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Supercapacitive microbial fuel cell: Characterization and analysis for improved charge storage/delivery performance

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HIGHLIGHTS

- Supercapacitive MFCs with various anode and cathode dimensions are investigated.
- Cathode is limiting bottle supercapacitive MFC performance.
- Increase in cathode area led to decrease in ohmic resistances and increase in capacitance.
- The performance of a hypothetical cylindrical MFC is linearly modelled.
- A 21 cm^3 cylindrical MFC can deliver a peak power of 25 mW at 70 mA and 1300 W m^{-3}.

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ABSTRACT

Supercapacitive microbial fuel cells with various anode and cathode dimensions were investigated in order to determine the effect on cell capacitance and delivered power quality. The cathode size was shown to be the limiting component of the system in contrast to anode size. By doubling the cathode area, the peak power output was improved by roughly 120% for a 10 ms pulse discharge and internal resistance of the cell was decreased by ~47%. A model was constructed in order to predict the performance of a hypothetical cylindrical MFC design with larger relative cathode size. It was found that a small device based on conventional materials with a volume of approximately 21 cm^3 would be capable of delivering a peak power output of approximately 25 mW at 70 mA, corresponding to ~1300 W m^{-3}.

1. Introduction

Microbial fuel cell (MFC) technology has been an area of interest over the past few decades as a potential source for sustainable alternative energy generation and simultaneous wastewater treatment (Pandey et al., 2016). Although power production of MFCs has increased greatly since the late 90's, MFCs still deliver current/power densities that are approximately three orders of magnitude lower than those of methanol or hydrogen based fuel cells (Logan, 2009). These low current densities make it difficult to employ MFCs to directly power devices which require high energy output. Improving the power quality delivered by MFCs is a key challenge in the development of this technology.

Microbial fuel cells utilize innate bacterial respiratory processes to convert organic materials to usable energy through the process of extracellular electron transfer. Electro-active bacteria oxidize organic substrates and electrons are conducted through the bacterial membrane to an extracellular electron acceptor using specialized proteins (c-type cytochromes) and appendages (nanowires) that are present on the bacterial surface (Busalmen et al., 2008; Gorby et al., 2006; Logan, 2009). In MFCs, a conductive anode serves as the final electron acceptor in the bacterial respiratory process. Conductive 3-D carbonaceous (Chen et al., 2012; Wei et al., 2011; Liu et al., 2012) or metallic (Dumas et al., 2007; Guerrini et al., 2014; Baudler et al., 2015) materials have been used as anode electrodes. The electrons flow through a circuit that is terminated with the reduction of oxygen at the cathode, creating

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a gradient in electrical potential and generating current. Oxygen is commonly used as the oxidant at the cathode due to its high electrochemical potential and its environmental availability. At near neutral pH, the cathodic reaction has a large overpotential, so a catalyst is necessary to complete the reaction (Zhao et al., 2006; Erable et al., 2012). Typically, this is accomplished through the use of platinum or platinum group metals (PGMs), enzymes, bacteria, high surface area carbon materials, or high surface area carbon materials with PGM-free catalyst.

While platinum is one of the most effective materials currently known for the electrocatalytic oxygen reduction, it is very cost prohibitive resulting in 47% of the capital cost of the device (Rozendal et al., 2008). Furthermore, platinum catalysts are also subject to poisoning in the conditions present in MFC environments, leading to reduced efficiency over time (Santoro et al., 2016a). In this work, we utilize a platinum group metal-free organic catalyst (Fe-AAPyr) to catalyze the oxygen reduction reaction (ORR). Fe-AAPyr is competitive with platinum-based catalysts with the advantage of being much more cost effective, sustainable and less prone to catalyst poisoning (Santoro et al., 2016a).

The maximum theoretical cell voltage, $V_{max,theoretical}$, of an MFC can be calculated by considering the equilibrium potentials of the anode and cathode reactions ($E_{cathode}$ and E_{anode} in V vs. SHE):

$$V_{max,theoretical} = E_{cathode} - E_{anode} = 0.805\ V - 0.300\ V = 1.105\ V \quad (1)$$

The above equation assumes that acetate is used as a fuel source (16.9 mM) for the anode at pH = 7 and oxygen, at a partial pressure of 0.2 atm, is the oxidant for the cathode (Fradler et al., 2014). During operation, losses occur as a result of ohmic, activation, and mass-transport limitations, resulting in lower cell potentials of around 0.3–0.5 V. These voltage levels are insufficient to operate low-power consuming devices such as microprocessors (270 uA, 2.2 V), LEDs (10–20 mA, 2 V), or photodiodes (10 mA, 3.3 V) (Fradler et al., 2014). Various approaches have been explored for improving cell potential and power output in MFCs including: stacking of individual MFCs with series and parallel connections (Ieropoulos et al., 2008; Ledezma et al., 2013), maximum power point tracking (MPPT) techniques (Park and Ren, 2012), and the use of external capacitors with DC/DC converters (Dewan et al., 2009; Rozendal et al., 2008; Wang et al., 2015).

Electrochemical supercapacitors (SCs) are an attractive energy storage technology that is capable of storing and delivering energy at high current and power densities with little variation in performance over the course of millions of charge/discharge cycles (Conway, 1999). In addition, SCs offer the advantage of duty cycles more compatible with BES technologies, whereby the charge/discharge cycles can be within minutes, rather than hours, days or months, which is the case for conventional batteries. SCs differ from conventional capacitors in that they do not make use of a solid dielectric material. Instead, they rely on the principles of electric double-layer capacitance and/or pseudocapacitance as the charge storage mechanisms (Conway, 1999).

As stated above, external SCs have been utilized as an energy storage system to harvest the low power produced by MFCs and to deliver higher current pulses in order to power small electronic devices (Dewan et al., 2009; Ieropoulos et al., 2010, 2013; Wang et al., 2015). Furthermore, it has been demonstrated that more energy can be harvested by operating MFCs intermittently rather than continuously. Dewan et al. showed a 111% increase in power by intermittent operation of the MFC connected to a SC when compared to continuous operation (Dewan et al., 2009; Ieropoulos et al., 2016; Papaharalabos et al., 2013). Another approach to improve power quality is the utilization of the inherent capacitive features of MFC electrodes. MFCs and SCs both utilize high surface area carbon as their electrode material. Recently, efforts have been made to integrate capacitive materials with MFC electrodes in order to improve power quality and charge storage capabilities (Deeke et al., 2015). In 2005, Ieropoulos et al. first demonstrated that biofilms in MFCs were capable of storing electrons when the device was left in open circuit for an extended period of time, providing higher power upon reconnection of the circuit (Ieropoulos et al., 2005). It has been shown that cytochromes present within MFC biofilms exhibit pseudocapacitive behavior and can act as electron sinks (Esteve-Núñez et al., 2008; Schrott et al., 2011; Uría et al., 2011).

Formation of a Helmholtz layer by electrolyte ion adsorption at the MFC/electrode interfaces further contributes to the observed capacitance of the cell (Fradler et al., 2014). Fradler et al. showed that double layer capacitance contributed approximately ten times the capacitance of the biofilm in a tubular MFC which was shown to achieve charge storage capacities comparable to SCs with minimal current leakage (Fradler et al., 2014). An integrated self-charging supercapacitive MFC has been constructed by integrating an additional high surface area carbon brush short-circuited with the cathode and operating an MFC in a controlled manner (Santoro et al., 2016b). The additional electrode (AdE) confers increased surface area available for formation of a Helmholtz double layer, thus increasing the device's capacitance. The AdE also leads to lower observed ohmic resistance during galvanostatic (GLV) discharge of the microbial supercapacitor. This design significantly improves recharge times of the system when compared to designs that incorporate external capacitors, allowing for more frequent use of the accumulated energy (Santoro et al., 2016b).

It was previously shown that the increase in cathode area affected positively on the performance output of the MFCs (Cheng and Logan, 2011; Kim et al., 2015). In the present study, we investigate a supercapacitive MFC (SC-MFC) system and the effect of relative anode and cathode size on the overall performance of the system. We use the experimental data from these experiments to construct a simple predictive linear model for a hypothetical SC-MFC with a cylindrical design in order to forecast performance of a larger scale device. We demonstrate that the performance of a SC-MFC based on conventional materials can be improved to levels suitable for powering practical electronic devices by optimizing design parameters.

2. Materials and method

2.1. MFC configuration

A single chamber glass bottle microbial fuel cell design with a volume of 125 mL was used to investigate the effect of relative anode and cathode geometric area on supercapacitive MFC (SC-MFC) performance (Fig. S1). The cell consisted of a Pyrex glass bottle modified with two lateral glass tubes to serve as attachment sites for cathode electrodes. The MFC was operated in a membraneless configuration with the anode fully immersed in the solution with air-breathing cathodes. One face of the cathode was exposed to the electrolyte and the other was exposed to the air. The effect of changing the relative area of the anode and cathode of the MSC was investigated.

2.2. Anode construction

Carbon brush electrodes (Millirose, USA) were employed as the anode material for all experiments. The carbon brushes used had a diameter of 3 cm and a length of 3 cm, giving a projected surface area of 9 cm^2. Prior to our experiments, all anodes were pre-colonized with electro-active bacterial biofilms by incubation