Micro photosynthetic power cell for power generation from photosynthesis of algae

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Devices such as solar and fuel cells have been studied for many decades and noticeable improvements have been achieved. This paper proposes a Micro Photosynthetic Power Cell (μPSC) as an alternative energy-harvesting device based on photosynthesis of blue-green algae. The effect of important biodesign parameters on the performance of the device, such as no-load performance and voltage-current (V–I) characteristics, were studied. Open-circuit voltage as high as 993 mV was measured while a peak power of 175.37 μW was obtained under an external load of 850 Ω. The proposed μPSC device could produce a power density of 36.23 μW/cm², voltage density of 80 mV/cm² and current density of 93.38 μA/cm² under test conditions.

Keywords: Micro Photosynthetic Power Cell; Polymer; MEMS; Energy Harvesting.

INTRODUCTION

Various compact power-generating devices have been developed in recent years among which fuel cells are the most promising systems. The advantages of fuel cells include the usage of continuously replenished reactants, absence of moving parts and reduced thermal conversion. The key disadvantage of the fuel cells is insufficient ionic conductivity of the electrolyte. Micro-scale fuel cells are being investigated as a solution to improve the ionic conductivity⁴,⁵.

Heat engines remain as the primary choice for power conversion at many large-scale power plants. Based on the generation scale, different energy sources ranging from natural gas to coal to nuclear are used. Hydrocarbon fuels containing chemical energy are used in micro heat engines. Although the second law of thermodynamics dictates a limit on the conversion efficiency of the heat engines, larger energy densities are still achieved compared to lithium-ion batteries⁶. Internal combustion engines and steam engines on the micro scale have also been developed and tested⁷. Large viscous losses resulting from thin boundary layers were found as one of the main disadvantages of these micro heat engines⁸.

Thermophotovoltaics (TPV) is another class of energy conversion systems. Here, the power generation is based on a heated emitter radiating photons which are then absorbed by a photocell and converted to electricity. This concept is very similar to that of solar cells with one major difference — the source of radiation⁹. Although the emitter can be heated by sunlight, extremely large beam concentrators are required in order to provide sufficient temperature for efficient operation, which makes it a less practical choice. Hence, the emitter is usually heated by combustion, providing a great deal of versatility in potential fuels. Higher power densities compared to solar cells are reported since the emitter and the photocell are in close proximity. The current challenges in TPV application on the large scale are design, fabrication and material selection⁹.

Solar cells are arguably the most thoroughly explored energy conversion systems. In a typical photovoltaic module, photons of a longer wavelength do not generate electron-hole pairs. The respective portions of the light energy are converted to heat. The working temperature is increased and the cell efficiency is reduced. Structural damage might also occur due to overheating. Thus, combined systems such as photovoltaic/thermal hybrid solar systems were introduced, enabling the production of both electricity and heat from one integrated system⁶,⁹. One example is a combination of TPV and solar-assisted heat pump systems with the TPV panel directly coupled to the heat pump⁷.

Another promising category of small-scale power-generating devices is the Micro Photosynthetic Power Cell (μPSC) studied in this work. As noted from the term, the μPSC employs photosynthesis — a process of converting light energy to chemical energy, responsible for sustaining life on Earth. The μPSC is similar to fuel cells but no resupply of fuel is required. Hence, parameters such as supply and exhaust are not considered as difficulties of design. Like solar cells, the μPSC operates under illumination, but one key difference is that the absence of light not only
Both photosynthesis and respiration form the basis of μPSC operation. Photosynthesis involves the conversion of light energy to chemical energy by living organisms including plants, bacteria, algae, and phytoplankton. Despite its complexity and variety, the fundamentals are quite similar across all organisms, although there are differences in the reactants and by-products. In higher plants and algae, photosynthesis splits water molecules to oxygen (liberated to the atmosphere) and hydrogen (protons). Carbon dioxide and hydrogen are combined into sugars (stored in the plants as a source of food). In the absence of light, the process takes place in reverse, termed respiration, using oxygen and sugar, liberating carbon dioxide and energy. Both photosynthesis and respiration involve electron transport chains which are fundamentals to the μPSC. The electrons are released in one step and taken up in another. The idea is to interfere with the electron-transport chain in such a way that the electrons were directed through an external load, resulting in an electric current. Equations (I) and (II) summarize the processes of photosynthesis and respiration:

\[
\begin{align*}
6 \text{CO}_2 + 12 \text{H}_2\text{O} &\rightarrow \text{C}_6\text{H}_12\text{O}_6 + 6 \text{O}_2 + 6 \text{H}_2\text{O}, \\
\text{C}_6\text{H}_12\text{O}_6 + 6 \text{O}_2 &\rightarrow 6 \text{CO}_2 + 12 \text{H}_2\text{O}.
\end{align*}
\]

**PHOTOSYNTHETIC POWER CELL**

The schematic of the μPSC developed in this work is shown in Fig. 1. The electrolyte chamber was divided into two compartments by a PEM, which was a sulfonated polymer (Nafion®). Electrodes were microfabricated on both sides of the PEM. The anolyte compartment contained a medium composed of live photosynthetic microorganisms such as algae and cyanobacteria. Ferro-cyanide solution was used as the electron acceptor and was located in the catholyte compartment. Electrodes were connected to an external load. The top and optionally bottom sides of the chamber were covered with glass, which allowed light into the chambers. Since the catholyte works as an electron acceptor, it did not need to be exposed to light neither under photosynthesis nor under respiration. Once electrons were released in the anolyte chamber, they were transferred through the external circuit to the other side of the chamber (catholyte). This transfer of electrons created an ionic gradient which was balanced by the PEM.

**Fabrication**

The fabrication process of the μPSC presented in this work differed from those of previously fabricated photosynthetic electrochemical cells. The designs were introduced with the aim of improving the overall efficiency of the μPSC in terms of output power. Different parameters possibly affecting the output power were tested through various experiments. These results are the main focus of the current work. Hence, the fabrication process will only be briefly mentioned below.

In contrast to the majority of the previously described μPSC model, the current device is polymer based. PDMS (polydimethylsiloxane) was used for the main body of the device. Figure 1b depicts the unassembled μPSC, followed by the fabricated device in Fig. 1c. The PEM was sandwiched between two identical half-cells. The half-cells were fabricated in a single step and included the chamber, the desired number of inlets/outlets and fluid ports. Glass covers were attached on both sides and precision tips were attached to the chip, which enabled usage of a peristaltic pump for fluid circulation. Electrodes (100-nm thick; made of gold) were directly patterned on the two sides of the PEM by a process that eliminated the use of a photoresist stripper solution, which was not compatible with the PEM. Moreover, chromium was not used as an auxiliary layer for gold electrode deposition and hence,
the electrode thickness was reduced by over 50% due to the absence of a chromium layer. The final assembly of the μPSC was achieved using oxygen plasma treatment and PDMS glue. Some dimensions of the proposed μPSC are presented in Fig. 1d. The rectangular PDMS chip measured 76 mm by 30 mm, with a thickness of 3 mm. Fluid ports included inlets/outlets which were 2 mm in diameter and circular fluid channels which were 0.5 mm in diameter and 12–18 mm in length. The designated electrode area was in the shape of a square measuring 22 mm by 22 mm.

Measurement setup

A set of resistors with nominal values of 1-kΩ, 20-kΩ and 100-kΩ switches was used as the external load with the μPSC. The switches served to engage each resistor as desired and acted as necessary ports for connections to the measuring system, a data acquisition system and a multi-meter. For some experiments where more resistance values within a certain range were required, such as determination of voltage–current (V–I) characteristics, a potentiometer was used.

In the experimental setup, the electrodes from the μPSC were connected to the designated ports on the external circuit. A data acquisition system was used to measure the output voltages across the μPSC. Data Translator USB data acquisition module is used as the hardware and Measure Foundry is used as the interface between the module and computer. The setup is designed such that one could continuously measure and monitor the Open Circuit Voltage (OCV) across the μPSC. For some experiments, one photosynthetic sample (green algae) was used, while providing proximity of the photosynthetic agents to the PEM are of great importance in electron transfer. Hence, the electrode configuration becomes a critical parameter for investigation. It must be noted that these might vary in relation to the species; for instance, the optimal shape, size and pitch of the pores in the electrodes might vary from one species to another. As mentioned earlier and to facilitate the experiments, one photosynthetic sample (green algae) was used, which enabled a focus on the optimal geometrical parameters for that species.

In order to study the effect of PEM thickness and electrode configurations on ionic and electron transfers, three different configurations of electrodes on three different thicknesses of PEMs were studied. In this study, three types of Nafion® of differing thickness were used as the PEMs (Table 1). Three patterns of electrodes were integrated on the respective PEMs on both sides. Design configurations of these electrodes are presented in Table 2. 100-nm gold was directly sputtered on the PEM surfaces with no chromium used as the external load. V–I characteristics as well as long-term no-load performance were also performed as standard experiments to elucidate the behavior of the μPSC.

Green algae (Chlamydomonas reinhardtii) were used as the photosynthetic microorganism in all experiments. Using the experimental setup explained earlier, the OCV was measured. In addition to current and voltage under certain loadings, current and power densities based on the μPSC’s electrode area were also calculated in order to compare our results with those of previous works.

Effect of PEM and electrode configurations

Ionic transfer in the μPSC is a function of photosynthetic samples, the PEM and electrode patterns. Ionic transfer across the membrane is strongly dependent on the thickness of the membrane, and it is assumed that the thinner the PEM, the more efficient the ionic transfer would be. Electrodes having a high surface-to-volume ratio while providing proximity of the photosynthetic agents to the PEM are of great importance in electron transfer. Hence, the electrode configuration becomes a critical parameter for investigation. It must be noted that these might vary in relation to the species; for instance, the optimal shape, size and pitch of the pores in the electrodes might vary from one species to another. As mentioned earlier and to facilitate the experiments, one photosynthetic sample (green algae) was used, which enabled a focus on the optimal geometrical parameters for that species.

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<table>
<thead>
<tr>
<th>Table 1</th>
<th>Nafion® properties.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEM</td>
<td>Typical thickness (μm)</td>
</tr>
<tr>
<td>Nafion® NRE – 212</td>
<td>50.8</td>
</tr>
<tr>
<td>Nafion® N – 115</td>
<td>127</td>
</tr>
<tr>
<td>Nafion® N – 117</td>
<td>183</td>
</tr>
</tbody>
</table>

Figure 2 (a) Changes in the electrode surface-to-volume ratio with number of pores. (b) Variation of Open Circuit Voltage (OCV) across the μPSC with electrode configurations of Nafion® 212.
Thus, $\Delta \sigma$ indicates the changes in the surface-to-volume ratio:

$$\Delta \sigma = \sigma_N - \sigma_0,$$

where $\sigma_N$ is the electrode surface-to-volume ratio corresponding to $N$ number of pores and $\sigma_0$ is the electrode surface-to-volume ratio with no pores ($N = 0$). As mentioned earlier, the electrode thickness in this work was 100 nm.

Thus, nine µPSC models with three different combinations of PEMs and three electrode patterns were fabricated and tested for performance. For each configuration, two devices were fabricated and the average output of the two measurements were used to present the results. Two percent (2%) potassium ferricyanide solution was used as the catholyte and the OCV was monitored and compared. Figure 2b presents a sample graph illustrating the variations of the OCV with different electrode configurations with Nafion® 212 as the PEM.

The average of maximum OCVs for every combination was considered as the maximum OCV and the average of the mean values obtained over a range was considered as the mean OCV (Fig. 3). It was observed that both the maximum and average OCV adopted the same trend. When the thinnest available membrane was used, the highest output was observed with the electrode configuration D3, whereas for the other two membranes, D2 and D3 outperformed D1. As seen from Fig. 3, the thinnest PEM did not produce a high OCV. These results indicate that one has to select the thickness of the membrane and associated pattern design depending on the fabrication process and other design parameters.

**Effect of potassium ferricyanide concentration**

As mentioned earlier, in this study, potassium ferricyanide was used as the catholyte solution as the electron acceptor. Potassium ferricyanide was used to present the results. Two percent (2%) potassium ferricyanide solution was used as the catholyte and the OCV was monitored and compared. Figure 2b presents a sample graph illustrating the variations of the OCV with different electrode configurations with Nafion® 212 as the PEM.

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**Table 2** Electrode configurations.

<table>
<thead>
<tr>
<th>Design</th>
<th>$D_i$ (μm)</th>
<th>$L_i$ (μm)</th>
<th>Pitch/Diameter</th>
<th>$\Delta \sigma$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1 – High</td>
<td>200</td>
<td>700</td>
<td>1.4</td>
<td>56.849</td>
</tr>
<tr>
<td>D2 – Med.</td>
<td>500</td>
<td>1,000</td>
<td>2</td>
<td>19.545</td>
</tr>
<tr>
<td>D3 – Low</td>
<td>800</td>
<td>1,300</td>
<td>2.6</td>
<td>9.271</td>
</tr>
</tbody>
</table>

Figure 3 (a) Variations of maximum OCV with varying electrode configurations on different PEMs. (b) Variations of mean OCV with varying electrode configurations on different PEMs. (c) Variations of maximum OCV with electrode configuration kept constant. (d) Variations of mean OCV with electrode configuration kept constant.
(K₃[Fe(CN)₆]) is a bright red salt and displays a greenish yellow fluorescence once dissolved in water. Its redox potential is such that it is easily reduced to its related ferrocyanide, making it a suitable solution to be used as the electron acceptor in many power cells. The general oxidation–reduction of ferricyanide is given below:

\[
[\text{Fe(CN)}_6]^{3-} \rightleftharpoons [\text{Fe(CN)}_6]^{4-} + e^-. \quad \text{(VIII)}
\]

Since the catholyte was directly involved in the electron transfer in the μPSC, it was believed that its concentration plays an important role and can affect the output. A μPSC with Nafion® 117 and electrode D2 was used in investigating the OCV with various potassium ferricyanide concentrations. The concentrations studied were 2, 5, 10, 15, 20 and 25%. Figure 4a illustrates the no-load performance of the mentioned μPSC with various concentrations of catholyte followed by Fig. 4b which presents a comparison of these concentrations and their effects on the maximum and mean OCVs.

It was observed that the concentration of potassium ferricyanide directly affects the output voltage. By using more concentrated solutions, both the maximum and mean OCVs show an increasing trend. The changes appeared to be very significant in the first few studied concentrations. In the higher concentrations (above 10%), these changes were not as significant. However, they were still noticeable (10–20%). Eventually, the OCV tended to stabilize at concentrations around 25%. As the performance saturated beyond 25%, this concentration (25%) was chosen for other experiments in this work.

Effect of volume and concentration

Another parameter possibly affecting the efficiency of electron transfer is proximity of the photosynthetic agents (algae in this study) to the PEM. For this study, 50 mL of green algae (Chlamydomonas reinhardtii) with an activity ratio of 0.742 and cell count of 81,600 cells/mL were used as a stock solution. Different concentrations were prepared by diluting the stock solution with water. The concentrations used are 0.5, 0.25 and 0.125 of the stock concentration. In order to examine the effect of proximity of the photosynthetic agents, four different volumes of algae were also used. The volumes of 2 mL, 1.5 mL, 1 mL and 0.5 mL were selected, while 2 mL was the maximum volume. Hence, a total of 16 experiments were performed under an external load of 20 kΩ, where the parametric variations previously mentioned were considered. Twenty-five percent (25%) potassium ferricyanide was used as the catholyte in a μPSC with the following configurations: Nafion® 117 and the electrode pattern D3. This is shown in Fig. 3c.
All experiments with maximum volume or concentration were performed for 45 min including two periods of OCV observation (0–5 min and 30–35 min). All other experiments were conducted for 20 min with the 20-kΩ external load. A sample result for the maximum volume with different concentrations is shown in Fig. 4c. Two outputs (voltage and current) were investigated for each experiment. The period in which the OCV was monitored is marked in gray on the chart. As no load was used in that period, no data for the current was plotted during the OCV measurements. By normalizing the volume and concentration values and averaging the output voltage under the external load for each experiment, eight graphs similar to those presented in Fig. 4d were obtained. Combining these results, an axonometric plot, as presented in Fig. 5a, could be generated.

It was found that there exists an optimal volume for each concentration used. Further experiments can provide a guideline to determine the optimal concentration given the volume of the μPSC, and vice versa. The existence of this phenomenon is most likely due to the interplay among the following considerations: photosynthesis is taking place only where algae are present; however, the zone which is of interest for ionic transfer is located in the vicinity of the PEM, where the released electrons are conducted by the electrode (gold). Increasing the volume of the medium does not change this active zone, but it increases the freedom of the cells to move away from it. As algal cells move farther from the electrode, they contribute less to electron transfer as well as block some photons from reaching the cells present in the active area.

Based on Fig. 5a, the contour plot in Fig. 5b illustrates the correlation between the volume and concentration of algae in impacting the output voltage. It can be observed that at higher concentrations, the volume of algae directly affects the output voltage, whereas at lower concentrations, an increase in volume results in a decrease in output.

At lower concentrations, the effective number of cells that are involved in ionic transfer and are of close proximity to the PEM decrease as volume increases, leading to a reduction in performance. As cells have a tendency to float away from the electrodes and be near to the surface, a lower volume is preferred for lower concentrations. As the concentration increases, the number of cells that are involved in ionic transfer and are of close proximity to the PEM also increases with volume, leading to an increase in performance.

Considering the various configurations of the μPSC and the external load, the maximum measured output voltage was 410 mV. Assuming 75% (300 mV) and greater as the acceptable range of operation, Fig. 5c represents the corresponding range of suitable concentration and volume.

**Effect of illumination**

Illumination is also an important parameter for photosynthetic cultures. Under illumination, photosynthesis is considered as the dominant process (although respiration takes place with a very low rate); on the other hand, in the absence of light, respiration would be the dominant process. A μPSC with Nafton® 117 as the PEM and electrode configuration D2 was used in an experiment for 80 min with...
10-min cycles of light and dark conditions. The OCV was monitored in the last two cycles, whereas in other cycles, a load of 1 kΩ was used as resistance. It was observed in previous experiments that the greater the resistance, the lower the output current would be. In this experiment, a lower resistance was chosen to increase the current for better observation of the variations. Twenty-five percent (25%) potassium ferricyanide was used as the catholyte.

Figure 6a illustrates the variations of voltage and current with light. In all experiments so far, light intensity was kept at 600–650 lux. In this experiment however, the measured photometric parameter of the illumination source reaching the surface of the μPSC was 1,100–1,200 lux. Photosynthetic samples and components of the μPSC were probably the most important factors in determining the functionality of the μPSC. Both the photosynthetic sample and μPSC used in this experiment were in relatively good condition, since improvements and optimizations were learned and implemented from previous experiments. That is probably one of the reasons that the outputs did not vary significantly. The lack of fluctuations in Fig. 6a was also believed to be related to the fluctuations of the photosynthetic sample as observed in previous experiments. In some studies, the highest outputs were reported to be produced from those under the absence of light. It should be noted, however, that these cycles helped the μPSC and more precisely the photosynthetic sample culture to restore itself, which undoubtedly affected the lifetime of the device before refilling the anolyte. Hence, illumination cycles are strongly recommended for extending the lifetime of the photosynthetic elements and the device.

Characteristics

V–I characteristics are useful in understanding the behavior of a power-generating device, as well as designing power converters and performing electrical modeling of the device. V–I characteristics of the μPSC studied in this work were obtained by testing a μPSC with Naﬁon® 117 and electrode pattern D2 which was found to be among the relatively better conﬁgurations according to the previous experiments. Potassium ferricyanide with 25% of concentration was used as the catholyte. Figure 6b shows variations of the output voltage and current while the resistance is increased.

As observed, V–I characteristics present a linear behavior with change in resistance. As resistance increases, there would be a greater amount of barrier against ﬂow of the electrons, which results in a decrease in current and increase in voltage. Beyond a certain point of increase in resistance, even though voltage still increases, the resulting current drastically decreases, causing the output power to decrease as well. Hence, studying the power-generation curve (Fig. 6c) allows the deﬁnition of an operational working range for the μPSC. With the varying conﬁgurations tested, the operational range of the device is suggested to be between 300 and 500 mV, providing the highest amount of generated power (approximately 175.37 μW corresponding to 36.23 μW/cm²).

Long-term analysis

Two μPSCs were used for the long-term analysis: one for OCV and the other for closed circuit voltage (CCV) with 20-kΩ resistance. For the experiment examining OCV, a μPSC with Naﬁon® 115 and...
electrode pattern D3 was used, while the µPSC with Nafton® 117 and electrode pattern D2 was used for the experiment examining CCV. Both experiments were performed for 25 h, in which 25% potassium ferricyanide was used as the catholyte. The results of the experiments are shown in Fig. 6d. The long-term analysis of the device demonstrated an increasing trend for the OCV. To a large extent, this is dependent on the conditions of the microorganisms. In this case, the sample was still in the growth stage and in a favorable condition. Since an open-chamber (anodic chamber without a glass cover) µPSC was used for these experiments, evaporation of the medium occurred at a faster rate. An OCV of more than 0.9 V was observed and deterioration was seen after the majority of the medium had evaporated, and the increasing trend became a decreasing one as shown in Fig. 6d. For the steady-state analysis with an external load, a 20-kΩ resistor was initially used. Since the results were plotted to a larger scale, some minor fluctuations were not visible. However, a close-up of the results (Fig. 6d) revealed cyclic fluctuations in the output similar to those observed in other experiments. Using this load, the output voltage tended to stabilize around 0.8 V. After approximately 17 h of continuous operation, the load was switched to 1 kΩ and the output voltage dropped as expected. Hence, the current was increased and the voltage was reduced. For verification, a load of greater resistance was used as well. For this, the current decreased while the voltage increased and neared the OCV after loading with a 100-kΩ resistor. Eventually after about 20 h, considerable evaporation of the medium resulted in a more obvious decreasing trend. It is possible to scale up the total power by integrating many devices in series and parallel, as it is produced through microfabrication techniques. In addition, the µPSC is able to generate power in both the day and night, via photosynthesis and respiration, respectively.

CONCLUSION

A novel polymer-based photosynthetic power cell was designed and fabricated. After verifying the functionality of the device, a series of experiments were conducted to obtain the most stable µPSC after considering the proposed fabrication method. Several parameters affecting the performance of the device were studied and behaviors such as long-term analysis and V–I characteristics were observed. Decreasing the thickness of the PEM and increasing the surface-to-volume ratio of the electrodes boosted the efficiency of ion transfer. This is however limited by the fabrication method as in this study, the thinnest PEM and electrodes with the highest pore density did not give rise to the most stable µPSC, which resulted in a relatively poor performance of the device. Hence, Nafton® 115 and 117 with different electrode patterns of medium pore density (Table 2) are suggested for the future experiments.

The performance of the µPSC was found to be directly dependent on the catholyte solution. Until a certain concentration (around 25%), increasing the concentration of potassium ferricyanide significantly increased the OCV. In addition, after 25% concentration was reached, performance became saturated.

For every measured concentration of the photosynthetic agent used, there exists a volume of the medium to be used in the µPSC for optimal performance. Using a smaller volume might not provide the maximal power-generation capacity, while using a greater volume might also be non-influential. Hence, one has to select the right combination of volume and concentration for optimal performance.

Long-term analysis showed an increasing trend of the output voltage for almost 20 h, after which evaporation of the medium resulted in a decrease in output. Thus, continuous circulation of the medium into the chamber to maintain a fixed desired volume at all times is suggested for efficient operation. V–I characteristics of the device indicated the optimal operation range to be 300–500 mV, which would lead to power generation of more than 175.37 µW corresponding to 36.23 µW/cm².

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