

Energy recovery from energy rich vegetable products with microbial fuel cells

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Abstract Two types of rapidly biodegradable vegetable products (the liquid fraction of clover and the glycerol-containing sidestream from biodiesel production) were selected for anodic oxidation in microbial fuel cells (MFC) equipped with a biocathode. As benchmark references, five abundant amino-acids in plant sap (L-glutamine, L-glutamic acid, L-asparagine, L-aspartic acid and L-alanine) were tested separately. Their performance was in the same order of magnitude of clover sap oxidation ($145\text{--}225\text{ A m}^{-3}\text{ MFC}$; $39\text{--}95\text{ W m}^{-3}\text{ MFC}$). Glycerol oxidation resulted in competitive current and power outputs ($111\text{ A m}^{-3}\text{ MFC}$; $23\text{ W m}^{-3}\text{ MFC}$).

Keywords Bio-electrochemical systems · Bioenergy · Biological cathode · Glycerol · Vegetable substrate

Introduction

All systems where micro-organisms catalyze at least one of the redox reactions in anode or cathode are defined as bio-electrochemical systems (BESs) (Rabaey et al. 2007). A microbial fuel cell (MFC) is an example of a BES as micro-organisms catalyze the oxidation of organic compounds in the anode.

Recently, also microbial catalysis in the cathode has been established in MFCs for O_2 or nitrate reduction (Clauwaert et al. 2007a, b).

Bio-electrochemical systems have been proposed as a novel technology for wastewater treatment with energy recovery, either as electrical power or as hydrogen gas. BES are typically operated at moderate temperatures and with a low sludge production rate (Logan and Regan 2006; Rabaey and Verstraete 2005; Rozendal et al. 2006). For laboratory scale tests, typically glucose or acetate have been used to demonstrate conversion rates up to $310\text{ A m}^{-3}\text{ MFC}$ ($2.2\text{ kg chemical O}_2\text{ demand (COD) m}^{-3}\text{ MFC d}^{-1}$) (Clauwaert et al. 2007b; Logan et al. 2007). Anodic oxidation of other sugars and volatile fatty acids (Catal et al. 2008; Cheng and Logan 2007; Du et al. 2007), ethanol (Kim et al. 2007) and wastewater (Aelterman et al. 2006, Rabaey et al. 2005a) has also been described.

The objective of this study was to test if some abundant aminoacids present in phloem sap can be used as a substrate in the anode of a MFC with a biological open air cathode. Also, clover sap and glycerol, a vegetable product from biodiesel production, were examined.

Methods and materials

Microbial fuel cells

Three microbial fuel cells (R1, R2 and R3) were constructed as previously described (0.143 l total

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anodic volume (TAC); 0.183 l MFC (complete electrode and liquid volume in the reactor); 127 cm² membrane) (Clauwaert et al. 2007b) (Fig. 1). The anodic liquid stream (modified M9 medium (Clauwaert et al. 2007b)) was recirculated in an upstream mode through the anodic compartment with a peristaltic pump (3 l h⁻¹) from a recirculation vessel (1 l in the case of R1, 80 ml in the case of R2 and R3).

After several months of operation with sodium acetate, the electron donor of R1 was subsequently switched to L-glutamine (18 mol electrons mol⁻¹ substrate for oxidation to CO₂), L-glutamic acid (18 mol e⁻ mol⁻¹ substrate), L-asparagine (12 mol e⁻ mol⁻¹ substrate), L-aspartic acid (12 mol e⁻ mol⁻¹ substrate), L-alanine (12 mol e⁻ mol⁻¹ substrate) and clover sap. For each amino-acid tested, the medium was renewed and 3 mmol was spiked per feeding cycle. Clover sap was obtained by mixing fresh clover (*Trifolium repens*) in a food processor. The anodic medium was spiked with clover sap (194 g COD l⁻¹) to obtain a concentration of 0.5 g COD l⁻¹.

After several months of operation with sodium acetate, the anodes of R2 and R3 were operated in a continuous mode by means of a peristaltic pump (0.333 l M9 medium d⁻¹) and a syringe pump with a concentrated analytical glycerol solution in order to obtain a volumetric COD loading rate of 1.28 kg COD m⁻³ MFC d⁻¹. After 453 h, industrial glycerol (min. 80% v/v glycerol, 6.5% w/v Na₂SO₄) originating from a biodiesel producing factory (Proviron, Belgium) was diluted to obtain the same volumetric COD loading rate with the help of the syringe pump for reactor R2 only.

The cathodes of R1 and R2 were operated as biocathodes as previously described (Clauwaert et al. 2007b). The cathodic medium, the same modified M9 medium as the anodic medium but without organic electron donor, was recirculated (3 l h⁻¹) from a recirculation vessel (2L). R3 was operated with a non-biologically catalyzed cathode, in which ferricyanide was used as the electron acceptor as previously described (Rabaey et al. 2005a). The pH of the electrolyte of the biological anodes and cathodes was adjusted when necessary as previously described (Clauwaert et al. 2007b).

Measurements

The graphite rod contacts of both the anodic and the cathodic electrode were connected to an external

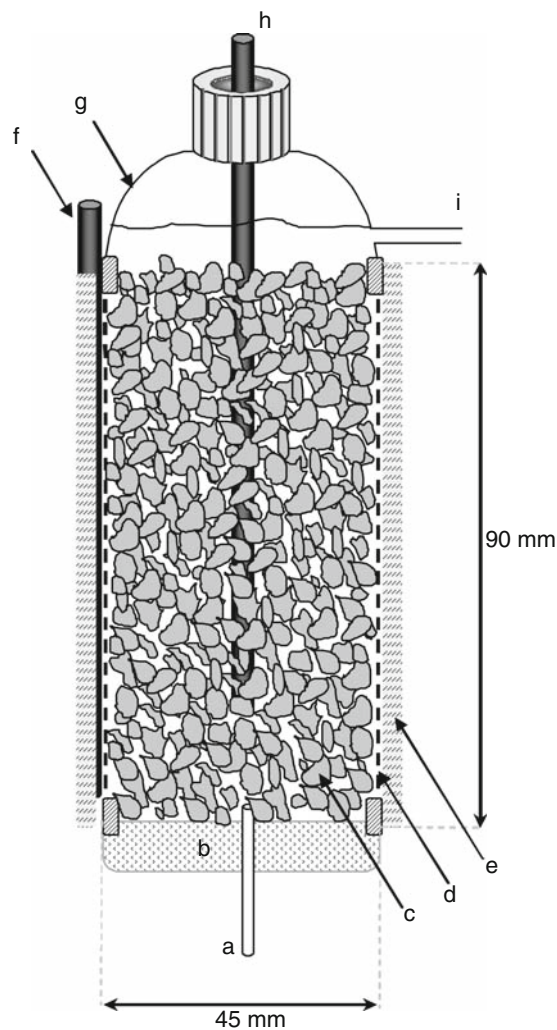


Fig. 1 Schematic MFC overview (a) inlet anodic liquid; (b) rubber stopper; (c) anodic granular graphite; (d) cation exchange membrane; (e) cathodic graphite felt; (f) cathodic graphite contact rod; (g) glass stopper with screw cap; (h) anodic graphite contact rod; (i) outlet anodic liquid

resistor (10 Ω) or to a Bi-Stat potentiostat (PAR Bi-Stat Potentiostat, Princeton Applied Research, France). A data acquisition unit (HP 34970A, Agilent, USA) recorded the voltage difference every minute. Only hourly averaged values of the cell voltage and the value of the external resistance were used for further calculations. Periods of substrate depletion and anode acidification (pH <6) or cathode alkalization (pH >8.5) were not taken into account. Calculations and polarization curves were performed as previously described (Clauwaert et al. 2007b). Chemical oxygen demand, volatile fatty acids and pH

were measured as previously described (Clauwaert et al. 2007a). All experiments were performed at room temperature ($22 \pm 2^\circ\text{C}$).

Results

Amino-acids and clover sap oxidation in microbial fuel cells

A microbial fuel cell (R1) with a biological anode and a biological cathode was allowed to adapt over a period of several months to a high conversion of acetate to current with an external resistance of 10Ω . Subsequently the electron donor was switched from acetate to L-glutamine (h 0–h 170). After 100 h lag phase, the current production rapidly increased and remained between 205 and 225 A m^{-3} MFC ($79\text{--}95 \text{ W m}^{-3}$ MFC). When the electron donor was changed from L-glutamine to L-glutamic acid (h 170–h 195), the current and power production remained at the same level. Then L-asparagine was fed (h 196–h 330) and the current production gradually increased over 71 h after replacing L-glutamic acid to L-asparagine and remained between 173 and 190 A m^{-3} MFC ($56\text{--}68 \text{ W m}^{-3}$ MFC). Subsequently, L-aspartic acid was used as the anodic substrate (h 331–h 406) and without lag phase, $145\text{--}167 \text{ A m}^{-3}$ MFC was produced ($39\text{--}52 \text{ W m}^{-3}$ MFC). After this test, L-alanine was dosed to the anodic vessel (h 407–h 552). After a lag phase of 20 h, the current production increased and remained between 151 and 178 A m^{-3} MFC ($43\text{--}59 \text{ W m}^{-3}$ MFC). The coulombic efficiency for all amino-acids was between 41 and 67%.

After the adaptation tests to different amino-acids, the anode of reactor R1 was supplied with $0.5 \text{ g COD-clover sap l}^{-1}$ in multiple feeding cycles (h 553–h 823). During a first 15 h, the current production was in the order of 50 A m^{-3} MFC (5 W m^{-3} MFC). Then the current sharply increased and remained between 123 and 193 A m^{-3} MFC ($28\text{--}70 \text{ W m}^{-3}$ MFC). The coulombic efficiency for substrate conversion in current production was between 46 and 70%. In the periods of optimal cell performance with each substrate, a polarization curve was obtained from this reactor (Fig. 2). The open circuit voltage (OCV, after 15 min of stabilization) for all substrates was between 0.778 and 0.850 V. The maximum power production during polarization was between 84

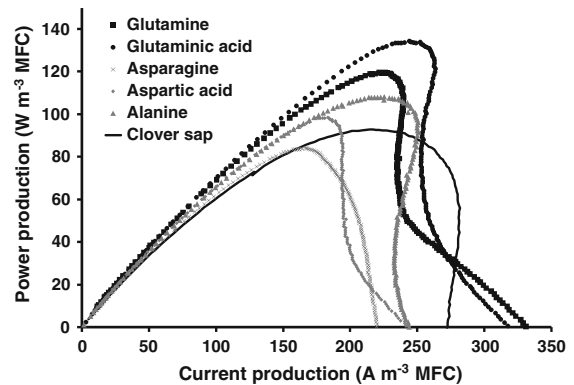


Fig. 2 Polarization curves (1 mV s^{-1}) with five different amino-acids and clover sap as anodic substrate performed on reactor R1

and 134 W m^{-3} MFC and the maximum current production (the short circuit current) was between 220 and 331 A m^{-3} MFC.

Anodic glycerol oxidation

The substrate of two microbial fuel cells (R2 and R3), adapted to acetate oxidation for several months, were continuously fed with analytical glycerol at a loading rate of $1.28 \text{ kg COD m}^{-3} \text{ MFC d}^{-1}$. Within 24 h the current was in the order of the average current production obtained during the test (Table 1). After 453 h operation, industrial glycerol originating from a biodiesel producing plant was supplied as anodic substrate to R2 instead of analytical glycerol at the same volumetric loading rate. There was no significant change in the current and power production by this change (Table 1). Polarization tests were performed on R2 and R3 (Fig. 3). The maximum power production during polarization was not very different ($82\text{--}93 \text{ W m}^{-3}$ MFC), however the short circuit current was ($150 \text{ vs. } 480 \text{ A m}^{-3}$ MFC).

Discussion

The COD oxidation rates of wastewater in MFCs have generally been much lower compared to oxidation rates of acetate, glucose or sucrose in mineral medium (Aelterman et al. 2006; He et al. 2006; Rabaey et al. 2005a). Since the phloem sap of plant tissues contains high concentrations of rapidly biodegradable compounds such as sugars (mainly sucrose) ($0.2\text{--}1 \text{ M}$) and

Table 1 Anodic glycerol oxidation of reactors supplied with 1.28 kg COD-glycerol m⁻³ MFC d⁻¹ (R_{ext} = 10 Ω, HRT = 11.4 h)

Reactor	R2	R2	R3
Duration (h)	453	181	470
Anode substrate	Analytical glycerol	Industrial glycerol	Analytical glycerol
Cathode system	Biocathode	Biocathode	K ₃ Fe(CN) ₆
OCV (V)	0.758–0.824	0.738–0.845	0.570–0.670
Av. cell voltage (V)	0.215 ± 0.026	0.204 ± 0.019	0.148 ± 0.042
Av. current (A m ⁻³ MFC)	117 ± 14	111 ± 10	81 ± 23
Av. power (W m ⁻³ MFC)	26 ± 6	23 ± 4	13 ± 9
Av. CE (%)	65 ± 8	62 ± 6	45 ± 13

Reactor R2 was operated with a biological cathode and R3 with a chemical cathode with ferricyanide as electron acceptor

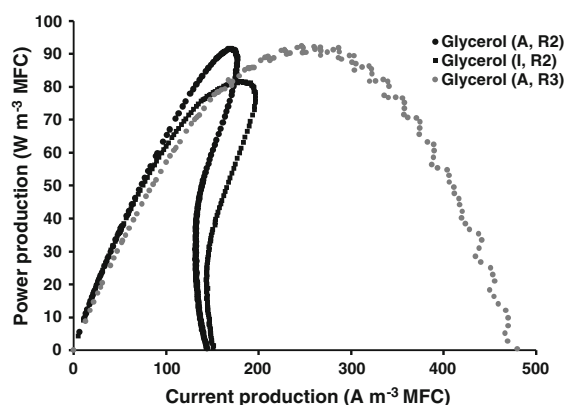


Fig. 3 Polarization curves (1 mV s⁻¹) with either analytical glycerol (A) or industrial glycerol (I) on reactors R2 and R3. R2 was operated with a biocathode and R3 with a chemical ferricyanide reducing cathode

amino-acids (0.03–0.6 M) (Amiard et al. 2004; Fukumorita and Chino 1982; Girousse et al. 1991), it can be an interesting substrate for biocatalyzed anode oxidations. Sucrose oxidation has already been demonstrated (He et al. 2006; Rabaey et al. 2005b) and, in this work, we have demonstrated that the most abundant amino-acids present in plant sap can easily be converted into current with a competitive power production in the order of 51–97 W m⁻³ MFC and a coulombic efficiency in the order of 60%. Maple syrup has been used as the electron donor in a MFC with ferricyanide as an artificial cathode system, resulting in a maximum current production of 13 A m⁻³ MFC (calculated value) (Rabaey et al. 2005b). Maple syrup, which is concentrated xylem sap from *Acer Saccharum*, contains mainly sucrose as the electron donor, with traces of fructose, glucose and malic acid (Stuckel and Low 1996).

Plant phloem sap can be of interest for powering electrical devices or sensors in natural habitats. When a MFC could be linked to the phloem sap of a living higher plant in a continuous way in which the minerals are returned to the plant, such a combination can constitute as a photo-electrical power producing unit. However, maintaining a continuous phloem sap drain from a growing plant will be challenging as plants have developed strategies to minimize phloem sap loss due to mechanical damage (Van Bel 2003).

To the authors knowledge, it is the first time that glycerol has been used as an electron donor in a BES, without the use of external added mediators (Emde et al. 1989). Glycerol oxidation was established in a continuous mode at an efficiency of 62% with glycerol loaded at 1.28 kg COD m⁻³ MFC d⁻¹, a waste product originating from industrial biodiesel production. No significant differences were noticed between analytical glycerol and industrial glycerol, which indicates that sulfate present in the industrial product is not interfering with the current production. During operation with a fixed external resistance of 10 Ω, the MFC that had a biocathode produced on average 20 to 30% more current than the reactor which had a ferricyanide containing cathode (Table 1). It is likely that the cathode selection had an influence on the anode potential, which might have influenced the development of the glycerol oxidizing communities in the anode. However, the continuous current production from glycerol (81 ± 23 A m⁻³ MFC) was still comparable to the current production in continuous acetate oxidizing MFCs where ferricyanide was used in the cathode (68–110 A m⁻³ MFC) (Clauwaert et al. 2008). The short circuit current during polarization of the MFC with the ferricyanide

cathode (480 A m^{-3} MFC) was much higher compared to the MFC with the biocathode (150 A m^{-3} MFC), and compared to the continuous current production with an external resistance. This indicates that a ferricyanide cathode allows short term acceleration of the bioanode activity during polarization at 1 mV s^{-1} , whereas a biocathode seems to curb this acceleration. This was also observed for acetate oxidizing MFCs (Clauwaert et al. 2007b).

Conclusions

- Amino-acids are interesting electron donors for MFCs, especially in combination with a biocathode resulting in a current production up to 225 A m^{-3} MFC and a power production up to 95 W m^{-3} MFC. Clover sap oxidation resulted in a maximum current production of 193 A m^{-3} MFC and a maximum power production of 70 W m^{-3} MFC.
- Continuous industrial glycerol oxidation in a MFC with a biocathode resulted in a current and power production of 111 A m^{-3} MFC and 23 W m^{-3} MFC respectively.

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