Biosensors and Bioelectronics 100 (2018) 504–511

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Flexible and stretchable microbial fuel cells with modified conductive and hydrophilic textile

Sumiao Pang, Yang Gao, Seokheun Choi*

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

ARTICLE INFO

Keywords:
Textile-based microbial fuel cells
Flexible and stretchable biofuel cells
Conductive and hydrophilic textile coating
Solid-state cathode
Bioelectricity

ABSTRACT

We built a flexible, stretchable microbial fuel cell (MFC) by laminating two functional components: a bioanode textile with a conductive and hydrophilic polymer coating and a solid-state cathode textile loaded with silver oxide. The textile MFC used *Pseudomonas aeruginosa* PAO1 as a biocatalyst to generate the maximum power and current density of 1.0 μW/cm^2 and 6.3 μA/cm^2, respectively, which are comparable with or even higher than other flexible MFCs such as paper-based devices (~ a few μW/cm^2). Additionally, the textile MFC generated consistent power even with repeated 70 cycles of 50% stretching. A simple batch fabrication method simultaneously produced 20 individual 2 cm × 2 cm devices by using brushing, spraying, ironing, and computerized sewing, a process that will revolutionize the mass production of textile MFCs. This achievement is scientifically meaningful because developing textile MFCs requires integration of both electronic and fluidic components into the textile three-dimensionally. This flexible and stretchable energy harvesting device is expected to be easily integrated with the next generation stretchable electronics for realizing low-power, stand-alone, self-sustainable systems.

1. Introduction

Microbial fuel cells (MFC) have been widely explored as an alternative energy technology, as they produce sustainable electricity from any biodegradable organic compound while revolutionizing wastewater treatment (Arends and Verstraete, 2012; Schröder, 2011; Lovley, 2012). Yet, despite advances, this MFC technique has never been successfully translated into practical applications because of its low power, expensive core parts and materials, and bottlenecks in scaling-up (Borole et al., 2011; Babauta et al., 2013; Logan, 2010). However, by miniaturizing MFCs to power battery-operated electronics that consume a small amount of energy their potential uses become radically expanded (Choi, 2015; Qian and Morse, 2011; Wang et al., 2011). In the past years, extensive efforts have been made to miniaturize standard macro-sized MFCs using micro-/nano-fabrication technologies (Jiang et al., 2017; Siu and Chiao, 2008; Qian et al., 2009; Gadhamshetty and Koratkar, 2012; Choi et al., 2011). Many unique and potential applications, such as power sources for implantable medical devices (Han et al., 2010), gastrobots (Wilkinson, 2000), and portable devices (Walter et al., 2017), have been demonstrated. Furthermore, the miniaturized MFCs have been identified as a promising energy harvesting technique for environmental sensors because of their self-sustainability, harnessing various environmental liquids ranging from wastewater to body fluids (Fraiwan et al., 2016; Mohammadifar and Choi).

In the meantime, with the rapid evolution of wireless sensor networks for the emerging Internet-of-Things (IoT), there is a clear and pressing need for flexible and stretchable electronics that can be easily integrated with a wide range of surroundings to collect real-time information (Jung et al., 2017; Song, 2015; Kim et al., 2017; Hussain and Hussain, 2016). Those electronics must perform reliably even while closely – even intimately when used on humans – attached while deformed toward complex and curvilinear shapes. To achieve the stand-alone and sustainable operation of the sensor networks, a flexible, stretchable, miniaturized MFC can now be considered as a truly useful energy technology because of their sustainable, renewable and eco-friendly capabilities. Previously, we, for the first time, demonstrated a flexible MFC on paper, generating electricity from bacteria-including liquid derived from renewable and sustainable wastewater (Fraiwan et al., 2013; Fraiwan et al., 2014; 2013, 2014a; Lee and Choi, 2015). The intrinsic porous and hydrophilic characteristics of paper allowed quick adsorption of the liquid through capillary force, rapidly generating electricity. Our latest paper-based device powered an on-chip, light-emitting diode by incorporating sixteen MFCs connected in series on a single sheet of flexible paper (Mohammadifar and Choi). Because of its light-weight, low-cost, disposable, and flexible features, a paper MFC can be potentially integrated into ubiquitous newspapers,

* Corresponding author.
E-mail address: sechoi@binghamton.edu (S. Choi).

http://dx.doi.org/10.1016/j.bios.2017.09.044
Received 17 July 2017; Received in revised form 25 September 2017; Accepted 25 September 2017
Available online 28 September 2017
0956-5663/

wrapping papers, wallpapers, and other objects (Gao and Choi, 2017). However, extremely harsh operating conditions, for example, those that require bending, twisting, folding, and stretching, demand development of a fully flexible and stretchable MFC. Textiles are attractive materials for flexible devices and offer superior elastomeric properties toward achieving conformal contact with non-planar, unsymmetrical surroundings (Huang et al., 2016; Yetsen et al., 2016). Low-cost and scalable fabrication based on well-established traditional textile manufacturing techniques can also be used, and other manufacturing techniques can add other functions. Furthermore, textiles are lightweight, inexpensive, and disposable. More specifically, textiles can be ideal supports for substrates and promise functional components for the development of flexible and stretchable MFCs. They offer many advantages, including (i) their easily patternable hydrophilic property allows for instrument-free liquid movement via capillary force and storage of biological and chemical reagents, (ii) their intrinsic macroporous structures ensure a large surface area and efficient mass transfer for bacterial growth and metabolism, and (iii) polymer-based biocompatible fibers improve correlations between cell growth and biofilm formation. Textile MFCs have superior self-repairing and self-assembling features even with repeated mechanical deformations from bending, twisting, and stretching. Several MFCs used textile-based anodes or cathodes mainly in order to improve the MFC performance but none of them were for flexible and stretchable applications (Xie et al., 2011; Xie et al., 20112011a, 2011b).

This work reports for the first time on a highly flexible and stretchable, entirely textile-based MFC that provides a stable power even with repeated severe mechanical deformations. Full integration of a high-performance MFC on textile was achieved by (i) forming all functional components in two pieces of fabric with precisely patterned microfluidic reservoirs, (ii) co-fabricating conductive and fluidic structures for holding exoelectrogenic bacterial inoculum, and (iii) using silver oxide/silver solid-state cathodic electron acceptors for maximized cathodic reaction. When the bacteria-containing liquid was added to the textile-based MFC, it was transported horizontally and vertically, filling the engineered reservoir of the device. The device generated high power (1.0 μW/cm^2) and current densities (6.3 μA/cm^2), which will be further improved by readily connecting the devices in series or in parallel for potentially powering practical applications. This technique should be adaptable enough to power practical low-power sensing applications, which will likely be made in coming years.

2. Results and discussion

All functional layers for the MFC structure were constructed within two commercially available fabrics consisting of 92% polyester and 8% spandex. Therein, twenty individual devices were simultaneously batch-fabricated by using facile, low-cost, scalable, and fabric-compatible methods including screen-printing, brushing, spraying, and computerized sewing and embroidery machining (Fig. 1a). A MFC typically consists of anode and cathode compartments, physically separated by an ion exchange membrane. Bacterial cells (i.e. exoelectrogens) in the anodic compartment degrade organic compounds and release protons and electrons (Choi, 2015). The electrons move from the anode to the cathode and produce an electrical current through an external circuit while protons travel to the cathode through the membrane. The top fabric layer is composed of a 3-D conductive and hydrophilic anodic reservoir for containing bacterial cells and a conductive thread as an anodic current collector. The bottom fabric layer is composed of an untreated hydrophilic region as a separator, the solid-state Ag_2O cathode, and sprayed-on carbon as a cathodic current collector (Figs. 1b & 1c). When the bacteria-containing solution is introduced to the top of the anode, it spreads over the entire 3-D anodic compartment of Textile #1 and the untreated hydrophilic region of Textile #2 by capillary forces (Fig. 1d). Then, bacterial respiration harvests electrons from the organic compounds in the solution, and the electrons flow to the anode. Proton transfer from the anode to the cathode is critical to maintaining fuel cell electroneutrality. These electrons and protons produced by the bacterial metabolism are moved to the cathode reducing Ag_2O to Ag. The corresponding reaction at the cathode is:

$$Ag_2O + 2H^+ + 2e^- \rightarrow 2Ag + H_2O \quad (1)$$

2.1. 3-D conductive and hydrophilic textile anodes

Several factors affect MFC performance, such as the types of bacterial inoculums, chemical substrates, ion-selective membranes and reactor configuration, but researchers have now reached a consensus that anode materials and architectures play the most profound role in influencing MFC performance (Xie et al., 2015; Lu et al., 2015; Mohan et al., 2014). Recently, studies have explored ways to increase anode surface area, porosity, biocompatibility, and conductivity using unconventional, 3-D micro- or nano-scale and micro-fabricated materials (Xie et al., 2015; Guo et al., 2015). The 3-D structure enables transport and colonization of bacterial cells deep inside the anode, ultimately increasing the MFC performance. Given the size of the bacterial cells (~2 μm) and thickness of the biofilm (> 50 μm), however, nano- and micro-scale pores are clogged by rapid microbial growth, which hinders the transport of nutrients and waste products; this makes the inner anode surface unusable for bacterial colonization (Fraiwan et al., 2014b). For this reason, high porosity and large pores will be an important factor in designing a high-performance bioanode. In this sense, a textile is an excellent anodic material, providing enough control to create pores that reach macro size and beyond, or at least 50 μm (Akbari et al., 2016; Turan and Okur, 2012). Furthermore, textiles are not only flexible for conformal contact with asymmetrical and non-uniform surfaces (e.g. human skin, organs, and tissues), but also reliable under extreme levels of deformation (e.g. stretching, twisting, and compressing). Despite their vast potential and promise, however, the full potential of the textile-based MFCs have not been realized yet and a standardized micro-sized device platform compatible with micro- and batch-fabrication has not been established. This deficiency is mainly caused by limitations in constructing conductive and hydrophilic textiles. A conductive textile allows the collection of electrons generated by all the bacteria throughout the fiber matrix, while the hydrophilic feature provides a fluidic compartment that holds bacteria-containing liquid and allows the mass transfer of ions. Patterning non-conducting textiles and conducting materials to create macro pores and hydrophilic features for liquid sample introduction is quite challenging.

In this work, poly(3,4-ethylened ioxythiophene):polystyrene sulfonate (PEDOT:PSS) was used as the conducting materials for the textiles. Its conductivity and hydrophilicity were greatly increased by adding ethylene glycol (EG) and 3-glycidoxypropy-trimethoxysilane (3 G), respectively, without damaging the fabric's mechanical features (Fig. 2a). The addition caused no change in the thin, tight and conformal deposition of the material (Fig. S1). To study the electrical conductivity of the engineered anode, we used the four-point probe method (Fig. S2). We measured its sheet resistance to be 7.84 Ω· cm, which is comparable to recent efforts to use conductive textile coating. Even after the length of the fabric-based device was stretched to become 50% larger, the resistance value (12.8 Ω cm) was not changed significantly compared to the overall internal resistance of the device (~kΩ), demonstrating the effectiveness of a highly conductive and stretchable fabric that uses EG/3G-modified PEDOT:PSS.

The commercial fabric with 92% polyester and 8% spandex comes with a thin layer of wax on the surface creating a hydrophobic property. Therefore, a hydrophilic pre-treatment process is usually necessary to build anodic reservoirs. However, our mixture of EG/3G-modified PEDOT:PSS disperses and adsorb immediately throughout even the initially hydrophobic textile without any pre-treatment techniques. The addition of the dielectric organic solvent EG dissolves the outer wax