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Self-powered supercapacitive microbial fuel cell: The ultimate way of boosting and harvesting power

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Santoro, C., Soavi, F., Serov, A., Arbizzani, C., Atanassov, P. (2016). Self-powered supercapacitive microbial fuel cell: The ultimate way of boosting and harvesting power. BIOSENSORS & BIOELECTRONICS, 78, 229-235 [10.1016/j.bios.2015.11.026].

Availability: This version is available at: https://hdl.handle.net/11585/521559 since: 2017-11-20

Published:

DOI: http://doi.org/10.1016/j.bios.2015.11.026

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This is the final peer-reviewed accepted manuscript of:

C. Santoro, F. Soavi^{*}, A. Serov, C. Arbizzani, P. Atanassov^{*}, Self-Powered Supercapacitive Microbial Fuel Cell: The Ultimate Way of Boosting and Harvesting Power, Biosensors and Bioelectronics, 78 (2016) 229-235.

The final published version is available online at: <u>https://doi.org/10.1016/j.bios.2015.11.026</u>

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1	Self-Powered Supercapacitive Microbial Fuel Cell: The Ultimate Way of Boosting
2	and Harvesting Power
3	
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26 In this work, for the first time, we demonstrate a supercapacitive microbial fuel cell 27 which integrates the energy harvesting function of a microbial fuel cell (MFC) with the 28 high power operation of an internal supercapacitor. The pursued strategies are: i) the 29 increase of the cell voltage by the use of high potential cathodes like bilirubin oxidase 30 (BOx) or iron-aminoantipyrine (Fe-AAPyr); ii) the use of an additional capacitive electrode (additional cathode, AdC) which is short-circuited with the MFC cathode and 31 32 coupled with the MFC anode (MFC-AdC). The high working potential of BOx cathode 33 and the low impedances of the additional capacitive electrode and the MFC anode permitted to achieve up to 19 mW (84.4 Wm⁻², 152 Wm⁻³), the highest power value ever 34 35 reported for MFCs. Exploiting the supercapacitive properties of the MFC electrodes 36 allows the system to be simpler, cheaper and more efficient without additional electronics 37 management added with respect to an MFC/external supercapacitor coupling. The use of 38 the AdC makes it possible to decouple energy and power and to achieve recharge times in 39 the order of few seconds making the system appealing for practical applications.

40

41 Keywords: microbial fuel cell, supercapacitor, additional cathode, EDLC, high
42 current/power

Microbial fuel cell (MFC) is a promising biotechnology for multiple applications such as 45 46 wastewater treatment and energy production from organic compounds (Rinaldi et al., 47 2008). Enhancement of MFCs performance through anode and cathode electrodes 48 materials development has been the main focus of the past decade for the scientists all 49 over the world (Rinaldi et al., 2008). In general, MFCs can be based on anodes made of 50 carbonaceous (Wei et al., 2011) and not carbonaceous electro-conductive materials 51 (Pocaznoi et al., 2012; Guerrini et al., 2014). Anodes feature high surface area in order to 52 accommodate electroactive bacteria that degrade organics and transfer electrons through 53 an external load. On the other side, cathode catalysts can be from different families of: i) 54 carbonaceous high surface materials (Watson et al. 2013), ii) platinum-based materials 55 (Liu et al., 2015), iii) non-platinum based materials (Antolini, 2015), iv) enzymatic 56 (Schaetzle et al., 2009; Higgins et al. 2011), and v) microbial (Jang et al., 2013; Ishii et 57 al. 2014). Such organic/inorganic materials as well as biotic matter work as catalysts or 58 co-catalyst enhancing the oxygen reduction rate and complete the redox reaction of the 59 MFC. It has been previously shown that at neutral working pH, enzymes (bilirubin 60 oxidase and laccase) based catalysis posses the highest open circuit potentials (OCPs) 61 among the existing catalysts for oxygen reduction reaction (ORR) (Mano et al., 2003; 62 Soukharev et al., 2004).

63 Current/power generated from MFC systems is over 3 orders of magnitude lower
64 compared to traditional hydrogen- or methanol-fuelled FC (Logan and Rabaey, 2012) and
65 therefore a smart design is necessary in order to harvest the low energy produced and for

the subsequent delivering of the high power pulses which are required for powering
devices. Supercapacitors are electrochemical energy storage systems which deliver high
specific power (up to 10 kW kg⁻¹) at required energy levels (Conway, 1999).
Electrochemical double layer capacitors (EDLC) use high surface area carbon electrodes
that store/deliver charge by an intrinsically fast and highly reversible electrostatic process
(Béguin et al., 2014).

72 Supercapacitors have been externally combined to the MFCs in order to harvest 73 appropriately the energy of the system. The external supercapacitors are recharged by the 74 MFCs and provide high power output during the discharge. This combination has been 75 already investigated by several groups (Wang et al.; 2015). The smart design and 76 efficient series/parallel connection of MFCs with external supercapacitors allowed to 77 power small electronics devices (Papaharalabos et al., 2013, 2014), sensors (Donovan et al., 2011, 2013; Di Lorenzo et al., 2014; Ewing et al., 2014; Dewan et al., 2014; Park et 78 79 al. 2012), a mobile phone (Ieropoulos et al., 2013), robotics prototypes (Ieropoulos et al., 80 2005, 2010, 2012) and the pump required to manage the wastewater flow in MFCs 81 (Ledezma et al., 2013).

The size of the supercapacitor to be connected with the MFC is a crucial design point. Indeed, the commercially available EDLCs with capacitance on the order of Farads require a substantial recharging time (on the order of several min or even hours) at the low current regimes of MFCs (on the orders of μ A). Every generated high current/power pulse requires a long time before its repetition, and consequently the tool that is powered by the MFC/external EDLC is switched on periodically, with long standby steps. The capacitive behavior of the MFC anode has been recently investigated (Deeke et al., 2012; Feng et al., 2012). It has been also reported an MFC anode decoration with ruthenium oxide to improve the capacitive response of MFCs (Lv et al., 2012) but its high cost prevents the usage in large scale MFCs.

92 Designing and improving the capacitive response of the MFC electrodes is a challenging 93 task for creating an integrated MFC-internal supercapacitor system. The capacitive 94 electrodes are expected to accomplish high power discharges, being simultaneously 95 recharged by the MFC redox reactions taking place at the electrode/organics containing 96 solution and electrode/ O_2 interfaces.

97 This approach has been already exploited in the field of biofuel cells where the first use 98 of enzymatic biofuel cells (BFC) as internal supercapacitor was recently demonstrated by 99 Pankratov et al. (2014a; 2014b). In this case, the high surface area, carbonaceous anode 100 and cathode of the BFC operated as the electrodes of the supercapacitor. Higher 101 performances have been recently obtained by Agnès et al. (2014) using a glucose-oxygen 102 enzymatic biofuel cell with maximum open circuit voltage of ≈ 800 mV. The BFC-103 supercapacitor hybrid system had the highest power achieved of approximately 18 mW 104 (Agnès et al., 2014).

To our best knowledge, for the first time, in this study we report on supercapacitive MFCs where anode and cathode simultaneously harvest energy from wastewater and work as self-powered EDLC. The power delivered by supercapacitors increases with cell voltage and with the decrease of the equivalent series resistance (ESR). We demonstrate how the power output of the MFC can be dramatically improved by two strategies: i) the use of non-platinum group metal, like iron-aminoantipyrine (Fe-AAPyr) and of bilirubin oxidase (BOx) cathodes to increase cell voltage, and ii) the usage of a third, capacitive electrode based on high surface area carbon to decrease ESR. The latter is an "additional cathode" (AdC) which is short-circuited with the MFC cathode and is coupled with the MFC anode to give a self-powered supercapacitor (MFC-AdC). This is the first time that the concept of AdC electrode is used. The proof-of-concept is demonstrated using a commercial high surface area carbon brush as the additional cathode and by galvanostatic tests at different currents from 1mA up to 45 mA.

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119 2. Materials and Methods

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121 **2.1 MFC configuration and electrolyte composition**

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Single glass bottle MFC (Cataldo Arbore, Milan, Italy) with 125 mL volume was used. A
lateral hole of 2.25 cm² allowed the insertion of the cathode that was there screwed using
a metallic clamp. Membraneless configuration allowed the exposure of anode and
cathode to the same electrolyte. A reference electrode (Ag/AgCl 3M KCl) was included
for the basic electrochemical studies.

The electrolyte was composed of a mixture of 50% volume of activated sludge from Albuquerque Southeast Water Reclamation Facility (New Mexico, USA) and 50% volume of phosphate buffer saline solution (PBS) and KCl 0.1M. PBS was made using KH₂PO₄ (1.77 g) and K₂HPO₄ (15.16 g). The pH of the electrolyte was 7.5 ± 0.02 . An air breathing cathode configuration was used and the tests were run in ambient conditions. The experiments have been carried out in Albuquerque at a constant temperature that was 134 22±1 °C and at 1600 meters above sea level. At that altitude, oxygen concentration is
135 roughly 20% lower compared to sea level due to the lower air pressure. This parameter
136 has to be taken into account when comparing the performance of air-breathing MFCs.

137

138 **2.2 MFC electrode materials and additional cathode material**

139

Anode electrodes were based on a carbon brush (Millirose, USA) of diameter 3 cm, length of 3 cm and projected area of 9 cm². The anodes were pre-colonized by mixed cultures bacteria taken from previous experiments running for over 4 months (Santoro et al., 2015a). Three different cathodes based on activated carbon (AC), ironaminoantipyrine (Fe-AAPyr) and bilirubin oxidase (BOx) enzymes were used. All the cathodes tested had the same current collector that was metallic stainless steel mesh (McMaster, USA).

147 AC-based cathode was prepared by mixing 70% wt high surface area AC (Norit SX Ultra, 148 Sigma Aldrich), 10%wt carbon black (CB, Alfa Aesar) and 20%wt PTFE (60% solution, 149 Sigma Aldrich) for 5 min in a coffee grinder. The carbon black was added to enhance the 150 composite electrode conductivity. After mixing, the composite material was pressed at 2 151 mT into a pellet die for 5 min (Santoro et al., 2014). The composite loading was 35±5 mg cm⁻², the geometric area was 2.25 cm² and this value was used for the power 152 153 normalization. The cathode has not been heated as previously shown (Santoro et al., 154 2014). The volume used for power normalization refers to the chamber volume of 125 155 mL.

The same procedure was followed to prepare Fe-AAPyr based cathode except that Fe-AAPyr was added into the mixture and mixed vigorously, before pressing at 2 mT. The preparation of Fe-AAPyr has been previously described (Santoro et al., 2015b). The Fe-AAPyr loading was 1.5 ± 0.1 mg cm⁻². Synthetic approach for preparation of Fe-AAPyr was based on Sacrificial Support Method developed at University of New Mexico. (Serov et al., 2014a, 2014b)

162 The preparation of BOx cathode instead was based on AC (70%wt), 10%wt CB and 163 20% wt PTFE ground for 5 min and then pressed at 2 mT for 5 min. After that, isopropanol (40 µL cm⁻²) was added on the top to create a hydrophilic/hydrophobic 164 165 gradient. A multi-walled nanotube paper (MWNTP, Buckeye Composite) was then fused 166 together on the top using pressure 0.25 mT for 5 min). At last, 10 mg of BOx (Amano 167 Enzyme, USA) dissolved in 50 mM PBS solution was then drop-casted onto the MWNTP 168 surface. The cathodes were kept at 4°C over night for enzyme immobilization. Before the 169 utilization, the liquid was dried and then the cathode was screwed on the lateral hole of 170 the bottle (Santoro et al., 2013).

171 The additional cathode for the supercapacitor was carbon brush (Millirose, USA) of diameter 2 cm and projected area of 4 cm² that was coated with a 95%wt AC- 5%wt 172 173 Nafion layer (0.3 g total). The carbon brush was immersed into a solution based on 174 Nafion (0.5% alcoholic solution Dupont, 1.0 mL), AC (100 mg) and water-isopropanol 175 solution (1 mL) and then was dried in ambient atmosphere over night. The addition of 176 AC allowed the increase in surface area of the carbon brush and consequently in the 177 capacitance of the overall additional cathode brush. The additional cathode was 178 completely immersed into the electrolyte and short-circuited with the MFC cathode.

180 **2.3 Electrochemical measurements**

181

182 Electrochemical measurements have been done using a potentiostat (SP-50, Bio-Logic, 183 France). Electrochemical tests consisted in the repetition of a sequence of the following 184 steps: rest (OCV) – galvanostatic (GLV) discharge at different currents (i_{pulse}, A) from 1 185 mA up to 45 mA) over 10 ms, 2 s or complete discharge down to 0V cell voltage. The 186 use of the reference electrode permitted to simultaneously monitor the MFC anode and 187 cathode (eventually short circuited with the AdC cathode) potentials as well as the cell 188 voltage during the sequence repetition. The analysis of the GLV discharge data is detailed 189 in the ESI section 190 191 3. Results and discussion 192 193 **3.1 Supercapacitive Microbial Fuel Cell** 194 195 PLEASE INSERT HERE FIGURE 1 196 197 In rest conditions, the cell voltage (V_{max}, _{OC}) of an MFC is determined by the equilibrium 198 potentials of the half-reactions taking place at the electrodes. The anaerobic anode 199 equilibrium potential of acetate oxidation at pH=7 is equal to ~-500 mV vs Ag/AgCl. The

200 theoretical potential for the oxygen reduction reaction at pH=7 is ~620 mV vs Ag/AgCl

201 (Erable et al., 2012). The anaerobic (bio-anode) and aerobic (cathode) environments of

the MFC polarize the carbon electrodes towards values that are more negative and
positive than the typical equilibrium potential (near 0 mV vs Ag/AgCl (Béguin et al.,
204 2014)) exhibited by metal and catalyst-free carbons in the de-aerated electrolytes (e.g.
supercapacitors electrolytes). The electrode processes cause the formation of
electrochemical double layers at the MFC electrode/electrolyte interfaces (Conway,
1999).

208 The excess of negative and positive charges, at the polarized anode and cathode surfaces 209 respectively, is balanced by positive and negative counter ions coming from the ionic 210 species dissolved in the solution. Electrolyte ions migrate to oppositely charged 211 electrodes forming an electrochemical double layer at each high-surface area 212 carbonaceous electrode of the MFC. The MFC is electrostatically storing charge at 213 $V_{max,OC}$, hence it is storing energy like in the case of an EDLC. The MFC anode and 214 cathode can be then discharged by a rapid electrostatic process. Their surface charges are 215 neutralized and ions are released in the bulk wastewater solution. The energy that was 216 electrostatically stored can thus be delivered by high and short galvanostatic discharge 217 pulses (GLV) and high power output is achieved. Subsequent rest, i.e. setting the MFC in 218 OC without any external load applied, restores the electrode equilibrium potentials. The 219 carbon electrodes are polarized again, the double-layers at each electrode are re-220 established, and the internal EDLC is recharged. Under these conditions, the system 221 operates a self-powered supercapacitor (Fig. 1.a and Fig. 1.b).

Fig. 1.c reports the cell voltage trend of a MFC under a rest (OC) - galvanostatic discharge pulse (GLV) - OC sequence. Fig. 1.c also highlights the parameters that were used for the evaluation of the system performance (see Supplemental Information).

226 PLEASE INSERT HERE FIGURE 2

227

228 For the first time, this concept was proven by the data reported in Figure 2 that shows the 229 MFCs cell voltage and electrode potential profiles under the sequence test reported in 230 Fig. 1.c, by 2 s (t_{pulse}) discharge pulse at 3 mA (i_{pulse}). The MFCs investigated had 231 different cathodes described before as AC, Fe-AAPyr and BOx and the cells are labeled 232 with the cathode acronyms. The AC, Fe-AAPyr and BOx MFCs features V_{max}, OC of 590 233 mV, 650 mV and 790 mV, respectively. This trend follows the equilibrium cathode 234 potentials of 105, 175 and 315 mV vs Ag/AgCl for AC, Fe-AAPyr and BOx cathodes. 235 Higher cathode potentials of BOx compared to other catalysts have been previously 236 shown (Mano et al., 2003). In all the investigated MFCs the equilibrium anode potential was \approx -500 mV vs Ag/AgCl which is close to the theoretical value. 237

238 The pulse caused the decrease of V_{max} , OC by ohmic (ΔV_{ohmic}) and capacitive 239 $(\Delta V_{capacitive})$ contributions (Fig. 1.c). The ΔV_{ohmic} cell voltage losses were in the range of 240 311 mV to 383 mV (Fig. 2 a,c,e) which were due to ESRs of 105-130 Ω (Table S1, 241 calculation in SI). Monitoring the MFC electrode potentials during the pulse permitted to 242 identify the cathode as the main contributor of ΔV_{ohmic} and, hence, of ESR for all the 243 MFCs (Fig. 2.b,d,f). Cathode overpotentials at i_{pulse} equal to 3 mA were 299 mV for BOx, 244 followed by Fe-AAPyr with 339 mV and AC with 344 mV and accounted for over 90% 245 of the total MFC ΔV_{ohmic} and ESR. The high electrode thickness ($\approx 1 \text{ mm}$) that is required 246 to avoid wastewater leakage through the breathing cathode could be one of the 247 parameters that determine the high cathode impedances (in the order of 100 Ω , as evaluated by dividing the cathode overpotential by i_{pulse}). The lowest ohmic losses of BOx cathode can be related to the utilization of CNT in the electrode preparation. CNT enhanced electronic conductivity compared to AC-based electrodes. The anodes based on carbon brush colonized by electro-active bacteria featured very low overpotentials within few mV (accounted for less than 10% of the total MFC ΔV_{ohmic} and ESR). This suggests that using high surface area and high conductivity carbon brush contributed to very low anode impedance that varied in a small range of 4-13 Ω.

For all the MFCs, the $\Delta V_{capacitive}$ cell voltage loss of the different MFCs was negligible and similar, indicating comparable cell capacitance (C) response. The values of C estimated by the cell voltage slope (s) (Conway, 1999) were between 80 and 100 mF (Table S1, calculation in SI). The electrode profile analyses indicated that anode and cathode almost equally contribute to C with electrode capacitances of ca. 200 mF.

Capacitance (C), equivalent series resistance (ESR), and maximum cell voltage under operation (V_{max}), which in turn depends on ESR (see SI), determine the practical maximum energy (E_{max}) and power (P_{max}) and the charge/discharge time constant (τ) of the supercapacitor. Indeed, these parameters are related by the following equations:

264
$$E_{max} = \frac{1}{2} C \times V_{max}^2$$
 (1)

$$265 \qquad P_{max} = i_{pulse} \times V_{max} \tag{2}$$

$$266 \quad \tau = \text{ESR} \times \text{C}. \tag{3}$$

267 C and ESR were used to estimate τ (Table S1) which was in the order of 10 s, thus 268 demonstrating the fast rate capability of the supercapacitive system. Table S1 reports the 269 practical values of E_{max} and P_{max} , and of the useful energy delivered during the pulse 270 (E_{pulse}) and average pulse power (P_{pulse}) evaluated by the GLV curves at 3 mA reported on Fig. 2. These values were calculated by taking into account that the highest feasible cell voltage (V_{max}) is the voltage of the charged cell in open circuit conditions (V_{max} , $_{OC}$) decreased by ΔV_{ohmic} after the pulse (see Figure 1.c), which in turn depends on i_{pulse} (eqs. SI9 and SI10). The energy and power values increase in the order AC < Fe-AAPyr < BOx, thus following the MFC voltage trend.

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277 PLEASE INSERT HERE FIGURE 3

278

279 On the basis of ΔV_{ohmic} and ESR that were evaluated by the test reported in Fig. 2, we calculated the P_{max} that can be delivered by the three MFCs at different i_{pulse} as described 280 281 in the Data Analysis Section of the SI, and the data are reported in Fig. 3. The Figure 282 reports P_{max} values that are 3-5 times higher compared to the highest values obtained 283 during conventional MFC operations that with the same configuration were equal to 2 Wm⁻² (BOx) (Santoro et al., 2013), 1.67 Wm⁻² (Fe-AAPyr) (Santoro et al., 2015b) and 284 1.17 Wm⁻² (AC) (Santoro et al., 2015b) referred to the geometric area of the cathode, the 285 286 limiting electrode.

Fig. 3 even indicates that the MFCs can deliver pulse currents up to 4 mA (AC and Fe-

288 AAPyr) and 5 mA (BOx). We calculated that the highest P_{pulse} of 1.47 mW (6.53 Wm⁻²,

- 289 11.76 Wm⁻³) can be delivered by the BOx MFC at 3.7 mA, followed by Fe-AAPyr-MFC
- 290 (0.90 mW (4 Wm⁻², 7.2 Wm⁻³) at 2.7 mA) and AC (0.67 mW (2.98 Wm⁻², 5.36 Wm⁻³) at
- 291 2.2 mA).

Data in Table S1 and Fig. 3 demonstrate that the utilization of cathodes with high working potentials is a reasonable option to increase the electric work and the power output of the designated current pulse.

295

296 **3.2 MFC-AdC Response**

297 ESR, C, i_{pulse} and t_{pulse} are the key parameters to be optimized in order to achieve high 298 maximum energy (E_{max}) and power (P_{max}) and, more importantly, high practical values of 299 energy (E_{pulse}) and power (P_{pulse}) delivered during the pulses. The practical values of E_{max} 300 and P_{max} depend on the highest feasible cell voltage (V_{max}), namely the voltage of the 301 charged cell in open circuit conditions ($V_{max, OCV}$) decreased by ΔV_{ohmic} after the pulse, 302 which in turn depends on ESR and i_{pulse} (see SI). ESR has to be minimized in order to 303 increase power output. The performance of the MFCs reported above was mainly 304 affected by the cathode ohmic losses. In order to overcome cathode limitation, an 305 additional cathode (denoted as AdC) was short-circuited with the MFC cathode, 306 embedded into the same electrolyte, and used as the positive electrode of the internal 307 supercapacitor (Fig. 1.b). The AdC was a carbon brush coated with activated carbon (AC) 308 to increase its surface area and electrode capacitance. The brush was used for its low 309 electrode resistance demonstrated in the previous section 3.1.

The AdC was short-circuited with the MFC cathode and it was brought to the high potential value of the latter. This caused the formation of an electric double-layer at the short-circuited brush/wastewater interface and the internal, positive charge of the AdC (Fig. 1.b). Coupling the AdC with the MFC anode provides an internal, self-powered EDLC that can be rapidly discharged by an electrostatic process to give high power output. According to the Kirchhoff law, the highest current will flow through the lowest
resistance branches of the circuit that models our system, i.e. the MFC anode and AdC
electrode resistances and the electrolyte resistance. The MFC cathode is then excluded
with positive effect on ESR and power output.

- 319 The MFC-AdC cells with AC, Fe-AAPyr and BOx cathodes short-circuited with the AdC
- 320 are labeled with AC-AdC, Fe-AAPyr-AdC, and BOx-AdC. Fig. 3 shows the cell voltage
- and electrode potential profiles under 2 s discharge pulse at 3 mA. The MFC-AdCperformances are summarized in Table S1.
- 323 Fig. 2 a, c, e demonstrate that the use of the AdC with i_{pulse} equal to 3 mA dramatically
- 324 decreases ΔV_{ohmic} down to 66 mV, 50 mV and 56 mV with AC, Fe-AAPyr and BOx
- 325 cathodes, without modifying the corresponding V_{max} , $_{OC}$. The MFC-AdC ESRs evaluated
- 326 by ΔV_{ohmic} are 6-8 times lower than MFCs' and reduced to 16-22 Ω . Fig. 2b, d, f evinces
- 327 that this result is due to the very low potential losses of the AdC-short circuited cathodes,
- 328 in turn related to their low impedances of $\approx 13 \Omega$. Given that the cell capacitance did not
- 329 significantly change (except for the cell with Fe-AAPyr-AdC which exhibited 60 mF),
- 330 the time response τ was substantially lowered to 2 s.
- Table S1 demonstrates that the decreases of ΔV_{ohmic} had the main effect on V_{max} and on energy and power values which substantially increased. The highest performance was achieved with the BOx-AdC cell which at 3 mA featured a practical operation voltage of 734 mV and P_{pulse} of 2 mW (t_{pulse} = 2 s). These are extremely high values that have never been reported before for microbial fuel cells.
- 336

337 PLEASE INSERT HERE FIGURE 4

339 The MFC-AdC cells were also tested at different pulse currents and the voltage profiles 340 analyzed to extract the P_{max} vs I_{pulse} plots reported in Fig. 4 (see SI). The significant 341 decrease in ESR allow to achieve pulse current up to 45-50 mA that were roughly 10 342 times higher than the 4-5 mA possible with MFC. P_{max} was 19 mW (84.4 Wm⁻², 152 Wm⁻ ³) with BOx cathode, 14 mW (62.2 Wm⁻², 112 Wm⁻³) with Fe-AAPyr and 6 mW (26.7 343 344 Wm⁻², 49 Wm⁻³) with AC cathode. These values are roughly one order of magnitude 345 higher than those achieved without AdC (Fig. 3), thus indicating the successful utilization 346 of the AdC.

347

348 PLEASE INSERT HERE FIGURE 5

349

350 Fig. 5 shows the MFC-AdC average pulse power P_{pulse} delivered at different currents over 351 10 ms and 2s pulses. Even under such test, the BOx-AdC cell outperformed the other 352 MFC-AdCs having 10 ms power output of 12 mW, followed by 9.5 mW of Fe-AAPyr-353 AdC and 4 mW of AC-AdC (Fig. 5.a). As it expected, the power decreases at pulse 354 length of 2 s and the highest P_{pulse} was 5 mW for BOx-AdC, followed by 3 mW for Fe-355 AAPyr-AdC and 2 mW for AC-AdC (Fig. 5.b). 356 357 3.3 Supercapacitive recharging time and durability experiments 358

- 359 PLEASE INSERT HERE FIGURE 6
- 360

361 Despite the higher OCP of the BOx, it has been shown previously that enzymes are not 362 durable for long period of time mainly due to denaturation or deactivation (Santoro et al. 363 2013). Moreover, currently, the cost of BOx is very high limiting practical utilization for 364 wastewater treatment purposes. At the contrary, Fe-AAPyr is a reliable catalyst for 365 oxygen reduction reaction at neutral pH due to its stability and low cost aiming to be a 366 good candidate for large-scale application (Santoro et al. 2015a). Consequently, the 367 recharging time and durability tests have been carried out considering the MFC-AdC with 368 Fe-AAPyr cathode for possible real and long terms application.

Fig. 6.a shows the voltage and electrode potential profiles of the Fe-AAPyr-AdC cell under an OC-GLV-OC sequence with 2s-pulses at 6 mA and 20 s rest. The rest of 20 s was enough to restore the equilibrium electrode potentials and "recharge" the cell at the V_{max} , _{OC} voltage (Fig. 6.b). Each cycle overlapped indicating the reversibility of the process. This underlines that the self-recharge of the internal EDLC is reversible and fast and can take place in the order of seconds.

The cycling stability of the Fe-AAPyr-AdC was proved over 1000 OC-GLV-OC steps which were performed by 10 ms-pulses at 10 mA followed by 10s rest. The first four (Fig. S1c) and last four (Fig. S1d) cycles are also reported. The cell voltage as well as the anodic and cathodic potentials during the initial and final cycles had very similar trend thus indicating that high current regimes (10 mA) do not affect the performances of the cell. Equilibria anode and cathode potentials are recovered in few seconds and this permits a stable, long-time operation.

382

383 **3.4 Significance of the Supercapacitive Microbial Fuel Cell**

385 In this first proof of concept, we demonstrate that current/power output is comparable 386 with MFC/external supercapacitor systems' with the advantage of much shorter 387 recharging time: sec/min instead of hours. This permits to increase power output 388 frequency that is an appealing feature for real applications where devices need to be 389 frequently powered. Notably, the AdC size can be independently sized which makes it possible to de-couple energy and power and to address target application requirements, 390 391 from sensor to external pump powering for self-sustainable systems. At last, the proposed 392 concept is sustainable in terms of materials, processes and energy cost. Further works 393 will be addressed to cell design and materials optimization for system scaling up.

394

395 4. Conclusions

396

397 To the best of our knowledge, for the first time a supercapacitive system with MFC anode 398 and cathode used as negative and positive electrodes of a self-rechargeable, internal 399 supercapacitor is demonstrated. The use of high voltage operation cathodes and the 400 additional capacitive cathode electrode permitted to achieve the exceptionally high power 401 of 19 mW under pulse currents as high as 45 mA. The power normalized to the geometric cathode area results 84 W m⁻². This is the highest performance ever achieved by an MFC 402 403 system. With respect to MFC/external supercapacitor coupling, MFC-AdC is a more 404 efficient, simple and cheap way of harvesting energy from the MFC system and does not 405 require any additional electronics management.

406

409	This project was funded by the Electrochemical Society and Bill & Melinda Gates
410	Foundation under initiative: "Applying Electrochemistry to Complex Global
411	Challenges". FS and CA acknowledge financial support by Alma Mater Studiorum -
412	Università di Bologna (Researcher Mobility Program).
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Figures Content

Figure 1. Microbial Fuel Cell configuration with anode and cathode of the MFC used as EDLC electrodes. Red and blue circles indicate cations and anions, respectively (a). MFC-AdC configuration with short circuited AdC-cathode and anode of the MFC used as EDLC electrodes (b). Current/Cell Voltage trends during the OC – GLV- OC sequence used for the electrochemical test. The labels indicate the parameters used for the evaluations of the system performance (c).

Figure 2. Cell voltage (a,c,e) and electrode potential (b,d,f) profiles of MFC and MFC-AdC cells with AC (a,b), Fe-AAPyr (c,d) and BOx (e,f) cathodes under 5s rest and 2 s pulses at 3 mA.

Figure 3. Calculated P_{max} vs. i_{pulse} plots of the MFCs assembled with AC, BOx and Fe-AAPyr cathodes.

Figure 4. P_{max} vs. i_{pulse} plots of the three MFCs having the additional cathode calculated at different pulse currents.

Figure 5. P_{pulse} vs. i_{pulse} plots for MFC-AdC cells for pulse time of 10 ms (a) and 2 s (b).

Figure 6. Cell voltage (a) and anode and cathode potentials (b) profile of a Fe-AAPyr-AdC cell under an OC-GLV-OC sequence with 2s-pulses at 6 mA and 20 s rest.

Figure 1







Figure 4



Figure 5



Figure 6

