A HIGH POWER DENSITY MEMS MICROBIAL FUEL CELL

S. Choi¹, H.-S. Lee², Y. Yang¹, B.E. Rittmann², and J. Chae^{1*}

¹ School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona, USA

² Center for Environmental Biotechnology, Biodesign Institute, Arizona State University, Tempe, Arizona, USA

ABSTRACT

We report a microfabricated microbial fuel cell (MFC) that produces a high power density using a *Geobacteraceae*-enriched mixed bacterial culture. The MFC features 4.5- μL anode/cathode chambers defined by 20- μm -thick photo-definable polydimethylsiloxane (PDMS). The short proton diffusion length (20 μm) in the anode lowers electrolyte resistance and consequently enhances power generation. A maximum current density of 16.3 mA/cm^2 and power density of 2.3 mW/cm^2 are achieved. The start-up time is only 2 days for maximum current generation. The MFC was operated under semi-continuous flow conditions, and L-cysteine was added in order to chemically scavenge the dissolved oxygen in the anode chamber.

INTRODUCTION

Microbial fuel cell (MFC) is an electrochemical device that converts organic substrates into electricity through microbial catabolism. Since the first microfabricated MFC in 2002 [1], interest in MEMS (Micro-Electro-Mechanical systems) MFCs has grown not only for miniaturized power sources [2-6], but for the studies of individual microorganism behavior [7, 8]. When it comes to the usefulness in studies of microbes, the MEMS MFCs have many advantages to characterize a small number of, or even a single, bacterial electron transfer due to the micro-sized electrode that can be in the size of individual microorganism. For miniaturized power sources, MEMS technology may be a potential solution to increase the power density in miniature MFCs by increasing the specific surface area, anode area divided by volume of the anode compartment. For example, Siu *et al.* presented a microfabricated polydimethylsiloxane (PDMS) MFC with embedded micropillar electrodes to increase the specific surface area up to 144 cm^{-1} [4]. Nevertheless, earlier MEMS MFCs had low power output [1-5, 7], short life time [1-4] and long start-up time [6], which are unacceptable for a practical portable power source. Those limitations were mainly due to the following two factors. First, the bacteria used in these MEMS MFCs (*Saccharomyces cerevisiae* or *Shewanella oneidensis MR-1*) are not efficient for generating high power density, as they require mediators to transfer electrons from donor substrate to the anode [1-5, 7]; *Saccharomyces cerevisiae* are unable to produce shuttling compounds, demanding exogenous mediators for current generation. The exogenous-mediator MFCs are impractical because of costs and mediator toxicity [9]. Second, high internal resistance in the micro-sized MFCs caused a substantial loss of power generation. A long distance between the anode and cathode can increase ohmic resistance, the main form of internal resistance [10], causes slow start-up and decreases power density [5, 10]. Siu *et al.* microfabricated a 100- μm -thick PDMS gasket that was manually assembled between anode and cathode; however, it is extremely hard to manually manipulate such a thin PDMS film to assemble the fuel cell [4]. Qian *et al.* reported a batch-fabricated MEMS technology to give short electrode spacing using a 100- μm -thick SU-8 spacer in a micro-scale MFC [5]. They accelerated the start-up period and showed long-term sustainability of power generation. However, their approach still had low power density at $15 \text{ }\mu\text{W}/\text{cm}^3$ ($0.15 \text{ }\mu\text{W}/\text{cm}^2$), which is even lower than that of the MFC using *Saccharomyces cerevisiae* [4, 5].

Figure 1: Schematic of the fabrication process

In this work, we report the possibilities of a micro-sized MFC as a power source by enhancing the power generation. We used *Geobacteraceae*-enriched mixed bacterial cultures to obtain high current, since these are anode-respiring bacteria (ARB) that produce a conductive biofilm matrix [11, 12]. We designed the MEMS MFC to have a short proton-transfer distance and a high specific surface area (500 cm^{-1}) to lower the internal resistance by using photo-definable PDMS, which increase the power density and decrease the start-up time.

MATERIALS AND METHODS

Device fabrication and assembly

Fig. 1 shows the fabrication process of the MFC. We cut two glass substrates (VWR International 75 mm x 25 mm x 1 mm) to 45 mm x 25 mm and mechanically drilled with six holes on each substrate: one inlet, one outlet, and four screws. The glass substrates were then coated with Ti/Au (20 nm/200 nm) by e-beam evaporator and patterned to define the electrodes (1.5 cm x 1.5 cm) using a lift-off process. After that, we spin-coated photo-definable PDMS (WL-5150, Dow corning) at 750 rpm for 30 sec. This PDMS layer was used for a spacer and the thickness of the layer can be controlled by the spin speed. The PDMS layer was prebaked at 110 $^{\circ}\text{C}$ for 120 sec. prior to UV exposure ($3000 \text{ mJ}/\text{cm}^2$) through a negative photo-mask. Following the exposure, the substrate was baked at 150 $^{\circ}\text{C}$ for 180 sec. and agitated in WL-9653 developer (Dow corning) for 30 sec. Finally, the PDMS-coated substrates were cured at 180 $^{\circ}\text{C}$ for 1 hr. The thickness of the PDMS was measured as 20 μm , corresponding to the depth of the anode/cathode chamber. The patterned PDMS defined a 4.5- μL volume for each (anode or cathode) chamber. The inlet and outlet of the microfluidic channel were accessed

from the back side of the substrates via nanoports (10-32 Coned assembly, IDEX Health & Science) and connected with fluidic tubing (outer diameter: 0.0625 inch, inner diameter: 0.002 inch, 1548, IDEX Health & Science). We used CMI 7000 (Membranes international Inc.) as cation exchange membrane (CEM) to permit only cation transport needed to maintain electroneutrality in both chambers. The CEM surface area was 1.7 cm x 1.7 cm. To assemble the dual-chamber MFC, we sandwiched the CEM between the anode and cathode chamber and clamped them with four screws (Fig 1 & Fig 2). The MFC was operated at 30°C.

Figure 2: (a) Device top view (b) side view (c) experiment setup for monitoring of the MFC power generation

Inoculum

The inoculum was obtained from an acetate-fed MFC mother reactor inoculated originally with a mixture of activated sludge and anaerobic digester sludge. 16S-rRNA gene clone libraries on the inoculum showed *Geobacter sulfurreducens*-enriched mixed bacterial culture [11]. Acetate was the sole electron donor present in the anode chamber at 25 mM in mineral medium. The composition of the mineral medium was (per L of deionized water): KH_2PO_4 1680 mg, Na_2HPO_4 12,400 mg, NaCl 1600 mg, NH_4Cl 380, 5 mg EDTA, 30 mg $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 5 mg $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 10 mg NaCl , 1 mg $\text{CO}(\text{NO}_3)_2$, 1 mg CaCl_2 , 0.001 mg $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.001 mg $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.1 mg $\text{AlK}(\text{SO}_4)_2$, 0.1 mg H_3BO_3 , 0.1 mg $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.1 mg Na_2SeO_3 , 0.1 mg $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 0.2 mg $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 1 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The initial pH in the anode chamber was 7.5 ± 0.1 [11]. 2.5 g/L L-cysteine was added in the anolyte to scavenge the dissolved oxygen in the anode chamber. The catholyte was 100 mM potassium ferricyanide and 100 mM phosphate buffer in which the initial pH was adjusted at 7.5 ± 0.2 with 0.1 M NaOH. Anolyte and catholyte solutions were continuously from a syringe pump at the speed of 1.5 $\mu\text{L}/\text{min}$.

Measurement setup

We measured the potential between the anode and cathode by a DAQ/68 data acquisition system (National Instrument) and recorded them every 1 min via LabVIEW (National Instrument). An external resistor was connected between electrodes of the MFC to close the circuit. We calculated the current through the resistor via ohm's law and the output power via $P=V \times I$. Current and power density were calculated based on the anode area (2.25 cm^2) or anode chamber volume (4.5 μL), respectively. The MFC system was closed with a 150- Ω external load. Inoculum and catholyte were injected to fill the 4.5- μL anode/cathode chamber by a syringe pump, and then the ends of tubing were sealed with silicone for biofilm formation at fed-batch mode.

MFC operation

With acetate being the substrate to the anode of the MFC,

protons, electrons, and CO_2 are the metabolic products of the ARB reaction, as shown in Equation (1). Electrons are transferred to the anode via the conductive matrix that the ARB forms and flow to the cathode through the external electrical circuit.

Protons released by the ARB reaction travel through CEM towards the cathode. At the cathode, potassium ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$, captures the electrons (Equation (2)) and the cycle is completed.

RESULTS AND DISCUSSION

Current generation

After we filled the anode chamber with inoculum and L-cysteine, the open circuit voltages (OCV) in batch- and continuous-mode were 346 mV and 745 mV in 20 hours, respectively (data not shown). The substantial drops of OCV in batch-mode could be attributed to O_2 intrusion into the anode chamber. O_2 can abiotically react with the anode when anode potential is negative enough to reduce O_2 into H_2O , which can significantly reduce OCV. In addition, O_2 in the anode chamber is a strong electron sink for the bacteria, which divert electron flow to O_2 oxidation instead of to current. Macro-sized MFCs also are adversely affected by O_2 intrusion into the anode, but the MEMS MFC is more sensitive to the presence of O_2 intrusion because even small rates of O_2 intrusion can divert significant electron flow when the system size is so small. Therefore, we added L-cysteine to reduce any O_2 entering the anode and operated MEMS MFC in semi-continuous flow conditions.

As shown in Fig 3, transient current generation was observed as soon as the inoculum including L-cysteine was injected. After we confirmed that the current increased to 0.5 μA , 5 hours after the injection of the inoculum, we fed fresh anolyte (a mixture of 25 mM acetate and 2.5 g/L L-cysteine in mineral medium) and catholyte solutions continuously to each chamber at 1.5 $\mu\text{L}/\text{min}$. Current increased to 50 μA in approximately 5 hours after the continuous feed of anolyte/catholyte. Once the current dropped to baseline due to the depletion of the solution in the 1-mL feeding syringe, we re-injected fresh anolyte/catholyte into both chambers, and the current increased to a peak value of 63.7 μA (14.2 mA/cm^3) in 2 days. The maximum current was 66.7 μA (14.8 mA/cm^3) in the third cycle.

Figure 3: Current produced from the MEMS MFC with a 150 Ω load

Repeated cycles of anolyte/catholyte addition showed good reproducibility of current generation. The current became stable and increased as the cycle was repeated. This reproducible current generation indicates that ARB oxidized acetate and transferred acetate electrons to the anode in the MEMS MFC. The current increase with operation cycles supports that the ARB attached to the gold anode and proliferated. Thus, one main factor for the rapid current generation was that the *Geobacter sulfurreducens*-enriched culture created its own conductive biofilm [12].

The results in Fig. 3 show that our MEMS MFC exhibited a significantly shorter start-up time compared to macro-sized MFCs. We believe that mitigation of O₂ intrusion by L-cysteine and a high specific surface area (500 cm²) of the anode increased ARB biofilm formation on the anode surface and led to fast start-up.

Polarization curve and power output

The voltage responses to different loads are shown in Fig 4. OCV of 687 mV was regained immediately upon load removal. We derived the polarization curve and power output from values of Fig. 4 and show them in Fig. 5. The maximum power output and current were 10.5 μW and 73 μA, respectively. The maximum current and power density per volume of anode chamber were 16.3 mA/cm³ and 2.3 mW/cm³, respectively.

Table 1 compares our output results with the literature [3-7]. We report the volumetric power density for micro-sized MFCs up to now; previous reports of volumetric power densities were only 0.34 to 32 μW/cm³. The main contributor for such high volumetric power density is the large specific surface area (500 cm²) in our MEMS MFC, compared to other MFCs [4-7]. Having high specific surface area allows high power density per unit volume. Yet, specific surface area is not the only parameter to determine the power density. A prior micro-sized MFC having similar specific surface area (510 cm²) only produced 2.3 μW/cm³ [3], orders of magnitude less than our maximum power density.

Another important factor for highest volumetric maximum power density is a small energy loss (voltage term), described by Equation (4).

$$E_{Device} = OCV - IR_{int} = I(R_a + R_m + R_c + R_e) \quad (4)$$

where R_a , R_m , R_c and R_e are anodic, membrane, cathodic and electrolyte resistance, respectively [14]. R_e can be expressed by:

Figure 4: Voltage response to different load resistors

Figure 5: Polarization curve (black square) and power output (blue circle) measured as a function of current

Table 1: Summary of microfabricated MFCs in literature

Biocatalyst	Operation	Anode mediator / Anolyte / Catholyte	Anode / Area [cm ²]	Cathode / Area [cm ²]	Membrane Area [cm ²]	Space; anode to membrane	Anode volume [cm ³]	Specific surface area [cm ⁻¹]	Max. Power (Current)	Start-up Time	Power density		Ref.
											P _S (μW/cm ²) ^c	P _V (μW/cm ³)	
Saccharomyces cerevisiae	Fed-batch	Yes / Glucose / [Fe(CN) ₆] ³⁻	Au/0.12 (0.51) ^e	Au/0.51	1	80 μm	0.001	510	2.3 mW (15 μA) under 10 Ω	NA ^d	0.019	2.3	[3]
Saccharomyces cerevisiae	Fed-batch	Yes / Glucose / [Fe(CN) ₆] ³⁻	Au/1.2 (2.16) ^e	Au/1.2	1.2	100 μm	0.015	144	0.48 μW (36 μA) under 1 KΩ	NA ^d	0.4	32.1	[4]
Shewanella oneidensis MR-1	Fed-batch	No / TSB ^a / [Fe(CN) ₆] ³⁻	Au/0.38	Carbon Cloth /0.38	0.38	1.2 cm	0.154	2.5	143.3 mW (0.6 μA) under 20 KΩ	NA ^d	0.377	0.93	[7]
Shewanella oneidensis MR-1	Fed-batch	No / TSB ^a / [Fe(CN) ₆] ³⁻	Au/0.15	Carbon Cloth /0.4	0.15	100 μm	0.0015	100	23 mW (0.8 μA) under 40 KΩ	2 Days	0.15	15	[5]
Geobacter Sulfurreducens	Continuous	No / Acetate / Fe(CN) ₆ ³⁻	Au/0.01	Coiled Au wire /1	0.5	NA ^d	0.35	0.03	0.12 μW (0.6 μA) under 330 KΩ	10 Days	12	0.343	[6]
Mixed Bacterial culture^b	Continuous	No / Acetate + L-cysteine / Fe(CN)₆³⁻	Au/2.25	Au/2.25	2.25	20 μm	0.0045	500	10.5 μW (26 μA) under 15 KΩ	2 Days	4.67	2333	This Work

^aTryptone soya broth; ^bGeobacteraceae-enriched culture; ^cEffective surface area;

^dNot Available; ^eCalculation based on geometric surface area

$$R_e = \frac{l}{A \cdot K} \quad (5)$$

where l is the distance (cm) and A is the cross-sectional area (cm²) over which the ionic conduction occurs, and K is the specific conductivity ($\Omega \cdot \text{cm}$)⁻¹ of the electrolyte [15]. Our electrode distance was 0.048 cm (membrane thickness 457 μm + spacer 20 μm), the conductivity of our medium was 0.017 ($\Omega \cdot \text{cm}$)⁻¹, and the cross sectional area of the membrane was 2.25 cm². Therefore, we computed R_e as only 1.26 Ω , and energy loss by electrolyte resistance was as small as 32 μV ($26 \mu\text{A} \times 1.26 \Omega$) at the maximum volumetric power density 2333 $\mu\text{W}/\text{cm}^3$. Resistance of CEM is 20 Ω ($45.1 \Omega \cdot \text{cm}^2$ ($R_m \cdot A$) divided by anode surface area 2.25 cm²) in phosphate buffer medium [14]. We estimated the energy loss by membrane resistance as 520 μV ($20 \Omega \times 26 \mu\text{A}$); thus, overall ohmic energy losses were only 555 μV for the maximum current density, which is negligible compared to the total energy losses 289 mV, OCV 687 mV – 398 mV (at the maximum power output) in Fig 5. These analyses indicate that electrode energy losses were the main energy bottleneck for our MEMS MFC.

Using the polarized curve in Fig 5, we estimated internal resistance (R_{ini}) from the point where the MFC polarization curve exhibited a near-linear drop (ohmic losses): from 10 μA to 60 μA . Linear fitting of the curve yielded a R_{ini} value of $\sim 10 \text{ k}\Omega$, which includes R_a , R_c , R_m , and R_e . The sum of R_m and R_e only is 21.3 Ω , and, therefore, electrode resistance ($R_a + R_c$) is computed at 9980 Ω . The linear-fitting approach is consistent to the early analysis that electrode energy losses are the main energy-barrier in the MEMS MFC.

CONCLUSION

We demonstrated that a microfabricated MFC utilizing a *Geobacter sulfurreducens*-enriched biofilm can give high power density. To achieve the high power density, we utilized a very thin photo-definable PDMS spacer patterned to define 4.5- μL anode/cathode chambers. The maximum current density of 16.3 mA/cm^2 and power density of 2.3 mW/cm^2 were by far the highest among all previously reported MEMS MFCs, and this was due to the high anode specific surface area, efficient ARB of *Geobacter sulfurreducens* capable of creating a conductive biofilm, elimination of O₂ exposure, and low ohmic losses. Moreover, the start-up time was only 2 days for maximum current generation.

REFERENCES

- [1] M. Chiao, K.B. Lam, Y. Su, and L. Lin, "A miniaturized microbial fuel cell," Technical Digest of the 2002 Solid-State Sensors and Actuators Workshop, Hilton Head Island, SC, pp. 59-60.
- [2] M. Chiao, K.B. Lam, and L. Lin, "Micromachined Microbial Fuel Cells," Proceedings of 16th IEEE International Conference on Micro Electro Mechanical Systems (MEMS) 2003, Kyoto, Japan, (2003), pp.383-386.
- [3] M. Chiao, K.B. Lam, and L. Lin, "Micromachined microbial and photosynthetic fuel cells," J. Micromech. Microeng., 16, 2547 (2006).
- [4] C. Siu, and M. Chiao, "A Microfabricated PDMS Microbial Fuel Cell," J. Microelectromech. Syst., 17, 1329 (2008).
- [5] F. Qian, M. Baum, Q. Gu, and D. E. Morse, "A 1.5 μL microbial fuel cell for on-chip bioelectricity generation," Lab on a Chip, 9, 3076 (2009).
- [6] E.A. Parra, and L. Lin, "Microbial fuel cell based on electrode-exoelectrogenic bacteria interface," Proceedings of

- 22nd IEEE International Conference on Micro Electro Mechanical Systems (MEMS) 2009, Sorrento, Italy, (2009), pp.31-34.
- [7] H. Hou, L. Li, Y. Cho, P. de Figueiredo, and A. Han, "Microfabricated Microbial Fuel Cell Arrays Reveal Electrochemically Active Microbes," PLOS one, 4, e6570, (2009).
- [8] E.A. Parra, A. Higa, C.R. Buie, J.D. Coates, and L. Lin, "Real-time biocatalyst loading and electron transfer via microfabricated btransparent electrode," Proceedings of 23rd IEEE International Conference on Micro Electro Mechanical Systems (MEMS) 2010, Hong Kong, (2010), pp.1183-1186.
- [9] D.R. Lovely, and K.P. Nevin, "Electricity Production with Electrocigens," Chapter 23, Bioenergy, ASM Press, Washington, DC, USA, 2008.
- [10] H. Liu, S. Cheng, and B.E. Logan, "Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration," 3 Environ. Sci. Technol., 9, 5488, (2005).
- [11] H. S. Lee, P. Parameswaran, A. Kato-Marcus, C.I. Torres, and B.E. Rittmann, "Evaluation of energy-conversion efficiencies in microbial fuel cells (MFCs) utilizing fermentable and non-fermentable substrates," Water Research, 42, 1501, (2008).
- [12] C.I. Torres, A.K. Marcus, H.S. Lee, P. Parameswaran, R. Krajmalnik-Brown, and B.E. Rittmann, "A kinetic perspective on extracellular electron transfer by anode-respiring bacteria," FEMS Microbiol Rev., 34, 3, (2010).
- [13] Z. He, J. Kan, Y. Wang, Y. Huang, F. Mansfeld, and K.H. Nealson, "Electricity production coupled to ammonium in a microbial fuel cell," Environ. Sci. Technol., 43, 3391, (2009).
- [14] F. Harnisch, U. Schroder, and F. Scholz, "The suitability of monopolar and bipolar ion exchange membranes as separators for biological fuel cells," Environ. Sci. Technol., 42, 1740, (2008).
- [15] Y. Fan, E. Sharbrough, and H. Liu, "Quantification of the internal resistance distribution of microbial fuel cells," Environ. Sci. Technol., 42, 8101, (2008).

CONTACT

*J. Chae, tel: +1- 480-965-2082; Junseok.Chae@asu.edu