Title: Intermittent load implementation in microbial fuel cells improves power performance.

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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 \mu W) than when under continuous loading (280 \mu W). 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.

**Key words:** ceramics, cation exchange membrane, pre-digester, continuous flow, intermittent loading, duty cycle.

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 decade (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 MFC systems (peripherals
included) to produce useful levels of power (Ieropoulos et al., 2005; Woodward et al.,
2010; Coronado et al., 2013).

Efforts to improve power output have generally focussed on changing either the
embodiment (Du et al., 2007; Jia et al., 2013) or the material employed (Logan & 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
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. Materials and 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 1.5kΩ 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 KH₂PO₄, 0.30 g L⁻¹ NH₄Cl, 1.30 g L⁻¹ MgCl₂.2H₂O, 0.50 g L⁻¹ KCl, 0.15 g L⁻¹ CaCl₂, 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 µM 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 (7cm long with a volume of 495\(\mu\)L) linked the output of one MFC, either anolyte or catholyte, to the input of the next one downstream, thus constituting a fluidic bridge. Each 5mL 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 (3mm ID; Saint Gobain Performance Plastics, FR). The anodes were made from a 64cm\(^2\) 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 160cm\(^2\) total surface area. Both electrodes were folded down to a cuboid with an exposed surface area of 3.36cm\(^2\). 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 5.12cm\(^2\).

Each MFC-cascade had identical membranes in all three constituent units. The water absorption (% of weight) of the 2mm 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 0.8mL h\(^{-1}\) from the lower to the upper MFCs, whilst the catholyte was pumped continuously at a rate of 80mL 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 hours 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 100mL glass bottle with a rubber butyl stopper, separating the vessel from the outside environment. The pre-digester was filled with 40mL of sterile medium and was inoculated with 10mL from the output of each MFC. The working volume was 50mL ± 2.5mL with a hydraulic retention time (HRT) of 62.5h ± 3.1h.

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 minutes, during the maturity period, and subsequently every 5 seconds 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 1MΩ - 11Ω, with 5 minutes 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 5V 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: 30s CC – 30s OC; 60s CC – 60s OC; 180s CC – 180s
OC; 60s CC – 90s OC; 60s CC – 180s OC; 90s CC – 15s OC; 180s CC – 60s OC; 300s CC – 180s 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 CC – 300 s OC. The external resistance for this phase was determined based on the results from polarisation experiments.

The amount of energy produced for each duty cycle was obtained by calculating the area under the curve. The energy produced by the two last duty cycles were normalised per day and then averaged (n=2).

3. Results & discussion

3.1 The introduction of a pre-digester enhanced power production.

During the first 40 hours when no pre-digester was used (Figure 1a), the current output was comparable to the results of previous studies employing similar systems (Ieropoulos et al., 2008). Under these conditions the MFCs with cation exchange membranes (cat-MFCs) outperformed the MFCs with ceramic membranes (cer-MFCs). When complex carbon sources are employed in MFCs, two main biological processes occur (Freguia et
al., 2008), namely: i) breaking down of complex organic matter into organic acids (e.g. lactate, butyrate, acetate), and ii) anaerobic respiration of those organic acids by electro-active microorganisms. Based on this principle, a pre-digester was introduced in the system to separate the two processes in specific and compartmentalised environments.

The aim was to increase both activities separately, thus increasing the systems total power output.

As shown in Figure 1a, when the fuel ran out, the current output decreased slowly until fresh medium was added (57 hours). Following the addition of fresh feedstock and the introduction of the pre-digester, the current output of the system recovered to previous levels. The voltage remained at a comparable level for approximately 65h (pre-digester HRT) before increasing for the next 130h. Following the addition of the pre-digester, the cascades with ceramic membranes outperformed those with cation exchange membranes (CEM) (Figure 1a). The load was changed from 1500Ω to 329Ω after 100h in steady-state conditions (plateau, Figure 1a) and then to 1000Ω. In both cases, the cer-MFC continued to outperform the cat-MFC (Figure 1a). The polarisation curves obtained confirmed these results (Figure 1b) where maximum power densities of 43.7 W.m\(^{-3}\) (cer-MFCs) and 24.8 W.m\(^{-3}\) (cat-MFCs) were produced. These data support the notion that ceramic MFCs are
leading contenders for advancing MFC technology by reducing the requirement for
expensive materials and/or pre-treatments (Dong et al., 2012).

3.2 Intermittent loading investigation.

The preliminary experiment described in section 3.1 demonstrated that i) power output
increased when a pre-digester stage was introduced, and that ii) ceramic membranes
performed better. The next step examined the effect of intermittent loading on the different
cascade systems.

The resistance value selected for use during intermittent loading, corresponded to the
same resistor value producing maximum power transfer during the polarisation
experiments for the cer-MFCs and cat-MFCs (329 Ω and 1000 Ω, respectively; Figure 1b).

Compared to continuous loading, intermittent loading allowed the cer-MFCs to produce
much higher bursts of power (Figure 2). Whilst not completely stable over time, these
bursts of power were all repeatable (60s CC / 180s OC, Figure 2b). Results indicate that
when the closed circuit time \( T_{CC} \) was longer than the open circuit time \( T_{OC} \) power bursts
decreased over time (Figure 2). This was only observed for \( T_{OC} \) lower than 180s, which
may indicate a low-level chemical capacitance effect (e.g. sulphide build-up). A previous
study has shown that capacitance effect appears with a minimal $T_{OC}$ of 20s (Ieropoulos et al., 2005). However, here, a capacitance behaviour is only visible with $T_{OC} = 30$ s (Figure 2a). For any longer $T_{OC}$, the power curves did not demonstrated any capacitance behaviour, thus suggesting that no chemical capacitance occurs with $60 \leq T_{OC} \leq 180$ s (see § 3.3).

As can be seen in Figure 2, in the case of the cer-MFCs, a plateau was always reached after 30s (Figure 2a). Independent of the applied duty cycle, the power output steady states of cer-MFCs were always higher than when the same MFCs were under continuous load (Figure 2). Therefore, in the context of pulse-width-modulation (PWM) any of those duty cycles would have been appropriate. When comparing the amount of energy produced, under intermittent load, only certain duty cycles generated more energy than under continuous load (Figure 3a). Results indicate that the power produced under intermittent loading was equivalent to that produced under continuous loading when $T_{CC}=T_{OC}$, and superior when $T_{CC}>T_{OC}$ (Figure 3a). For this comparison, the time lengths considered for averaging the energy produced were identical, i.e. the data were covering the same amount of time for both conditions.
Duty cycles could not have been applied for a long time period (hours) with similar time lengths (seconds) due to physical experimental limitations. In order to make the comparison possible, the employed time ratios were in the same range as for short duty cycles: 1/0.25 and 1/0.08, 60min CC/15min OC and 60min CC/5min OC respectively. Since duty cycles covered a period of 10 hours, values were compared to the steady state power of the cer-MFC after 10h under continuous load (Figure 4a). Results confirmed that those time ratios resulted in the production of higher power than when under continuous load (Figure 3b, 5a).

Depending on the time length of the duty cycles, with similar time ratios, the transient response of the cer-MFCs varies significantly. Although with long duty cycles the energy generated was comparatively higher than under continuous load, it was still less than when the cer-MFCs were under short time duty cycles (< 20 J d^{-1}, Figure 3). These results indicate that cer-MFCs would be more efficient if the duty cycles were of short time length with T_{CC} > T_{OC}. In the context of such short duty cycles and of MFC stacks, PWM of the harvesting electronics would be of significant interest since it allows the system to operate at higher voltage and power levels.
The resistance applied to the cat-MFCs corresponded to the values obtained from measurement of maximum power transfer (1000 Ω, Figure 1b). Compared to the voltage and power levels of the cat-MFCs under continuous load, the bursts of power were equivalent. Cation exchange membrane MFCs (cat-MFCs) produced higher power than continuous load only under three duty cycles (60cc/180oc, 180cc/180oc, and 60cc/90oc, time in seconds) but the difference was minimal (approx. 20 µW; Figure 5). Moreover, the energy produced daily was always lower for the intermittent loading, and this was independent of applied duty cycle (Figure 3a). Therefore, the results suggest that short duty cycles were not appropriate for cat-MFCs and that long duty cycles allowed better stability. Compared to cer-MFCs, they reached steady state immediately (Figure 4b).

These results confirm that intermittent loading does not increase the power produced by cat-MFCs, since the levels of voltage and power bursts were similar to continuous loading. Thus, even with an adapted PWM system, the generated total energy would bear no improvement over continuous loading.

3.3 Synergy of electroactive organic degradation and capacitance.

The efficiency of the experimental approach was confirmed by recording a 10-fold increase of power output (Figure 1a). Moreover, the cer-MFCs were more powerful than
the cat-MFCs only when the pre-digester was present (Figure 1b). These two facts need to be considered in relation to the stability of power output in cer-MFCs, when $T_{OC} > 180$s, to understand the observed capacitance-like behaviour.

The stability of the cer-MFCs power output, when $T_{OC}$ was longer than 180s and $T_{CC} > T_{OC}$ (Figure 2), was not observed with the cat-MFCs, since regardless of the duty cycle applied, the power output was stable over time and either lower or equal to when it was under continuous load (Figure 5). If a capacitance-like behaviour was occurring in cer-MFCs, it should have also been observed in the cat-MFCs, when placed under duty cycles with $T_{OC} \geq 180$s. Such behaviour was not observed with cat-MFCs.

The difference between the two tested MFC setups was that the ceramic membranes were far more permeable than the cation exchange membranes. Because cation exchange membranes were less porous than ceramic membranes, it may be assumed that the diffusion between the anolyte and catholyte was also much lower. This interpretation is supported by the response of cat-MFCs to short duty cycles ($T_{OC} < 90$ s; Figure 5): the voltage only reaches 85% of the open circuit value with $T_{OC} = 60$s; 75% with $T_{OC} = 30$s; 60% with $T_{OC} = 15$s. This limitation was also clear for the power to reach steady-state
when $T_{CC} < 90s$ (Figure 5). Therefore, the porosity of the cation exchange membranes can be considered as the limiting factor for the slow electro-active response of cat-MFCs, due to slow ion diffusion.

When the MFCs are running under longer duty cycles (Figure 4), power output levels of both MFC types follow the same behaviour as those for short duty cycles, with $T_{CC} > T_{OC}$ power output levels being stable for cat-MFCs and deceasing for cer-MFCs. After the power decrease of cer-MFCs in the early stages, it reached a steady state that was approximately equivalent to the power produced under continuous load (Figure 4). If the porosity of CEM was considered to be limiting the exchange between anodic and cathodic compartments, this was not the case for ceramic membranes. Thus, the synergy between fermenting and electro-active microorganisms could explain both the instability of the power output when $T_{CC} > T_{OC}$, and stability when $T_{CC} \leq T_{OC}$.

Since porosity allows faster exchange in cer-MFCs, it can be postulated that the equilibrium between production of organic acids and their electro-active consumption is reflected by the observed behaviour of power outputs (Figure 2). When ceramic membranes are employed the electro-active consumption rate of organic acids appeared
higher than their production rate. The increase of power observed when the pre-digester was introduced in the system tends to confirm such hypothesis (Figure 1a), where power output levels increased for both types of MFC, but were more marked for the cer-MFCs.

To confirm this hypothesis, it should be shown that if more organic acids were present, more power would be produced. In the present study, the organic acid content was not analysed. However, an indirect way of doing so was to increase $T_{OC}$ whilst keeping an equal ratio of loading time, i.e. $T_{CC} = T_{OC}$, since increasing $T_{OC}$ allows more time for organic acids to be produced due to non electro-active respiration occurring. The results of such a duty cycle (2 hours under load and 2 hours in open circuit) support the hypothesis that no power decrease over time was observed for cer-MFCs and the steady state reached was higher than under continuous loading (Figure 6a). Moreover, the shape of the curves indicated that a capacitance-like effect was occurring when the MFCs were operated under such a duty-cycle. However, cer-MFCs reached steady state slower and kept higher power output. Thus, the results confirm that the capacitance-like effect observed was due to the accumulation of organic acids that would be produced by fermenting organisms at a slower rate than they were consumed by electro-active microorganisms in cer-MFCs at a higher rate. Regarding cat-MFCs, even if a similar behaviour to cer-MFCs was observed, power output remained stable at an equivalent level.
to continuous loading (Figure 6b). It has recently been shown that higher magnitude bursts of power are possible, from intermittent loading, however the overall energy output is lower than under continuous loading (Fradler et al., 2014). The present study has demonstrated that both bursts of power and overall energy (area under curve) are possible with ceramic membranes under intermittent loading, and in fact better than continuous loading.

4. Conclusions

Results have shown that separating the production of organic acids from the electro-active respiration increased the power outputs, mainly for ceramic membranes. The alternated load demonstrated that the capacitance-like behaviour of cer-MFCs was probably due to a lower rate of organic acid production and accumulation than its utilisation by electro-active respiration.

The repetition of duty cycles has shown that when $T_{cc} \geq T_{oc}$, more power was produced than under continuous loading, independent of the time length of each duty cycle. This was only valid for ceramic membranes, thus indicating that they are more suitable for PWM harvesting electronics.
4. Acknowledgments

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References:


Figure caption:

**Figure 1**: Characterisation of the MFCs electrical output. **a)** Evolution of the voltage after the addition of the pre-digester. **b)** Polarisation curves of the two MFC setups. *

Disconnection and reconnection of the resistor. ** Campus power cut.

**Figure 2**: Voltage and power evolution of the MFCs assembled with ceramic membranes when intermittently placed under load (300Ω). The duty cycle in the numerator indicates the time (in seconds) under load (CC) and at the denominator, the time under open circuit (OC). The grey areas show the two duty cycles, of each time sweep, used for the calculation of the normalised daily energy. Red baselines are the average of the MFCs prior to starting intermittent loading. \( T_{CC} / T_{OC} \) are in seconds. Because all duty cycles could not fit on one single time axis, data were split in two independent graphs (a and b).

**Figure 3**: Diagram representing the energy produced depending on the time ratio of the loaded circuits (CC) over the open circuit (OC). **a)** Time ratio at the minute scale (n=2 for all except for 1/1 and 1/3 with n=6 and n=4, respectively). **b)** Time ratio at hour scale (3600 s CC – 900 s OC; 3600 s CC – 300 s OC). "Cont. CC" stands for continuously
loaded. “Cont. CC–10h” stands for the energy produced after 10h under continuous load.

Error bars indicate standard deviation (n=2).

**Figure 4:** Comparison between long intermittent sweep and continuously loaded MFCs. 

a) MFCs assembled with ceramic membranes. b) MFCs assembled with cation exchange membranes. Timescale for the intermittent sweeps are at the top of the graphics. Indicated time sweeps are in minutes. The grey areas show the two duty cycles used for the calculation of the normalised daily energy. The striped areas designate the duty cycles that serve for the energy calculation of both the intermittent load and continuous load. \( T_{CC} \) and \( T_{OC} \) are in minutes.

**Figure 5:** Voltage and power evolution of the MFCs assembled with cation exchange membranes when intermittently placed under load (1000 Ω). The duty cycle in the numerator indicates the time (in seconds) under load (CC) and at the denominator, the time under open circuit (OC). The grey areas show the two duty cycles, of each time sweep, used for the calculation of the normalised daily energy. Red baselines are the average of the MFCs prior starting intermittent loading. \( T_{CC} / T_{OC} \) are in seconds. Because
all duty cycles could not fit on one single time axis, data were split in two independent graphs (a and b).

**Figure 6:** Comparison between 2 hours intermittent sweep and continuously loaded MFCs. **a)** MFCs assembled with ceramic membranes. **b)** MFCs assembled with cation exchange membranes. The striped areas designate the duty cycles that serve for the energy calculation of both the intermittent loading and continuous loading. The projected red dotted line, was taken for energy calculations. $T_{CC}$ and $T_{OC}$ are in minutes.
**FIGURE 1**

(a) 

Voltage (mV) vs. Time (h)
- Ceramic membrane
- Cation exchange membrane

Key Events:
- New media + pre-digester
- Media finishing

Resistance Points:
- 65 h: 1500 Ω
- 130 h: 329 Ω

(b) 

Power (µW) vs. Current (µA)
- Ceramic membrane
- Cation exchange membrane
a) Continuously under load

b) Continuously under load
Figure 3: Normalised produced energy (J d$^{-1}$) for Ceramic membranes and Cation exchange membranes for different duty cycle ratios (CC/OC).

(a) Duty cycle Ratios (CC/OC): 1/3, 1/1.5, 1/1, 1/0.6, 1/0.33, 1/0.16, Cont. CC - 10 h.

(b) Duty cycle Ratios (CC/OC): 1/1, 1/0.25, 1/0.08, Cont. CC - 10 h.
Continuously under load

<table>
<thead>
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<th>Voltage (mV)</th>
<th>Power (µW)</th>
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<td>156</td>
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**Figure 5**
FIGURE 6

(a) 120cc / 120oc

(b) 120cc / 120oc