A MICROFABRICATED BIO-SOLAR CELL FOR SELF-SUSTAINABLE FIELD APPLICATIONS

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ABSTRACT

We report an entirely self-sustainable microfabricated bio-solar cell from which the power is generated through microbial photosynthetic and respiratory activities. The self-sustained bio-solar cell can continuously generate electricity from solar energy without the need for external input of organic matter (anolyte) and electron acceptor (catholyte). To enhance the bacterial attachment/electron coupling and solar energy capture, screen-printed carbon ink based anode was used instead of conventional transparent indium tin oxide and the anode structure was designed to face the sun while the produced protons traveled toward the cathode through perforations at the periphery of the anode. We generated a maximum power density of 90 nW/cm² through photosynthetic reactions of cyanobacteria, *Synechocystis sp.* PCC 6803.

INTRODUCTION

With increasing concerns about the energy crisis and global warming, solar energy is gaining more attention since it is extremely abundant and is a carbon-free, renewable energy source. However, the techniques for harnessing solar energy are limited primarily due to the semiconductor-based photovoltaic devices which have many enduring issues, including sustainability, high costs of materials and fabrication, and limited operational lifetimes. A new approach to convert solar energy into electricity has evolved with advances in microbial fuel cell technologies [1, 2].

Bio-solar cells are microbial fuel cells that utilize natural photosynthetic microorganisms such as cyanobacteria or algae. During photosynthesis, the microorganisms harvest solar energy to convert carbon dioxide and water into oxygen and carbohydrates, which will subsequently be used for their respiratory reaction, regenerating carbon dioxide and water [3]. During these reactions, electrons are released through extracellular electron transfer pathways and flow to the cathode through the external electrical circuit (Fig. 1). Simultaneously, the released protons diffuse from the anodic chamber to the cathode, where they re-combine with electrons and O₂ to re-form H₂O.

As a result, the bio-solar cell can continuously generate electricity from solar energy without additional organic matter since light energy absorbed by the photosynthetic reaction splits water and generates oxygen, protons, and electrons [4]. Only requiring sunlight, water and carbon dioxide to operate, bio-solar cells will offer advantages over current microbial fuel cells, chemical fuel cells, or photovoltaic cells, in that the catalytic microorganisms used in the devices are self-sustainable, relatively inexpensive, and capable of power production during the day and night. This system resembles the Earth's natural ecosystem, where living organisms work in conjunction with the nonliving components of their environment to offer self-sustainable and self-maintainable features as a system. To date, successive efforts have focused on demonstrating the photosynthetic electrogenic activities of various cyanobacteria or algae [1-5]. However, the metabolic

Figure 1: Principle of operation in a bio-solar cell. Schematic representation of the photosynthetic and respiratory electron transport pathways in cyanobacteria

pathways involved are only partially understood, and their significantly low power density and low energy efficiency makes them unsuitable for practical applications.

Recently, we reported a micro-sized bio-solar cell (57 μ L) that can produce sustainable energy through the photosynthetic reactions of cyanobacteria, *Synechocystis sp.* PCC 6803, in the anode [6]. We significantly increased the power density of micro-sized bio-solar cells by increasing surface area-to-volume ratio, obtaining a maximum power density of 7.09 nW/cm². This is 170 times more power than ever previously reported for MEMS bio-solar cells, however, the bio-solar cell performance is still insufficient for applied use and complete self-sustainable power generation is not yet possible. One of the major issues with our previous bio-solar cells is that the anode material and the device architecture were inappropriate for adequate solar energy capture/bacterial attachment and light penetration into the first layer of any biofilm growing on the surface. This resulted in a decrease in power/current generation, mainly because the bio-solar cell had a conventional dual-chamber device configuration with a face-to-face arrangement of electrodes. In addition, the thin gold anode showed poor interaction between the bacteria and anode. Another concern about our previous bio-solar cell system was the need to continuously introduce potassium ferricyanide as an electron acceptor (catholyte). Although this chemical has the advantages of fast cathodic reaction and low overpotential, these liquid-state electron acceptors may be impractical and unsustainable for applied use due to their requirement to regenerate chemicals.

In this paper, we developed a novel single-chambered device structure that is different from the conventional, dual-chambered

Figure 2: Principles of operation of our new bio-solar cell. The anode structure was designed to face the sun while produced protons travel toward the cathode through holes at the periphery of the anode.

microbial fuel cells with a face-to-face electrode arrangement. Both the anode and cathode were configured upright (face-up) to ensure that (i) the capture of solar energy can be maximized and (ii) the carbon-based materials can be utilized as an anode material instead of an inefficient, transparent indium tin oxide or thin gold for bacterial attachment/electron coupling (Fig. 2). Produced protons travel toward the cathode through perforations on the anode instead of through aqueous cathode systems.

Based on this innovative device structure, we significantly increased the power density of the MEMS bio-solar cell up to one order of magnitude larger than that of our previous device [6].

MATERIALS AND EXPERIMENTAL SET-UP

Device Fabrication and operation

Fig. 3 and Fig. 4 show the schematic of the bio-solar cell and of the fully assembled micro-fabricated bio-solar cell, respectively. The device consisted of five functional layers: anode chamber layers, an anode layer, a proton exchange membrane, an air-cathode layer, and supporting layers. A thin rubber layer ($\sim 100\ \mu\text{m}$) was sandwiched between each layer and the entire device was assembled by the two supporting frames with bolts and nuts. The bio-solar cell had a $\sim 300\text{-}\mu\text{L}$ single chamber defined by laser-machined PMMA substrates. Carbon anodes were deposited on the poly(methyl methacrylate) (PMMA) substrate using screen/stencil printing methods. Previously reported air-cathode techniques were applied for this small-scale bio-solar cell system; the catalyst layer directly faced the liquid, and the opposite side faced air, with diffusion layers to avoid water leakage and limit oxygen diffusion into the anode chamber [7]. The air-cathode bio-solar cell allowed the use of freely-available oxygen in the air as the electron acceptor, considerably improving the process's sustainability and decreasing the cell's operational costs. The bio-solar cell generated power/current output without the need to add organic fuel (anolyte) or electron acceptor (catholyte), making it entirely self-sustainable.

Figure 3: Schematic of the individual layers in the microfabricated bio-solar cell. There are holes at the periphery of the anode layer.

Figure 4: (a) A photo-image of the fully assembled MEMS bio-solar cell, (b) its top-view, and (c) its bottom-view. The cell has a $\sim 300\text{-}\mu\text{L}$ single chamber defined by PMMA and rubber layers.

Inoculum

Cultures of *Synechocystis sp.* PCC 6803 were grown at $30\ ^\circ\text{C}$ in BG-11 medium under continuous aeration and illumination provided by a fluorescent lamp. BG-11 medium contains 1.5 g NaNO_3 , 40 mg K_2HPO_4 , 75 mg MgSO_4 , 36 mg CaCl_2 , 1 mg of EDTA, and 6 mg of citric acid and of ferric ammonium citrate per 1 L distilled water. The anolyte with bacteria was injected continuously at a rate of $1\ \mu\text{L}/\text{min}$ until the anode chamber was completely filled. Once the chamber was fully filled, the supply of the anolyte stopped and the microfluidic tubings were sealed with clamps.

Measurement Setup

We measured the potential between the anode and the cathode by a data acquisition system (NI, USB-6212) and recorded the results every 1 min via a customized LabVIEW interface. An

Figure 5: Positive light response of the bio-solar cell under 100 k Ω resistor. The device was examined under 2 hour light/dark intervals. The white bars indicate the illuminated period and the shadow indicates the dark period.

external resistor was used to close the circuit by connecting the anode and cathode. The current through the load was calculated via Ohm's rule and the output power was calculated via $P=V \times I$. Current and power densities were normalized to the anode area.

RESULTS AND DISCUSSION

Biofilm formation

Cultivation of photosynthetic bacterial biofilms directly onto anode surfaces appears to be critical for high performance bio-solar cells. Microorganisms in the device can be planktonic cells (suspension) and/or biofilms [8]. Many bio-solar cells use planktonic cells and exploit an exogenously-supplied redox mediator to transfer electron from the cell surface to the anode [4, 9]. Therefore, power outputs from the planktonic cells are very low and the use of exogenous mediators is undesirable for sustainable field applications. More recently, the use of exogenous mediators has been avoided by growing photosynthetic bacterial biofilms directly onto anode surfaces to exploit the endogenous exoelectrogenic properties associated with biofilm development [4, 10]. Moreover, microorganisms in biofilms play a more important role in increasing bioelectricity. Davila et al. showed that the contribution of suspended bacteria was only about 20% of the total power generation in the microbial fuel cell [11]. In this work, noticeable biofilm growth was also observed over time. Along with the biofilm formation, the gradual increase in current density was monitored as shown in Fig. 5. It should be noted that *Synechocystis* sp. PCC 6803 can grow and form biofilm without the need of additional nutrition.

Current and power generation

Fig. 5 shows a current profile of the bio-solar cell under a 100 k Ω resistor. The current showed a decreasing trend immediately after the supply of the anolyte stopped and the microfluidic tubings were sealed with clamps. However, the current generation gradually increased over time. During operation at 2h/2h light/dark cycles, the device showed positive light response: the current increased under illumination and decreased in dark. After 40 h of operation, significant increase in current density was observed with a noticeable green biofilm formation on the anode. The difference of the current generation between the light/dark periods became distinct at 40h. This is mainly due to the biofilm formation. During dark, the current output was not zero due to the cellular

Figure 6: Polarization curve and output power measured as a function of current (a) under dark and (b) light conditions

respiration creating energy from the carbohydrates produced during the day. Temperature remained constant at 30 ± 2 °C throughout the experiment and changes in current output did not correlate to the minor fluctuations in temperature observed. This indicates that the current/power responses monitored were mainly light dependent.

Fig. 6 shows polarization curves and power outputs of the bio-solar cell under light and dark conditions. The values were derived and calculated based on the maximum current value at a given external resistance (4.7 M, 1M, 470k, 100k, 47k, 22k, & 10k Ω). We obtained a maximum power density of 90nW/cm² under four fluorescent lamps, which is the highest power density among all miniaturized bio-solar cells [6, 12, 13]. However, this power density is still in several orders of magnitude lower than that of even the smallest power microbial fuel cells [14]. The current limit in the performance of the bio-solar cell is primarily due to the high internal resistance, resulting in reduced power densities. Using the polarization curve in Fig. 6, we estimated their internal resistance in that the increased current is accompanied with a maximum power output when the external resistance approaches the internal resistance [15]. The internal resistance of the bio-solar cell yielded about 470 k Ω both during light and at night, which are several orders magnitude higher internal resistance than that of other biofuel cells (several Ω) [16]. The high internal resistance observed in our experiments might be due to the poor electron transfer from cyanobacteria to the anode surface and from the

inefficient interactions between the biological material and anode. However, a proper understanding of their metabolic pathways involved in extracellular electron transfer is still lacking. The evolution of this technology requires comprehensive understanding of (i) the behavior and physiology of those photosynthetic bacteria and (ii) their interaction with the electrode at a new level of detail and efficiency. In that sense, micro-sized bio-solar cells can facilitate studies of those microbial behaviors in a smaller group of cells with excellent control over the microenvironment.

CONCLUSION

We developed a micro-sized bio-solar cell for self-sustainable field applications. A carbon-based single-chambered device with a face-to-face electrode arrangement was designed so that capture of solar energy can be maximized and bacterial cell attachment/electron coupling can be enhanced. The maximum power density of 90 nW/cm² at a current density of 300 nA/cm² was generated through photosynthetic reactions of cyanobacteria, *Synechocystis sp.* PCC 6803, which is the highest power density among all miniaturized bio-solar cells. This sustainable micropower source will be essential for a large array of military mobile and wireless applications, including perimeter defense networks, environmental protection sensors and micro vehicle applications. Furthermore, this work will (i) contribute to an in-depth understanding of the interplay between miniature device architectures and photosynthetic microorganisms and reveal fundamental problems in electron transfer at the microbial/anode interface, and (ii) result in a barrier-transcending advancement in bio-solar cells, attaining higher power density and energy efficiency that can release bio-solar cell technology from its restriction to conceptual research, advancing its translational potential toward practical, real-world applications.

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