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Intermittent load implementation in microbial fuel cells improves power performance

X.A. Walter [a,b], J. Greenman [b], I.A. Ieropoulos [a,*]

[a] Bristol Robotics Laboratory, Universities of Bristol and of the West of England, T-building, Frenchay Campus, BS16 1QY, United Kingdom
[b] Microbiology Research Laboratory, School of Biological, Biomedical and Analytical Sciences, Faculty of Health and Applied Sciences, Frenchay Campus, University of the West of England, Bristol BS16 1QY, United Kingdom

HIGHLIGHTS

- Intermittent loading of MFCs allows 1.8 times higher power output bursts.
- Higher energy is produced under specific duty cycles.
- Ceramics respond better than cation exchange membranes.
- The presence of a pre-digester greatly improves power output.

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ABSTRACT

This study reports on the response of small-scale MFCs to intermittent loading, in terms of power output over time. The aim was to understand the evolution with time of power output under different duty cycles, in conditions close to practical implementation. Inexpensive ceramic membranes were compared to cation exchange membranes, under continuous flow and with a pre-digester connected. Results show that at the minute-scale, all the duty cycles investigated, produced 78% higher power bursts from the MFCs (500 μW) than when under continuous loading (280 μW). These results were recorded from MFCs employing ceramic membranes, whereas the difference in performance for MFCs employing commercially available cation-exchange-membranes was insignificant. When normalising to daily energy production, only specific duty cycles produced more power than continuous loading. Furthermore, the introduction of a pre-digester increased the MFC power outputs 10-fold, thus confirming that separating fermentation from electro-active respiration, significantly enhances the system performance.

1. Introduction

Microbial fuel cells (MFCs) are energy transducers comprising an anode, a cathode and typically a cation-selective membrane. Microorganisms consume organic matter as their source of nutrients, carbon-energy and electrons, and the anode electrode serves as the end-terminal electron acceptor. This degradation of organic substrates, in the anodic compartment, also produces protons that pass to the cathode through the exchange membrane. The electrons and the protons react together and reduce the oxidant present at the cathode (i.e. oxygen) (Liu et al., 2004). Research on MFCs was first reported in 1911 (Potter, 1911) but mostly gained interest during the last two decades (Logan et al., 2006; Pant et al., 2010). This interest is motivated by the potential to treat organic waste from various sources (e.g. agricultural, industrial, anthropogenic) without having to spend energy, as is the case with existing processes (Rozendal et al., 2008). One of the recent research avenues pursued in this field is to improve the ability of MFC systems (peripherals included) to produce useful levels of power (Ieropoulos et al., 2005; Woodward et al., 2010; Coronado et al., 2013).

In general, efforts to improve power output have focussed on changing either the embodiment (Du et al., 2007; Jia et al., 2013) or the material employed (Logan and Regan, 2006). However, most of these studies involve costly materials and processes such as nanotubes (Qiao et al., 2007; Feng et al., 2011; Ghasemi et al., 2013), platinum coated cathodes (Martin et al., 2011; Santoro et al., 2013), and/or membrane-electrode assemblies (Pham et al., 2005; Guo et al., 2012; Kim et al., 2013). With respect to energy

* Corresponding author. Tel.: +44 117 32 86 318.
E-mail address: loannis.leropoulos@brl.ac.uk (I.A. Ieropoulos).

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harvesting, it has already been reported (Ieropoulos et al., 2005) that intermittent loading and unloading of MFCs (subjecting the system to a duty-cycle) may be beneficial. Recent studies (Grondin et al., 2012; Liang et al., 2013; Fradler et al., 2014) have confirmed that by intermittently loading and unloading an MFC, more power can be produced, than under a continuous load. The main focus has been to adjust the resistive load and use the capacitive-properties of MFCs to increase power harvesting by pulse-width-modulation (PWM). These studies have demonstrated well the principle of intermittent loading, however experiments have been conducted under controlled temperature conditions, with simple organic fuel sources (e.g. acetate), pure cultures (e.g. *Shewanella oneidensis*), platinum-based cathodes, or chemical catholytes (e.g. ferricyanide) and in batch mode, which would be difficult to implement in practical applications. Furthermore, the time sweeps studied previously were short and would have probably captured the transient response of the MFCs, and not the long-term stability.

The aim of the present study was to verify if this principle could be applied to MFCs running under more realistic conditions, which would be closer to a real environment implementation i.e. continuous flow, no pH control, ambient temperature and no expensive catalysts. The MFCs were continuously fed with a complex carbon source to allow the development of a more complex biological community, and inoculation was with activated sludge. The MFCs had inexpensive ceramic membranes and plain carbon fibre veil electrodes. These MFCs were then operated under different duty cycles, defined as the ratio between the time during which the MFCs were under load and the time during which they were under open circuit conditions. The power output was recorded in order to measure the influence of repetition of different duty cycles over time.

2. Methods

2.1. Strain and culture media

The anodes were inoculated with activated sludge (Wessex Water, Saltford UK). The microbial fuel cells (MFCs) were maintained in batch mode for 2 weeks with a 1.5 kΩ load connected, and subsequently operated under continuous flow at a flow rate of 1.2 mL h^{-1}. The semi-synthetic medium used as the anolyte consisted of: 0.20 g L^{-1} KH_2PO_4, 0.30 g L^{-1} NH_4Cl, 1.30 g L^{-1} $MgCl_2{\cdot}2H_2O$, 0.50 g L^{-1} KCl, 0.15 g L^{-1} $CaCl_2$, 7 g L^{-1} NaCl, 10 g L^{-1} tryptone, 5 g L^{-1} yeast extract (complex carbon source), 1 mL L^{-1} of SL10 trace elements solution (Atlas, 2004), and 1 mL L^{-1} of Selenite–Tungstate microelements solution (11 and 12 μM, respectively). The pH was adjusted to 7.01 prior to autoclaving. Tap water was employed as the catholyte and the actual experiments started 3 months following inoculation.

2.2. MFC design and operation

The different ceramic membranes were tested under a cascade arrangement, as previously described (Winfield et al., 2012). These consisted of three MFCs, which were connected electrically in parallel. A short tube (7 cm long with a volume of 495 μL) linked the output of one MFC, either anolyte or catholyte, to the input of the next one, thus constituting a fluidic bridge. Each 5 mL anodic compartment was built in black acrylic material to avoid any development of phototrophic organisms. For the same reason the tubing consisted of black ISO-Versinic coating (3 mm ID; Saint Gobain Performance Plastics, FR). The anodes were made from a 64 cm^2 sheet of carbon fibre veil (20 g m^{-2}) (PRF Composite Materials Poole, Dorset, UK). The cathode consisted of the same electrode but with a 160 cm^2 total surface area. Both electrodes were folded down to a cuboid with an exposed surface area of 3.36 cm^2. Two types of membrane were employed, namely cation exchange membrane (CMI-7000, Membrane International, USA), and terracotta plates (CTM potter supplies, UK), the membrane area of which was 5.12 cm^2. Each MFC-cascade had identical membranes in all three constituent units. The water absorption (% of weight) of the 2 mm thick terracotta membranes was 9.1 ± 0.3% (Winfield et al., 2013). The terracotta membranes were kilned at 1080 °C.

The anolyte was supplied at a flow rate of 0.8 mL h^{-1} from the lower to the upper MFCs, whilst the catholyte was pumped continuously at a rate of 80 mL h^{-1} from the upper to the lower MFCs. The anolyte was pumped upstream in order to prevent accumulation of gas bubbles in the anode chambers. The catholyte was pumped downstream into a funnel and was inherently carrying air bubbles, therefore allowing the aqueous oxygen content to be in constant equilibrium with the atmospheric pO_2 (open to air reservoir, high flow rate). The reservoir of anolyte was separated from the MFC setup using two anti-grow-back systems in order to maintain sterile conditions. After 40 h of operation, a pre-digester was added between the medium reservoir and the MFC setup, at the same time as feedstock was replaced. The pre-digester was introduced to separate the production of organic acids from their electro-active consumption. The pre-digester comprised a 100 mL glass bottle with a rubber butyl stopper, separating the vessel from the outside environment. The pre-digester was filled with 40 mL of sterile medium and was inoculated with 10 mL from the output of each MFC. The working volume was 50 ± 2.5 mL with a hydraulic retention time (HRT) of 62.5 ± 3.1 h.

2.3. Data capture

MFC output was measured in millivolts (mV) against time using a PicoTech data logger (ADC-24, Pico Technology Ltd.). The voltage was recorded every 2 min, during the maturity period, and subsequently every 5 s when applying intermittent loads. The current I in Amperes (A) was calculated using Ohm's law, $I = V/R$, where V is the measured voltage in Volts (V) and R is the known value of the resistor. The power output P in Watts (W) was calculated as $P = I \times V$. Polarisation curves were performed at the beginning and at the end of the study, using a computer-controlled resistorstat (Degrenne et al., 2012). The polarisation ranged from 1 MΩ to 11 Ω, with 5 min sample rates for each resistance.

2.4. Intermittent load sweeps

A load switch box was built in order to alternate rapidly between open and closed circuit. This consisted of a single side stable 5 V double pole double throw relays (G6K-2G surface mounting relay, Omron Corp.). These relays were programmed to "open" thus enabling open-circuit conditions, when current was applied, and to connect the resistor when no current was drawn, from a separate power supply (mains).

A switch was set between the electrical mains supply and the load switch box. This switch was actuated manually in order to connect/disconnect a load simultaneously to all MFCs. Different time ratios, between closed circuit (CC) and open circuit (OC) were investigated, which were aimed at understanding more the stability of the system, in addition to the transient response. These were: 30 s CC–30 s OC; 60 s CC–60 s OC; 180 s CC–180 s OC; 60 s CC–90 s OC; 60 s CC–180 s OC; 90 s CC–15 s OC; 180 s CC–60 s OC; 300 s CC–180 s OC. The same load switch box was subsequently connected to a plug-in-mains timer switch that allowed longer sweep periods: 3600 s CC–900 s OC; 3600 s CC–300 s OC. The external resistance for this phase was determined based on the results from polarisation experiments.