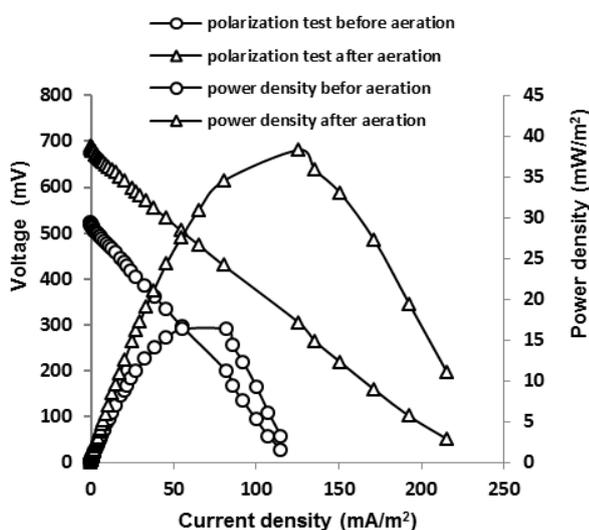


Figure 5. Comparison of Polarization and power density produced by SMFC before and after the aeration.

As shown in figure 5. the maximum power density before and after aeration were 16.36mW/m² and 38.31mW/m², respectively. These amounts show improvement nearly 234%.

4. CONCLUSION

In this research, the obtained results demonstrated that SMFC performance was enhanced by increasing

electrical conductivity. The enhanced power density confirmed that power increases with increasing electrolyte conductivity which attributed to the reduction of internal resistance. Increasing conductivity by NaCl could be an economical way to enhance power generation from SMFCs. Maximum generated power and current density were 32.76mW/m² and 330.14mA/m², respectively, for NaCl. Likewise, the cell with KCl produced maximum power and current density of 28.79mW/m² and 234.16mA/m², respectively. The maximum conditions were obtained at concentrations of 1.2 M NaCl and 0.8 M KCl.

Also, with aeration, the voltage increases from 580mV to 670mV; as a result with aeration the dissolved oxygen level, which is an electron acceptor, increased in cathode portion and thereby, power density enhanced from 16.36mW/m² to 38.31mW/m² which is 234% more than before aeration.

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