A MICRO PHOTOSYNTHETIC ELECTROCHEMICAL CELL
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ABSTRACT
A micro photosynthetic electrochemical cell (µPEC) was fabricated and tested as a potential self-sustained power source for mobile MEMS devices such as remote sensors. The µPEC harnesses the natural metabolic processes (photosynthesis and respiration) of the blue-green algae Anabaena to convert light energy into electrical power. In both light and dark conditions, the µPEC produced an open-circuit potential of over 400 mV, a current density of over 30 µA/cm² with a 10-Ω load, and a power density of 61 µW/L. These results are generally comparable to the microfabricated microbial fuel cell by Chiao et al. [8], though lower than those of micro solar cells and of macro-scale MFCs and PECs. However, unlike solar cells, the µPEC has the ability to produce power in the dark; and unlike methanol or microbial fuel cells, no fuel is required.

INTRODUCTION
The development of autonomous, mobile MEMS devices such as remote sensors and micro-robots [1] has elucidated the need for micro-scale mobile power sources that can be integrated monolithically with these devices. Toward this end, various researchers have presented such micro power sources as batteries [2,3], solar cells [4], and fuel cells. In the latter category, various types have been investigated, most notably methanol- and hydrocarbon-based polymer electrolyte fuel cells [5-7].

However, virtually no research has been done in the micro scale on a potentially important class of fuel cells: bio-electrochemical cells. Chiao et al. made progress in this area when they reported the first micromachined microbial fuel cell (µMFC) [8,9], which harnessed the natural metabolic processes of the microorganism Saccharomyces cerevisiae (commonly known as baker’s yeast) to “catalyze” glucose (the fuel) to produce electrical power [10-12].

Yet, all fuel cells require that their fuel be replenished periodically, which is an unlikely scenario for autonomous, mobile MEMS devices. To address this drawback, we present the first micro photosynthetic electrochemical cell (µPEC). The µPEC is able to provide dual functionality: (1) if light is available, it acts like a self-sustained solar cell by utilizing the natural photosynthetic processes of the blue-green algae Anabaena to convert light into electrical power; and (2) if light is unavailable, it behaves as a “conventional” µMFC by catalyzing into electrical power the glucose reserves that it has built up by photosynthesis [13].

PRINCIPLES OF OPERATION
The fundamental biochemical processes underlying the dual operation of the µPEC are photosynthesis and respiration:

Photosynthesis: \[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow_{\text{light}}^{\text{light}} (\text{CH}_2\text{O}) + \text{O}_2 \]

Respiration: \[ (\text{CH}_2\text{O}) + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2 + \text{ATP} \]

where (CH₂O) represents carbohydrates such as glucose [14]. Photosynthesis occurs in the cells of plants and other organisms like blue-green algae, providing energy sources in the form of carbohydrates (e.g. glucose) for themselves as well as non-photosynthetic organisms that consume them. By way of respiration, cells then further catabolize the carbohydrates into the smaller energy units ATP (adenosine triphosphate) to power their internal functions. Both photosynthesis and respiration are comprised of (different) electron transport chains in which protons \((\text{H}^+)\) and electrons \((\text{e}^-)\) are temporarily donated to the intermediate molecules NADP (in photosynthesis) or NAD (in respiration). The reduced forms of NADP and NAD—NADPH and NADH, respectively—thus may serve as sources of electrons from which electrical power may be “extracted” [10,13].

![Figure 1. Principles of operation of the µPEC.](image-url)
Figure 1 is a schematic of the µPEC in which the anode and cathode are separated by a proton-exchange membrane (PEM) but whose electrodes are connected by an external circuit. In the anode, the electrons (and protons) are “extracted” from NADPH (during photosynthesis) or from NAD (during respiration) inside the cells of the microorganism and deposited at the anodic electrode by the action of an electron mediator that has been added to the media of the algae. The electron mediator (methylene blue in this case) is able to play these dual roles because it has a redox potential $E_0$ such that it can (1) oxidize the reduced intermediate (NADH or NADPH) inside the cells of the microorganisms and (2) be oxidized by the anode electrode [12]. The electrons deposited the anodic electrode then travel through the external circuit to power a load and enter the cathode, where they reduce an electron acceptor such as ferricyanide. Meanwhile, the proton gradient in the anode drives the protons across the PEM into the cathode, where they combine with $O_2$ and electrons from ferricyanide to release $H_2O$.

For simplicity, we have implied that photosynthesis occurs when light is available and respiration when light is not; in actuality, respiration also persists when light is available and, thus, contributes to the total power production in the light. It is not known what the relative contributions of photosynthesis and respiration to the total power are in the light, and further investigations are necessary.

**DESIGN AND EXPERIMENT**

As illustrated in Fig. 1, the designs of the anode and cathode of the µPEC are interchangeable and, thus, were fabricated identically. The micromachining process is shown in Fig. 2 and 3. Low-stress nitride 1000 Å thick was deposited by LPCVD and patterned on both sides to define the reaction chamber (9 mm × 5 mm) and fluid ports on the back side and the $H^+$ pass-through holes (280 µm × 280 µm) on the front side. KOH at 80 °C was used to time-etch a 350 µm-deep chamber in the back side and, simultaneously, to etch through the wafer for the $H^+$ pass-through holes from the front side. The nitride on both sides was then etched away, and a 500/2000 Å thick Cr/Au electrode was thermally evaporated onto the front side. Figure 4 is a SEM of the fluid port that feeds the reaction chamber, where the electrode through-holes can be seen. Finally, the chamber was capped with a glass cover (which allows light to enter).
and the PEM was sandwiched between the Cr/Au electrodes of two such chambers, forming the anode and cathode. The PEM, DuPont Nafion 117, previously had been prepared in baths of 80 °C DIW, H₂O₂, and H₂SO₄ [15].

Cultures of *Anabaena* in Alga-Gro Freshwater medium were purchased from Carolina Biological Supply Company and kept under illumination until the experiments. The anolyte for the experiments was prepared using samples of *Anabaena* in its Alga-Gro medium and 0.01 M methylene blue as the electron mediator (but no glucose). The catholyte consisted of 0.02 M potassium ferricyanide in a 0.1 M sodium phosphate buffer (pH 7).

Two series of experiments were done at different times: (1) after 2 days of culturing in Alga-Gro under illumination and (2) after 4 days of culturing. The first series is intended to measure the electrical output of the blue-green algae during its exponential growth phase, when it is most metabolically active; whereas the second series was intended to measure output during the less-active stationary phase [16]. In both series, open-circuit potential was measured in the light (Fig. 5) and in the dark (Fig. 6). In addition, the current under a 10 Ω resistive load was measured in the light and dark for series 1 and given as current density in Fig. 7. Because of the low magnitude of the current, there was considerable scatter in the data, so polynomial fits were used to represent the data. Current density in PEM fuel cells is defined as the current normalized by the area of the PEM available for H⁺ transfer [17]; in the μPEC, the PEM area was 0.031 cm². In each experiment, 16 μL of anolyte and catholyte were injected by syringe into the anode and cathode, respectively, immediately before the electrical measurements were recorded.

**RESULTS AND DISCUSSION**

Inspection of Fig. 5 – 7 shows that the voltage and current levels were comparable in the light and dark, which is perhaps surprising at first. Indeed, the peak voltage of 500 mV in the dark (Fig. 6) is even greater than the peak of 400 mV in the light (Fig. 5). Furthermore, Fig. 7 shows comparable current output in both light and dark in the range of 30 - 40 μA/cm². However, these results should not be surprising because, as described above, analogous electron transport chains in photosynthesis and respiration are active in the light and dark, respectively, to serve as sources of electrons.

The length of time the *Anabaena* has been cultured, though, does appear to affect the electric output. As shown in Fig. 5 and 6, the voltage output after 2 days of culturing is higher than after 4 days, in both light and dark. The open-circuit voltage in the dark peaked at about 200 mV in the light and 250 mV in the dark. This outcome supports the postulate that the algae after 2 days of culturing was in a more metabolically active phase than after 4 days.

The peak power and power density of the μPEC were calculated to be about 1 nW and 63 μW/L, respectively. By estimating an irradiation of 1 mW/mm² from the light source used in the experiments, the light energy conversion efficiency was calculated to be less than 1%. As seen in Table 1, which summaries the figures of merit of macro and micro bio-electrochemical cells, the performance of the μPEC is comparable to the μMFC but an order of
Table 1. Comparison of solar cells, MFCs, and PECs.

<table>
<thead>
<tr>
<th></th>
<th>Power Density (mW/mm²)</th>
<th>Current Density (µA/cm²)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar Cell [18]</td>
<td>1</td>
<td>N/A</td>
<td>15</td>
</tr>
<tr>
<td>PEC [13]</td>
<td>35</td>
<td>300</td>
<td>3.3</td>
</tr>
<tr>
<td>µMFC [9]</td>
<td>0.50</td>
<td>10</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>µPEC</td>
<td>0.061</td>
<td>30</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

magnitude less powerful than the macro MFC and PEC [10-13]. This discrepancy may probably be attributed to the lack of an anaerobic environment in the µPEC—a condition that was imposed in the referenced PEC experiments—for O₂ present in the anode will tend to oxidize the electron mediator, so that fewer electrons would be transmitted to the anodic electrode to produce electricity.

CONCLUSION

Utilizing light energy and metabolic processes of the blue-green algae Anabaena, the µPEC produced over 400 mV open-circuit, 30 µA/cm² current density with a 10 Ω load, and 1 nW power output in both light and dark. These output levels are roughly equivalent to those of the µMFC but less than those of micro solar cells and of the macro bio-electrochemical cells. However, the µPEC uniquely combines the capability of continuing to produce power in the dark (versus solar cells) with not requiring external sources of fuel (compared to other PEM fuel cells).

Currently, the µPEC generates sufficient power to meet estimated power requirements of certain remote MEMS sensors [1,18]. In the near future, we aim to increase power output by at least an order of magnitude by investigating platinum as the electrode material, alternative electron mediators, and improved algae culturing protocols.

ACKNOWLEDGEMENTS

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REFERENCES


