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Electricity Generation by Photosynthetic Biomass

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1. Introduction

Biofuel cells generate electricity through biological processes. Conventional microbial fuel cells (MFCs) operate by converting organic substrates, such as glucose, acetate, starch, and lactate, to electrical bioenergy through microbial oxidation processes [1-3]. A typical MFC consists of an anodic and a cathodic chamber with electrodes partitioned by a proton exchange membrane (PEM) or a cation exchange membrane. This membrane functions as an insulator for maintaining the redox potential and only allows specific ion exchange [4].

While MFCs use suspension cultivation of microorganisms in the anodic chamber [5], some MFCs attach microorganisms to the electrodes to form a biofilm [6]. As microbial oxidation consumes the supplied substrates, the anode surface generates electrons and conducts them to the cathode through an external circuit. The resulting cations pass through the membrane to the cathode in the electrolyte. However, the following three factors limit MFC performance: (1) electron activation on the anode and cathode surfaces, (2) electron transfer from microbial cells to the anode, and (3) internal resistances of the circuit and anions passing through the membrane. Researchers have developed electrode modification, mediator addition, and membrane-free designs to address these issues and improve MFC performance [5]. Different electrode materials produce different activation polarization losses; for example, the noble metal platinum (Pt) offers superior catalytic activity. But, graphite, graphite felt, Pt-coated graphite, and other metal-coated materials are employed as cost-effective electrodes [5,7,8].

Since the cell surfaces of microorganisms are not electrically conductive, the electrons inside the cells cannot directly transfer to the surrounding electrolyte [9,10]. For this reason, previous designs adopt several kinds of toxic and unstable electro-chemicals as electrochemical mediators, or electron shuttles: neutral red (NR), methylene blue (MB), thionint, and phenolic compounds [4,10]. However, these active chemicals are expensive and toxic, rendering them unsuitable for long-term operation [4]. Exchange membranes are the most expensive components of typical MFC [10]. These membranes insulate and separate different kinds and/or concentrations of electrolytes into two chambers and restrict specific ion exchange. Once the permeability of the exchange membrane becomes poor, the resulting increase in ohmic resistance decreases MFC performance [11]. A membrane-free system may address these concerns. In a membrane-free system, the diffusion gradient of the dissolved reactants between the anode and cathode maintains the electrochemical

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potential with a sufficiently long distance [5]. However, this sufficient long distance leads to a large internal resistance [4,10].

Many operational MFCs employ microbes such as *Clostridium* sp., *Geobacter* sp., *Shewanella* sp., *Synechocystis* sp. and some photosynthetic microorganisms as microbial catalysts for electricity generation [4, 12, 13]. These non-photosynthetic and photosynthetic microorganisms require external substrates to live and generate electricity in the heterotrophic cultivation mode. Several recent studies apply mediator-free and membrane-free MFCs for energy recovery in wastewater treatment [10, 11, 14, 15]. This promising design for MFC is also applied in our study. The current study uses the photosynthetic microorganism *Spirulina platensis* for electricity generation. When *S. platensis* attaches to the anode, it maintains the chemical potential using the attached biomass and conducts the produced electrons to the anode directly instead of transporting them through a mediator, exchange membrane, or reactant gradient. Both photosynthetic reaction in light and respiration reaction in dark can generate electrical power. The attractive design factors of a photosynthetic microbial fuel cell (PMFC), not only include its mediator-free and membrane-free design, but also instant electricity generation instead of a long cultivation time [16]. This study attempts to operate a PMFC in buffer solution using the batch mode with no organic substrate. This study also examines the effects of electrode spacing, electrolyte pH, temperature, and light on OCV associated on the PMFC power output.

2. Materials and methods

2.1 Cultivation of *Spirulina platensis*

S. platensis was obtained from the Fisheries Research Institute in Pintung, Taiwan, and it was cultivated in Zarrouk medium containing 16.00 g/L $NaHCO_3$, 1.60 g/L NaCl, 1.00 g/L KCl, 0.50 g/L K_2HPO_4, 0.2 g/L $MgSO_4.7H_2O$, 0.10 g/L $(NH_2)_2CO$, 0.04 g/L $CaCl_2{\cdot}2H_2O$, and 0.01 g/L $FeSO_4{\cdot}7H_2O$ [17]. Cultivation was conducted in a 2000 ml Duran bottle with a 1700 ml working volume. The aeration rate of air was 2LPM and a white fluorescent lamp provided a continuous illumination of 30 μmole photon m^{-2} s^{-1}. The cultivation system was operated at temperatures ranging from 28 to 30 °C for 7 days before *S. platensis* was harvested and weighed for the experiments.

2.2 Configuration of a membrane-free and mediator-free PMFC

The proposed PMFC chamber was constructed of transparent poly-acrylic plastic material. The length, width, and height of the PMFC chamber were 4cm, 2cm, and 2cm, respectively. Two platinum electrodes measuring 5cm long, 0.5cm wide, and 0.1cm thick were installed at each end of the PMFC with 2cm and 4cm spacing. One of the electrodes served as the anode for *S. platensis* attachment. Medium solution, carbonic acid, sodium bicarbonate, and sodium carbonate were employed as electrolytes. Using the medium as the electrolyte prepared the mediator-free and membrane-free PMFC for use, as Fig. 1 shows.

3. PMFC operation and measurements

The experiments in this study operated the PMFC in a continuous light illuminated and temperature controlled environment. *S. platensis* with biomass weight of 0.2g was attached to the 0.25cm^2 anode. The PMFC's voltage and current readings were collected every 10 seconds by a dual-channel multi-meter (PROVA 903, manufactured in Taiwan) connected to

the Pt electrodes and a laptop PC through a RS-232 interface. Experiments used different temperatures (20°C, 30°C, and 40°C), light conditions (0 and 30μmol m^{-2} s^{-1}), electrolyte pH values (pH 5.5, 8.5 and 9.9), and spacing between electrodes (2cm and 4cm) to determine their effects on the output voltage and current. Resistances of 22MΩ, 10MΩ, 3.9MΩ, 1MΩ, 500KΩ, 220KΩ, 100KΩ, 56KΩ, 18KΩ, 1KΩ, and 2.5Ω were loaded to reveal the relationship between working current and PMFC voltage in the external circuit. Furthermore, two equally-sized PMFCs were connected in series and in parallel to investigate the effect of setup on overall performance.

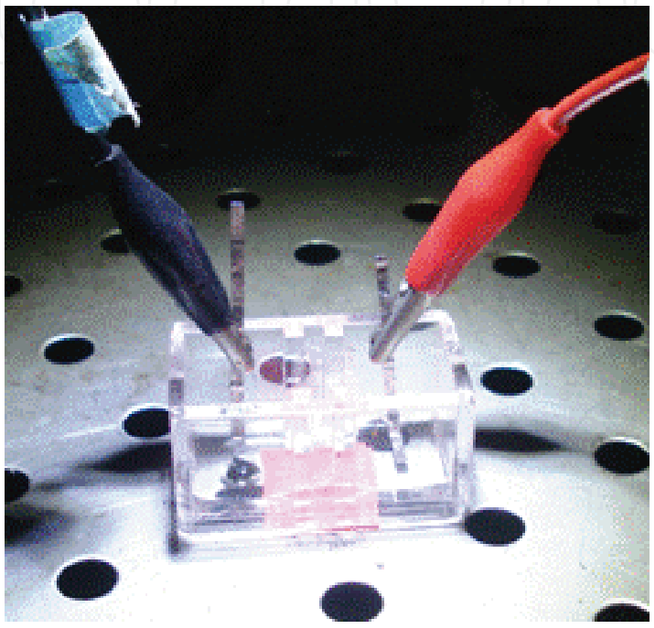

Fig. 1. The mediator-free and membrane-free PMFC with *S. platensis*, which attached to the left side.

4. Results and discussion

4.1 Initialization and instant application

Initially, 0.2g *S. platensis* biomass weight was attached to the anode surface under dark conditions, and the distance between the electrodes was 4cm. Since the biomass attaching onto the anode is a step change for the PMFC, the OCV increased from zero to 0.33V in 13 minutes after the biomass attachment. Figure 2(a) shows the associated responses to the mentioned step change in the OCV readings. Equation 1 indicates that the OCV transition time depends on the time constant (*RC*), which is the product of the internal resistance (*R*) and capacitance (*C*) of the PMFCs:

$$RC = \frac{-t}{\ln(1 - \frac{V}{V_m})} \tag{1}$$

where *R* is the internal resistance of the PMFC, *C* is the capacitance, V is the voltage, *t* is the time, and V_m is the maximum OCV.

Applying the least squares method to the recorded OCV data indicates that the time constant, *RC*, is approximately 4.4 minutes. The time constant represents the time required to reach 63.2% maximum OCV. Reducing the internal resistance decreases the time constant decreases, and simultaneously increases power output [18]. The time constant indicates that the developed PMFC is capable of instant usage.

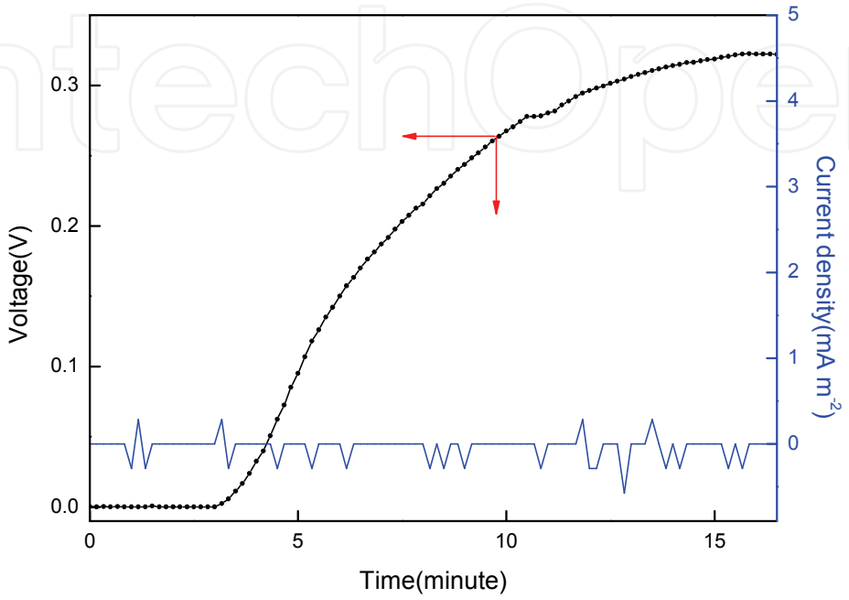

Fig. 2.(a) The response of the OCV associated with the zero current density caused by a step change of 0.2g biomass attachment on the anode.

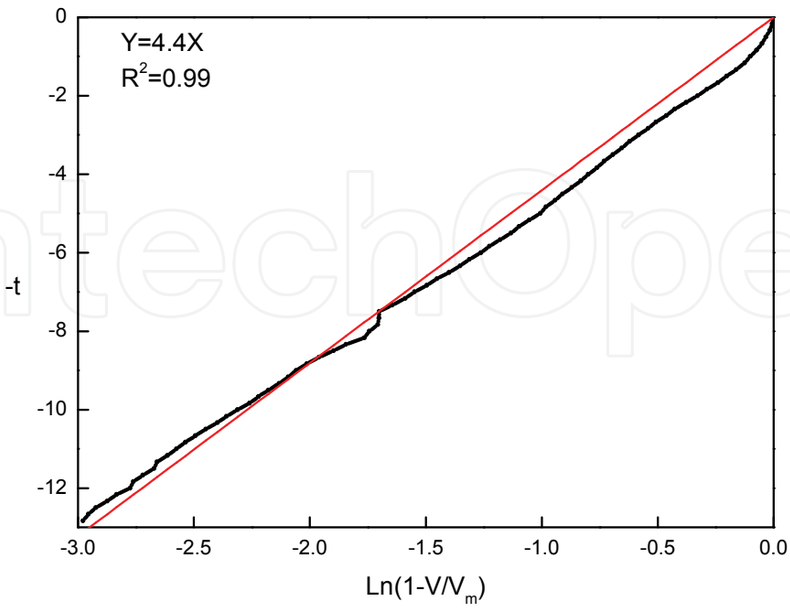

Fig. 2.(b) Determination of the time constant, *RC*, by the least squares method with the collected OCV data.

4.2 Effects of light conditions

The proposed *S. platensis* PMFC was operated in the dark until the OCV approached a pseudo-steady-state level in the first eight minutes. A light intensity of 30μmol photon m^{-2} s^{-1} was applied to the PMFC. The PMFC responses the step change coming from the light intensity by the OCV dropped from 0.24V to 0.19V, as shown in Fig. 3. This negative response in lighting is different from other studies, indicating that the OCV increased with the light intensity [13,19].

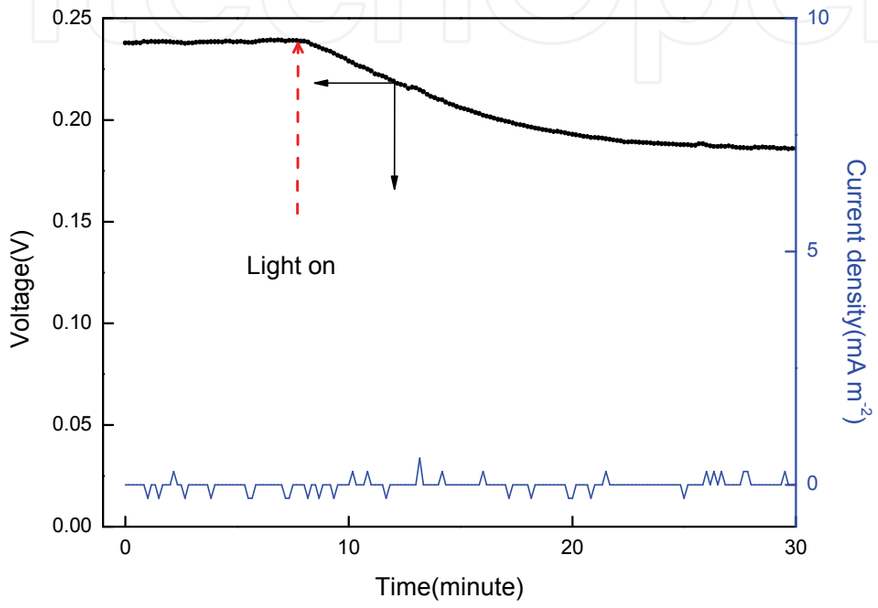

Fig. 3. Effects of lighting on the OCV and output current density.

4.3 Effects of resistance

The PMFC was connected to various levels of external resistances to generate electricity in both dark and light conditions. The OCV of the PMFC was initially 0.24V in the dark condition. A step change of 22MΩ resistor created a voltage drop of 0.22V, and the current density increased from zero to 0.3mA m^{-2}. Resistances of 10MΩ, 3.9MΩ, 1MΩ, 500KΩ, 220KΩ, 100KΩ, 56KΩ, 18KΩ, 1KΩ, and 2.5Ω, were sequentially applied to determine the resistance effects on PMFC voltage and current densities. The resistance change took about five minutes to approach a new pseudo-steady-state level. Decrease of the external resistanceed led to a decrease of working voltages and an increase of current densities until voltage readings approaching zero, as shown in Fig. 4.

4.4 Effects of spacing in dark and light conditions

Spaces between the electrodes were provided to evaluate the output of the voltages and current densities under both the light and dark conditions. The PMFC with 4cm electrode spacing was first operated in dark and light conditions, and responded to the applied light with an OCV drop. Various levels of external resistances were sequentially loaded to

determine the associated current densities and voltages in dark conditions. Results indicate that a shorter spacing distance created higher voltage, current density, resistance, and output. The PMFC under light conditions achieved a lower power density in the same external resistance than that under dark condition.

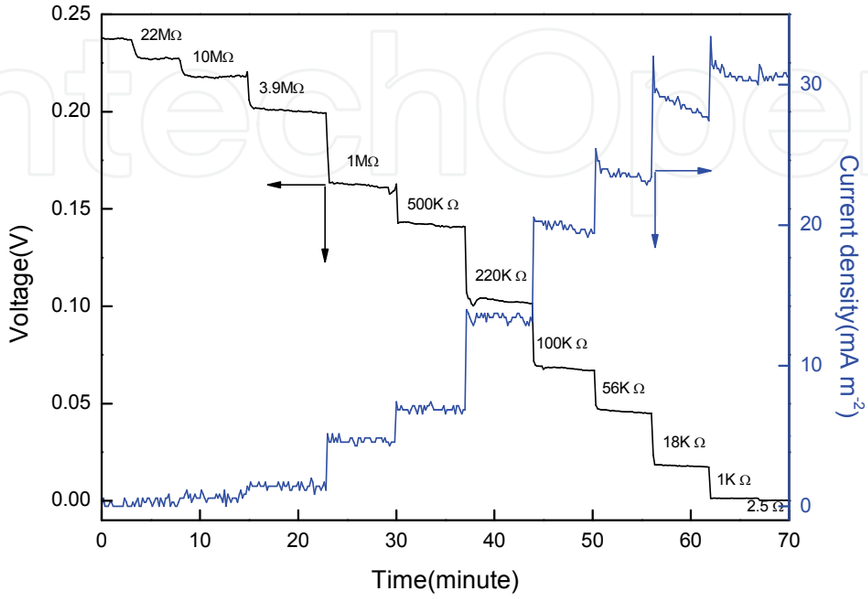

Fig. 4. Time courses of voltage associated with the current density readings of a PMFC with 4 cm electrode spacing after sequentially loading various resistances.

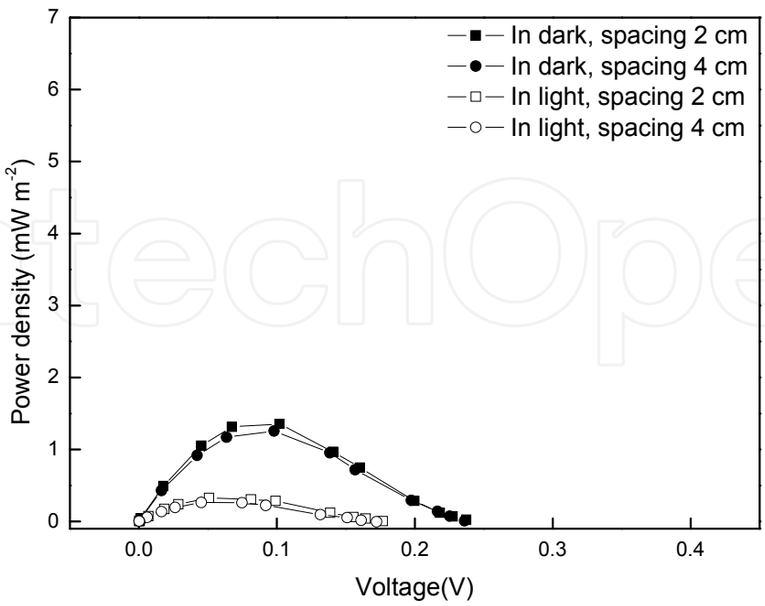

Fig. 5. Power density curves of the PMFC with different electrode spaces of 2 cm and 4 cm under dark and light conditions (pH 9.9, 30°C, and biomass density of 1g cm^{-2}).

4.5 Effects of electrolyte pH

Three pH levels of 5.5, 8.3, and 9.9, maintained by carbonic acid, sodium bicarbonate and sodium carbonate, respectively, were applied to the PMFC to evaluate the effects of pH on power output. Experimental results demonstrate that the highest OCV of 0.39V occurred at pH 5.5; while the lowest OCV of 0.24V occurred under basic conditions (pH 8.3 and pH 9.9) The received maximum power output were approximately 5mWm^{-2}, as Fig 6 shows. These results indicate that the PMFC performed better in acidic conditions. A possible explanation is that the carbonic acid increased the PMFC's ionic strength of H^+ and reduced the internal resistance of PMFC [20].

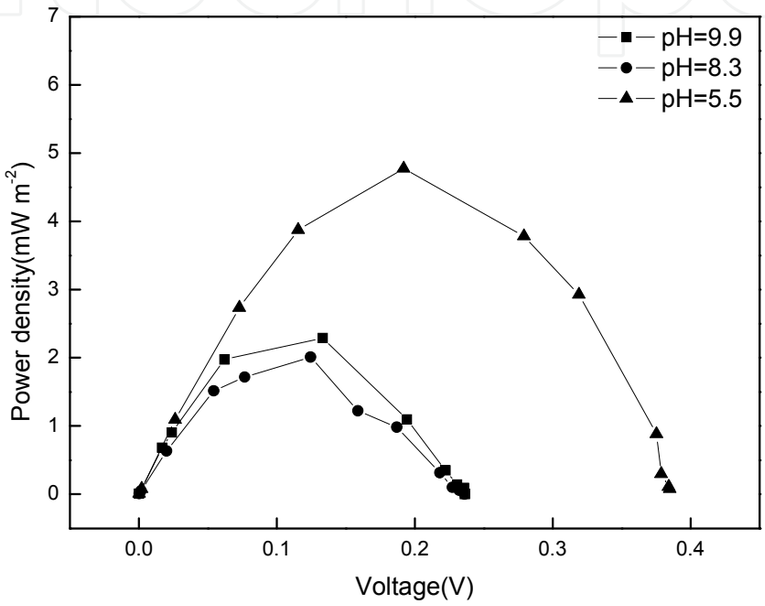

Fig. 6. Power density curves of the PMFC with *S. platensis* at various pH levels of 5.5, 8.3, and 9.9 (in dark, 30°C, and biomass density of 1g cm^{-2}).

4.6 Effects of temperature

The PMFC was operated at 20°C, 30°C, and 40°C to determine effects of temperature on electrical output. The OCV increased as the temperature increased, and the maximal value of 0.39V appeared at 40°C. Figure 7 shows the power density curves of the PMFC loaded with various external resistors. These results show that PMFC achieved higher power output at higher temperatures. A possible explanation is that higher temperatures increased the reaction rate and transportation of electrons [21-23].

4.7 Effects of PMFC connections

Since the negative light response in this study differs from other studies, subsequent experiments examined the effects on the connection of two PMFCs in parallel and in series. External resistors were loaded sequentially to obtain voltage and current density readings. The resulting current-voltage curves in Fig. 8 present that the OCV readings for parallel and series connections were 0.31V and 0.45V, respectively, and the maximum current densities were 40 and 25mA m^{-2}. These results indicate that PMFCs connected in parallel and series

achieved greater current densities and OCVs, respectively. The maximal power density was approximately 2.5mW m^{-2} for both cases.

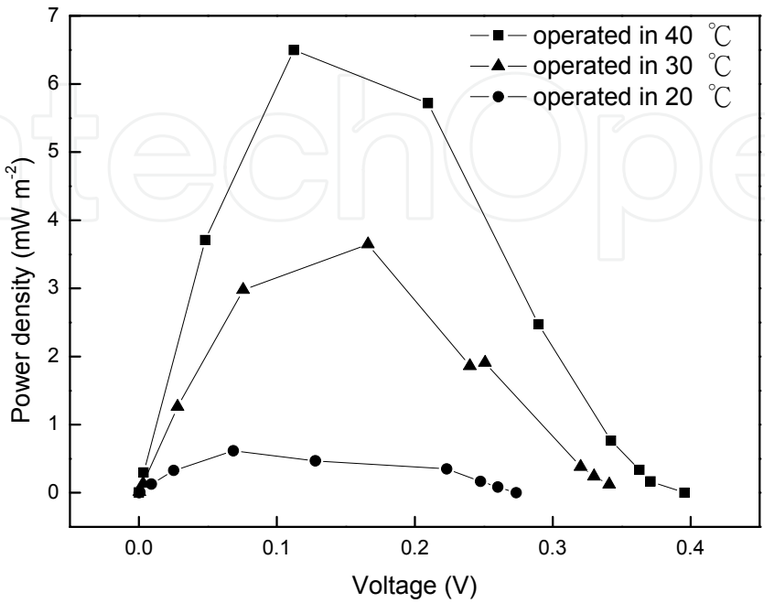

Fig. 7. Power density curves of the PMFC with *S. platensis* under temperature conditions of 20°C, 30°C, and 40°C (in dark, pH 9.9, and biomass density of 1g cm^{-2}).

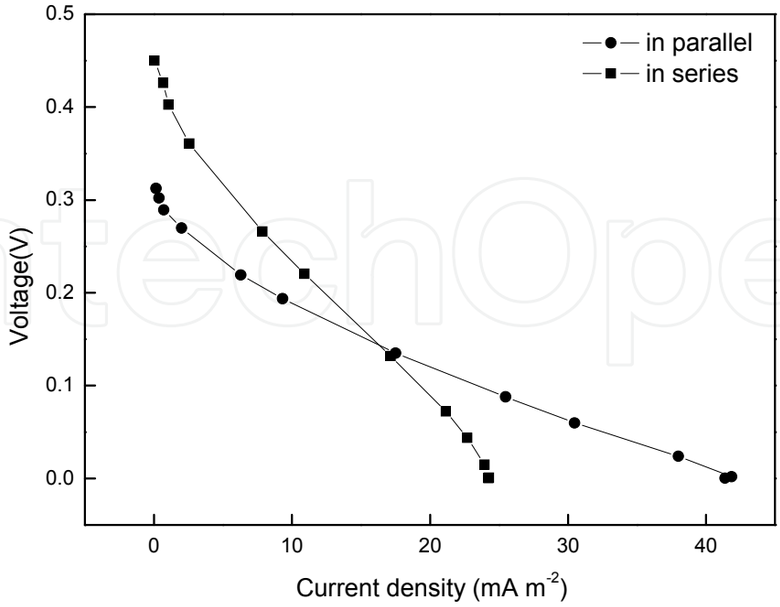

Fig. 8. The polarization curves of two equally-sized PMFCs connected in series and in parallel (in dark, pH 9.9, 30°C, and biomass density of 1g cm^{-2}).

5. Conclusion

The proposed PMFC employs the living bio-catalyst *S. platensis* to generate electricity without membranes and mediators. This study examines PMFC performance under different lighting conditions, electrode spaces, electrolyte pH values, temperatures, and connection types. The proposed PMFC achieved the highest power output in the conditions of dark, 2cm between the electrodes, pH 5.5, and a temperature of 40°C. When two PMFCs of the same size were connected, they exhibited a higher voltage in series and greater current density in parallel.

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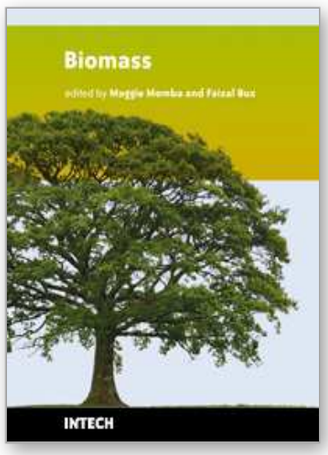

Biomass

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Due to demands placed on natural resources globally and subsequent deterioration of the environment, there is a need to source and develop appropriate technology to satisfy this requirement. For decades mankind has largely depended on natural resources such as fossil fuels to meet the ever increasing energy demands. Realizing the finite nature of these resources, emphasis is now shifting to investigating alternate energy source governed by environmentally friendly principles. The abundance of biomass and associated favorable techno-economics has recently changed global perceptions of harnessing biomass as a valuable resource rather than a waste. To this end this book aims to make a contribution to exploring further this area of biomass research and development in the form of a compilation of chapters and covering areas of ecological status of different types of biomass and the roles they play in ecosystems, current status of biomass utilization and deriving energy and other value added products from biomass. In this context biomass can be defined as large plants and trees and different groups of microorganisms. This book will serve as an invaluable resource for scientists and environmental managers in planning solutions for sustainable development.

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