Korean J. Chem. Eng., 33(1), 154-158 (2016)
DOI: 10.1007/s11814-015-0123-x

pISSN: 0256-1115
eISSN: 1975-7220

Improvement of sediment microbial fuel cell performance by application of sun light and biocathode

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(*Received 6 February 2015 • accepted 8 June 2015*)

Abstract−Three series of experiments were conducted to improve sediment microbial fuel cell (SMFC) performance. At first, dissolved oxygen level of catholyte was increased with native seaweed of the Caspian Sea. Power output was improved about 2-fold, and maximum power density of 46.148 mW/m^2 was produced in the presence of seaweed as biocathode in cathode compartment. Secondly, the best depth to embed anode was then determined. Anode was embedded in 3, 6, 9 and 12 cm below the sediment/water interface. The best depth to bury the anode was finally determined in 3 cm below the sediment/water interface, maximum generated power and current density of 42.156 mW/m^2 and 282.92 mA/m^2, were respectively obtained in this depth. In addition, influence of agitated flow on power generation from SMFC was investigated.

Keywords: Sediment Microbial Fuel Cell, Power Density, Biocathode, Turbulence Flow, Dissolved Oxygen

INTRODUCTION

Direct power production from biodegradable organic/inorganic components presented in aquatic sediments are one of the most exciting findings in the field of microbial fuel cell (MFC) researches [1-4]. Sediment microbial fuel cells (SMFC) have appeared in the MFC family in recent years [5-7]. SMFC uses natural redox gradients bewteen anoxic sediments and oxic water to produce electrical power [8-10]. These systems involve an embedded anode in sediment and a placed cathode in overlying water. Electricigenic bacteria, inhabitant in sediment, produce electrons by oxidation the organic/inorganic materials, and transfer electrons to anode electrode [11-13]. Produced electrons flow to the cathode via external circuit, at the cathode surface reduce dissolved oxygen and form water then. SMFC has gained a remarkable attention case of simple configuration of SMFC compared to the MFC and advantages such as the elimination of proton exchange membrane, no need of mediator and power generation for long time [14-18]. Moreover, SMFC generates electricity and remediates contaminated sediments simultaneously [19-22]. In spite of low electricity generation from SMFC, it has been demonstrated that this system is used successfully to power low-power electronic devices in aquatic ecosystems [8,23-27]. Nevertheless, SMFC technology is facing many challenges to be a reliable renewable energy source. research in this field of fuel cell must be continued to improve SMFC performances.

Shortage of electron acceptor in cathode portion is one of the power generation limiting factors [28]. Concentration of electron acceptor directly has an effect on power output from SMFC [29-31]. In most of a fuel cell's cathodic reaction, oxygen is the final electron acceptor [32]. When cathode portion is maintained in the atmospheric condition, dissolved oxygen (DO) is the most important limiting factor [32]. This influence of oxygen is due to its two important roles: electron accepting in cathode portion and the inhibitory effects on anode anaerobic bacteria [33]. Note that large amounts of oxygen could lead to oxygen back-diffusion to the anode portion and heterotrophic bacteria which competition with electricity-producing bacteria growth, as a result the efficiency performance of SMFC reduce [29]. However, oxygen is the most widely used final electron acceptor caused by availability and non-toxicity.

He et al. used rotating cathode to increase DO level in catholyte [29]. Moreover, Fuentes-Albarrán et al. [31], and Hong et al. [30] studied the effect of DO concentration, but all researchers have used electrical consumer devices to produce oxygen, which is not economically feasible. Because the designed SMFC by them consumed much electricity more than produced. In this work, catholyte DO level was increased with seaweed and mixer. Caspian seaweed was applied to provide sufficient DO to cathodic reaction without using any electrical consumer instrument. Algae are a very varied group of predominantly marine photosynthetic organisms that report almost 50% of the photosynthesis which occurs on earth [34]. Mixer was employed to study effect of turbulent flow, which increased DO level on performance of cells. Also, An et al. [35] demonstrated that depth of anode and power generated from SMFC have direct relation and for different sources optimum depth is diverse; therefore, determining the best depth of anode bury for Caspian sea sediment source was another propose of this reserch study.

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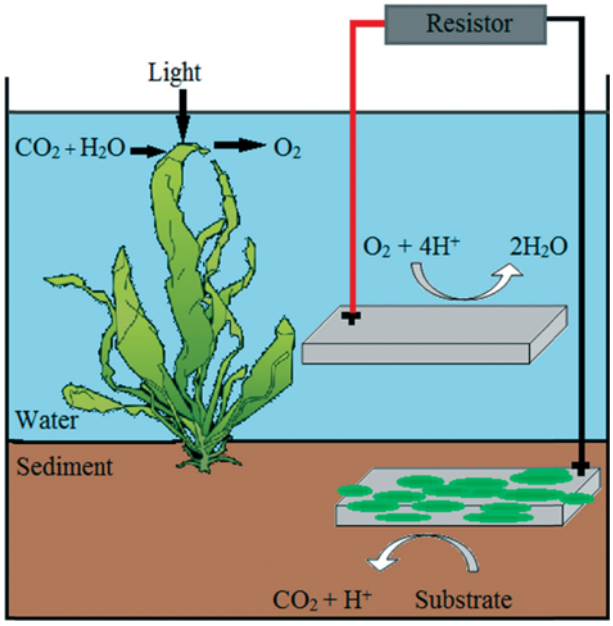

Fig. 1. Experimental setup of SMFC with biocathode.

MATERIALS AND METHODS

1. Sampling

Subsurface sediments (0-15 cm below the sediment/water interface) and associated seawater were gathered from Noor beach on the Caspian Coast of Iran. Sediments were sieved at 5 mm, and homogenized mechanically. Seaweed samples were also collected 10 cm below the water surface from similar location with three days interval. The collected algae was enteromorpha intestinal, which is a species of the genus ulvaceae [36]. Enteromorpha is also called Ulva. It is tubular green intestine like, bright grass green. This species is a summer annual plant and grows in environments from freshwater to full seawater. All samples placed into plastic container to transfer to laboratory.

2. SMFC Setup and Operation

In this study, two types of SMFCs were used. All SMFCs were cylindrical and made of polycarbonate with inner diameter of 80 mm (Fig. 1). First type of SMFCs which were used for studying effect of seaweed and agitated flow have height of 150 mm, while the second SMFCs type have height of 240 mm to determine the best depth of embedding anode. The first SMFCs type filled with 600 ml wet sediment and second type with 800 ml. Each SMFC contained 200 ml seawater. Both applied anodes and cathodes were made of plain graphite plates (ENTEGRIS, INC. FCBLK-508305-00004, USA) with dimension of 30 mm * 30 mm * 3.6 mm. To decrease acclimation effect on performance of SMFCs, a clean electrode was used to test of each parameter. Anode was located 6 cm below the sediment/water interface in type one, and for type two placed at depth of 3, 6, 9 and 12 cm to determine the best anode embedding depth. All SMFCs were assembled as soon as sample arrival except that used to determine the best anode depth experiments; they were left for three weeks to settle the bacteria on depth of sediment which is the habit in nature. Also, experiments operated in triplicate to ensure that the results are trustworthy. During the testing SMFC were operated at ambient temperature and temperature was not controlled throughout the operation. Water lost by evaporation was manually replenished with distilled water to constant level of dissolved oxygen concentration, electrical conductivity, pH and salinity identical to the natural environment.

3. Instrumentation and Analyses

The open circuit voltage (OCV) produced from SMFCs was measured with a homemade 16-channel datalogger instrument, which was connected to a personal computer. Power and current were calculated based on following equations:

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

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

where P is produced power, V is the voltage difference between the anode and the cathode; R_{ext} is an external resistance and I indicates produced current. To draw the polarization (I-V) and power curves Datalogger automatically changes the resistance between anode and cathode electrodes from 65,000 to 1 Ω with 5-minute interval. For the sake of calculating power and current density these values are normalized with surface area of the anode [6]. Electrolyte DO was measured with a DO meter (Mettler Toledo* CH-8603, Switzerland), and a mixer (IKA* 16 RW basic) was used for agitating the catholyte. To study differences in the internal resistance in connection with depth of the embedded anode, the internal resistances were estimated from the slope of the polarization curve [32].

RESULTS AND DISCUSSION

1. Effect of Seaweed Implements

Experiments were carried out in three stages. Initially, performance of SMFC was studied in presence of seaweed as biocathode in cathodic chamber. For this experiment two types of SMFC were run, early both of SMFC's were operated without any seaweed, At first, the potential rapidly rose to about 480 mV after a short lag phase (~11 hr) and remained relatively constant over the next two days. At this time (four days after the test at 5 pm), seaweeds were planted in one of the SMFC's and another one was left without seaweed as control. Fig. 2 shows OCV of SMFC with biocathode and control during 10-day of experiment. The gray area in Fig. 2 corresponds to night hours and the light area related today hours. DO levels in seawater is dropped by entering the seaweed because of getting dark and low photosynthesis. As plants, seaweeds produce oxygen during the day and, they begin to excrete carbon dioxide when it gets dark [37], so DO levels w ere changed at different times of day and voltage curves were swinging [38,39]. This test was done in the time the weather was usually partially cloudy.

Average DO level was about 8.9 mg/*l* and 11.87 mg/*l* at 11 am and 1 pm, respectively, on cloudy days. At 2 and 4 pm when cells produce maximum power density, DO was about 18.5 mg/*l* and this amount dropped to approximately 7 mg/*l* at 4 am. Polarization tests were performed after inserting seaweed, when conditions were fixed. As shown in Fig. 3 maximum power and current density produced by control was 22.48 mW/m^2 and 207.33 mA/m^2, respectively. In comparison, cells with biocathode generated maximum

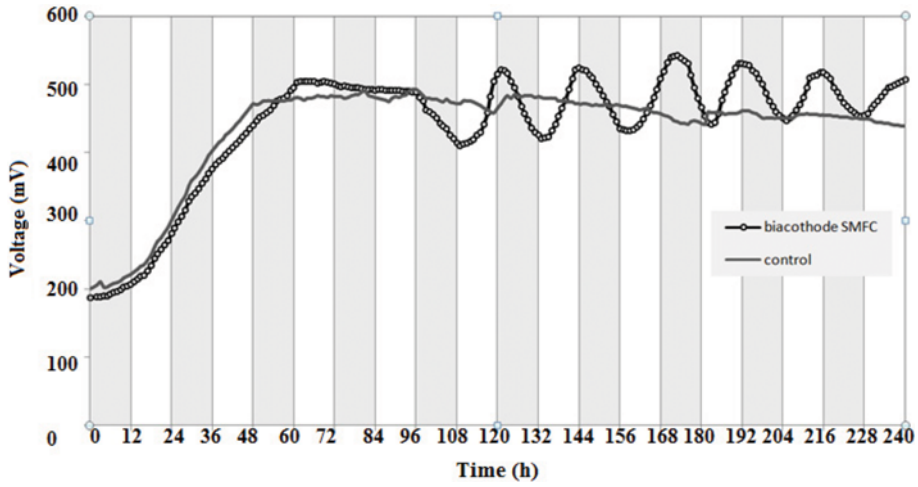

Fig. 2. OCV curves of SMFC with biocathode and control during 20 days of experiment.

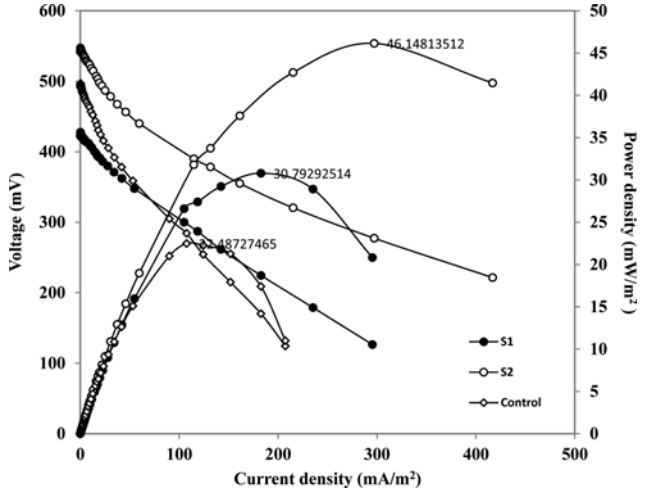

Fig. 3. Polarization and power density curves of SMFC with biocathode at state of maximum (S2) and minimum (S1) produced voltage and control cell.

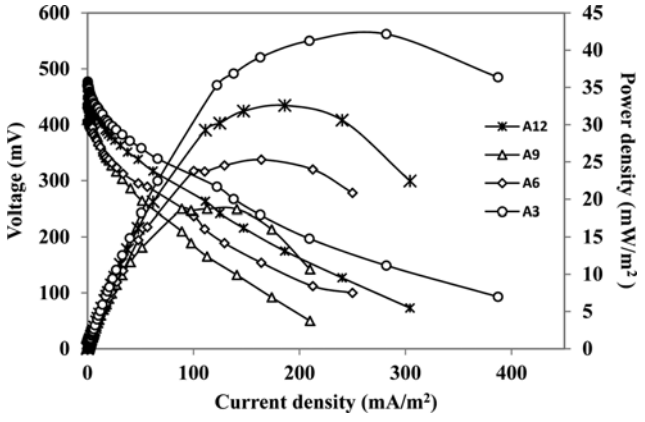

Fig. 4. Polarization and power density curves of SMFC with embedded anode in deferent depth of 3, 6, 9 and 12 cm below the sediment/water interface.

power and current density of 46.148 mW/m^2 and 416.89 mA/m^2. Furthermore, in the lowest produced voltage by biocathode cells, maximum power and current density was 30.79 mW/m^2 and 295.41 mA/m^2, which is more than control. It is obvious that applying seaweed improved power and current density by nearly two-fold.

The obtained data show that DO of cathode solution has an important role in performance of SMFCs. DO in cathode chamber before adding algae was 5.2 mg/*l* and it was increased up to 18.5 mg/*l*. The relation between DO and maximum generated power is summarized in Table 1.

Table 1. Relation between of DO and performance of fabricated SMFs

Do in cathode chamber (mg/*l*)	Maximum generated power (mW/m^2)
5.2	22.48
11.87	38.19
18.5	46.148
7	30.79

2. Determining the Best Depth of Anode Embedding

Embedding anode in depth in which anodophile or electrophiles, such as metal or sulfate-reducing bacteria are natively presented, can improve power generation. On the other hand, internal resistance of system is enhanced by increasing depth of anode, which leads to a decrease in cell performance. Therefore, depth of anode embedding must be optimized. Anode electrodes were buried in 3 (A3), 6 (A6), 9 (A9) and 12 (A12) cm below the sediment water interface. Experiments were carried out in triplicate for accuracy of data. As shown in Fig. 4, maximum power and current density of 42.156 mW/m^2 and 281.92 mA/m^2 were, respectively, produced in A3. Power generation was decreased in A6 and it was 25.3 mW/m^2. This trend continued to 9 cm below the water/sediment interface. The internal resistance was measured by the slope of the polarization curve and results presented in Table 2. The internal resistance increased according to depth; however, the proportion of this increase is different at diverse depths because embedding depth of

Table 2. Internal resistances according to embedding depth of anode

Internal resistance (Ω)	Depth of embedding anode (distance from sediment/water interface) (cm)
491	12
375	9
370	6
266	3

anode isn't the only effective parameter on internal resistance in SMFC and other factors are involved [32,35].

Enhanced internal resistance was observed with increasing burial depth which resulted in decrease in SMFC performance. However, with increasing depth from A6 to A12 the generated power density increased (32.58 mW/m^2). This phenomenon is probably due to the presence of sulfate or metal-reducing bacteria, which offset some of internal resistance caused by burial depth. However, produced power is also lower than A3.

3. Effect of Agitation

A mixer, with three rates of 160, 280 and 400-rpm rotational speed, was used to investigate the effect of agitated flow on power generation. Experiments were carried out when OCV was stable on the maximum condition. Before agitating the flow, power and current density were obtained 43.08 mW/m^2 and 287.32 mA/m^2, respectively (Fig. 5); also the DO level was 6.42 mg/*l*. Upon running the mixer with 160-rpm rotational speed, DO level greatly increased and reached to 8.30 mg/*l*; as a result power and current density increased to 54.12 mW/m^2 and 363.25 mA/m^2, respectively. Afterward, with increasing impeller rotational speed to 280 and 400-rpm, DO level slightly increased (8.39 mg/*l*), in spite of enhanced produced voltage and DO level, the power density decreased and reached to 51.99 mW/m^2. This phenomenon is due to the disarrangement of the sediment layers and diffusion of oxygen to the electrode surface, which this issue leads the microorganisms to become aerobic and subsequently worse SMFC operation. As a result, the optimal rotational speed is required.

4. The Structure of the Electrode Surface

At the end of electrochemical tests, the scanning electron microscopy (SEM) images of the biofilms taken from anode electrode. Images from surface of anode electrode by SEM before and after the work are shown in Fig. 6. As can be observed, before operation, there is no biomass on electrode but after operation, the accumulation of biomass observed as a biofilm on the electrode surface.

CONCLUSION

Results of this inquiry demonstrate the improved performance of SMFC by applying seaweed to supply additional oxygen. The

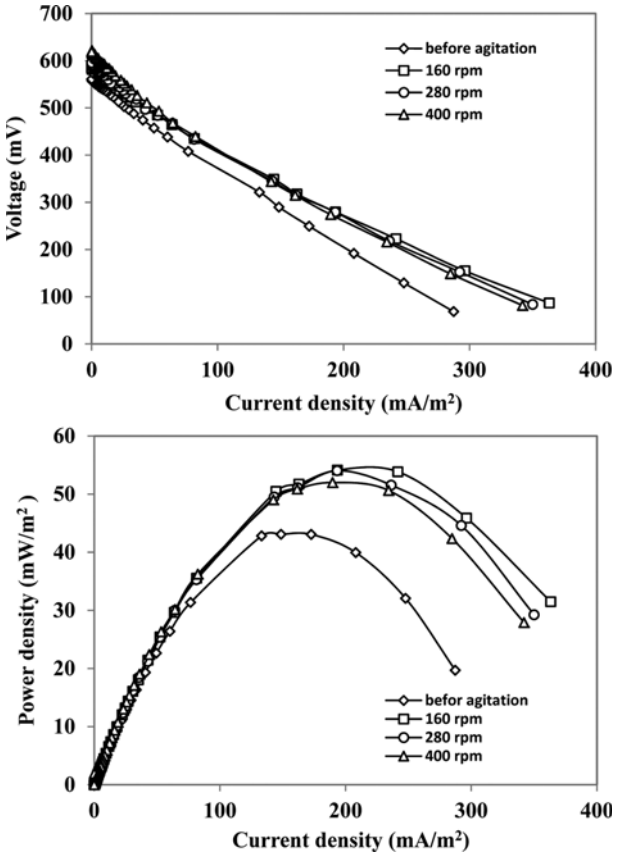

Fig. 5. Polarization and power density curves of SMFC at three rates of 160, 280 and 400 rpm of impeller.

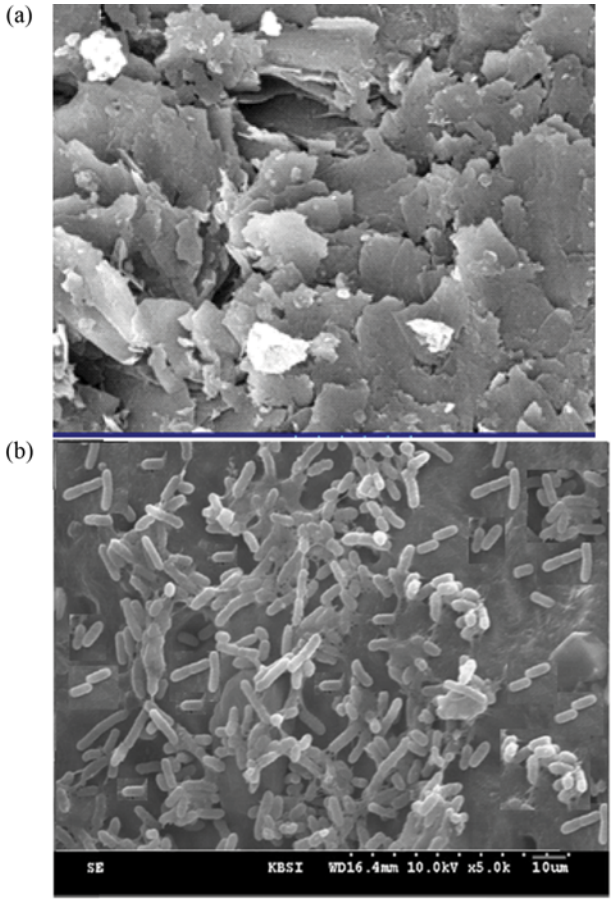

Fig. 6. SEM images from electrode surface (a) before operation (b) after operation.

biocathode is promising when natural seaweed is available. Compared to control, the maximum power density was enhanced from 22.48 to 46.148 mW/m^2, and it showed a double increase. Also, the best depth to embed anode in sediment source from the Caspian Sea was determined at 3 cm below the sediment water interface. It demonstrated that at greater depth SMFCs show weaker performance due to larger internal resistance. Likewise, the positive effect of agitated flow on power generation was shown. In the lower rotational speed, power and current density enhanced; nevertheless, with making stronger the velocity of speed power and current density reduced. Consequently, an optimum rotational speed is required to approach fine cell performance. In this experiments optimum rotational speed was 160-rpm, which developed the power density from 43.08 mW/m^2 to 54.12 mW/m^2.

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