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## Publisher's version / Version de l'éditeur:

https://doi.org/10.1016/j.biortech.2013.08.005 Bioresource Technology, 147, pp. 65-70, 2015-08-09

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# Pulse-width modulated external resistance increases the microbial fuel cell power output

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нісніснтя

• MFC is operated with pulse-width modulated connection of the electrical load.

• At operating frequencies above 100 Hz power output increases by 22–43%.

• Process dynamics can be described by a simple equivalent circuit model.

#### ARTICLE INFO

 3 9

 21
 Article history:

 22
 Received 30 April 2013

 23
 Received in revised form 31 July 2013

 24
 Accepted 2 August 2013

 25
 Available online xxxx

26 Keywords:

27 MFC 28 Perio

31

28 Periodic operation29 Pulse-width modulation

29 Pulse-width modulation30 Power output maximization

#### 41 **1. Introduction**

43 Environmental and economic sustainability requires a number of changes in the existing energy production and consumption 44 practices. Not only would fossil fuels be replaced with renewable 45 sources of energy, but also our energy consumption should be re-46 47 duced by using energy-efficient technologies. With this regard, 48 electricity production from organic wastes in Microbial Fuel Cells 49 (MFCs) offers a new technological solution capable of converting 50 otherwise energy-consuming wastewater treatment into an energy-neutral, and potentially an energy-producing process. 51

Advances in MFC design and materials helped to improve volumetric power output by several orders of magnitude (Logan, 2010). Yet, to be competitive with the existing wastewater treatment technologies, power densities should be further improved. While researchers continue to make progress by improving the electrode materials and MFC design (Logan, 2010; Saito et al., 2011; Song et al., 2010), the need for an adequate electrical system for optimized

0960-8524/\$ - see front matter  $\odot$  2013 Published by Elsevier Ltd. http://dx.doi.org/10.1016/j.biortech.2013.08.005

ABSTRACT

This study describes MFC operation with a pulse-width modulated connection of the external resistor (R-PWM mode) at low and high frequencies. Analysis of the output voltage profiles acquired during R-PWM tests showed the presence of slow and fast dynamic components, which can be described by a simple equivalent circuit model suitable for process control applications. At operating frequencies above 100 Hz a noticeable improvement in MFC performance was observed with the power output increase of 22–43% as compared to MFC operation with a constant external resistance.

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energy collection also becomes more and more apparent (Premier et al., 2011; Woodward et al., 2010; Woodward et al., 2009).

In order to utilize MFCs for powering electrical devices, a relatively low output voltage, which typically ranges from 0.2 to 0.5 V, should be converted to a higher value using an electronic device (boost converter or up-converter). Recently, several power management systems for up-converting MFC output voltage have been suggested (Park and Ren, 2012a; Tender et al., 2008; Wu et al., 2012; Yang et al., 2012), including a synchronous boost converter (Park and Ren, 2012a), a transformer – based power management system (Yang et al., 2012), and a custom-made power conditioner, which transformed the voltage from 0.35 to 6 V (Tender et al., 2008).

In addition to voltage conversion, MFC power output might be maximized by matching the external impedance with MFC internal impedance. Based on the principle of power supply by means of commuting (switching) circuits, hysteresis controllers have been implemented to track the Maximum power point (MPP) of a MFC (Park and Ren, 2012b). Also, a perturbation-observation algorithm was used to optimize MFC electrical load in real time showing a considerably improved power output (Pinto et al., 2011b; Woodward et al., 2010). In addition, a simple heuristic approach was

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implemented to automatically control the electrical load attached
 to the MFC (Premier et al., 2011).

83 At least one recent study suggested that by operating an MFC 84 with intermittent connection/disconnection of the electrical load (external resistance), the MFC power output could be improved 85 86 (Grondin et al., 2012). The study presented below elaborates on 87 the approach of intermittent (periodic) connection of the electrical 88 load by analyzing the MFC frequency response in a range of 0.1-89 1000 Hz and operating the MFC at a sufficiently high switching frequency, equivalent to a pulse-width modulated connection of the 90 external resistance (R-PWM mode of operation). 91

#### 92 2. Methods

#### 93 2.1. MFC design, inoculation, and operation

Two membrane-less air-cathode MFCs were constructed using 94 95 nylon plates as described elsewhere (Grondin et al., 2012). The an-96 odes were 5 mm thick carbon felts measuring  $10 \text{ cm} \times 5 \text{ cm}$  (SGL 97 Canada, Kitchener, ON, Canada) and the cathodes were 98 10 cm × 5 cm manganese-based catalyzed carbon E4 air cathodes 99 (Electric Fuel Ltd, Bet Shemesh, Israel). The electrodes were sepa-100 rated by a nylon cloth. Two MFCs, MFC-1 and MFC-2, were built. Both MFCs had an anodic compartment volume of 50 mL. MFC-1 101 contained two 10 cm × 5 cm carbon felt anodes with a total thick-102 103 ness of 10 mm and two cathodes (one on each side connected by a 104 wire) with a total surface area of 100 cm<sup>2</sup>. MFC-2 had one 105  $10 \text{ cm} \times 5 \text{ cm}$  carbon felt anode with a thickness of 5 mm and one  $50^{\circ}$  cm<sup>2</sup> cathode. 106

107 Each MFC was inoculated with 5 mL of anaerobic sludge with 108 volatile suspended solids (VSS) content of approximately 40-50 g 109 L<sup>-1</sup> (Lassonde Inc., Rougemont, QC, Canada) and 20 mL of effluent from an operating MFC. The MFCs were maintained at 25 °C and 110 111 were continuously fed with sodium acetate and trace metal solu-112 tions using a syringe pump and a peristaltic pump, respectively. The acetate stock solution was composed of (in  $g L^{-1}$ ): sodium ace-113 114 tate (37.0), yeast extract (0.8), NH<sub>4</sub>Cl (18.7), KCl (148.1), K<sub>2</sub>HPO<sub>4</sub> (64.0), and KH<sub>2</sub>PO<sub>4</sub> (40.7). The infusion rate of the acetate stock 115 solution was varied in order to obtain the desired influent concen-116 tration. The trace metal solution was prepared by adding 1 mL of 117 118 the trace elements stock solution to 1 L of deionized water. A de-119 tailed composition of the stock solution of the trace elements is gi-120 ven elsewhere (Pinto et al., 2011a).

121 An influent acetate concentration of 900 mg  $L^{-1}$  and a hydraulic 122 retention time of 6–7 h were typically maintained, with an excep-123 tion of the high-load test, where the influent acetate concentration 124 was doubled to 1800 mg  $L^{-1}$ . Fig. 1A shows the schematic diagram 125 of the experimental setup, while a detailed description of MFC de-126 sign, stock solution composition, and operating conditions can be 127 found elsewhere (Grondin et al., 2012).

#### 128 2.2. External resistance connection

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Pulse-width modulated connection of the external resistor ( $R_{ext}$ ) to MFC terminals was achieved by adding an electronic switch (IRF540, International Rectifier, El Sequndo, CA, USA) to the external electrical circuit (denoted as SW in Fig. 1B, the corresponding resistance is shown as  $R_{SW}$ ). Duty cycle (D) was defined as:

$$D = \frac{t_{\rm on}}{t_{\rm off} + t_{\rm on}} 100\% \tag{1}$$

138Where  $t_{on}$  is the "on" time within each cycle during which  $R_{ext}$  is139connected and  $t_{off}$  is the disconnection ("off") time. The electronic140switch was computer-controlled using a Labjack U3-LV data

Technol. (2013), http://dx.doi.org/10.1016/j.biortech.2013.08.005





Fig. 1. Schematic diagrams of the experimental setup (A) and electrical circuit (B).

acquisition board (LabJack Corp., Lakewood, CO, USA). The data acquisition board was also used to record MFC voltage at a maximum rate of 22,500 scans/s.

As shown in Fig. 1B, the data acquisition board measured MFC output voltage ( $U_{MFC}$ ) and voltage after the switch ( $U_{sw}$ ). Electrical connections corresponding to these measurements are shown in Fig. 1B as  $V_{MFC}$  and  $V_{SW}$ , respectively. Voltage over the resistive load ( $U_{Load}$ ) was calculated as the difference between  $U_{MFC}$  and  $U_{sw}$  ( $U_{Load} = U_{MFC} - U_{sw}$ ). Electric current was calculated as  $I = U_{Load}/R_{Load}$  by applying Ohm's law over the external load resistance ( $R_{Load}$ ).

For calculation purposes, the switching device was considered as an ideal switch in series with a resistance  $R_{sw}$  to represent power losses in the switch.  $R_{sw}$  value was estimated by dividing the voltage over the switch by the current. In the following discussion,  $R_{ext}$  denotes the sum of the external load connected to the circuit and the switch resistance ( $R_{ext} = R_{Load} + R_{sw}$ ) with a corresponding external voltage  $U_{ext}$ , as follows from the diagram shown in Fig. 1B. The voltage measurements described above and the calculation method accounted for power losses due to the fast switching.

#### 2.3. Frequency and duty cycle tests

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Frequency and duty cycle tests were carried out with either16315 min or 1 h intervals between parameter changes. The tests were164performed in a broad range of frequencies from 0.1 to 1000 Hz.165Duty cycle was set to 50% when frequency tests were carried out.166For the duty cycle analysis, duty cycles were varied between 5%167and 100% at a constant frequency of 500 Hz. Between the R-PWM168

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tests, the MFCs were operated using the Perturbation/Observationalgorithm described below.

MFC performance was expressed in terms of average (per cycle)
 output voltage, current, and power output. Average values per cy cle were obtained as follows:

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$$M = \frac{1}{T} \int_0^T m(t) dt$$
 (2)

177 where  $\underline{m}(t)$  is either the voltage, current, or power measurements at 178 each moment of time t, *T* is the cycle duration ( $T = t_{on} + t_{off}$ ), and  $\overline{M}$ 179 is the corresponding average value. Integrals were numerically cal-180 culated. To reduce errors due to sampling noise at least 100 average 181 (per cycle) values were acquired and then the mean values were 182 calculated.

#### 183 2.4. Perturbation/observation algorithm

184 The perturbation observation (P/O) algorithm for maximum power point tracking (MPPT) was used to optimize MFC perfor-185 mance during the tests with a fixed external resistor (control tests) 186 and between frequency and duty cycle tests. At each iteration, the 187 188 P/O algorithm modified  $R_{\text{ext}}$  (digital potentiometer) with a prede-189 termined amplitude ( $\Delta R$ ) at each iteration. The direction of resis-190 tance change was selected by comparing the value of the power 191 output with that at the previous resistance. Once the algorithm 192 converges to a vicinity of the optimum resistance value, the  $R_{ext}$ 193 will oscillate around this optimum with a maximum distance of 194  $\Delta R$ . A computer-controlled digital potentiometer with a resistance 195 variation range from 4 to  $130 \Omega$  and a step of  $1.25 \Omega$  was used 196 (Innoray Inc, Montreal, QC, Canada). A detailed description of the 197 P/O algorithm can be found in Woodward et al. (2010).

#### 198 2.5. Numerical methods

199 Computer simulations were carried out using the equivalent 200 circuit model and model solutions described in the Appendix. 201 Parameter estimation was carried out using Fmincon function of 202 Matlab R2010a (Mathworks, Natick, MA, USA). In the parameter 203 estimation procedure the root mean square error (RMSE) between 204 the model outputs and measured values of  $U_{\rm MFC}$  was minimized 205 using data of five on/off cycles. At an R-PWM frequency of 0.1 Hz this corresponded to 637 data points. At a frequency of 100 Hz, 206 207 1000 data points were used to estimate model parameters.

#### 208 3. Results and discussion

In order to evaluate the effect of a pulse-width modulated con-209 nection of the external resistance (R-PWM mode of operation), 210 211 MFC-1 and MFC-2 were operated at several frequencies ranging 212 from 0.1 Hz to 1000 Hz. At each tested frequency,  $R_{\text{ext}}$  was connected to the MFC during the first half of the cycle and discon-213 nected for the rest of the cycle, thus corresponding to a duty 214 cycle of 50%. Fig. 2A shows the average voltage output  $(\overline{U}_{ext})$  calcu-215 216 lated over the external resistor ( $R_{ext}$ ) of MFC-1 during the R-PWM tests. The frequency tests were carried out with Rext values of 8 and 217 218 47  $\Omega$ . It can be seen that in all tests the average voltage increased 219 with the initial frequency increase, then a plateau was reached at 220 around 100-500 Hz.

Initially, frequency tests were carried out with 15 min intervals between each frequency change. The tests were also repeated with 1 h intervals between the changes. A comparison of  $\overline{U}_{ext}$  profiles obtained with 15 min and 1 h intervals shows a qualitatively similar dependence (Fig. 2A). However, the average voltage was always higher in the tests carried out with 1 h intervals, i.e., the average (per cycle) power output was improved. This suggests that



**Fig. 2.** Average external voltage  $\overline{U}_{ext}$  as a function of  $R_{ext}$  connection – disconnection frequency.

a 15 min interval was insufficient to establish steady-state conditions corresponding to a new operating frequency. Also, it appeared that the R-PWM mode of operation led to an overall performance improvement, as power outputs were consistently higher as compared to a fixed  $R_{\text{ext}}$ . To insure reproducibility, the frequency tests were repeated in MFC-2 with  $R_{\text{ext}}$  values of 7.5 and 12  $\Omega$ . Once again, a similar trend was observed with a near linear increase of  $\overline{U}_{\text{ext}}$  as the operating frequency increased from 0.1 Hz to 500 Hz (Fig. 2B). This increase in average voltage and, accordingly, in average power output was followed by  $\overline{U}_{\text{ext}}$  stabilization at around 100–500 Hz.

MFC response to periodic connection/disconnection of  $R_{\text{ext}}$  was also characterized by observing the dynamics of MFC output voltage ( $U_{\text{MFC}}$ ) during each cycle. Fig. 3 compares  $U_{\text{MFC}}$  values acquired during MFC-1 operation at a low frequency of 0.05 Hz (Fig. 3A, D = 75%) and at a high frequency of 100 Hz (Fig. 3B, D = 90%). It should be understood that when  $R_{\text{ext}}$  is connected, the output and external voltages are equal, i.e.  $U_{\text{MFC}} = U_{\text{ext}}$ . However, if  $R_{\text{ext}}$  is disconnected, then  $U_{\text{ext}} = 0$ , while  $U_{\text{MFC}} > 0$ . At both frequencies, MFC output voltage ( $U_{\text{MFC}}$ ) abruptly decreases when  $R_{\text{ext}}$  is connected (closed circuit with switch ON), while it increases when  $R_{\text{ext}}$ is disconnected (open circuit with switch OFF). Also, when  $R_{\text{ext}}$  is connected to the MFC, current demand increases and a voltage divider is created between the MFC's internal impedance and the external resistance, causing  $U_{\text{MFC}}$  to decrease.

At 0.05 Hz two different dynamics components are evidenced during each on-off or off-on transition (Fig. 3A). At first, there is an abrupt change of  $U_{MFC}^{-}$  until reaching some intermediate value. This fast transition is followed by an exponential curve, which approaches the steady-state value at a much slower rate. At a frequency of 100 Hz (Fig. 3B), only fast dynamics appear in the  $U_{MFC}$ curve, while the slow dynamics disappears and  $U_{MFC}$  essentially 247

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**Fig. 3.** Profiles of MFC voltage ( $U_{MFC}$ ) measured at  $R_{ext}$  connection/disconnection frequencies of (A) 0.05 Hz (D = 75%) and (B) 100 Hz (D = 90%).

switches between two levels, with higher voltage corresponding to 260 the open circuit state and lower voltage corresponding to the 261 closed circuit state. This dynamics is consistent with the results 262 263 of the frequency tests shown in Fig. 2 and can be described by a 264 simple equivalent circuit model (Randles model, (Randles, 1947)) previously used for modeling batteries (Durr et al., 2006). The same 265 266 equivalent circuit model was also recently used to simulate a MFC 267 power management system (Yang et al., 2012). The model includes 268 two resistors and a capacitor, which enables the description of the 269 slow and fast output voltage responses observed during the tests. 270 Fig. 4 shows the model diagram, where U<sub>oc</sub> corresponds to MFC's 271 open circuit voltage (ideal voltage), C represents the actual MFC 272 capacitance, R<sub>1</sub> accounts for the MFC's ohmic losses, and R<sub>2</sub> repre-273 sents the resistive component accounting for both the activation and concentration losses (Yang et al., 2012). 274

This equivalent circuit model might have a limited predictive capacity as it assumes that all the electrical elements are constant. Furthermore, this model does not consider any changes in biomass



concentration, microbial activity, and carbon source concentration, 278 i.e., constant values of these parameters are assumed. The MFC 279 internal resistance and open circuit voltage were already demon-280 strated to be strongly dependent on biofilm density, on carbon 281 source concentration in the anodic liquid, and on temperature 282 (Pinto et al., 2010; (Pinto et al., 2011b). Therefore, the equivalent 283 circuit model might be lacking the predictive capacity of bioelec-284 trochemical models such as recently developed two-population 285 bio-electrochemical MFC model (Pinto et al., 2010) and the con-286 duction-based MFC model (Marcus et al., 2007) and cannot be used 287 to predict the influence of various process inputs, such as the or-288 ganic loading rate and the operating temperature, on MFC perfor-289 mance. Nevertheless, it offers some insight on the fast process 290 dynamics linked to the electrical properties of a MFC. Indeed, when 291 the electrical circuit is operated in the continuous mode (i.e.,  $R_{\text{ext}}$  is 292 constant), the internal capacitor is fully charged and the total inter-293 nal resistance can be expressed as  $R_{int} = R_1 + R_2$ . The capacitor 294 dynamics may only be evidenced when the system is disturbed, 295 for example by means of a switch operated at a low frequency. 296 Fig. 3 compares the equivalent circuit model outputs with voltage 297 measurements at low (Fig. 3A) and high (Fig. 3B) frequencies of  $R_{ext}$ 298 connection/disconnection. For this simulation, model parameters 299 were estimated by minimizing RMSE between the measured volt-300 age values and corresponding model outputs, as described above. 301 The following parameters were estimated:  $U_{0c} = 0.33 \text{ V}$ , 302  $R_1 = 4.24 \Omega$ ,  $R_2 = 3.25 \Omega$ , C = 0.38 F. The comparison of simulated 303 and measured voltage values shows that that the model ade-304 quately describes process dynamics at both frequencies, although 305 at the high operating frequency the model appears to somewhat 306 underestimate the output voltage. As mentioned above, although 307 process dynamics is adequately described within each cycle, the 308 model is too simplified to predict the output voltage over extended 309 periods of time. 310

While the equivalent circuit model analysis might suggest that the power output is maximized at D equal to 100%, our previous study demonstrated improved MFC power output at D values below 100%, at least when the MFC was operated at very low frequencies below 0.1 Hz (Grondin et al., 2012). Consequently, the performance of MFC-1 and MFC-2 was evaluated in a series of tests (D tests) performed at a frequency of 500 Hz and various D values ranging from 5% to 100%, the latter corresponding to a fixed resistor. 311

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Notably, MFC power output might also be dependent on the selected value of  $R_{\text{ext}}$ . Indeed, power output is maximized if external and internal impedances are matched. Therefore, prior to *D* tests total internal resistances ( $R_{\text{int}}$ ) of MFC-1 and MFC-2 were estimated by conducting polarization tests and calculating  $R_{\text{int}}$  values using linear parts of each polarization curve. Based on this technique, both MFCs showed internal resistance values in a range of 12– 15  $\Omega$ .

Fig. 5A shows MFC-1 power output at different values of the 328 duty cycle and different external resistances. When D tests were 329 conducted with  $R_{\text{ext}} = 17 \Omega$ , which is slightly above the estimated 330 value of  $R_{int}$  based on the corresponding polarization test, power 331 output was maximized at D = 95%. A duplicate test performed 332 immediately after the first test demonstrated excellent reproduc-333 ibility. Following this test, to compare R-PWM and mode of opera-334 tion with the power output corresponding to a constant  $R_{ext}$ , MFC-335 1 was operated at D = 100% for three days. A slow decline in power 336 output over time was observed with the power output stabilizing 337 at 2.23 mW (Fig. 5A, D = 100%). Interestingly, a re-evaluation of  $R_{int}$ 338 suggested an increase to 20  $\Omega$ . A third *D* test conducted following 339 MFC-1 operation with a constant  $R_{\text{ext}}$  confirmed a power output 340 decrease (Fig. 5A). 341 342

*D*-tests were also performed in MFC-2 with  $R_{\text{ext}}$  = 13.5  $\Omega$ , which corresponded to an estimated value of  $R_{\text{int}}$ . In this test, MFC power

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Fig. 5. MFC Power outputs of MFC-1 (A) and MFC-2 (B) as a function of their duty cycles. Power output at D = 100% corresponds to MFC operation with fixed external resistance. All D-tests were carried out at a frequency of 500 Hz.

output at D = 100% was estimated using the same experimental 344 procedure previously performed for other *D* values, i.e., the voltage 345 346 was measured after 1 h of MFC-2 operation with a fixed resistor. 347 Consequently, the power output decrease at D = 100% was much 348 smaller as compared to D = 95% (Fig. 5B). When the test was re-349 peated at  $R_{\text{ext}}$  = 21  $\Omega$ , which was above the estimated value of  $R_{\text{int}}$ , 350 there was no difference between power outputs at D = 95% and 351 D = 100%. For the tests conducted at  $R_{\text{ext}} = 6 \Omega$  (well below  $R_{\text{int}}$  esti-352 mation), the power output was maximized at around D = 45%, as 353 can be seen from the data presented in Fig. 5B. Although this maximum was below the highest power output observed at  $R_{\text{ext}}$ - $R_{\text{int}}$ , 354 the R-PWM mode of operation prevented a sharp drop in power 355 356 output typically observed at  $R_{\text{ext}} \ll R_{\text{int}}$ . and improved MFC stability by limiting the current. This feature might be especially useful 357 to prevent voltage reversal in a stack of MFCs (Oh and Logan, 358 2007). 359

D-curves shown in Fig. 5 were in agreement with the results 360 361 presented by Grondin et al.(2012), where the external load connec-362 tion was governed by the upper and lower boundaries of the MFC 363 output voltage, thus resulting in a variable switching frequency, 364 which was below 0.1 Hz. Overall, *D*-tests suggested an increase in power output as a result of MFC operation in R-PWM mode. 365 To elaborate on this observation, MFC-1 and MFC-2 were operated 366 367 for 3-5 days in the R-PWM mode with 95% duty cycle and external resistance values chosen based on  $R_{int}$  estimations obtained in the 368 polarization tests. Then the operating mode was changed to 369 370 constant connection and the MFCs were operated for another 371 3–5 days. To ensure optimal performance during this period,  $R_{\text{ext}}$ 372 value was optimized in real time using the P/O algorithm described 373 in the Section 2. This sequence of testing was repeated several 374 times. Power outputs obtained during each MFC operation by the P/O algorithm, were used as a basis for comparison (control) with 375 the R-PWM mode of operation, i.e., the R-PWM mode was com-376 377 pared with the highest attainable MFC power output. The results 378 of this comparison are summarized in Table 1 (current and power

#### Table 1

A comparison of average currents, power outputs an Coulombic Efficiencies (CE) obtained during Rext-PWM and perturbation/observation tests carried out at two influent acetate concentrations.

Influent acetate(mg L <sup>-1</sup> )	Cell	R-PWM mode			Perturbation/observation		
		Current (mA)	Power (mW)	CE%	Current (mA)	Power (mW)	CE%
900	MFC- 1	16.4	3.63	91.5	14.4	2.83	80.3
900	MFC- 2	13.6	3.62	76.1	14.1	2.55	78.6
1800	MFC- 1	15.1	3.84	42.2	17.1	3.07	47.9
1800	MFC- 2	20.6	3.60	57.6	19.6	3.46	54.9

outputs were estimated based on the last 24 h of operation). Interestingly, similar currents (and therefore similar Coulombic efficiencies) were observed, while both in MFC-1 and MFC-2 voltages and power outputs were consistently higher during R-PWM tests. Since at an influent acetate concentration of 900 mg  $L^{-1}$  the anodic liquid measurements showed acetate-limiting conditions with acetate levels below 40 mg  $L^{-1}$ , the tests were repeated where the influent concentration of acetate was doubled  $(1800 \text{ mg L}^{-1})$ . The increased acetate load led to higher acetate concentrations in the anodic liquid  $(600-700 \text{ mg L}^{-1})$  and somewhat lower Coulombic efficiency. Nevertheless, the results given in Table 1 once again confirmed improved power output during **R-PWM** operation.

Overall, power outputs observed during R-PWM tests were in a range of 3.6–3.8 mW corresponding to a volumetric power density of  $72-76 \text{ mW L}^{-1}$ . This power density is not only higher than that observed during MFC operation using the P/O algorithm (2.6-4.5 mW or 51-70 mW L<sup>-1</sup>, Table 1), but also is higher in comparison to the recently reported performance of a continuously operated MFC with a power density of  $30-50 \text{ mW L}^{-1}$  (Ahn and Logan, 2012).

Interestingly, the periodic and pulse modes of operation of catalytic reactors were observed to lead to an increased catalyst activity and therefore an increased volumetric performance (Silveston et al., 1995). Several mechanisms were proposed to explain the increased catalyst activity, including a change in the catalyst state in response to reactant concentration, a higher catalyst activity due to a transient state, and non-linear reaction kinetics (Roopsingh and Chidambaram, 1999; Silveston et al., 1995). While a direct comparison between the periodic operation of chemical reactors and the R-PWM mode of MFC operation might not be always justified, both systems feature catalysts with non-linear reaction kinetics. It can 410 be suggested that at high-frequencies the R-PWM mode of MFC 411 operation leads to a reduced activation and/or concentration losses 412 due to changes in the biocatalytic activity. These losses are repre-413 sented as  $R_2$  in the equivalent circuit model (Fig. 4). Considering 414 poor mixing within the carbon felt anode, carbon source (acetate) 415 transport through the porous anode might be one of the important 416 limiting factors, *i.e.*, acetate concentration within the anode is ex-417 pected to be significantly lower than its concentration in the bulk 418 419 anodic liquid during MFC operation in the continuous mode ( $R_{ext}$  is constant). Importantly,  $R_{\text{ext}}$  disconnection during  $t_{\text{off}}$  part of each 420 duty cycle (Eq. (1)) in the R-PWM mode of operation might termi-421 nate acetate consumption by anodophilic bacteria. Consequently, 422 acetate concentration within the anode could be hypothesized to 423 be increasing during  $t_{off}$  part of each cycle. As the cycle continues 424 and  $R_{\text{ext}}$  is re-connected, the metabolism of anodophilic bacteria 425 resumes, presumably at a higher acetate concentration. Several

Please cite this article in press as: Coronado, J., et al. Pulse-width modulated external resistance increases the microbial fuel cell power output. Bioresour. Technol. (2013), http://dx.doi.org/10.1016/j.biortech.2013.08.005

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427 previous studies demonstrated a strong link between carbon 428 source availability and MFC performance, including the effect of 429 carbon source on R<sub>int</sub> values (Martin et al., 2010; Pinto et al., 430 2011a). As metabolic activity of the anodophilic microorganisms resumes upon R<sub>ext</sub> reconnection, the improved acetate availability 431 is hypothesized to positively affect MFC performance. Indeed, the 432 433 anodophilic microorganisms were shown to exhibit a non-linear (Monod or Haldane-like) kinetics of carbon source consumption 434 with lower internal resistances observed at carbon source-non-435 limiting conditions (Hamelers et al., 2011; Manohar and Mansfeld, 436 2009; Marcus et al., 2007; Pinto et al., 2010). These hypotheses 437 438 might require extensive validation using experimental methods such as electrode potential monitoring and EIS measurements 439 (Martin et al., 2013) followed by a thorough model-based analysis. 440

#### 441 4. Conclusion

442 R-PWM mode of MFC operation increased the average output 443 voltage and the power output at operating frequencies above 444 100 Hz. By comparing power outputs of MFCs operated in the R-445 PWM mode and with a constant resistance equal to the estimated total internal resistance value, the R-PWM mode operation was 446 demonstrated to improve MFC performance by up to 22-43%. 447 448 Analysis of the output voltage profiles acquired during R-PWM tests showed the presence of slow and fast dynamic components. 449 This process dynamics was successfully simulated by a simple 450 equivalent circuit model suitable for real-time MFC control and 451 performance optimization. 452

#### 453 Acknowledgement

This research was partially funded by the Natural Sciences andEngineering Research Council of Canada (NSERC).

#### 456 Appendix A. Equivalent circuit model

The equivalent circuit model consisted of two internal resistors  $(R_1 \text{ and } R_2)$  and one internal capacitor (C) as shown in Fig. 4. The following first order differential equation describes voltage dynamics at the capacitor:

$$\frac{\partial U_c(t)}{\partial t} = \frac{U_{\rm oc}}{C(R_1 + R_{\rm ext})} - \frac{R_1 + R_2 + R_{\rm ext}}{R_2 C(R_1 + R_{\rm ext})} U_c(t) \tag{A1}$$

where  $U_c(t)$  is the voltage at the internal capacitor,  $R_{ext}$  is the external resistance,  $U_{oc}$  is the apparent open circuit voltage.

466 By applying Kirchhoff's circuit law to the diagram in Fig. 4, the 467 following analytical solution can be used to obtain MFC output 468 voltage ( $U_{MFC}$ ) as a function of time at low operating frequencies:

471 
$$U_{\rm MFC}(t) = (U_{\rm oc} - U_{\rm c}(t)) \frac{R_{\rm ext}}{(R_1 + R_{\rm ext})}$$
 (A2)

472 where,

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$$U_c(t) = U_{\text{final}} + (U_c|t_0 - U_{\text{final}})e^{-\frac{t}{\tau}}$$
(A3)

476 Here, the capacitance final voltage  $U_{\text{final}}$  and the time constant  $\tau$  are 477 defined as:

480 
$$U_{\text{final}} = U_{\text{oc}} \frac{R_2}{R_1 + R_2 + R_{\text{ext}}}, \tau = \frac{R_2(R_1 + R_{\text{ext}})}{(R_1 + R_2 + R_{\text{ext}})}C$$
 (A4)

At high frequencies of  $R_{\text{ext}}$  connection/disconnection, the voltage over the capacitance is considered to be a constant equal to the value of  $U_{\text{final}}$ .

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