

Electricity Production from Carbon Monoxide and Syngas in a Thermophilic Microbial Fuel Cell

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1. Introduction

Microbial fuel cells (MFCs) represent a novel technological solution for electricity production from biomass. In its most simple configuration, a microbial fuel cell is a device that uses microorganisms to produce an electrical current. The technology exploits the ability of microorganisms that are capable of extracellular electron transfer to an insoluble electron acceptor, such as an electrode. Logan (2008) defined microorganisms as exoelectrogens because of their capability of exocellular electron transfer. Other researchers described the microorganisms as electrochemically active bacteria (Manish and Banerjee 2008), anode-respiring bacteria (Moon et al. 2004) and electricigens (Logan 2004). The oxidation of organic chemicals by microorganisms liberates both electrons and protons. Electrons are then transferred from microorganisms to the anode and subsequently to the cathode through an electrical network. Simultaneously, protons (electron acceptor) migrating to the cathode combine with electrons and an electron acceptor, such as oxygen, to produce water. The electrical current generated is similar to that in chemical fuel cells; however, in MFCs the microbial catalysts are attached to the anode surface (Franks and Nevin 2010).

For microorganisms to produce electricity in MFCs, the cells need to transfer electrons generated along their membranes to their surfaces. While anodes and cathodes can function in microbial respiration, research has been focused on understanding microbial anodic electron transfer. Anode-respiring bacteria catalyze electron transfer in organic substrates onto the anode as a surrogate for natural extracellular electron acceptors (e.g., ferric oxides or humic substances) by a variety of mechanisms (Lovley et al. 2004; Lovley 2006; Lovley 2008; Logan 2009). Microorganisms transfer electrons to anodes either directly or via mediated mechanisms. In a direct electron transfer, microorganism requires physical contact with the electrode for the current production. The contact point between the bacteria and the anode surface requires outer membrane-bound cytochromes or putatively conductive pili called nanowires. In mediated electron transfer mechanisms, bacteria either produce or take advantage of indigenous soluble redox compounds such as quinones and flavins to shuttle electrons between the terminal respiratory enzyme and the anode surface.

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MFCs have been successfully operated on a wide range of substrates, such as acetate, CO, H₂, glucose, galactose, butyrate, starch, marine sediments, swine wastewater, etc. (Pant et al. 2010; Hussain et al. 2011). In principle, any biodegradable material could be utilized as a fuel for electricity generation in an MFC. An ideal MFC can produce current while sustaining a steady voltage if a steady supply of substrate is maintained. MFCs do not need to use metal catalysts at the anode; instead, they use microorganisms (exoelectrogens) that biologically oxidize organic matter and transfer electrons to the electrode. Exoelectrogens, inoculated in MFCs for electricity generation, are found in marine sediment, soil, wastewater, freshwater sediment or activated sludge (Nevin et al. 2008).

The gasification of biomass at high temperatures leads to the generation of synthesis gas (syngas). Carbon monoxide (CO) and hydrogen account for 60-80% of the syngas composition with CH₄, CO₂, SO₂, H₂S and NH₃ present in smaller amounts (Sipma et al. 2006; Munasinghe and Khanal 2010). Syngas can be transformed into biofuels (such as ethanol, butanol, methane and hydrogen) that can be performed using the chemical as well as biological catalysts or by microbial transformation (Henstra et al. 2007; Tiquia 2014a; Pomaranski and Tiquia-Arashi 2016). It can also be used to generate electricity. The microbial transformation of CO/syngas is carried out by carboxydrotrophic bacteria. Carboxydrotrophic bacteria use CO as their sole carbon source (Henstra et al. 2007; Oelgeschlager and Rother 2008; Nguyen et al. 2013; Tiquia-Arashi 2014b). The ability of these microorganisms to oxidize and metabolize CO is connected to the existence of the enzyme CO-dehydrogenase (Henstra et al. 2007; Nguyen et al. 2013; Tiquia-Arashi 2014b) that is often found in carboxydrotrophic methanogens and acetogens (Sipma et al. 2006; Tiquia-Arashi 2014c) and result predominantly in methane and acetate production, respectively. The metabolic activity of carboxydrotrophic bacteria also results in the formation of H₂, ethanol, butyrate, butanol and acetate (Henstra et al. 2007; Nguyen et al. 2013; Tiquia-Arashi 2014d; Pomaranski and Tiquia-Arashi 2016). Some of these metabolic products can be utilized by exoelectrogens for electricity production in a mediatorless MFC in which the exoelectrogenic microorganisms transfer electrons to the anode via nanowires or self-produced mediators (Faaij et al. 1997; Steele et al. 2001; Song 2002; Liu and Logan 2004; Hussain et al. 2011; Tiquia-Arashi 2014d). This review focuses on recent advances that have been made in electricity production from CO/syngas in a thermophilic MFC accomplished by a consortium of carboxydrotrophic and CO-tolerant exoelectrogenic microorganisms.

2. Exoelectrogens

Exoelectrogens (e.g., anodophilic, electricigens or anode-respiring bacteria) are microorganisms that can transfer electrons extracellularly (Niessen et al. 2006). Different genetic groups of bacteria have shown exoelectrogenic activity in MFCs, including β -*Proteobacteria* (*Rhodospirillum rubrum*) (Chaudhuri and Lovley 2003), γ -*Proteobacteria* (*Shewanella* and *Pseudomonas*) (Kim et al. 1999, 2002; Ren et al. 2007), δ -*Proteobacteria* (*Aeromonas*, *Geobacter*, *Geopsychrobacter*, *Desulfuromonas*, and *Desulfobulbus*) (Bond et al. 2002; Holmes et al. 2004a, 2004b; Pham et al. 2003), *Firmicutes* (*Clostridium*) (Park et al. 2001) and *Acidobacteria* (*Geothrix*) (Bond and Lovley 2005). It has been demonstrated that cell-bound outer membrane cytochromes and conductive pili (nanowires) play a key role in electron transfer for some *Geobacter* and *Shewanella* species (Lovely et al. 2004; Reguera et al. 2005; Gorby et al. 2006). Alternatively, some exoelectrogens, such as *Pseudomonas aeruginosa* (Rabaey et al. 2004) and *Geothrix fermentans* (Bond and Lovley 2005), excrete mediators to shuttle electrons to surfaces. Many of the exoelectrogens that produce current in an MFC are dissimilatory metal-reducing bacteria, originally isolated based on their ability to reduce insoluble metals (e.g., Fe(III) or Mn(IV) oxides) in the natural environment (Lovley 2006; Logan and Regan 2006). *Geobacter sulfurreducens* secretes riboflavin in its monolayer biofilms that interact with outer membrane c-type cytochromes (OM c-Cyts) (Malvankar and Lovley 2012). It also produces conductive nanowires i.e., type IV pili (made up of PilA monomer units) and OM c-Cyts (chiefly OmcZ) that mediate the DET (Jayapriya and Ramamurthy 2012; Sneider et al. 2012). *S. oneidensis*, the most versatile exoelectrogen because of its ability to reduce diverse electron acceptors (Jain et al. 2012; Leung et al. 2013), secretes two types of flavins (riboflavin and flavin mononucleotide) that help to transfer the electrons exogenously to the electrode surface (Brutinel

and Gralnick 2012; Kotloski and Gralnick 2013). A single cell of *G. sulfurreducens* can generate ca. 90 fA amount of current in the MFC (Biffinger 2013), while *S. oneidensis* MR-1 can transfer the electrons to the anode surface across the cell membrane with a rate of $1.3 \times 10^6 \text{ e}^- \text{ cell}^{-1} \text{ s}^{-1}$ (Mclean et al. 2010). Thermophilic exoelectrogens have been reported in several studies (Choi et al. 2004; Wrighton et al. 2008; Marshall and May 2009; Fu et al. 2013a, Fu et al. 2013b; Fu et al. 2015).

3. Carbon Monoxide/Syngas as Substrates for Electricity Generation in MFCs

The possibility of electricity production from CO and syngas in an MFC has been demonstrated by Kim and Chang (2009) in a two-stage reactor system in which CO is first microbiologically converted to fermentation products (dominantly acetate) and subsequently fed to an MFC seeded with anaerobic sludge. A maximum power output of 1.6 mW L^{-1} (normalized to the total reactor volume) and coulombic efficiency (CE) of $\sim 5\%$ were reported. Mehta et al. (2010) for the first time reported the electricity generation in an MFC directly fed with CO or syngas (a mixture of CO and H_2). The maximum volumetric power output and coulombic efficiency achieved in their study were 6.4 mW L^{-1} and 8.7%, respectively. Although the overall performance of the MFC directly fed with CO or syngas was marginally better than the two-stage process utilized in the study of Kim and Chang (2009), it clearly demonstrated that the microbial communities of an MFC could utilize CO or syngas as the electron donor for electricity generation. However, the adoption of an efficient gas-liquid mass transfer mechanism and reactor design optimization need to be put in place for the performance of an MFC on CO/syngas.

Based on the analysis of metabolic products, Mehta et al. (2010) concluded that the production of electricity from CO or syngas in an MFC proceeds through a multi-step biotransformation process. Several concurrent pathways are hypothesized; one is the pathway involved in CO transformation to acetate by acetogenic carboxydrotrophic (CO-oxidizing) microorganisms followed by oxidation of acetate by CO-tolerant exoelectrogenic microorganisms. This pathway is hypothesized to be the foremost step responsible for electricity generation. Notably, the ability of the electricity-producing microorganisms to utilize H_2 as an electron donor has also been documented (Bond and Lovley 2003). Based on this observation a pathway of electricity production through H_2 and acetate followed by acetate conversion to electricity has been suggested. The experimental observations from the studies of Kim and Chang (2009) and Mehta et al. (2010) shows that the electricity production from syngas in an MFC poses several engineering and microbiological challenges pertaining to gas transfer limitations, selection and enrichment of microorganisms capable of efficient syngas transformation to electricity and selection of cathodic catalysts resistant to poisoning by CO and sulfur compounds. The subsequent sections of this chapter review the microbial communities and reactor designs suitable for MFC operation on CO/syngas at thermophilic temperatures.

4. Electricity Generation in Thermophilic CO/Syngas-Fed MFCs

The search for microorganisms that is capable of catalyzing the reduction of an electrode within a fuel cell has primarily been focused on bacteria that operate at mesophilic temperatures. However, anaerobic digestion studies have reported on the superiority of thermophilic operation and demonstrated a net energy gain in terms of methane yield. Microorganisms that function optimally under extreme conditions are beginning to be examined because they may serve as more effective catalysts (e.g. higher activity, greater stability, longer life, capable of utilizing a broader range of fuels) in MFCs. Considering that at the exit of the gasification process syngas temperature could be in a range of 45 to 55°C, the operation of the MFC at thermophilic temperatures might be preferable because it eliminates the need for syngas cooling and might lead to a higher biocatalytic activity (Jong et al. 2006; Mathis et al. 2008). The thermophilic conditions would also lead to a reduced oxygen solubility that is beneficial considering even trace amounts of unreacted O_2 diffusing through the cathode can inhibit the anaerobic carboxydrotrophic microorganisms which are highly sensitive to the presence of O_2 (Tiquia-Arashiro 2014d).

Although the exoelectrogens studied for the generation of electricity in an MFC are predominantly mesophilic (e.g., *Geobacter sulfurreducens* or *Geobacter metallireducens*), successful MFC operation under thermophilic conditions (50 to 55°C) has been demonstrated (Choi 2004; Jong et al. 2006; Hussain et al. 2011). Hussain et al. (2011) demonstrated for the first time that electricity can be generated in a thermophilic MFC fed with syngas. The thermophilic conditions led to a higher power density and improved syngas transformation efficiency as compared to a similar MFC operated under mesophilic conditions. The Coulombic CE is also improved to 20-26% as compared to 6-9% reported for the mesophilic MFC. The supply of CO to the anodic liquid was also improved (Hussain et al. 2011). Several reasons can be cited to explain the improved MFC performance under thermophilic conditions. Firstly, thermophilic conditions affect the activation, ohmic and diffusion losses at the anode. The activation losses contribute to 5-10% of the total internal resistance in a mesophilic MFC (Logan 2008; Zhang and Liu 2010). Secondly, the electrochemical reaction rates increase with increasing temperature and thus leading to lower activation losses. Thirdly, the higher temperature affects the diffusion of the substrates in the anodic liquid, thereby influencing the concentration losses that account for 45-50% of the total internal resistance of the MFC (Logan 2008; Zhang and Liu 2010). Likely, the operation of the syngas-fed MFC at thermophilic temperatures increases the transfer rate of CO and H₂ not only to the anodic liquid but also facilitates the transport of the dissolved gasses through the stagnant liquid layer adjacent to the anode fibers, thus reducing the diffusion losses. Overall, the internal resistance of the thermophilic MFC at optimized performance is less than 50 Ω, whereas the mesophilic MFC internal resistance is above 120 Ω (Mehta et al. 2010; Hussain et al. 2011). Finally, thermophilic conditions increase the activity of the microorganisms. Up to a certain temperature, the biomass growth and substrate conversion rates increase with temperature according to the Arrhenius relationship. In general, thermophilic microorganisms feature higher growth and reaction rates as compared to the mesophilic cultures (Min et al. 2008). Therefore, a higher carboxydrotrophic activity could be expected at thermophilic temperatures. In a mesophilic CO-fed MFC, the step of CO conversion to acetate appeared to limit the overall transformation rate (Mehta et al. 2010). Another advantage of the thermophilic process is the reduced O₂ solubility at elevated temperatures. While most of the O₂ diffusing through the cathode surface is consumed by the cathodic reaction, the residual O₂ diffuses to the anodic liquid and thus results in the inhibition of the anodophilic and carboxydrotrophic populations (Oelgeschlager and Rother 2008) as well as competes with the anode as the final electron acceptor. The presence of trace amounts of O₂ in the anodic chamber is observed to significantly impair the power output of the mesophilic syngas-fed MFC (Hussain et al. 2011).

Mathis et al. (2008) studied thermophilic bacteria selected from sediments that 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 *Firmicutes*. Interestingly, 48 clones (out of 64) of *Firmicutes* had RFLP patterns and sequences (99%) most similar to that of *Thermincola carboxydophila*, a hydrogenogenic CO-oxidizing thermophilic microorganism (Mathis et al. 2008). These findings indicate that temperate aquatic sediments are a good source of thermophilic electrode-reducing bacteria. *Firmicutes* spp. have been also identified during thermophilic MFC operation by Wrington et al. (2008) whose findings provided a detailed analysis of microbial community dynamics in an acetate-fed MFC inoculated with sludge collected from a thermophilic anaerobic digester. Several thermophilic metal-reducing bacteria have been studied including *Ferroglobus placidus* and *Geoglobus ahangari* that can grow at 85°C by coupling acetate oxidation to Fe (III) reduction (Tor et al. 2001). *Deferribacter thermophilus* (isolated from a petroleum reservoir in the UK) grows by the reduction of Fe (III) and 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). The bacterium, *Geothermobacter ehrlichii* (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 of 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* (Zavarzina et al. 2007). Population analysis of the exoelectrogenic

microorganisms suggests a possible involvement of *Caloramator*-related bacteria in electricity generation (Fu et al. 2013b). Pure culture of *Caloramator australicus* shows electricity-generating ability, indicating that the bacterium is a new thermophilic exoelectrogen (Fu et al. 2013b). Overall, this broad range of thermophilic exoelectrogens might be capable of forming a syntrophic consortium with thermophilic carboxydrotrophic microorganisms for efficient operation of a syngas-fed MFC.

5. Thermophilic Carboxydrotrophs

The utilization of CO by thermophilic carboxydrotrophs is catalyzed by Ni-containing CO dehydrogenases (CODHs) and acetyl-CoA synthases (ACSs). CODHs and CODH/ACS complexes are widespread among anaerobes and are found in acetogens, methanogens, sulfate reducers and iron reducers. CODH/ACS complexes catalyze both catabolic and anabolic acetyl-CoA synthesis and cleavage reactions in which CO is an intermediate that travels along a hydrophobic channel between the CODH and ACS active sites (Ragsdale 2004).

Many acetogens can grow on CO (Drake et al. 2006). CO conversion has been documented for 10 acetogens, including four moderate thermophiles e.g., *M. thermoacetica*, *Moorella thermoautotrophica*, *Thermoanaerobacter kivui* and *Moorella perchloratireducens*, described by Balk et al. (2008). *Moorella thermoautotrophica* and *M. thermoacetica* can grow on CO at high partial pressures as the sole energy source (Savage et al. 1987; Daniel et al. 1990).

The methanogenic carboxydrotrophs identified by Hussain et al. (2012) in syngas-fed MFC operated at 50°C include *Methanothermobacter wolfeii*, *Methanothermobacter thermoautotrophicum* and *Methanobrevibacter arboriphilicus*. These microorganisms use H₂ and CO₂ for growth and CH₄ formation (Daniels et al. 1977; Winter et al. 1983). The ability of *M. thermoautotrophicum* and *M. arboriphilicus* to remove CO in the gas phase while growing on CO₂ and H₂ has been reported by Daniels et al. (1977), who found that *M. thermoautotrophicum* can utilize CO as the sole energy source by disproportionating CO to CO₂ and CH₄. This ability can be attributed to the presence of carbon monoxide dehydrogenase (CODH) and acetyl-CoA synthase (ACS) in the microorganism, the two metalloenzymes fundamental for growth on CO (Oelgeschlager and Rother 2008). The other uncultured archaea identified in the MFC that possess the hydrogenotrophic pathway for CH₄ formation belong to the genera *Methanobacterium* and *Methanobrevibacterium* (Wasserfallen et al. 2000).

The capacity of some sulfate-reducing bacteria to oxidize CO at low concentrations (4–20%) is long known (Yagi 1959). CO conversion by four thermophilic sulfate-reducing bacteria—*Desulfotomaculum thermoacetoxidans* CAMZ (DSM 5813) (Min and Zinder 1990), *Thermodesulfovibrio yellowstonii* ATCC 51303 (Henry et al. 1994), *Desulfotomaculum kuznetsovii* DSM 6115 (Nazina et al. 1988; Nazina et al. 1999), and *Desulfotomaculum thermobenzoicum* subsp. *thermosyntrophicum* DSM 14055 (Plugge et al. 2002)—was studied in pure cultures and co-cultures with the thermophilic hydrogenogenic carboxydrotrophic bacterium *C. hydrogenoformans* (Parshina et al. 2005).

Dissimilatory Fe(III)-reducing thermophilic bacteria such as *Thermosinus carboxydovorans*, *Carboxydotherrmus ferreducens*, *Carboxythermus siderophilus* and *Thermicola ferriacetica* produce H₂ during the oxidation CO to CO₂. *Thermosinus carboxydovorans* grows at temperatures between 40 and 68°C (with an optimum at 60°C). This bacterium can utilize CO as its sole energy source with a doubling time of 1.15 hours leading to the formation of H₂ and CO₂ in equimolar quantities. Fe (III) is also reduced during its growth on sucrose and lactose. The dissimilatory Fe(III)-reducing, moderately thermophilic bacterium *Carboxydotherrmus ferreducens* (Slobodkin et al. 2006) can grow by utilizing organic substrates or H₂ as electron donors. Apart from Fe(III) or AQDS, it can also reduce sulfite, thiosulfate, elemental sulfur, nitrate and fumarate (Slobodkin et al. 1997; Henstra and Stams 2004). *Carboxydotherrmus ferreducens* can grow on CO, without hydrogen or acetate production, with ferrihydrite as the electron acceptor, forming magnetite precipitate (Slobodkin et al. 2006) or with AQDS or fumarate as electron acceptors (Henstra and Stams 2004). *Carboxydotherrmus siderophilus* (isolated from hot spring of Geyser Valley) produces H₂ and CO₂ along with Fe (III) and AQDS reduction during its growth on CO (Slepova

et al. 2009). *Thermicola ferriacetica* (isolated from ferric deposits of a terrestrial hydrothermal spring in Kunashir Island, Russia) utilizes H₂ and acetate as energy sources with Fe (III) serving as the electron acceptor. It is also able to grow in an atmosphere of 100% CO as the sole energy source, leading to the formation of H₂ and CO₂. However, it requires 0.2 g L⁻¹ of acetate as its carbon source during its growth on CO (Zavarzina et al. 2007).

Carboxydrotrophic hydrogenogenic microorganisms are capable of lithotrophic metabolism based on the reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ (Svetlitchnyi et al. 2001). All thermophilic hydrogenogenic CO oxidizers isolated so far are obligate anaerobes, including *Thermolithobacter carboxydivorans*, *Carboxydotherrmus hydrogeniformans*, *Thermincola carboxydophila*, *Carboxydocella thermoautotrophica*, *Thermolithobacter carboxydivorans* and *Carboxydibrachium pacificum*, that produce H₂ from CO oxidation under thermophilic growth conditions (Slepova et al. 2006; Sokolova et al. 2007; Sokolova et al. 2009; Sokolova and Lebedinsky 2013; Tiquia 2014d).

Similar to the mesophilic co-culture, a co-culture of the thermophilic CO-utilizing acetogens, methanogens, sulfate reducers, iron reducers and hydrogenogens mentioned above can be co-cultured with H₂ utilizing thermophilic exoelectrogens for electricity generation in a syngas-fed MFC.

6. Design Considerations of MFCs Operating at Thermophilic Temperatures

Although the majority of MFCs have been tested at ambient or mesophilic temperatures, thermophilic systems warrant evaluation because of the potential for increased microbial activity rates on the anode. MFC studies, at elevated temperatures, have been scattered and most used designs that are already established, including the air-cathode single chambers and two-chamber designs. Previous modular MFC design by Rismani-Yazdi et al. (2007) have shown to work under mesophilic conditions (39°C) but failed at 60°C possibly because this design is not a closed system and permitted evaporation from the cathode chamber. Between 50 to 70% of the anode working volume was lost within two days. The concentrated anolyte can be detrimental to microbial metabolism and activity due to the enrichment of metabolites and cell debris. Thermophilic studies have not addressed these problems other than to note periodic anolyte and catholyte replacement (Mathis et al. 2008; Marshall and May 2009).

Jong et al. (2006) utilized a continuous flow rather than batch or fed-batch that allowed constant replacement of anolyte and catholyte in the thermophilic mediatorless MFC. The best MFC performance was achieved with 338 cm³ h⁻¹ and 11 cm³ h⁻¹ catholyte and anolyte flow rates, respectively. The catholyte required a higher flow rate likely due to the continuous evaporation of liquid from the open cathode chamber. A maximum power density of 1030 ± 340 mW/m² was generated continuously at 55°C with an anode retention time of 27 minutes (11 mL h⁻¹) and continuous pumping of air-saturated phosphate buffer into the cathode compartment at the retention time of 0.7 minutes (450 mL h⁻¹). While the constant replacement of anolyte and catholyte prevents the drastic liquid loss, electricity production relies on the electrochemically active biofilm alone since suspended cells are removed with the continuous flow of the anolyte. Several MFC studies have tested a range of operating temperatures and demonstrated consistently higher power densities with higher temperatures within the limits of the microbial populations (Choi 2004; Moon et al. 2006).

Carver et al. (2011) described a thermophilic MFC design that prevents evaporation that is based on the original concept elucidated by Min et al. (2008). The MFC utilized an anaerobic, glass reactor design in combination with a cathode chamber submersed in anolyte. Rather than having extensive layers of gaskets, membrane, carbon paper and polycarbonate as in the previous design (Min et al. 2008), the cathode chamber has a single rubber o-ring that prevents liquid or air crossover. The components of the cathode assembly, including the stainless screws, foil and graphite discs, have all been shown to be conducive and were securely connected. Analyses of the glucose-fed thermophilic MFC showed improved performance over 120 hours with increased maximum power of 3.3-4.5 mW m⁻² (Carver et al. 2011). The polarization curve has three distinct sections of irreversible voltage losses: activation loss,

ohmic loss and mass transfer loss. The typical initial and drastic voltage drop was not apparent, indicating lower than normal activation losses (Carver et al. 2011). This is attributed to increased reaction rates at thermophilic temperatures that lowered the activation energy and therefore the voltage necessary to maintain active anaerobic metabolism. Ohmic loss can be observed in the center of the polarization curve with the gradual decrease of voltage as current density increases (Carver et al. 2011). The slope of this overpotential section, equivalent to the voltage over current, yields an internal resistance of $9.25 \pm 0.15 \Omega$. This value is in the general range reported for other MFCs although the experimental conditions are not comparable among the studies reviewed in the literature (He et al. 2005; Ieropoulos et al. 2010). The work by Carver et al. (2011) suggests the potential for stable, thermophilic MFC operation although optimization of biological and engineering components is necessary prior to the application of the design.

A CO or syngas-fed MFC system requires a CO-tolerant cathode. Mehta et al. (2010) used a CoTMPP cathode to generate electricity from CO with a Co load of 0.5 mg cm^{-2} . A maximum power density of 6.4 mW L^{-1} was reported. 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.

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

7. Conclusions

Electricity generation from CO/syngas predominantly takes place by a two-step process in which syngas is first converted to acetate that is then oxidized by the exoelectrogenic microorganisms to produce electricity. This pathway is accomplished by a syntrophic association of exoelectrogenic and carboxydrotrophic microorganisms. With the performance of a syngas-fed MFC with mixed cultures already demonstrated, a detailed study of the CO-operated MFC might be of interest and warrant exploration. Studies can focus on (1) improving gas transfer efficiency, (2) understanding the complex transformation pathways in mixed cultures/co-cultures under thermophilic conditions and (3) determining the energetics of syntrophic cooperation between thermophilic carboxydrotrophs and exoelectrogens.

The benefits of operating biochemical systems at thermophilic conditions include higher microbial activity, better substrate solubility, higher mass transfer rate and lower risk of contamination. However, one drawback is higher rates of evaporation. This review noted two answers to this problem are possible, either to run the MFC in continuous mode allowing replacement of the anolyte and catholyte or to utilize an MFC that precludes evaporation as designed by Carver et al. (2011). Further development will likely result in more efficient reactor designs and stackable MFC capable of efficient operation on gaseous substrates such as CO and H_2 and with power outputs suitable for commercial applications.

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