

Light intensity affects the performance of photo microbial fuel cells with *Desmodesmus* sp. A8 as cathodic microorganism



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HIGHLIGHTS

- The DO within alga biofilm under different light intensities was investigated.
- Effects of illumination on biocathode performance was investigated from the electrochemical perspective.
- Power generation of photo-MFC and DO change within the biofilm exhibited a similar trend with light intensity.

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ABSTRACT

The performance of photo microbial fuel cells (photo-MFCs) with *Desmodesmus* sp. A8 as cathodic microorganism under different light intensities (0, 1500, 2000, 2500, 3000, 3500 lx) was investigated. The results showed that illumination enhanced the output of the photo-MFC three-fold. When light intensity was increased from 0 to 1500 lx, cathode resistance decreased from 3152.0 to 136.7 Ω while anode resistance decreased from 13.9 to 11.3 Ω . In addition, the cathode potential increased from -0.44 to -0.33 V (vs. Ag/AgCl) and reached a plateau as the light intensity was increased from 1500 lx to 3500 lx. Accompanied with the potential change, dissolved oxygen (DO) within the cathode biofilm increased to 13.2 mg L⁻¹ under light intensity of 3500 lx and dropped to 7.5 mg L⁻¹ at 1500 lx. This work demonstrated that light intensity profoundly impacted the performance of photo-MFC with *Desmodesmus* sp. A8 through changing the DO.

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1. Introduction

Nowadays, energy crisis has encouraged people to explore sources of renewable energy. Microbial fuel cell (MFC) is a technology that can derive green energy from pollutants [1]; it presents a possibility for high strength wastewater treatment [2]. Many microorganisms such as *Geobacter sulfurreducens* [3], *Shewanella putrefaciens* IR-1 [4] and some photosynthetic microorganisms [5] have been studied to improve the performance of MFCs and to expand their functions [6]. Microalgae produce approximately half of the atmospheric oxygen and simultaneously consume the greenhouse gas of carbon dioxide to grow photoautotrophically [7]. Owing to their high photosynthesis efficiency and lipid content, microalgae have the potential to produce new biofuel energy [8].

MFCs containing photosynthetic microorganisms are known as photo-MFCs [9]. It is emerging as a promising technology and capable of converting solar energy into electricity through the

metabolic reactions of photosynthetic microorganisms [9]. In addition to bioelectricity generation, photo-MFCs can also sequester carbon dioxide and remove nitrogen contaminants [10–12]. Recently, microalgae have received increasing attention in cathode reaction due to its low operation cost and self-regeneration ability [13]. It was demonstrated that adopted microalgae can provide oxygen as electron acceptor for the cathode reaction and decrease the over-potential of the oxygen reduction reaction [14]. In spite of the advantages, relevant studies are still in the infancy stages and power generation yields remain relatively low [9,15]. However, the investigation of photo-MFC performance on limiting factors is emergent. Therefore, investigation of factors that can affect the performance of microalgae biocathode is significantly meaningful.

The cathode reaction of an MFC strongly depends on the oxygen concentration within a cathode chamber [12,16]. Microalgae can provide a substantial amount of oxygen through photosynthesis [17]. Light supply is one of the most important factors that can affect the photosynthesis efficiency and metabolic pathway of microalgae [18]. Both insufficient and excessive light could prevent the algae's logarithmic growth [19]. Therefore, optimal utilization of light energy is a great scientific and technological challenge to

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the development of photo-MFCs. Moreover, although dissolved oxygen (DO) within biofilm has been verified to play an important role in the performance of bioelectrochemical systems [20], little information is available on the change of DO within microalgae biofilm with light intensity.

Microalgae *Desmodesmus* sp. is suitable for the coupling system of biodiesel production and wastewater treatment [21]. In the present study, the effect of light intensity on the performance of photo-MFC incubated with *Desmodesmus* sp. (strain A8) was investigated. Furthermore, the effect of light intensity on DO concentration within the biofilm under different light intensity was revealed with microelectrode technology, which provides deep insight of the effect of light intensity on the performance of photo-MFC with microalgae as cathodic microorganism.

2. Materials and methods

2.1. Microalga

The *Desmodesmus* sp. A8, previously isolated was used as cathodic microorganism in this study [22]. The alga was kept in an illuminated autoclaved Erlenmeyer flask with BG11 medium [23].

2.2. Photo-MFC construction and operation

Two-chamber photo-MFCs were constructed with Plexi-glass. Anode and cathode chambers were separated with a cation exchange membrane (16 cm², Zhejiang Qianqiu Group Co., Ltd., China) as a separator. Each chamber had a working volume of 125 ml. Both anode and cathode were made of plain graphite felt (Haoshi Carbon Fiber Co., Ltd., China), with a projected surface area of 16 cm² (4 × 4 cm). The external circuit was connected using titanium wire with a loading of 1000 Ω. The electrodes were held in position by the rubber stopper of the chamber. The Ag/AgCl electrode (3 M KCl) was introduced as the reference electrode.

Anodic effluent from a MFC was used as inoculum of anodic biofilm. The anode chambers were filled with 0.125 L artificial wastewater containing (g L⁻¹): 0.82 CH₃COONa, 6.28 KH₂PO₄, 2.0 NaHCO₃, 10.0 K₂HPO₄, 0.5 Na₂SO₄, 0.5 NaCl and 0.2 MgSO₄·7H₂O; the cathode chambers were filled with BG11 medium and inoculated with *Desmodesmus* sp. A8. One parallel setup without inoculum in the cathode chamber was operated as a control. Throughout the experiment, the anode chamber was wrapped with aluminum foil to avoid the growth of photosynthetic bacteria.

At the beginning of experiment, we measured the concentration of A8, i.e. we inoculated the same concentration of *Desmodesmus* sp. A8 (OD₆₈₀ = 0.4) to the cathode chamber of each photo-MFCs. All photo-MFCs were operated in batch mode with an external resistance of 1000 Ω at 28 °C in an illumination incubator with a cool white fluorescent light source. The light intensities studied were 1500, 2000, 2500, 3000 and 3500 lx, which were controlled by varying the distance between lamps and photo-MFCs as well as the number of fluorescent lamps. In order to keep the same algae amount in our work, the performance of photo-MFC under each light intensity was tested in 10 h.

2.3. Measurement and analysis

The cell voltage (V_{cell}) was recorded every 5 min with a digital multimeter (Keithley Instruments, Inc., USA). Polarization curves were obtained by varying the external resistances using a fuel cell test system (Maccor, USA). The voltage of MFC and cathode potential (P_c) were recorded during the polarization measurement. The anode potential (P_a) was calculated as $P_a = P_c - V_{cell}$. Power (P) was determined as $P = VI$, where V is the cell voltage, and I is the

current. Power density and current density were normalized to the electrode projected surface area.

Electrochemical impedance spectroscopy (EIS) analysis was conducted in the frequency range of 100 kHz to 10 mHz with an electrochemical workstation (AutoLab, Netherlands). The cathode served as the working electrode and the anode served as both the reference and counter electrode. The data was simulated and fitted by Nova Version1.7 (AutoLab, Netherlands).

The concentration of alga was measured with absorbance at 680 nm in an F-4600 spectrophotometer (Hitachi, Japan). DO within biofilm at 200 μm depth was determined with the microelectrode (Unisense, Denmark), more details can be find in previous study [22]. We conducted the experiments with at least duplications to obtain consolidate results; we performed the significant difference determined at the level of $P < 0.05$ using independent-samples T -test.

3. Results and discussion

3.1. Microalga promoted voltage output

The photo-MFCs were incubated with A8 as cathodic microorganism under illumination at light intensity of 1500 lx to facilitate the formation of biofilm on the cathode. Fig. 1 shows the voltage of the photo-MFC and the abiotic control with an external resistance of 1000 Ω. There was an 80 h lag period for the photo-MFC. Thereafter, an increase in voltage up to an average of 182 mV was observed. However, the voltage of the abiotic control remained at approximately 3 mV. The stable voltage indicated that the microalgae cells were successfully enriched on the cathode, providing more oxygen for the reduction reaction of the electrode compared to the control.

3.2. Illumination affected the power generation

After the voltage of the photo-MFC was stable, illumination was provided at a cycle of light and dark to evaluate the effect of illumination on photo-MFC performance. As demonstrated in Fig. 2, illumination mainly affected the performance of biocathode, for which the potential decreased from -368.9 to -526.8 mV (vs. Ag/AgCl) when the light was turned off, resulting in a decrease of the cell voltage from 185.7 mV to 54.7 mV. Anode potential also decreased by 26.9 mV with an illumination shift. Polarization analysis illustrated that the illumination enhanced the maximum power density from 11.3 to 64.2 mW m⁻² (Fig. 3). Light dependent performance was also observed with cyanobacteria [24,25]. Similar trends were observed in eukaryotic algae [12]. However, *Spirulina platensis*

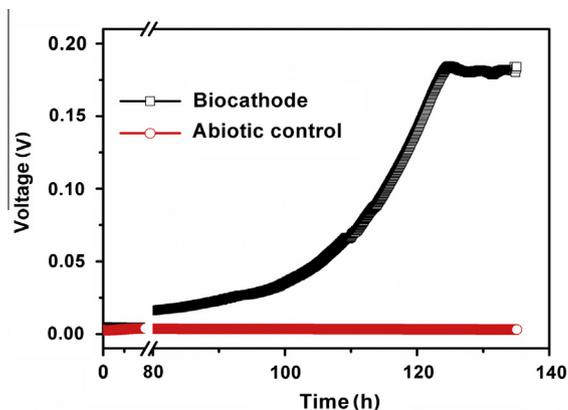


Fig. 1. Voltage change of biocathode photo-MFC and the control during the startup period.

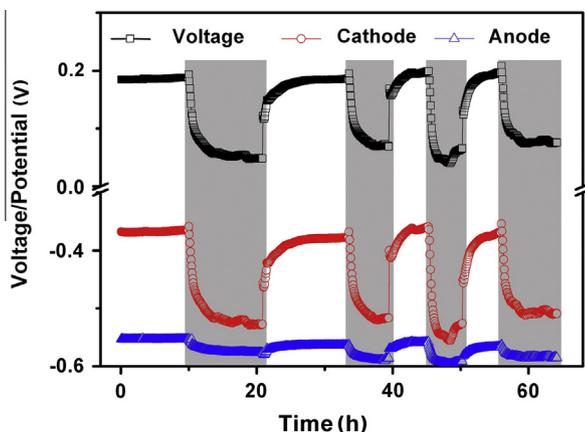


Fig. 2. Variation of electrode potentials (vs Ag/AgCl) and voltage of the photo-MFC in alternate light and dark conditions (shadow indicates no illumination, external resistance = 1000 Ω).

attached to the anode of an MFC generated higher power density in darkness than that in the light [26]. The different findings on the effect of light on MFCs could be caused by the fact that microalgae can have varying roles in reduction reaction of cathode and oxidation reaction of anode.

Internal resistance (R_{int}) is a key limitation on the power output of MFCs [27]. More knowledge about the R_{int} will help to enhance the performance of the MFC. R_{int} of MFCs was the sum of ohmic internal resistance (R_s), cathode resistance (R_c) and the anode resistance (R_a), described as follows:

$$R_{int} = R_s + R_c + R_a \quad (1)$$

where R_s comprises of ohmic resistance of electrolyte and membrane, R_c and R_a include charge-transfer related resistance and diffusion related resistance of cathode and anode, respectively [28]. Three electrode system can be used to estimate the value of anode and cathode resistances and verify R_c and R_a .

EIS analysis revealed that the major difference was the R_c which decreased from 3152.0 to 136.7 Ω while the light was turned on (Table 1). Meanwhile, DO concentration increased from 4.3 to 7.5 mg L⁻¹ in the cathode (Fig. S2), demonstrating that illumination enhanced the photosynthetic efficiency respective to oxygen release, which was further related to the decrease in the cathode resistance.

3.3. Light intensity affected the biocathodes performance

To further validate the effect of light intensity on the performance of the photo-MFC, cell voltage and electrode potentials were evaluated at light intensities of 1500, 2000, 2500, 3000 and 3500 lx (Fig. 4). The voltage output rose from 0.18 to 0.26 V as the light intensity increased from 1500 lx to 3000 lx. When light intensity further increased to 3500 lx, the voltage output was enhanced by 0.01 V. Cathode potential synchronously varied with the cell voltage, increasing by 0.11 V as light intensity increased from 1500 to 3500 lx, while the anode potential increased by only 0.01 V. These results were consistent with the effect of light intensity on chronoamperometric responses of the strain A8 (Fig. S3).

The polarization curves of the photo-MFC at light intensities of 1500, 3000 and 3500 lx are shown in Fig. 5. The maximum power density of photo-MFC at intensities of 3000 lx was 99.09 mW m⁻², 1.5 times higher than that at 1500 lx. When the light intensity was enhanced to 3500 lx, the maximum power density of photo-MFC increased by 4.79 mW m⁻². The utilization efficiency of light energy and the dependence of algal growth on light intensity differed

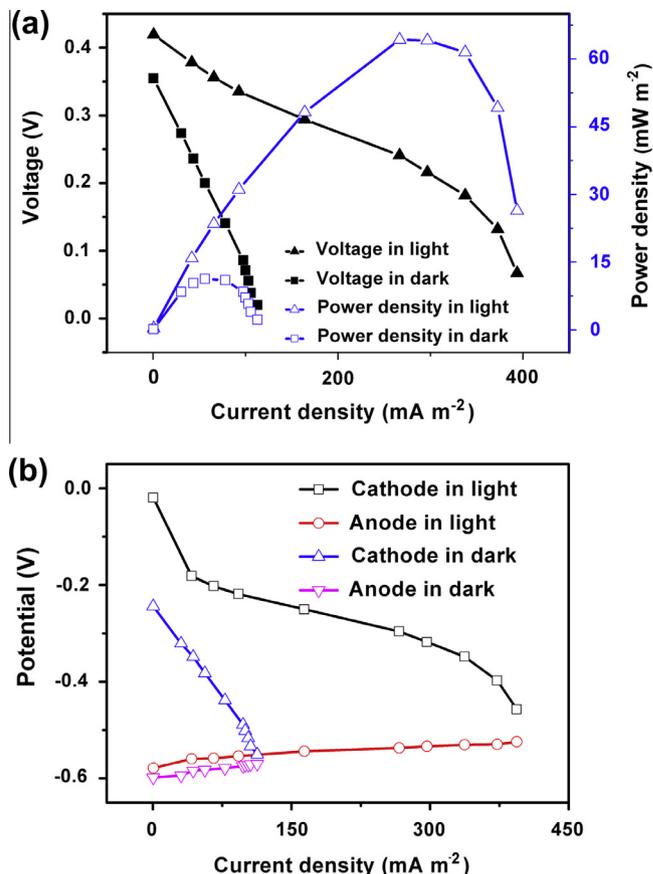


Fig. 3. (a) Power output and (b) electrode potentials (vs Ag/AgCl) as a function of current density in light and in dark.

widely with different strains [15]. Even low light intensity ($\lambda = 550$ nm, 1500 lx) can saturate the electrogenic activity of *Syn-echocystis* [9]. Light saturation of *Chlorella kessleri* was obviously observed when the light intensity increased to 120 $\mu\text{mol m}^{-2} \text{s}^{-1}$, however when light intensity increased to 200 $\mu\text{mol m}^{-2} \text{s}^{-1}$ for *C. protothecoides*, the specific growth rate was considerably enhanced [18]. The utilization efficiency of light energy differed widely with various alga strains maybe due to the difference in genetic make-up and culture condition.

3.4. Oxygen concentration varied with light intensity

In MFCs, oxygen is considered as the optimal cathode electron acceptor due to its high potential and ease of availability [29]. The cathode potential depends on the DO level within the cathodic chamber [11]. Accompanied with the voltage changes of the photo-MFC, the DO within biofilm rose from 7.5 to 13.2 mg L⁻¹ when the light intensity increased from 1500 to 3500 lx (Fig. 6).

Table 1
Composition analysis of internal resistances.

	R_{int}		
	R_s (Ω)	R_a (Ω)	R_c (Ω)
In dark	39.0	13.9	3152.0
In light	51.3	11.3	136.7

R_{int} : the internal resistance of photo-MFC.
 R_s : ohmic resistance derived from photo-MFC.
 R_c : the cathode resistance of photo-MFC.
 R_a : the anode resistance of photo-MFC.

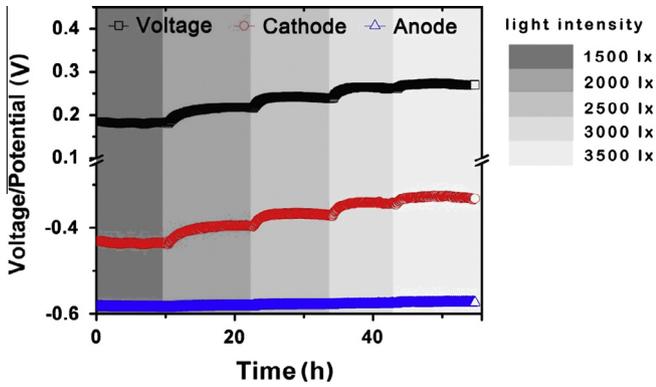


Fig. 4. Variation of electrode potentials (vs Ag/AgCl) and voltage output of the photo-MFC under different light intensity (external resistance = 1000 Ω).

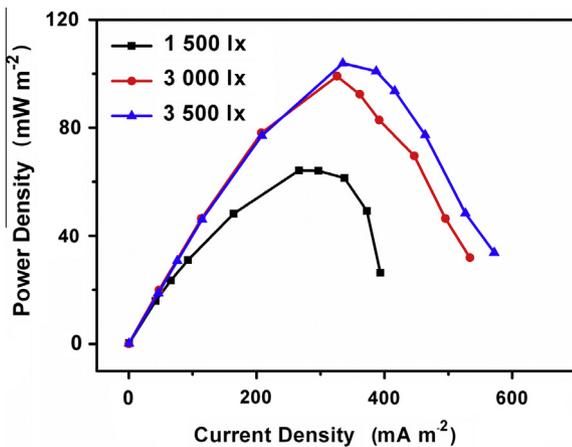


Fig. 5. Polarization curves of the photo-MFC under different light intensity.

The microalga attached to the cathode can continuously provide substantial oxygen through photosynthesis under illumination. Oxygen diffused from biofilm to the solution, and thus the DO in electrolyte is super saturation. Increasing the DO concentration was supposed to be responsible for the voltage change. Voltage output of photo-MFC and DO concentration within the cathodic biofilm exhibited a similar trend with light intensity, demonstrating that O_2 produced by *Desmodesmus* sp. A8 affected the voltage output. The DO concentration in anodic chamber is below 1 mg/L

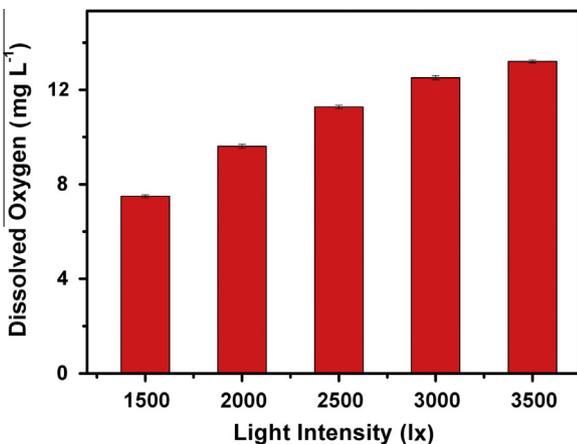
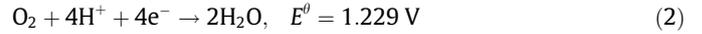


Fig. 6. DO concentration within the *Desmodesmus* sp. A8 biofilm as a function of light intensity revealed with microelectrode technique.

during the experiment, this low concentration will not affect the reaction of the microbes in anode.

Oxygen is reduced to water in the cathode chamber with electrons and protons according to the following equation [30]:



The equilibrium potential of oxygen reduction in cathode could be described with the Nernst Eq. (2):

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}} \quad (3)$$

where E and E^0 are the actual and the standard electrode potentials for each half cell reaction. a_{Red} and a_{Ox} are the activity of reducing species and oxidizing species in the solution of the cathode chamber, respectively. T is the absolute temperature, R ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) is the universal gas constant, F ($9.648 \times 10^4 \text{ C mol}^{-1}$) is the Faraday constant, while n is the number of electrons involved. In this work, the theoretical electrode potentials of O_2 reduction could be described as follows:

$$E_{\text{O}_2/\text{H}_2\text{O}} = E_{\text{O}_2/\text{H}_2\text{O}}^0 - \frac{RT}{4F} \ln \frac{1}{a_{\text{O}_2} \times a_{\text{H}^+}^4} \quad (4)$$

In this study, the pH of the catholyte was 9.12, when the light intensity was increased from 1500 to 3500 lx, while DO concentration within algae biofilm rose from 7.50 to 13.21 mg L^{-1} (Fig. 5). Improving the cathode performance resulted in the increased voltage due to the light intensity being raised (Fig. 4). Poor catalytic activity of graphite reducing oxygen is another factor affecting the performance of the cathode.

Several studies have demonstrated that oxygen in the cathode chamber was reduced to H_2O_2 [20,31]. The possible reactions and the standard electrode potentials can be described as:



The risks of cellular damage may arise through oxidizing proteins when H_2O_2 compounds are over produced [32]. In addition, the increase in pH of the catholyte to 9.12, can influence the microbial electro-activity and increase the oxygen reduction over-potential. Both of them inhibit the performance of the microalgae.

When the light intensity increases to higher values, the effect of light intensity on microalgae growth could be classified as four phases, that is the lag, light limitation, light saturation, and light inhibition phase [33]. Therefore, the effect of light intensity on the performance of photo-MFC may also be classified as four phases corresponding to the increase in light intensification, including (1) lag phase in which voltage output remains unchanged as light intensity increases; (2) light limitation phase in which voltage output rises with increasing light intensity; (3) light saturation phase in which voltage output stays constant as light intensity increases, and (4) light inhibition phase in which voltage output declines when light intensity increases. In this study, the light limitation phase and light saturation phase were observed when the light intensity increased from 1500 to 3500 lx. When light intensity exceeded 3000 lx, the stable current output of three electrode systems inoculated with *Desmodesmus* sp. A8 was clearly noticed.

4. Conclusion

This study demonstrated that *Desmodesmus* sp. A8 significantly enhanced electricity generation under light illumination. Light intensity showed a profound impact on the cathode potential of photo-MFC, while anode potential varied a little during light intensity changes. The DO within biofilm synchronously varied with light intensity. The dependence of the voltage output responses

of photo-MFCs varied with light intensity, thus when light intensity increased to 3000 lx, the voltage output of photo-MFC increased to a plateau. This study presented an insight into improving the performance of photo-MFCs.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apenergy.2013.11.066>.

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