



Further Improving the Current and Power Density of Miniaturized Microbial Fuel Cells

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INTRODUCTION

In recent years, due to the advancement of research in distributed wireless sensor networks, wearable sensors, and implantable medical devices, miniaturized power sources have become an active research area. A variety of miniaturized power sources have been extensively studied, including piezoelectric nano-generators (Wang and Song, 2006), triboelectric nano-generators (Fan et al., 2012; Zhang et al., 2018, 2019), fast charge-discharge batteries (Heeger, 2001), biofuel cells (Yu et al., 2016), and high-power micro-super capacitors (Pech et al., 2010; Pu et al., 2016, 2018). These devices benefit from small size, high surface area to volume ratio, and short charging time. In addition, miniaturized power sources generally benefit from micro/nanofabrication and batch manufacturing, thereby achieving precisely controlled geometry and low cost. The trend of miniaturizing power sources has also been adopted in the field of microbial fuel cell (MFC).

Microbial fuel cells are bionic-based electrochemical fuel cells that directly convert the chemical energy of organic compounds in biomass into electrical energy. This is accomplished through the catalytic reaction of specific microorganisms called exoelectrogens or Anode-Respiring Bacteria (ARB) (Ren et al., 2012, 2015a, 2016a). MFCs are very suitable as a long-term, maintenance-free stable power supply for the sensor network in remote areas of rivers and oceans, mainly due to (1) its direct and efficient power conversion efficiency; (2) abundance of river and ocean sediments and exoelectrogen or ARB in rivers and oceans, which means no external energy source need to be supplied; (3) electricity-producing bacteria can metabolize and reproduce by themselves, so theoretically it can supply electricity for an unlimited amount of time. Compared with large and medium sized MFCs, miniaturized MFCs have advantage of small size and high surface area to volume ratio, which generally results in a high current and power density. At present, the world records of the areal power density and volumetric power density of MFCs are 7.72 and 11,220 W/m³, respectively, which are achieved by miniaturized MFCs. However, the current and power densities are still one order of magnitude lower than traditional lithium ion batteries (Pikul et al., 2013; Ren et al., 2016a,b). It is critical to further improve the power density of MFCs. The important factors affecting power density, such as MFC configuration, anode/cathode materials and exoelectrogen or ARB, need to be investigated further.

MINIATURIZED MICROBIAL FUEL CELLS

A microbial fuel cell is a bionic-based electrochemical fuel cell that directly convert the chemical energy of organic compounds in biomass into electrical energy. Generally, MFCs are composed of two chambers, the anode chamber and the cathode chamber. The two chambers are separated by a proton exchange membrane or ion exchange membrane. Exoelectrogen or ARB forms on the anode in the anode chamber, and during the catalytic process of exoelectrogen or ARB, the microbe

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breaks down organic substance, such as sodium acetate to H_2O , CO_2 , and electrons inside the microbe. The electrons are transferred by extracellular electron transfer to the anode surface, and then through an external load to the cathode in the cathode chamber to be oxidized by oxidant, such as oxygen. Without extracellular electron transfer capability, the electrons generated by the microbe cannot be transferred to the anode and oxidized at the cathode. Miniaturized MFCs have smaller chamber volume compared with large or medium sized MFCs, and they are generally fabricated by microfabrication techniques. The surface area to volume ratio of miniaturized MFCs is high, resulting in higher current and power density. Miniaturized MFCs are firstly reported by Chiao et al. (2002), using *Saccharomyces cerevisiae* as exoelectrogen to decompose glucose to generate electricity. The electrode of this MEMS-based MFC is a flat gold electrode with a size of 0.07 cm^2 . Its power density is low, only 5.95 nW/m^2 (Chiao et al., 2002). In 2008, Siu and Chiao fabricated micropillars as electrodes on a polydimethylsiloxane (PDMS) substrate. The areal and volumetric power density is 4 mW/m^2 and 40 W/m^3 (Siu and Chiao, 2008). In 2009, Qian et al. proposed a miniaturized MFC as a power source for lab on a chip. *Shewanella oneidensis* was implemented as exoelectrogen and gold was used as electrodes and an areal power density of 1.5 mW/m^2 and a volumetric power density of 15 W/m^3 is reported (Qian et al., 2009). In 2009, Parra and Lin used *Geobacter sulfurreducens* for the first time as the electricity-producing bacteria for MEMS MFCs. Compared with other exoelectrogens, the power density of *Geobacter sulfurreducens* is higher. The areal power density obtained by the MFC is 0.12 W/m^2 , and the volumetric power density is 0.34 W/m^3 (Parra and Lin, 2009). In 2011, Choi et al. reported a miniaturized MFC based on *Geobacter sulfurreducens*, with a flat gold electrode as the anode. An areal power density of 47 mW/m^2 and a volumetric power density of $2,333 \text{ W/m}^3$ was reported, the highest volumetric power density of all MFCs reported at that time (Choi et al., 2011). In 2015, Lee and Choi presented an origami 3-D paper-based MFC. *Shewanella oneidensis* MR1 was implemented as exoelectrogen, and a maximum power density of $9.3 \mu\text{W/m}^2$ was reported (Lee and Choi, 2015). In 2017, Jiang et al. presented an integrated microfluidic flow-through MFC. *Shewanella oneidensis* was implemented as exoelectrogen and three-dimensional graphene foam was implemented as anode. High volumetric power density of 745 W/m^3 and a surface power density of 0.894 W/m^2 was reported (Jiang et al., 2017). In 2018, Pang et al. presented a flexible and stretchable MFC with conductive and hydrophilic textile. *Pseudomonas aeruginosa* PAO1 was implemented as exoelectrogen, and a maximum power density of 0.01 W/m^2 is achieved (Pang et al., 2018). In 2020, Gao et al. reported a yarn-based MFC. *Shewanella oneidensis* MR1 was implemented as exoelectrogen, and Ag_2O electron acceptor was implemented at the cathode. A maximum current and power density of 315.45 A/m^3 and 22.12 W/m^3 was reported (Gao et al., 2020). In 2016, Ren et al. implemented two-dimensional and three-dimensional graphene scaffold to improve the conductivity of biofilms and reduce the acidification in biofilms on power density, thereby increasing the power density. This study obtained a volumetric power density that is

much higher than in previous studies- $11,220 \text{ W/m}^3$ (Ren et al., 2016a).

DISCUSSION

Compared with large and medium-sized MFCs, miniaturized MFCs benefit from the scale effect and have a higher surface area to volume ratio, resulting in higher power density (Choi, 2015). The record in current power density in the field of MFCs is obtained by miniaturized MFC in 2016 by Ren et al. (2012, 2016a,b). As a result, in order to further improve the power density of MFCs, further improving the performance of miniaturized MFCs is critical.

Electrode materials are also critical to the performance of MFCs. In order to improve the performance of MFCs, many studies have adopted electrode materials with high surface area to volume ratio and high conductivity (Ren et al., 2012). In recent years, nano-structured carbon-based materials have been widely implemented as two or three dimensional anodes due to their higher electrical conductivity, higher surface area to volume ratio, and mechanical and thermal stability compared with traditional carbon-based materials. The two-dimensional carbon-based electrodes allow nanostructured carbon materials grow on a planar electrode, such as carbon nanotubes and graphene, and the biofilm grows on the surface of the two-dimensional electrode. To date, the maximum reported areal and volumetric power density is 0.83 W/m^2 and 3320 W/m^3 , respectively (Mink and Hussain, 2013; Ren et al., 2015a). Compared to two-dimensional electrodes, three-dimensional electrodes are more attractive because they allow the growth of thicker electro-generating biofilms. According to previous studies on the extracellular electron transfer, the exoelectrogens located tens of micrometers away from the anode have difficulty transferring electrons to the anode due to extracellular electron transfer limitations, while the three-dimensional electrode can grow thicker biofilms due to the large electrode thickness, thereby improving the performance of microbial fuel cells (Bond et al., 2012; Liu and Bond, 2012; Malvankar et al., 2012; Strycharz-Glaven and Tender, 2012; Ren et al., 2020). Microbial fuel cells with various three-dimensional nanostructured carbon-based electrodes have been reported, including carbon nanotube textiles (Xie et al., 2010), conductive polypyrrole/reduced graphene oxide (Gnana Kumar et al., 2014), reduced graphene oxide/carbon nanotube coated scaffold, Polyaniline hybrid graphene (Chou et al., 2014; Qiao et al., 2014), reduced graphene oxide carbon fiber (Xiao et al., 2012), carbon nanotube/polyaniline (Qiao et al., 2007), carbon nanotube/chitosan composite (Liu et al., 2011), reduced graphene oxide on sponge (Xie et al., 2012), and three-dimensional graphene on nickel sponge (Wang et al., 2013). In recent years, three dimensional electrodes have been adopted by many studies of miniaturized MFCs, including 3-D paper-based electrode by Lee and Choi (Lee and Choi, 2015), 3D graphene foam by Jiang et al. (2017), 3D textile based electrode by Pang et al. (2018), 3D yarn based electrode by Gao et al. (2020), and 3D graphene scaffold by Ren et al. (2016a). Currently the highest volumetric power density of all MFCs is achieved with 3D graphene scaffold

by Ren et al. at $11,220 \text{ W/m}^3$ (Ren et al., 2016a). As a result, to further improve the current and power density of miniaturized MFCs, adopting 3D electrodes as anode and cathode is critical.

Another important limiting factor for improving the performance of microbial fuel cells is exoelectrogen or ARB. A variety of electricity-producing microorganisms have been reported. The most important two are *Geobacter sulfurreducens* and *Shewanella oneidensis* (Ren et al., 2012). The current world record of power density for microbial fuel cells is obtained by *Geobacter sulfurreducens* (Ren et al., 2016a,b). The mechanism and bottleneck of extracellular electron transfer of electricity-producing microorganisms are critical to the power density of microbial fuel cells. However, the mechanism and bottleneck of the extracellular electron transfer of *Geobacter sulfurreducens* are still unclear to researchers worldwide. Elucidating the mechanism and bottleneck of extracellular electron transfer of *Geobacter sulfurreducens* is not only an important scientific discovery, but also has a vital influence on improving the performance of microbial fuel cells and even microbial electrochemical technology. There are two theories regarding the extracellular electron transfer of *Geobacter sulfurreducens*: (1) electron hopping (Snider et al., 2012); (2) microbes grow metallic nanowires that can conduct electrons (Malvankar et al., 2011; Dhar et al., 2018). The process of *Geobacter sulfurreducens* catalyzed decomposition of organic matter and transferring electrons to the electrode is generally divided into four steps: (a) *Geobacter sulfurreducens* decomposes organic matter to produce carbon dioxide, protons and electrons; (b) electrons from inside the outer cellular membrane of *Geobacter sulfurreducens* transfer to the outside of the cellular outer membrane; (c) Electrons are transferred from outside the cell to the vicinity of the electrode through electron hopping or conductive nanowires; (d) Electrons are transferred from the vicinity of the electrode to the electrode (Bonanni et al., 2012; Strycharz-Glaven and Tender, 2012). At present, the mechanism of the first and fourth steps are elucidated by researchers, yet the mechanism of the second and third steps is still unclear to researchers. For the second step, how electrons are transferred from the inside of the cellular outer membrane to the outside of the cellular outer membrane, there are currently few reports, and for the third step, as mentioned above, there is debate on whether the electron transfer is caused by electron hopping or microbial conductive nanowires (Ren et al., 2015b). The mechanism of microbial extracellular electron transfer is very important to the performance of microbial fuel cells. Probing the mechanism of microbial extracellular electron transfer can reveal the factors limiting the performance of microbial fuel cells, thereby elucidating it allows researchers to alleviate the bottleneck in a targeted manner and improve the performance of microbial fuel cells. In recent years, *Geobacter sulfurreducens* and *Shewanella oneidensis* have been adopted by many studies of miniaturized MFCs, and high performance has been achieved. In addition, screening for exoelectrogen with higher current and

power generation capability is also critical. Hou et al. presented 24 miniaturized MFC arrays to perform direct and parallel comparisons of microbial electrochemical activities of different exoelectrogen (Hou et al., 2009). Tahernia et al. presented 64 and 96 well-miniaturized MFC arrays to perform direct and parallel comparisons of genetically engineered exoelectrogen (Tahernia et al., 2019, 2020). By large MFC array screening, potential exoelectrogen with highly efficient EET capability may be found, which will improve the current and power density of MFCs.

Furthermore, due to the advantage of microfabrication for miniaturized MFCs, series/parallel MFC stacks/arrays with identical dimensions are fabricated by batch fabrication, which mitigate the problem of current reversal in MFC stacks/arrays (Ren et al., 2012). Miniaturized MFCs connected in series and parallel have been demonstrated. Choi and Chae presented 3 miniaturized MFCs in series which provide a power density of 667 W/m^3 at an output voltage of 1.8V (Choi and Chae, 2012). Gao et al. presented 3 series, 2 parallel MFCs with power densities of 22.10 and 19.14 W/m^3 (Gao et al., 2020). Because miniaturized MFC arrays/stacks can provide higher voltage output compared with single cells and exoelectrogens in each MFC in the stacks/arrays can efficiently transfer electrons to the anode when the dimension of each MFC is small, the current and power density can be potentially improved. In the future, by stacking large arrays of identical-sized miniaturized MFCs fabricated by batch fabrication, not only the current and power density can be enhanced, the output voltage can also be boosted to 10–100 s of volts. At such a high output voltage, the MFC stacks/arrays can potentially provide power to electronics directly without DC-DC converters.

OUTLOOK

According to the theoretical research on the scale effect of miniaturized MFCs, the current and power density of microbial fuel cells still have a room of improvement of one order of magnitude (Ren et al., 2012). If the current and power density of miniaturized MFCs can be successfully increased by an order of magnitude by adopting 3D electrode material and exoelectrogen with highly efficient EET capability, it will be able to make MFCs widely adopted in distributed wireless sensor networks, wearable sensors, implanted medical devices and other fields.

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and has approved it for publication.

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Conflict of Interest: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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