Application of Biocathodes in Microbial Fuel Cells: Opportunities and Challenges

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The heavy reliance on fossil fuels, especially oil and gas has triggered the global energy crisis. Continued use of petroleum fuels is now widely recognized as unsustainable because of their depleting supplies and degradation to the environment. To become less dependent on fossil fuels, current world is shifting paradigm in energy by developing alternative energy sources mainly through the utilization of renewable energy sources. In particular, bioenergy recovery from wastes with the help of microorganism is viewed as one of the promising ways to mitigate the current global warming crisis as well as to supply global energy. It has been proved that microorganism can generate power by converting organic matter into electricity using microbial fuel cells (MFCs). MFC is a bioelectrochemical device that employs microbes to generate electricity from bio-convertible substrate such as wastewaters including municipal solid waste, industrial, agriculture wastes, and sewage. Sustainability, carbon neutral and generation of renewable energy are some of the major features of MFCs. However, the MFC technology is confronted with a number of issues and challenges such as low power production, high electrode material cost and so on. This paper reviews the recent developments in MFC technology with due consideration of electrode materials used in MFCs. In addition, application of biocathodes in MFCs has been discussed.

Key words: Microbial fuel cell, Electricity, Sustainability, Economic, Biocathode

Introduction

Universally, energy is recognized as fundamental inputs for social and economic activities (Bauen, 2006; Mulder and Tembe, 2008; Katuwal and Bohara, 2009). Thus, per capita energy consumption is considered as one of the major determinants for wealth and quality of life for a nation (Bauen, 2006; Katuwal and Bohara, 2009). Global primary energy supply in 2009 was 12,150 Mtoe in which more than 80% of the energy demand is met by fossil fuels sector (Fig. 1) (Weiland, 2010; IEA, 2011). Till date, fossil fuels play pivotal role in meeting the global energy demand both in developed and developing countries (Bauen, 2006; Umbach, 2010). In recent years, the global energy demand has increased rapidly mainly due to economically booming developing countries like China, Brazil and India (Geller et al., 2004; Bauen, 2006; Umbach, 2010; Leung, 2011). Energy scientists have predicted that global energy demand will continue to rise

during this century by a factor of two to three (IEA, 2006).

Nevertheless, use of fossil fuels confronted with a number of major issues and challenges mainly due to fuel-derived CO_2 emissions and burning of coals that increase the concentrations of green house gases (GHGs) in the atmosphere (IPCC, 2000; Bauen, 2006; Weiland, 2010). The rapid increase in consumption of fossil fuels has already shown detrimental impacts to environment by polluting air, water and soil (IPCC, 2000; Bauen, 2006). In addition, majority of the fossil fuels are concentrated in
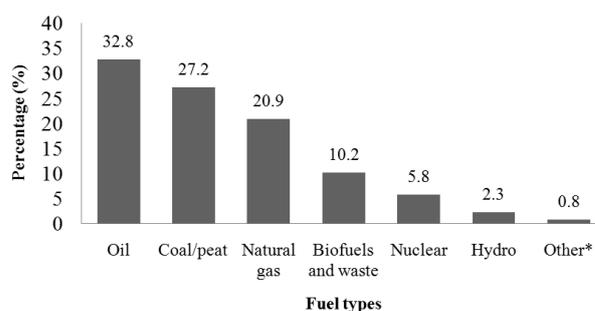
*other includes geothermal, solar, wind and heat, etc.

Fig. 1. World total primary energy supply by fuel type in 2009 (IEA, 2011).

the politically unstable regions such as in Middle East, which can further worsen the global energy security (Umbach, 2010; Weiland, 2010).

The growing demand for energy, depletion of fossil fuels, hike in oil price and increasing concerns of environmental issues have challenged scientists to develop new technological processes to generate clean and sustainable energy mainly through the utilization of renewable energy sources (Bauen, 2006; Logan et al., 2006; Umbach, 2010). In this regard, the recovery of renewable energy from waste biomass such as food wastes, residues and energy crops will play a key role in mitigating the global warming as well as supply alternative energy (Weiland, 2010). This paper was written with due consideration of recent developments in microbial fuel cell (MFC) technology highlighting the electrode materials used in MFC. In addition, application of biocathodes in MFCs for recovering renewable energy from organic substrates has been discussed.

Depending on the end-use applications, microorganism can produce fuels like ethanol, methanol and hydrogen from organic matter (Oh and Logan, 2005; Mohan et al., 2007). It has been reported that microorganism can also generate power by converting organic matter into electricity using MFCs (Potter, 1931; Berk, 1964; Rao et al., 1976; Logan et al., 2006). MFC is a bioelectrochemical device that employs microbes to generate electricity from bio-convertible substrate such as wastewaters including municipal solid waste, industrial and agriculture wastes, and sewage (Min et al., 2005; Oh and Logan, 2005; Logan et al., 2006). In recent years, bioelectricity generation through MFC using variety of substrates is being studied extensively.

A conventional two chamber MFC consists of anode and cathode compartments separated by cation specific membrane (proton exchange membrane; PEM) (Logan et al., 2006). The anode compartment is typically maintained under anoxic conditions, whereas the cathode compartment can be suspended in aerobic solutions or exposed to air (Rabaey and Verstraete, 2005a; He and Angenent, 2006; Logan et al., 2006). Microbes in the anode compartment oxidize fuel (electron donor) generating electron (e^-) and proton (H^+) through the anaerobic respiration of organic substrates (Logan et al., 2006; Wrighton and Coates, 2009). Electrons are transferred to the cathode compartment through an external circuit and the proton through the membrane (Wrighton and Coates, 2009; Huang et al., 2011a). Electrons and protons are

consumed in the cathode compartment, reducing oxygen to water (Rabaey and Verstraete, 2005a). The potential difference between the respiratory system and electron acceptor generates the current and voltage needed to generate electricity (Logan et al., 2006; Mohan et al., 2007).

Although abiotic cathodes such as ferricyanide and manganese are effective in transferring electrons to oxygen as the terminal electron acceptor, these substances are expensive and not applicable for real time applications in MFCs (Rabaey and Verstraete, 2005a; Logan et al., 2006; Rismani-Yazdi et al., 2008; Zhou et al., 2011). In recent years, researchers are able to circumvent this problem by developing biocathode as an alternative to chemical cathodes (He and Angenent, 2006; Clauwaert et al., 2007a; Clauwaert et al., 2007b). Biocathode has provided new door in the field of MFC, where bacteria are used as catalysts to recover electrons directly from the cathode which are then transferred to a final electron acceptor such as oxygen, nitrogen, sulphur, carbon dioxide, etc., (He and Angenent, 2006). Low cost, good stability, sustainability and multiple functions for wastewater treatment are the important characteristics of biocathodes (He and Angenent, 2006; Huang et al., 2011a; Wei et al., 2011a; Wei et al., 2011b).

Application of Microbial Fuel Cells (MFCs)

In recent years, MFC technology is considered as potential technology for generating electricity using waste biomass, especially wastewaters (Liu et al., 2004; Min and Logan, 2004; Min et al., 2005; Oh and Logan, 2005; Lu et al., 2009). Use of wastewaters as substrates in MFCs have emerged as promising technology to meet increasing energy needs, which can generate electricity and treat wastewater simultaneously thereby reducing the operational costs of wastewater treatment plant (Huang and Logan, 2008; Li et al., 2008; Wang et al., 2008; Lu et al., 2009; Mohanakrishna et al., 2010; Nam et al., 2010; Pant et al., 2010; Zhou et al., 2011). In general, MFCs have very broad range of application including electricity generation, bio-hydrogen production, wastewater treatment, biosensors and bioremediation (Logan et al., 2005; Oh and Logan, 2005; Rozendal et al., 2008; Liu et al., 2011; Sun et al., 2011). Table 1 summarizes the use of MFCs in wastewater treatment.

As depicted in the Table 1, different wastewaters can

Table 1. Use of MFCs in real wastewater treatment.

Anode material	Cathode material	Wastewater	P_{max}	COD removal	References
			mW m^{-2}	%	
Carbon paper	Carbon cloth[a]	Domestic sewage	22	43	(Min and Logan, 2004)
Carbon paper	Carbon cloth[a]	Food-processing wastewater	81	95	(Oh and Logan, 2005)
Carbon paper	Carbon paper[a]	Swine wastewater	261	92	(Min et al., 2005)
Carbon paper	Carbon paper[a]	Starch wastewater	239.4	98	(Lu et al., 2009)
Carbon cloth	Carbon cloth[a]	Brewery wastewater	205	87	(Wang et al., 2008)
Graphite fiber brush	Graphite fiber brush	Paper-recycling wastewater	672	29	(Huang and Logan, 2008)
Carbon felt	Graphite paper	Electroplating wastewater	1600	99.5	(Li et al., 2008)
Activated carbon+carbon cloth	Carbon cloth[a]	Fermented wastewater	2981	93	(Nam et al., 2010)
Graphite plate	Graphite plate	Distillery wastewater	124.35	72.8	(Mohanakrishna et al., 2010)
Graphite rod	Carbon cloth[a]	Primary clarifier effluent	26	80	(Liu et al., 2004)

[a]Pt coated.

be treated in MFCs, in which the COD removal efficiencies differ from MFC to MFC (the COD removals vary from 30% to 98%). Nevertheless, domestic wastewaters might be the most common substrates for MFCs, which is important source of sewage (Min and Logan, 2004; Zhou et al., 2011). In addition, use of MFCs in wastewater treatment has many advantages such as high theoretical energy conversion rate, less sludge production and no gas processing require as compared to other biological wastewater treatment processes (Zhou et al., 2011).

Although electrochemical reactions in MFCs are comparable, the overall performance of a MFC is influenced by various factors such as pH, temperature, ionic strength, electrode materials, electrode spacing, reactor size, electron acceptor, substrates, circuit resistance, proton transfer through the membrane and so on (Liu et al., 2005; Logan et al., 2006; Oh and Logan, 2006; Rismani-Yazdi et al., 2008; Wei et al., 2011a). For example, when the anodic potential is very low, bacteria will switch to fermentation and can extract only one-third of the electron available in the substrate (Rabaey and Verstraete, 2005a). On the other hand, if the anodic potential is very high, bacterial growth is encouraged thereby shortening the lag phase

for generation of electricity (Aelterman et al., 2008).

Anode materials used in MFCs

Different configurations of MFCs are being constructed to generate electricity in which anode and cathode electrodes are made up of different materials (Logan et al., 2006). However, a good anode material should have some novel characteristics such as good electrical conductivity, biocompatibility, large surface area, chemical stability and appropriate mechanical strength (Logan et al., 2006; Zhou et al., 2011). Carbon materials such as carbon paper, carbon felt, carbon cloth, graphite rod, graphite fiber brush, graphite granules and so on are the commonly used electrode materials in MFCs (Logan et al., 2006; Zhou et al., 2011; Wei et al., 2011b). Graphite rods or plates are the most widely used materials for anode electrodes due to their excellent electrical conductivity, chemical stability, easy to handle and relatively cheap (Logan et al., 2006; Zhou et al., 2011). It is reported that roughened graphite electrode produces a higher power density compared to flat graphite electrodes (Ter Heijne et al., 2008).

In recent years, anode electrode has been modified using different materials to provide better bacterial adhesion and electron transfer to the anode surface (Wei et

Table 2. Summary of anode modification methods and the improvement in performance of MFCs.

Base material	Treatment methods	Treatment	Improvement	References
Carbon clothes	Surface treatment	NH_3 gas treatment	20% increase in power density, reduce start-up time by 50%	(Cheng and Logan, 2007)
Graphite felt	Surface treatment	HNO_3 treatment	Power density increase by 2-fold	(Scott et al., 2007)
Carbon mesh	Surface treatment	Heat treatment	Power density increase by 3%	(Wang et al., 2009)
Carbon brush	Surface treatment	H_2SO_4 treatment	Power density increase by 8%	(Feng et al., 2010)
Graphite felt	Surface treatment	Electrochemical oxidation	Current density increase by 39.5%	(Tang et al., 2011)
Carbon paper	Surface coating	Carbon nanotube	Power density increase by 20%	(Sun et al., 2010)
Glassy carbon	Surface coating	Carbon nanotube	Current density increase by 82 fold	(Peng et al., 2010)
Carbon brush	Surface treatment	Heat and acid treatment	Power density increase by 25%	(Feng et al., 2010)
Carbon brush	Surface treatment	Heat treatment	Power density increase by 25%	(Feng et al., 2010)
Graphite felt	Surface coating	Polyaniline	Power density increase by 1.8 fold	(Scott et al., 2007)
Graphite plates	Surface coating	NR	Power density reached 900 mW/m^2	(Wang et al., 2011)
Carbon paper	Surface coating	Iron oxide	Power density increase 2.75-fold	(Kim et al., 2005)
Graphite disk	Surface coating	Au nanoparticle	Current density increase 20-fold	(Fan et al., 2011)
Graphite disk	Surface coating	Pd nanoparticle	Current density increase by 50-150%	(Fan et al., 2011)

al., 2011b). Table 2 shows the summary of treatment methods of anode modification and improvement in the performance of the MFCs. The most common methods of modification for anode electrode are: surface treatment with physical or chemical methods, addition of highly conductive or electro-active coatings and use of metal-graphite composite (Kim et al., 2005; Cheng and Logan, 2007; Scott et al., 2007; Wang et al., 2009; Feng et al., 2010; Peng et al., 2010; Sun et al., 2010; Fan et al., 2011; Tang et al., 2011; Wang et al., 2011; Wei et al., 2011b). For example, Cheng and Logan (2007) modified the carbon cloth using surface treatment method. They treated a carbon cloth using 5% NH_3 gas in a helium carrier gas at 700℃, and this surface treatment method increased power 1640 to 1970 mW m^{-2} and reduced the start-up time by 50%.

Cathode materials in MFCs

The performance efficiency of a MFC is also greatly influenced by the cathode materials (Logan et al., 2006). Graphite, carbon cloth and carbon paper are the commonly used cathode materials in MFCs (Logan et al., 2006; Zhou et al., 2011). As depicted in the Table 3, oxygen is the most popular terminal electron acceptor in a MFC because of its abundance and high standard redox potential as well as produces no byproducts (Logan et al., 2006; Rismani-Yazdi et al., 2008). However, incomplete reduction of oxygen results in low energy conversion efficiency of a MFC (Rismani-Yazdi et al., 2008). Highly active catalyst such as Pt is used to increase the reduction rate of oxygen and reduce the cathodic reaction activation energy (Logan et al., 2005; Cheng et al., 2006; HaoYu et al., 2007; Watanabe, 2008; Erable et al., 2009; Deng et al., 2010; Zhang et al., 2010). However, use of Pt is not sustainable for actual applications due to its high cost and possible poisoning by components in the substrates solution (Bard and Faulkner, 2001; Zhou et al., 2011).

Chemical such as ferricyanide ($K_3[Fe(CN)_6]$) is used as an alternative electron acceptor to enhance the cathodic reduction reaction in MFCs (Park and Zeikus, 2003). Ferricyanide has faster reduction kinetics as compared to dissolved oxygen on the cathode and has relatively large redox potential (Park and Zeikus, 2003; Oh and Logan, 2006; Rismani-Yazdi et al., 2008). Use of ferricyanide as terminal electron acceptor in the cathode chamber increases the power by 1.5 to 1.8 times compared to Pt-coated cathode and dissolved oxygen in H-type reactor (Oh and Logan, 2006). Although use of ferricyanide as electron acceptor in the cathode can increase the power significantly, it has some drawback as well (Logan et al., 2006). Since ferricyanide has to be regenerated chemically, it is not sustainable for real applications (Rabaey et al., 2005b; Logan et al., 2006). Moreover, use of ferricyanide in the cathode chamber for long term operation can affect the system by diffusing across the PEM and into anode chamber (Logan et al., 2006). Thus, use of ferricyanide as

Table 3. Comparison of the maximum power density obtained from MFCs with different cathodic catalysts.

Cathode material	Catalyst	Electron acceptor	Maximum power density	References
Carbon clothes, Nafion (binder)	Pt	O_2	400-480 mW/m^{2a}	(Cheng et al., 2006)
Stainless steel mesh	Pt	O_2	1610 mW/m^{2a}	(Zhang et al., 2010)
Carbon clothes, PTFE (binder)	Pt	O_2	331-360 mW/m^{2a}	(Cheng et al., 2006)
Carbon cloth	Pt	O_2	474 mW/m^2	(HaoYu et al., 2007)
Activated carbon fiber felt		O_2	315 mW/m^{2b}	(Deng et al., 2010)
Nitric acid and thermal activated graphite		O_2	8.1 W/m^{3c}	(Erable et al., 2009)
Carbon paper	Pt	O_2	33 mW/m^{2d}	(Logan et al., 2005)
Carbon cloth	CoTMPP	O_2	369 mW/m^{2a}	(Cheng et al., 2006)
Carbon cloth	CoTMPP	O_2	483 mW/m^2	(HaoYu et al., 2007)

[a]projected area of cathode, [b]cross-sectional area of separator, [c]cathode liquid chamber volume, [d]anode area, PTFE=polytetrafluoroethylene, CoTMPP= cobalt tetramethoxyphenylporphyrin.

reducing agent in the cathode chamber is not applicable for large- scale MFCs.

Application of biocathode in MFCs

In recent years, biocathode has become a rapidly emerging research topic in MFC, which provides opportunity to enhance the economic viability and environmentally sustainability of MFC systems by eliminating the use of noble metal, such as Pt for oxygen reduction (Sun et al., 2011; Huang et al., 2011a). Apart from recovering electricity, the biocathode also has potential approach for wastewater treatment and biosynthesis where bacteria reduce metals such as Cr^{6+}, Fe^{3+}, Mn^{4+} and nutrients including nitrogen and sulfur from wastewater due to its variety of terminal electron acceptors in the cathode (Rhoads et al., 2005; He and Angenent, 2006; Sun et al., 2011; Wei et al., 2011b). Similar to abiotic cathodes, carbonaceous materials are also the most widely used materials for cathode electrodes in biocathodes (Wei et al., 2011b). At present carbon-based materials like graphite plate, carbon felt, granular graphite, graphite fiber brush, glassy carbon, gassy carbon rod and graphite felt are used in biocathodes. (Lojou et al., 2002; Strycharz et al., 2008; Cheng et al., 2009; You et al., 2009; Aulenta et al., 2010; Cournet et al., 2010; Jeremiasse et al., 2010; Steinbusch et al., 2010; Villano et al., 2010). In addition stainless steel mesh is also used as cathode electrode in biocathode for power generation (Dumas et al., 2008).

Clauwaert and his colleagues developed a microbial biocathode as a potential alternative for noble catalysts such as Pt at which bacteria catalyze the electron transfer

from the cathode to electro positive terminal electron acceptors (Clauwaert et al., 2007a). This biocathode was obtained by enriching a biofilm of different types of aerobic and anaerobic sludge and sediment on granular graphite and they obtained power density of 10 W m^{-3} using nitrate as the terminal electron acceptor. Wei et al. (2011a) operated MFCs with two inexpensive semicoke and activated carbon packed bed biocathode. Using semicoke and activated carbon packed biocathode; they obtained a maximum power density of 20.1 W m^{-3} and 24.3 W m^{-3}, respectively. In another study, Mao et al. (2010) operated a biocathode MFC biocatalyzed by ferro/manganese- oxidizing bacteria and obtained the maximum power density of 32 W m^{-3}

Huang et al. (2011b) evaluated the biocatalytic cathode materials in tubular MFCs for reducing Cr^{6+} and subsequent generation of electricity. They observed that at cathode to anode surface area ratio of 3, specific Cr^{6+} reduction rates ranging from 12.4 to 20.6 mg g^{-1} VSS h^{-1} and power generation from 6.8 to 15 W m^{-3} were achieved using the biocatalytic graphite fiber cathode MFCs. Zhang et al. (2012) operated biocathodes into a three-chamber MFC to generate electricity from sewage sludge and reported maximum power density of 13.21.7 W m^{-3} during polarization. Very recently, Chen et al. (2012) operated sediment MFC using biocathode that was buried in the rice rhizosphere and found to be capable of delivering electrons to root excreted oxygen for oxygen reduction reactions.

The practical voltage obtained in MFC is always less than the voltage predicted thermodynamically mainly due to three reasons; activation losses, ohmic losses and mass

transport losses (Rismani-Yazdi et al., 2008; Rozendal et al., 2008). In case of abiotic cathode, efforts have been made in minimizing the internal resistances by modifying the reactor configuration (Liu et al., 2005; Rismani-Yazdi et al., 2008; Mao et al., 2010). However, in biocathode there was apparent decrease in activation losses at oxygen-reducing biocathodes since bacteria accelerate cathodic electron transition in biocathode (Chen et al., 2008; You et al., 2009; Mao et al., 2010). Chen et al. (2008) observed that during the growth of bacteria in both anode and cathode chambers, the internal resistance reduced from 40.2 to 14.0 Ω. You et al. (2009) observed that the charge transfer resistance of the cathode decreased from 188 to 17 Ω with the use of aerobic inoculation of electrochemically active bacteria in biocathode. In addition, Mao et al. (2010) obtained internal resistance of 14 Ω while operating MFC biocathode using ferro/manganese-oxidizing bacteria.

Electron transfer mechanism in biocathode

Electricity can be produced from MFC technology when microorganism switch from the natural electron acceptor (oxygen or nitrate) to an insoluble electron shuttles (Rabaey and Verstraete, 2005a; Rabaey et al., 2011). For this to be happened, electrons have to be transferred from central metabolism extracellulary to the electrode that will enable cellular respiration in an MFC and conversion of substrates (electron donors) to CO_2 (Bond and Lovley, 2003; Franks et al., 2010). Similar to electron transfer mechanism in bioanode MFCs, two mechanisms have been reported in biocathode, namely direct and indirect electron transfer (Rosenbaum et al., 2011; Huang et al., 2011a). Direct electron transfer requires a physical contact between the microorganism and the cathode electrode surface, in which electrons move between the bacterial cell and the cathode electrode (Bond and Lovley, 2003; Wrighton and Coates, 2009; Rosenbaum et al., 2011; Huang et al., 2011a). The outer membrane redox macromolecules such as cytochromes play a pivotal role in direct biocatodic electron transfer between the bacterial cell membrane and the cathode electrodes surface (Huang et al., 2011a). Several electro-chemically active microorganism have been identified that can transfer electrons directly to the cathode surface thereby by eliminating the need for a mediator in an MFC (Franks et al., 2010). This kind of electron transfer

mechanism was best studied with the *Geobacter* species or other mixed cultures, where different compounds such as CO_2, fumarate, nitrate, O_2, Cr^{6+}, U^{6+}, or tetrachloroethene are used as terminal electron acceptor (Gregory and Lovley, 2005; Dumas et al., 2008; Cao et al., 2009; Tandukar et al., 2009).

In the case of indirect electron transfer, microorganism itself cannot transfer electron to the cathode electrode, however, they acquire reducing power via soluble or miscible shuttles (Park and Zeikus, 1999; Huang et al., 2011a). Electrochemically inactive bacterial cells excrete or they can excrete redox-active compounds to carry out indirect electron transfer with electrodes (Rosenbaum et al., 2011; Huang et al., 2011a). Apart from self-excreted redox-active compounds, chemical mediators such as neutral red, methyl viologen, thionine, methylene blue, etc., have been used to indirectly accept electrons from the electrode (Park and Zeikus, 1999; Bond et al., 2002; Huang et al., 2011a). Because of such great versatility of electron acceptors in the cathode chamber, there is a great possibility to promote the application of biocathodes in MFCs, which is crucial for scale up and commercialization of MFCs (Aulenta et al., 2010; Cournet et al., 2010; Villano et al., 2010).

Type of biocathode

Depending on the terminal electron acceptor adopted in the cathode, biocathode can be classified as aerobic and anaerobic (Sun et al., 2011). Oxygen is used as the terminal electron acceptor in an aerobic biocathode (Sun et al., 2011). Microorganisms can also assist in the oxidation of transition metal compounds such as Mn^{2+}/Mn^{4+} or Fe^{2+}/Fe^{3+} by catalyzing the re- oxidation of redox couples from cathode to oxygen, resulting oxygen reduction (Bergel et al., 2005; Rhoads et al., 2005; He and Angenent, 2006; Ter Heijne et al., 2007; Lefebvre et al., 2008a). In recent years, use of manganese and iron compounds in microbial biocathode have shown positive aspect in improving the performance of a MFC (Mao et al., 2010). Use of these compounds in biocathode is also sustainable due to their abundance (Nealson and Saffarini, 1994). For example, MnO_2 on solid state cathode was first reduced to an intermediate product, MnOOH via electrons from the cathode, releasing Mn^{2+} into the solution and then with the help of manganese-oxidizing bacteria (*Leptothrix discophora*), Mn^{2+} was re-oxidize to MnO_2 by releasing two electrons to oxygen (Rhoads et al., 2005; He and

Table 4. Summary of electrode-oxidizing microorganism and electron acceptors in biocathodes.

Biocatalyst	Cathode material	Electron acceptor	Operational mode	Standard potential of the electron acceptor	References
Anaerobic sludge	Granular graphite	NO_3^-	anodic and cathodic liquids separately recirculated	+0.74 V	(Clauwaert et al., 2007a)
Anaerobic sludge	Manganese treated graphite felt	O_2	anode fed-batch, cathodic liquid recirculated	+0.820 V	(Clauwaert et al., 2007b)
Anaerobic digester effluent	Graphite plates	Cr^{6+}	Two-chamber, batch-fed	+1.33V	(Tandukar et al., 2009)
Geobacter sulfurreducens	Unpolished graphite rod	U^{6+}	Two-chamber, batch-fed	+0.334V	(Gregory and Lovley, 2005)
Methanobacterium palustre	Graphite fiber brush	CO_2	Two-chamber, batch-fed	-0.244V	(Cheng et al., 2009)
Geobacter sulfurreducens	Graphite plate	Fumarate	One-chamber, batch-fed	+0.031 V	(Dumas et al., 2008)
Anaerobic sludge		NO_3^-	Two-chamber, batch-fed	+0.74 V	(Lefebvre et al., 2008b)
Aerobic activated sludge	Graphite brush	O_2	Two-chamber, batch-fed	+0.820 V	(You et al., 2009)
Phototrophic mixed culture	Graphite felt	CO_2	Two-chamber, batch-fed	-0.420 V	(Cao et al., 2009)
Hydrogenophilic mixed culture	Graphite felt	H_2	Two-chamber, continuous mode	-0.414 V	(Jeremiasse et al., 2010)
Hydrogenophilic methanogenic culture	Carbon paper	H_2	Two-chamber, batch-fed	-0.414 V	(Villano et al., 2010)
Desulfovibrio vulgaris	Glassy carbon	H_2	One-chamber, batch-fed	-0.414 V	(Lojou et al., 2002)
Hydrogenophilic dechlorinating culture	Carbon paper	Trichloroethene	Two-chamber, batch-fed	+0.550 V	(Aulenta et al., 2010)
Kingella denitrificans	Gassy carbon rod	O_2	One-chamber, batch-fed	+0.820 V	(Cournet et al., 2010)
Anaerobic sludge	Graphite felt	Acetate	Two-chamber, batch-fed	-0.433 V	(Steinbusch et al., 2010)

Angenent, 2006; Huang et al., 2011a).

In an anaerobic biocathode, compounds such as nitrate, sulphate, iron, manganese, selenate, arsenate, urinate, fumarate and carbon dioxide are used as terminal electron acceptors (Stams et al., 2006; Lefebvre et al., 2008a). Nitrate, iron and manganese are the commonly used compounds in anaerobic biocathode and have a relative metabolic activity close to oxygen (He and Angenent, 2006). Nitrate is the most widely used terminal electron acceptors in the biocathode due to the relatively high redox potential of the couple NO_3^-/N_2 (E'=+0.74 V) (He and Angenent, 2006; Lefebvre et al., 2008b). Table 4

summarize some of the important research being conducted in biocathode.

Challenges and future perspective of MFCs

The ultimate goal of MFC technology is to achieve practical implementation in a wastewater treatment system, which can improve their economic feasibility for recovering energy and wastewater treatment (Lu et al., 2009; Zhou et al., 2011; Wei et al., 2011b). Despite the power generation from MFCs have improved considerably in recent years, the technology is still confronted with a number of issues

and challenges (Pant et al., 2010). At present, the greatest challenge in MFC technology is the low output of power (Zhou et al., 2011). A typical MFC produces an open circuit voltage (OCV) in the range of 0.7-1.0 V, however, the working voltage decreased when connected to a load resistor i.e 0.35-0.5 V (Oh and Logan, 2007). To be considered for practical applications, current power and power density have to be increased by 10 to 100 fold (Wrighton and Coates, 2009). Thus, scale-up is one of the big challenges currently persistent in the MFC technology.

In recent years, efforts have been made in generating higher power from MFCs by connecting multiple units of MFCs in series (Aelterman et al., 2006; Shin et al., 2006; Oh and Logan, 2007; Zhuang and Zhou, 2009). As a common configuration for chemical fuel cell, voltage can be increased by stacking or connecting multiple individuals cells in series (Knights et al., 2003). Same principle can be adopted in MFCs to increase the power output (Oh and Logan, 2007). In an effort to increase voltage, Aelterman et al. (2006) connected six individual MFCs in series with $K_3[Fe(CN)_6]$ catholyte and obtained the stack voltage of 4.14 V (OCV). Zhuang and Zhou (2009) evaluated the stack performance using two individual tubular MFCs with aerated cathode in series, and obtained the total stack voltage of 1.307 V (OCV). Shin et al. (2006) operated the bipolar stack performance (five single cells are connected in series) using $K_3[Fe(CN)_6]$ and obtained the stack voltage of 2.5 V (OCV).

Nevertheless, connection of two or more MFCs in series result in 'voltage reversal' (Knights et al., 2003; Oh and Logan, 2007). Voltage reversal is mainly attributed when one of the working cell in the circuit is weak as compared to other cell (Knights et al., 2003; Oh and Logan, 2007). During the process of voltage reversal, the overall performance of the cell is reduced due to polarity reversal (Oh and Logan, 2007). Voltage reversal also occurred due to variation in internal impedance, which is associated with the PEM fouling (Hu, 2008; Ieropoulos et al., 2010). In addition to PEM fouling, the high cost of cation exchange membranes limits the real implementation of MFCs (Hu, 2008; Pant et al., 2010).

Despite the rapid progress in design of MFCs including reactor configuration, electrode materials and other chemical parameters, the MFC technology is still in its infancy condition to be applicable in industrial sector (Osman et al., 2010; Zhou et al., 2011; Wei et al., 2011b). To achieve practical implementation in a wastewater treatment system, the cost of electrode materials, especially cathode electrode cost should be reduced (Rozendal et al., 2008; Zhou et al., 2011). In a typical MFC, the contribution of the anode and cathode electrodes to the total capital was 9.4% and 47%, respectively, and thus, still the cost of electrode limits their practical application (Rozendal et al., 2008; Zhou et al., 2011). Electrode materials should have high conductivity and need to be more catalytic which can overcome the problems due to fouling of the active surfaces, corrosion and other degradation mechanisms (Logan et al., 2006; Osman et al., 2010; Wei et al., 2011b).

Reactor configuration needs to be designed in such a manner which will maximize the cell voltage while reducing electrode potentials and internal resistances (Rabaey and Verstraete, 2005a; Logan et al., 2006; Osman et al., 2010). For example, most of the electrode areas used in the MFC studies for wastewater treatment ranged from several to 100 cm^2, which is not applicable for real wastewater systems (Min and Logan, 2004; Kim et al., 2005; Min et al., 2005; Zhou et al., 2011). In recent years, biocathode is viewed as alternative to reduce cathode cost (Wei et al., 2011a). However, the capital costs of biocathodes currently used in MFCs based on electrode materials are several times more costly than those of conventional wastewater treatment systems (Wei et al., 2011b). Thus, till date MFC studies are restricted to lab scale though few pilot-scales MFC has tested (Zhou et al., 2011).

Conclusions

The MFC technology is considered as a promising technology in recovering energy from waste biomass, especially wastewaters. However, the overall performance of a MFC is influenced by various factors such as reactors configuration, electrode materials, substrate type, pH, DO, electrolyte strength and temperature. During the past two decades many efforts have been made in the development and modification of reactors configuration and electrode materials (both cathode and anode) to promote the performance of MFCs. However, scale-up in MFCs is still a major challenge to achieve its implementation in industrial sector. Therefore, development of cost- effective materials and architecture are the main challenges, which are crucial to the successful scale up and commercialization of MFCs.

Acknowledgment

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