Research review paper

A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy

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Abstract

A microbial fuel cell (MFC) is a bioreactor that converts chemical energy in the chemical bonds in organic compounds to electrical energy through catalytic reactions of microorganisms under anaerobic conditions. It has been known for many years that it is possible to generate electricity directly by using bacteria to break down organic substrates. The recent energy crisis has reinvigorated interests in MFCs among academic researchers as a way to generate electric power or hydrogen from biomass without a net carbon emission into the ecosystem. MFCs can also be used in wastewater treatment facilities to break down organic matters. They have also been studied for applications as biosensors such as sensors for biological oxygen demand monitoring. Power output and Coulombic efficiency are significantly affected by the types of microbe in the anodic chamber of an MFC, configuration of the MFC and operating conditions. Currently, real-world applications of MFCs are limited because of their low power density level of several thousand mW/m². Efforts are being made to improve the performance and reduce the construction and operating costs of MFCs. This article presents a critical review on the recent advances in MFC research with emphases on MFC configurations and performances.
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Keywords: Microbial fuel cells; Wastewater treatment; Electricity generation; Biohydrogen; Biosensor

Contents

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1. Introduction

The use of fossil fuels, especially oil and gas, in recent years has accelerated and this triggers a global energy crisis. Renewable bioenergy is viewed as one of the ways to alleviate the current global warming crisis. Major efforts are devoted to developing alternative electricity production methods. New electricity production from renewable resources without a net carbon dioxide emission is much desired (Lovley, 2006, Davis and Higson, 2007). A technology using microbial fuel cells (MFCs) that convert the energy stored in chemical bonds in organic compounds to electrical energy achieved through the catalytic reactions by microorganisms has generated considerable interests among academic researchers in recent years (Allen and Bennetto, 1993; Gil et al., 2003; Moon et al., 2006; Choi et al., 2003). Bacteria can be used in MFCs to generate electricity while accomplishing the biodegradation of organic matters or wastes (Park and Zeikus, 2000; Oh and Logan., 2005). Fig. 1 shows a schematic diagram of a typical MFC for producing electricity. It consists of anodic and cathodic chambers partitioned by a proton exchange membrane (PEM) (Wilkinson, 2000; Gil et al., 2003).

Microbes in the anodic chamber of an MFC oxidize added substrates and generate electrons and protons in the process. Carbon dioxide is produced as an oxidation product. However, there is no net carbon emission because the carbon dioxide in the renewable biomass originally comes from the atmosphere in the photosynthesis process. Unlike in a direct combustion process, the electrons are absorbed by the anode and are transported to the cathode through an external circuit. After crossing a PEM or a salt bridge, the protons enter the cathodic chamber where they combine with oxygen to form water. Microbes in the anodic chamber extract electrons and protons in the dissimilative process of oxidizing organic substrates (Rabaey and Verstraete, 2005). Electric current generation is made possible by keeping microbes separated from oxygen or any other end terminal acceptor other than the anode and this requires an anaerobic anodic chamber.
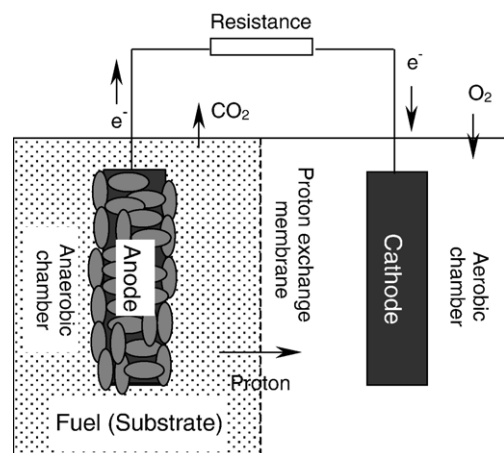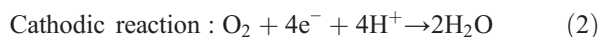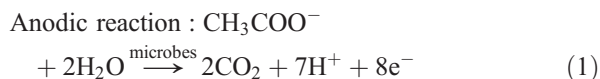

Fig. 1. Schematic diagram of a typical two-chamber microbial fuel cell.

Typical electrode reactions are shown below using acetate as an example substrate.

$$\text{Anodic reaction}: CH_3COO^-$$
$$+ 2H_2O \xrightarrow{\text{microbes}} 2CO_2 + 7H^+ + 8e^- \qquad (1)$$

$$\text{Cathodic reaction}: O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad (2)$$

The overall reaction is the break down of the substrate to carbon dioxide and water with a concomitant production of electricity as a by-product. Based on the electrode reaction pair above, an MFC bioreactor can generate electricity from the electron flow from the anode to cathode in the external circuit.

In recent years, rapid advances have been made in MFC research and the number of journal publications has increased sharply in the past three years with more researchers joining the research field. Several reviews on MFC are available, each with a different flavor or emphasis. Logan et al. (2006) reviewed MFC designs, characterizations and performances. The microbial metabolism in MFCs was reviewed by Rabaey and Verstraete (2005). Lovley (2006) mainly focused his review on the promising MFC systems known as Benthic Unattended Generators (BUGs) for powering remote-sensing or monitoring devices from the angle of microbial physiologies. Pham et al. (2006) summarized the advantages and disadvantages of MFCs compared to the conventional anaerobic digestion technology for the production of biogas as renewable energy. Chang et al. (2006) discussed both the properties of electrochemically active bacteria used in mediatorless MFC and the rate limiting steps in electron transport. Bullen et al. (2006) compiled many experimental results on MFCs reported recently in their review on biofuel cells. This work here presents a state of the art review on MFC with emphases on the recent advances in MFC reactor designs, MFC performances and optimization of important operating parameters. A brief MFC history is also presented.

2. History of microbial fuel cell development

Theoretically, most microbes can potentially be used as a biocatalyst in MFC. The earliest MFC concept was demonstrated by Potter in 1910 (Ieropoulos, 2005a). Electrical energy was produced from living cultures of *Escherichia coli* and *Saccharomyces* by using platinum electrodes (Potter, 1912). This didn't generate much interest until 1980s when it was discovered that current density and the power output could be greatly enhanced by the addition of electron mediators. Unless the species

in the anodic chamber are anodophiles, the microbes are incapable of transferring electrons directly to the anode. The outer layers of the majority of microbial species are composed of non-conductive lipid membrane, peptidi-doglycans and lipopolysaccharides that hinder the direct electron transfer to the anode. Electron mediators accelerate the transfer (Davis and Higson, 2007). Mediators in an oxidized state can easily be reduced by capturing the electrons from within the membrane. The mediators then move across the membrane and release the electrons to the anode and become oxidized again in the bulk solution in the anodic chamber. This cyclic process accelerates the electron transfer rate and thus increases the power output. Good mediators should possess the following features (Ieropoulos et al., 2005a): (1) able to cross the cell membrane easily; (2) able to grab electrons from the electron carries of the electron transport chains; (3) possessing a high electrode reaction rate; (4) having a good solubility in the anolyte; (5) non-biodegradable and non-toxic to microbes; (6) low cost. And how efficient the oxidized mediator gets reduced by the cells reducing power is more important compared with other features. Although a mediator with the lowest redox would in theory give the lowest anodic redox and thus maximize the redox difference between anode and cathode (i.e. give biggest voltage difference) it would not necessarily be the most efficient at pulling electrons away from the reduced intracellular systems (NADH, NADPH or reduced cytochromes) within the microbes. A mediator with a higher E^o redox would give a higher overall power than a mediator with the lowest redox (Ieropoulos et al., 2005a). Typical synthetic exogenous mediators include dyes and metallorganics such as neutral red (NR), methylene blue (MB), thionine, meldola's blue (MelB), 2-hydroxy-1,4-naphthoquinone (HNQ), and Fe(III)EDTA (Park and Zeikus, 2000; Tokuji and Kenji, 2003; Veag and Fernandez, 1987; Allen and Bennetto, 1993; Ieropoulos et al., 2005a). Unfortunately, the toxicity and instability of synthetic mediators limit their applications in MFCs. Some microbes can use naturally occurring compounds including microbial metabolites (Endogenous mediators) as mediators. Humic acids, anthraquinone, the oxyanions of sulphur (sulphate and thiosulphate) all have the ability to transfer electrons from inside the cell membrane to the anode (Lovley, 1993). A real breakthrough was made when some microbes were found to transfer electrons directly to the anode (Kim et al., 1999a, Chaudhuri and Lovley, 2003). These microbes are operationally stable and yield a high Coulombic efficiency (Chaudhuri and Lovley, 2003; Scholz and Schroder, 2003). *Shewanella putrefaciens*

(Kim et al., 2002), *Geobacteraceae sulferreducens* (Bond and Lovley, 2003), *Geobacter metallireducens* (Min et al., 2005a) and *Rhodoferax ferrireducens* (Chaudhuri and Lovley, 2003) are all bioelectrochemically active and can form a biofilm on the anode surface and transfer electrons directly by conductance through the membrane. When they are used, the anode acts as the final electron acceptor in the dissimilatory respiratory chain of the microbes in the biofilm. Biofilms forming on a cathode surface may also play an important role in electron transfer between the microbes and the electrodes. Cathodes can serve as electron donors for *Thiobacillus ferrooxidans* suspended in a catholyte (Prasad et al., 2006) for an MFC system that contained microbes in both anodic and cathodic chambers. *G. metallireducens* and *G. sulfurreducens* (Gregory et al., 2004) or other seawater biofilms (Bergel et al., 2005) may all act as final electron acceptors by grabbing the electrons from cathode as electron donors. Since the cost of a mediator is eliminated, mediator-less MFCs are advantageous in wastewater treatment and power generation (Ieropoulos et al., 2005a).

3. Microbes used in microbial fuel cells

Many microorganisms possess the ability to transfer the electrons derived from the metabolism of organic matters to the anode. A list of them is shown in Table 1 together with their substrates. Marine sediment, soil, wastewater, fresh water sediment and activated sludge are all rich sources for these microorganisms (Niessen et al., 2006, Zhang et al., 2006). A number of recent publications discussed the screening and identification of microbes and the construction of a chromosome library for microorganisms that are able to generate electricity from degrading organic matters (Logan et al., 2005; Holmes et al., 2004; Back et al., 2004).

The anodic electron transfer mechanism in MFC is a key issue in understanding the theory of how MFCs work. As mentioned above, microbes transfer electrons to the electrode through an electron transport system that either consists of a series of components in the bacterial extracellular matrix or together with electron shuttles dissolved in the bulk solution. *Geobacter* belongs to dissimilatory metal reducing microorganisms, which

Table 1
Microbes used in MFCs

| Microbes	Substrate	Applications
Actinobacillus succinogenes	Glucose	Neutral red or thionin as electron mediator (Park and Zeikus, 2000; Park and Zeikus, 1999; Park et al., 1999)
Aeromonas hydrophila	Acetate	Mediator-less MFC Pham et al. (2003)
Alcaligenes faecalis, Enterococcus gallinarum, Pseudomonas aeruginosa	Glucose	Self-mediate consortia isolated from MFC with a maximal level of 4.31 W m^{-2}. Rabaey (2004)
Clostridium beijerinckii	Starch, glucose, lactate, molasses	Fermentative bacterium Niessen et al. (2004b)
Clostridium butyricum	Starch, glucose, lactate, molasses	Fermentative bacterium (Niessen et al., 2004b; Park et al., 2001)
Desulfovibrio desulfuricans	Sucrose	Sulphate/sulphide as mediator (Ieropoulos et al., 2005a; Park et al., 1997)
Erwinia dissolven	Glucose	Ferric chelate complex as mediators Vega and Fernandez, (1987)
Escherichia coli	Glucose sucrose	Mediators such as methylene blue needed. (Schroder et al., 2003; Ieropoulos et al., 2005a; Grzebyk and Pozniak, 2005)
Geobacter metallireducens	Acetate	Mediator-less MFC Min et al. (2005a)
Geobacter sulfurreducens	Acetate	Mediator-less MFC (Bond and Lovley, 2003; Bond et al., 2002)
Gluconobacter oxydans	Glucose	Mediator (HNQ, resazurin or thionine) needed Lee et al. (2002)
Klebsiella pneumoniae	Glucose	HNQ as mediator biomineralized manganese as electron acceptor (Rhoads et al., 2005; Menicucci et al., 2006)
Lactobacillus plantarum	Glucose	Ferric chelate complex as mediators (Vega and Fernandez, 1987)
Proteus mirabilis	Glucose	Thionin as mediator (Choi et al., 2003; Thurston et al., 1985)
Pseudomonas aeruginosa	Glucose	Pyocyanin and phenazine-1-carboxamide as mediator (Rabaey et al., 2004, 2005a)
Rhodoferax ferrireducens	Glucose, xylose sucrose, maltose	Mediator-less MFC (Chaudhuri and Lovley, 2003; Liu et al., 2006)
Shewanella oneidensis	Lactate	Anthraquinone-2,6-disulfonate (AQDS) as mediator (Ringeisen et al., 2006)
Shewanella putrefaciens	Lactate, pyruvate, acetate, glucose	Mediator-less MFC (Kim et al., 1999a,b); but incorporating an electron mediator like Mn (IV) or NR into the anode enhanced the electricity production (Park and Zeikus, 2002)
Streptococcus lactis	Glucose	Ferric chelate complex as mediators (Vega and Fernandez, 1987)
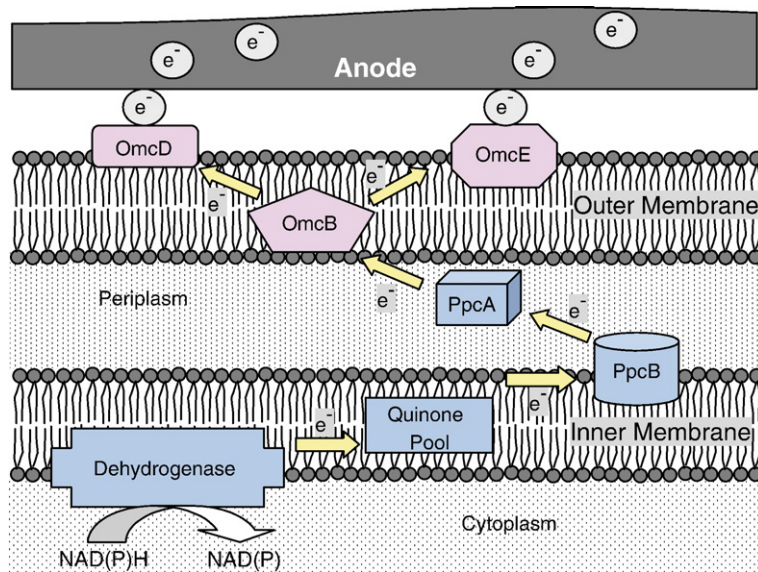
Fig. 2. Summary of components proposed to be involved in the electron transport from cells to the anode in MFCs using metal reducing microorganisms (*Geobacter* species). (Figure drawn with modifications after Lovley et al., 2004.)

produce biologically useful energy in the form of ATP during the dissimilatory reduction of metal oxides under anaerobic conditions in soils and sediments. The electrons are transferred to the final electron acceptor such as Fe_2O_3 mainly by a direct contact of mineral oxides and the metal reducing microorganisms (Lovley et al., 2004; Vargas et al., 1998). The anodic reaction in mediator-less MFCs constructed with metal reducing bacteria belonging primarily to the families of *Shewanella, Rhodoferax,* and *Geobacter* is similar to that in this process because the anode acts as the final electron acceptor just like the solid mineral oxides. Fig. 2 illustrates the chemical compounds proposed to be involved in the electron transportation from electron

carriers in the intracellular matrix to the solid-state final electron acceptor (anode) in dissimilatory metal reducing microorganisms (Lovley et al., 2004; Vargas et al., 1998; Holmes et al., 2004). *S. putrefaciens, G. sulferreducens, G. metallireducens* and *R. ferrireducens* transfer electrons to the solid electrode (anode) using this system.

Though most of the real mediator-less MFCs are operated with dissimilatory metal reducing microorganisms, an exception was reported with *Clostridium butyricum* (Oh and Logan, 2006; Park et al., 2001). Mediators such as dye molecules and humic substances
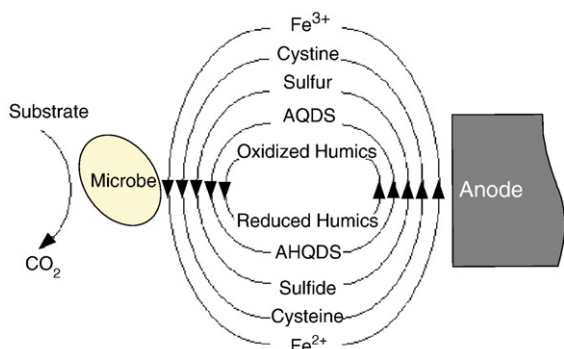
Fig. 3. Model for various compounds serving as electron shuttles between a bioelectrochemically active microorganism and the anode. (Figure drawn with modifications after Lovley et al., 1996).

Table 2
Basic components of microbial fuel cells

Items	Materials	Remarks
Anode	Graphite, graphite felt, carbon paper, carbon-cloth, Pt, Pt black, reticulated vitreous carbon (RVC)	Necessary
Cathode	Graphite, graphite felt, carbon paper, carbon-cloth, Pt, Pt black, RVC	Necessary
Anodic chamber	Glass, polycarbonate, Plexiglas	Necessary
Cathodic chamber	Glass, polycarbonate, Plexiglas	Optional
Proton exchange system	Proton exchange membrane: Nafion, Ultrex, polyethylene.poly (styrene-co-divinylbenzene); salt bridge, porcelain septum, or solely electrolyte	Necessary
Electrode catalyst	Pt, Pt black, MnO_2, Fe^{3+}, polyaniline, electron mediator immobilized on anode	Optional

also have some effects on the mediator-less MFCs even though the anodophiles can transfer the electrons to the anode directly especially in the early stage of biofilm formation. Electron mediators like Mn^{4+} or neutral red (NR) incorporated into the anode noticeably enhance the performance of MFCs using anodophile *S. putrefaciens* (Park and Zeikus, 2002). Mediators play an important role in electron transport for those microbes that are unable to transfer the electrons to the anode. Basic processes are shown as follows (Fig. 3) (Lovley et al., 1996, 2004; Ieropoulos et al., 2005a). Mediators shuttle between the anode and the bacteria transferring the electrons. They take up the electrons from microbes

and discharge them at the surface of the anode. *Actinobacillus succinogenes*, *Desulfovibrio desulfuricans*, *E. coli*, *Proteus mirabilis*, *Proteus vulgaris*, *Pseudomonas fluorescens* need extraneous mediators while some microbes can provide their own. For example, *Pseudomonas aeruginosa* produces pyocyanin molecules as electron shuttles.

When an MFC is inoculated with marine sediments or anaerobic sludge, mixed cultured microbes are in the anode chamber. Usually mixed culture MFCs have good performances. Using complex mixed cultures (anodic microcosm) allows much wider substrate utilization. It means that the MFCs have much wider substrate

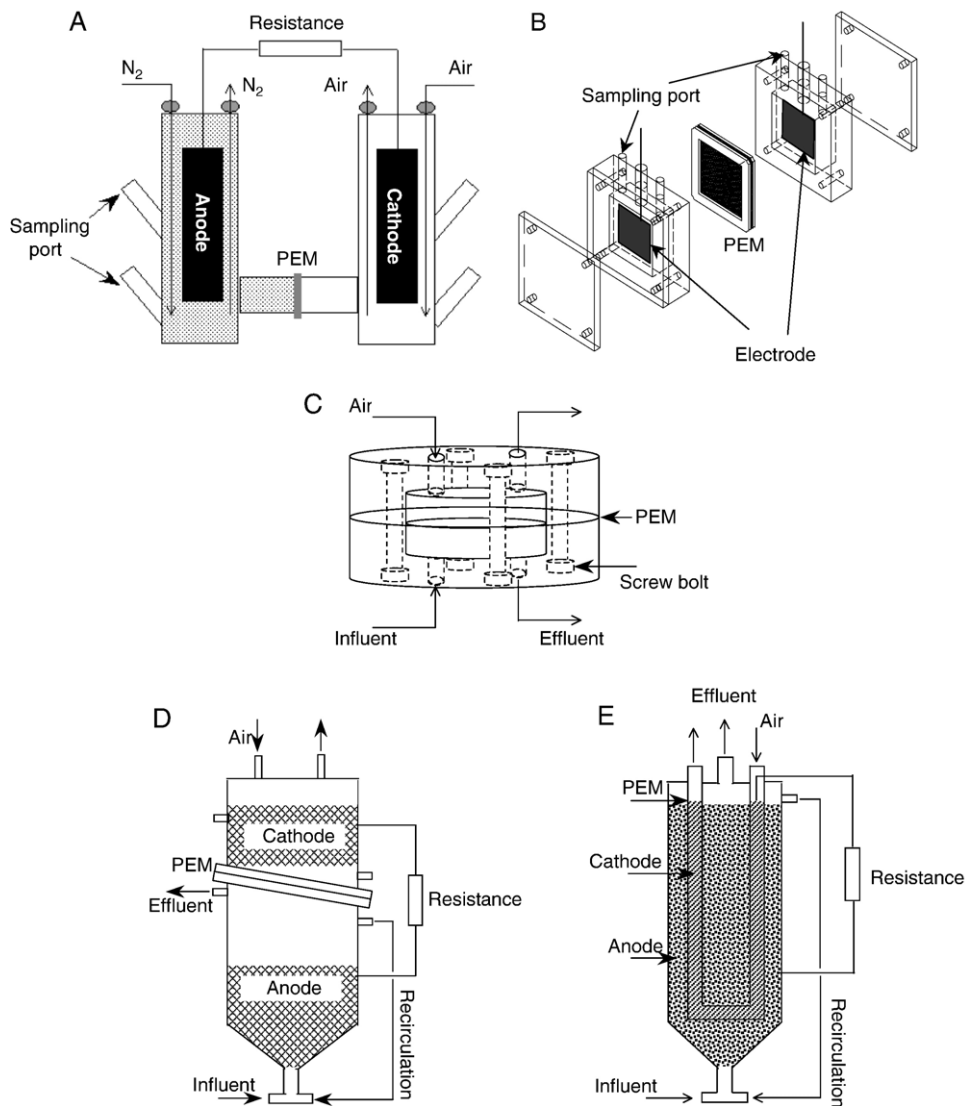Fig. 4. Schematics of a two-compartment MFC in cylindrical shape (A), rectangular shape (B), miniature shape (C), upflow configuration with cylindrical shape (D), cylindrical shape with an U-shaped cathodic compartment (E). (Fig. 4A drawn to illustrate a photo in Min et al., 2005a,b. The rest drawn with modifications after Delaney et al., 1984; Allen and Bennetto, 1993; Ringeisen et al., 2006; He et al., 2005, 2006, respectively.)

specificity when mixed than do pure cultures. In mixed culture MFCs (with anaerobic sludge) there are both electrophiles/anodophiles and groups that use natural mediators together in the same chamber. Ieropoulos et al. (2005b) showed a relationship between power output and levels of sulphur compounds. Since there are always some naturally occurring levels of S-containing material in sludge, they showed that up to 70–80% of the power was due to sulphate/sulphide mediated system and only 20–30% due to electrophiles.

4. Design of microbial fuel cells

4.1. MFC components

A typical MFC consists of an anodic chamber and a cathodic chamber separated by a PEM as shown in Fig. 1. A one-compartment MFC eliminates the need for the cathodic chamber by exposing the cathode directly to the air. Table 2 shows a summary of MFC components and the materials used to construct them (Logan et al., 2006; Rabaey and Verstraete, 2005; Bullen et al., 2006; Lovley, 2006).

4.2. Two-compartment MFC systems

Two-compartment MFCs are typically run in batch mode often with a chemically defined medium such as glucose or acetate solution to generate energy. They are currently used only in laboratories. A typical two-compartment MFC has an anodic chamber and a cathodic chamber connected by a PEM, or sometimes a salt bridge, to allow protons to move across to the cathode while blocking the diffusion of oxygen into the anode. The compartments can take various practical shapes. The schematic diagrams of five two-compartment MFCs are shown in Fig. 4. The mini-MFC shown in Fig. 4C having a diameter of about 2 cm, but with a high volume power density was reported by Ringeisen et al. (2006). They can be useful in powering autonomous sensors for long-term operations in less accessible regions. Upflow mode MFCs as shown in Fig. 4D and E are more suitable for wastewater treatment because they are relatively easy to scale-up (He et al., 2005, 2006). On the other hand, fluid recirculation is used in both cases. The energy costs of pumping fluid around are much greater than their power outputs. Therefore, their primary function is not power generation, but rather wastewater treatment. The MFC design in Fig. 4E offers a low internal resistance of 4 Ω because the anode and cathode are in close proximity over a large PEM surface area.

Min and Logan (2004) designed a Flat Plate MFC (FPMFC) with only a single electrode/PEM assembly. Its compact configuration resembles that of a conventional chemical fuel cell. A carbon-cloth cathode that was hot pressed to a Nafion PEM is in contact with a single sheet of carbon paper that serves as an anode to form an electrode/PEM assembly. The FPMFC with two non-conductive polycarbonate plates is bolted together. The PEM links the anodic and the cathodic chambers as shown in Fig. 5B. The anodic chamber can be fed with wastewater or other organic biomass and dry air can be pumped through the cathodic chamber without any liquid catholyte, both in a continuous flow mode (Min and Logan, 2004).

4.3. Single-compartment MFC systems

Due to their complex designs, two-compartment MFCs are difficult to scale-up even though they can be operated in either batch or continuous mode. One-compartment MFCs offer simpler designs and cost savings. They typically possess only an anodic chamber without the requirement of aeration in a cathodic chamber. Park and Zeikus (2003) designed a one-compartment MFC consisting of an anode in a rectangular anode chamber coupled with a porous air-
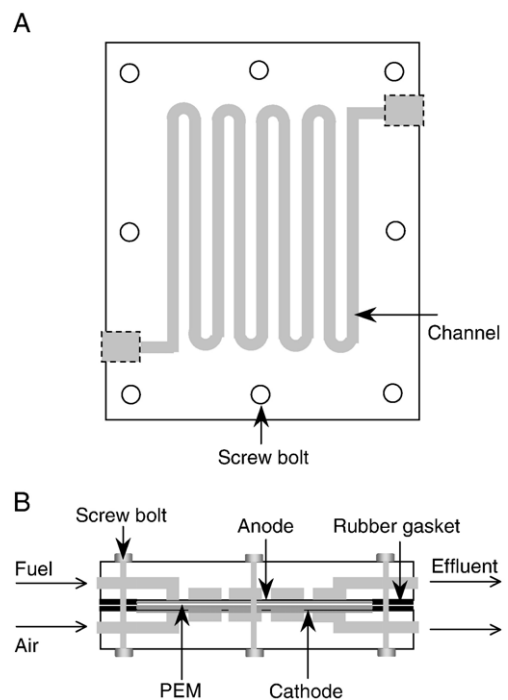
Fig. 5. Schematics of top (A) and side (B) views of a flat plate MFC. (Figures drawn with modifications after Min and Logan, 2004.)
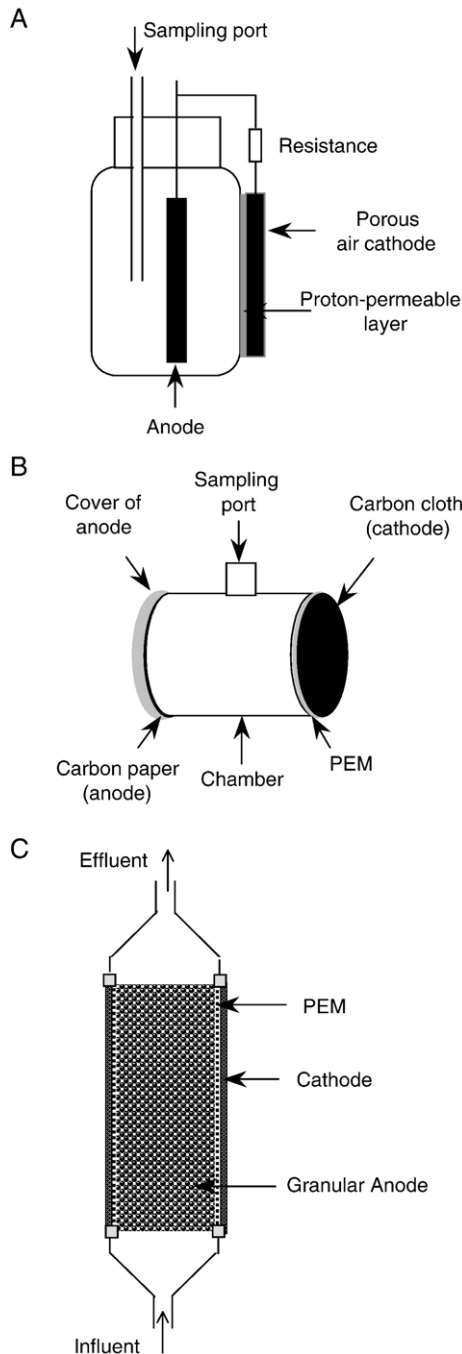
Fig. 6. An MFC with a proton permeable layer coating the inside of the window-mounted cathode (A), an MFC consisting of an anode and cathode placed on opposite side in a plastic cylindrical chamber (B), and a tubular MFC with outer cathode and inner anode consisting of graphite granules (C). ((A) drawn to illustrate a photo in Park and Zeikus, 2003. (B) and (C) drawn with modifications after Liu and Logan, 2004; Rabaey et al., 2005b, respectively.)

cathode that is exposed directly to the air as shown in Fig. 6A. Protons are transferred from the anolyte solution to the porous air-cathode (Park and Zeikus, 2003). Liu and Logan (2004) designed an MFC consisting of an anode placed inside a plastic cylindrical chamber and a cathode placed outside. Fig. 6B shows the schematic of a laboratory prototype of the MFC bioreactor. The anode was made of carbon paper without wet proofing. The cathode was either a carbon electrode/ PEM assembly fabricated by bonding the PEM directly onto a flexible carbon-cloth electrode, or a stand alone rigid carbon paper without PEM (Liu and Logan, 2004; Liu et al., 2005a; Cheng et al., 2006a). A tubular MFC system with an outer cathode and an inner anode using graphite granules is shown in Fig. 6C (Rabaey et al., 2005b). In the absence of a cathodic chamber, catholyte is supplied to the cathode by dripping an electrolyte over the outer woven graphite mat to keep it from drying up. Rabaey et al. (2005b) pointed out that the use of sustainable, open-air cathodes is critical to practical implementation of such MFCs. Another type of SC-MFC reactor was reported by Liu et al. (2004). Their
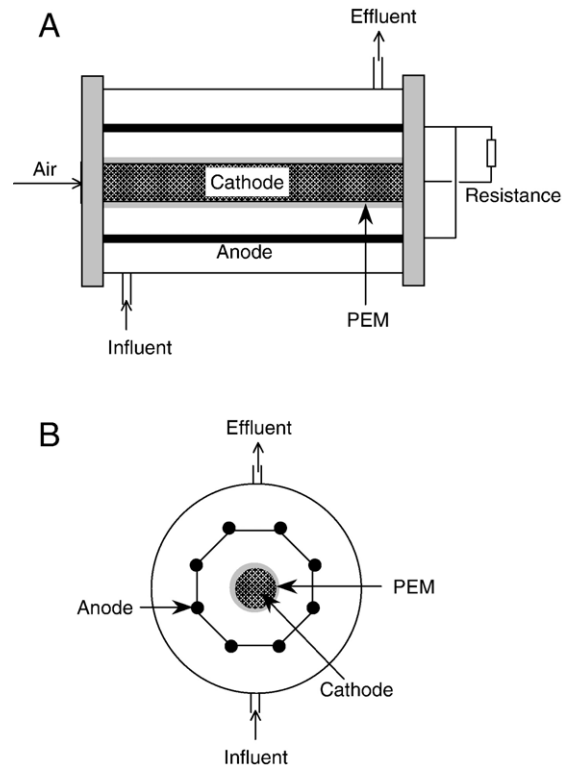

Fig. 7. Schematics of a cylindrical SC-MFC containing eight graphite rods as an anode in a concentric arrangement surrounding a single cathode. ((A) drawn with modifications after Liu et al., 2004. (B) drawn to illustrate a photo in Liu et al., 2004.)
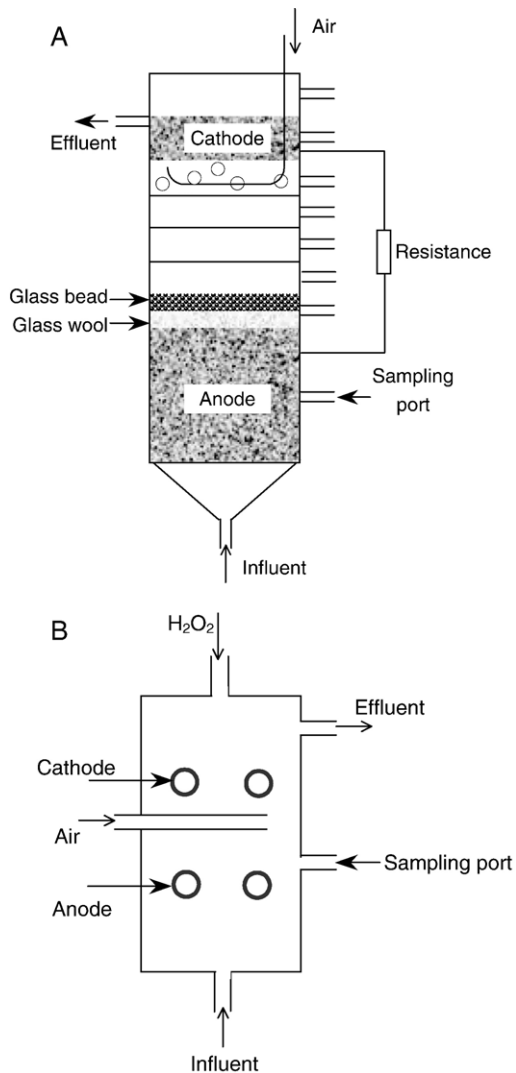
Fig. 8. Schematics of mediator-and membrane-less MFC with cylindrical shape (A), and with rectangular shape (B). (Figures drawn with modifications after Jang et al., 2004; Tartakovsky and Guiot, 2006, respectively.)

SC-MFC housed both the anode and the cathode in one chamber. It consisted of a single cylindrical Plexiglas chamber with eight graphite rods (anode) in a concentric arrangement surrounding a single cathode as shown in Fig. 7. A carbon/platinum catalyst/proton exchange membrane layer was fused to a plastic support tube to form the air-porous cathode in the center (Liu et al., 2004).

4.4. Up-flow mode MFC systems

Jang et al. (2004) provided another design (Fig. 8A) of an MFC working in continuous flow mode. A Plexiglas

cylinder was partitioned into two sections by glass wool and glass bead layers. These two sections served as anodic and cathodic chambers, respectively as shown in Fig. 8A. The disk-shaped graphite felt anode and cathode were placed at the bottom and the top of the reactor, respectively. Fig. 8B shows another MFC design inspired by the same general idea shown in Fig. 8A but with a rectangular container and without a physical separation achieved by using glass wool and glass beads (Tartakovsky and Guiot, 2006). The feed stream is supplied to the bottom of the anode and the effluent passes through the cathodic chamber and exits at the top continuously (Jang et al., 2004; Moon et al., 2005). There are no separate anolyte and catholyte. And the diffusion barriers between the anode and cathode provide a DO gradient for proper operation of the MFCs.

4.5. Stacked microbial fuel cell

A stacked MFC is shown in Fig. 9 for the investigation of performances of several MFCs connected in series and in parallel (Aelterman et al., 2006). Enhanced voltage or current output can be achieved by connecting several MFCs in series or in parallel. No obvious adverse effect on the maximum power output per MFC unit was observed. Coulombic efficiencies (In fact it is not real Coulombic efficiency but Coulombic percent conversion. Coulombic efficiency describes how much of the electrons can be abstracted from the electron-rich substrates via the electrodes. It is not a measurement of electron transfer rate, while the authors described how much substrate was used for electricity generation before the stream flowed out of the MFCs or MFC stacks) differed greatly in the two arrangements with the parallel connection giving about an efficiency six times
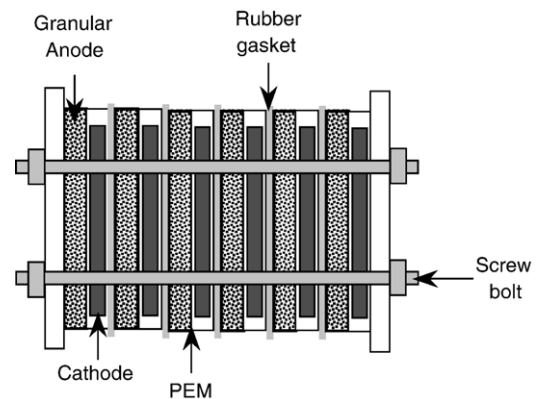

Fig. 9. Stacked MFCs consisting of six individual units with granular graphite anode. (Figure drawn to illustrate a photo in Aelterman et al., 2006.)

Table 3
MFC electrode reactions and corresponding redox potentials

| Oxidation/reduction pairs	$E^{o'}$ (mV)
H^+/H_2	−420
$NAD^+/NADH$	−320
S^0/HS^-	−270
SO_4^{2-}/H_2S	−220
$Pyruvate^{2-}/Lactate^{2-}$	−185
2,6-AQDS/2,6-AHQDS	−184
$FAD/FADH_2$	−180
Menaquinione ox/red	−75
Pyocyanin ox/red	−34
Humic substances ox/red (Straub et al., 2001)	−200 to +300
Methylene blue ox/red	+11
$Fumarate^{2-}/Succinate^{2-}$	+31
Thionine ox/red	+64
Cytochrome b(Fe^{3+})/Cytochrome b(Fe^{2+})	+75
Fe(III) EDTA/Fe(II) EDTA	+96
Ubiquinone ox/red	+113
Cytochrome c(Fe^{3+})/Cytochrome c(Fe^{2+})	+254
O_2/H_2O_2	+275
Fe(III) citrate/Fe(II) citrate	+372
Fe(III) NTA/Fe(II) NTA	+385
NO_3^-/NO_2^-	+421
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	+430
NO_2^-/NH_4^+	+440
O_2/H_2O	+820

higher when both the series were operated at the same volumetric flow rate. The parallel-connected stack has higher short circuit current than the series connected stack. This means that higher maximum bioelectro-chemical reaction rate is allowed in the connection of MFCs in parallel than in series. Therefore to maximize Chemical Oxygen Demand (COD) removal, a parallel connection is preferred if the MFC units are not independently operated (Aelterman et al., 2006).

5. Performances of microbial fuel cells

5.1. Ideal performance

The ideal performance of an MFC depends on the electrochemical reactions that occur between the organic substrate at a low potential such as glucose and the final electron acceptor with a high potential, such as oxygen (Rabaey and Verstrate, 2005). However, its ideal cell voltage is uncertain because the electrons are transferred to the anode from the organic substrate through a complex respiratory chain that varies from microbe to microbe and even for the same microbe when growth conditions differ. Though the respiratory chain is still poorly understood, the key anodic reaction that determines the voltage is between the reduced redox potential of the mediator (if one is employed) or the final

cytochrome in the system for the electrophile/anodo-phile if this has conducting pili, and the anode. For those bacterial species that are incapable of releasing electrons to the anode directly, a redox mediator is needed to transfer the electrons directly to the anode (Stirling et al., 1983; Bennetto, 1984). In such a case the final anodic reaction is that the anode gains the electrons from the reduced mediator. Eq. (3) illustrates the anodic reaction with AQDS (on the right side of the equation), the major component of the humics (Lovley et al., 2004; Nevin and Lovley, 2000), as the mediator. The anodic potential is consequently defined by the ratio of AHQDS and AQDS.

$$ \tag{3} $$
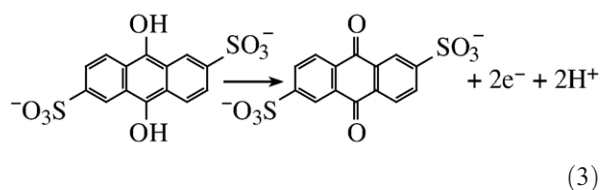
In mediator-less MFCs utilizing anodophiles such as *G. sulfurreducens* and *R. ferrireducens,* microbes form a biofilm on the anode surface and use the anode as their end terminal electron acceptor in their anaerobic respiration. Section 2 mentioned the possible electron transport process. Though the respiratory chain is still not well understood, the anodic potential can be evaluated by the ratio of the final cytochrome of the chain in reduced and oxidized states. The electrode reactions for various types of MFCs and their cor-responding redox potentials of those substrates involved in electrode reactions are presented in Table 3 (Hernan-dez and Newman, 2001; Straub et al., 2001; Rabaey and Verstraete, 2005; Madigan, 2000). The ideal potentials of MFCs can be calculated by the Nernst equation for these reactions and they range from several hundred mV to over 1000 mV.

5.2. Actual MFC performance

The actual cell potential is always lower than its equilibrium potential because of irreversible losses. The following equation (Appleby and Foulkes, 1989) reflects various irreversible losses in an actual MFC

$$ V_{cell} = E_{cathode} - |\eta_{act,c} + h_{conc,c}| - E_{anode} - |\eta_{act,a} + \eta_{conc,a}| - iR_i \tag{4} $$

where $\eta_{act,c}$ and $\eta_{act,a}$ are activation polarization losses on cathode and anode, respectively. $\eta_{conc,c}$ and

$\eta_{conc,a}$ are concentration polarization in cathodic and anodic chambers, respectively. Ohmic losses η_{ohm} occur because of resistance to the flow of ions in the electrolyte and resistance to flow of electrons through the electrode. Since both the electrolyte and the electrodes obey Ohm's law, it can be expressed as iR_i, in which i is the current flowing through the MFC, and R_i is the total cell internal resistance of the MFC.

Activation polarization is attributed to an activation energy that must be overcome by the reacting species. It is a limiting step when the rate of an electrochemical reaction at an electrode surface is controlled by slow reaction kinetics. Processes involving adsorption of reactant species, transfer of electrons across the double-layer cell membrane, desorption of product species, and the physical nature of the electrode surface all contribute to the activation polarization. For those microbes that do not readily release electrons to the anode, activation polarization is an energy barrier that can be overcome by adding mediators. In mediator-less MFCs, activation polarization is lowered due to conducting pili. Cathodic reaction also faces activation polarization. For example, platinum (Pt) is preferred over a graphite cathode for performance purpose because it has a lower energy barrier in the cathodic oxygen reaction that produces water. Usually activation polarization is dominant at a low current density. The electronic barriers at the anode and the cathode must be overcome before current and ions can flow (Appleby and Foulkes, 1989).

The resistance to the flow of ions in electrolytes and the electron flow between the electrodes cause Ohmic losses. Ohmic loss in electrolytes is dominant and it can be reduced by shortening the distance between the two electrodes and by increasing the ionic conductivity of the electrolytes (Cheng et al., 2006b). PEMs produce a transmembrane potential difference that also constitutes a major resistance.

Concentration polarization is a loss of potential due to the inability to maintain the initial substrate concentration in the bulk fluid. Slow mass transfer rates for reactants and products are often to blame. Cathodic overpotential caused by a lack of DO for the cathodic reaction still limits the power density output of some MFCs (Oh et al., 2004). A good MFC bioreactor should minimize concentration polarization by enhancing mass transfer. Stirring and/or bubbling can reduce the concentration gradient in an MFC. However, stirring and bubbling requires pumps and their energy requirements are usually greater than the outputs from the MFC. Therefore, balance between the power output and the energy consumption by MFC operation should be carefully considered. A polarization curve analysis

(Rhoads et al., 2005) of an MFC can indicate to what extent the various losses listed in Eq. (4) contribute to the overall potential drop. This can point to possible measures to minimize them in order to approach the ideal potential. These measures may include selection of microbes and modifications to MFC configurations such as improvement in electrode structures, better electrocatalysts, more conductive electrolyte, and short spacing between electrodes. For a given MFC system, it is also possible to improve the cell performance by adjusting operating conditions (Gil et al., 2003).

5.3. Effects of operating conditions

So far, performances of laboratory MFCs are still much lower than the ideal performance. There may be several possible reasons. Power generation of an MFC is affected by many factors including microbe type, fuel biomass type and concentration, ionic strength, pH, temperature, and reactor configuration (Liu et al., 2005b). Effects of reactor configuration and types of microbe used in the MFC have been addressed in Sections 2 and 3. With a given MFC system, the following operating parameters can be regulated to decrease the polarizations in order to enhance the performance of an MFC.

5.3.1. Effect of electrode materials

Using better performing electrode materials can improve the performance of an MFC because different anode materials result in different activation polarization losses. Pt and Pt black electrodes are superior to graphite, graphite felt and carbon-cloth electrodes for both anode and cathode constructions, but their costs are much higher. Schroder et al. (2003) reported that a current of 2–4 mA could be achieved with platinumized carbon-cloth anode in an agitated anaerobic culture of *E. coli* using a standard glucose medium at 0.55 mmol/L, while no microbially facilitated current flow is observed with the unmodified carbon-cloth with the same operating conditions. Pt also has a higher catalytic activity with regard to oxygen than graphite materials. MFCs with Pt or Pt-coated cathodes yielded higher power densities than those with graphite or graphite felt cathodes (Oh et al., 2004; Jang et al., 2004; Moon et al., 2006).

Electrode modification is actively investigated by several research groups to improve MFC performances. Park and Zeikus (2002, 2003) reported an increase of 100-folds in current output by using NR-woven graphite and Mn(IV) graphite anode compared to the woven graphite anode alone. NR and Mn(IV) served as

mediators in their MFC reactors. Doping ions such as Fe (III) and/or Mn(IV) in the cathode also catalyze the cathodic reactions resulting in improved electricity generations. The principle for their catalytic activity is the same as that of electron shuttles. The electron driving force generated is coupled to the quantivalence change cycles of Fe(III)-Fe(II)-Fe(III) or Mn(IV)-Mn (III)) or Mn(II)-Mn(IV) on the cathode. Four times higher current can be achieved with the combination of Mn(IV)-graphite anode and Fe^{3+}-graphite cathode compared to plain graphite electrodes (Park and Zeikus, 1999, 2000, 2003). One drawback of using Pt or Pt black electrodes is that their activities are reduced by the formation of a PtO layer at the electrode surface at positive potentials. Schroder et al. (2003) investigated the function of a polyaniline overlay on a Pt black anode. Their current density increased from 0.84 with Pt black anode to 1.45 mA^{-1} cm^{-2} with a polyaniline coated Pt black anode. The fluorinated polyanilines poly (2-fluoroaniline) and poly(2,3,5,6-tetrafluoroaniline) outperformed polyaniline as electrode modifiers (Niessen et al., 2004a, 2006). These conductive polymers also serve as dissolved mediators thanks to their structural similarities to conventional redox mediators (Schroder et al., 2003). Cathode reaction has a Monod-type kinetic relationship with the dissolved oxygen concentration (Oh et al., 2004; Pham et al., 2004). Iron(II) phthalocyanine (FePc) and cobalt tetramethoxyphenylporphyrin (CoTMPP) based oxygen cathodes are inexpensive and are efficient alternatives for use in MFCs because they demonstrate similar performances as Pt oxygen electrodes (Zhao et al., 2005, 2006). Catalysts such as Pt, CoTMPP, Mn(IV) and Fe(III) deposited on an air-cathode improve power output by increasing their affinity for oxygen and decreasing the activation energy of the cathodic reaction that reduces O_2 to H_2O (Cheng et al., 2006c). Seafloor MFCs also benefit from electrode modifications. Anodic modifications including AQDS or 1,4-naphthoquinone (NQ) adsorption and Mn^{2+}, Ni^{2+}, Fe_3O_4 or Fe_3O_4/Ni^{2+} incorporation increased the power density of *in situ* marine sediment MFCs in their long-term operations (Lowy et al., 2006). Some people tend to think that a large cathodic surface area would facilitate electrode reactions on the cathode's surface. However, it was reported that different cathode surface areas had only a small effect on internal resistance and the power output (Oh and Logan, 2006; Oh et al., 2004).

5.3.2. pH buffer and electrolyte

If no buffer solution is used in a working MFC, there will be an obvious pH difference between the anodic and cathodic chambers, though theoretically there will be no pH shift when the reaction rate of protons, electrons and oxygen at the cathode equals the production rate of protons at the anode. The PEM causes transport barrier to the cross membrane diffusion of the protons, and proton transport through the membrane is slower than its production rate in the anode and its consumption rate in the cathode chambers at initial stage of MFC operation thus brings a pH difference (Gil et al., 2003). However, the pH difference increases the driving force of the proton diffusion from the anode to the cathode chamber and finally a dynamic equilibrium forms. Some protons generated with the biodegradation of the organic substrate transferred to the cathodic chamber are able to react with the dissolved oxygen while some protons are accumulated in the anodic chamber when they do not transfer across the PEM or salt bridge quickly enough to the cathodic chamber. Gil et al. (2003) detected a pH difference of 4.1 (9.5 at cathode and 5.4 in anode) after 5-hour operations with an initial pH of 7 without buffering. With the addition of a phosphate buffer (pH 7.0), pH shifts at the cathode and anode were both less than 0.5 unit and the current output was increased about 1 to 2 folds. It was possible that the buffer compensated the slow proton transport rate and improved the proton availability for the cathodic reaction. Jang et al. (2004) supplied an HCl solution to the cathode and found that the current output increased by about one fold. This again suggests that the proton availability to the cathode is a limiting factor in electricity generation. Increasing ionic strength by adding NaCl to MFCs also improved the power output (Jang et al., 2004; Liu et al., 2005b), possibly due to the fact that NaCl enhanced the conductivity of both the anolyte and the catholyte.

5.3.3. Proton exchange system

Proton exchange system can affect an MFC system's internal resistance and concentration polarization loss and they in turn influence the power output of the MFC. Nafion (DuPont, Wilmington, Delaware) is most popular because of its highly selective permeability of protons. Despite attempts by researchers to look for less expensive and more durable substitutes, Nafion is still the best choice. However, side effect of other cations transport is unavoidable during the MFC operation even with Nafion. In a batch accumulative system, for example, transportation of cation species other than protons by Nafion dominates the charge balance between the anodic and cathodic chambers because concentrations of Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+} are much higher than the proton concentrations in the anolyte and

catholyte (Rozendal et al., 2006). In this sense, Nafion as well as other PEMs used in the MFCs are not a necessarily proton specific membranes but actually cation specific membranes.

The ratio of PEM surface area to system volume is important for the power output. The PEM surface area has a large impact on maximum power output if the power output is below a critical threshold. The MFC internal resistance decreases with the increase of PEM surface area over a relatively large range (Oh and Logan, 2006).

Min et al. (2005a) compared the performance of a PEM and a salt bridge in an MFC inoculated with G. metallireducens. The power output using the salt bridge MFC was 2.2 mW/m^2 that was an order of magnitude lower than that achieved using Nafion. Grzebyk and Pozniak (2005) reported that they prepared interpolymer cation exchange membranes with polyethylene/poly(styrene-co-divinylbene) by sulfonation with a solution of chlorosulfonic acid in 1,2-dichloroethane. Their MFC using this different membrane instead of Nafion had a relative low performance. The highest voltage achieved in their MFC (with E. coli) was 67 mV with a total resistance of 830 Ω and graphite electrodes with a working surface area of about 17 cm^2 for both anode and cathode. Park and Zeikus (2003) used a porcelain septum made from kaolin instead of Nafion as the proton exchange system in a one-compartment MFC. The maximum electrical productivities obtained with sewage sludge as biocatalyst and a Mn^{4+}-graphite anode and a Fe^{3+}-graphite cathode were 14 mA current, 0.45 V potential, 1750 mA/m^2 current density, and 788 mW/m^2 of power density. No obvious disadvantages in performance were observed with the kaolin septum to Nafion.

Membranes and Kaolin septum are prone to fouling if the fuel is something like municipal wastewater. Membrane-less MFCs are desired if fouling or cost of the membrane becomes a problem in such applications.

5.3.4. Operating conditions in the anodic chamber

Fuel type, concentration and feed rate are important factors that impact the performance of an MFC. With a given microbe or microbial consortium, power density varies greatly using different fuels. Table 1 shows the performances of some MFCs operated using different microbes and fuels. Many systems have shown that electricity generation is dependent on fuel concentration both in batch and continuous-flow mode MFCs. Usually a higher fuel concentration yields a higher power output in a wide concentration range. Park and Zeikus (2002) reported that a higher current level was achieved with lactate (fuel) concentration increased until it was in excess at 200 mM in a single-compartment MFC inoculated with S. putrefaciens. Moon et al. (2006) investigated the effects of fuel concentration on the performance of an MFC. Their study also showed that the power density was increased with the increase in fuel concentration (Moon et al., 2006). Gil et al. (2003) found that the current increased with a wastewater concentration up to 50 mg/L in their MFC. Interestingly, the electricity generation in an MFC often peaks at a relatively low level of feed rate before heading downward. This may be because a high feed rate promoted the growth of fermentative bacteria faster than those of the electrochemically active bacteria in a mixed culture (Moon et al., 2006; Kim et al., 2004; Rabaey et al., 2003). However, if microbes are growing around the electrodes as biofilms, the increased feed rate is unlikely to affect the flora. One possible reason is that the high feed rate brings in other alternate electron acceptors competing with the anode to lower the output.

5.3.5. Operating conditions in the cathodic chamber

Oxygen is the most commonly used electron acceptor in MFCs for the cathodic reaction. Power output of an MFC strongly depends on the concentration level of electron acceptors. Several studies (Oh et al., 2004; Pham et al., 2004; Gil et al., 2003) indicated that DO was a major limiting factor when it remained below the air-saturated level. Surprisingly, a catholyte sparged with pure oxygen that gave 38 mg/L DO did not further increase the power output compared to that of the air-saturated water (at 7.9 mg/L DO) (Oh et al., 2004; Min and Logan, 2004; Pham et al., 2004;). Rate of oxygen diffusion toward the anode chamber goes up with the DO concentration. Thus, part of the substrate is consumed directly by the oxygen instead of transferring the electrons though the electrode and the circuit (Pham et al., 2004). Power output is much greater using ferricyanide as the electron acceptor in the cathodic chamber. So far, reported cases with very high power outputs such as 7200 mW/m^2, 4310 mW/m^2 and 3600 mW/m^2 all used ferricyanide in the cathodic chamber (Oh et al., 2004; Schroder et al., 2003; Rabaey et al., 2003, 2004), while less than 1000 mW/m^2 was reported in studies using DO regardless of the electrode material. This is likely due to the greater mass transfer rate and lower activation energy for the cathodic reaction offered by ferricyanide (Oh et al., 2004). Using hydrogen peroxide solution as the final electron acceptor in the cathodic chamber increased power output and current density according to Tartakovsky and Guiot (2006). As a consequence, aeration is no longer needed for single-compartment MFCs with a cathode that is directly exposed to air. Rhoads et al. (2005) measured the cathodic polarization curves for oxygen and manganese and found

that reducing manganese oxides delivered a current density up to 2 orders of magnitude higher than that by reducing oxygen.

Surely changing operating conditions can improve the power output level of the MFCs. However, it is not a revolutionary method to upgrade the MFCs from low power system to a applicable energy source at the very present. The bottleneck lies in the low rate of metabolism of the microbes in the MFCs. Even at their fastest growth rate (i.e. μ_{max} value) microbes are relatively slow transformers. The biotransformation rate of substrates to electrons has a fixed ceiling which is inherently slow. Effort should be focused on how to break the inherent metabolic limitation of the microbes for the MFC application. High temperature can accelerate nearly all kinds of reactions including chemical and biological ones. Use of thermophilic species might benefit for improving rates of electron production, however, to the best of our knowledge, no such investigation is reported in the literature. Therefore this is probably another scope of improvement for the MFC technology from the laboratory research to a real applicable energy source.

6. Applications

6.1. Electricity generation

MFCs are capable of converting the chemical energy stored in the chemical compounds in a biomass to electrical energy with the aid of microorganisms. Because chemical energy from the oxidization of fuel molecules is converted directly into electricity instead of heat, the Carnot cycle with a limited thermal efficiency is avoided and theoretically a much higher conversion efficiency can be achieved (>70%) just like conventional chemical fuel cells. Chaudhury and Lovley (2003) reported that *R. ferrireducens* could generate electricity with an electron yield as high as 80%. Higher electron recovery as electricity of up to 89% was also reported (Rabaey et al., 2003). An extremely high Coulombic efficiency of 97% was reported during the oxidation of formate with the catalysis of Pt black (Rosenbaum et al., 2006). However, MFC power generation is still very low (Tender et al., 2002; Delong and Chandler, 2002), that is the rate of electron abstraction is very low. One feasible way to solve this problem is to store the electricity in rechargeable devices and then distribute the electricity to end-users (Ieropoulos et al., 2003a). Capacitors were used in their biologically inspired robots named EcoBot I to accumulate the energy generated by the MFCs and worked in a pulsed manner. MFCs are especially suitable for powering small telemetry systems and wireless sensors that have only low power requirements to transmit signals such as temperature to receivers in remote locations (Ieropoulos et al., 2005c; Shantaram et al., 2005). MFCs themselves can serve as distributed power systems for local uses, especially in underdeveloped regions of the world. MFCs are viewed by some researchers as a perfect energy supply candidate for Gastrobots by self-feeding the biomass collected by themselves (Wilkinson, 2000). Realistic energetically autonomous robots would probably be equipped with MFCs that utilize different fuels like sugar, fruit, dead insects, grass and weed. The robot EcoBot-II solely powers itself by MFCs to perform some behavior including motion, sensing, computing and communication (Ieropoulos et al., 2003b; Ieropoulos et al., 2004; Melhuish et al., 2006). Locally supplied biomass can be used to provide renewable power for local consumption. Applications of MFCs in a spaceship are also possible since they can supply electricity while degrading wastes generated onboard. Some scientists envision that in the future a miniature MFC can be implanted in a human body to power an implantable medical device with the nutrients supplied by the human body (Chai, 2002). The MFC technology is particularly favored for sustainable long-term power applications. However, only after potential health and safety issues brought by the microorganisms in the MFC are thoroughly solved, could it be applied for this purpose.

6.2. Biohydrogen

MFCs can be readily modified to produce hydrogen instead of electricity. Under normal operating conditions, protons released by the anodic reaction migrate to the cathode to combine with oxygen to form water. Hydrogen generation from the protons and the electrons produced by the metabolism of microbes in an MFC is thermodynamically unfavorable. Liu et al. (2005c) applied an external potential to increase the cathode potential in a MFC circuit and thus overcame the thermodynamic barrier. In this mode, protons and electrons produced by the anodic reaction are combined at the cathode to form hydrogen. The required external potential for an MFC is theoretically 110 mV, much lower than the 1210 mV required for direct electrolysis of water at neutral pH because some energy comes from the biomass oxidation process in the anodic chamber. MFCs can potentially produce about 8–9 mol H_2/mol glucose compared to the typical 4 mol H_2/mol glucose achieved in conventional fermentation (Liu et al., 2005c). In biohydrogen production using MFCs, oxygen is no longer needed in the cathodic chamber. Thus, MFC efficiencies improve because oxygen leak to the

anodic chamber is no longer an issue. Another advantage is that hydrogen can be accumulated and stored for later usage to overcome the inherent low power feature of the MFCs. Therefore, MFCs provide a renewable hydrogen source that can contribute to the overall hydrogen demand in a hydrogen economy (Holzman, 2005).

6.3. Wastewater treatment

The MFCs were considered to be used for treating waste water early in 1991 (Habermann and Pommer, 1991). Municipal wastewater contains a multitude of organic compounds that can fuel MFCs. The amount of power generated by MFCs in the wastewater treatment process can potentially halve the electricity needed in a conventional treatment process that consumes a lot of electric power aerating activated sludges. MFCs yield 50–90% less solids to be disposed of (Holzman, 2005). Furthermore, organic molecules such as acetate, propionate, butyrate can be thoroughly broken down to CO_2 and H_2O. A hybrid incorporating both electrophiles and anodophiles are especially suitable for wastewater treatment because more organics can be biodegraded by a variety of organics. MFCs using certain microbes have a special ability to remove sulfides as required in wastewater treatment (Rabaey et al., 2006). MFCs can enhance the growth of bioelectrochemically active microbes during wastewater treatment thus they have good operational stabilities. Continuous flow and single-compartment MFCs and membrane-less MFCs are favored for wastewater treatment due to concerns in scale-up (Jang et al., 2004; Moon et al., 2005; He et al., 2005). Sanitary wastes, food processing wastewater, swine wastewater and corn stover are all great biomass sources for MFCs because they are rich in organic matters (Suzuki et al., 1978; Liu et al., 2004; Oh and Logan, 2005; Min et al., 2005b; Zuo et al., 2006). Up to 80% of the COD can be removed in some cases (Liu et al., 2004; Min et al., 2005b) and a Coulombic efficiency as high as 80% has been reported (Kim et al., 2005).

6.4. Biosensor

Apart from the aforementioned applications, another potential application of the MFC technology is to use it as a sensor for pollutant analysis and *in situ* process monitoring and control (Chang et al., 2004, 2005). The proportional correlation between the Coulombic yield of MFCs and the strength of the wastewater make MFCs possible biological oxygen demand (BOD) sensors (Kim et al., 2003). An accurate method to measure the

BOD value of a liquid stream is to calculate its Coulombic yield. A number of works (Chang et al., 2004; Kim et al., 2003) showed a good linear relationship between the Coulombic yield and the strength of the wastewater in a quite wide BOD concentration range. However, a high BOD concentration requires a long response time because the Coulombic yield can be calculated only after the BOD has been depleted unless a dilution mechanism is in place. Efforts have been made to improve the dynamic responses in MFCs used as sensors (Moon et al., 2004). A low BOD sensor can also show the BOD value based on the maximum current since the current values increase with the BOD value linearly in an oligotroph-type MFC. During this stage, the anodic reaction is limited by substrate concentration. This monitoring mode can be applied to real-time BOD determinations for either surface water, secondary effluents or diluted high BOD wastewater samples (Kang et al., 2003). MFC-type of BOD sensors are advantageous over other types of BOD sensor because they have excellent operational stability and good reproducibility and accuracy. An MFC-type BOD sensor constructed with the microbes enriched with MFC can be kept operational for over 5 years without extra maintenance (Kim et al., 2003), far longer in service life span than other types of BOD sensors reported in the literature.

7. MFCs in the future

The MFC technology has to compete with the mature methanogenic anaerobic digestion technology that has seen wide commercial applications (Holzman, 2005; Lusk, 1998) because they can utilize the same biomass in many cases for energy productions. MFCs are capable of converting biomass at temperatures below 20 °C and with low substrate concentrations, both of which are problematic for methanogenic digesters (Pham et al., 2006). A major disadvantage of MFCs is their reliance on biofilms for mediator-less electron transport, while anaerobic digesters such as up-flow anaerobic sludge blanket reactors eliminate this need by efficiently reusing the microbial consortium without cell immobilization (Pham et al., 2006). It is likely that the MFC technology will co-exist with the methanogenic anaerobic digestion technology in the future.

To improve the power density output, new anodophilic microbes that vastly improve the electron transport rate from the biofilm covering an anode to the anode are much needed (Angenent et al., 2004). Lovley claimed that an MFC's current flow could increase by four orders of magnitude if *Geobacter*

transports electrons to the anode at the same rate as its does to its natural electron acceptor that is ferric iron (Holzman et al., 2005). Mutagenesis and even recombinant DNA technology can conceivably be used in the future to obtain some "super bugs" for MFCs. Microbes may be used as a pure culture or a mixed culture forming a synergistic microbial consortium to offer better performance. One type of bacterium in a consortium may provide electron mediators that are used by another type of bacterium to transport electrons more efficiently to an anode (Rabaey and Verstraete, 2005). It is possible in the future that an optimized microbial consortium can be obtained to operate an MFC without extraneous mediators or biofilms while achieving superior mass transfer and electron transfer rates.

As aforementioned, MFCs can potentially be used for different applications. When used in wastewater treatment, a large surface area is needed for biofilm to build up on the anode. A breakthrough is needed in creating inexpensive electrodes that resist fouling. It is unrealistic to expect that the power density output from an MFC to match that of conventional chemical fuel cell such as a hydrogen-powered fuel cell. The fuel in an MFC is often a rather dilute biomass (as in wastewater treatment) in the anodic chamber that has a limited energy (reflected by its BOD). Another limitation is the inherent naturally low catalytic rate of the microbes. Even at their fastest growth rate microbes are relatively slow transformers. Although Coulombic efficiency over 90% has been achieved in some cases, it has little effect on the crucial problem of low reaction rate. Although some basic knowledge has been gained in MFC research, there is still a lot to be learned in the scale-up of MFC for large-scale applications.

Acknowledgement

References

Aelterman P, Rabaey K, Pham HT, Boon N, Verstraete W. Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. Environ Sci Technol 2006;40:3388–94.

Allen RM, Bennetto HP. Microbial fuel-cells: electricity production from carbohydrates. Appl Biochem Biotechnol 1993;39/40:27–40.

Angenent LT, Karim K, Al-Dahhan MH, Wrenn BA, Domíguez-Espinosa R. Production of bioenergy and biochemicals from industrial and agricultural wastewater. Trends Biotechnol 2004;9:477–85.

Appleby AJ, Fouldes FR. Fuel cell handbook. New York: Van Nostrand Reinhold; 1989.

Back JH, Kim MS, Cho H, Chang IS, Lee J, Kim KS, et al. Construction of bacterial artificial chromosome library from electrochemical microorganisms. FEMS Microbiol Lett 2004;238:65–70.

Bennetto HP. Microbial fuel cells. Life Chem Rep 1984;2:363–453.

Bergel A, Feron D, Mollica A. Catalysis of oxygen reduction in PEM fuel cell by seawater biofilm. Electrochem Commun 2005;7:900–4.

Bond DR, Holmes DE, Tender LM, Lovley DR. Electrode-reducing microorganisms that harvest energy from marine sediments. Science 2002;295:483–5.

Bond DR, Lovley DR. Electricity production by *Geobacter sulfurreducens* attached to electrodes. Appl Environ Microbiol 2003;69:1548–55.

Bullen RA, Arnot TC, Lakeman JB, Walsh FC. Biofuel cells and their development. Biosens Bioelectron 2006;21:2015–45.

Chang IS, Jang JK, Gil GC, Kim M, Kim HJ, Cho BW, et al. Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor. Biosens Bioelectron 2004;19:607–13.

Chang IS, Moon H, Jang JK, Kim BH. Improvement of a microbial fuel cell performance as a BOD sensor using respiratory inhibitors. Biosens Bioelectron 2005;20:1856–9.

Chang IS, Moon H, Bretschger O, Jang JK, Park HI, Nealson KH, et al. Electrochemically active bacteria (EAB) and mediator-less Microbial fuel cells. J Microbiol Biotechnol 2006;16:163–77.

Chaudhuri SK, Lovley DR. Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. Nat Biotechnol 2003;21:1229–32.

Cheng S, Liu H, Logan BE. Increased performance of single-chamber microbial fuel cells using an improved cathode structure. Electrochem Commun 2006a;8:489–94.

Cheng S, Liu H, Logan BE. Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing. Environ Sci Technol 2006b;40:2426–32.

Cheng S, Liu H, Logan BE. Power densities using different cathode catalyst (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells. Environ Sci Technol 2006c;40:364–9.

Chia M. A miniaturized microbial fuel cell. Technical digest of solid state sensors and actuators workshop, Hilton Head Island; 2002. p. 59–60.

Choi Y, Jung E, Kim S, Jung S. Membrane fluidity sensing microbial fuel cell. Bioelectrochemistry 2003;59:121–7.

Davis F, Higson SPJ. Biofuel cells—recent advances and applications. Biosens Bioelectron 2007;22:1224–35.

Delaney GM, Bennetto HP, Mason JR, Roller SD, Stirling JL, Thurston CF. Electron-transfer coupling in microbial fuel cells. 2. Performance of fuel cells containing selected microorganism-mediator-substrate combinations. J Chem Tech Biotechnol 1984;34B:13–27.

Delong EF, Chandler P. Power from the deep. Nat Biotechnol 2002;20:788–9.

Gil GC, Chang IS, Kim BH, Kim M, Jang JY, Park HS, et al. Operational parameters affecting the performance of a mediator-less microbial fuel cell. Biosens Bioelectron 2003;18:327–34.

Gregory KB, Bond DR, Lovley DR. Graphite electrodes as electron donors for anaerobic respiration. Environ Microbiol 2004;6:596–604.

Grzebyk M, Pozniak G. Microbial fuel cells (MFCs) with interpolymer cation exchange membranes. Sep Purif Technol 2005;41:321–8.

Habermann W, Pommer EH. Biological fuel cells with sulphide storage capacity. Appl Microbiol Biotechnol 1991;35:128–33.

He Z, Minteer SD, Angenent L. Electricity generation from artificial wastewater using an upflow microbial fuel cell. Environ Sci Technol 2005;39:5262–7.

He Z, Wagner N, Minteer SD, Angenent LT. An upflow microbial fuel cell with an interior cathode: assessment of the internal

resistance by impedance spectroscopy. Environ Sci Technol 2006;40:5212–7.

Hernandez ME, Newman DK. Extracellular electron transfer. Cell Mol Life Sci 2001;58:1562–71.

Holmes DE, Bond DR, O'Neil RA, Reimers CE, Tender LR, Lovley DR. Microbial communities associated with electrodes harvesting electricity from a variety of aquatic sediments. Microbial Ecol 2004;48:178–90.

Holzman DC. Microbe power. Environ Health Persp 2005;113:A754–7.

Ieropolulos I, Greenman J, Melhuish C. Imitation metabolism: energy autonomy in biologically inspired robots. Proceedings of the 2nd international symposium on imitation of animals and artifacts; 2003a. p. 191–4.

Ieropolulos I, Melhuish C, Greenman J. Artificial metabolism: towards true energetic autonomy in artificial life. Lect Notes Comput Sc 2003b;2801:792–9.

Ieropoulos I, Melhuish C, Greenman J. Energetically autonomous robots. In: Groen F, et al, editor. Intelligent autonomous systems, vol. 8. Amsterdam: IOS Press; 2004. p. 128–35. (March, 2004).

Ieropoulos IA, Greenman J, Melhuish C, Hart J. Comparative study of three types of microbial fuel cell. Enzyme Microb Tech 2005a;37:238–45.

Ieropoulos I, Greenman J, Melhuish C, Hart J. Energy accumulation and improved performance in microbial fuel cells. J Power Sources 2005b;145:253–6.

Ieropoulos I, Melhuish C, Greenman J. EcoBot-II: an artificial agent with a natural metabolism. Adv Robot Syst 2005c;2:295–300.

Jang JK, Pham TH, Chang IS, Kang KH, Moon H, Cho KS, et al. Construction and operation of a novel mediator-and membrane-less microbial fuel cell. Process Biochem 2004;39:1007–12.

Kang KH, Jang JK, Pham TH, Moon H, Chang IS, Kim BH. A microbial fuel cell with improved cathode reaction as a low biochemical oxygen demand sensor. Biotechnol Lett 2003;25:1357–61.

Kim BH, Kim HJ, Hyun MS, Park DH. Direct electrode reaction of Fe (III)-reducing bacterium, Shewanella putrifaciens. J Microbiol Biotechnol 1999a;9:127–31.

Kim HJ, Hyun MS, Chang IS, Kim BH. A microbial fuel cell type lactate biosensor using a metal-reducing bacterium, Shewanella putrefaciens. J Microbiol Biotechnol 1999b;9:365–7.

Kim HJ, Park HS, Hyun MS, Chang IS, Kim M, Kim BH. A mediator-less microbial fuel cell using a metal reducing bacterium, Shewanella putrefaciens. Enzyme Microb Tech 2002;30:145–52.

Kim BH, Chang IS, Gil GC, Park HS, Kim HJ. Novel BOD (biological oxygen demand) sensor using mediator-less microbial fuel cell. Biotechnol Lett 2003;25:541–5.

Kim BH, Park HS, Kim HJ, Kim GT, Chang IS, Lee J, et al. Enrichment of microbial community generating electricity using a fuel-cell type electrochemical cell. Appl Microbiol Biotechnol 2004;63:672–81.

Kim JR, Min B, Logan BE. Evaluation of procedures to acclimate a microbial fuel cell for electricity production. Appl Microbiol Biotechnol 2005;68:23–30.

Lee SA, Choi Y, Jung S, Kim S. Effect of initial carbon sources on the electrochemical detection of glucose by Gluconobacter oxydans. Bioelectrochemistry 2002;57:173–8.

Liu H, Logan BE. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. Environ Sci Technol 2004;38:4040–6.

Liu H, Ramnarayanan R, Logan BE. Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environ Sci Technol 2004;28:2281–5.

Liu H, Cheng S, Logan BE. Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell. Environ Sci Technol 2005a;39:658–62.

Liu H, Cheng S, Logan BE. Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration. Environ Sci Technol 2005b;39:5488–93.

Liu H, Grot S, Logan BE. Electrochemically assisted microbial production of hydrogen from acetate. Environ Sci Tchnol 2005c:4317–20.

Liu ZD, Lian J, Du ZW, Li HR. Construction of sugar-based microbial fuel cells by dissimilatory metal reduction bacteria. Chin J Biotech 2006;21:131–7.

Logan BE, Murano C, Scott K, Gray ND, Head IM. Electricity generation from cysteine in a microbial fuel cell. Water Res 2005;39:942–52.

Logan BE, Hamelers B, Rozendal R, Schroder U, Keller J, Freguia S, et al. Microbial fuel cells: methodology and technology. Environ Sci Technol 2006;40:5181–92.

Lovley DR. Dissimilatory metal reduction. Annu Rev Microbial 1993;47:263–90.

Lovley DR, Coates JD, Blunt-Harris EL, Phillips EJP, Woodward JC. Humic substances as electron acceptors for microbial respiration. Nature 1996;382:445–8.

Lovley DR, Holmes DE, Nevin KP. Dissimilatory Fe(III) and Mn(IV) reduction. Adv Microb Physiol 2004;49:219–86.

Lovely DR. Microbial fuel cells: novel microbial physiologies and engineering approaches. Curr Opin Biotech 2006;17:327–32.

Lowy DA, Tender LM, Zeikus JG, Park DH, Lovley DR. Harvesting energy from the marine sediment–water interface II kinetic activity of anode materials. Biosens Bioelectron 2006;21:2058–63.

Lusk P. Methane recovery from animal manures: a current opportunities casebook. NREL/SR-580-25145; 1998. Sept.

Madigan MT, Martinko JM, Parker J. Brock biology of microorganisms. Upper Saddle River: Prentice Hall; 2000.

Melhuish C, Ieropoulos I, Greenman J Horsfield I. Energetically autonomous robots: food for thought. Auton Robot 2006;21:187–98.

Menicucci J, Beyenal H, Marsili E, Veluchamy RA, Demir G, Lewandowski Z. Procedure for determining maximum sustainable power generated by microbial fuel cells. Environ Sci Technol 2006;40:1062–8.

Min B, Logan BE. Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell. Environ Sci Technol 2004;38:5809–14.

Min B, Cheng S, Logan BE. Electricity generation using membrane and salt bridge microbial fuel cells. Water Res 2005a;39:1675–86.

Min B, Kim JR, Oh SE, Regan JM, Logan BE. Electricity generation from swine wastewater using microbial fuel cells. Water Res 2005b;39:4961–8.

Moon H, Chang IS, Kang KH, Jang JK, Kim BH. Improving the dynamic response of a mediator-less microbial fuel cell as a biochemical oxygen demand (BOD) sensor. Biotechnol Lett 2004;26:1717–21.

Moon H, Chang IS, Jang JK, Kim BH. Residence time distribution in microbial fuel cell and its influence on COD removal with electricity generation. Biochem Eng J 2005;27:59–65.

Moon H, Chang IS, Kim BH. Continuous electricity production from artificial wastewater using a mediator-less microbial fuel cell. Bioresource Technol 2006;97:621–7.

Nevin KP, Lovley DR. Lack of production of electron-shuttling compounds or solubilization of Fe(III) during reduction of insoluble Fe(III) oxide by Geobacter metallireducens. Appl Environ Microbiol 2000;66:2248–51.

Niessen J, Schroder U, Rosenbaum M, Scholz F. Fluorinated polyanilines as superior materials for electrocatalytic anodes in bacterial fuel cells. Electrochem Commun 2004a;6:571–5.

Niessen J, Schroder U, Scholz F. Exploiting complex carbohydrates for microbial electricity generation — a bacterial fuel cell operating on starch. Electrochem Commun 2004b;6:955–8.

Niessen J, Harnisch F, Rosenbaum M, Schroder U, Scholz F. Heat treated soil as convenient and versatile source of bacterial communities for microbial electricity generation. Electrochem Commun 2006;8:869–73.

Oh SE, Logan BE. Hydrogen and electricity production from a food processing wastewater using fermentation and microbial fuel cell technologies. Water Res 2005;39:4673–82.

Oh SE, Logan BE. Proton exchange membrane and electrode surface areas as factors that affect power generation in microbial fuel cells. Appl Microbiol Biotechnol 2006;70:162–9.

Oh SE, Min B, Logan BE. Cathode performance as a factor in electricity generation in microbial fuel cells. Environ Sci Technol 2004;38:4900–44.

Park DH, Zeikus JG. Utilization of electrically reduced neutral red by *Actinobacillus succinogenes*: physiological function of neutral red in membrane-driven fumarate reduction and energy conservation. J Bacteriol 1999;181:2403–10.

Park DH, Zeikus JG. Electricity generation in microbial fuel cells using neutral red as an electronophore. Appl Environ Microb 2000;66:1292–7.

Park DH, Zeikus JG. Impact of electrode composition on electricity generation in a single-compartment fuel cell suing *Shewanella putrefaciens*. Appl Microbiol Biotechnol 2002;59: 58–61.

Park DH, Zeikus JG. Improved fuel cell and electrode designs for producing electricity from microbial degradation. Biotechnol Bioeng 2003;81:348–55.

Park DH, Kim BH, Moore B, Hill HAO, Song MK, Rhee HW. Electrode reaction of *Desulfovibrio desulfuricans* modified with organic conductive compounds. Biotechnol Tech 1997;11:145–58.

Park DH, Laivenieks M, Guettler MV, Jain MK, Zeikus JG. Microbial utilization of electrically reduced neutral red as the sole electron donor for growth and metabolite production. Appl Environ Microbiol 1999;65:2912–7.

Park HS, Kim BH, Kim HS, Kim HJ, Kim GT, Kim M, et al. A novel electrochemically active and Fe(III)-reducing bacterium phylogenetically related to *Clostridium butyricum* isolated from a microbial fuel cell. Anaerobe 2001;7:297–306.

Pham CA, Jung SJ, Phung NT, Lee J, Chang IS, Kim BH, et al. A novel electrochemically active and Fe(III)-reducing bacterium phylogenetically related to *Aeromonas hydrophila*, isolated from a microbial fuel cell. FEMS Microbiol Lett 2003;223:129–34.

Pham TH, Jang JK, Chang IS, Kim BH. Improvement of cathode reaction of a mediatorless microbial fuel cell. J Microbiol Biotechnol 2004;14:324–9.

Pham TH, Rabaey K, Aelterman P, Clauwaert P, De Schamphelaire L, Boon N, Verstraete W. Microbial fuel cells in relation to conventional anaerobic digestion technology. Eng Life Sci 2006;6:285–92.

Potter MC. Electrical effects accompanying the decomposition of organic compounds. Proc R Soc Ser B 1912;84:260–76.

Prasad D, Sivaram TK, Berchmans S, Yegnaraman V. Microbial fuel cell constructed with a micro-organism isolated from sugar industry effluent. J Power Sources 2006;160:991–6.

Rabaey K, Verstraete W. Microbial fuel cells: novel biotechnology for energy generation. Trends Biotechnol 2005;23:291–8.

Rabaey K, Lissens G, Siciliano S, Verstraete W. A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. Biotechnol Lett 2003;25:1531–5.

Rabaey K, Boon N, Siciliano SD, Verhaege M, Verstraete W. Biofuel cells select for microbial consortia that self-mediate electron transfer. Appl Environ Microb 2004;70:5373–82.

Rabaey K, Boon N, Hofte M, Verstraete W. Microbial phenazine production enhances electron transfer in biofuel cells. Environ Sci Technol 2005a;39:3401–8.

Rabaey K, Clauwaert P, Aelterman P, Verstraete W. Tubular microbial fuel cells for efficient electricity generation. Environ Sci Technol 2005b;39:8077–82.

Rabaey K, Van De Sompel K, Maignien L, Boon N, Aelterman P, Clauwaert P, et al. Microbial fuel cells for sulfide removal. Environ Sci Technol 2006;40:5218–24.

Rhoads A, Beyenal H, Lewandowshi Z. Microbial fuel cell using anaerobic respiration as an anodic reaction and biomineralized manganese as a cathodic reactant. Environ Sci Technol 2005;39:4666–71.

Ringeisen BR, Henderson E, Wu PK, Pietron J, Ray R, Little B, et al. High power density from a miniature microbial fuel cell using *Shewanella oneidensis* DSP10. Environ Sci Technol 2006;40:2629–34.

Rosenbaum M, Schroder U, Scholz F. Investigation of the electrocatalytic oxidation of formate and ethanol at platinum black under microbial fuel cell conditions. J Solid State Electrochem 2006;10:872–8.

Rozendal RA, Hamelers HVM, Buisman CJN. Effects of membrane cation transpoet on pH and microbial fuel cell performance. Environ Sci Technol 2006;40:5206–11.

Scholz F, Schroder U. Bacterial batteries. Nat Biotechnol 2003;21:1151–2.

Schroder U, Nieben J, Scholz F. A generation of microbial fuel cells with current outputs boosted by more than on e order of magnitude. Angew Chem Int Ed 2003;42:2880–3.

Shantaram A, Beyenal H, Veluchamy RRA, Lewandowski Z. Wireless sensors powered by microbial fuel cells. Environ Sci Technol 2005;39:5037–42.

Stirling JL, Bennetto HP, Delaney GM, Mason JR, Roller SD, Tanaka K, et al. Microbial fuel cells. Biochem Soc Trans 1983;11:451–3.

Straub KL, Benz M, Schink B. Iron metabolism in anoxic environments at near neutral pH. FEMS Microbiol Ecol 2001;34:181–6.

Suzuki S, Karube I, Matsunaga T. Application of a biochemical fuel cell to wastewater. Biotechnol Bioeng Symp 1978;8:501–11.

Tartakovsky B Guiot SR. A comparison of air and hydrogen peroxide oxygenated microbial fuel cell reactors. Biotechnol Prog 2006;22:241–6.

Tender LM, Reimers CE, Stecher HA, Holmes DE, Bond DR, Lowy DA, et al. Harnessing microbially generated power on the seafloor. Nat Biotechnol 2002;20:821–5.

Thurston CF, Bennetto HP, Delaney GM, Mason JR, Roller SD, Stirling JL. Glucose metabolism in a microbial fuel cell. Stoichiometry of product formation in a thionine-mediated *Proteus vulgaris* fuel cell and its relation to Coulombic yields. J Gen Microbiol 1985;131:1393–401.

Tokuji I, Kenji K. Vioelectrocatalyses-based application of quinoproteins and quinprotein-containing bacterial cells in biosensors and biofuel cells. Biochim Biophys Acta 2003;1647:121–6.

Vargas M, Kashefi K, Blunt-Harris EL, Lovley DR. Microbiological evidence for Fe(III) reduction on early earth. Nature 1998;395:65–70.

Vega CA, Fernandez I. Mediating effect of ferric chelate compounds in microbial fuel cells with *Lactobacillus plantarum*, *Streptococcus lactis*, and *Erwinia dissolvens*. Bioelectrochem Bioenerg 1987;17: 217–22.

Wilkinson S. "Gastrobots" — benefits and challenges of microbial fuel cells in food powered robot applications. Auton Robot 2000;9:99−111.

Zhang E, Xu W, Diao G, Shuang C. Electricity generation from acetate and glucose by sedimentary bacterium attached to electrode in microbial-anode fuel cells. J Power Sources 2006;161:820–5.

Zhao F, Harnisch F, Schroder U, Scholz F, Bogdanoff P, Herrmann I. Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. Electrochem Commun 2005;7:1405–10.

Zhao F, Harnisch F, Schroder U, Scholz F, Bogdanoff P, Herrmann I. Challenges and constraints of using oxygen cathodes in microbial fuel cells. Environ Sci Technol 2006:5193–9.

Zuo Y, Maness PC, Logan BE. Electricity production from steam-exploded corn stover biomass. Energ Fuel 2006;20:1716–21.