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# Bioresource Technology

journal homepage: [www.elsevier.com/locate/biortech](http://www.elsevier.com/locate/biortech)



## Enhanced performance of an air–cathode microbial fuel cell with oxygen supply from an externally connected algal bioreactor



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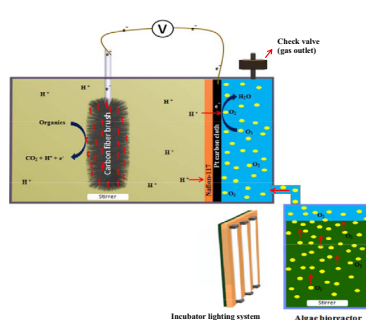
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### HIGHLIGHTS

- MFC power generation was enhanced with high oxygen levels from algae bioreactor.
- Cathodic reduction current was increased with oxygen from algae bioreactor.
- MFC performance was well maintained with algae oxygen supply in long term operation.
- Algae bioreactor aeration kept membrane well hydrated without salt depositions.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 30 April 2015

Received in revised form 12 June 2015

Accepted 13 June 2015

Available online 30 June 2015

#### Keywords:

Air-cathode microbial fuel cell

Algae bioreactor

Cell voltage

Cathode potential

Oxygen supply

### ABSTRACT

An algae bioreactor (ABR) was externally connected to air–cathode microbial fuel cells (MFCs) to increase power generation by supplying a high amount of oxygen to cathode electrode. The MFC with oxygen fed from ABR produced maximum cell voltage and cathode potential at a fixed loading of 459 mV and 10 mV, respectively. During polarization analysis, the MFC displayed a maximum power density of 0.63 W/m<sup>2</sup> (at 2.06 A/m<sup>2</sup>) using 39.2% O<sub>2</sub> from ABR, which was approximately 30% higher compared with use of atmospheric air (0.44 W/m<sup>2</sup>, 20.8% O<sub>2</sub>). The cyclic voltammogram analysis exhibited a higher reduction current of –137 mA with 46.5% O<sub>2</sub> compared to atmospheric air (–115 mA). Oxygen supply by algae bioreactor to air–cathode MFC could also maintain better MFC performance in long term operation by minimizing cathode potential drop over time.

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### 1. Introduction

Electricity generation from wastewater with use of bacteria as catalyst on the MFC anode is an inventive and environmental friendly technology (Vologni et al., 2013). Generation of electricity from MFC involves oxidation of substrate in anode producing electrons and protons (Kakarla and Min, 2014b), which combine with oxygen in the cathode chamber to form water (Min et al., 2012).

However, the operational, maintenance and material costs of MFC should be considered to improve the feasibility of field scale MFC operation (Oliveira et al., 2013). In addition, other drawbacks including high system internal resistance due to long distance between anode and cathode are reported to limit MFC performances. Immersing cathode electrode into non-sustainable cathode electrolyte such as ferricyanide or oxygenated chemicals makes MFC less productive. The aeration (oxygen) required for oxygen reduction reaction (ORR) can subside the net energy production (Liu et al., 2014).

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The MFC without a cathode chamber, in which the cathode electrode was exposed to air, seems to have low construction and operating costs due to simple configuration and no necessity of aeration in the cathode. The air–cathode MFC also has higher power production due to less internal resistance compared to double chambered MFC with immersed cathode in aqueous media (Pant et al., 2010). However, air–cathode performance was affected by several factors such as anolyte evaporation, membrane dehydration (Fan et al., 2007), and salt deposition which resulted in limited proton diffusion from anode to cathode and pH imbalance (Cheng and Logan, 2011). However, the reported maximum power densities from air–cathode MFC studies were with the use of atmospheric oxygen (Wei et al., 2011). This maximum power density can be limited by several factors including use of atmospheric air (20.8% oxygen), which can be improved with use of higher oxygen concentrations. The use of higher oxygen levels than atmospheric oxygen can have several benefits such as (1) increased MFC voltage due to the increased ORR by higher oxygen partial pressure, as per the Nernst equation (Fornero et al., 2008; Mateo et al., 2015), (2) the cathode activation energy can be reduced, as most of cathode catalytic site will be involved in the reduction process, and (3) the high concentration of oxygen can minimize the mass transportation and concentration losses on the surface of cathode as well (Fornero et al., 2008).

In the present study, an innovative single chamber air–cathode MFC configuration with a cover arrangement on cathode was developed and tested. Oxygen supply to cathode was provided from atmospheric air or oxygen generated from algae bioreactor (ABR). Air–cathode MFC power generation with oxygen from ABR was compared to atmospheric air. Polarization tests were conducted to evaluate the MFC performance by obtaining maximum power density at different oxygen concentrations and to determine system internal resistances. In long term (5-month) the performance of cathode was investigated using cyclic voltammogram (reduction current) with atmospheric air and oxygen from ABR.

## 2. Methods

### 2.1. Wastewater and algae culture media

The wastewater used as inoculum and media for MFC biofilm development and to isolate mixed culture of algae was collected from Giheung Respia, wastewater treatment plant (Yongin, Korea). The reported wastewater characteristics were SCOD 180 to 210 mg/L, TN 39 mg/L, TP 4.5 mg/L and pH 7.2. The mixed culture algae used in this study was isolated by illuminating wastewater and then grown using Bold Basal Medium (BBM) (Agrawal and Sarma, 1982). During this growth period algae was provided with filtered air (400 mL/min) with alternating light (intensity of 1600 lumens, with stirring) and dark (without stirring) conditions under at around  $28 \pm 4$  °C temperature.

### 2.2. Algae bioreactor (ABR) configuration and operation

A glass bottle was used as an algae bioreactor with a working volume of 580 ml (Bold Basal Medium) and 30 mL head space. Two ports were made on the top of the algae bioreactor for gas out let and measurement of headspace oxygen levels with help of an oxygen sensor. Initially the ABR was feed with BBM having 2 g/L of sodium bicarbonate as a carbon source and algae (0.9 g/L algae dry biomass). However, the concentration of sodium bicarbonate was varied (1–6 g/L) based on the experimental condition as mentioned. Both the ABR and air–cathode MFC were purged with pure nitrogen gas to remove all DO and headspace oxygen

before connecting ABR outlet to air–cathode MFC inlet. This step was repeated every time throughout the experiment whenever a new operation cycle was performed.

### 2.3. Microbial fuel cell configuration and operation

A cube type air–cathode MFC made of plexiglass with a cover arrangement on cathode was used in this study (Fig. S1). Anode half cell inner dimensions were  $7 \times 5 \times 6$  cm ( $L \times W \times H$ ), accounting a total volume of 210 mL and a working volume of 205 mL. Several ports were made on top of the anode chamber for anode electrode, reference electrode and sampling. The cover on cathode had an inner dimension of  $1.5 \times 5 \times 6$  cm ( $L \times W \times H$ ) accounting a total empty space of 45 mL. Several ports were installed on the top of the cathode chamber for oxygen, humidity sensors and gas outlet which was fitted with a check valve (Fisher Scientific) to allow only one way movement of gases (from inside to out). On the front side small opening ( $6.6$  cm<sup>2</sup>) was made for gas inlet (for air diffusion or connected to oxygen from ABR). The MFC half cells (anode and cathode) were separated by using a proton exchange membrane (Nafion-117, Nano letters, Korea) which was placed in between two silicone gaskets to prevent media leaking from anode and cathode. The Carbon fiber brush ( $3 \times 2.5$  cm) (Kemsung brush, South Korea) was used as anode. Carbon cloth coated with Platinum (wet proofed,  $0.5$  mg/cm<sup>2</sup>) with a surface area of  $30$  cm<sup>2</sup> ( $5 \times 6$  cm) was used as cathode (Fuel Cell Earth, USA). Which catalyst side was placed towards Nafion membrane and gas side exposed to atmospheric air or oxygen from algae bioreactor (ABR). The anode chamber and cathode cover were assembled with coated crews, and the distance in between anode and cathode electrodes were measured to be around 3 cm.

In the start-up of MFC reactor, anode was filled with 205 mL of wastewater and acetate (2 g/L). The anolyte was sparged with pure nitrogen gas for about 5–7 min and the headspace of the reactor for 1 min to prepare anaerobic environment. This method was repeated whenever the voltage generations dropped below 30 mV with wastewater or GM media. After 30 days of MFC start up with wastewater voltage generations started to increase up to around 0.30 V. The anolyte solution was changed to GM media having 2 g/L acetate after getting stable voltage generations with wastewater. The total MFC operation was carried in a temperature ( $30 \pm 1$  °C) controlled incubator having built-in lightening system which can provide an illumination of 5000 lumens (Vision, Korea). Continuous measurement of cell voltage and cathode potential was carried out along with measurement of ABR headspace oxygen concentration. Initial voltage generation of air–cathode MFC was supported by allowing the atmospheric air (20.8% oxygen) to diffuse through  $6.6$  cm<sup>2</sup> opening on cathode cover. When MFC voltage was stabilized with atmospheric air, and then the aeration was switched to use oxygen provided from ABR. The algae bioreactor was connected to MFC cathode chamber by using a tube and headspace oxygen was measured continuously using an oxygen sensor fitted to it. The algae and algae media in the algae bioreactor was replenished with begin of every MFC experimental cycle. This process was repeated throughout experiment with use of oxygen from ABR.

### 2.4. Measurement and analysis

MFC and its cathode potentials were measured continuously with a data acquisition system for every five minutes across a fixed resistor of 600  $\Omega$  (Keithly 2700, Keithley Instruments, US). Cathode potential was measured using Ag/AgCl (197 mV vs. SHE) as reference electrode (Bio-analytical Systems Inc, USA). The polarization tests were conducted with various loads ranging from 4000  $\Omega$  to 10  $\Omega$  using a resistance box. Current was calculated according to

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