A SWEAT-BASED SELF-CHARGING POWER SYSTEM: INTEGRATION OF MICROBIAL ENERGY HARVESTING AND STORING DEVICES

Yang Gao[1], *and Seokheun Choi*[1,2*]
[1]Bioelectronics & Microsystems Laboratory, Department of Electrical & Computer Engineering, State University of New York at Binghamton (SUNY Binghamton), Binghamton, New York, USA
[2]Center for Research in Advanced Sensing Technologies & Environmental Sustainability, SUNY Binghamton, Binghamton, New York, USA

ABSTRACT

We demonstrate the first example of a wearable self-charging power system that offers (i) the high-energy harvesting function of a microbial fuel cell (MFC) and (ii) the high-power operation of a supercapacitor through charging and discharging. The MFC uses human skin bacteria as a biocatalyst to transform the chemical energy of human sweat into electrical power through bacterial metabolism, while the integrated supercapacitor stores the generated electricity for constant and high-pulse power generation even with the irregular perspiration of individuals. The all-printed paper-based power system integrates the horizontally structured MFC and the planar supercapacitor, representing the most favorable platform for wearable applications because of its lightweight and easy integrability into other wearable devices. The self-charging wearable system attains higher electrical power and longer-term operational capability, demonstrating considerable potential as a power source for wearable electronics.

KEYWORDS

Self-charging power systems, sweat-activation, microbial energy harvesting, wearables, supercapacitors

INTRODUCTION

Sweat-based energy harvesting techniques have attracted tremendous attention as a reliable and practical power solution for next-generation wearable electronics [1]. Sweat contains a large variety of chemical and biochemical substances that store sufficient energy to be harvested [2]. To date, the studies have been centered mainly around enzymatic fuel cells where redox enzymes convert the chemical energy of sweat into electrical energy [3-8]. However, due to their inherent short-term stability, the enzymatic catalysts have rendered the fuel cells unreliable and unstable for actual long-lasting wearable applications [3-8]. In 2020, our group, *for the first time,* used microorganisms as living enzymatic catalysts for sweat-based energy generation and successfully created a wearable microbial fuel cell (MFC) for longer and more stable power generation than the enzymatic fuel cells [9]. Because microorganisms contain many reproducible enzymatic catalysts and they can self-sustainably maintain their viability, microbial power generation can be more stable, reliable and robust for long-term wearable applications. We confirmed that many skin bacteria have electrogenic capability feeding off human sweat. Very recently, we enabled long-lasting microbial power generation using a spore-forming bacterium, *Bacillus subtilis*, which are usually found on plantar skin [10]. The spore-forming bacterium produced a sustainable power responding to the sweat availability through repeated sporulation and germination. However, this technology has suffered from its low performance.

In this work, a spore-forming MFC is integrated with a supercapacitor in paper, so that the harvested biological energy from the sweat can be charged and discharged for higher power generation (Figure 1). For simple fabrication and integration on a single paper, the MFC and the supercapacitor units are innovatively designed as a planar configuration. The MFC is horizontally structured where the anodic and the cathodic components are formed having a hydrophobic wax between them (Figure 1). The

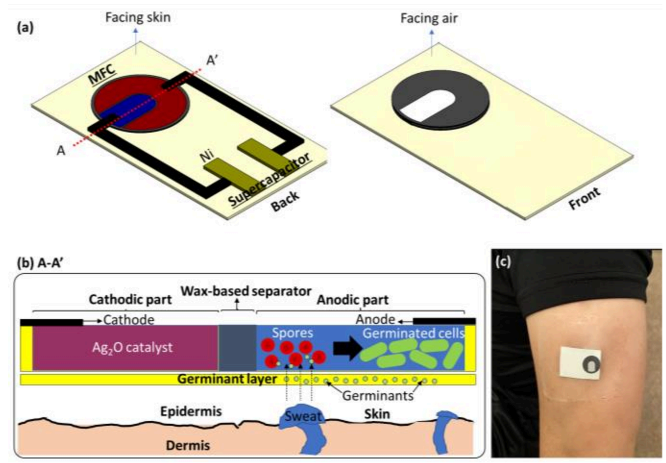

Figure 1: (a) Schematic illustrations of the self-charging power system integrating the MFC and the supercapacitor (back and front view), (b) the MFC inoculated with B. subtilis spores and its operating principle with sweat, and (c) the system applied to human.

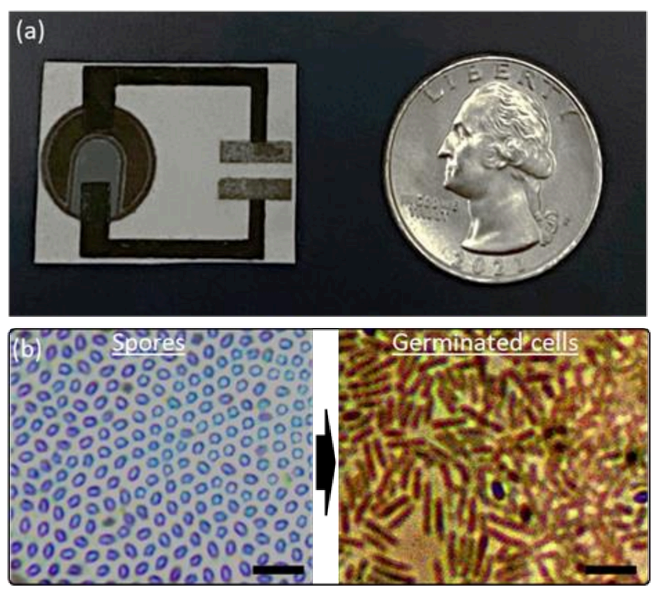

Figure 2: (a) Image of the assembled device and (b) microscopic images showing spore germination.

cathodic part is prepared with Ag_2O for the cathodic reaction. A germinant paper layer is placed on top of the spore-loaded anodic compartment, which allows for the MFC to be initiated by the sweat, as it washes the germinant into the anodic layer to begin germination and return to metabolic vegetative cells while generating power (Figure 2).

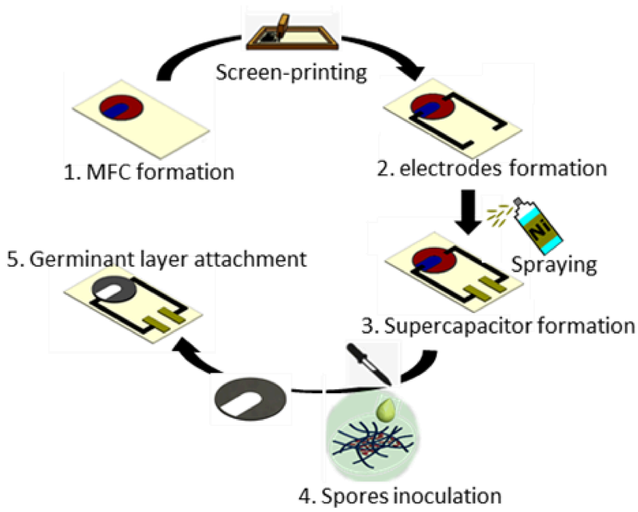

Figure 3: Device fabrication steps

EXPERIMENTAL PROCEDURE

Device fabrication

Previously, our group developed many paper-based MFCs, but all were limited to a vertical configuration where an anode, an ion exchange membrane, and a cathode were vertically aligned [11-13]. The vertical configuration needs multilayers and their precise alignment, requiring more complicated and high-cost manufacturing steps. Here, we, *for the first time*, created a horizontal MFC structure where all the device components were simply prepared in a single sheet of paper (Figure 1). Even the planar-type supercapacitor was readily constructed on the same paper with the MFC. Whatman Grade 1 filter paper was selected as the paper substrate for the self-charging system. The paper has the pore size of 11 μm which allowed inoculation of the bacterial spores (~ 1 μm in diameter) and conversion of the spores into the vegetative cells (~ 2~6 μm long and 1 μm in diameter) (Figure 2) [14, 15]. Detailed device fabrication steps are shown in Figure 3. All device boundaries and the ion exchange membrane for the MFC were prepared by printing the wax on both sides of the paper (Xerox Phaser, ColorQube 8570) and allowing the wax impregnation into the entire paper at 150 ºC for 45 seconds. The anodic part was first engineered with a conformal coating of conductive polymer, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). The cathodic part was prepared with Ag_2O for the cathodic reaction [11]. The solid-state supercapacitor was constructed with two Ni-spayed planar electrodes and poly(vinyl alchohol)/KCl electrolyte between them. The MFC and the supercapacitor were electrically connected by screen-printing a graphite ink. Then, the electricity-producing bacteria, *Bacillus subtilis*, were inoculated as spores. The dormancy of *B. subtilis* spores can preserve the bacteria for a long-term storage without denaturation or degradation. The germinant paper layer having L-Valine (10 mM) and AGFK (10 mM L-Asparagine, 33.6 mM D-Glucose, 33.6 mM D-Fructose, 60 mM KCl) was prepared in Whatman Grade 410 filter paper and attached to the MFC [14, 15]. *B. subtilis* spores are well-studied about their germination process where GerA, GerB, and GerK germinant receptors interact with L-Valine and AGFK and trigger the spore gemination. Because the 410 filter paper has much smaller pores than the MFC paper, we can minimize a potential risk of bacterial leakage from the MFC [15].

Cultivation and sporulation of *Bacillus subtilis*

We purchased *Bacillus subtilis* strain 168 from the American Type Culture Collection (ATCC) and cultivated them in Luria Broth (LB) medium at 37°C for 24 hours. Then, the cultured bacterial cells were induced to sporulate by nutrient exhaustion on agar plates [14, 15]. The formed spores were obtained from the plate and centrifuged for 4 minutes at 4000 rpm to pellet. The collected spores were washed, resuspended in distilled water, and stored at 4°C until use.

Electrical measurement setup

The voltage drops across 15 external resistors (No resistor, 470 kΩ, 240 kΩ, 160 kΩ, 100 kΩ, 75 kΩ, 47 kΩ, 33 kΩ, 22 kΩ, 15 kΩ, 10 kΩ, 2 kΩ, 1.5 kΩ, 470 Ω, and 360 Ω). were measured by using a data acquisition system (DATAQ Instruments), generating polarization curves and power outputs. The charging and discharging were carried out by using our customized electric relay circuit with Arduino software. The relay controlled the on and off states of the external circuit through the given resistor.

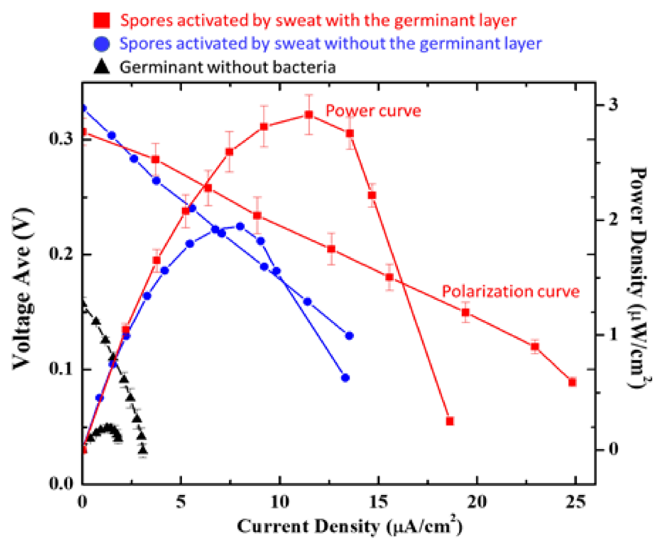

Figure 4: Polarization curves and power outputs of the MFCs (w/ and w/o a germinant layer) actuated by sweat. The control does not include bacterial cells.

RESULTS AND DISCUSSION

MFC performance

As shown in Figure 4, we characterized the MFC power generation by providing real human sweat samples taken from our group members with their consent. Our horizontally structured MFC generated significantly high power and current compared to the control without bacterial cells, indicating that the electricity production originates from the spore germination and their electron transfer activity. The MFC produced a maximum power density of 3 μW/cm^2 which is about 20 times larger than the control. It should be noted that the MFC even without the germinant layer produced a certain amount of power (1.9 μW/cm^2), which is in good agreement with our previous study showing that human sweat contains potential chemicals to trigger the spore germination [10].

Supercapacitor performance

As shown in Figure 5, we characterized the supercapacitive function by intermittently connecting external resistors (1 kΩ, 10 kΩ, and 100 kΩ). After the device was fully charged, it was discharged through the given resistors, showing stable output performance under charging-discharging cycles. The external resistors controlled the discharging rate of the stored energy during the discharging operation. The 1 kΩ resistor allowed a more rapid discharge of the accumulated charges while the higher resistors provided a slower rate at discharge with a smaller current generation (Figure 5).

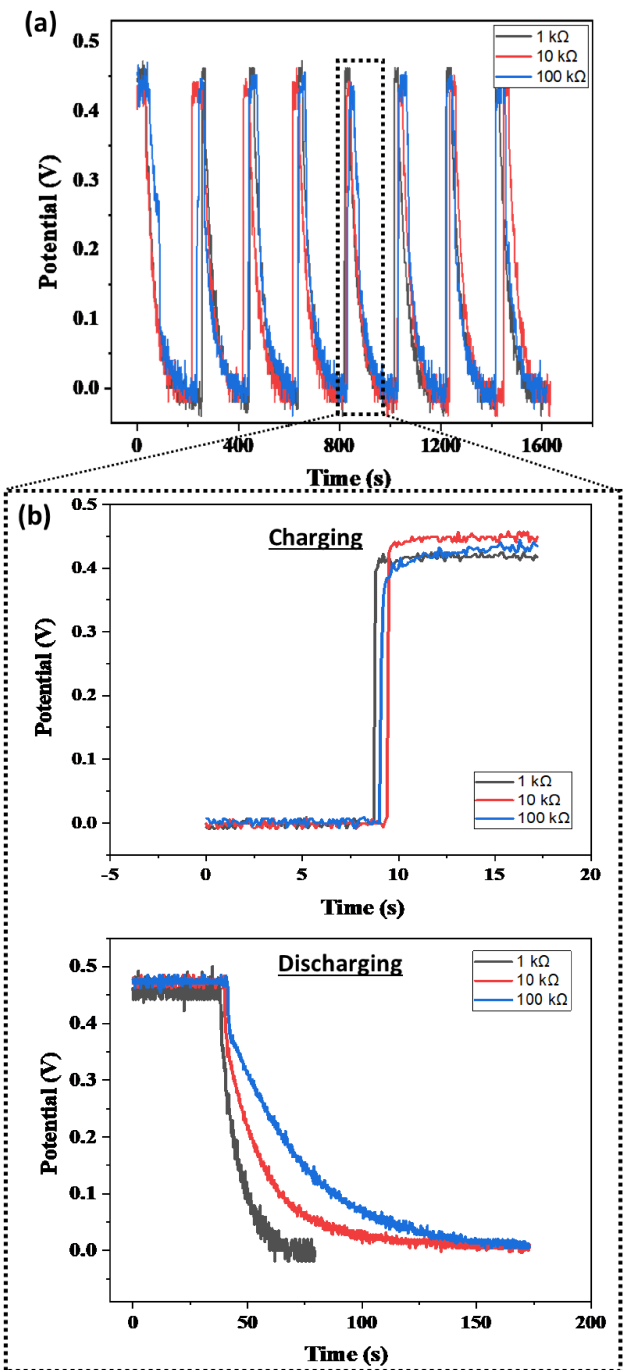

Figure 5: (a) Charging-discharging cycles of the supercapacitor with different external resistors. (b) A charge/discharge cycle

Performance of the self-charging power system

The low and short power generation of existing miniature MFCs have limited their capability to power useful applications in practice [16-19]. Increasing the size of the single device or stacking multiple devices in series/parallel can produce more power but it is not a suitable strategy for wearable applications where the device must be small enough to fit anywhere within the human body. Alternatively, energy storage devices like supercapacitors have been externally connected to the MFCs to boost their low power in a way that the supercapacitors are recharged by the MFCs and produce high electrical output during the discharge [21, 21]. However, the connection of the paper-based MFC to these external capacitors is more complicated, increasing the cost of the system with the performance degradation. As shown in Figure 1, the paper-based self-charging power system consisting of the horizontally structured MFC, and the supercapacitor was constructed on a single sheet of paper. Because this paper device is flexible, small, and thin, it can be applied directly to nonuniform small area of the human skin (Figure 1). This self-charging power system simultaneously generated electric energy from the bacterial metabolism with human sweat in the MFC and stored the energy in the supercapacitor. As shown in Figure 6, the self-charging hybrid power system generates much higher and longer voltage generation than the MFC only. This is because the energy electrostatically stored in the integrated supercapacitor can be delivered with higher and longer discharge output [22]. Moreover, microorganisms in MFCs can provide self-assembling, self-repairing, and self-maintaining operational capabilities with long-term stability [23-27]. The self-charging wearable system generated higher electrical power (~twice larger than the MFC only) and longer-term operational capability (stable current pulses for 25 minutes) (Figure 6).

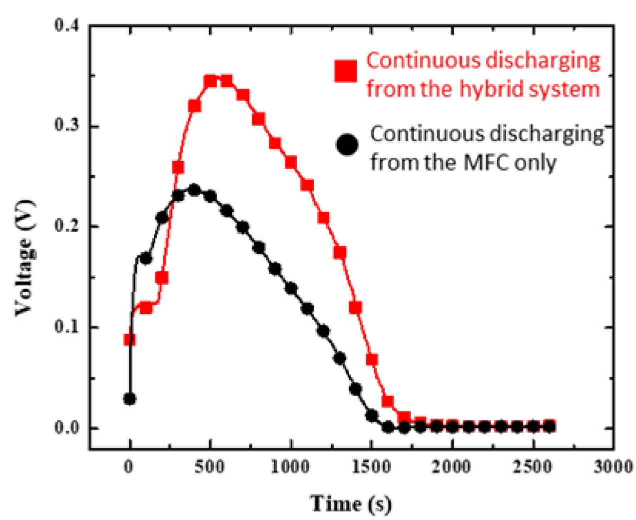

Figure 6: Continuous discharging profiles from the hybrid system and MFC only.

CONCLUSION

In this work, we, *for the first time*, report an integration of sweat-based MFC and a supercapacitor with an all-planar configuration on a single sheet of paper. The energy biochemically harvested from the sweat can be charged and discharged for higher and longer power generation than the MFC only. The spore-forming bacterium, *Bacillus subtilis*, were used as the living biocatalysts. The MFC produced electricity when human sweat triggered the spore germination and reverted the spores to vegetative cells. Because the spores can withstand very unfavorable external conditions, the MFC shelf-life can be significantly extended without requiring special procedures. The germinant paper layer having small pore size innovatively enclosed the spore-loaded anodic compartment to promote the spore germination with sweat. In addition, the layer could minimize a potential risk of bacterial leakage from the MFC. The MFC produced 0.32 V of open circuit voltage, 3 $\mu W/cm^2$ of power density, and 18 $\mu A/cm^2$ of current density. The supercapacitor constructed with two planar electrodes and solid-state electrolyte on the same paper substrate exhibited reversible charge-discharge reactions, demonstrating stable output performance.

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CONTACT

*Prof. S. Choi, tel: +1-607-777-5913; sechoi@binghamton.edu