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A MICROFLUIDIC PLATFORM FOR EVALUATING ANODE SUBSTRATES FOR MICROBIAL FUEL CELLS

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ABSTRACT

Microbial fuel cell technology is a new technology for producing green energy from wastewater. While lab scale and commercial microbial fuel cells typically utilize graphite as the film substrate, it is difficult to rapidly prototype micro-patterned graphite and it has not been used to date. Our design sandwiches graphite sheets under a channel layer creating a microfluidic microbial fuel cell with graphite electrodes. The microfluidic microbial fuel cell uses Geobacter sulfurreducens fed with acetate in a phosphate buffer media. Ferricyanide is used as the catholyte so that the system is anodically limited. Current versus time and open circuit voltage are reported showing biofilm growth microbial fuel cell operation.

NOMENCLATURE

\( A_c \) Cross-sectional area  
\( \text{COD} \) Chemical Oxygen Demand \([\text{g O}_2 \text{ L}^{-1}]\)  
\( D_h \) Hydraulic diameter, \([\text{m}]\) \( D_h = A_c/P \)  
\( I \) Current, \([\text{A}]\)  
\( I_{sc} \) Short circuit current, current when the voltage is 0 \( \text{V} \) \([\text{A}]\)  
\( \mu \) Viscosity of solvent \([\text{Pa} \cdot \text{s}]\)  
\( OCV \) Open Circuit Voltage\([\text{V}]\)  
\( P \) Wetted perimeter  
\( P_{max} \) Maximum power density \([\text{mW m}^{-3}]\)  
\( Re_{D_h} \) Reynolds number based on the hydraulic diameter  
\( \rho \) Density of solvent \([\text{kg} \cdot \text{m}^{-3}]\)  
\( SA \) Surface area of the electrode \([\text{m}^2]\)

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INTRODUCTION

A microbial fuel cell (MFC) is a device in which bacteria consume sugar and other hydrocarbons and ‘exhale’ \( \text{CO}_2 \), protons and electrons. The electrons travel to a corrosion resistant metal (the anode) while the protons diffuse away from the bacteria to be combined at another electrode (the cathode) with the electrons that have passed through a circuit.

Our lab started looking at MFCs around the same time that Lee & Kjeang reviewed existing scaled down microbial fuel cells [1]. In this review, they made a strong case for using microfluidic fuel cell architecture to study and possibly improve microbial fuel cells. Specifically, this made a case for using the laminar flow fuel cell (LFFC) architecture that had produced exceptionally large power densities for standard fuel cell chemistries. Similar designs in microfluidic devices have greatly reduced culturing times [2]. Since then, two groups published results exploring the possibilities with this design [2, 3].

The laminar flow fuel cell architecture takes the anolyte and catholyte of a fuel cell and runs them parallel to each other at flow rates low enough to achieve laminar flow. The flow can either go on top, in between or through the anode and cathode electrodes/current collector. In laminar flow, the only mixing between streams is due to diffusive mixing, so the anolyte and catholyte can be kept separate for longer lengths at faster flow rates or wider spacing of the electrodes. As the separation is due
to the flow, these devices have been called membraneless fuel cells. The simplest and some of the first designs were Y-shaped channels flowing above gold electrodes.

Gold is the gold standard of microfabrication. Gold is less conductive (\(\sim 4 \times 10^7\) S m\(^{-1}\)) than copper (\(\sim 6 \times 10^7\) S m\(^{-1}\)) and silver (\(\sim 6 \times 10^7\) S m\(^{-1}\)), but it is less reactive and less bactericidal than copper or silver. It is more conductive than platinum and less bactericidal. It is not cheap (\(\sim 50,000\) USD kg\(^{-1}\)) but can be deposited in thin (100 nm) stable conductive layers, reducing the cost. It is used frequently, even in biological platforms, because there is a breadth of knowledge in manufacturing from the semiconductor industry. To bridge the gap between biocompatibility and ease of manufacturing, gold electrodes have been chemically modified by functionalization with alkanethiols or sulfate linked carbon nanotubes [4]. This reduces the catalytic effect and increases charge transfer resistance. It is not clear how this impacts the bacteria.

Carbon is the gold standard of microbial fuel cell anodes. Carbon is not bactericidal, is conductive (\(\sigma \sim 10^5\) S m\(^{-1}\)), and is a cheap (\(\sim 3\) USD/kg) anode material. We surveyed 80 publications from the past 10 years and found that 26 distinct anodes have been used in microbial fuel cells. Of these, only 3 were not alternate packaging of carbon. Within the 23 carbon packagings, an additional 23 mechanical, thermal, or chemical treatments were applied to those anodes. Mechanical modifications try to increase the available surface area and the surface area to volume ratio [5]. Chemical modifications include but are not limited to etching with oxygen plasma, pyrolysis in an ammonium environment, immersion in acetone, acetone and nitric acid, to list a few [6–9]. Carbon is not easily microfabricated although printing carbon electrodes is a promising new technology [10]. This last reason is most likely the reason, the recent membraneless microfluidic fuel cells have used gold electrodes [7, 8].

Our goal was to create a microfluidic microbial fuel cell that was able to use graphite as the electrode. Along the way, we designed the device to be oxygen impermeable and reusable.

**METHODS**

A microfluidic microbial fuel cell was designed to maximize surface to volume ratios and minimize internal resistance. The design was a Y channel similar to those of [3, 11, 12] except that the outlet was separated into 3 streams for recirculation of the anolyte and catholyte (see Fig 1). Whereas microfluidic biological platforms are made from poly(dimethylsiloxane) (PDMS) for rapid prototyping [13], this design is milled from optically clear acrylic (poly(methyl methacrylate)) (McMaster-Carr, Los Angeles, CA). The main channel is 1.1 mm wide by 0.055 mm deep and was milled on a micro-mill (Microlution Inc, Chicago, IL) using a 0.01” (0.254 mm) end mill (Performance Micro Tool, Janesville, WI). This manufacturing technique takes 1 hr from acrylic sheet to device. The 60 x 60 mm plates, interconnects and screw holes were cut using a laser cutter. The interconnects were made using 22 gauge luer tips with metallic epoxy. Acrylic is oxygen and water impermeable giving precise control of the oxygen environment. The total volume of the chamber was \(V = 1.21\) mm\(^3\) while the volume directly over the anode was \(V_{An} = 0.385\) mm\(^3\). The anode and the cathode were spaced 0.4 mm apart with equal area of 0.35 mm x 20 mm. It follows that the anode to cathode ratio is 1 and while the surface area to volume ratio is \(\frac{\alpha S}{V} = 1.8 \times 10^4\) m\(^{-1}\). Equal anolyte and catholyte flow rates of \(Q = 0.66\) mm\(^3\)/s (40 \(\mu\)L/min) were created using a peristaltic pump (Ismatec, Wertheim-Mondfeld, GER). This resulted in a Reynolds number based on the hydraulic diameter of

\[
Re_D_h = \frac{p v D_h}{\mu} = \frac{4 p Q}{\mu P} = 2
\]

so the flow is laminar. In addition to experimentation using colored dyes (images not shown), crossover was modeled using COMSOL 4.3 as shown in 2. In the simulation, acetate diffuses 0.2 mm past the midplane at a concentration of \(\sim 1.5\) mM while ferricyanide (results not shown), diffuses over to the same distance at 0.8 mM at the trailing edge of the electrode. This model did not include reactions, which would decrease the concentration available for diffusive mixing.

The electrodes were pyrolytic graphite sheets Panasonic PGS type EYG with adhesive backing (Digikey, Thief River,
results and discussion

The microfluidic MFC with PG electrodes produced a steady current at ~ 50 nA or 20.43 ± 4.76 mA · m⁻² at +0.2 V/Ag/AgCl within 6 hrs. Open circuit voltage was ~ 95 mV.

The steady-state current density is similar to the maximum current found by Li et al (2011) [3]. The maximum current would happen at a much smaller voltage (~ 0 V) which implies that the maximum current density here would be larger. This probably is due to the use of ferricyanide as the catholyte instead of dissolved oxygen. The current density here is 3 orders of magnitude smaller than that found by Li et al (2012) [2] who similarly used ferricyanide. This is most likely due to the higher poised potential (0.7 V/vs [Fe(CN)₆]³⁻/[Fe(CN)₆]²⁻). Compared to other microbial fuel cells of similar volume our devices steady state current is an order of magnitude less than the maximum current found [1]. A comparison of open circuit voltage between our device and the other two membraneless microfluidic microbial fuel cells is not possible. Compared with microfluidic fuel cells with membranes, the open circuit voltage is 0.3 V less [1]. The current stabilized within 5-9 hrs, as shown in Fig 3, faster than both of the existing membraneless microfluidic fuel cells. While culturing times in microfluidic devices are typically much faster than bulk culture vessels [13], microscale MFCs have not shown similar improvement [1]. Instead, using cultures from established fuel cells decreases start-up time and improves current production [16] which was probably the case here.

The interaction of transmembrane proteins and substrate is important for adhesion and electron transfer. The adhesion process is an interplay of electrochemical and mechanical forces. The electrochemical forces include the displacement of the solution shell around the protein and the double-layer on the electrode surface [17]. It also includes the potentially irreversible adsorption of protein and subsequent displacement of the atoms within the crystal structure [18,19]. The electron transfer process of Geobacter sulfurreducens occurs through transmembrane proteins [20]. The same problems that face binding proteins would face proteins engaged in electron transfer: irreversible binding, denaturing, blockage of active sites. The identity of the protein, activity of the substrate, and solution conductivity all affect the binding strength and nature of the binding [21]. Work thus far has shown that electron transfer to car-

FIGURE 2. A MODEL OF THE FLOW OF THE ANOLYTE (ACETATE, 40 mM) INTO THE BOTTOM LEFT, SHOWS THAT THE ACETATE DIFFUSE 0.2 mm PAST THE MIDPLANE AT A CONCENTRATION OF ~ 0.01 mM.

FIGURE 3. RESULTING STEADY STATE CURRENT OUTPUT OF THE LAMINAR FLOW MICROBIAL FUEL CELL FROM STARTUP OVER 24 HRS AT +0.2 V/Ag/AgCl WAS 20.43 ± 4.76 mA · m⁻². THE LAMINAR FLOW MICROBIAL FUEL CELL WAS RUN USING THE EFFLUENT FROM THE ANODE OF AN EXISTING MICROBIAL FUEL CELL. A PERISTALTIC PUMP WAS USED TO KEEP THE FLOW AT 0.66 mm³·s⁻¹.
bon electrodes is optimal, followed by humic/thiols substance and last gold and other metals [4, 22, 23]. Our test of gold versus carbon electrodes in a macrofuel cell produced OCVs of 189 mV and 590 mV for gold and carbon respectively after 1 week. This may further explain differences between our system and the existing microfluidic microbial fuel cells.

CONCLUSION & FUTURE WORK

A microfluidic microbial fuel cell has been created using graphite electrodes similar to those used in lab scale MFCs. The device was inoculated using an existing fuel cell culture and achieved steady-state current of 20 mA · m⁻² in 24 hrs. A low open circuit voltage of 95 mV compared to standard Geobacter fuel cells (660 mV) shows that there is room for improvement. The device allows for interchangeable electrodes and future work will compare the graphite electrode with gold and other metals that can be microfabricated.

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