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Publisher's version / Version de l'éditeur:
https://doi.org/10.1007/s00253-011-3188-4
Applied Microbiology and Biotechnology, 90, 3, pp. 827-836, 2011-03-13

Appl Microbiol Biotechnol (2011) 90:827–836
DOI 10.1007/s00253-011-3188-4

MINI-REVIEW

Electricity generation from carbon monoxide and syngas in a microbial fuel cell

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Received: 23 November 2010 / Revised: 15 February 2011 / Accepted: 16 February 2011 / Published online: 13 March 2011

Abstract Electricity generation in microbial fuel cells (MFCs) has been a subject of significant research efforts. MFCs employ the ability of electricigenic bacteria to oxidize organic substrates using an electrode as an electron acceptor. While MFC application for electricity production from a variety of organic sources has been demonstrated, very little research on electricity production from carbon monoxide and synthesis gas (syngas) in an MFC has been reported. Although most of the syngas today is produced from non-renewable sources, syngas production from renewable biomass or poorly degradable organic matter makes energy generation from syngas a sustainable process, which combines energy production with the reprocessing of solid wastes. An MFC-based process of syngas conversion to electricity might offer a number of advantages such as high Coulombic efficiency and biocatalytic activity in the presence of carbon monoxide and sulfur components. This paper presents a discussion on microorganisms and reactor designs that can be used for operating an MFC on syngas.

Keywords Microbial fuel cell · Syngas · Carbon monoxide

Introduction

A steady increase in energy consumption in the developed countries and a surge in energy demands in the fast growing developing countries might lead to a shortage of fossil fuels in the foreseeable future. This anticipated shortage and the concerns about atmospheric pollution and global warming are acting as a major impetus for research into alternative renewable energy technologies. A number of studies have suggested biomass to be one of the most promising sources of renewable energy (Kim and Chang 2009; Song 2002). Microbial digestion, fermentation, and gasification are well-known processes, among many, for biomass conversion to a wide range of biofuels and bioproducts. Wet biomass with up to 25–35% of solids such as urban organic waste and high moisture agricultural waste (vegetables, sugar cane, sugar cane beet, etc.) is best suited for microbial degradation, while gasification is most appropriate for dry biomass such as woody waste and low moisture agricultural waste (Demirbas 2001).

The gasification of biomass at high temperatures leads to the generation of synthesis gas (syngas). Carbon monoxide and hydrogen account for 60–80% of the syngas composition, with CH_4, CO_2, SO_2, H_2S, and NH_3 present in smaller amounts (Sipma et al. 2006; Munasinghe and Khanal 2010). Although most of the syngas today are produced from nonrenewable sources, such as natural gas and coal, syngas production from renewable biomass or poorly degradable organic matter makes energy generation from syngas a sustainable process (Faaij et al. 1997; Henstra et al. 2007).

Fermentation is one way of producing an energy carrier from syngas, which has been advocated by many studies (Bredwell et al. 1999; Sipma et al. 2006; Henstra et al. 2007). As well, electricity generation from syngas in conventional fuel cells has been studied (Steele and Heinzel 2001; Ormerod 2003; Baschuk and Li 2001; Song 2002). Syngas can be used in polymer electrolyte membrane fuel cells (PEMFC) or solid oxide fuel cells (SOFC). However, Pt or Pt-based alloys used in PEMFCs are extremely sensitive to CO and sulfur compounds with 10 ppm of CO and 0.1 ppm

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of sulfur compounds, respectively, leading to irreversible inhibition of the catalyst (Kim and Chang 2009; Ormerod 2003). Even SOFCs, which generally employ nickel as the anode catalyst, are poisoned by small amounts (greater than 1 ppm) of sulfur compounds (Ormerod 2003; Kim and Chang 2009; Song 2002; Baschuk and Li 2001).

Recently, Kim and Chang (2009) have shown syngas conversion to electricity by a bioelectrochemical process, where a CO fermenter was connected to a microbial fuel cell (MFC). Subsequently, Mehta et al. (2010) for the first time reported electricity generation in an MFC directly fed with CO or a mixture of CO and H_2. The MFC technology employs the electricigenic bacteria, which are capable of extracellular electron transfer to an exogenous electron acceptor such as the anode (Logan and Regan 2006; Lovley 2008; Lefebvre et al. 2010). Microbial fuel cells have been successfully operated on a wide range of substrates, including, acetate, H_2, butyrate, marine sediments, and swine wastewater (Chaudhuri and Lovley 2003; Bond and Lovley 2003; Rabaey and Verstraete 2005; Mathis et al. 2008; Min et al. 2005; Niessen et al. 2004). MFCs have also been operated both under mesophilic and thermophilic conditions (Logan 2008; Demirbas 2007; Mathis et al. 2008; Choi 2004; Jong et al. 2006).

Although the microbiology, design, and operation of MFCs fed with conventional carbon sources (i.e., non-gaseous, such as acetate or wastewater) have been extensively presented (e.g., Logan 2008, 2009; Lovley 2006b; Lefebvre et al. 2010), a syngas-fed MFC represents a novel approach, which has not yet been reviewed. MFC operation on syngas presents a number of challenges related to gas transfer limitations, selection of microorganisms capable of efficient syngas transformation to electricity, and selection of cathodic catalysts resistant to poisoning by CO and sulfur compounds. This paper introduces the concept of electricity generation from syngas in an MFC and provides a discussion of the expected transformation pathways as well as reactor designs suitable for MFC operation on syngas.

Microbial community of a syngas-fed MFC

So far, electricity production from syngas has been demonstrated in MFCs seeded with a mixed microbial population of anaerobic sludge (Mehta et al. 2010; Kim and Chang 2009). Based on the analysis of metabolic products, Mehta et al. (2010) concluded that the production of electricity proceeds through a multi-step biotransformation process. Several concurrent pathways, as shown in Fig. 1, were observed. One pathway involved CO transformation to acetate by acetogenic carboxidotrophic microorganisms followed by oxidation of acetate by CO-tolerant electricigenic microorganisms (pathways 1 and 4 in Fig. 1). This pathway was

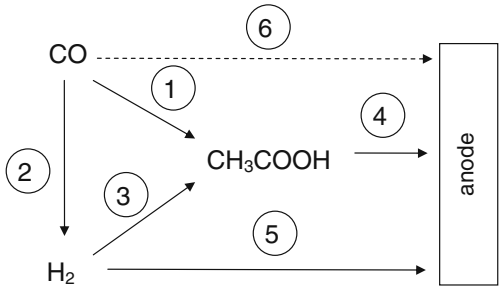

Fig. 1 Pathways of electricity production from syngas observed in a CO-fed MFC (based on Mehta et al. (2010)). *1* CO conversion to acetate by acetogenic carboxidotrophs, *2* CO conversion to H_2 by hydrogenogenic carboxidotrophs, *3* H_2 conversion to acetate by homoacetogens; *4*, *5* acetate and H_2 consumption by anodophilic microorganisms, *6* CO consumption by anodophilic carboxidotrops (hypothesized)

suggested to be the foremost responsible for electricity generation. However, hydrogen was also found in the off-gas samples during MFC operation solely on CO, which indicated the presence of hydrogenogenic carboxydotrophic microorganisms. It was suggested that H_2 is used for electricity production by the electricigenic microorganisms (pathways 3 and 5 in Fig. 1). The importance of this pathway should be greater in the syngas-fed MFC where a significant amount of hydrogen is present. Notably, the ability of the electricigenic microorganisms to utilize H_2 as an electron donor has been documented (Bond and Lovley 2003). The presence of acetate when the MFC was fed only with hydrogen also indicated the presence of homoacetogenic microorganisms. Based on this observation, a pathway of electricity production through H_2 and acetate followed by acetate conversion to electricity was also suggested (pathways 2, 3, and 4 in Fig. 1). The work of Mehta et al. (2010) also raised a possibility of another pathway, which involved direct electron transfer to the anode by metal-reducing carboxidotrophic bacteria (pathway 5 in Fig. 1). The following review discusses these pathways in more detail.

Syngas conversion to electricity by acetogenic and electricigenic microorganisms ($CO/H_2 \rightarrow$ acetate $\rightarrow e^-$)

Mesophilic acetogenesis and electricigenesis

Acetogens have the ability of utilizing a wide range of substrates for metabolic needs (Drake and Daniel 2004). *Clostridium carboxidivorans* (ATCC BAA 624), *Clostridium autoethananogenum* (DSM 10061), *Peptostreptococcus productus* (ATCC 35244), *Eubacterium limosum* (ATCC 10825), and *Acetobacterium woodii* (DSM 1030) are some of the mesophilic bacterial acetogens capable of using CO as their sole source of energy while forming acetate and CO_2 (Henstra et al. 2007; Lorowitz and Bryant

1984; Genthner and Bryant 1987). This biotransformation can be presented by the following stoichiometric equation:

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \quad (1)$$

P. productus isolated from an anaerobic sewage digester was the first acetogenic anaerobic coccus observed to utilize CO as an energy source. The doubling time with 90% CO was 1.15 h at an optimum temperature of 30 °C (Lorowitz and Bryant 1984). Similarly, *E. limosum* can utilize CO, forming acetate and CO_2. The generation time of *E. limosum* on CO, within the temperature range of 38–39 °C, was reported to be 7 h. *A. woodii* grew on CO at 30 °C without requiring any adaptation period, with a generation time of 13 h.

Acetate is also formed by certain bacteria by acetogenic hydrogenation where H_2 and CO_2 are converted to acetate according to the following stoichiometric equation (pathway 3 in Fig. 1):

$$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O \quad (2)$$

This ability under mesophilic conditions has been demonstrated by *Clostridium aceticum* (DSM 1496), *Acetobacterium wieringae* (DSM 1911), *Ruminococcus hydrogenotrophicus* (DSM 10507), etc. (Braun et al. 1981; Bernalier et al. 1996). *C. aceticum* is an obligate anaerobe which grows chemolithotrophically on H_2 and CO_2 forming acetate. The optimum temperature and pH for growth was reported to be 30 °C and 8.3, respectively, with a doubling time of 25 h (Braun et al. 1981). Similarly, *A. wieringae* coupled H_2 and CO_2 for acetate formation. The doubling time was less than 10 h at the optimal growth temperature and pH of 30 °C and 7.6, respectively (Braun and Gottschalk 1982). *R. hydrogenotrophicus* is a strict anaerobe that grew autotrophically on H_2 and CO_2 forming acetate (Bernalier et al. 1996).

For electricity generation under mesophilic conditions, the above-mentioned bacteria could be used in co-culture with electricigenic microorganisms capable of using acetate as an electron donor such as *Geobacter sulfurreducens* (ATCC 51573; Bond and Lovley 2003), leading to a syntrophic relationship with the acetogens. The following stoichiometric equation can be used to describe the corresponding acetate transformation reaction (Logan 2008):

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+ \quad (3)$$

Equations (1–3) imply a yield of $2e^-$/mol either on CO or on H_2 for a syngas-fed MFC. A detailed review of electricigenic microorganisms can be found elsewhere (Logan and Regan 2006; Lovley 2008; Logan 2009).

Interestingly, genome sequencing of *G. sulfurreducens*, often found in mixed microbial populations of MFCs, revealed the presence of carbon monoxide dehydrogenase, which is known to catalyze the reaction of CO conversion to CO_2 and H_2 (Methe et al. 2003). Although growth of *G. sulfurreducens* on CO has not been reported, it can be suggested that this strain can be at least tolerant to the presence of CO, thus growing in a co-culture with carboxydotrophic strains producing acetate.

Thermophilic acetogenesis and electricigenesis

The growth of acetogens on CO and electricity generation through the acetate pathway can also be anticipated under thermophilic conditions. Savage et al. (1987) reported the ability of CO-dependent chemolithotrophic acetogenesis and growth by *Moorella thermoautotrophicum* (ATCC 33924; formerly *Clostridium thermoautotrophicum*), with supplemental CO_2 required for efficient growth on CO. The CO/CO_2 ratio of 2:4 yielded optimal doubling times at a temperature of 58 °C. This microorganism has the ability to grow autotrophically and heterotrophically using various electron donors and acceptors (Sokolova et al. 2009; Savage et al. 1987). *Clostridium thermoaceticum* (ATCC35608) also demonstrated CO-dependent growth and acetogenesis under chemolithotrophic conditions, with a doubling time of 10 h at a temperature of 55 °C (Daniel et al. 1990). The recently isolated thermophilic bacterium *Moorella perchloratireducens* (ATCC BAA 1531), which is closely related to the above-mentioned bacterial species, resorted to acetogenesis on CO in the absence of perchlorate (Balk et al. 2008).

Acetogenic hydrogenation (Eq. 2) has also been observed in thermophiles. *C. thermoaceticum*, capable of growth on CO, grew chemolithotrophically on H_2 and CO_2 forming acetate. The doubling time was 18 h at a temperature of 55 °C (Kerby and Zeikus 1983). A similar growth physiology was also observed in *Acetogenium kivui* (ATCC 33488; Daniel et al. 1990). This thermophilic anaerobic bacterium formed acetate by chemolithotrophic growth on H_2 and CO_2, with a doubling time of 2 h, at a temperature of 66 °C, and pH of 6.8.

For generation of electricity in an MFC, the above-mentioned thermophilic bacterial species should be co-cultured with thermophilic electricigenic microorganisms capable of using acetate as an electron donor. Although the microorganisms studied for generation of electricity in an MFC are predominantly mesophilic (e.g., *G. sulfurreducens* or *Geobacter metallireducens*), successful MFC operation under thermophilic conditions has been demonstrated. Choi (2004) used thermophilic bacteria *Bacillus licheniformis* and *Bacillus thermoglucosidasius* (with a redox mediator) for electricity generation. The best efficiency was achieved within the temperature range of 50–60 °C. Mediatorless MFC operation under thermophilic conditions was also reported by Jong et al. (2006). The MFC was inoculated

with anaerobic digester effluent and fed with sodium acetate. The maximum power density was achieved during MFC operation at 55 °C. Based on the 16S rRNA analysis, only 13 different patterns of anodic bacterial populations were observed, of which 5 patterns showed the highest homology to an uncultured clone E4, which was initially identified as a member of a thermophilic microbial community in a lab scale methanol-fed anaerobic digester. Seven patterns were related to genus *Coprothermobacter*, and one pattern was related to *Thermodesulfovibrio* spp.

In the study by Mathis et al. (2008), thermophilic bacteria selected from sediment MFC were used to colonize the anode of acetate and cellulose-fed MFCs. Cloning and sequencing of the biofilm formed at the anode of the acetate-fed MFC showed the presence of *Deferribacters* and *Fermicutes*. Interestingly, 48 clones (out of 64) of *Fermicutes* had RFLP patterns and sequences (99%) most similar to that of *Thermincola carboxydophila*, a hydrogenogenic CO-oxidizing thermophilic microorganism (Mathis et al. 2008). *Firmicutes* spp. were also identified during thermophilic MFC operation by Wrighton et al. (2008). This study provided a detailed analysis of microbial community dynamics in an acetate-fed MFC inoculated with sludge collected from a thermophilic anaerobic digester. The dominant members of the electricity-producing community were identified using clone library analysis. The results showed the dominance of *Firmicutes* spp. (80% of the clone library sequences). Within *Firmicutes*, sequences belonging to *Thermicanus*, *Alicyclobacillus*, and *Thermincola* were identified representing 27%, 25%, and 22% of the total clones, respectively. The study was well complemented by the demonstration of electricity production in an MFC inoculated with a pure strain of *Thermincola* sp. Strain JR, representing direct anode reduction by a member of *Fermicutes* phylum (Wrighton et al. 2008).

As electricity generation has never been an evolutionary pressure per se, but rather the capacity for electron transfer to natural extracellular electron acceptors, it is likely that the ability of the microorganism to produce electricity is closely correlated to its capacity to transfer electrons onto extracellular acceptors, such as Fe^{3+} and Mn^{4+} oxides and humic substances (Lovley 2006a; Lovley et al. 2004; Logan 2009). Hence, the prospect for electricigenic microorganisms could include any microorganism capable of extracellular electron transfer, even if their capacity for electricity generation has not yet been experimentally evidenced (Lovley et al. 2004).

With this respect, hyperthermophiles *Ferroglobus placidus* (DSM 10642) and *Geoglobus ahangari* (ATCC BAA 425) were reported to grow at 85 °C by coupling acetate oxidation to Fe(III) reduction (Tor et al. 2001). Also, *Deferribacter thermophilus* (DSM 14813) isolated from a petroleum reservoir (UK) was able to grow by the reduction of Fe (III), Mn(IV), and nitrate in the presence of acetate, yeast extract, peptone, and other carbon sources in the temperature range of 50–65 °C (Greene et al. 1997). Kashefi et al. (2003) reported the isolation of a bacterial strain belonging to the *Geobacteraceae* family exhibiting thermophilic growth. The bacterium, *Geothermobacter ehrlichii* (DSM 15274) isolated from a hydrothermal vent coupled acetate oxidation to Fe (III) reduction, with an optimum growth temperature of 55 °C. This strain is the first member in the *Geobacteraceae* family reported to be capable of thermophilic growth. Fe(III) reduction coupled to acetate oxidation has also been demonstrated by the bacterium *Thermincola ferriacetica* (DSM 14005; Zavarzina et al. 2007). Overall, a broad range of thermophilic electricigenic microorganisms might be capable of forming a syntrophic consortium with thermophilic carboxidotrophic microorganisms for efficient operation of a syngas-fed MFC.

Syngas conversion to electricity by hydrogenogenic and electricigenic microorganisms ($CO \rightarrow H_2 \rightarrow e^-$)

Biological water–gas shift reaction and electricigenesis at mesophilic temperatures

This pathway leads to CO conversion to H_2 through the biological water–gas shift reaction followed by H_2 utilization as an electron donor by electricigenic bacteria. Indeed, the ability of CO-dependent H_2 production by mesophilic bacteria such as *Rubrivivax gelatinosus* (Maness et al. 2005), *Rhodospirilum rubrum* (Singer et al. 2006), *Rhodopseudomonas palustris* P4, and *Citrobacter* sp. Y19 (Henstra et al. 2007) has been reported. *R. gelatinosus* uses CO as its sole carbon source (with a doubling time of 2 days), leading to the generation of H_2 according to the following stoichiometric equation, which describes the water–gas shift reaction (Maness et al. 2005):

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (4)$$

Similarly, the exposure of *R. rubrum* to CO leads to H_2 production according to Eq. (4) due to the stimulation of a CO oxidizing–H_2 evolving enzymatic system (Singer et al. 2006). In a syngas-fed MFC, this pathway is expected to maximize the Coulombic efficiency of syngas transformation, as compared to H_2 utilization through acetate formation. To conclude, a mixed culture of electricigenic and mesophilic carboxydotrophic hydrogenogenic bacteria would allow for CO conversion to H_2 and the subsequent use of the H_2 produced from CO and H_2 present in syngas for electricity generation.

Biological water–gas shift reaction and electricigenesis at thermophilic temperatures

The sequence of bioreactions described above is also expected to proceed under thermophilic conditions since thermophilic oxidation of CO leading to H_2 evolution is a widespread trait found among several recently isolated carboxydotrophic microorganisms. Carboxydotrophic microorganisms such as *Thermolithobacter carboxydivorans* (DSM 7242), *Carboxydothermus hydrogenoformans* (DSM 6008), *T. carboxydophila* (DSM 17129), *Carboxydocella thermoautotrophica* (DSM 12326), and *Carboxydibrachium pacificum* (ATCC BAA 271) produce H_2 from CO oxidation under thermophilic conditions (Sokolova et al. 2009, 2007, 2005, 2002). A number of carboxydotrophic microorganisms capable of hydrogenogenic activity have been isolated from marine hydrothermal vents (Henstra et al. 2007; Sokolova et al. 2009). *C. pacificum*, isolated from a submarine hot vent, grew chemolithotrophically on CO producing equimolar quantities of H_2 and CO_2. Its growth was observed between 50 °C and 80 °C, with an optimum temperature of 70 °C (Sokolova et al. 2002). Likewise, *C. thermautotrophica*, a thermophilic CO utilizing bacterium isolated from a terrestrial hot vent on the Kamchatka Peninsula (Russia) produced H_2 to CO_2, with a generation time of 1.1 h, at a temperature of 58 °C, and pH 7. *Carboxydocella sporoproducens* (DSM 16521), also isolated from hot springs of Karymshoe Lake, Kamchatka Peninsula (Russia), grows chemolithoautrophically on CO (doubling time of 1 h) producing equimolar quantities of CO_2 and H_2. The temperature and optimum pH were observed to be 60 °C and 6.8, respectively (Slepova et al. 2006). Sokolova et al. (2005) reported the isolation of the alkali-tolerant carboxydotrophic hydrogenic bacterium, *T. carboxydophila*, from a hot spring of the Baikal Lake region, Russia. CO was found to be the sole source of energy for this bacterium. For lithotrophic growth of *T. carboxydiphila*, acetate or yeast extract was required, but these substrates did not support growth in the absence of CO. Neither acetate nor methanol formation was detected during growth on CO.

Similar to the mesophilic co-culture, a co-culture of thermophilic hydrogenogenic carboxydotrophic microorganisms with H_2 utilizing thermophilic electricigenic microorganisms such as *D. thermophilus* or *Pyrobaculum islandicum* (DSM 4184) could be used for electricity generation in a syngas-fed MFC. *D. thermophilus* was able to grow by the reduction of Fe(III), Mn(IV), and nitrate in the presence of H_2. Similarly, *P. islandicum* is able to reduce Fe(III) and Mn(IV) with H_2 as an electron donor (Kashefi and Lovley 2000). *Thermolithobacter ferrireducens* (ATCC 700985) reduces Fe(III), anthraquinone-2,6-disulfonate (AQDS), thiosulfate, and fumarate with H_2 serving as the electron donor in a temperature range of 50–75 °C (Sokolova et al. 2007).

Direct conversion of CO to electricity by axenic cultures of Fe(III)-reducing thermophiles

While direct conversion of H_2 to electricity has been experimentally demonstrated (Bond and Lovley 2003), electricigenic bacteria growth on CO has not yet been demonstrated. Nevertheless, Sokolova et al. (2004) reported the isolation of a new anaerobic facultative carboxydotrophic bacterium from a hot spring at Norris basin (Yellowstone National Park, US). The bacterium, *Thermosinus carboxydivorans* (DSM 14886), grew at temperatures between 40 °C and 68 °C (with an optimum at 60 °C) at neutrophilic conditions. The bacterium could utilize CO as its sole energy source, with a doubling time of 1.15 h leading to the formation of H_2 and CO_2 in equimolar quantities. Fe(III) was also reduced during its growth on sucrose and lactose. The species was the first metal-reducing carboxydotrophic bacterium to be reported (Sokolova et al. 2004). Similarly, *Carboxydothermus ferrireducens* (DSM 11255), also isolated from Yellowstone National Park (Sokolova et al. 2009; Henstra and Stams 2004), has the ability to use CO as an electron donor for AQDS and fumarate reduction. Fumarate, AQDS, ferric iron, and thiosulfate could serve as electron acceptors during its growth on H_2. Hydrogen or acetate production was not observed during its growth on CO. In contrast, *Carboxydothermus siderophilus* (DSM 21278), isolated from the hot spring of Geyser Valley (Kamchatka Peninsula, Russia), produced H_2 and CO_2 along with Fe(III) and AQDS reduction during its growth on CO (Slepova et al. 2009). However, the doubling time for *C. siderophilus* (9.3 h) on CO was much longer than that of *T. carboxydivorans* (1.15 h). Balk et al. (2008) reported the isolation of *M. perchloratireducens*, the thermophilic gram-positive bacterium with the ability to use perchlorate as a terminal electron acceptor. This strain was able to use CO, methanol, pyruvate, glucose, fructose, mannose, xylose, pectin, and cellobiose for growth.

T. ferriacetica (DSM 14005), isolated from ferric deposits of a terrestrial hydrothermal spring (Kunashir Island, Russia), is a thermophilic facultative chemolithoautotrophic anaerobic bacterium. It was able to utilize H_2 and acetate as energy sources, with Fe(III) serving as the electron acceptor. Also, it was able to grow in an atmosphere of 100% CO, leading to the formation of H_2 and CO_2. However, it required 0.2 g/L of acetate as its carbon source during its growth on CO (Zavarzina et al. 2007). *C. hydrogenoformans*, a close relative of *T. ferrireducens*, oxidized CO and H_2 using AQDS as an electron acceptor. CO_2 and H_2 were formed during its growth on CO.

It has to be noted that most of the metal-reducing carboxydotrophic organisms are thermophiles. High temperatures could be more favorable as less cooling of syngas would be required (Henstra et al. 2007). Although MFC

operation at thermophilic temperatures is expected to have a detrimental effect on the CO solubility in the anodic liquid, this is counteracted by the increase in the mass transfer rate with increasing temperature (Drew 1981). Elevated temperatures would also lead to reduced O_2 solubility, which is beneficial considering the sensitivity of carboxydotrophs to O_2 (Davidova et al. 1994).

Design considerations

Apart from the biological system, the efficient generation of electricity in a syngas-fed MFC also requires the optimization of the MFC architecture to counter the two major challenges posed by a gaseous substrate: the gas to liquid mass transfer limitations and the poisoning of the cathode by CO and other toxic gases.

Membrane systems for improved mass transfer efficiency

For sparingly soluble gases such as CO and H_2, the primary resistance to gas transport is in the liquid film at the gas–liquid interface. Although the conventional continuous stirred tank reactors could be used, the high impeller speeds require a high power input (Henstra et al. 2007; Hickey et al. 2008) and leads to biofilm shearing, causing a decrease in the growth of shear-sensitive microorganisms (Munasinghe and Khanal 2010).

Bubble-free gas transfer to liquid can be accomplished by the selection of a membrane system with a high selectivity for the gaseous substrate. The membrane systems offer an efficient and a relatively inexpensive method for gas–liquid mass transfer (Scott and Hughes 1996). A wide range of microporous and nonporous membranes are commercially available and can be selected based on the gaseous substrate and process conditions. In a dense polymer membrane, the gas is absorbed in the polymer at the high pressure end and is carried to the liquid (lower pressure side) by diffusion across the membrane. In contrast, the gas in a microporous system is transported to the liquid through the pore system rather than through the polymer. Although the gas pressure is then maintained below the bubble point, bubbles might be formed at the surface of the membrane, but kept attached to the membrane due to surface tension. Dense polymer membranes offer an advantage over microporous membranes as they can be operated at high pressures, which increases the concentration gradient and hence the mass transfer rate (Côté et al. 1989; Ahmed and Semmens 1992).

In particular, silicone membranes are dense membranes which offer the advantage of high mechanical strength, flexibility, and stability under high temperature and pressures. They have been reported to be ideal for membrane-based bubble-less aeration without vigorous mixing, where a conventional system is unable to meet the O_2 requirements of a high rate system (Côté et al. 1989). Such membranes could be easily incorporated in a conventional MFC design as shown in Fig. 2a. Depending upon the type of membrane system selected, they offer the flexibility of being folded into different geometries (e.g., tubular or flat membrane, etc.) to increase the surface to volume ratio. A gas compartment containing syngas can be attached to the anodic compartment with the selected membrane system acting as a wall between the anodic liquid and gas phase. The details of different membrane systems made up of polyvinyl fluoride, polyethylene, polyvinyl chloride, and other polymeric materials can be found elsewhere (Hickey et al. 2008; Scott and Hughes 1996).

In order to validate the applicability of the bubble-less gas transfer in an MFC, the CO gas–liquid mass transfer coefficient for a silicone membrane and a silicone tube was estimated in our laboratory. The tests were carried out in 50-mL MFCs designed as shown in Fig. 2a, b. A 50-cm^2 silicone membrane (Specialty Silicone Products Inc., NY, USA) and a thin wall silicone tube (VWR International LLC, Radnor, PA, USA) were used in these tests. The K_La values were determined by measuring the change in concentration of dissolved CO with time at a constant gas flow rate set prior to the start of the experiment. It was assumed that the reactor operates in a batch mode, the CO pressure in the gas compartment is constant at all times, the liquid phase is well mixed, and the CO concentration in the liquid at the gas–liquid interface is in equilibrium with the CO concentration in the gas. The mass transfer coefficient was calculated using the analytical solution of the dissolved CO material balance (Riggs and Heindel 2006).

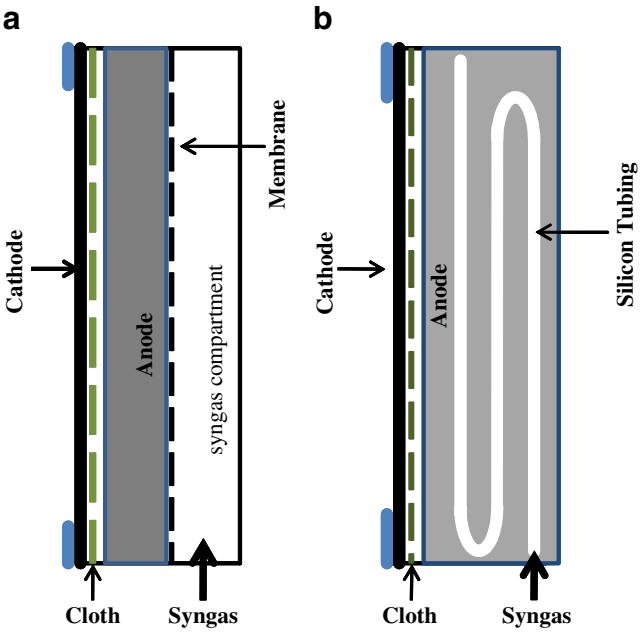

Fig. 2 Design of an MFC with a **a** flat membrane and **b** microporous tubes embedded in the anode

Based on the laboratory tests, the CO K_La values for the MFCs equipped with the silicone membrane and a thin wall silicone tube were estimated to be 0.63 h^{-1} and 0.76 h^{-1}, respectively. Riggs and Heindel (2006) obtained considerably higher CO K_La in the range of 11–155 h^{-1} for a stirred tank reactor, while the K_La for CO in a syngas mixture in a continuous stirred tank reactor was in the range of 14.2–101 h^{-1} (Bredwell et al. 1999; Munasinghe and Khanal 2010). Nevertheless, an optimum operation of an MFC requires that the rate of gas transfer matches the rate of its consumption. Mehta et al. (2010) observed a CO consumption rate of 2.1 L $(L_R \text{ day})^{-1}$ for an MFC equipped with a sparger, i.e., providing a sufficient membrane area, the K_La values obtained in our tests were sufficient to match the observed CO consumption. Excessive CO transfer might lead to CO-related inhibition of carboxidotrophic organisms (Henstra et al. 2007; Sipma et al. 2006; Sokolova et al. 2009). Furthermore, sparger replacement with a membrane offers the advantage of a more compact design. Indeed, the sparger used in the experiments carried out by Mehta et al. (2010) required a 50% increase of the anodic compartment. Thus, a membrane-based MFC is expected to have a higher volumetric efficiency.

Apart from the membrane systems discussed above, other promising alternatives to the conventional stirred tank reactors for increased gas–liquid mass transfer include monolith packing and columnar reactors. Monolith packing consists of a number of narrow, straight, and parallel flow channels with a large open frontal area which allows for a low flow resistance, leading to low pressure drops and low energy losses. High volumetric mass transfer rates of ~1 s^{-1} and a 50–80% reduction in power consumption as compared to conventional reactors make monolith reactors an economically viable option (Munasinghe and Khanal 2010; Hickey et al. 2008). Similarly, columnar reactors such as bubble column, trickle bed, and airlift reactors offer the advantage of a high gas–liquid mass transfer rate with low operational and maintenance costs. K_La values within the range of 18–860 h^{-1} have been reported for such reactors (Bredwell et al. 1999; Munasinghe and Khanal 2010; Charpentier 1981). Various reactor design improvements such as the low-frequency vibration of liquid phase in a bubble column reactor, the addition of static mixers, baffles, perforated plates, jet loop, and forced circulation loop in internal and external loop airlift reactors promises a further increase in the gas–liquid mass transfer efficiency (Ellenberger and Krishna 2003; Gavrilescu et al. 1997; Fadavi and Chisti 2005; Chisti et al. 1990; Vorapongsathorn et al. 2001; Krichnavaruk and Pavasant 2002; Ugwu and Ogbonna 2002).

Non-noble catalysts for improved cathode stability

The development of an efficient MFC system for the generation of electricity from CO or syngas requires a CO-tolerant cathode. The most extensively used cathode material in a conventional MFC consists of carbon paper with a Pt/C catalyst (Logan 2008). Even though the Pt-based cathode demonstrates high electrochemical activity, the use of Pt is undesirable due to high costs and easy inhibition by CO (Logan 2008; Herrmann et al. 2009). Even at small concentrations, CO can fully cover the Pt surface, thereby reducing the reaction site. CO is easily able to absorb to Pt due to the negative free energy of adsorption (Baschuk and Li 2001). This phenomenon also poses a challenge for other conventional fuel cells such as the direct methanol fuel cells and proton exchange membrane fuel cells (PEMFC), where even trace amounts of CO, present as fuel impurity, can seriously dampen the cells' performance due to the relatively high loading of Pt at the anode and cathode (Steele and Heinzel 2001; Baschuk and Li 2001; Song 2002; Ormerod 2003).

Jasinski (1964) was the first to report that transition metal porphyrins and phthalocyanines demonstrated electrochemical activity towards the oxygen reduction reaction and therefore can be used as a cathode catalyst in fuel cells. Studies testing less expensive porphyrins and phthalocyanines as cathode catalysts in MFCs such as Fe(II) phthalocyanine (FePc), and Fe(III) tetramethoxyphenyl porphyrin (FeTMPP), and Co tetramethoxyphenylporphyrin (CoTMPP) showed that these non-noble metal cathode catalysts can generate power equal to that obtained from Pt-based carbon cathodes (Zhao et al. 2005; Birry et al. 2010; HaoYu et al. 2009; Harnisch et al. 2009). The use of CoTMPP as a cathode catalyst was also demonstrated by Cheng et al. (2005), where the performance of a CoTMPP air cathode was tested in a single-chamber MFC. A maximum power density of 369±8 mW/m^2 was obtained using CoTMPP/C catalyst, which was only 12% lower than that obtained with a Pt/C catalyst (Cheng et al. 2005). When the Fe loading was optimized for FePc-based cathodes, a similar power output was obtained in MFCs operated with FePc cathodes containing 0.01–0.16 mg Fe/cm^2 and 0.5 mg Pt/cm^2 (Birry et al. 2010).

In the study conducted by Mehta et al. (2010), a CoTMPP cathode was used for generation of electricity from CO with a Co load of 0.5 mg cm^{-2}. This was the first time that a CoTMPP cathode was used in an MFC operated on CO. A maximum power density of 6.4 mW/L was reported. In another study (unpublished results), we also tested pyrolised CoTMPP, FeTMPP, and CoTMPP/FeTMPP cathode catalysts with a load of 0.5 mg/cm^2. The cathode performance was tested in acetate and CO-fed MFCs. MFC operation on CO showed the best performance with the CoTMPP/FeTMPP/C cathode catalyst. Considering the high cost of Pt-based cathodes and the plausible decrease in activity with time, the use of CoTMPP/FeTMPP/C or FePc cathodes is a step forward in increasing the efficiency of CO-operated MFCs.

Perspectives

Increasing energy demands, dwindling fossil fuel reserves, and environmental and health concerns have forced us to look for clean and sustainable sources of energy. If produced from biomass, syngas represents a renewable source of energy. The conversion of syngas to electricity in an MFC, though at a very early experimental stage, offers some major advantages such as high conversion efficiency, operation at temperatures in a range of 30–70 °C, low maintenance requirements and operating costs, and resistance to CO poisoning. With the performance of a syngas-fed MFC with a mixed culture already demonstrated, a detailed study of the CO-operated MFC might be of interest. This study includes a detailed characterization of the syngas transformation pathways observed in a mixed culture under mesophilic and thermophilic conditions as well as an attempt at developing an axenic culture for an MFC featuring direct electron transfer from CO to the anode. Furthermore, MFC design improvements might be expected to result in the development of a stackable MFC capable of efficient operation on gaseous substrates such as CO and H_2 and with power outputs suitable for commercial applications.

Acknowledgments The authors are grateful to the Natural Sciences and Engineer Research Council of Canada (NSERC) for financial support (NRC publication no. 53353).

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