Performance Enhancement Of Mems-Based Microbial Fuel Cells (μMFC) For Microscale Power Generation

PERFORMANCE ENHANCEMENT OF MEMS-BASED MICROBIAL FUEL CELLS (µMFC) FOR MICROSCALE POWER GENERATION

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Abstract. This paper reports the design, fabrication, and testing of a microliter scale Microbial Fuel Cell (µMFC) based on silicon MEMS fabrication technology. µMFC systems are operated under different loads or open circuit to compare the effect of different acclimatization conditions on start-up time. *Shewanella oneidensis* MR-1 is preferred to be the biocatalyst. The internal resistance is calculated as 20 kΩ under these conditions. Acclimatization of µMFC under a finite load resulted in shorter start-up time (30 hours) when compared to the open load case. Power and current densities normalized to anode area are 2 µW/cm^2 and 12 µA/cm^2 respectively. When the load resistance value is closer to the internal resistance of the µMFC, higher power and current densities are achieved as expected, and it resulted in a shorter start-up time. Further studies focusing on the different acclimatization techniques for µMFC could pave the way to use µMFCs as fast and efficient portable power sources.

1. Introduction

Microbial fuel cells (MFC) are defined as bioreactors that convert the energy in the chemical bonds of organic compounds into electrical energy through catalytic activity of microorganisms under anaerobic conditions [1-3]. Adopting MFCs as portable power sources has been a popular research field for the last fifteen years [4-6]. However, the miniaturization of MFCs is necessary to be employed as portable power sources [7-8]. In this scope, MEMS technology is attractive for creating microscale microbial fuel cells (µMFC) due to the potential of miniaturization, economical mass production and large surface-area-to-volume ratio [9]. To be able to employ µMFCs as power sources, their performance parameters, namely power density, current density and start-up time, must be enhanced. The power and current densities depend on the biofilm (complex structure adhering to surfaces and consisting of colonies of bacteria) and the type of electrode surface. The biofilm varies from Gram-positive to Gram-negative bacteria and depends on the operational mode of the MFC, whether MFC is operated in closed circuit or open circuit system [10-11]. The growth of the microbial biofilm is found to decrease the anode polarization resistance and

facilitate the kinetics of the electrochemical reactions [12]. Anode polarization resistance is one of terms forming the overall internal resistance, which limits the power and current generation, of µMFC. Thus, when the biofilm grows on the anode surface, the internal resistance decreases providing an enhancement on the performance [13]. In the light of these facts, to obtain higher performance µMFCs, the internal resistance of µMFC and the start-up time should decrease. Optimization of chamber and/or cell geometries, chamber or electrode materials, and electrode surface characteristics is crucial to increase µMFC performance. Furthermore, to enhance the biofilm formation, acclimatization of bacteria (giving time to bacteria to adjust to the conditions of growth) may be preferred. Thus, this study focused on a MEMS based µMFC with micro-liter volume to decrease the internal resistance and acclimatization of bacteria to decrease the start-up time.

2. Experimental methods and materials

2.1. Device fabrication and assembly

Since gold is biocompatible, conductive, and compatible with conventional microfabrication techniques, it was preferred as the electrode material. µMFC electrodeswere designed to have gold conductive areas and access holes inside the device. The masks were prepared with Cadence software, the flow inside the chambers modelled with COMSOL software (data not shown) and the microfabrication (figure 2) was performed in class 1000 clean room area.

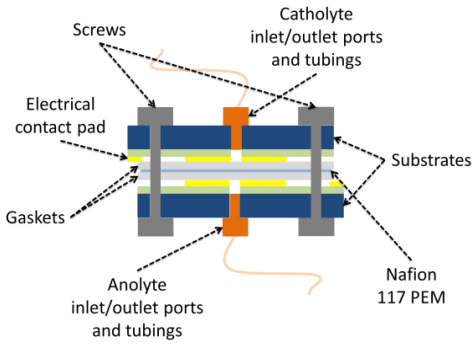

Figure 1. Schematic of µMFC.

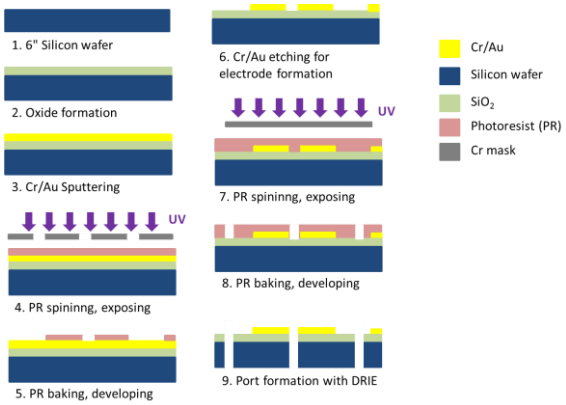

Figure 2. µMFC electrode fabrication steps.

Thermal oxide was formed on a polished 6″ polished silicon wafer by PECVD in order to provide passivation. Cr/Au layers (30 nm / 300 nm) were sputtered on the mentioned passivation layer and patterned by standard photolithography process. The access holes were drilled via DRIE. A picture of the microfabricated electrode is shown in figure 3.

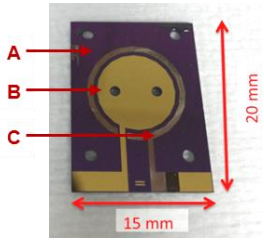

Figure 3. Microfabricated µMFC electrode. When two electrodes on substrates faced each other at 180°, the gold contact pads are exposed for electrical wiring. (A: Silicon substrate, B: Gold electrode, C: Silver electrode for further studies (the brownish thin circular electrode around the gold electrode is the oxidized silver layer to be processed as the reference electrode).

Two pieces of Gel-Pak WF 1.5-X4 gel films (170 µm x 15 mm x 17 mm) were sandwiched as gaskets between the two electrodes facing each other at 180°. The anode and cathode were separated by a proton exchange membrane (Nafion 117) placed between the gaskets. All layers were manually stacked and tightly kept together by screws and/or clamps. The assembled µMFC (figure 1) had four holes for fluidic inlet/outlet and eight holes for screws. It had two chambers (10.4 µL each) defined as anode and cathode chambers. The exposed conductive electrodes area per chamber was 0.61 cm^2. The

inlet and outlet of the µMFC were accessed from the backside of the silicon substrates via nanoports (LabSmith) and transparent medical tubing (Ø 1 mm). Figure 1 depicts the schematic of the assembled µMFC.

2.2. Bacterial inoculum and µMFC operation

Shewanella oneidensis MR-1 (ATCC, USA), a facultative anaerobic electroactive bacterium, was grown on Triptic Soy Agar (Merck) at 30°C for 24 hours by streak plate method to obtain single colonies of bacteria. Then, the one grown single colony was cultured in Triptic Soy Broth (TSB) (Merck) medium on a shaker (150 rpm) at 30°C for 24 hours under aerobic conditions. To be fed as the anolyte, fresh TSB and bacteria inoculum was mixed (1:1). The anolyte (including inoculum) and catholyte solutions were continuously supplied using a syringe pump (KD Scientific) at rates of 3 µL/min and 5 µL/min respectively to anode and cathode chambers independently. The catholyte was 100 mM ferricyanide (Sigma-Aldrich) in a 100 mM phosphate buffer in which pH was adjusted at 7.5±0.1 with 0.1 M NaOH. The µMFC was operated at 25±1 °C. Three different µMFC assemblies were connected to either 10 kΩ or 25 kΩ external loads or operated under open circuit conditions.

2.3. Performance evaluation

The potential between the anode and the cathode was measured via a digital multimeter (Agilent 3441A) with a data acquisition system (National Instrument) and recorded the results every 1 min via Keysight IntuiLink interface. The start-up time of the biofilm formation was determined from the voltage versus time plot as the point when the voltage started to increase dramatically. The biofilm formation was accepted as terminated when the voltage reached a steady value. The polarization curve (V vs I) was obtained by changing the external resistors between 1 MΩ and 1 kΩ while recording the voltage. Linear fitting of the curve at the ohmic loss region resulted in the total internal resistance of the µMFC. The current through the resistors was calculated via Ohm's law, I = V/R, and the output power via Joule's law, P = V×I. Current and power densities were normalized to the anode area (0.61 cm^2) and anode chamber volume (10.4 µL).

3. Results and discussion

3.1. Start-up performance

The start-up time of the biofilm formation was investigated by plotting voltage versus time plot (figure 4). Acclimatization of µMFC under a load resulted in shorter start-up time (table 1).

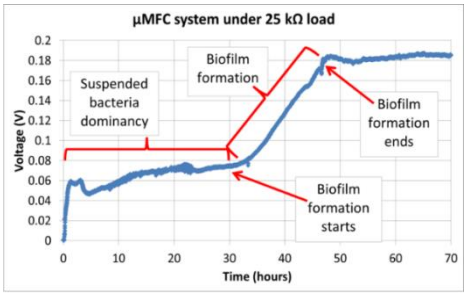

Figure 4. Effect of load on biofilm formation.

Table 1. Comparison of start-up values.

System	Start-up time of biofilm formation	Duration to reach maximum current
25 kΩ loaded µMFC system	~30 hours	~47 hours
10 kΩ loaded µMFC system	~31 hours	~84 hours
Open circuit µMFC system	~47 hours	~200 hours

3.2. Power generation performance

The results obtained showed the performance enhancement in terms of power and current densities and start-up time with respect to similar microliter scale microbial fuel cells with the same biocatalyst used given literature. Power density (133 µW/cm^3) and start-up time (30 hours) obtained with 25 kΩ loaded µMFC is better than to similar literature study by Qian et al. [7] and Li et al. [14] (table 2). The internal resistance was calculated as 20 kΩ under the mentioned conditions via polarization curve linear fitting (data not shown). It is observed that when the load is closer to internal resistance of the µMFC, higher power and current densities are achieved. However, power and current densities of this

study are smaller than the densities of MFC made of carbon paper by Vigolo et al. [15]. Bacteria prefer to adhere to carbon-based materials but they are difficult to integrate in MEMS processes when compared to gold as an electrode material.

Table 2. Comparison of performance values.

	25 kΩ loaded (this study)	10 kΩ loaded (this study)	Qian et al., 2009 [7]	Li et al., 2011 [14]	Vigolo et al., 2014 [15]
Bacteria	*S. oneidensis* MR-1	*S. oneidensis* MR-1	*S. oneidensis* MR-1	*S. oneidensis* MR-1	*S. oneidensis* MR-1
Fuel cell geometry	Double chamber with Nafion-117	Double chamber with Nafion-117	Double chamber with Nafion-117	Double chamber with laminar flow	Double chamber with Nafion-117
Anode area	0.61 cm^2	0.61 cm^2	0.15 cm^2	0.014 cm^2	0.5 cm^2
Anode volume	10.4 µL	10.4 µL	1.5 µL	0.3 µL	5 µL
Chamber depth	170 µm	170 µm	100 µm	50 µm	100 µm
Anode/cathode materials	Au/Au	Au/Au	Au/carbon cloth	Au / Au	Carbon paper / Carbon paper
Load	25 kΩ	10 kΩ	100 Ω	N/A	100 kΩ
Start-up time	30 hours	31 hours	47 hours	36 hours	15 hours
Internal resistance	20 kΩ	20 kΩ	30 kΩ	N/A	49 kΩ
Volumetric power density	133 µW/cm^3	26 µW/cm^3	15 µW/cm^3	N/A	900 µW/cm^3
Volumetric current density	716 µA/cm^3	500 µA/cm^3	1300 µA/cm^3	127 µA/cm^3	6180 µA/cm^3
Areal power density	2 µW/cm^2	0.4 µW/cm^2	0.15 µW/cm^2	N/A	9 µW/cm^2
Areal current density	12 µA/cm^2	9 µA/cm^2	13 µA/cm^2	2.542 µA/cm^2	61.8 µA/cm^2

4. Conclusions

A MEMS-based µMFC is demonstrated to operate with short start-up time in this study. With the designed 10.4 µL double-chamber µMFC, the internal resistance was calculated as 20 kΩ which is still an important bottleneck to overcome. Power and current densities obtained is comparable to similar literature study. In addition to higher power and current densities, when the bacteria is acclimatized under a load closer to the internal resistance of the µMFC, shorter start-up time is achieved. Further studies focusing on the different acclimatization techniques for µMFC could pave the way to use µMFCs as fast and efficient portable power sources.

Acknowledgments

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