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Microbial Fuel Cells

On August 1, 2012, The National Petroleum Council (NPC) in approving its report, *Advancing Technology for America's Transportation Future*, also approved the making available of certain materials used in the study process, including detailed, specific subject matter papers prepared or used by the study's Task Groups and/or Subgroups. These Topic Papers were working documents that were part of the analyses that led to development of the summary results presented in the report's Executive Summary and Chapters.

These Topic Papers represent the views and conclusions of the authors. The National Petroleum Council has not endorsed or approved the statements and conclusions contained in these documents, but approved the publication of these materials as part of the study process.

The NPC believes that these papers will be of interest to the readers of the report and will help them better understand the results. These materials are being made available in the interest of transparency.

Microbial Fuel Cells

Future Fuel Technologies, National Petroleum Council (NPC) Study

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Microbial Fuel Cells

Energy needs in the U.S and the world continue to increase and in an effort to aid energy independence, research initiatives are focused on alternate, renewable and carbon neutral energy sources. Production of electrical energy using microorganisms through microbial fuel cells (MFC) is one such renewable and sustainable technology that is considered to be one of the most efficient (HaoYu et al., 2007; Salgado, 2009) and carbon neutral energy sources (Lovley, 2006). MFCs are fuel cells that are capable of converting chemical energy available in organic substrates into electrical energy using bacteria as a biocatalyst to oxidize the biodegradable substrates (www.microbialfuelcell.org). The fact that bacteria can oxidize the substrates to produce electricity makes MFCs an ideal solution for wastewater treatment and domestic energy production (Schwartz, 2007). Logan (2010) reported that MFCs can generate power densities as much as $1kW/m^3$ of reactor volume. MFCs as a source of bioenergy production have accelerated the research worldwide and the technical aspects of MFCs have been reviewed extensively (Pant D, 2010). This paper briefly focuses on the MFC technology, technical challenges, future outlook, key players and their research on MFC.

The basic MFC design consists of an anode, a cathode, a proton exchange membrane (PEM) and an electrical circuit, as shown in Fig.1 (Logan, 2008). In an MFC, bacterial community present in the anode compartment uses organic substrates as fuels to produce electrons and protons through biological processes (Rabaey and Verstraete, 2005)(www.microbialfuelcell.org). These electrons are accepted by nicotinamide adenine dinucleotide (NADH) in the electron transport chain and subsequently transferred to terminal electron acceptors such as nitrate, sulphate and oxygen and then reaches the outer membrane proteins (Logan and Regan, 2006; Salgado, 2009). Bacteria then transfer these electrons to anode from where electrons reach the cathode via an external electrical circuit, thus producing electric current, which is measured by a voltmeter or ammeter connected to the device (Salgado, 2009). The protons generated are diffused through

the PEM to the cathode and subsequently combine with the electrons and oxygen to form water. The anode compartment is typically maintained under anaerobic conditions as oxygen inhibits electricity generation whereas the cathode is exposed to oxygen (Logan, 2008; Rahimnejad Mostafa, 2009). Du et al., 2007 reported that the electrode reaction is the breakdown of the biodegradable substrate to carbon dioxide and water along with production of electricity using acetate as a substrate.

Anode reaction: $CH_3COO^- + 2H_2O \longrightarrow 2CO_2 + 7H^+ + 8e^-$

Cathode reaction: $O_2 + 4e^- + 4H \rightarrow 2H_2O$

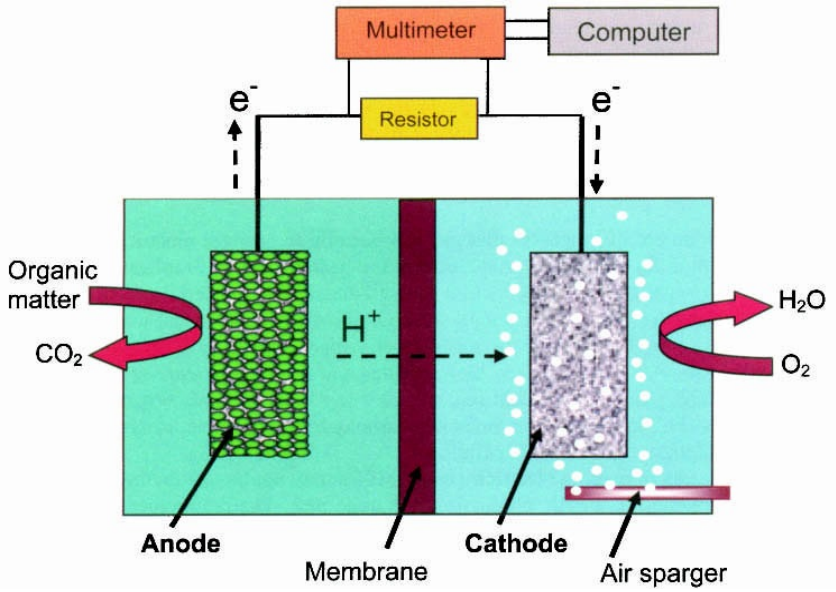


Fig 1: Graphical representation of microbial fuel cells (Logan, B.E. 2008.Microbial fuel cells)

Electron transfer mechanisms

In MFCs, the bacterial transfer of electrons from the substrates to electrodes is mainly through two ways (Fig.2). The mechanism of electron transfer may be of either direct transfer (mediator-less) or indirect electron transfer (mediator MFC) (Yan-ping, 2008).

Direct electron transfer:

There are several microorganisms (Eg. *Shewanella putrefaciens, Geobacter sulferreducens, G. metallireducens and Rhodoferax ferrireducens*) that transfer electrons from inside the cell to extracellular acceptors via c-type cytochromes, biofilms and highly conductive

pili (nanowires) (Derek R, 2008). These microorganisms have high Coulombic efficiency[1] and can form biofilms on the anode surface that act as electron acceptors and transfer electrons directly to the anode resulting in the production of more energy (Chaudhuri and Lovley, 2003; Kim et al., 2002).

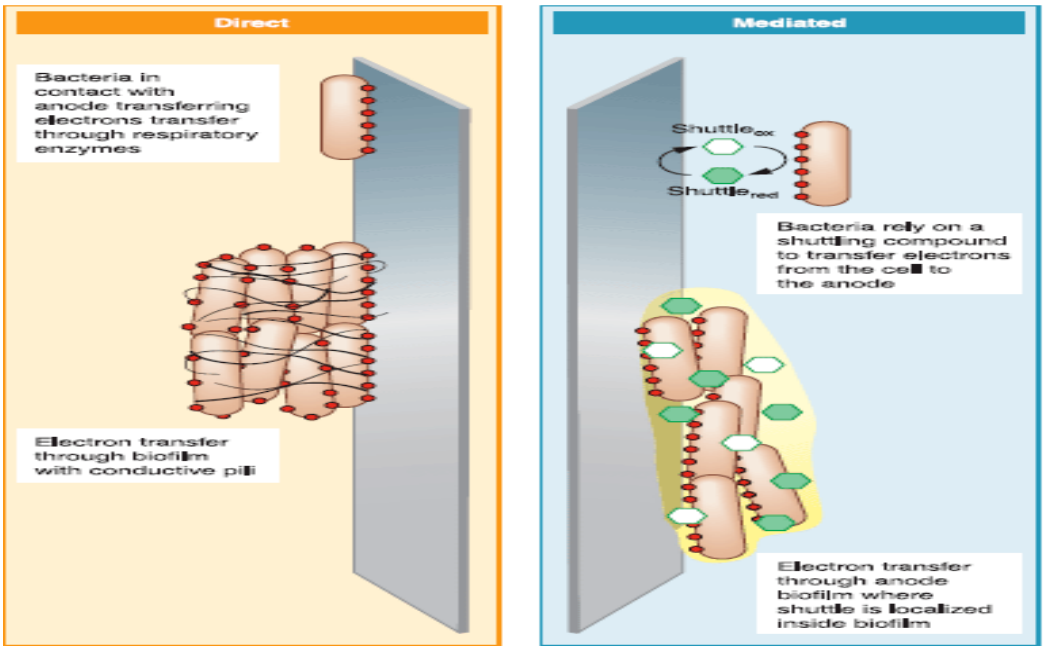


Fig 2: Electron transfer mechanisms (Derek Lovely, 2009)

Electron transfer by own /artificial mediators:

In this mechanism, electrons from microbial carriers are transported onto the electrode surface either by a microorganism's (*Shewanella oneidensis, Geothrix ferementans)* own mediator which in turn facilitate extracellular electron transfer or by added mediators. The MFCs that use mediators as electron shuttles[2] are called mediator MFCs. Mediators provide a platform for the microorganisms to generate electrochemically active reduced products. The reduced form of the mediator is cell permeable, accept electrons from the electron carrier and transfer them onto the electrode surface (Lovley, 2006). Usually neutral red, thionine, methylene blue, anthraquinone-2, 6-disulfonate, phenazines and iron chelates are added to the reactor as redox mediators (Du et al., 2007). Mediators are required in MFCs that use *Proteus vulgaris,*

[1] Coulombic efficiency: The amount of electrons recovered as current versus the maximum recovery from the substrate (Logan, B.E., and Regan, J.M., 2006; Balat, M. 2009).

[2] Mediators / electron shuttles: They carry the electrons from inside the cell to exogenous electrodes.

Escherichia coli, Streptococcus lactis, and *Pseudomonas* species as these bacteria cannot transfer electrons outside the cell. To be effective, the mediator should be able to penetrate the cell membranes easily, able to grab the electrons from the electron carriers of the electron transport chains, should increase electron transfer from the metabolite, stable during long periods of redox cycling and non-toxic to microbes (Du et al., 2007; Ieropoulos et al., 2005; Osman et al., 2010).

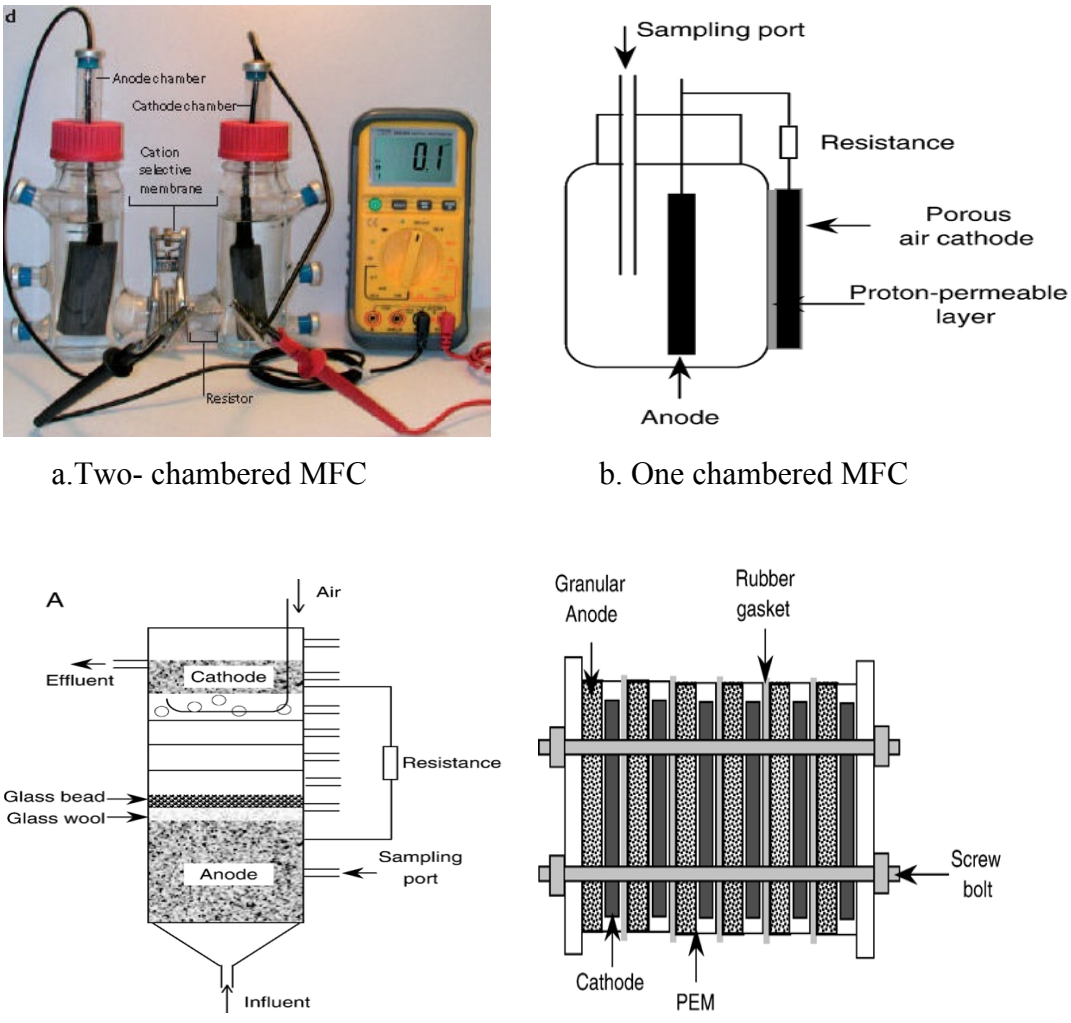
MFC designs

There are many types of reactors but they all share the same operating principles. Different configurations of MFCs are being developed using a variety of materials. They are operated under different conditions to increase the performance, power output and reduce the overall cost (Fig 3).

- Two chamber MFC: This is the most widely used design consisting of two chambers with the anode and cathode compartments separated by an ion exchange membrane (Fig3a). This design is generally used in basic research and literature suggests that the power output from these systems are generally low due to their complex design, high internal resistance and electrode based losses (Du et al., 2007; Logan and Regan, 2006; Nwogu, 2007).
- Single chamber MFC: This design has only one compartment that contains both the anode and the cathode. The anode is either placed away or close to the cathode separated by PEM. Liang et al. (2007) reported that if the anode is closer to the cathode, it reduces internal ohmic resistance by avoiding the use of catholyte as a result of combining two chambers and thus increases the power density. Compared to the two chamber MFC, it offers simple, cost effective design and produces power in a more efficient way (Du et al., 2007). However, in the membrane-less configuration, microbial contamination and back diffusion of oxygen from cathode to anode without PEM are the major drawbacks (Kim 2008)Fig3b).
- Up-flow MFC: The cylinder shaped MFC consists of the anode (bottom) and the cathode (top) partitioned by glass wool and glass beads layers. The feed is supplied from the bottom of the anode passes upward of the cathode and exits at the top (Fig3c). The diffusion barrier among the electrodes provides a gradient for proper operation of the MFCs (Du et al., 2007; Kim 2008; Schwartz, 2007). This design has no physical

separation and so there are no proton transfer associated problems and is attractive for wastewater treatment (Kim 2008).

- Stacked MFC: In this design, several single cell MFCs are connected together in series or in parallel to achieve high current output (Du et al., 2007). Due to higher electrochemical reaction rate, a parallel connection can generate more energy than a series connection when operated at the same volumetric flow but is prone to higher short circuiting compared to a series connection (Fig3d)(Aelterman et al., 2006; Schwartz, 2007).



a.Two- chambered MFC

b. One chambered MFC

c. Up-flow mode MFC

d. Stacked MFC

Fig 3: Examples of different MFC configurations (Zhuwei et al., 2007)

Electrode materials

The choice of electrode material affects the performance of MFCs. Various materials have been investigated as electrodes to increase the performance and power output of the MFCs. For anode, carbon cloth, carbon felt, graphite felt, carbon mesh and graphite fiber brush are frequently used due to their stability, high electric conductivity and large surface area (Logan, 2010; Logan and Regan, 2006). For cathodes, platinum (Pt), platinum black, activated carbon (AC), graphite-based cathodes and biocathodes are used (Chen et al., 2008; Du et al., 2007). Though platinum coated electrodes are more efficient and superior in power production due to higher catalytic activity with oxygen than other electrodes, they are not cost effective (Logan, 2010; Oh et al., 2004) Alternate catalysts for platinum include ferric iron, manganese oxides, iron and cobalt based compounds. Ferricyanide ($K_3(Fe(CN)_6$) is frequently used as an electron acceptor in the MFCs due to its good performance and low overpotential[3] (Logan and Regan, 2006). Biocathodes increases the power by decreasing the overpotential (Huang et al., 2011). Alternately, the cathode can contain oxygen and is preferred because it simplifies the operation of the cell and is the most commonly used electron acceptor in MFC.

The power output depends on proton transfer from anode to cathode. Transfer of protons to the cathode is a slow process that causes high internal resistance (Kazuya, 2008; Osman et al., 2010). Most of the MFCs require a salt bridge or PEM to separate the anode and cathode compartments. The PEM is commonly made from polymers like Nafion and Ultrex (Schwartz, 2007). Although membrane-less, single chamber MFCs are reported to produce higher power density, membrane absence would increase oxygen to the anode and thus lowers the coulombic efficiency and bioelectrocatalytic activity of the microbes (Logan, 2010; Wen et al., 2010).

Microbes in MFC

A wide variety of bacterial communities are found to have the ability to oxidize organic compounds and transfer electrons to the anode. MFCs make use of both the mixed cultures and pure bacterial cultures (Cheng et al., 2005). Rabaey et al (2005) reported that the mixed cultures have high resistance for process disturbances, substrate consumption and higher power output. The electrochemically active bacteria in MFCs may be aerobes or facultative anaerobes and the

[3] Overpotential: The difference between the real voltage (E) and theoretical voltage (E_t) (44).

reaction temperature in MFCs depend on the bacterial tolerance to temperature (mesophilic/thermophilic) (Logan, 2008; Rabaey and Verstraete, 2005). Not only the electrochemically active, iron-reducing bacteria (*Shewanella* and *Geobacter)* but also other group of bacteria (*Klebsiella pneumonia, Rhodopseudomonas palustris,Dessulfobulbus propionicus*) that are isolated from the wastewater showed great potential to be used in MFCs (Sharma and Kundu, 2010). A number of recent reports reviewed screening, identification of microbes, their ability to generate electric current and power densities in detail (Logan, 2009; Logan et al., 2005)

Substrate in MFC

Substrate provides not only energy for the bacterial cells to grow in the MFCs but also influences the economic viability and overall performance such as power density and coulombic efficiency of MFCs. The composition, concentration and type of the substrate also affect the microbial community and power production (Cheng and Logan, 2011; Pant D, 2010). Many organic substrates including carbohydrates, proteins, volatile acids, cellulose and wastewater have been used as feed in MFC studies. It can range from simple, pure, low molecular sugars to complex organic matter containing waste water to generate electricity. In most of the MFCs, acetate is commonly used as a substrate due to its inertness towards alternative microbial conversions (fermentations and methanogenesis) that lead to high coulombic efficiency and power output (Pant D, 2010). Power generated with acetate found to be higher when compared with other substrate (Chae et al., 2009; Liu et al., 2005). Different substrate and their columbic efficiency and power output have been reviewed by many authors (Lee et al., 2008; Niessen et al., 2004; Pant D, 2010; Zuo et al., 2006). However, the economics of substrate is not known. Table 1 presents a list of substrates used in MFCs.

Table 1: List of substrates in MFC studies

Substrate type	**Concentration**	**Current density (mA/cm^2)**
Acetate	1g/L	0.8

Lactate	18mM	0.005
Glucose	6.7mM	0.7
Sucrose	2674mg/L	0.19
Glucuronic acid	6.7mM	1.18
Phenol	400mg/L	0.1
Sodium fumarate	25mM	2.05
Starch	10g/L	1.3
Cellulose particles	4g/L	0.02
Xylose	6.7mM	0.74
Domestic wastewater	600mg/L	0.06
Brewery wastewater	2240mg/L	0.2

(Pant D, 2010)

Current maturity of the technology

MFC is an active research field and scientific research has advanced rapidly increasing power density from a few Wm^{-2} to over $1kWm^{-3}$ of reactor volume under ideal conditions (Logan, 2010). The use of MFCs in wastewater treatment and remote power generation is being tested at a pilot scale. Schwartz (2007) reported that biosensors powered by MFCs are close to market readiness. As of now only benthic[4] MFCs have been described to be useful in generating power in remote locations (Osman et al., 2010). Recent advances on new types of MFC designs, electrode materials and significant progress in optimizing other parameters and a few pilot scale demonstrations at Queensland, Australia, University of Connecticut and Cambrian Innovation, MA indicate that this technology can be deployed for sustainable energy production and other applications within a few years (Logan, 2010; Viscarolasaga, 2008) Currently, different MFC

[4] Benthic MFC – Generates power from the organic matter in anoxic marine sediments.

designs (single chamber, tubular, series) are used with enhanced electrode materials and various substrates to enhance the MFC power output (Min et al., 2005). Aelterman et al . (2006) reported that power output can be increased when the MFC cells are connected in series. However, getting a high power output from MFC still remains a technically challenging task and requires further increase in power generation for market readiness. Also, the cost of new materials and their performance for long-term use need to be evaluated (Schwartz, 2007). Further, bacteria are evolved to oxidize different substrates (Table 1) it is essential to understand the metabolic pathway and gene regulatory systems of bacteria to achieve enhanced electricity production. As noted earlier, microbial fuel cells function by harnessing the metabolic pathways of certain species of bacteria to catalyze the substrate to electrical energy. Depending on the operational parameters such as substrate and anode potential of the MFC, different metabolic pathways are used by the bacteria. So it is also important to map the transcriptional and metabolic pathways in different species of bacteria to enhance the power output with high efficiency. Continued research on scientific advancements that will lead to cost effective materials and designs would accelerate commercialization of this technology in the next few years.

Key Findings

- Identification of bacterial species such as *Clostridium butyricum* and *Pseudomonas aeruginosa* that produces their own mediators reduced the addition of artificial chemical mediators to MFC for electron transport from bacteria to the electrode (Osman et al., 2010). The direct communication of exoelectrogens like *Geobacter* species that are capable of oxidizing organic compounds and their efficiency in transferring electrons to electrodes via highly conductive filaments were considered remarkable in MFC research (Derek R, 2008).
- Mixed bacterial cultures can produce power densities equal to pure cultures (Liu et al., 2004) and gradual increases in power densities (Rabaey et al. 2003) accelerated the research interest on MFCs.
- Wastewater as a fuel source while achieving waste water treatment has aided numerous startups to focus on the commercial potential of MFC technology.

Challenges

To date, MFCs have emerged as a promising, yet challenging technology to extract energy from different sources and turn them into electricity. Despite the rapid progress, there are some areas in which further research needs to be done to overcome the constraints associated with MFC.

Low power

- The major challenge in the application of MFCs is its low power density. The voltage generated by MFC is so low that it can only be used in limited applications and the actual current densities that can be generated are not yet known. Saldago (2009) reported that the current generation is only 14mA, which could power only small devices. Kim et al. (2007) reported that even using similar biocatalyst and substrate showed differences in the power density. Abhijeet el al. (2009) reported that the power obtained from MFCs is about 300 Wm^{-3} which is low for commercial applications.

Microbe/electrode interaction

- Though the electron transfer mechanism is understood in some bacteria, further research is needed to create genetically engineered strains to generate more current (Lovely 2008). Current production by bacteria in MFC is a complex process that is regulated by more than few genes and requires further insight into the process of electron transfer (Franks and Nevin, 2010). Cheng et al. (2006) reported that biofouling of cathode affect MFC performance. As the electrode properties affect microorganism wiring and MFC performance, there is a need to develop higher catalytic material with superior performance to avoid biofouling, corrosion and other degradation mechanisms of electrodes (Huang et al., 2011).

Large scale

- The main challenge in implementing MFC on a large scale is in maintaining low costs, minimizing hazards while maximizing power generation (Schwartz, 2007). The performance of the MFCs is influenced by current, power density, fuel oxidation rate, loading rate and coulombic efficiency (Balat, 2009; Kim et al., 2007). The power density is affected by high internal resistance or over potential related ohmic, activation and mass

transfer losses (Logan and Regan, 2006) whereas the fuel oxidation rate is influenced by anode catalytic activity, fuel diffusion, proton and electron diffusion and consumption (Balat, 2009).

- Min et al (2005) described that diffusion of oxygen into the anode chamber lowers the couloumbic efficiency by more than half (55% to 19%) and reduces the power output. It has also been suggested that coulombic efficiency and maximum theoretical amount of energy depend on complete oxidation of substrate to CO_2 (Franks and Nevin, 2010). *Geothrix fermentans* and *Geobacter* has the ability to oxidize the substrate completely (94-100% coulombic efficiency by oxidizing acetate), whereas *Shewanella oneidensis* has only partial oxidation ability (56%).
- The internal resistance can be minimized by reducing the electrode spacing, increasing the electrode surface area, using highly selective proton membrane and increasing catalyst activity (Oh and Logan, 2006). Liu et al. (2005) showed that closer electrode spacing increased the power density by 68%. Chaudhuri and Lovely (2003) described threefold increase in current with larger surface area of electrode material.

  The performance is also affected by factors such as pH, temperature, substrate, microbial activity, resistance of circuit and electrode material. Yong Yuan et al. (2011) found that alkaline conditions (pH 9) favor electricity generation by enhancing electron transfer efficiency. However, Gil et al. (2003) reported that the highest current was obtained in the pH 7 –pH 8 range but not at pH 9.

- Oh and Logan (2007) reported that voltage reversal[5] is a problem in fuel cells due to substrate starvation in cells that resulted in reduced power generation. High resistance remains a barrier in MFCs (Nwogu, 2007). The power density decreases as the system size increases and further improvements are needed to construct highly efficient reactors with reduced internal resistance and electrode over-potential to maximize power in large scale systems (Cheng and Logan, 2011).

[5] Voltage reversal: When the voltage in the cells is not matched or when one cell suffers the loss of fuel or showshigher resistance than other cells.

Other factors

- One of the limiting factors is cost of the electrode and membrane materials like Nafion. However, reviews suggest that low cost materials are being tested to reduce the cost with slightly reduced performance (Logan, 2010).
- Polarization resistance of anode and slow rate of proton movement from the biofilm to cathode and accumulation within the biofilm inhibits power production (Franks and Nevin, 2010; Wen et al., 2010).
- Cathode is an important factor for better performance of MFCs but oxygen reduction at the cathode occurs at a very slow pace that leads to high over potential, which is a limiting factor in obtaining high current density (Kim 2008).
- Optimizing MFC conditions and it performance needs to be evaluated over time to identify the variations such as change in fuel composition, build-up of metabolites and electrode fouling that affect the performance in large scale applications (Osman et al., 2010).
- Better understanding of fluid flow, ion migration and its concentration, proton mass transfer and bio-chemical pathway used by the exo-electricigens for higher metabolic rate and transfer of electrons to acceptors outside the cell need further investigation.

Applications

- Electricity generation
- Biohydrogen production
- Wastewater treatment
- Bioremediation
- Biosensors for pollution analysis

Future outlook

MFC is a promising technology for bioelectricity generation and waste water treatment. Recent research and development and analysis of literature review show that higher power densities can be obtained from improved MFC designs with the use of cost effective materials. Intensive research on this topic significantly reduced the complexity of rate-limiting steps which in turn has enhanced higher current output. Some companies (*mfc tech*, *Opencel*) have emerged to use

MFC technology for fuel and other potential applications including remote power, bioremediation and biosensors (Caspermeyer, 2011; MFCtech) proving that this technology could have greater impact in development of clean energy within a few years.

Players and Research

In recent years, there are many research projects worldwide exploring MFC as a new source of energy. As a result of rapid advances in MFC research, several research publications have been reported in peer reviewed journals. Logan (2010) reported that the citation on the topic MFC have increased from 2,415 to 10,700 within a few years (2002-2009). A number of recently established startups and academic groups have collaborated to explore the commercial applications of MFC. Cambridge based IntAct's lab (Cambrian Innovation) obtained funding from National Science Foundation (NSF) and the U.S. Department of Agriculture for developing MFCs for wastewater treatment projects. It has plans to startup a pilot plant for wastewater remediation. Similarly, Lebone, which was founded in 2007, obtained $200,000 grant from the World Bank and launched a pilot program in Tanzania and Namibia using MFC technology to provide power to small equipments like cell phone chargers and LEDs (Craven, 2010). The University of Glamorgan, UK has been awarded one million dollars for microbial fuel cell research to develop sustainable power (Lane, 2010). Emefcy, an Israeli biotechnology company is developing MFCs for electricity generation from wastewater and has plans for commercial implementation of MFCs by 2012 (Clary, 2011). Bruce Logan's group at Penn state university is funded by ARPA-E for development of fuel using *Rhodobacter* (Logan) and have collaborations with National Renewable Energy Laboratory (NREL) and the Department of Energy (DOE) for fuel cell development. There are many research projects worldwide including academia and companies that are exploring MFC on a variety of technical aspects. As noted earlier there are several groups working on MFC, this table (table2) is a non-comprehensive list of players and their research.

Table 2: Players and their research

Name	Institution	Research
Bruce Rittmann	Biodesign Institute, Arizona state University	Anode electrochemistry
Largus Angenent	Cornell University, NY	Electron transfer mechanism
Bruce Logan	Penn State University	Reactor design and scaling up power generation
Harold May	Medical University of South Carolina	Bacterial community
Gregory Stephanopoulos	MIT	Bacterial metabolism, system biology
Abhijeet Borole	Oak Ridge National Laboratory, TN	Bioelectrochemical process
Hong Liu	Oregon State University	Electrode development and performance
Tingyue Gu	Ohio University	Biofilm, bioproducts from MFC
Arum Han	Texas A&M University	Screening electricigens
Keith Scott (2)	New castle University, UK	Anode biofilm & electrochemistry
Derek Lovley (3)	University of Massachusetts	Electron transfer mechnism
John Regan	Penn State University	Biocathodes and electron transfer mechnism
Zhiyong Ren	University of Colorado, Denver	Anode biofilm & architecture
Akeel Shah, Frank Walsh (7)	University of Southampton	Modeling of MFC, PEM
Tim Gardner	Boston University	Bioengineering bacteria
Peter Girguis	Harvard University	Sediment based biofuel
Korneel Rabaey	University of Queensland	Bioelectrochemical systems
Liping Huang	Dalian University of technology	Biocathode and electron transfer mechanism
Peter Aelterman	Ghent University	Electrodes and bioreactors
Willy Verstraete	Ghent University	Anaerobic digestion
Bert Hamelers	Wageningen University	Electrodes

Bradley Ringeisen	Naval research laboratory	Reactors and membranes
Kenneth Nealson	University of Southern California	Metal oxidation
Kelly Nevin	University of Massachusetts	Fuel cell biology

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