



Up to 399 mV bioelectricity generated by a rice paddy-planted microbial fuel cell assisted with a blue-green algal cathode

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Abstract

Microbial fuel cells are used as an alternative source of energy and for microbial degradation of waste and pollutants. Different types of microbial fuel cells include sediment microbial fuel cells, waste treatment microbial fuel cells, constructed wetland microbial fuel cells and plant microbial fuel cells. Plant microbial fuel cells use plant–microbe relationships for producing bioelectricity. For this cell, the development of efficient, low-cost cathode is a key challenge. Here, a plant microbial fuel cell using algal-assisted cathode was designed. This cell uses rhizodeposits of plants as carbon source in the anode chamber and photosynthesis of algae to generate the oxygen that acts as a terminal electron acceptor in the cathode chamber. Results show that a maximum power density of 29.78 mW/m³ and a current density of 610 mA/m³ were recorded from the polarization curve during the light phase. The maximum voltage recorded was 399 mV in the light phase and 390 mV in the dark phase. This is the first design of a rice paddy-planted microbial fuel cell assisted with a blue-green algal cathode, capable of operating in self-sustainable mode using entirely natural processes without any external input of organics or oxidant.

Keywords Plant microbial fuel cell · Microbial fuel cell · Cathode · Algae · Photosynthesis

Introduction

In recent years, plant microbial fuel cell has emerged as a promising clean technique for generating electricity from plants and their residues (Yadav 2010; Nitorisavut and Regmi 2017; Khudzari et al. 2018). In the plant microbial fuel cell, plants synthesize organics through photosynthesis, which is made available to the electrochemically active bacteria to generate electricity (Deng et al. 2012; Yadav et al. 2018; Wang et al. 2018). The electrochemically active bacteria present in the anode compartment of the plant microbial fuel cell convert organic compounds into carbon dioxide, protons and electrons. The electron goes to the anode electrode placed in the anode chamber. Subsequently, the electrons flow through an electrical circuit to the cathode

electrode and are consumed by the oxygen and protons to form water molecules (Yadav et al. 2012; Mathuriya and Yakhmi 2014; Srivastava et al. 2018; Ilamathi and Jayapriya 2018). However, power produced in plant microbial fuel cell is still low for the real-world application. Non-efficient cathode reaction due to activation, ohmic and mass transport losses is assumed for low power production in plant microbial fuel cell and other microbial fuel cell (Rismani-Yazdi et al. 2008). Improvement in power generation and low-cost efficient cathode development are among the top major challenges for the real field application of plant microbial fuel cell (Chen et al. 2012). The ample availability of oxygen in the surrounding environment and its positive redox potential make it the most suitable electron acceptor for the cathode reaction (Chen et al. 2012; Zhao et al. 2006; Srivastava et al. 2017). Photosynthetic activities of algae are being used for producing in situ oxygen at the cathode of microbial fuel cell (Yadav et al. 2015).

This study designed and developed a rice paddy-planted microbial fuel cell with integration of algal (*Cyanobacterium phormidium*)-assisted cathode. It presents a system, which completely runs by natural processes. For imitating the real conditions, this study performed the experiment without adding the external carbon source, outside electrochemically

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active bacteria, or external oxidant. The electrochemically active bacteria present in the anode compartment were supported by the rice paddy plants for their carbon requirements. Similarly, the cathode reaction was supported by algal photosynthesis for their oxygen requirements.

Materials and methods

Microcosms setup and start-up of plant microbial fuel cell assisted with algae cathode

Figure 1 shows the schematic of plant microbial fuel cell assisted with algae cathode used in this study. A two-chamber plant microbial fuel cell assisted with algae cathode microcosm was designed and constructed in the laboratory. The anode chamber was constructed using a piece of polyvinyl chloride-based pipe (length 20 cm; ϕ 11.0 cm), and the cathode chamber was constructed using a transparent plastic rectangular container (length 22.5 cm, width 13.0 cm and height of 10.0 cm). Plastic flanges were bolted together to join these two chambers. A circular piece of Nafion 117 membrane (3.0 cm diameter) was placed between the flanges before bolting them. The anodic chamber was packed with 100 g of graphite granules (average size 0.5–1.0 cm, occupied volume of \sim 1370 ml) which act as an anode electrode. A square graphite rod (size of 2.2 cm length \times 2.2 cm width \times 12.5 cm height, surface area 116 cm²) connected with copper wire was inserted into the graphite granules to collect the electrons. In the cathode chamber, a piece

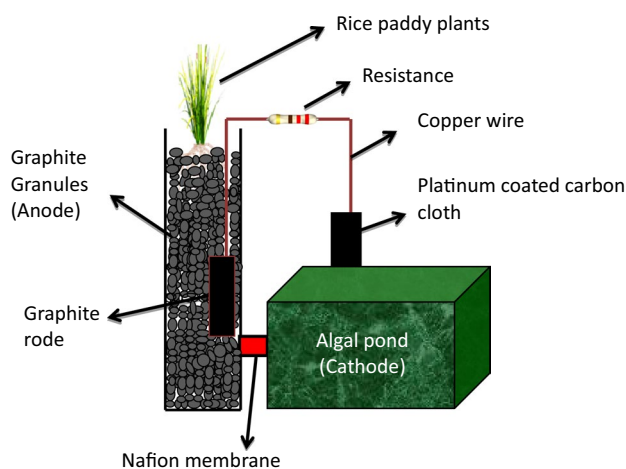


Fig. 1 Schematic of plant microbial fuel cell assisted with algae cathode (not scaled). The plant microbial fuel cell assisted with algae cathode was design to use rhizodeposits of plants as carbon source in anode chamber and photosynthesis of algae to generate the oxygen which acts as a terminal electron acceptor in cathode chamber. The proposed design of plant microbial fuel cell assisted with algae cathode gives self-sustainability to it with regard to fuel substrate and oxidant. It is successfully demonstrated in this study

of 0.8 mg/cm² platinum-coated carbon cloth (6.0 cm width \times 8.0 height cm, surface area 96 cm²) connected with copper wire was used as a cathode. The total volume of the cathode chamber was 1.0 l, whereas the void volume of the anode chamber after packing with graphite granules was 0.8 l. Open ends of the wire were attached using an external resistance.

In the cathode chamber, blue-green algae (*Cyanobacterium phormidium*) were grown using BG11 media for algal growth Stanier et al. (1971). 10.0 ml of a pre-grown culture of algae was used as inoculums. In the anode chamber, seven rice paddy plants (total weight of 9.6 g) were planted. These plants were collected from a 20-day-old rice paddy plant field situated near Nandankanan Zoological Park, Bhubaneswar. The rice variety was a short-duration variety (80–110 days). Such variety of rice plants spends about 50 days in the vegetative phase, 30 days in the reproductive phase and 30 days in the ripening phase. After collecting them from the field, they were brought to the laboratory and rinsed with tap water to remove the excess soil from the root areas. For plant growth, Hoagland's solution was used in an anodic chamber. The composition of Hoagland's solution was adopted from Hoagland and Arnon (1950). The said solution is a mixture of macronutrient and micronutrient (ml of stock solution for 1 l of Hoagland's solution) as given here: stock (g/l): 202.0 KNO₃, 2.5 ml/l; 472.0 Ca (NO₃)₂·4H₂O, 2.5 ml/l; 15 iron (sprint 138 iron chelate), 1.5 ml/l; 493 MgSO₄·7H₂O, 1 ml/l; 80 NH₄NO₃ 1 ml/l. Micronutrient stock (g/l): 2.86 H₃BO₃, 1 ml/l; 1.81 MnCl₂·4H₂O, 1 ml/l; 0.22 ZnSO₄·7H₂O, 1 ml/l; 0.051 CuSO₄·5H₂O, 1 ml/l; 0.09 H₂MoO₄·H₂O, 1 ml/l; 0.12 Na₂MoO₄·2H₂O, 1 ml/l and 136 KH₂PO₄ (pH 6.0), 0.5 ml/l. During the initial 4 weeks, the anode portion of microcosm was fed with a half portion of new Hoagland's solution and a half portion of old used Hoagland's solution for promoting and retaining the electrochemically active bacteria and attaching them to graphite granules. No external microbial inoculums were added in anode chamber as some of the native microorganisms were attached to roots and rhizospheric zone (Reid et al. 2017; Moronta-Barrios et al. 2018). Subsequently, all anode portion media were replaced with new media. During the remaining experimental period, media utilized in the anode chamber to support the plants growth were changed with new media every 48 h as voltage drops were observed after this period. Similarly, after the initial 15 days of algal growth without any change in the initially provided BG11 medium, the media were changed every 7 days to maintain the algae growth as algae die off observed after this period. Minimum wastage of algal biomass was assured by using filtration through Whatman filter paper, grade 1. Voltage was recorded four times a day, twice in the morning toward the end of the dark phase of 12 h and twice in the evening toward the end of the light phase of 12 h. A spiral white compact florescent bulb of 85 watts

(light intensity of 5000 lm) was arranged to provide light to the whole experimental setup. This bulb was manually operated for creating the light and dark phases of the experiment. All the experiments were carried out at controlled room temperature of $27\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. Analyses of various samples were carried out in triplicates to ensure the accuracy of the experimental results.

Experimental details and analysis

Chemical oxygen demand and dissolved oxygen were measured according to the procedure given by the standard methods (APHA, WEF, 2005). pH was measured using a pH meter (Eutech Instruments CyberScan pH 1500, Eutech Instruments Pte Ltd, Singapore). The voltage (V) was measured using a digital handheld multimeter (Sanwa CD772, Sanwa Electric Instrument Co. Ltd, Japan) on a fixed resistance. Analysis of chemical oxygen demand of the anode solution was first performed at the starting stage (2nd week) and twice (4th and 6th week) in the middle of the experiment and lastly at the final period (13th week) of the experiment. Chemical oxygen demand of the initial Hoagland's solution and the solution after 48 h contact with plants roots present in the anode chamber was analyzed. After acclimatization of plant microbial fuel cell assisted with algae cathode, the experiment was run for another 13 weeks and continuously monitored for electricity generation. Polarization curve was drawn using resistances between 10,000 Ω and 1 Ω . The power (P) and current (I) were determined by basic electrical calculations using the standard relations. The power density and the current density were calculated by dividing the power and current with the volume (m^3) of the used solution.

Result and discussion

Dissolved oxygen, pH and chemical oxygen demand

Dissolved oxygen level was always high in the cathode compartment while it was low in the anode compartment (Fig. 2). With the progression of the experiment, the level of dissolved oxygen concentration increased in the cathode compartment. However, in the anode compartment, dissolved oxygen concentration did not change and it slightly decreased. The above observation is understandable as with time, biomass at the root zone increased which can increase the utilization of the dissolved oxygen. In the case of the cathode compartment, more biomass leads to further photosynthesis and releases a higher amount of oxygen. The dissolved oxygen of the cathode was always high in the light condition due to photosynthetic activity of algae, whereas it was low in anode portion in both light and dark conditions. The initial dissolved oxygen of the cathode portion

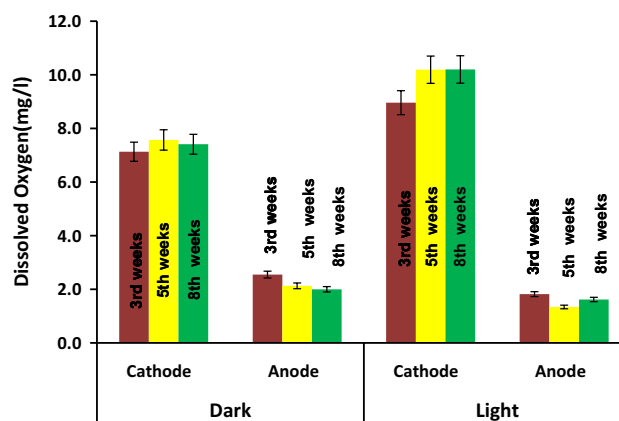


Fig. 2 Dissolved oxygen profile of cathode and anode in light and dark conditions. Results show that dissolved oxygen concentration level at cathode is sufficient to run efficient cathode reaction of a microbial fuel cell. The difference in dissolved oxygen concentration level between anode and cathode also indicates that there is sufficient potential difference to run a microbial fuel cell effectively

was 7.93 mg/l, and the anode portion was 2.16 mg/l. In the light condition, the highest measured dissolved oxygen was 10.19 mg/l in the cathode portion and 1.34 mg/l in the anode portion. In this study, the pH level at both the cathode and anode compartments was also measured. Initially, pH of the cathode portion increased from 6.5 to 8.3 during the acclimatization phase and in the initial phase (up to 20 days). Subsequently, it stabilized at 6.5 ± 0.3 . pH of the anode portion was measured and found to be around 5.9 ± 0.2 . A pH is an important parameter for the operation of microbial fuel cell, and it significantly affects the microbial growth as well as the growth of algae. Both of the organisms perform their vital functions across a limited pH condition. Acidic pH (in the range 3.0–6.2) and an alkaline pH (in the range 8.6–9.0) retard the growth of algae Sorensen et al. (1996). pH difference between both chambers increases the proton diffusion from anode to cathode chamber and plays an important role in the electricity generation Du et al. (2007). The previous study also depicted that the significant pH difference between anode and cathode may enhance the power output in microbial fuel cell (Jadhav and Ghangrekar 2009).

To measure the level of the organic substrate in liquid presented in the anode portion, chemical oxygen demand was measured. The initial chemical oxygen demand of the Hoagland's solution utilized for plant growth was found to be $16.5 (\pm 4.39)$ mg/l. The chemical oxygen demand of the Hoagland's solution after 48 h of contact period with plant roots in the 2nd, 4th, 6th and 13th week of the experiments was 20.18, 57.04, 216.31 and 512.74 mg/l, respectively. It is evident from the results that when rice paddy plants start aging, they release more organics from their root systems that ultimately become available to the electrochemically active bacteria.

Electricity generation

The voltage profile of plant microbial fuel cell assisted with algae cathode is shown in Fig. 3a. Voltage generation by plant microbial fuel cell assisted with algae cathode was dynamic throughout the operational period. During the first week of the experiment, voltage generation increased in light phase and decreased in the dark phase. This trend gradually changed and voltage generation decreased in light phase and increased in dark phase from the 2nd week onwards. The same pattern was observed up to the 8th week of the experiment. Subsequently, there was a slight change in the trend, and again voltage generation increased in light phase and decreased in the dark phase. This pattern was not steady for a long period, and fluctuations were observed in dark and light phases. The pattern of voltage generation in plant microbial fuel cell assisted with algae cathode was similar to voltage production reported by (He et al. 2009). It was also observed at some point that the voltage generation was higher in the dark phase as compared to the light phase. Juang et al. (2012) and Yadav et al. (2015) also reported similar trends while using algae in an microbial fuel cell's cathode. An hourly voltage profile for 10 h in the light phase

was recorded to measure the effect of light on the reactor performance (Fig. 3b). When the light was turned on, the recorded voltage was 159 mv in the starting phase. It was observed that voltage decreased sharply during the first 2 h, and then, there was a sudden rise in voltage and subsequently a fall in the voltage. There was no voltage generation pattern; however, it can be seen that a long-time exposure to light leads to a decrease in voltage generation. Wu et al. (2013) also reported that a long-time exposure to light may lead to the production of oxygen generation and may enhance electricity production. However, extended exposure to light decreases electricity generation. The performance of various plant microbial fuel cells studied in recent years with Hoagland's solution was compiled and is presented in Table 1. Overall, all performances of plant microbial fuel cell assisted with algae cathode are notable among listed studies, although the reported value of plant microbial fuel cell assisted with algae cathode is normalized over volume of the anode chamber.

Polarization curve was also recorded in the 9th week of the experiments and is presented in Fig. 3. Important information on major losses such as activation loss, ohmic loss and concentration loss, which hinder the current

Fig. 3 Voltage profile: **a** weekly voltage profile in dark and light phase, **b** hourly voltage profile in light phase. Results show that plant microbial fuel cell assisted with algae cathode generates variable voltage in light phase (day time) and dark phase (night time). Similarly, due to photosynthesis activities of plants and algae, voltage generation varies throughout day time and night time which may correlate with the light, oxygen availability, etc

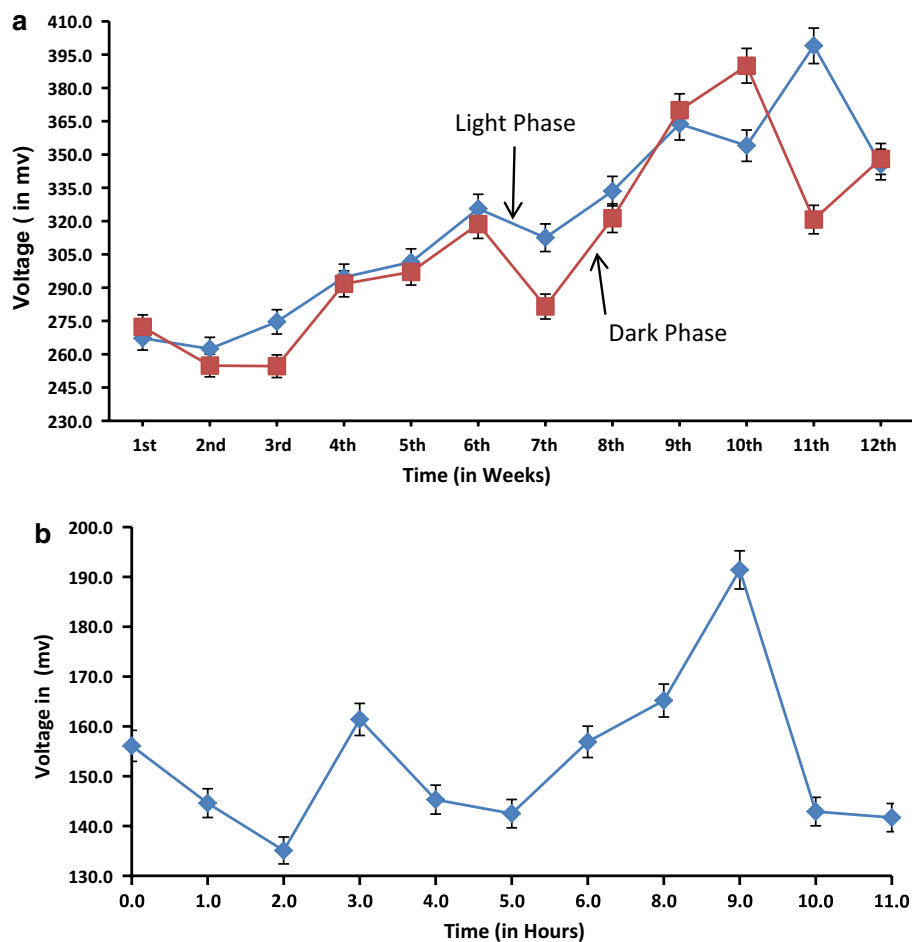


Table 1 Performance of plant microbial fuel cell assisted with algae cathode (modified from Nitisravut and Regmi 2017)

Sr. No.	Plant species	Reactor configuration		Cathode	Average voltage (mV)	Current density (mA/m ²)		Power density (mW/m ²)	Electron acceptor	References
		Reactor type	Anolyte			Anode	Average			
1.	<i>Lolium perenne</i>	Membrane less	1/2 Hoagland's solution	Graphite granule	–	–	–	–	Cr(VI)	Habibul et al. (2016)
2.	<i>Oryza sativa</i>	Proton exchange membrane	Professional growing medium	Carbon fiber	98.5	–	–	0.980 GJha ⁻¹ year ⁻¹	Potassium ferri-rieyanide	Bombelli et al. (2013)
3.	<i>Echinochloa glabrescens</i>	Proton exchange membrane	Professional growing medium	Carbon fiber	98.2	–	–	0.088 GJha ⁻¹ year ⁻¹	Potassium ferri-rieyanide	Bombelli et al. (2013)
4.	<i>Spartina anglica</i>	Proton exchange membrane	Modified Hoagland's solution	Graphite granule	–	84	–	10 79	Oxygen	Timmers et al. (2010)
6.	<i>Spartina anglica</i>	Proton exchange membrane	Modified Hoagland's solution	Graphite granule	–	214	–	50 100	Potassium ferri-rieyanide	Timmers et al. (2010)
8.	<i>Glyceria maxima</i>	–	Hoagland's solution	Graphite granule	–	32	153	4 67	Oxygen	Strik et al. (2008)
9.	<i>Spartina anglica</i>	Cation exchange membrane	Hoagland's solution	Graphite rod in graphite grains	–	–	–	21 222	Potassium ferri-rieyanide	Helder et al. (2010)
10.	<i>Arundinella anomala</i>	Cation exchange membrane	Hoagland's solution	Graphite rod in graphite grains	–	–	–	10 22	Potassium ferri-rieyanide	Helder et al. (2010)
11.	<i>Oryza sativa</i>	Membrane less	–	Graphite felt	–	–	52	– 5.75	Oxygen	Kaku et al. (2008)
12.	<i>Oryza sativa</i>	Membrane less	–	Graphite felt	–	–	163	– 14	Oxygen (with platinum catalyst)	Takanezawa et al. (2010)
13.	<i>Oryza sativa</i>	Proton exchange membrane	Hoagland's solution	Graphite granule	–	–	610 mA/m ³	– 29.77 mW/m ³	Oxygen (with platinum catalyst)	Present Study

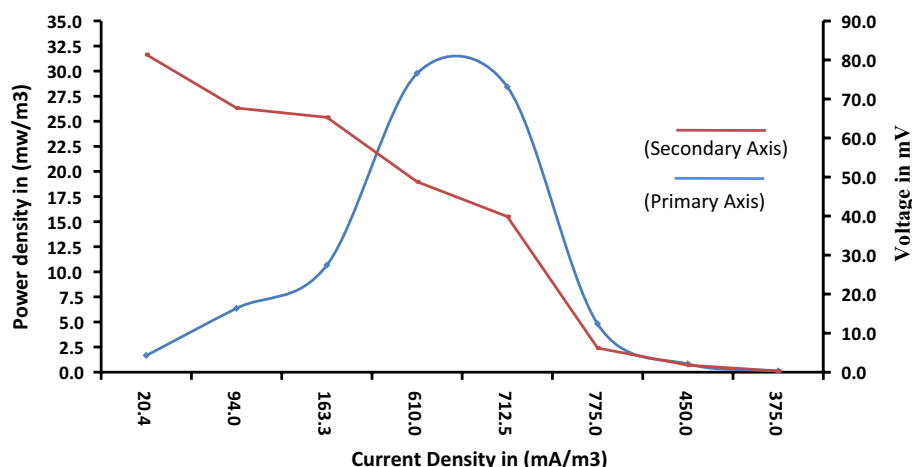


Fig. 4 Polarization curve. From the above polarization curve obtained from plant microbial fuel cell assisted with algae cathode, it is concluded that the first initial sharp drop in voltage reflects the activation losses; second, slow linear-like fall in voltage represents the ohmic

losses; and third, fast drop in the voltage at higher current directs the concentration losses. With minimization of these losses, plant microbial fuel cell assisted with algae cathode can generate more power and current; thus, it should be studied in further research

production, can be extracted from a polarization curve. Srivastava et al. (2015) described the important characteristic features of the polarization curve. They concluded that the first initial sharp drop in voltage reflects the activation losses; second, slow linear-like fall in voltage represents the ohmic losses; and third, fast drop in the voltage at higher current directs the concentration losses. Figure 4 shows that the plant microbial fuel cell assisted with algae cathode microcosm suffers all three major losses. Figure 4 also follows the classical trend where voltage drops with drops in applied resistor loads Srivastava et al. (2015).

Conclusions

The present study successfully demonstrates a low-cost algal-assisted oxygen generation for cathode reaction and rhizodeposits and root exudates of rice paddy plant-based carbon supply as fuel for anode reaction. Further research on other aspects of the current technology such as the effect of greenhouse gas emission from rice paddy plant at anode portion and carbon dioxide utilization at the cathode portion is needed to examine other advantages of using plant microbial fuel cell assisted with algae cathode.

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