A Review on Development of Microbial Fuel Cell for Waste Water Treatment

H. Asodariya*, P. Patel

Department of Chemical Engineering, Institute of Technology, Nirma University-382481

Abstract: ***The world needs sustainable, efficient, and renewable energy production. With the current interest in alternative methods of energy production and increased utilization of existing energy sources, Microbial Fuel Cells (MFC) have become an important field of research. MFC is a biochemical-catalyzed system which generates electrical energy through the oxidation of biodegradable organic matter in the presence of either fermentative bacteria or enzyme under mild reaction conditions. Bacterial energy is directly converted to electrical energy. To close the cycle, salt bridge is connected from anode to cathode. Present paper focuses on the development and performance based evaluation of a laboratory scale Microbial Fuel Cell. Electricity generation using organic matter from the wastewater as substrate is the prime principle of this particular cell. If power generation in MFC can be increased, this technology may provide a new method to offset wastewater treatment plant operating costs, with less excess sludge production.***

Keywords: *Microbial Fuel Cell, Microorganism, Waste Water Treatment*

1. Introduction

MFC technology is an emerging research field, in which electrons derived from the metabolism of biodegradable organic matter are converted to electricity. Barriers to the application of the technology include the use of expensive components (i.e., platinised cathode and proton exchange membrane) and low power densities, caused by poor electron transfer from the bacteria to the anode. In addition to generating electricity, the process can also treat wastewaters. However, in order for this technology to be a viable source of power or wastewater treatment method, further improvements in MFC performance are needed.

It is well known that microorganisms can produce fuels such as ethanol, methane and hydrogen from organic matter. More recently, it has been reported that microorganisms can also convert organic matter into electricity using MFCs. MFC is a biochemically catalyzed system, which generates electricity by oxidizing biodegradable organic matter in the presence of either fermentative bacteria or enzymes. The biocatalyst present in the anode chamber of MFC generates electrons (e–) and protons (H+) through anaerobic respiration of organic substrates. Electron transfer occurs through the electrode (anode) integrated with an external circuit to the cathode. Protons diffuse through the proton exchange membrane (which separates the cathode and anode chamber) into the cathode chamber, where they combine with the electron acceptor.

The potential difference between the respiratory system and electron acceptor generates the current and voltage needed to generate electricity. Harvesting electricity from organic wastes through MFC is an attractive source of energy as organic waste is 'carbonneutral' and oxidation of organic matter only releases recently fixed carbon back into the atmosphere. According to Lovley et al., MFC could fill a niche that is significantly different from that of the better known abiotic hydrogen and methanol-driven fuel cells. Abiotic fuel cells require high temperatures and expensive catalysts which are toxic, to promote oxidation of the electron donors. Naturally occurring microorganisms catalyse the oxidation of fuels in MFC at room temperature and could potentially be designed to function at any temperature at which microbial life is possible. MFC can be considered as a promising alternative for the harnessing of electrical energy from various substrates using different cell configurations, and electron transfer mechanisms.

Electrons and protons are generated during the oxidization of substrates by microorganisms. The generated electrons flow from the anode via an external circuit to the cathode, where they typically combine with protons and oxygen to form water. Electricity is thus produced and harnessed by inserting a load between the two electrodes. This provides MFCs promising potentials to generate renewable electricity while accomplishing the biodegradation of organic matters or wastes when they are assembled and integrated in wastewater treatment process.

Most studies have focused on how different MFC reactor configurations, substrates, operating parameters

*Corresponding author – email id: hardik.asodariya@gmail.com

and different types of electrodes affect power generation. . However, if it is to achieve practical application as a wastewater treatment technology, several important challenges need to be faced. Most of all, the capital costs of MFCs have to be significantly reduced so that MFCs can match the traditional wastewater treatment technology in terms of performance–cost ratio.

In general, a microbial fuel cell (MFC) is a device that generates electric power by utilizing bacteria. Compared to other present alternative energy with many respective shortcomings, such as solar power (low efficiency), wind power (limited by location) and nuclear power (lack of safety and high investment), which restrict their wide application like fossil fuel, MFCs reserve common advantages of normal fuel cells which are high fuel conversion efficiency and simplicity of design; moreover, MFCs are more environmentally friendly in that they are capable of utilizing a wide range of renewable fuels. Actually, one attractive advantage of MFC is capacity of generating power when fed with wastewater; that requires the bacteria can consume different kinds of substrates in anode medium from inorganic compounds to organic compounds.

There have been a lot of attempts to improve and develop this concept of Microbial fuel Cells, as it is a renewable source of energy. Though the Microbial Fuel Cell is unlikely to replace the conventional sources, that are satisfying the needs of human beings today, it can be very useful for its novel applications such as waste water treatment, desalination of water, for locations devoid of conventional fuels etc.

There are many challenges remaining to fully exploit the maximum power production possible by MFCs, to find ways to make the systems economical, and to create wastewater treatment systems based on MFC bioreactors. Power densities still need to be increased but this must be done under realistic conditions. For example, work with chemical catholytes such as ferricyanide should be abandoned and the focus should be squarely placed on using oxygen in air at the cathode. Materials, and different methods to treat materials, must be examined that are efficient both in terms of power generation and cost.

2. Microorganisms in microbial fuel cell

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. 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

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 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 mainly by a direct contact of mineral oxides and the metal reducing microorganisms.

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.

Mediators in oxidized state are easily reduced by capturing electrons from within the membrane of microorganisms.

The mediators then transfer across the membrane and release the electrons to the electrode and become oxidized again in anodic chamber and thus are reutilized. Good mediators should have following characteristics [5]:

- It should be cell membrane permeable.
- It should have electron affinity more than the electron carries of the electron transport chains.
- It should possess a high electrode reaction rate.
- It should be well soluble.

- It should be completely non-biodegradable and non-toxic to microbes.
- it should be of low cost. These characteristics describe the efficiency of mediators.

Contrary to lower redox potential mediators being theoretically better the higher redox potential mediators for high affinity for electrons absorbing from electron carriers in cell are the best. Methylene blue, neutral red, thionine, Meldola's blue, Fe(III)EDTA are sysnthetic mediators but the problem is their toxicity which limits their use in MFCs.

Microbes in anodic chamber of an MFC oxidize added substrate and generate electrons and protons in the process. Carbon dioxide is produced as an oxidation product. However there is no net 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 transferred to the cathode through an external circuit. After crossing Proton Exchange Membrane (PEM) or a salt bridge, the proton enter the cathodic chamber where they combine with the oxygen to form water.

Typical electrode reactions are shown below using glucose as a fuel example.

Anodic reaction:

$$C_6H_{12}O_6 + H_2O \longrightarrow 6CO_2 + 24e^- + 24H^+$$

Cathodic reaction:

$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O$$

As Rabaey et al Referred to such microbial communities as adapted anodophilic consortia. Anodophilic bacteria from different evolutionary lineages from the families of Geobacteraceae, Desulfuromonaceae, Alteromonadaceae, Enterobacteriaceae, Pasteurellaceae, Clostridiaceae, Aeromonadaceae, and Comamonadaceae were able to transfer electrons to electrodes. Methanogens also reported to have a capacity to transfer electrons. Because the power output of MFCs is low relative to other types of fuel cells, reducing their cost is essential, if power generation using this technology is to be an economical method of energy production.

The overall limiting steps to enhance the power production are showed in the Fig 1. Further research is required to enhance the power production by overcoming these limitations. The main disadvantage of a two chamber MFC is that the solution cathode must be aerated to provide oxygen to the cathode.

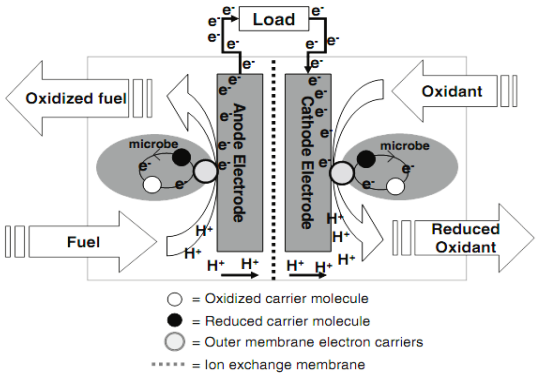


FIG.1: Microbial fuel cell schematic for wastewater management [5]

In addition to microorganisms that can transfer electrons to the anode, the presence of other organisms appears to benefit MFC performance. It is reported that, a mixed culture generated a current that was six fold higher that that generated by a pure culture. Hence, the microbial communities that develop in the anode chamber may have a similar function as those found in methanogenic anaerobic digesters, except that microorganisms that can transfer electrons to the electrode surface replace methanogens.

3. Design of Microbial Fuel Cell

There are basic component of MFCs which are important in construction. Electrodes, wirings, glass cell, and salt bridge have an important role. Salt bridge can replaced with proton exchange membrane in PEM fuel cell. Though it enhance the cost but handling and the power generation both get enhanced, thus portability and efficiency of the system. Apart from that fuel cell can be classified into two types.

1. Double chamber fuel cell
2. Single chamber fuel cell.

3.1 Double Chamber Fuel Cell

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.

TABLE 1: Microorganisms used in Microbial Fuel Cell (MFC)

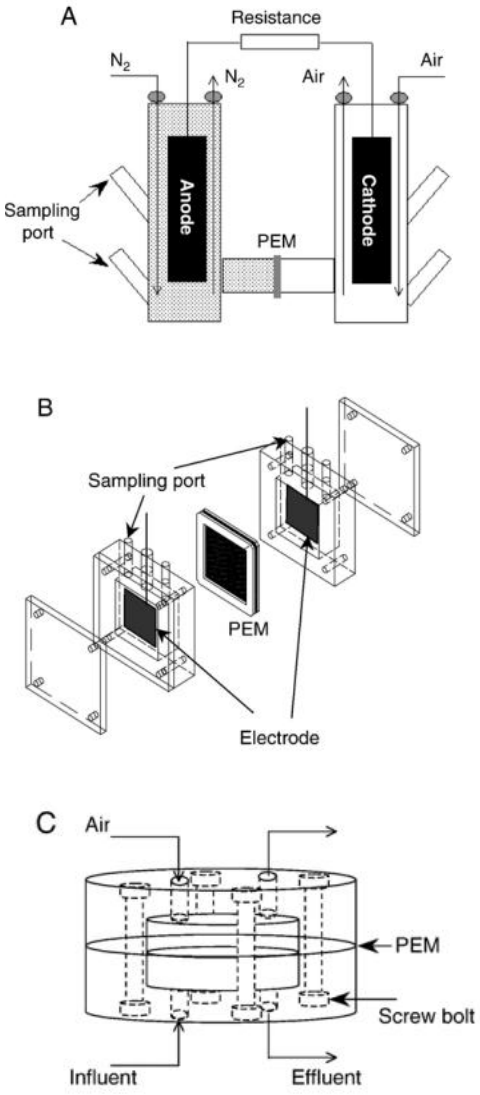
MICROORGANISMS	SUBSTRATES	MEDIATORS	REFERENCES
Saccharomyces cerevisiae	Hydrolyzed Lactose	MB, NR	[23]
Escherichia coli	Glucose	NR	[24]
Enterobacter cloacae	Glucose	Methyl Viologen, MB	[1]
Saccharomyces cerevisiae	Glucose	Resorufin	[25]
Aeromonas hydrophila	Glucose, Acetate	Without mediator	[26]
Enterococcus faecium	Glucose	Pyocyanin	[27]
Streptococcus lactis	Glucose	Ferric Chelate complex	[28]
Proteus vulgaris	Glucose, Maltose, Galactose	Thionin	[29]
Shewanella putrefaciens	Lactate	Without mediator	[30]
Rhodoferax ferrireducens	Glucose	Without mediator	[31]
Activated sludge	Waste water	Without mediator	[32]
Mixed consortium	Glucose, Sucrose	Without mediator	[33]
Actinobacillus succinogenes	Glucose	NR, Thionine	[34]
Klebsiella pneumoniae	Glucose	HNQ	[35]
Micrococcus luteus	Glucose	Thionine	[36]
Shewanella oneidensis Escherichia coli Proteus vulgaris	Lactate Glucose, Acetate Glucose, Sucrose	Anthraquinone-2,6-disulfonate(AQDS) NR, 2-Hydroxy-1,4-Naphthoquinone, MB Thioninee	[37], [37-40], [41–44]
Shewanella putrefaciens	Lactate, Pyruvate, Acetate	NR	[45]
Proteus mirabilis	Glucose	Thionine	[46]
Shewanella putrefaciens	Glucose, Lactate	Without mediator	[30]

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. 2.

The mini-MFC shown in Fig. 2C having a diameter of about 2 cm, but with a high volume power density was reported by Ringeisen et al. They can be useful in powering autonomous sensors for long-term operations in less accessible regions. 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. 3E 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 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. 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.



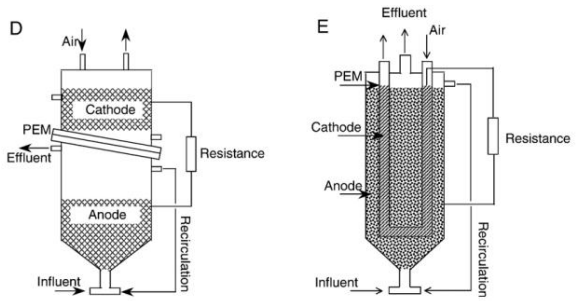


Fig.2. Schematics of a two-chamber MFC in [4]
(a) Cylindrical shape,
(b) Rectangular shape,
(c) Miniature shape,
(d) Up flow configuration with cylindrical shape,
(e) Cylindrical shape with an U-shaped cathodic compartment

3.2 Single chamber MFC system

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 designed a one compartment MFC consisting of an anode in a rectangular anode chamber coupled with a porous air- cathode that is exposed directly to the air as shown in Fig. 3A. Protons are transferred from the anolyte solution to the porous air-cathode. Liu and Logan designed an MFC consisting of an anode placed inside a plastic cylindrical chamber and a cathode placed outside. Fig. 3B 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.

There are many other types of MFCs have developed in recent years as the advancement of technology to improve the power density. Table 2 shows the main basic component of MFC.

1. Two-Chamber MFC system
2. Single Chamber system
3. Up-flow mode MFC systems
4. Stacked MFC

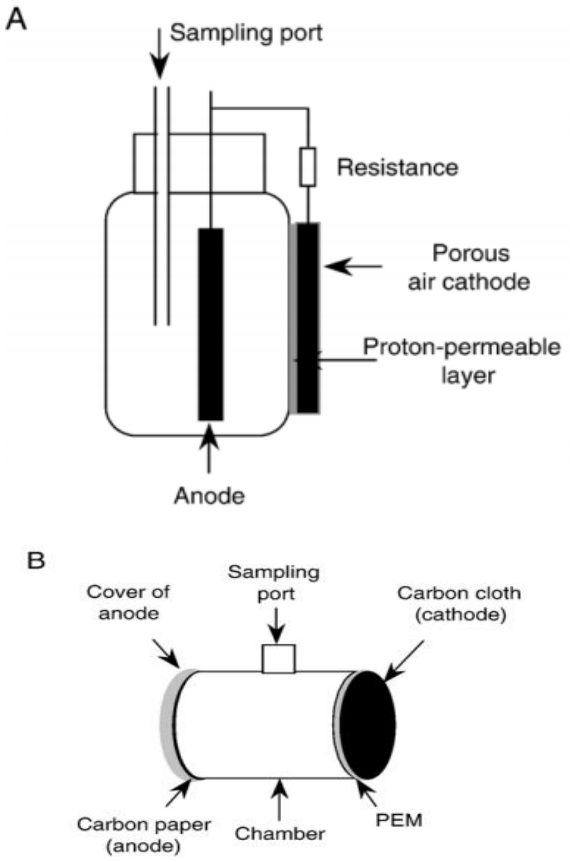


Fig 3. Single chamber MFC[4]

A. An MFC with a proton permeable layer coating the inside of the window-mounted cathode,

B. an MFC consisting of an anode and cathode placed on opposite side in a plastic cylindrical chamber.

Table 2: Basic component of MFC [4]

Items	Materials	Remarks
Anode	Graphite, Carbon paper, Carbon cloth, Pt, Pt black	Necessary
Cathode	Graphite, Carbon paper, Carbon cloth, Pt, Pt black	Necessary
Anodic chamber	Glass, Plexi glass Polycarbonate	Necessary
Cathodic chambe	Glass, Plexi glass Polycarbonate	Optional
Proton Exchange Membrane	PEM: Nafion ultrex, salt bridge porcelain septum	Necessary
Electrode catalyst	Pt, Pt black,MnO Fe^{3+},	Optional

4. Recent development on MFC

A membrane-less microbial fuel cell (ML-MFC) with the internal resistance of 3.9 Mwas used to enrich a microbial consortium oxidizing electron donors with concomitant current generation. Within 4 weeks the system generated a stable current of 2 mA. The current yield was less than 10%. Forced aeration to the cathode compartment generated higher current, but the yield was similar. Use of a cathode with a high eraffinity for oxygen could improve the current yield. Additions of NaCl or HCl increased the current generation further with the current yield of 15%. Aerobic microbes turned out to be the predominant oxygen consumer at the cathode. Based on these findings suggestions are made for a ML-MFC configuration with better performance.[21]

The COD removal efficiency was 526.67 g/m^3 day with the efficiency over 90%. These results show that the ML-MFC can be used as a wastewater treatment process.

The utilization of this electron acceptor in the single dual-chambered and double dual-chambered MFC's in parallel and series was observed to produce an open circuit voltage of 1560mV, 1400mV and 2860mV respectively. Maximum power density was observed to be 12.26mW/m, 20.71mW/m^2[17]

Current densities at maximum power for the single dual-chambered and double dual chambered in parallel were observed to be 16.09mA/m and 35.77mA/m^2 with internal resistances 4000Ω and 600Ω respectively. [17]

Electricity generation with whey degradation was investigated in a two compartment cell with and without mediators in the microbial fuel cell. Saccharomyces cerevisiae (PTCC 5269) was able to utilize the carbohydrate exist in the whey for generation of bioelectricity. The open circuit potential in absence of mediator was 500 mV at ambient temperature (25±2°C). Maximum power generation and current were 50 µW and 470 µA, respectively. [41]

The influence of the pH on the conversion appeared to be of no significant importance in the obtained range Table 3. Decrease of the bacterial external electron transfer was observed for glucose loading rates of 3.5 g l −1 d−1 and higher.

Table 3: Microbial fuel cell mass balance and final reactor parameters. Changes were calculated relative to the initial concentration at t = 0. All values were expressed as COD [10]

Experiment	Amount COD added (mg)	ΔBiomass (mg COD)	VFA (mg COD)	Electricity (mg COD)	Total (mg COD)	Recovery (%)	Final pH
1	262	18 ± 11	−28 ± 27	232 ± 47	222 ± 55	85 ± 21	6.5 ± 0.9
2	326	71 ± 5	−13 ± 5	263 ± 60	321 ± 60	99 ± 19	6 ± 0.7
3	304	53 ± 9	−22 ± 9	200 ± 31	231 ± 34	76 ± 11	7.1 ± 0.6
4	416	70 ± 1	− 1 ± 10	312 ± 32	381 ± 34	92 ± 8	5.2 ± 0.2
5	366	59 ± 14	− 6 ± 16	234 ± 38	287 ± 44	78 ± 12	7.2 ± 0.5
6	392	52 ± 4	28 ± 9	255 ± 46	335 ± 47	85 ± 12	6.2 ± 0.6
7	416	51 ± 7	51[a]	78 ± 30	180 ± 31	43 ± 7	6.4 ± 0.4
8	595	94 ± 1	89 ± 21	61 ± 29	244 ± 36	41 ± 6	4.7 ± 0.1

[a] Data from one single reactor.

5. Factor affecting MFC efficiency

5.1 Electrode Material

There are different types of electrode material have been used for increasing the efficiency for the MFC. The Type of material used in electrode preparation will show vital effect on MFCs efficiency. Better performing electrode materials usage will always improve the performance of 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. 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. 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. [34, 35]

5.2 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. [36]

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. It was possible that the buffer compensated the slow proton transport rate and improved the proton availability for the cathodic reaction. 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 [37] possibly due to the fact that NaCl enhanced the conductivity of both by anolyte and the catholyte.

5.3 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. However, side effect of other cations transport is unavoidable during the MFC operation with Nafion. But its usage is better in the sense of charge balance between the anodic and cathodic chambers. Hence 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 MFC internal resistance decreases with the increase of PEM surface area over a relatively large range [38]. 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.

6. Conclusion

At present the field of MFCs is in its infancy and also this is an exciting time in microbial fuel cell research. The MFCs technology has evolve to compete with well advanced methanogesis technology where biomass is used as substrate. In contrast to methanogenesis MFCs are capable to convert biomass to electricity at low temperatures and substrate concentration. The discovery and usage of new anodophilic microbes that vastly

enhance the electron transport rate from the biofilm covering an anode to the anode are much needed to improve the power density output in MFCs.

Furthermore, there are many microorganisms yet to be discovered that might be beneficial for electricity production. The well coordination efforts of different scientific fields like electrochemists, materials scientists, engineers and microbiologists is well require in the development of the several potential practical applications of microbial fuel cells.

The ultimate achievement in for MFCs will be when they can be used solely as a method of renewable energy production. Right now, the high costs of materials for MFCs and the relatively cheap price of fossil fuels makes it unlikely that electricity production can be competitive with existing energy production methods. Microbial fuel cell is one of the most upcoming technologies for power generation and is being developed so as to obtain a consistent high power.

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