Methanol opportunities for electricity and hydrogen production in bioelectrochemical systems

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Highlights

- Syntrophic consortia development for methanol-driven bioelectrochemical systems
- Methanol is reported as a potential substrate for power generation
- Homoacetogenic bacteria avoid net H_2 production from methanol in single chamber MEC
- Hydrogen is produced from methanol fed in double-chamber MECs for the first time

ABSTRACT

An anodic syntrophic consortium (exoelectrogenic plus fermentative bacteria) able to use methanol as sole carbon source was developed for the first time in a bioelectrochemical system. In this frame, promising results were obtained in single chamber MFC, comparable to those obtained with readily biodegradable substrates. Regarding MEC operation, the presence of homoacetogenic bacteria led to electron recycling, avoiding net hydrogen production in single chamber MEC. In a double chamber MEC, satisfying results (in terms of coulombic efficiency and cathodic gas recovery) were obtained even though energy recovery still restrained the feasibility of the process. The approach used in this work with methanol opens a new range of possibilities for other complex substrates as electron donors for bioelectrosynthesis.

KEYWORDS

Hydrogen, methanol, microbial fuel cell (MFC), microbial electrolysis cell (MEC), syntrophic consortia

1. INTRODUCTION

The forecast of fossil fuels shortage and the negative impact of its usage on environment drive the need to search for alternate sustainable fuel sources [1]. In this frame, bioelectrochemical applications may facilitate wastewater treatment for reuse and valorization, for example for power or hydrogen generation. These are considered as promising systems and have the potential to occupy a prominent place in future renewable energy generation, bioremediation, and wastewater treatment [2]. The opportunities of bioelectrochemical systems (BES) would lay on their capability of converting chemical energy of non-fermentable and fermentable substrates into electricity or other high added-value products under relatively mild conditions and using a wide variety of substrates with inexpensive metals as catalysts. The most common BES nowadays are microbial fuel cells (MFC) aiming at electricity generation and microbial electrolysis cells (MEC) to form products such as hydrogen. The key of BES is the enrichment of the anode in exoelectrogenic bacteria (also known as anode respiring bacteria, ARB) which have the ability to transfer their electrons extracellularly to a solid anode [3]. The anodic oxidation reactions are equivalent in both MFC and MEC, while the reduction reaction occurring on the cathode varies depending on the system. In a MFC, electricity is generated as a result of an overall thermodynamically favorable reaction where oxygen is reduced to water, whereas in MEC, additional energy is required to drive the overall reduction reaction [4].

In determining the type of carbon source for BES, cost and availability impacts the total economy of the technology. Conversion of substrates other than volatile fatty acids (VFA) is essential in view of their practical implementation. ARB can use a limited range of substrates and fermentative bacteria do not have external electron transfer abilities. Nevertheless, the utilization of fermentable substrates (glucose, xylose, sucrose), non-fermentable substrates (acetate, propionate and butyrate) and wastewaters of domestic, swine, brewery, paper

92 recycling, starch and food processing wastewaters for the generation of power or hydrogen
93 through BES has been reported [5-10].
94 Among all the different carbon sources used, methanol has never been reported to be a
95 successful carbon source for BES. Understanding previous failures and achieving methanol-
96 driven BES is interesting not only for potential methanol utilization but also as a pathway to
97 follow for the utilization of other complex carbon sources. When compared to other alcohols
98 such as ethanol, methanol is a more economical approach due to its availability from different
99 sources. Biomethanol can currently be obtained from any organic waste source that can be
100 first converted to synthesis gas [11]. Also, unlike ethanol, it does not interfere with human
101 food chain and its purification process is simpler.
102 Methanol interaction in BES systems is also interesting in the frame of utilizing crude
103 glycerol as carbon source, a target waste product to valorize. Crude glycerol as a raw material
104 for processes such as BES for hydrogen production was reported to be an interesting carbon
105 source [12,13] but Chignell and Liu [14] observed a decrease in hydrogen production yield
106 when methanol was present in this waste stream. Direct utilization of methanol for operation
107 of BES was attempted by Kim et al. [15], studying the feasibility of alcohols (ethanol and
108 methanol) for power generation using double chamber MFC, succeeding with ethanol and
109 reporting non-appreciable electricity generation with methanol. Regarding MEC, direct
110 methanol utilization has never been reported and its effect on hydrogen production is rather
111 unknown. Finally, the utilization of methanol in BES is a challenging task due to its possible
112 inhibitory and toxic effect at high concentration.
113 Hence, in the present investigation, we have evaluated the performance of methanol in BES
114 for bioelectricity and biohydrogen production with syntrophic consortia developed using
115 ARB and anaerobic sludge. To the best of our knowledge, this is the first successful attempt
116 of methanol utilization as a sole carbon source in BES.

2. MATERIALS AND METHODS

2.1. Microbial Fuel and Electrolysis Cells

MFC were 28mL methacrylate vessels provided with a lateral aperture (3.8cm diameter), where a PTFE diffusion layer stuck to the cathode permitted oxygen diffusion into the cell while preventing water leakage [16,17]. The anode was a titanium wire connected to a graphite fiber brush (20mm diameter x 30mm length; 0.21m^2 specific surface area made with fibers of diameter 7.2 µm (type PANEX33 160K, ZOLTEK). It was thermally treated at 450ºC for 30 minutes to enhance biomass adhesion and inoculated from an already working MFC [18]. The cathode consisted of graphite fiber cloth (3.8cm diameter, 7cm^2 total exposed area) coated with platinum (5mg Pt/cm^2, ElectroChem Inc.). The two electrodes, spaced 2.5 cm apart, were connected through a 1000Ω external resistance.

MEC were homologous to MFC, but the cathode was not exposed to air and the cell had a glass cylinder at the top, tightly sealed with a PTFE rubber cap that enabled gas collection. The gas produced was further collected in a gas-tight bag (Ritter, Cali-5-bond) connected to the glass cylinder. Both electrodes were connected to a power source (HQ Power, PS-23023) applying a potential of 0.8V. Current production was measured quantifying the voltage drop across a 12 ohms external resistance serially connected to the circuit. The cell was easily converted to a double chamber MEC by coupling an identical module and placing an anion exchange membrane in between (AMI-7001S, Membranes International INC). The membrane was soaked overnight in a 10% sodium chloride solution. Under this configuration the distance between electrodes increased to 7cm.

The cells operated with methanol as sole carbon source in fed-batch mode unless otherwise stated. The medium contained per liter: 1.6 g methanol, 172 mL PBS stock solution, 2.925 g $KHCO_3$ and 12.5 mL mineral media. The medium was completely replaced with fresh one

when voltage response decreased below 20 mV. MEC were sparged with nitrogen for 10 minutes after feeding to guarantee anaerobic conditions. The PBS stock solution contained per liter: 70g Na_2HPO_4 and 12g KH_2PO_4. Mineral media solution contained per liter: 1g EDTA, 0.164g $CoCl_2 \cdot 6H_2O$, 0.228g $CaCl_2 \cdot 2H_2O$, 0.02g H_3BO_3, 0.04g $Na_2MoO_4 \cdot 2H_2O$, 0.002g Na_2SeO_3, 0.02g $Na_2WO_4 \cdot 2H2O$, 0.04g $NiCl_2 \cdot 6H_2O$, 2.32g $MgCl_2$, 1.18g $MnCl_2 \cdot 4H_2O$, 0.1g $ZnCl_2$, 0.02g $CuSO_4 \cdot 5H_2O$ and 0.02g $AlK(SO_4)2$. Cobalt (II) chloride was added to the system to enhance the growth of acetogens versus methanogens [19]. A 50mM 2-bromoethanesulfonate concentration was used according to the work of Parameswaran et al. [20], where it was stated that such concentration would selectively inhibit methanogenic bacteria. 2-bromoethanesulfonate had been previously stated to inhibit methanogenic activity [21,22] and to be more effective than other chemical inhibitors or changes in system conditions such as pH and temperature [23]. In the double chamber MEC configuration the catholyte was a 100mM PBS solution. Cells were kept at room temperature during all the operational period.

Voltage evolution was monitored by means of a 16-bit data acquisition card (Advantech PCI-1716) connected to a personal computer with a software developed in LabWindows CVI 2013 for data acquisition.

2.2. MFC start-up

During the start-up of the MFC, the cell was inoculated with the media removed from a previously working MFC (originally inoculated with anaerobic digester sludge) that had been running in fed batch mode for over one year. The MFC was fed with acetate as carbon source to enhance the growth of ARB and their enrichment in the anode. Once a stationary response in terms of current intensity was achieved (in about two weeks time), the MFC was fed with methanol following three different strategies to obtain a methanol-driven MFC: i) direct replacement of acetate for methanol, ii) progressive replacement of acetate for methanol and

iii) two-step consortium development with methanol fermenting bacteria and ARB. The methanol fermenting population was grown anaerobically at 37ºC in Schott bottles using anaerobic digester sludge (Granollers urban WWTP, Barcelona) as inoculum and operated under fed batch mode (5 days cycles). Every time the system was fed, the mixed liquor was centrifuged (4 minutes at 5000rpm) to enhance high biomass retention, the medium was discarded, and the sludge was resuspended in fresh medium identical to the one used for MFC and MEC. Methanol was used as sole carbon source and also a concentration of 50mM 2-bromoethanesulfonate was used to limit the methanogenic activity. Methanol and acetate concentrations were measured to assess the development of the fermenting community and gas analyses from the headspace allowed to ensure that no methane was being produced.

2.3. Chemical and electrochemical analyses

Methanol and acetate concentration was analyzed with gas chromatography (Agilent Technologies, 7820-A) using a flame ionization detector and helium as carrier gas. Hydrogen and methane were also measured with gas chromatography using a thermal conductivity detector and argon as carrier gas. Gas production was evaluated as in Ambler and Logan [24]. pH and conductivity were measured offline.

MFC internal resistance was assessed from polarization curves [25]. The polarization curve was performed allowing the cell to reach the open circuit voltage for a period of one hour and then progressively changing the external resistance (from high to low resistance) and measuring the resulting cell voltage after 10 minutes. The set of external resistances used for the polarization curves were 470kΩ, 218kΩ, 44.2kΩ, 24.1kΩ, 12.1kΩ, 6.6kΩ, 3.3kΩ, 2.0kΩ, 1.65kΩ, 1.0kΩ, 825Ω, 470Ω, 250Ω, 218Ω, 100Ω, 50Ω and 25Ω.

2.4. Microbial analyses

High-throughput 16S rRNA gene pyrosequencing was performed in a 454 Titanium FLX system by the Research and Testing Laboratory (Lubbock, TX) based upon RTL protocols

192 from cathode and anode DNA samples (20 ng/ μL, quality ratio of 1.8). Sequence checking,
193 chimeras detection, sorting and trimming and quantitative assessment are detailed elsewhere
194 [26].

195 **2.5. Calculations**

196 Cell current intensity and power were calculated according to Ohm's law (Equations 1, 2):

197 $$I = V/R_{ext} \quad (1)$$

198 $$P = V \cdot I \quad (2)$$

199 where V is the voltage drop in the resistance (V), R_{ext} is the external resistance (Ω), I is the
200 current intensity (A) and P is the power output (W). Maximum power output (Pmax) was
201 calculated with Equation 2 considering the maximum voltage reached during a batch cycle.
202 Coulombic efficiency (CE) was calculated as stated in Equation 3:

203 $$CE = \frac{\int_{t0}^{t} I(t)dt}{F \cdot b \cdot \Delta S \cdot V_R} \quad (3)$$

204 where t is time (s), F is Faraday's constant (96485 C/mol-e^-), b is the stoichiometric number
205 of electrons produced per mol of substrate (6 mol-e^-/mol methanol), ΔS is the substrate
206 consumption (mol/L) and V_R the liquid volume (L).

207 Cathodic gas recovery (r_{CAT}) was calculated as the ratio of moles of hydrogen measured and
208 moles of hydrogen produced based on current intensity measured, as presented in Equation 4:

209 $$r_{CAT} = \frac{n_{H2}}{\frac{\int_{t0}^{t} I(t)dt}{2F}} \quad (4)$$

210 where n_{H2} is the number of moles of hydrogen measured, calculated according to the ideal
211 gases law knowing the hydrogen volume measured. 2 is the number of moles of electrons per
212 mole of hydrogen.

213 The overall efficiency (r_{H2}) was calculated as stated in Equation 5:

214 $$r_{H_2} = r_{CAT} \cdot CE \quad (5)$$

Energy recovery, i.e. the amount of energy produced as hydrogen with respect to the energy input, was calculated based on electricity input (η_w) and based on both electricity and substrate inputs (η_{ws}) according to Equations 6 and 8 respectively.

$$\eta_W = \frac{n_{H2}}{n_{in}} \quad (6)$$

where n_{in} is the number of moles based on electricity input, calculated as:

$$n_{in} = \frac{\int_{to}^{t}(I \cdot E_{ps} - I^2 R_{ext})dt}{\Delta H_{H2}} \quad (7)$$

where E_{ps} is the voltage applied (V), R_{ext} is the external resistance (ohm) and ΔH_{H2} is the heat of combustion for hydrogen (286 kJ/mol).

$$\eta_{WS} = \frac{\Delta H_{H2} \cdot n_{H2}}{\int_{to}^{t}(I \cdot E_{ps} - I^2 R_{ext})dt + \Delta H_S \cdot n_S} \quad (8)$$

where ΔH_S (638.2 kJ/mol) is the heat of combustion of methanol and n_S is the number of moles of methanol consumed during the period of time considered.

3. RESULTS AND DISCUSSION

3.1. Development of syntrophic consortium for methanol utilization in BES

The development of a syntrophic consortium able to degrade methanol and generate current intensity in MFC was tested for three different strategies: the direct replacement of acetate for methanol (ST1), a progressive replacement of acetate for methanol (ST2) and a two-step consortium development bioaugmenting ARB with methanol fermenting bacteria (ST3). The idea beneath the syntrophic consortium of anaerobic methanol-degraders and ARB is that the anaerobic fraction (essentially, acetogens) would degrade methanol, while ARB would live off the degradation byproducts (e.g. acetate) enabling exoelectrogenesis. For this aim, a first step, where methanol-degrading acetogens were selected against other methanol degraders (essentially methanogens) from an anaerobic sludge, was necessary. Methanogens were

absolutely undesired in this consortium since they could use both methanol and acetate for methanogenesis becoming, then, competitors to both ARB and acetogens. Once the anaerobic sludge was enriched in methanol-degrading acetogens, it was used as bioaugmentation agent in a MFC where an acetate-degrading population had been previously developed, i.e. a MFC already enriched in ARB.

Figure 1 presents the performance of three different MFC during the inoculation period using the three different strategies tested. It can be observed that for strategies ST1 (direct replacement) and ST3 (syntrophic consortium) an acclimation time was required before current intensity generation was boosted, which was shorter for ST3 (Figure 1A). On the other hand ST2 (progressive replacement) kept generating a much higher current intensity as a result of being fed also with acetate. After 80 days of operation under inoculation conditions, the cells were changed to the operational mode with methanol as sole carbon source (Figure 1B, change of axis scale to ease reading). The cell inoculated with ST2 (progressive replacement of acetate for methanol) suffered an abrupt decrease in cell performance. The current intensity with ST3 kept rising after the switch to methanol. The results indicated that the two-step consortium development was the most efficient in terms of higher CE, higher power density and lower internal resistance (Table 1).

The cell inoculated with ST3 was maintained for a longer term (Figure 2). Its performance was enhanced and reached an increase up to ten fold on power output (220μW). These results are comparable to previous values (250-300μW) obtained using acetate as sole carbon source in other studies with the same cells. In addition, these values are also comparable to those reported with conventional carbon sources. In analogous configurations, Logan et al. [5] obtained a power output of 325μW feeding acetate as carbon source and Liu and Logan [27] obtained 270.4μW feeding glucose. The highly comparable values obtained here represent a

high spot of this work since this is, to best of our knowledge, the first report of a methanol-driven MFC in the literature.

3.2. Methanol-driven bioelectrochemical hydrogen production

The methanol-driven single chamber MEC was started up with the anode of a methanol-driven MFC inoculated following the syntrophic consortium strategy. Figure 3 presents the voltage profile of the last batch cycle performed in that MFC. As can be observed, methanol degradation was fast whereas acetate concentration was low indicating that the process was not limited by ARB, i.e. the fermentation products were fast consumed by ARB. However, the presence of other acetate sinks different from ARB could not be ruled out. The low acetate presence in the bulk was consistent with the fact that the growth of the consortium as biofilm was enhanced throughout the cell operation, since after every batch cycle the media was completely replaced by fresh one. Thus, only the acetate that had not been consumed by ARB in the biofilm could diffuse into the bulk.

The results when operating as MEC for hydrogen production (Figure 4A) were not as satisfactory as expected; the classical performance evaluation indexes were unrealistic (CE = 296%), the cycle was remarkably long (about 28 days) and, despite the significant current density obtained (5.7mA/m^2), no hydrogen was detected during all the batch cycle. These observations evidenced the occurrence of electron recycling from the cathode to the anode, together with the presence of hydrogen scavengers, i.e. H_2 oxidizing ARB and/or homoacetogenic bacteria.

Equations 9 to 12 present the most probable chemical reaction scheme occurring in the MEC. Equation 9 describes the methanol conversion to acetate, which is further oxidized by ARB to bicarbonate (Equation 10). Equation 11 describes the hydrogen consumption by

285 homoacetogenic bacteria and finally Equation 12 shows the possible hydrogen utilization by
286 ARB. The last two reactions are responsible for the electron recycling scenario.

287 $4CH_3OH + 2\ HCO_3^- \rightarrow 3CH_3COO^- + H^+ + 4H_2O$ (9)

288 $CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$ (10)

289 $2HCO_3^- + 4H_2 + H^+ \rightarrow CH_3COO^- + 4H_2O$ (11)

290 $H_2 \rightarrow 2H^+ + 2e^-$ (12)

291

292 In this case, methanogenic bacteria, although being potential hydrogen consumers, could be
293 ruled out since i) a chemical methanogenic inhibitor, 2-bromoethanesulfonate, was used, ii)
294 methane was never detected and iii) their metabolic activity would not have caused such an
295 electron recycling effect. The role of hydrogen scavengers in similar systems has already
296 been discussed [20]. Ruiz et al. [28] demonstrated that the utilization of CE and r_{CAT} to
297 evaluate the MEC performance would only be valid when neither methanogenesis nor H_2-
298 recycling is occurring and hence different performance indexes should be used.
299 The presence of homoacetogenic bacteria in these methanol-fed systems was assessed and
300 confirmed with microbiological techniques. A sample from this anodic biofilm was analyzed
301 with high-throughput 16S rRNA gene pyrosequencing (Figure 5), detecting a microbial
302 community with a high diversity. The main genus detected was *Geobacter* sp. (39%), which
303 is commonly found in high proportion (around 70 %) in similar acetate-fed BES [20]. Note
304 that acetate is not the external carbon source in this system, but only a potential intermediary
305 of methanol degradation. Regarding homoacetogenic bacteria, *Acetobacterium* sp. are the
306 homoacetogens in higher proportion in our sludge. Indeed, their presence could be expected,
307 since it is known that acetogens metabolize C1-compounds, such as CO_2 and methanol, to
308 acetate [29], [30]. *Desulfovibrio* (standing for 6% of anode population) are also
309 homoacetogens and can excrete acetate into the medium from hydrogen [31].

Moreover, an extra test was performed in order to further study whether the so called electron recycling was consequence of the presence of H_2 oxidizing bacteria or it was only caused by homoacetogenic bacteria (Figure 4B). In Period I, during the first 20 hours, the circuit was opened, the cell was fed with fresh medium without methanol and sparged during 5 minutes with hydrogen. At the end of the period, acetate was detected in the medium but at a very low concentration (less than 5mg/L). In Period II fresh medium without methanol was fed and the circuit was closed in MFC configuration, giving an initial voltage of 25mV. Hydrogen was then sparged into the system as in Period I. A lag time of about ten hours was required for observing a voltage increase, in agreement with hydrogen not being directly used as electron donor. In the same way, when no more substrate was available (presumably acetate rather than hydrogen) the response of the cell decreased to 0mV. According to the experimental results, the existence of this lag-time indicates that H_2-oxidizing ARB activity was minimal. The cell voltage monitored at the very beginning of Period II could be a sign of homoacetogenic bacteria presence in the anodic biofilm, where the acetate produced in Period I could have remained and eventually be consumed by ARB. Again this would be consistent with the fact that biofilm growth was enhanced along all the cell operation.
Thus, hydrogen production from methanol in a single chamber MEC was not possible due to the presence of homoacetogenic bacteria, which could not be avoided since they were in charge of methanol conversion to acetate, a preferred substrate for ARB.
To avoid the problem of electron recycling, the system was changed to work as a MEC in double chamber configuration. Under this arrangement a clear current intensity profile was obtained for each batch cycle (Figure 6), i.e. the cell experienced a current intensity increase as methanol was being converted to acetate and it decreased when the substrate was being depleted. This evidenced that electron recycling was avoided. Also hydrogen was detected during this period and CE was assessed to be lower than 100% for each batch cycle.

Throughout the double chamber operational period, maximum current intensity achieved in every batch cycle increased, obtaining at the steady state a CE of 90%, r_{CAT} of 40% and r_{H2} of 28%, with a production of 0.1m^3 $H_2 \cdot m^{-3}$ reactor$\cdot d^{-1}$. Energy recovery based on electricity input stabilized around 60% and energy recovery based on both electricity and substrate input was only around 20%, still being far from considering the system energetically feasible. In any case, this is, to the best of our knowledge, the first time where methanol-driven hydrogen production using bioelectrochemical systems is reported.

When working in a double chamber configuration, current density doubled reaching a stable response of 10.7mA/m^2 despite the membrane inclusion, which should had increased the cell internal resistance. However, as a consequence of physically separating both anolyte and catholyte a pH change was observed. pH decreased in the anolyte (final pH about 6.5), where protons were produced, and increased in the catholyte (final pH about 11), where hydroxides were produced. Methanol was not detected when the cycle was over, i.e. when current density decreased. During the cycle, maximum current intensity remained rather constant, inferring from this that the decrease in current density was not a consequence of the change in pH but of the complete depletion of the substrate.

3.3. PRACTICAL IMPLICATIONS

The results presented are not only significant in terms of methanol utilization in BES systems but the approach used in this work could open a new range of possibilities and, similarly, other complex substrates can be used as electron donors for bioelectrosynthesis. The syntrophic consortium was developed in the biofilm (i.e. the biological activity in the suspended liquid was negligible). Growing the consortium as biofilm is interesting in view of practical implementation, because: (i) a pretreatment tank to carry out the fermentation could be omitted, (ii) slow growing biomass in the biofilm is protected against washout when

operating at low hydraulic retention times and (iii) operation at low hydraulic retention time would decrease the chances for other non-desired communities such as methanogenic bacteria to grow.

Methanol was not among the reported substrates in bioelectrochemical systems and therefore its potential for power generation and hydrogen production in BES was unknown. The work presented becomes relevant when the aim is using biodiesel waste water streams in BES, where methanol is commonly found. Glycerol from biodiesel, and methanol as impurity, could be effectively used a substrate for current production in single chamber MFC, but a more engineered system would be required if hydrogen production was the goal of the process, increasing the installation and operation costs of the system. For instance a physical separation of both electrolytes with an ionic membrane would enhance net hydrogen production but such configuration could lead to higher internal resistance of the system, and thus higher energy supply needs, as well as higher maintenance costs.

4. CONCLUSIONS

A syntrophic consortium of fermentative and exoelectrogenic bacteria was developed aiming at improving the starting-up step of a methanol-driven BES. The cell inoculated with this consortium, reached about twofold CE and power output as well as lower internal resistance than other inoculation strategies concerning direct replacement of acetate for methanol and a progressive replacement of acetate for methanol.

The development of such anodic consortium allowed current generation in MFC, where homoacetogenic bacteria metabolized methanol to acetate, playing a key role in this system. Power output reached 220μW, values comparable to those obtained with readily biodegradable carbon sources.

384 The presence of homoacetogenic bacteria in single chamber MEC prevented net hydrogen
385 production due to hydrogen being also consumed for homoacetogenic metabolism, clearly
386 leading to an electron recycling situation, what caused a CE of 296%. As a consequence, a
387 physical separation between both anolyte and catholyte was needed for hydrogen production,
388 reaching under this double chamber MEC configuration a CE of 90%, r_{CAT} of 40% and r_{H2} of
389 28%, with a production of 0.1m^3 $H_2 \cdot m^{-3}$ reactor$\cdot d^{-1}$. Although the hydrogen production from
390 methanol in BES is demonstrated in this work, further improvements in energy recovery
391 (60% based on electricity input and 20% based on both electricity and substrate input) are
392 still required to consider the system energetically feasible.
393
394

ACKNOWLEDGEMENTS

Discussions with S. Guri and L. Vega from Carburos Metálicos are gratefully acknowledged. Financial support was provided by Carburos Metálicos, Air Products Group and the Spanish Government, under the project BIOSOS (CDTI, program Ingenio 2010). The authors are members of the GENOCOV group (Grup de Recerca Consolidat de la Generalitat de Catalunya, 2009 SGR 815). Vijay Kumar Garlapati is thankful for the postdoctoral research fellowship at UAB inside the Alliance4universities program**.** Laura Rago is grateful for the grant received from the Spanish government (FPI).

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Methanol opportunities for electricity and hydrogen production in bioelectrochemical systems

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Tables

Table 1 MFC performance characterization for the three inoculation strategies presented.

	CE	P_{MAX} (mW)	R_{INT} (□)	Maximum power density (mW/m^2)
ST1 (Methanol)	13.4±3.1	0.008±0.003	3080	0.84
ST2 (Acetate+Methanol)	14.5±1.2	0.017±0.003	1575	1.19
ST3 (Syntrophic consortium)	26.7±1.0	0.021±0.002	966	1.87

LIST OF FIGURES

Figure 1. MFC performance with the three different inoculation strategies tested. Top: ST1, direct replacement of acetate for methanol. Middle: ST2, progressive replacement of acetate for methanol. Bottom: ST3, syntrophic consortium. (A) Inoculation period. (B) Operation with methanol as sole carbon source.

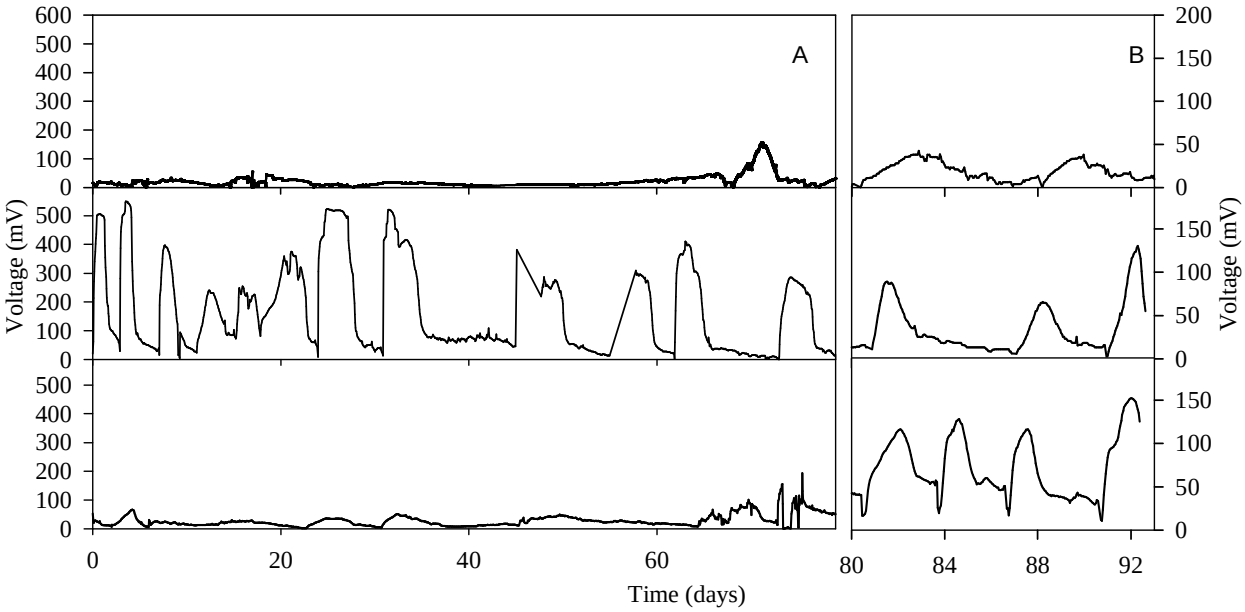
Figure 2. Performance evolution of the methanol-driven MFC with a syntrophic consortium (ST3).

Figure 3. Voltage and metabolites evolution in a methanol driven MFC. Solid line: Voltage, ●: acetate and □: methanol concentration.

Figure 4. A: Current intensity evolution in a single chamber methanol-driven MEC. **B:** Homoacetogenic detection in a MFC fed with hydrogen and carbonate. Period I open circuit. Period II closed circuit.

Figure 5. Anodic genus microbial distribution through high-throughput 16S rRNA gene pyrosequencing. Genera making less than 1 % of total sequences were classified as others.

Figure 6. Current intensity evolution in a double chamber methanol-driven MEC. Solid: current intensity; ●: CE.



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527

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530 for methanol. Bottom: ST3, syntrophic consortium. (A) Inoculation period. (B) Operation
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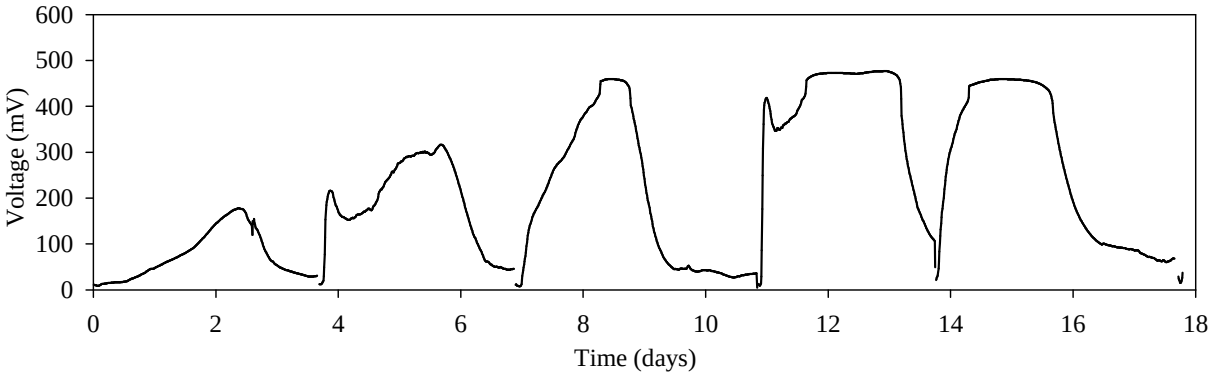

533

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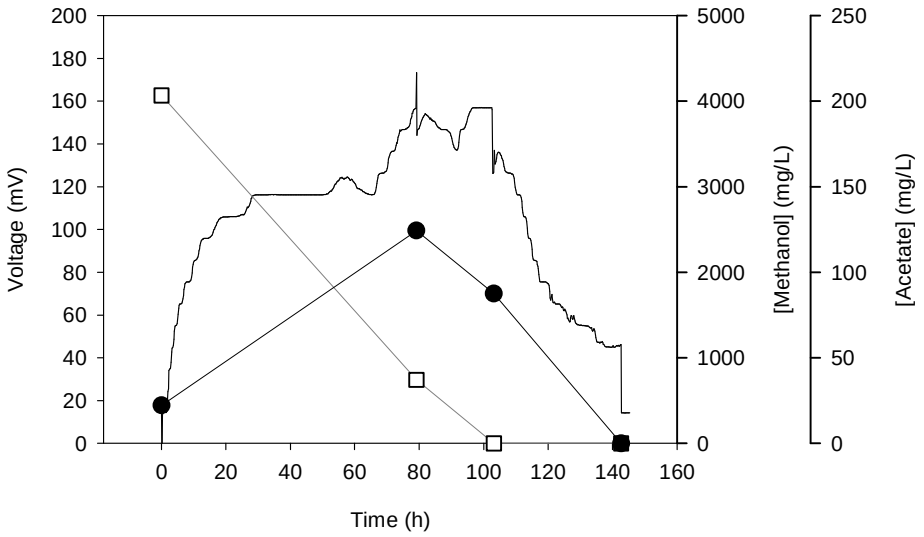

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539 ●: acetate and □: methanol concentration.

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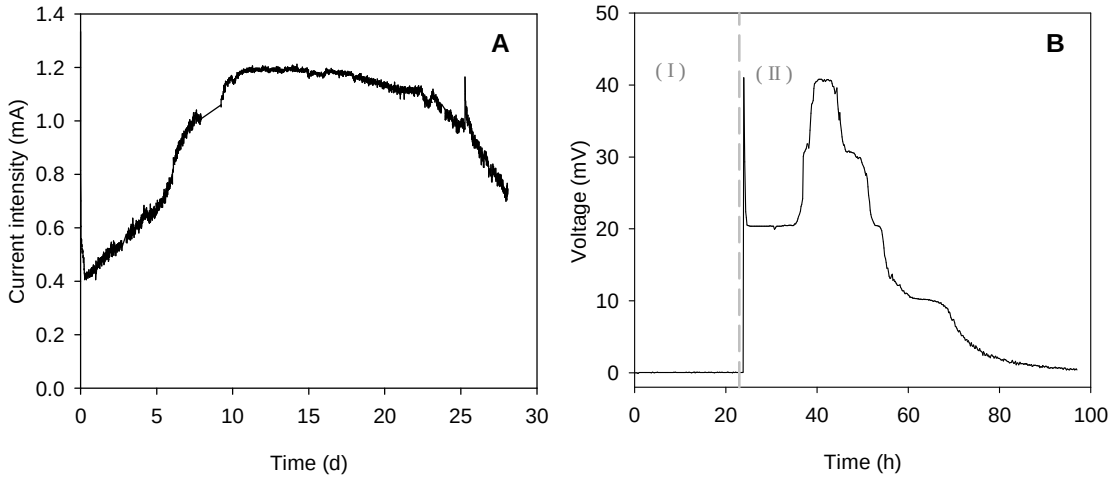

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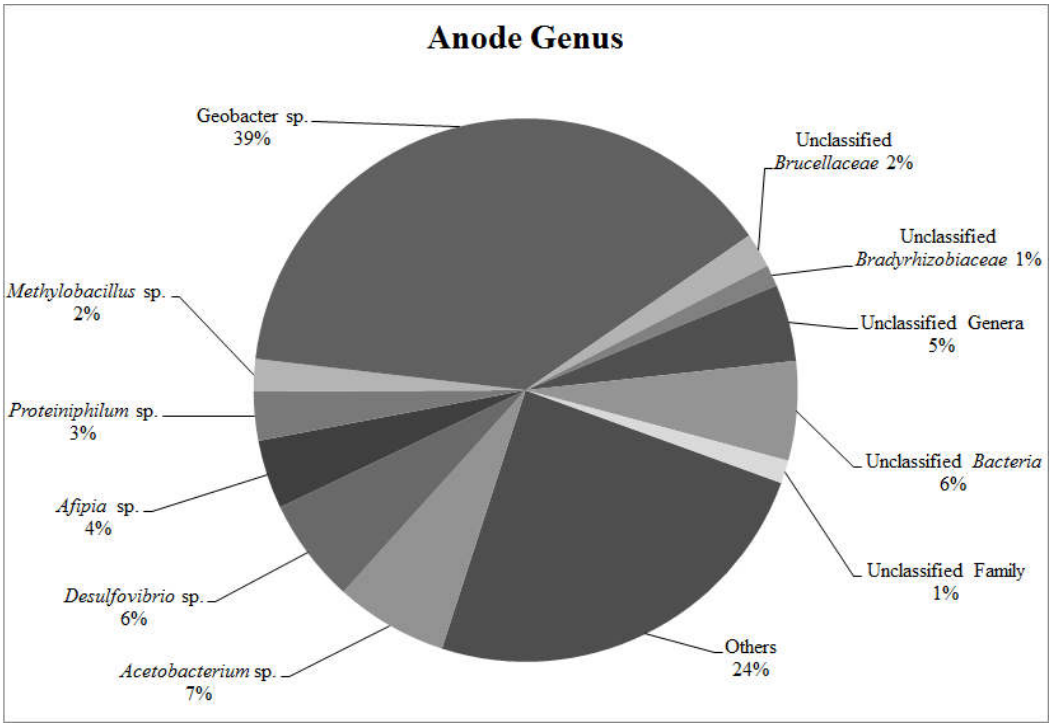
542 **Figure 4. A**: Current intensity evolution in a single chamber methanol-driven MEC. **B:**

543 Homoacetogenic detection in a MFC fed with hydrogen and carbonate. Period I open circuit,

544 unmonitored signal. Period II closed circuit.

545



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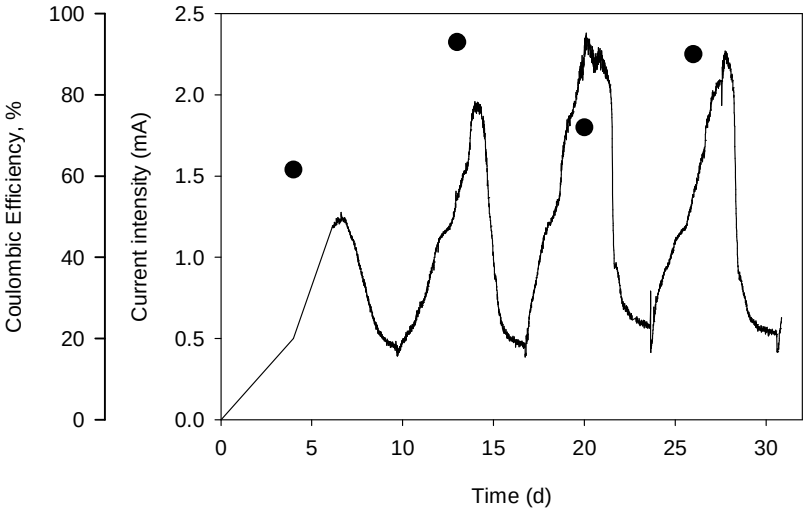

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