

# Supercapacitive Micro-Bio-Photovoltaics

**Lin Liu, Maedeh Mohammadifar and Seokheun Choi\***

Bioelectronics & Microsystems Laboratory, Department of Electrical & Computer Engineering, State University of New York-Binghamton, Binghamton, NY 13902, USA

\*Corresponding author: Seokheun Choi, Associate Professor, SUNY-Binghamton, Email: [sechoi@binghamton.edu](mailto:sechoi@binghamton.edu)

**Abstract.** We created innovative supercapacitive micro-bio-photovoltaic systems (or micro-BPVs) with maximized bacterial photoelectrochemical activities in a well-controlled, tightly enclosed micro-chamber. The technique was based on a 3-D double-functional bio-anode concurrently exhibiting bio-electrocatalytic and charge-storage features so that it offers the high-energy harvesting function of BPVs and the high-power operation of an internal supercapacitor for charging and discharging. During the charging-discharging operation with 3 min of charging and 2 min of discharging, our device produced a maximum power density of  $19.12 \mu\text{W}/\text{cm}^2$  and current density  $212.09 \mu\text{A}/\text{cm}^2$ , a performance significantly greater than that of the continuous discharging mode. This work creates a microscale hybrid energy-harvesting device that combines a biological photovoltaic device and a supercapacitor for self-sustainable field applications.

## 1. Introduction

Micro-bio-photovoltaic systems (or micro-BPVs) can be the most suitable power source for unattended environmental sensors because the technique resembles the earth's natural ecosystem -- living organisms work in conjunction with non-living components of their environment to create a self-assembling and self-maintaining system [1, 2]. Micro-BPVs can continuously generate electricity from microbial photosynthetic and respiratory activities over day-night cycles, offering a clean and renewable power source with self-sustaining potential. However, the promise of this technology has not been translated into practical applications because of its relatively low power and current short life-times. To fulfil the potential of micro-BPV technology as a superior substitute for conventional batteries and other energy harvesting devices for future wireless sensing applications, there is a clear and pressing need to discover powerful yet simple approaches for high-performance, self-sustaining, long-life micro-BPVs, and to ensure their practical feasibility as a power source for those wireless sensor networks (WSNs). Recently, extensive research efforts have been made to improve the energy density of supercapacitors without sacrificing their high-power capability [3]. This path toward a high energy-density supercapacitor is currently undergoing exciting development with an entirely new kind of electric power device: a self-charging supercapacitor in which electric energy is simultaneously acquired and stored. This new hybrid device integrates the energy harvesting function of an electrochemical energy storage device (e.g. fuel cells) with the high-power operation of an internal supercapacitor (Figure 1). In particular, several proposals and preliminary demonstrations of the hybrid devices combine supercapacitors and bioelectrochemical systems such as enzymatic fuel cells, microbial fuel cells, and

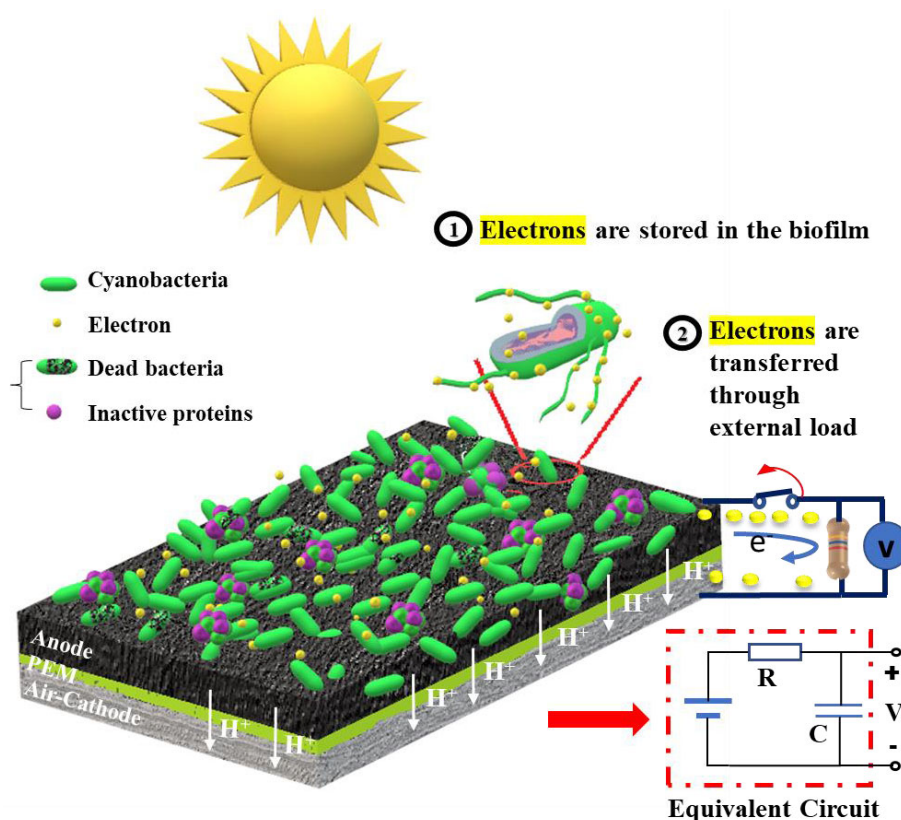


Figure 1: Conceptual diagram of the self-charging bio-supercapacitor and the equivalent circuit

photosynthetic enzymatic (or sub-cellular) fuel cells [4, 5]. This concept indicates the possibility that even low-performance biological fuel cells can become a superior substitute to conventional batteries or other energy harvesting techniques. However, the full potential of the hybrid devices for high-performance energy production and power storage has not been realized yet, nor has a standardized micro-sized device platform compatible with micro- and nano-fabrication been established. Furthermore, cellular BPVs using living photosynthetic organisms have never been integrated with supercapacitors.

## 2. Methods and materials

### 2.1. Electrodes

The anode was prepared on a treated carbon cloth with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). The anode was brush-painted with a mixture of 1wt% PEDOT:PSS and 15 wt% dimethyl sulfoxide (DMSO). The DMSO was added to increase the PEDOT:PSS conductivity. The anode was exposed to oxygen plasma for 1min for hydrophilization.

The air-cathode was constructed on 30% wet-proofed carbon cloth with four layers of a mixture of carbon powder and polytetrafluoroethylene (PTFE) solution. The other side of the cathode was coated by 10% Pt on carbon black and a binder solution including 5wt% Nafion solution, DI water, and isopropanol. The anodes and cathodes were pierced with a 0.5mm thick Ti wire as a current collector.

### 2.2. Device fabrication

The Nafion 117 membrane was hot-pressed directly between the anode and the air-cathode to form the sandwich electrode configuration. Fabrication details can be found in our pervious paper [6].

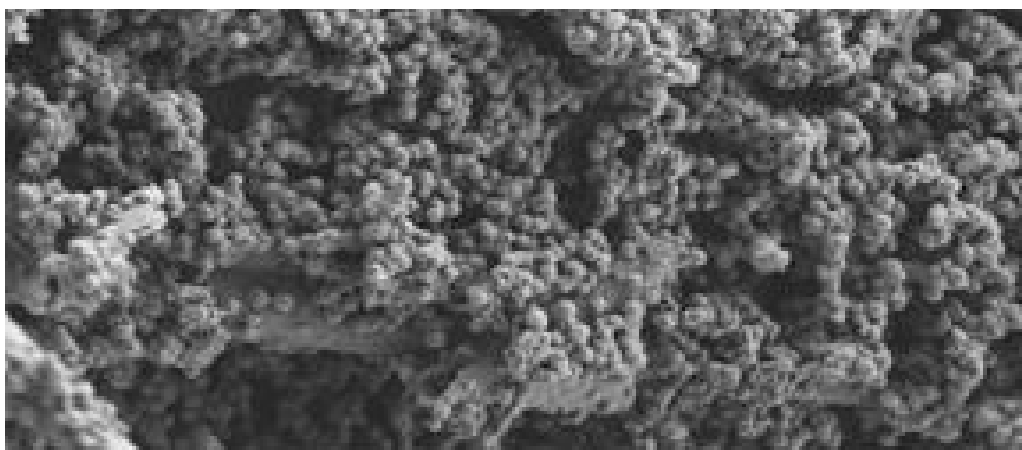


Figure 2: SEM image of cyanobacteria biofilms on the anode

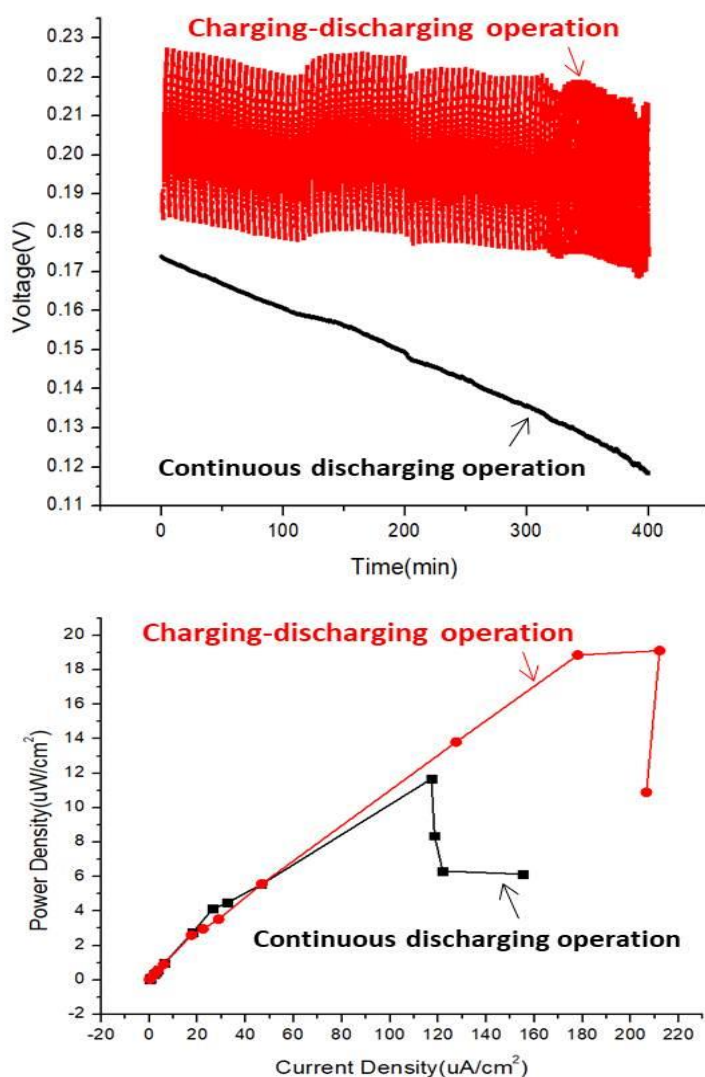


Figure 3: (a) charge-discharge cycles and (b) power output of the device as a function of current.

### 2.3. Inoculum

*Synechocystis* sp. PCC 6803 were grown from  $-80^\circ\text{C}$  glycerol stock cultures by inoculating 15mL of BG-11 medium with gentle shaking under 12-hour light and dark intervals. The BG-11 contained 1.5 g  $\text{NaNO}_3$ , 40 mg  $\text{K}_2\text{HPO}_4$ , 75 mg  $\text{MgSO}_4$ , 36 mg  $\text{CaCl}_2$ , 1 mg of EDTA, and 6 mg of citric acid and of ferric ammonium citrate per 1 L of distilled water. Fluorescent lamps-controlled chamber provided the continuous aeration at  $30 \pm 2^\circ\text{C}$  and illumination for 2 weeks. Growth was monitored by measuring the optical density at 600 nm ( $\text{OD}_{600}$ ) and the culture reached an  $\text{OD}_{600}$  of 1.2.

### 2.4. Measurement setup

We measured the potentials between the anodes and the cathodes with a data acquisition system (National instrument, USB-6212), and recorded the readings every 1 min via a customized LabView interface. An external resistor connected

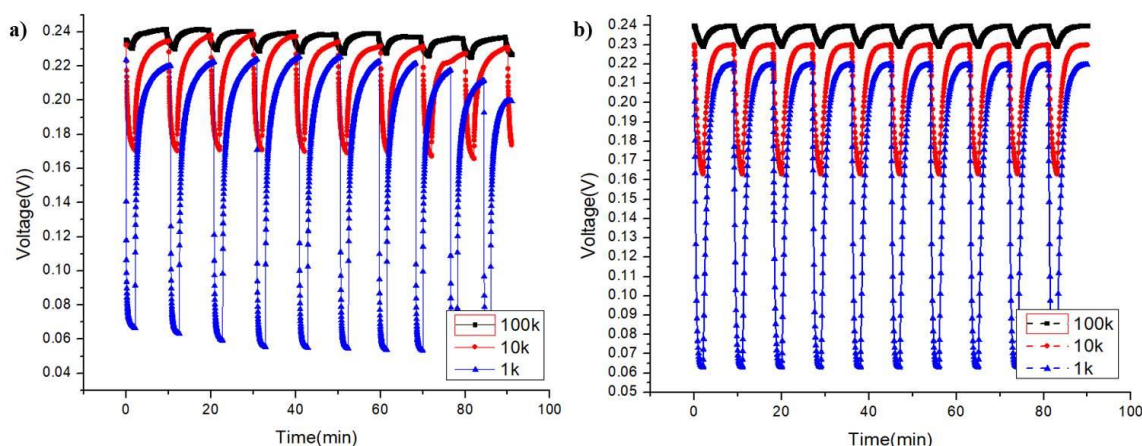


Figure 4: Comparison between the experimental results (a) and the model simulation (LTspice) (b)

the anode and cathode and closed the circuit. The current through this resistor was calculated using Ohm's law.

### 3. Results and discussion

The supercapacitive micro-BPV consisted of three functional layers; an anode with photosynthetic bacterial biofilm, a proton exchange membrane, and an air-cathode (Fig. 1 & 2). In open circuit mode, device voltage was determined by the equilibrium potentials of the electrodes. The photo-bio-electrocatalytic and redox reactions polarized the anode/cathode toward values that are more negative and positive than the typical equilibrium potential. Excess negative and positive charges at the electrodes were balanced by counter ions from the electrolyte forming an electrochemical double layer at each electrode of the device. In this way, the hybrid device electrostatically stored charge/energy (Fig. 3 & 4). The device can be then discharged by a rapid electrostatic process under short circuit conditions.

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