



NRC Publications Archive Archives des publications du CNRC

Electricity generation from carbon monoxide in a single chamber microbial fuel cell

Mehta, P.; Hussain, A.; Tartakovsky, B.; Neburchilov, V.; Raghavan, V.; Wang, H.; Guiot, S. R.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.enzmictec.2010.02.010>

Enzyme and Microbial Technology, 46, 6, pp. 450-455, 2010-05-05

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=833ea871-ff3c-4a87-9b87-d8e84384ad68>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=833ea871-ff3c-4a87-9b87-d8e84384ad68>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

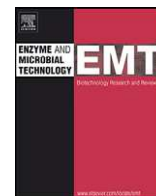
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





Electricity generation from carbon monoxide in a single chamber microbial fuel cell

P. Mehta^a, A. Hussain^{a,b}, B. Tartakovsky^{a,*}, V. Neburchilov^c, V. Raghavan^b, H. Wang^c, S.R. Guiot^a

^a Biotechnology Research Institute, National Research Council of Canada, 6100 Royalmount Ave, Montreal, QC, Canada H2P 2R2

^b Department of Bioresource Engineering, McGill University, Ste-Anne-de-Bellevue, QC, Canada H9X 3V9

^c Institute for Fuel Cell Innovation, National Research Council of Canada, 4250 Wesbrook Mall, Vancouver, BC, Canada V6T 1W5

ARTICLE INFO

Article history:

Received 15 September 2009

Received in revised form 10 February 2010

Accepted 16 February 2010

Keywords:

MFC

Carbon monoxide

Syngas

Carboxydophilic microorganisms

ABSTRACT

Electricity production from carbon monoxide (CO) is demonstrated in a single chamber microbial fuel cell (MFC) with a CoTMPP-based air cathode. The MFC was inoculated with anaerobic sludge and continuously sparged with CO as a sole carbon source. Volumetric power output was maximized at a CO flow rate of $4.8 \text{ L L}_R^{-1} \text{ d}^{-1}$ reaching 6.4 mW L_R^{-1} . Several soluble and gaseous degradation products including hydrogen, methane, and acetate were detected, resulting in a relatively low apparent Coulombic efficiency of 8.7%. Tests also demonstrated electricity production from hydrogen and acetate with the highest and fastest increase in voltage exhibited after acetate injection. It is hypothesized that electricity generation in a CO-fed MFC is accomplished by a consortium of carboxydophilic and carbon monoxide – tolerant anodophilic microorganisms.

Crown Copyright © 2010 Published by Elsevier Inc. All rights reserved.

1. Introduction

Fossil fuel depletion and the pollution that results from its extraction and combustion have forced us to look at alternative and cleaner forms of energy, from preferably non-edible biomass such as agricultural wastes, grasses, and wood. Several bioconversion routes exist to turn biomass into gas or liquid fuels. However, microbial degradation of this biomass is slow and challenging due to its heterogeneous and polymeric nature. An alternative would be to gasify the organic matter, when relatively dry (e.g. moisture content <40%), and produce synthesis gas (syngas).

Syngas is considered to be a cheap source of hydrogen gas but many applications are inhibited by the high CO concentration. There are many efforts underway to generate electricity using syngas in conventional fuel cells. A prime example is the solid oxide fuel cell (SOFC) [1], which operates at high temperatures and can use syngas as fuel but the anode is easily poisoned by fuel impurities.

Another method of syngas utilization involves microbial transformation. Carboxydophilic bacteria can use CO as their only carbon source [2–4], at low temperatures and pressures. Their ability to oxidize and metabolize CO is connected to the existence of the enzyme CO-dehydrogenase [3], often found in carboxydophilic methanogens and acetogens [5], resulting pre-

dominantly in methane and acetate production, respectively. Metabolic activity of carboxydophilic mesophilic bacteria also results in the formation of H_2 , ethanol, butyrate, butanol, and acetate [3,6]. Notably, at least some of these metabolic products can be utilized by anodophilic (exo-electrogenic) microorganisms for electricity production in a mediator-less microbial fuel cell (MFC), where the anodophilic microorganisms transfer electrons to the anode via nanowires or self-produced mediators [7–10]. A MFC may be designed where carboxydophilic microorganisms in a consortium with anodophilic microorganisms produce electricity from carbon monoxide or syngas. This process can be conducted at low temperatures and with high Coulombic efficiency. Kim and Chang [11] connected a CO fermenter containing carboxydophilic microorganisms to a MFC to produce electricity from syngas in a two-stage reactor system. In the study presented below we explore the feasibility and demonstrate that a single chamber MFC with a consortium of anaerobic microorganisms, instead of a two-stage reactor system, can accomplish electricity production from CO or syngas.

2. Materials and methods

2.1. MFC design, operation, and characterization

The air-cathode MFC was custom-made (Wolltech, Montreal, Canada) from Makrolon (polycarbonate) plates. The 1.0 cm thick plates had $10 \text{ cm} \times 5 \text{ cm}$ windows forming a 100 mL anodic chamber equipped with a 5 mm thick graphite felt anode measuring $10 \text{ cm} \times 5 \text{ cm}$ (Speer Canada, Kitchener, ON, Canada). The outside wall of the chamber was formed by an additional polycarbonate plate. A membraneless MFC design was used in all tests [9] since preliminary experiments comparing mem-

* Corresponding author. Tel.: +1 514 496 2664; fax: +1 514 496 6265.

E-mail addresses: Boris.Tartakovsky@nrc-cnrc.gc.ca, boris.tartakovsky@nrc-cnrc.gc.ca (B. Tartakovsky).

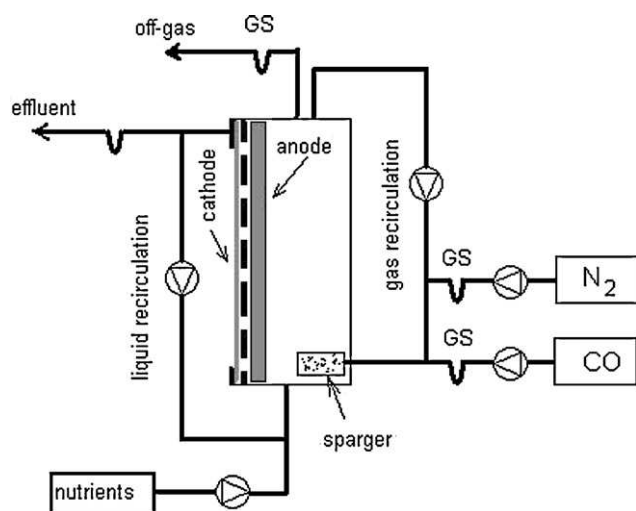


Fig. 1. Diagram of the experimental setup showing liquid and gas recirculation streams. GS denotes U-tubes used as gas counters.

braneless and Nafion-based MFCs showed superiority of the membraneless design (data not shown). A carbon paper cathode containing cobalt tetramethoxyphenylporphyrin (CoTMPP) as a catalyst [12] was attached to a side of the anodic chamber and separated from the anode by a piece of J-cloth [13], such that the estimated distance between the electrodes was 0.7 mm. The MFC was equipped with lines for influent, effluent, liquid recirculation, gas exit and entry (Fig. 1). A solution of nutrients and trace metals was prepared and fed to the MFC at a rate of 75 mL d⁻¹, using a peristaltic pump.

Two 5 L gas bags (Control Concepts Inc., Calgary, Alberta, Canada) were attached to the line for gas entry and used for continuous supply of CO and N₂ to the anodic chamber through a sparger. Also an external gas recirculation loop was used to increase gas transfer efficiency, as shown in Fig. 1. Gas flow rates were controlled by a programmable timer. In order to estimate the maximal CO consumption rate, several CO flow rates were tested, as outlined in Table 1, where gas flow rates are expressed in L of gas per L of anodic chamber volume per day (LL_R⁻¹ d⁻¹). Each flow rate was maintained for at least 5 days, starting at a low CO flow rate and progressively increasing the flow rate to its highest value.

Also, in one of the tests N₂ was replaced with H₂ in order to estimate MFC performance on syngas. In addition, substrate tests were carried out where a H₂/CO₂ mixture (80:20 v/v) was sparged for a period of 24 h (hydrogen test) or acetate was injected to obtain an initial acetate concentration of 2.4 g L⁻¹. Prior to these tests the MFC was operated on N₂ for at least 24 h to remove all metabolic products.

MFC temperature was maintained at 30–31 °C by means of a thermocouple placed in the anodic chamber, a temperature controller (Model JCR-33A, Shinko Technos Co., Ltd., Osaka, Japan) and a 5 cm × 10 cm heating plate attached on the outside of the anodic chamber wall. The voltage was measured on-line at 20 min intervals using a data acquisition system (Labjack U12, Labjack Corp., Lakewood, CO, USA).

Except for during the startup and substrate tests, the external resistance connected to the MFC was periodically adjusted such that it was about 50–60 Ω higher than the total MFC internal resistance calculated by polarization tests. The substrate tests were performed at an external resistance of 500 Ω. The polarization tests were carried out as follows. First, open circuit voltage (OCV) was measured by disconnecting the external resistance for 30 min. Then the external resistance was re-connected and progressively decreased in 5–7 steps with an interval of 10 min between each step to allow for voltage stabilization. Output voltage measurements were conducted at the end of each interval. The measurements were started at 5000 Ω or 1000 Ω and terminated if a sharp drop in current was observed (typically between 100 Ω and 20 Ω). These measurements were used to plot polarization (voltage vs. current) and power (output power vs. current) plots. The linear part of the polar-

ization curve, which corresponded to ohmic losses, was used to estimate the total internal resistance as a slope of linear approximation of the selected data points [14]. In addition, internal resistance was estimated using measurements of OCV and a current observed at a given external resistance ($R_{\text{int}} = \text{OCV}/I_{\text{R}_{\text{ext}}} - R_{\text{ext}}$, [15]).

Apparent Coulombic efficiency (CE_a) of the MFC was estimated as:

$$CE_a = \frac{I \cdot \Delta t \cdot M_{\text{CO}}}{F \cdot n \cdot (M_{\text{CO, in}} - M_{\text{CO, out}})} 100\% \quad (1)$$

where I is the average measured current (A), Δt is the time interval during which current was measured (s), M_{CO} is the CO molecular weight (g), F is the Faraday's constant (C/mol), n is the number of electrons (electron/mol), $M_{\text{CO, in}}$ is the amount of CO supplied to MFC during Δt (g), $M_{\text{CO, out}}$ is the amount of CO recovered in the off-gas line during Δt (g).

CE_a can be corrected to account for CO consumption for the production of acetate (not used for electricity production), methane, and hydrogen. CO utilized by microorganisms to produce these metabolic products was subtracted from the total amount of CO consumed in the anodic chamber. The corrected (true) Coulombic efficiency (CE_c) was estimated as follows:

$$CE_c = \frac{I \cdot \Delta t \cdot M_{\text{CO}}}{F \cdot n \cdot (M_{\text{CO, in}} - M_{\text{CO, out}} - M_{\text{CH}_4, \text{out}} - M_{\text{H}_2, \text{out}} - M_{\text{Ac, out}})} \quad (2)$$

where $M_{\text{CH}_4, \text{out}}$, $M_{\text{H}_2, \text{out}}$, $M_{\text{Ac, out}}$ are the CO equivalents required for the production of methane, hydrogen, and acetate (measured in the effluent), respectively.

2.2. Media composition and inoculum

The stock solution of nutrients was composed of (g/L): 1.87 NH₄Cl, 14.81 KCl, 6.40 K₂HPO₄, 4.07 KH₂PO₄, 0.415 yeast extract. For acetate injection test 34.59 g of NaC₂H₃O₂ (anhydrous) was added to the nutrients stock solution. The trace metal stock solution was prepared according to Tartakovsky et al. [16]. The stock solution was filter sterilized and maintained at 4 °C until used. The chemicals used were all of analytical grade. MFC was fed with a solution prepared by adding 35 mL of the nutrient solution and 1 mL of the trace metal solution to 1 L of de-ionized water. This solution had a conductivity of 14 mS cm⁻¹ and a pH of 7.0–7.2. The MFC was inoculated with 10 mL of anaerobic sludge originating from a food processing plant (Lassonde Inc., Rougemont, QC, Canada). The sludge was stored at 4 °C, pH 6.8–7.0, under anaerobic conditions prior to use.

2.3. Cathode manufacturing

The cathode was manufactured by dissolving CoTMPP (Sigma–Aldrich, Canada, Oakville, ON, Canada) in acetone by sonication using an ultrasonic probe. The solution was sonicated for 0.5 s/1 s, for 30 min. This was followed by stirring at 20 °C, until completely dissolved. Carbon black Vulcan XC72R powder was dissolved in the CoTMPP solution by sonication for 0.5 s/1 s, for 1 h followed by 15 h stirring at 20 °C (ratio of solvent to carbon black = 20 mL:1 g). The solution was subsequently evaporated at 80 °C on a hot plate. The solute was washed and dried at 80 °C, and ground at 25,000 rpm for 2 min. The resulting CoTMPP/C powder was heat treated at 800 °C for 1 h in 100% N₂.

Ink fabrication and spraying was accomplished by dispersion of CoTMPP/C powder in isopropyl alcohol:H₂O = 1:1 by ultrasonic probe treatment for 0.5 s/1 s, at 20 °C, during 30 min. The cathode was prepared by manual spraying of the catalyst ink on a gas diffusion layer with microporous sub-layer (95% C + 5% Teflon) on a hot plate at 80 °C followed by drying at 90 °C for 20 min.

2.4. Analytical measurements

Acetate, and volatile fatty acids (VFAs) were analyzed in an Agilent 6890 gas chromatograph (Wilmington, DE) equipped with a flame ionization detector. Method details are provided in Tartakovsky et al. [17].

Gas inflow and outflow were measured by bubble counters connected to glass U-tubes and interfaced with a data acquisition system [17]. The gas composition was measured using a gas chromatograph (6890 Series, Agilent Technologies, Wilmington, DE) equipped with a 11 m × 3.2 mm 60/80 mesh Chromosorb 102 column (Supelco, Bellefonte, PA, USA) and a thermal conductivity detector. The carrier gas was argon. The pH and conductivity of the effluent were measured daily using a pH meter and a conductivity meter, respectively.

3. Results

The MFC operation was initially started with a flow rate of 2 LL_R⁻¹ d⁻¹ of CO and an $R_{\text{ext}} = 500 \Omega$. Less than 1 mV was recorded prior to MFC inoculation. After a 3-week delay the voltage increased to 260 mV corresponding to a power output of 1.35 mW LL_R⁻¹ (where R is the anodic chamber volume). The effluent and the off-gas composition of the MFC were measured periodically, and as shown in Table 2, there was acetate in the effluent and methane and hydrogen in the off-gas.

Table 1
Phases of MFC operation.

Test #	CO flow rate (LL _R ⁻¹ d ⁻¹)	N ₂ flow rate (LL _R ⁻¹ d ⁻¹)
1	2	0
2	10.2	0
3	4.8	2
4	7.5	2
5	11.6	2
6	4.8	4.8 ^a

^a H₂ was fed instead of N₂ to simulate syngas.

Table 2
MFC performance at different flow rates of carbon monoxide.

Test #	CO (LL _R ⁻¹ d ⁻¹)	Power output (mWL ⁻¹)	Effluent acetate (mg L ⁻¹)	H ₂ (%)	CH ₄ (%)	CO (%)	R _{int} (Ω)	CE _{ap} (%)	CE _c (%)	CO removal (%)
1 ^a	2	1.35	172.0	7.6	5.2	71.4	596	9.1	14.0	20.7
2 ^a	10.2	0.02	70.0	0.0	0.1	90.0	1018	0.5	0.5	2.7
3	4.8	6.4	17.6	0.1	4.48	35.8	93.2	8.7	33.0	53.0
4	7.5	5.75	66.1	0.6	5.45	35.1	145	6.0	16.4	46.8
5	11.6	5.13	219.6	1.4	4.2	48.8	158	4.7	11.2	60.7
6 ^c	4.8	4.52	49.0	22.1	22.1	25.0	124	9.2	n/c ^b	52.6

^a For tests #1 and #2 R_{ext} was set to 500 Ω.

^b Not calculated because of significant methane production from hydrogen.

^c Syngas test.

Once the reactor had reached its initial steady state we tested CO, acetate, and H₂/CO₂ as substrates to determine the pathway(s) by which electricity was being produced. Prior to each test the anodic compartment was fed with the solution of nutrients and microelements and sparged with N₂ for at least 24 h to flush the MFC of the former metabolic gaseous products from the previous test and allow for washout of the metabolic products in the liquid phase. VFA analysis at the beginning of each test showed acetate to be below the level of detection (0.5–1 mg L⁻¹). A voltage of only 3–4 mV was measured at R_{ext} = 500 Ω, demonstrating the absence of significant power production by electrochemical reactions or from nutrients present in the influent.

When the MFC was fed with a CO/N₂ mixture at 4.8 LL_R⁻¹ d⁻¹ of CO, the power output increased to 450 mV as compared to 4 mV when only N₂ was fed. At the end of the CO substrate test, analysis of the effluent composition showed an acetate concentration of 35 mg L⁻¹. The appearance of acetate, which accompanied the increase in voltage during the test, is an indicator of carboxydotrophic activity. When only H₂/CO₂ (80:20 v/v) was continuously fed to the MFC an increase in MFC voltage was also observed, although the voltage was not higher than 160 mV (Fig. 2B). As in the previous test, acetate appearance in the anodic chamber was observed (29.4 mg L⁻¹). When acetate was injected into the anodic chamber the voltage instantly increased to 420 mV (Fig. 2C).

After the substrate tests, the CO flow rate was restored to 2 LL_R⁻¹ d⁻¹ and then further increased to 10.2 LL_R⁻¹ d⁻¹. This resulted in a significant decrease in voltage, which dropped to 20–40 mV, and a disappearance of degradation products, such as H₂ and CH₄, with acetate being the only measurable metabolite (Table 2). Since no improvement was observed within 5 days of MFC operation, it was re-inoculated with 10 mL of anaerobic sludge and CO was sparged into the anodic chamber at a reduced flow rate of 4.8 LL_R⁻¹ d⁻¹. Furthermore, the CO concentration in the anodic chamber headspace and therefore the concentration of dissolved CO was also reduced by simultaneously feeding N₂ at a flow rate of 2 LL_R⁻¹ d⁻¹ (test #3 in Table 1). After an initial delay of 3 days the voltage increased and reached 320 mV (at R_{ext} = 160 Ω). The flow rate of CO was subsequently increased to 7.5 LL_R⁻¹ d⁻¹ (phase 4) and then further increased to 11.6 LL_R⁻¹ d⁻¹ (phase 5), whilst the N₂ flow rate remained at 2 LL_R⁻¹ d⁻¹ as specified in Table 1. Fig. 3 and Table 2 show that under these conditions the off-gas analysis detected CH₄, CO₂, and traces of H₂ (Fig. 3), and effluent measurements demonstrated that the concentration of acetate increases with the increase in the CO flow rate (Table 2). Also, trace amounts of propionate were detected in tests #4 and #5 (7 and 12 mg L⁻¹, respectively).

At each CO flow rate a polarization curve was produced to estimate MFC internal resistance as shown in Fig. 4. The OCV values varied between 550 and 560 mV (Fig. 4A) and the internal resistances estimated using linear parts of the polarization curves were similar at each flow rate (R² between 0.88 and 0.97), including that which resulted from the MFC fed with CO and H₂ (Table 2). A sharp drop in current and power was observed at R_{ext} below 100 Ω in all

tests with the exception of phase 3, likely due to diffusion-limited transport of substrates or ions under non-optimal conditions. The MFC fed with CO, with a flow rate of 4.8 LL_R⁻¹ d⁻¹, resulted in the highest power output and Coulombic efficiency when operated at a R_{ext} of 160 Ω (Fig. 5). The polarization tests confirmed these results and demonstrated that the MFC fed with CO flow rate of 4.8 LL_R⁻¹ d⁻¹ (Fig. 4B) had the highest power output and the absence of a sharp drop in current and power at an R_{ext} below 100 Ω.

4. Discussion

Electricity production in the CO-fed MFC was accomplished by a mixed anaerobic microbial consortium. The activity of carboxydotrophic microorganisms in the anodic compartment was evidenced by the conversion of CO into hydrogen and methane in the off-gas and acetate and propionate in the effluent. In our experiments electricity production was always associated with the presence of acetate in the anodic chamber. Substrate tests showed a significant delay in electricity production after the onset of CO feeding (Fig. 2A), which was accompanied by the appearance of acetate in the anodic chamber. At the same time, the immediate increase of MFC voltage upon acetate injection was observed (Fig. 2C). These observations strongly suggest that at least one pathway of electricity production consists of CO transformation to acetate by carboxydotrophic bacteria described by:



Acetate formation from CO was conceivably followed by acetate oxidation, resulting in power generation, by CO-tolerant anodophilic microorganisms. Anaerobic carboxydotrophic bacteria such as *Clostridium carboxidivorans* are known to produce acetate [6]. Also, mesophilic *Archaea*, such as *Methanosarcina barkeri* can produce CH₄ from CO [3].

Another potential pathway would involve direct transfer of electrons to the anode by Fe(III)-reducing carboxydotrophic bacteria, which were shown to reduce iron, therefore suggesting that direct electron transfer from CO to the anode can be achieved, at least under thermophilic conditions [18]. However in our tests the indirect formation of electricity from acetate seems to be predominant, either due to a lack of the necessary microbial consortia, the insignificant contribution of this pathway to overall production of electricity or lack of being able to measure the CO directly converted into electricity.

Electricity production was also observed in the H₂/CO₂ addition test (Fig. 2B). In the CO-fed MFC hydrogen can be produced according to the following stoichiometric equation [3]:



Although less power was produced from hydrogen than from acetate this pathway cannot be excluded from consideration. A lower current density was also observed when hydrogen was fed to a pure culture of *Geobacter sulfurreducens* [10]. Effluent analysis during the hydrogen addition test showed the presence of acetate,

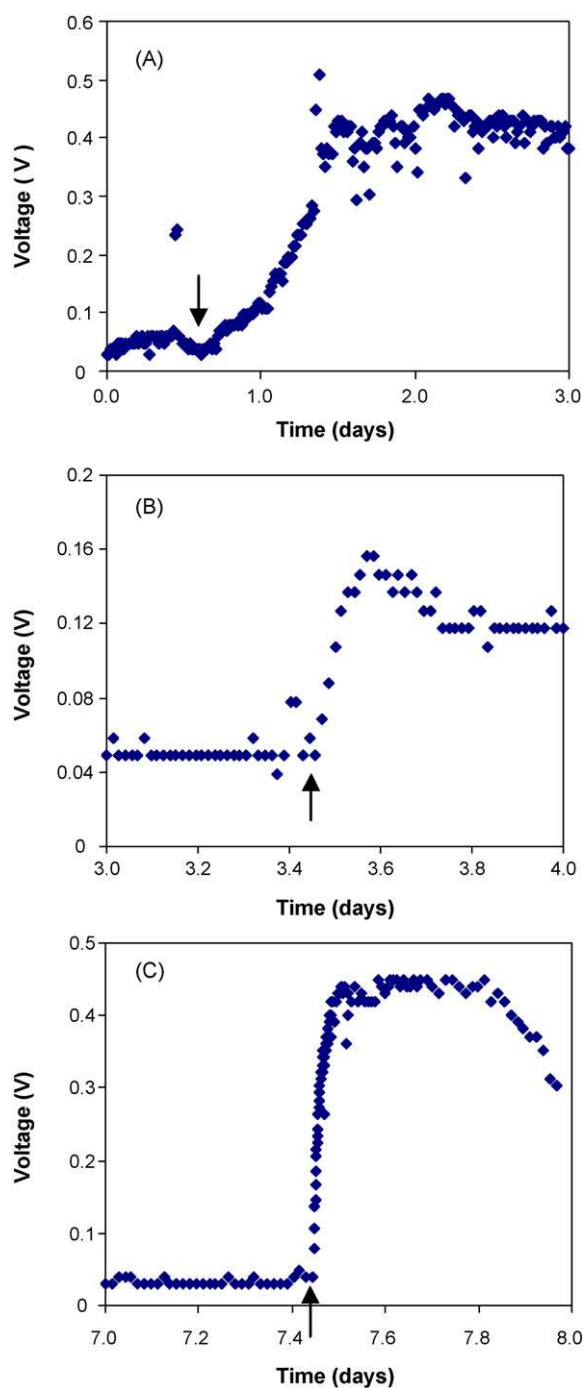
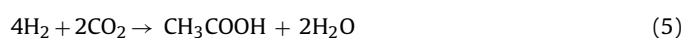


Fig. 2. Substrate addition tests showing MFC voltage response to the addition of (A) CO at a flow rate of 4.8 LL_R⁻¹ d⁻¹ while maintaining N₂ flow at 2 LL_R⁻¹ d⁻¹; (B) H₂/CO₂ (80:20 v/v) at a flow rate of 4.8 LL_R⁻¹ d⁻¹; and (C) injection of 3 mL of a 40 g L⁻¹ acetate stock solution. R_{ext} was kept at 500 Ω for all tests. In CO and H₂/CO₂ tests gas was fed continuously. In the acetate test a stock solution was added to obtain initial acetate concentration of 2.4 g L⁻¹. The arrows indicate startup of each test.

which might be attributed to the activity of homoacetogenic bacteria [19]. This biotransformation can be described as:



Therefore the electricity generated during hydrogen addition test is either the result of its direct conversion into electricity or the result of a two-step process where hydrogen is converted into acetate, which is then consumed by anodophilic microorganisms.

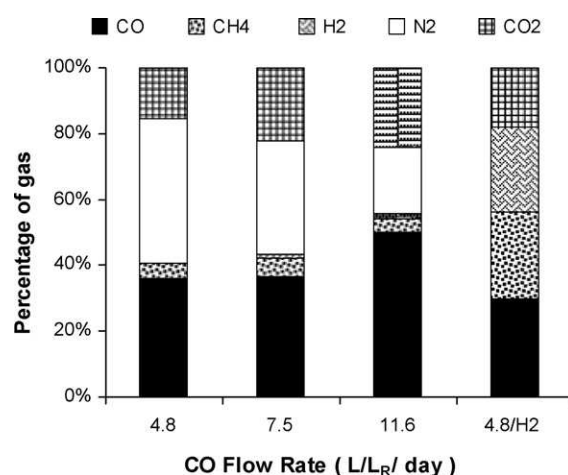


Fig. 3. A comparison of the MFC off-gas composition produced at different flow rates of carbon monoxide. For all CO flow rates except test #6 (last column) N₂ was mixed with the CO stream as specified in Table 1.

Also, acetate can be produced by carboxydutrophic acetogenic bacteria, which utilize H₂ and CO [3,4].

In addition to electricity production, methane can be directly produced from carbon monoxide (Henstra et al. [3]), as follows:



Methane can also be formed by hydrogenotrophic methanogens from hydrogen and CO₂ or acetoclastic methanogens from acetate, which can be produced directly from CO. Indeed, when a CO/H₂ mixture was fed to the MFC in order to test MFC operation on syn-gas, methane production increased 5 times and the concentration of CO₂ fell by 40–50% (Table 2) indicating hydrogenotrophic activity.

There was very little difference in the power production that resulted from the different flow rates of CO, when N₂ was added to the gas stream. However, at a flow rate of 10.2 LL_R⁻¹ d⁻¹ in phase 2 where pure CO was sparged only 10% of the CO was removed. In phase 5, a CO/N₂ mixture was sparged and 60.7% of the CO was removed. A comparison of MFC performance in phases 2 and 5 and assuming an equilibrium between the gas and liquid phase CO concentrations, it can be hypothesized that high levels of dissolved CO in the anodic chamber liquid were inhibitory both to carboxydutrophic and anodophilic microorganisms. Nevertheless, microbial consortium adaptation cannot be ruled out, since phase 5 tests were carried out after a longer exposure of microorganisms to CO. It can also be concluded that a flow rate of 4.8 LL_R⁻¹ d⁻¹ was sufficient for a given MFC configuration. At this CO flow rate, a volumetric rate of CO consumption of 2.1 LL_R⁻¹ d⁻¹ was reached.

Our results confirmed those previously obtained by Sipma et al. [5] using methanogenic sludge specimens from various anaerobic wastewater treatment plants. While having never been exposed to CO as in our case, in batch tests all the sludges converted CO at an initial headspace concentration of 95% CO and 5% N₂. The conversion resulted in the production of acetate and CO₂ in some cases and in other cases CH₄ and CO₂. In all cases only trace amounts of H₂ were detected and other major CO conversion products were absent. In their studies they also found that acetate seemed to be the main intermediate of methane production since it was inhibited when 2-bromoethanesulfonic acid, an inhibitor of methanogenesis, was added.

When the MFC was operated at a CO flow rate of 4.8 LL_R⁻¹ d⁻¹ (phase 3), the apparent Coulombic efficiency approached 8.7% and the volumetric power output was at 6.4 mW L_R⁻¹ (Fig. 5). More importantly, concomitant production of methane and other degradation products resulted in relatively low apparent Coulombic

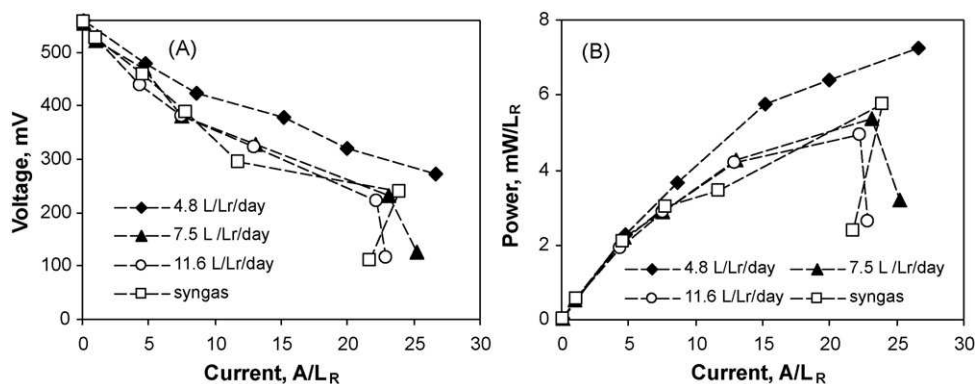


Fig. 4. Polarization (A) and power (B) curves produced in phases 3–6. Anodic chamber volume was 100 mL and cathode area was 50 cm².

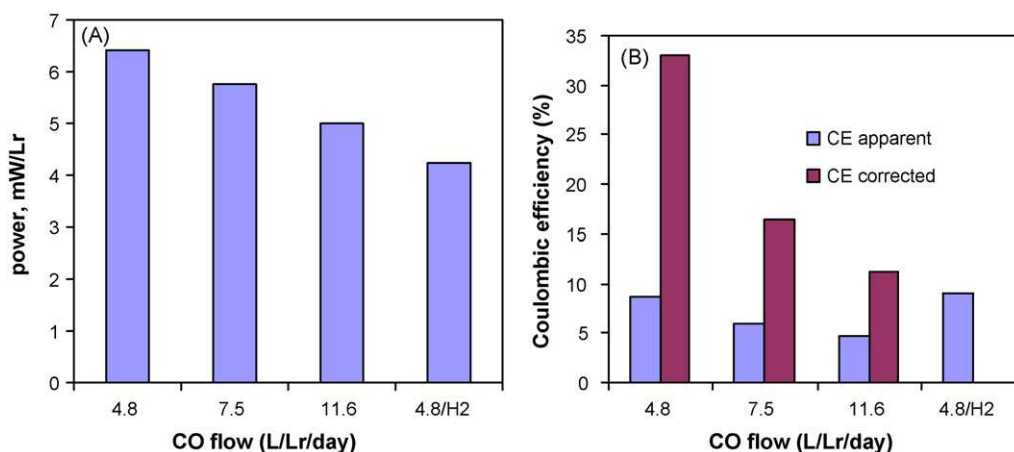


Fig. 5. The volumetric power output (A) and Coulombic efficiency (B) of a MFC operated at different flow rates of CO and with CO/H₂ mixture.

efficiency. When the Coulombic efficiency calculations were modified to take into account the formation of methane and acetate (Eq. (2)) the corrected (true) Coulombic efficiency approached 33% (Table 2 and Fig. 5B). This Coulombic efficiency and power output are only marginally lower than those reported for acetate-fed MFCs, which are in the range of 10–100 mW L⁻¹ for MFCs with a comparable design [20,21]. Operation of a similar MFC with an anodic chamber volume of 50 mL using acetate as a sole source of carbon showed a power output of 34 mW L_R⁻¹ (results not shown). Notably, because of sparger installation in the anodic chamber, the chamber volume had to be increased to 100 mL, while the anode occupied only 25 mL of the anodic chamber. By recalculating the volumetric power output per anode volume a value of 25.6 mW L_{anode}⁻¹ (per litre of anode volume) was obtained. This implies that by optimizing the anodic chamber and providing efficient methods of CO transfer to liquid while avoiding CO-related inhibition of anodophilic populations, volumetric efficiency can be further increased.

5. Conclusion

This study presents a demonstration of electricity production from carbon monoxide in a single chamber air-cathode MFC. MFC inoculation with a mixed microbial community of anaerobic sludge resulted in a complex pathway of CO transformation. It can be hypothesized that electricity formation was mostly accomplished through CO conversion to acetate followed by acetate consumption by anodophilic microorganisms. However electricity production, directly from CO, or indirectly from H₂ through homoacetogenesis, cannot be excluded.

MFC operation for an extended period of time demonstrated a stable power output of 6.4 mW L_R⁻¹ and a CO consumption rate of 2.1 L L_R⁻¹ d⁻¹. Moreover, CO related inhibition of anodic activity was only observed when feeding the MFC with pure CO at high flow rates (i.e. 10.2 L L_R⁻¹ d⁻¹). Inhibition was not observed when the MFC was fed with a mixture of CO and N₂ or H₂ due to a decreased CO partial pressure. Furthermore, no CO-related inhibition of the CoTMPP cathode was observed throughout the tests suggesting that this non-noble catalyst can be used to reduce MFC construction costs. This study suggests the feasibility of syngas transformation to electricity in a MFC. In comparison to electricity production by an internal combustion engine, such a process might have an advantage of high Coulombic efficiency if the production of hydrogen and methane are kept to a minimum. Further studies might be focused on improving gas transfer efficiency and on understanding the complex transformation pathways.

Acknowledgement

This research was supported by the National Research Council of Canada (NRC article #00000)

References

- [1] Ormerod RM. Solid oxide fuel cells. *Chem Soc Rev* 2003;32:17–28.
- [2] Davidova MN, Tarasova NB, Mukhitova FK, Karpilova IU. Carbon monoxide in metabolism of anaerobic bacteria. *Can J Microbiol* 1994;40:417–25.
- [3] Henstra AM, Sipma J, Rinzeema A, Stams JM. Microbiology of synthesis gas fermentation for biofuel production. *Curr Opin Biotechnol* 2007;18:200–6.

- [4] Oelgeschlager E, Rother M. Carbon monoxide – dependent energy metabolism in anaerobic bacteria and archaea. *Arch Microbiol* 2008;190:257–69.
- [5] Sipma J, Lens PNL, Stams AJM, Lettinga G. Carbon monoxide conversion by anaerobic bioreactor sludges. *FEMS Microbiol Ecol* 2003;44:271–7.
- [6] Liou JS-C, Balkwill DL, Drake GR, Tanner RS. *Clostridium carboxidivorans* sp. nov., a solvent-producing clostridium isolated from an agricultural settling lagoon, and reclassification of the acetogen *Clostridium scatologenes* strain SL1 as *Clostridium drakei* sp. nov. *Int J Syst Evol Microbiol* 2005;55:2085–91.
- [7] Kim HJ, Park HS, Hyun MS, Chang IS, Kim M, Kim BH. A mediator-less microbial fuel cell using a metal reducing bacterium, *Shewanella putrefaciens*. *Enzyme Microb Technol* 2002;30:145–52.
- [8] Rabaey K, Boon N, Siciliano S, Verhaege M, Verstraete W. Biofuel cells select for microbial consortia that self-mediate electron transfer. *Appl Environ Microbiol* 2004;70(9):5373–82.
- [9] Liu H, Logan BE. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ Sci Technol* 2004;38:4040–6.
- [10] Bond DR, Lovley DR. Electricity production by *Geobacter sulfurreducens* attached to electrodes. *Appl Environ Microbiol* 2003;69:1548–55.
- [11] Kim D, Chang IS. Electricity generation from synthesis gas by microbial processes: CO fermentation and microbial fuel cell technology. *Bioresour Technol* 2009;100:4527–30.
- [12] Cheng S, Lui H, Logan B. Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (nafion and PTFE) in single chamber microbial fuel cells. *Environ Eng Sci* 2006;40(3):364–9.
- [13] Fan Y, Hu H, Liu H. Enhanced Coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration. *J Power Sources* 2007;171:348–54.
- [14] Fan Y, Sharbrough E, Liu H. Quantification of the internal resistance distribution of microbial fuel cells. *Environ Sci Technol* 2008;42:8101–7.
- [15] Ieropoulos I, Greenman J, Melhuish C. Microbial fuel cells based on carbon veil electrodes: stack configuration and scalability. *Int J Energy Res* 2008;32:1228–40.
- [16] Tartakovsky B, Manuel MF, Neburchilov V, Wang H, Guiot SR. Biocatalyzed hydrogen production in a continuous flow microbial fuel cell with a gas phase cathode. *J Power Sources* 2008;182:291–7.
- [17] Tartakovsky B, Manuel MF, Wang H, Guiot SR. High rate membrane-less microbial electrolysis cell for continuous hydrogen production. *Int J Hydrogen Energy* 2009;34(2):672–7.
- [18] Sokolova T, Hanel J, Onyenwoke RU, Reysenbach A-L, Banta A, Geyer RJMG, et al. Novel chemolithotrophic, thermophilic, anaerobic bacteria *Thermolithobacter ferrireducens* gen. nov., sp. nov. and *Thermolithobacter carboxydivorans* sp. nov. *Extremophiles* 2007;11:145–57.
- [19] Dolfing J. Acetogenesis. In: Zehnder AJB, editor. *Biology of anaerobic microorganisms*. New York: John Wiley & Sons Inc.; 1988. p. 417–68.
- [20] Lovley DR. The microbe electric: conversion of organic matter to electricity. *Curr Opin Biotechnol* 2008;19:564–71.
- [21] Logan BE, Hamelers B, Rozendal RA, Schroder U, Keller J, Freguia S, et al. Microbial fuel cells: methodology and technology. *Environ Sci Technol* 2006;40(17):5181–92.