

VERSATILE 3-D STACKING OF 2-D PAPER-BASED BIOBATTERIES

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ABSTRACT

We demonstrated a novel fabrication technique of 3-D biobattery packs by folding or stacking 2-D paper-based biobatteries for their series and/or parallel connections. A stackable, high-performance bacteria-powered battery was developed by folding two functional components (i.e. a conductive hydrophilic reservoir as an anode and a solid electron acceptor as a cathode) integrated into a single sheet of chromatography paper. Upon adding one drop of bacteria-containing liquid on the device, bacterial respiration transferred electrons from the organic liquid to the electrode, providing power to an external load. The various battery folding and/or stacking strategies with different series and/or parallel combinations significantly improved the power and current outputs. This battery manufacturing technique on paper can improve performance, simplify fabrication and connection, and revolutionize mass-production of large-scale flexible paper batteries, enabling the development of new types of powered, paper-based electronics.

INTRODUCTION

The field of paper electronics has recently obtained a great deal of attention as a game-changing platform for next-generation applications in healthcare, display, flexible electronics and batteries [1-2]. The most challenging task for those future applications lies in the requirement of the external power supply, so that the paper electronics can work independently and self-sustainably, even in challenging field conditions, where people lack access to a reliable electrical supply [3]. Paper-based bacteria-powered batteries (or microbial fuel cells (MFCs)) have attracted tremendous research interest, as a new type of power source for those paper-based devices [4-5]. The paper-based MFCs have four main advantages over other types of paper-based energy storage devices. First, they are capable of generating electricity from various kinds of organic matter, such as urine, biomass, wastewater, and even commercial beverages. Second, the devices' structures are much simpler than the others. Third, the materials and fabrication methods used are more cost effective. Last, the devices are environmentally friendly, so that they can be cleanly disposed of by incineration.

However, despite their vast potential and promise, significant challenges remain in the making of 3-D paper-based MFCs with foldable, batch-fabricable, and scalable solutions for simple and easy-to-use paper-based applications. Furthermore, there are many challenging areas for stacking batteries in a series and/or in parallels, required to produce higher power output and operating voltages. Typically, MFCs are limited to a low-output working voltage of about 0.3V at maximum power delivery [6]. By directly connecting individual MFCs [7] or applying the origami technique [3, 8, 9], paper-based MFCs can be connected in series or in parallel. However, their device configuration/operation becomes substantially

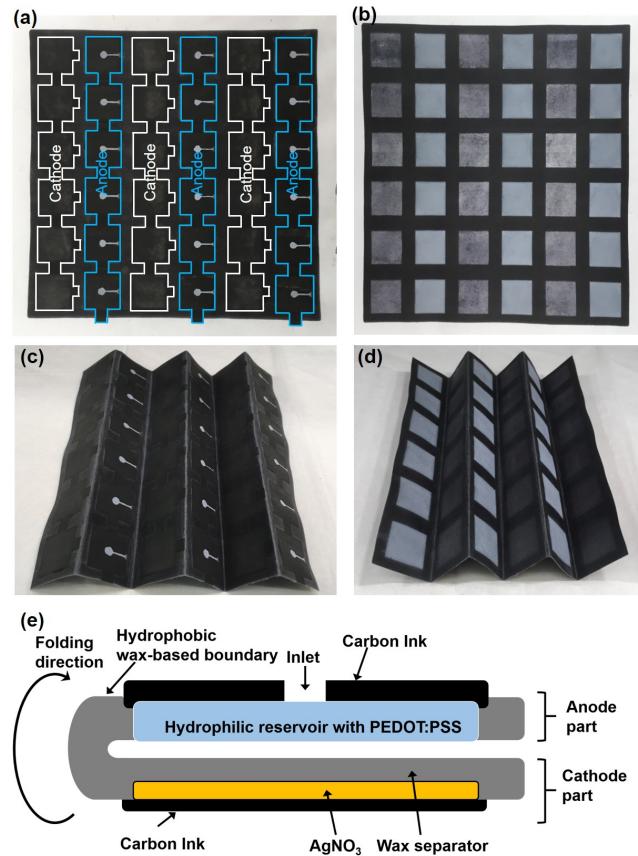


Figure 1: (a) ~ (d) Photo images of the paper-based biobatteries batch-fabricated on a 2-D single sheet of paper. (a) & (c) the front side and (b) & (d) the back side of the foldable 2-D batteries along pre-defined creases. (e) Schematic diagram of the cross section of the single battery unit.

complicated, rendering them insufficient for practical applications. Moreover, two very common cathodic techniques (i.e. cathodic chemicals [7, 8] and air-cathodes [3, 8]) are not suitable for development of the paper-based MFCs. The cathodic chemicals are expensive and not environmentally friendly [10] while the air-cathodes require the large cathodic areas to be exposed to the air [8] and suffer from extremely low power performance because of their high cathodic over-potential [11, 12]. Constructing a novel cathode with high-performance feature and low-cost material remains a significant challenge for the paper-based MFCs.

In this work, we demonstrate a technique that overcomes all two of these limitations by creating a solid-state cathode on paper, preparing all the MFC components on a single sheet of paper and folding/stacking the 2-D sheet of the paper for a 3-D MFC stack (Figure 1). This technique will greatly improve performance, simplify fabrication and operation, and revolutionize the mass production of the paper-based MFCs.

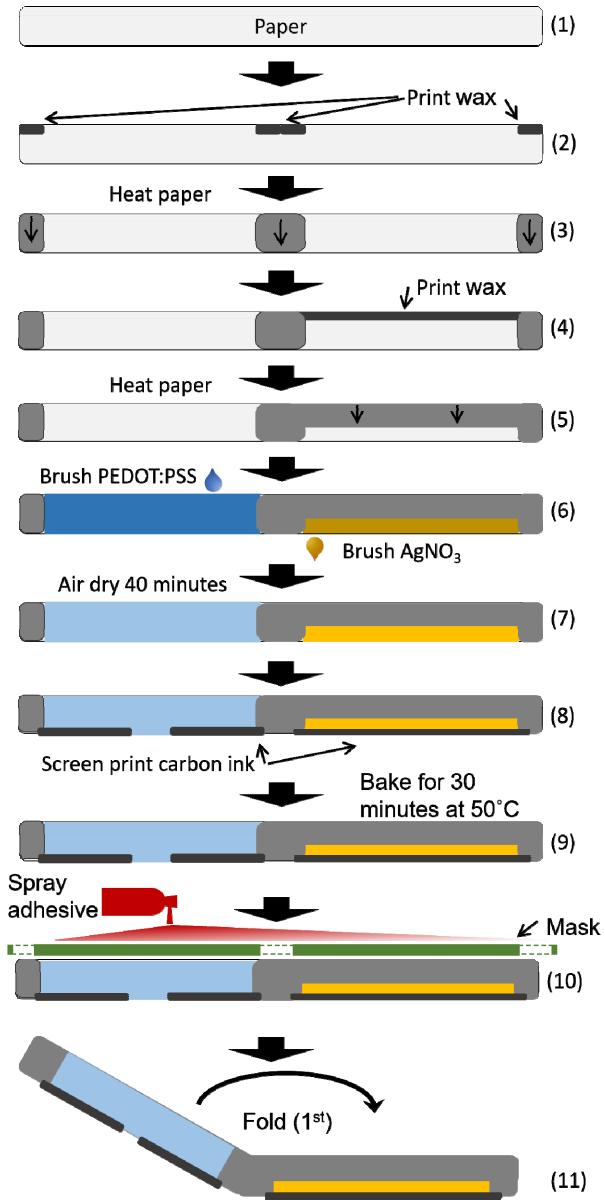


Figure 2: Schematic diagrams for the fabrication process of the paper-based MFC

METHODS AND MATERIALS

The functional components were first micro-fabricated on a large sheet of Whatman #1 chromatography paper, and then folded (1st folding) to create a 2-D battery. The batteries batch-fabricated on the sheet of paper can be further folded (2nd folding) or stacked for their series/parallel connections. The conductive poly(3,4-ethylened ioxithiophene):polystyrene sulfonate (PEDOT:PSS) was embedded within the anode reservoir, making it conductive while retaining its porosity and hydrophilicity [1, 13]. The cathodic electron transfer kinetics were enhanced by using low-overpotential silver nitrate as a solid electron acceptor, eliminating the need for the air-cathode or toxic chemicals.

Device configuration

A single MFC consists of two parts, (i) an anodic

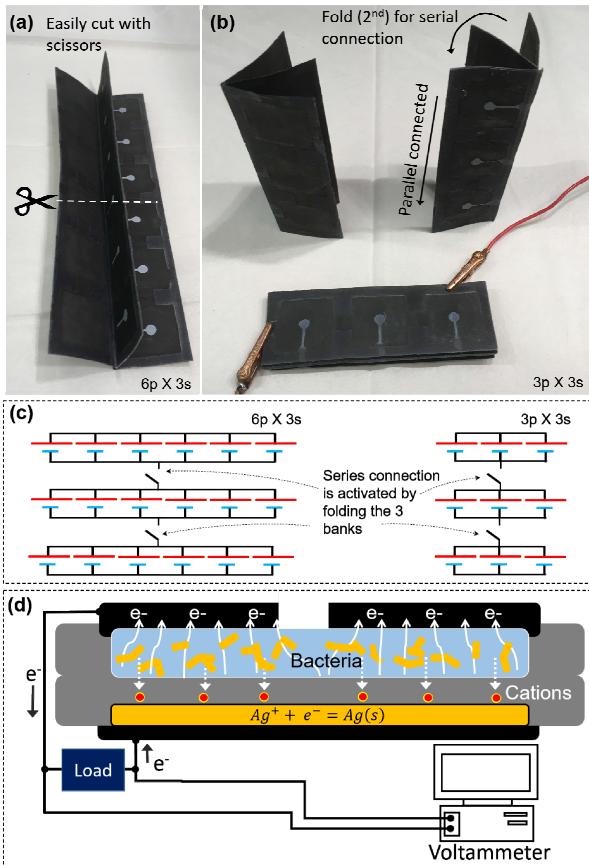


Figure 3: (a) & (b) Photo images of various folding/stacking strategies of the 2-D paper-based biobatteries. (c) Circuit diagram for 6p X 3s and 3p X 3s stacks, and (d) schematic diagram of the MFC operating principle and its test set-up.

compartment with a conductive anodic reservoir and a carbon-based current collector, and (ii) a cathodic compartment with a wax-based proton exchange membrane (PEM), a silver nitrate cathode and a carbon-based current collector (Figure 1 & 2). The anodic and cathodic compartments were fabricated simultaneously as shown in Figure 2. By folding (1st folding) the paper, the two compartments were combined to form a 2-D biobattery. The functional parts of the device were delineated with a hydrophobic wax boundary by printing wax on the paper substrate with commercially available solid-wax printer (Xerox phaser printer) and subsequently heating the paper in 130 °C for 70 seconds.

Anode and conductive anode reservoir

A mixture of 1wt% PEDOT:PSS (Sigma-Aldrich), 5wt% dimethyl sulfoxide (DMSO, Sigma-Aldrich) and deionized (DI) water was pipetted into the defined anode reservoir to make it conductive/porous and 3-glycidoxypyropyltrimethoxysilane was added to improve hydrophilicity (Figure 2). After the reservoir was air-dried in a fume hood, carbon ink was screen printed on the electrode side of the reservoir, and subsequently baked in a ventilated oven.

Silver-based cathode

The silver-based cathode was constructed on top of the

wax-based proton exchange membrane (PEM) by using silver nitrate ink. First, hydrophobic wax was printed on the cathode part of paper and then the wax was penetrated through the paper with heat treatment. A hydrophilic region was defined on the other side of paper as the penetration depth of the wax was controlled by adjusting the heating time. 50 μ L of silver nitrate solution (0.1 M) was dropped to the hydrophilic region to form the cathode (Figure 2).

Stacking strategies

On the large 2-D single sheet of the filter paper, 18 cells were batch manufactured (Figure 1). Individual cells were pre-connected by the anode and cathode so that every 6 cells were connected in parallel. By folding it further (2nd folding), three 6-cell packs connected in parallel were connected in series ($6p \times 3s$). The various device folding and stacking strategies with different series and parallel combinations can be proposed. One of examples is that $6p \times 3s$ battery pack can be readily cut in half to form two $3p \times 3s$ battery packs (Figure 3a, 3b, & 3c).

Inoculum Preparation

Pseudomonas aeruginosa wild-type PAO1 were grown from -80°C glycerol stock cultures by inoculating 20 mL of L-broth (LB) medium with gentle shaking for 24 h at 37°C. The culture was then centrifuged, at 5000 rpm for 5 min to remove the supernatant, and resuspended in fresh L-broth medium. Growth was monitored by measurement of the optical density at 600 nm (OD₆₀₀)

Test Setup

Electrical potentials between the anodes and cathodes were monitored by a data acquisition system (NI, USB-6212) with a customized LabVIEW interface (Figure 3d). To determine the currents generated by the individual units, external resists (10 k Ω and 1 k Ω) were used to connect the anode and cathode, and the current flow through the resistors was calculated by using Ohm's law. Then, polarization and power curves were derived from the voltages generated from stacked MFCs.

RESULTS AND DISCUSSION

Individual MFC units

To determine the performances of the single MFC units, we cut them into individual 18 cells and dropped 60 μ L-bacteria inoculum samples on the anode reservoir inlets of individual MFC units (Figure 4a). The liquid infiltrated underneath the carbon-based collector and spread over the conductive anodic reservoir. The hydrophilic, PEDOT:PSS treated conductive anode reservoir rapidly adsorbed the bacteria-containing liquid, which promoted bacterial cell attachment to the conductive paper matrix. Then, bacterial respiration transferred electrons from the organic matter to the anode, from which they flowed through an external load connecting the anode to the cathode. The protons or cations were transferred through the wax-based PEM and were reduced with the solid-state cathode, as well as the electrons, which had traveled from the anode. The wax membrane became saturated with the sample liquid and provided an optimal environment for

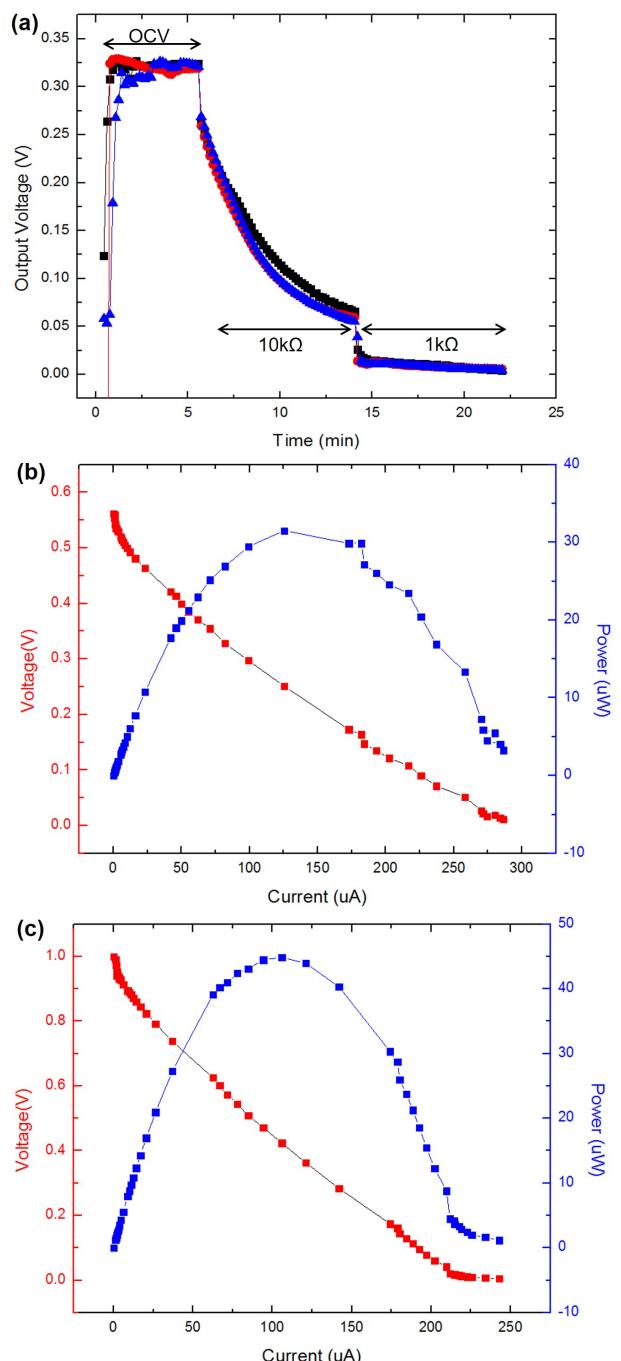
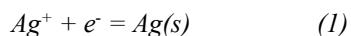


Figure 4: Voltages measured from (a) single MFC units. Power outputs and polarization curves of (b) $6p \times 3s$ and (c) $6p \times 6s$ MFC stacks.

movement of the protons or cations and reduction of the silver nitrate to the silver ions in the cathode. The silver ions combined with the electrons formed a solid silver. Thus, the cathode half-cell reaction is as follows,



The single MFC units generated average values of the open circuit voltage (OCV), the current density and the power density of 0.29V, 3.37 μ A/cm² (with 1k Ω) and 0.04 μ W/cm² (with 1k Ω), respectively (Figure 4a).

MFC stacks

After confirming that the individual MFCs can supply the desirable performance from the 3-D paper-based device, we prepared two MFC stacks; (i) $6p \times 3s$ and (ii) $6p \times 6s$ by stacking two $6p \times 3s$ packs together. The polarization curves and power outputs of the MFC stacks were measured and calculated based on the saturated current value at a given external resistance (Figure 4b & 4c). The OCV of the $6p \times 3s$ stack was 0.562V, which indicates that the average OCV of three $6p \times 1s$ MFC stacks is about 0.187V. This value is smaller than that of the individual MFC units (~0.29V). The OCV of the $6p \times 6s$ stack was 1V, which shows that the average of OCV of six $6p \times 1s$ MFC stacks is about 0.17V. The overall OCV values decreased with the number of MFC packs connected in series. The maximum power of the $6p \times 3s$ stack was $31.51\mu W$ at $125.53\mu A$ (Figure 4b), while the $6p \times 6s$ one generated $44.85\mu W$ at $105.89\mu A$ (Figure 4c). From the polarization curves, we estimated internal resistance from the point where the polarization curve showed a near-linear drop (i.e. ohmic losses) [14]. Linear fitting of the curve generated internal resistances of $1.79k\Omega$ and $4.27k\Omega$ for $6p \times 3s$ and $6p \times 6s$ MFC stack, respectively. As the more MFC cells were connected in series, the internal resistance of the stack increased further, decreasing the MFC performance. This is mainly because of the enhanced contact resistance of the MFC stack and the abiotic oxygen intrusion [15] as the number of cells increases. Further studies are required to improve the MFC stack performance.

CONCLUSION

In this work, we proposed an origami-inspired fabrication technique for forming 3-D MFC stacks. A solid electron cathode and PEDOT:PSS treated conductive anode reservoir were first applied for the paper-based MFC technique, which revolutionized the MFC fabrication on paper and provided compact and versatile MFC stacking strategies. A maximum power of $31.51\mu W$ at $125.53\mu A$ and $44.85\mu W$ at $105.89\mu A$ were generated from $6p \times 3s$ and $6p \times 6s$ stack configuration, respectively. The battery stack developed here could greatly reduce fabrication costs, simplify manufacturing processes, and establish an innovative strategy for paper-based MFC stacks.

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REFERENCES

- [1] M.M. Hamed, A. Ainla, F. Guder, D.C. Christodouleas, M. Fernandez-Abedul, and G.M. Whitesides, “Integrating Electronics and Microfluidics on Paper,” *Advanced Materials*, vol. 28, pp. 5054-5063, 2016.
- [2] D. Tobjörk and R. Österbacka, “Paper electronics,” *Advanced Materials*, vol. 23, pp. 1935-1961 2011.
- [3] A. Fraiwan, L. Kwan and S. Choi, “A disposable power source in resource-limited environments: A paper-based biobattery generating electricity from wastewater,” *Biosensors and Bioelectronics*, vol. 85, pp. 190-197, 2016.
- [4] T.H. Nguyen, A. Fraiwan and S. Choi, “Paper-based batteries: A review,” *Biosensors and Bioelectronics*, vol. 54, pp. 640-649, 2014.
- [5] K. Zuo, H. Liu, Q. Zhang, P. Liang, X. Huang and C.D. Vecitis, “A Single□Use Paper□Shaped microbial fuel cell for rapid aqueous biosensing,” *ChemSusChem*, vol. 8, no. 12, pp. 2035-2040, 2015.
- [6] P. Aelterman, K. Rabaey, H.T. Pham, N. Boon and W. Verstraete, “Continuous electricity generation at high voltages and currents using stacked microbial fuel cells,” *Environ. Sci. Technol.*, vol. 40, no. 10, pp. 3388-3394, 2006.
- [7] A. Fraiwan, and S. Choi, “Bacteria-Powered Battery on Paper,” *Physical Chemistry Chemical Physics*, vol. 16, pp.26288-26293, 2014.
- [8] H. Lee, and S. Choi, “An origami paper-based bacteria-powered battery,” *Nano Energy*, vol.15, pp. 549-557, 2015.
- [9] A. Fraiwan, and S. Choi, “A Stackable, Two-chambered, Paper-based Microbial Fuel Cell,” *Biosensors and Bioelectronics*, vol. 83, pp. 27-32, 2016.
- [10] S. Mukherjee, S. Su, W. Panmanee, R.T. Irvin, D.J. Hassett, and S. Choi, “A microliter-scale microbial fuel cell array for bacterial electrogenic screening,” *Sensors and Actuators: A. Physical*, vol. 201, pp.532-537, 2013.
- [11] X. Xie, M. Ye, P.-C. Hsu, N. Liu, C. S. Criddle, and Y. Cui, “Microbial battery for efficient energy recovery,” *PNAS*, vol. 110, pp. 15925-15930, 2013.
- [12] X. Xie, M. Ye, C. Liu, P. Hsu, C.S. Criddle, and Y. Cui, “Use of low cost and easily regenerated Prussian Blue cathodes for efficient electrical energy recovery in a microbial battery,” *Energy and Environmental Science*, vol. 8, pp. 546-551, 2015.
- [13] M.M. Hamed, V.E. Campbell, P. Rothemund, F. Guder, D.C. Christodouleas, J. Bloch, and G.M. Whitesides, “Electrically Activated Paper Actuators,” *Advanced Functional Materials*, vol. 26, pp. 2446-2453, 2016.
- [14] Y. Fan, E. Sharbrough, and H. Liu, “Quantification of the internal resistance distribution of microbial fuel cells,” *Environ. Sci. Technol.*, vol. 42, pp. 8101-8107, 2008.
- [15] S. Choi, H.-S. Lee, Y. Yang, P. Parameswaran, C.I. Torres, B.E. Rittmann and J. Chae, “A μL -scale Micromachined Microbial Fuel Cell Having High Power Density,” *Lab on a Chip*, vol.11, pp.1110-1117, 2011.

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