A BIO-SOLAR CELL POWERED BY SUB-CELLULAR PLANT PHOTOSYSTEMS

Kien B. Lam[1], *Eric Johnson*[2], and *Liwei Lin*[1]

[1]Berkeley Sensor and Actuator Center, [2]Department of Plant and Microbial Biology
[1]Phone: 510-642-8983, Fax: 510-642-6163, Email: kblam@me.berkeley.edu
University of California, Berkeley, CA, 94720, USA

ABSTRACT

A microfabricated biomimetic solar cell was demonstrated that harnesses the sub-cellular thylakoid photosystems isolated from spinach cells to convert light energy into electricity. Subject to light intensity of 2000 µmol photons/m^2/s, it generated an open circuit voltage of 470 mV and a current density of 1.0 µA/cm^2 at 5.2 µV, output that is comparable to other microfabricated biological fuel cells. In the present anode/PEM/cathode configuration, the bio-solar cell can serve as a power source for micro-scale devices like remote sensors or autonomous robots. Yet, because it directly interfaces with forms of cellular energy (NADPH, proton-motive force, ATP) generated by photosynthesis, the bio-solar cell can also be a potential power source for nano-scale molecular motors like ATP synthase, kinesin, and myosin.

1. INTRODUCTION

We present for the first time a biomimetic solar cell that directly harnesses the sub-cellular photosystems isolated from plant cells to perform bio-conversion of light energy into electricity. This bio-solar cell has potential application as a power source for two diverging classes of technologies. The first class consists of micro-scale mobile devices such as remote distributed sensors [1] and autonomous robots [2]; second class comprises nano-scale molecular motors such as the ATP synthase enzyme that generates ATP in all living cells [3] and the kinesin and myosin motors that power intracellular movement [4].

For micro-scale devices, various micro power sources such as rotary engines [5], batteries [6], thin-film solar cells [7], and direct methanol fuel cells [8] have been reported. However, less work has been done in the area of micro biological power cells—only recently, at MEMS 2003, were a microbial fuel cell [9] and a photosynthetic electrochemical cell (µPEC) [10] presented. The µPEC, which utilized live cultures of photosynthetic cyanobacteria, is the only previous microfabricated device that has demonstrated bio-conversion of solar energy into electricity. In comparison to the µPEC, the innovation of the present bio-solar cell is the reduction of biological complexity by eliminating all non-photosynthetic biological systems of a living cell and harnessing only the sub-cellular components essential for photo-electrical conversion—the thylakoid photosystems.

Moreover, the thylakoid photosystems generate cellular energy in the forms of proton-motive force and ATP, which can power the ATP synthase and kinesin/myosin motors, respectively. Thus, the bio-solar cell can also potentially serve as a power source for nano-scale molecular motors.

2. PRINCIPLES OF OPERATION

Photosynthetic organisms such as plants and certain bacteria capture solar energy to drive the reduction of CO_2 using electrons from H_2O to produce carbohydrates (CH_2O), the biological fuel on which all non-photosynthetic life on earth depends [11].

$$\text{Photosynthesis:} \quad CO_2 + H_2O \xrightarrow{\text{light}} (CH_2O) + O_2 \quad (1)$$
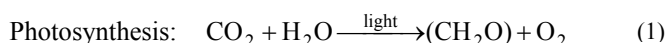
Equation (1) comprises a complex series of reactions, many of which, in higher plants, occur in the sub-cellular photosystems. These photosystems (PS) are networks of light-absorbing pigments (e.g. the green chlorophylls) and electron transporters that are arranged in two arrays, PSI and PSII ("Z-Scheme" of Fig. 1c). These networks are embedded in the outer membranes of structures known as thylakoids (Fig. 1b), which themselves are internal to organelles called chloroplasts that reside inside plant cells (Fig. 1a). Under illumination, the pigments capture the energy of incident photons and funnel it to PSII to oxidize
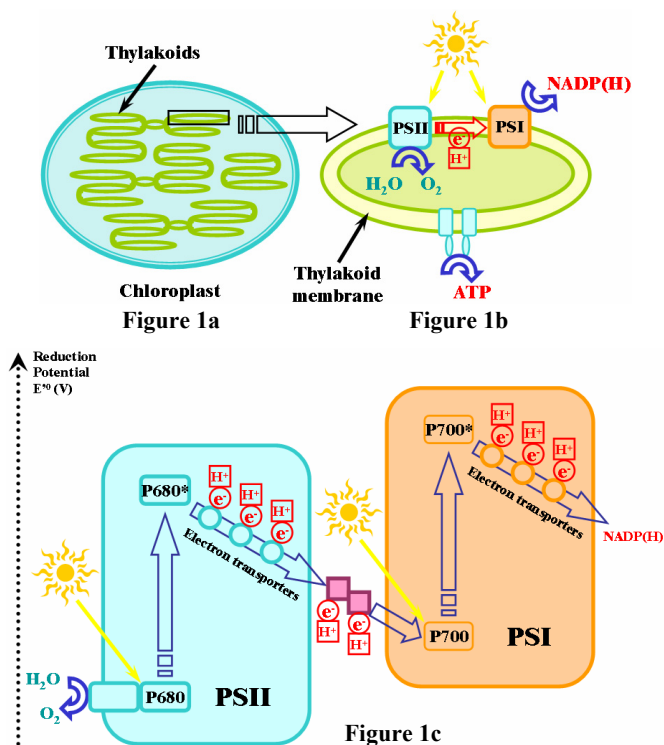
Figure 1. (a) Chloroplast, an organelle inside plant cells. (b) Structures internal to chloroplasts, thylakoids have Photosystems I and II and ATP synthase embedded in their outer membranes. (c) Light energy powers photosynthesis "Z-Scheme," which splits $2H_2O$ into O_2, releasing electrons that are transported through the photosystems to reduce $NADP^+$ into NADPH.
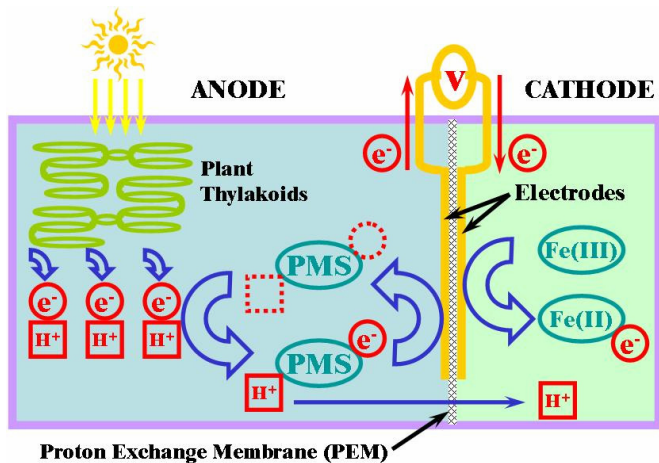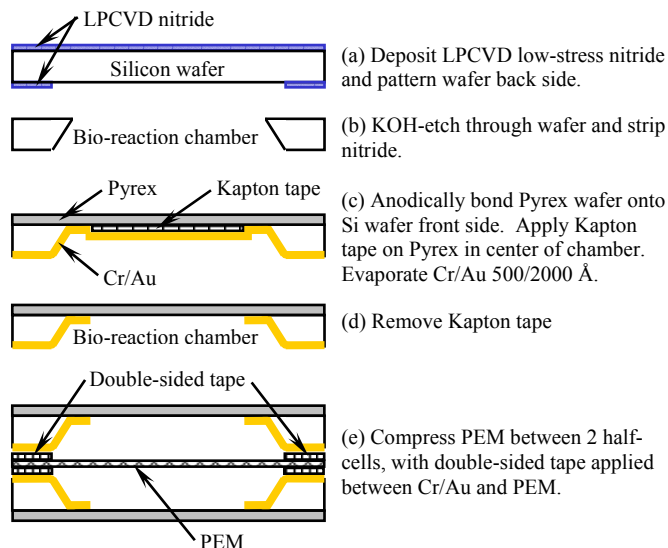
Figure 2. During photosynthesis, electrons are transported through the photosystems in thylakoid membranes. Redox mediator PMS "siphons" these electrons (and protons, H^+) from the thylakoids and transports them to the anodic electrode. They then travel through an external load to the cathodic electrode, where they reduce oxidant Fe(III) to Fe(II). Simultaneously, protons (H^+) diffuse from the anode across the PEM into the cathode.

Figure 3. Microfabrication and assembly.

Figure 4. (a) A half-cell before assembly; ref. Fig. 4d. (b) Fully-assembled bio-solar cell; ref. Fig. 4e. The PEM and double-sided tape, pressed between the half-cells, are barely visible.

$2H_2O$ into O_2. This splitting of H_2O releases electrons (in the form of hydrogen atoms, H) that then are transported from PSII to PSI. At the terminus of PSI, the electrons reduce $NADP^+$ into NADPH, a biological electron carrier (Fig. 1c).
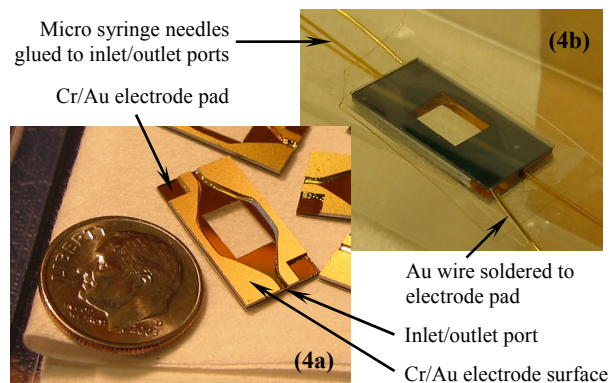
Simultaneously, electron transport through the photosystems pumps protons (H^+) across the thylakoid membrane from outside the thylakoid to inside. This creates a proton electrochemical gradient across the membrane (a proton-motive force) that powers the ATP synthase motor to produce ATP, the universal biological energy molecule (Fig. 1b) [11]. The energy transferred to NADPH and ATP by this "photo"-driven electron transport is then used to fuel the reduction of CO_2 into carbohydrates (CH_2O) in various anabolic pathways, thus forming the "synthesis" half of photosynthesis [11].

The bio-solar cell generates electrical power, in essence, by harnessing electrons from the photosystems during photosynthesis using the scheme shown in Fig. 2. Thylakoids were isolated from baby spinach—which interrupts the normal transport of electrons through the photosystems—and suspended in a buffer solution with the redox mediator phenazine methosulfate (PMS). The PMS "siphons" electrons (and protons) being transported through the photosystems and transfers them to the anodic electrode. From there, the electrons flow through an external load and arrive at the cathodic electrode, where they reduce the oxidant ferricyanide Fe(III) into Fe(II). Simultaneously, the protons accumulating inside the anode diffuse across the PEM into the cathode.

The bio-solar cell, as described above, thus can potentially be a power source for micro-scale devices. In addition, although less obvious, the bio-solar cell contains the biomimetic machinery for potentially powering certain nano-scale molecular motors. For example, the ATP synthase motor is powered by a proton electrochemical gradient (proton-motive force) across a biological membrane. In the bio-solar cell, an analogous proton gradient is formed across the PEM (Fig. 2); such a gradient may facilitate the development of biomimetic ATP synthase-like motors embedded in biomimetic synthetic membranes. As another example, the kinesin and myosin motors are powered by ATP, which may potentially be generated by the ATP synthase already embedded in the thylakoid membranes of the bio-solar cell. In the present bio-solar cell as described above, these ATP synthases are not utilized in that capacity.

3. DESIGN AND EXPERIMENT

The bio-solar cell was fabricated and assembled as shown in Fig. 3 and 4. Low-stress nitride of 1300 Å was deposited by LPCVD on a Si wafer and patterned on the back side to define the flow ports and bio-reaction chamber, which was then formed by a through-wafer etch in KOH. After stripping off the nitride in 49% HF, a Pyrex (7740) wafer was anodically bonded onto the front (polished) side of the Si wafer. Then a 5 mm × 7 mm piece of Kapton tape was applied onto the Pyrex in the center of the chamber to mask that area of Pyrex from the evaporation of Cr/Au 500/2000 Å thick onto the Si backside. The Cr/Au serves as the electrode

surface. The Si-Pyrex stack was then diced into 1 cm × 2 cm half-cells, and the Kapton tape was removed. Before final assembly, micro syringe needles (World Precision, Microfil 28 gauge, 250 μm ID) were glued to the ports of each half-cell to facilitate inlet and outlet flow; and Au wires were soldered onto the electrode pads. Finally, the bio-solar cell was assembled by sandwiching a PEM (Nafion N-117, 183 μm thick) between 2 half-cells, with double-sided Scotch tape applied between the Cr/Au and PEM as a bonding agent and fluidic seal. The Nafion PEM had been prepared in H_2O_2, H_2SO_4, and deionized water as described in [12].

Thylakoids were isolated from spinach using a procedure in [13]—yielding 2.4 mg chlorophyll/mL, which was then suspended in 400 mM sucrose, 20 mM Tricine (pH 8.0), and 10 mM NaCl. The thylakoids were diluted into an anode reaction mixture of 50 mM Tricine (pH 8.0), 50 mM NaCl, 4 mM $MgCl_4$, and 300 μM PMS to a final volume of 10 mL, resulting in 240 μg chlorophyll/mL. The cathode reaction mixture consisted of 20 mM potassium ferricyanide in deionized water. During the experiments, the anode and cathode reaction mixtures were pumped through their respective chambers in the bio-solar cell at 0.1 mL/min in counter-flowing directions using a syringe pump interfacing with the micro syringe needles. Two lighting conditions were imposed on the bio-solar cell: complete darkness or direct illumination of the anode by a light source calibrated to 2000 μmol photons/m^2/s to approximate the solar intensity during a cloudless, sunny day. All experiments were conducted at room temperature.

4. RESULTS AND DISCUSSION

The open circuit voltage (OCV) response of the bio-solar cell is shown in Fig. 5a. After flow was turned on, OCV climbed to 330 mV after 4 minutes in the dark; then, upon being subject to direct illumination, OCV sharply increased to and stabilized at 470 mV within 2 min. In repeated experiments, the maximum OCV ranged from 440 – 475 mV. When darkness was again imposed, OCV returned to 330 mV. The discharge current density (Fig. 5b) with a 1 kΩ load resistor climbed from 0.2 μA/cm^2 in the dark to 1.1 μA/cm^2 under direct illumination in about 2 min.

The flow of anodic and cathodic reaction mixtures through their respective chambers in the bio-solar cell brings some noteworthy effects that are illustrated by Fig. 6. At time = 0, before flow was turned on and while in the dark, the OCV floated at about 60 mV (not shown). After flow was introduced (while still in the dark) and the both chambers were filled, OCV climbed to 330 mV within 5 min (Region 1 in Fig. 6). Why was the OCV non-zero even when there was no light? We conjecture that because the anodic reaction mixture was prepared under ambient lighting conditions, a certain concentration of PMS would have already been reduced even before it was pumped through the bio-solar cell and subject to direct illumination. Thus, pumping an anodic mixture with pre-reduced PMS through the bio-solar cell would produce a non-zero OCV. But, as shown in Region 2 of Fig. 6, when the flow of "fresh" reaction mixtures was turned off while in the dark, OCV
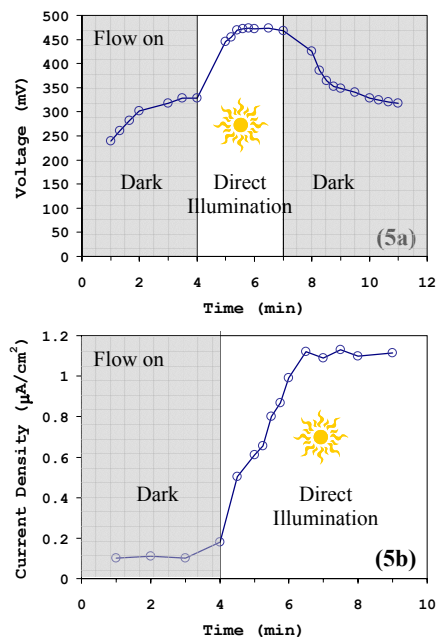
Figure 5. (a) Open circuit voltage. **(b)** Discharge current density with load R = 1 kΩ. Direct illumination = 2000 μmol photons/m^2/s. Flow of reaction mixtures through reaction chambers = 0.1 mL/min.
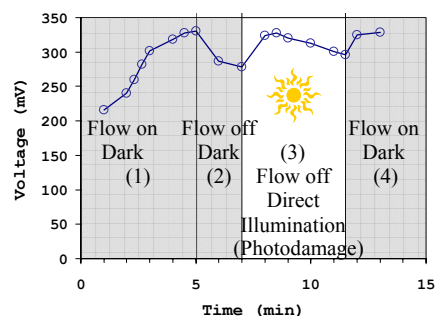
Figure 6. Effect of flow and light on open circuit voltage.
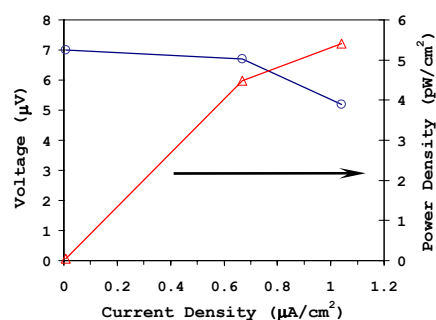
Figure 7. Voltage and power density versus current density under direct illumination with flow.

declined from 330 mV to 280 mV as the PMS (in the anode) and ferricyanide (in the cathode) were gradually oxidized.

In Region 3 of Fig. 6, direct illumination was switched on even though flow was still off. Now, the photosynthetic reactions of the photosystems re-reduced (i.e. "recharged") the PMS that had been oxidized in Region 2, causing OCV to climb back up to 320 mV—but only briefly. Within 2

minutes, the OCV again decreased because, under intense illumination, PSII suffered photo-oxidative damage and lacked the necessary repair mechanisms [14]. In addition, with flow still off, fresh thylakoids with "active" photosystems were not being supplied to the bio-solar cell. Finally, in Region 4 of Fig. 6, the bio-solar cell was again subject to darkness, but the flow was turned back on. Since these were the same conditions as Region 1, it is consistent that OCV returned to 330 mV within 2 min. Open circuit voltage under the conditions of direct illumination with flow was already described for Fig.5a.

The performance of the bio-solar cell over a range of current densities is characterized in Fig. 7. As is characteristic of fuel cells [15], a trade-off exists between voltage and power. The greatest achievable power density is desirable (5.4 pW/cm^2 at 1.0 μA/cm^2), but that is obtained at lower voltages (5.2 μV compared to about 6.5 μV at lower current densities), which translates to lower efficiency. However, even at the peak voltage of 6.7 μV, the calculated efficiency for the bio-solar cell was less than 1%. Moreover, the electrical output of the bio-solar cell was comparable to other microfabricated biological fuel cells [9, 10], though generally lower than larger biological fuel cells [16].

5. CONCLUSION

The bio-solar cell converts solar energy into electrical output by utilizing sub-cellular photosynthetic systems isolated from spinach. Under direct illumination of 2000 μmol photons/m^2/s with anode and cathode flow of 0.1 mL/min, it generated an open circuit voltage of 470 mV and a peak current density of 1.0 μA/cm^2 at 5.2 μV, which are comparable to other microfabricated biological fuel cells. Peak power density was 5.4 pW/cm^2. However, at less than 1%, its efficiency was poor. Continuous flow of "fresh" reaction mixtures into the bio-solar cell was necessary for sustaining electrical output; otherwise, the PMS and ferricyanide in the stagnant chambers became oxidized, and the thylakoid photosystems suffered photo-oxidative damage.

The bio-solar cell can potentially serve as a power source for micro-scale mobile sensors and robots, although its output is inadequate with the present configuration and parameters. However, we expect to be able to increase current densities by optimizing illumination intensity, flow rate, and chemical concentrations in the reaction mixtures. In particular, using a thinner PEM should increase current output by reducing ohmic losses.

Moreover, the bio-solar cell provides an interface with the thylakoid photosystems and, thus, gives access to the photosynthetic machinery that generates NADPH, proton-motive force, and ATP. In this way, the bio-solar cell shows promise as a power source for nano-scale molecular motors such as the ATP synthase, kinesin, and myosin.

REFERENCES

[1] B. Warneke, M. Last, B. Liebowitz, and K. S. J. Pister, "Smart dust: communicating with a cubic-millimeter computer," *Computer*, vol.34, no.1, *IEEE Comput. Soc*, Jan. 2001, p.44-51.

[2] S. Hollar, A. Flynn, C. Bellew, and K. S. J. Pister, "Solar powered 10 mg silicon robot," ," in *Proc. IEEE Conf. on Micro Electro Mechanical Syst.(MEMS 2003)*, Kyoto, Japan, Jan. 19-23, pp. 706-711, 2003.

[3] H. Wang and G. Oster, "Energy transduction in the F1 motor of ATP synthase," *Nature*, vol. 396, pp. 279-282, 1998.

[4] R. D. Vale and R. A. Milligan, "The way things move: Looking under the hood of molecular motor proteins," Science, vol. 288, pp. 88-95, 2000.

[5] K. Fu *et. al.*, "Design and Experimental Results of Small-Scale Rotary Engines," in *Proc. 2001 International Mechanical Engineering Congress and Exposition (IMECE),* New York, November 11-16, 2001.

[6] K. B. Lee, F. Sammoura, and L. Lin, "Water activated disposable and long shelf life microbatteries," in *Proc. IEEE Conf. on Micro Electro Mechanical Syst.(MEMS 2003)*, Kyoto, Japan, Jan. 19-23, pp. 387-390, 2003.

[7] A. Cuevas, R. A. Sinton, N. E. Midkiff, and R. M. Swainish, "26-percent efficient point-junction concentrator solar cells with a front metal grid," *IEEE Electron Device Letters*, vol. 11, no. 1, pp. 6-8, 1990.

[8] S. C. Kelley, G. A. Deluga, and W. H. Smyrl, "Miniature fuel cells fabricated on silicon substrates," *AIChE Journal*, 2002, vol. 48, no. 5, pp. 1071-1081, 2002.

[9] M. Chiao, K. B. Lam, and L. Lin, "A microfabricated microbial fuel cell," in *Proc. IEEE Conf. on Micro Electro Mechanical Syst.(MEMS 2003)*, Kyoto, Japan, Jan. 19-23, 2003, pp. 383-386.

[10] K. B. Lam, M. Chiao, and L. Lin, "A micro photosynthetic electrochemical cell," in *Proc. IEEE Conf. on Micro Electro Mechanical Syst.(MEMS 2003)*, Kyoto, Japan, Jan. 19-23, 2003, pp. 391-394.

[11] D. L. Nelson and M. M. Cox, *Lehninger Principles of Biochemistry*, 3rd ed., New York, NY: Worth Publishers, 2000, pp. 691-714, 746-764.

[12] S. J. Lee, "Effects of Nafion impregnation on performance of PEMFC electrodes," Electrochimica Acta, vol. 43, no. 24, pp. 3693-3701, 1998.

[13] A. Melis, L. Zhang, M. Forestier, M. L. Ghirardi, M. Seibert, "Sustained photobiological hydrogen gas production upon reversible inactivation of oxygen evolution in the green algae Chlamydomonas Reinhardtii," *Plant Physiol.*, vol. 122, pp. 127-135, 2000.

[14] A. Melis, "Photosystem-II damage and repair cycle in chloroplasts: what modulates the rate of photodamange *in vivo*?" *Trends in Plant Science*, vol. 4, no. 4, pp. 130-135, 1999.

[15] Parsons Inc., EG&G Services, *Fuel Cells: A Handbook,* 5th ed., US Department of Energy, 2000, pp. 2.1–2.26.

[16] E. Katz, A. N. Shipway, and I. Willner, "Biochemical fuel cells," in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, W. Vielstich, A. Lamm, and H. A. Gasteiger, Ed, vol. 1, Chichester, West Sussex: John Wiley & Sons, 2003, pp. 355-381.