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A REVIEW ON MICROBIAL FUEL CELL USING ORGANIC WASTE AS FEED

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ABSTRACT

Microbial fuel cells (MFCs) are devices that can use bacterial metabolism to produce an electrical current from wide range organic substrates. Sustainable energy production from organic wastes is gaining a research interest from last few years. But only a few marine sediment MFCs have been used for providing current for low power devices practically. The greatest value of MFC technology may not be the production of electricity but the ability of electrode associated microbes to degrade wastes and toxic chemicals. The effects of operational conditions of a microbial fuel cell were tested and optimized for the best performance of a mediator-less microbial fuel cell. The optimal pH was 7. The resistance higher than 500 Ω was the rate-determining factor by limiting electron flow from anode to cathode. At the resistance lower than 200 Ω , proton and oxygen supplies to the cathode were limited. A non-compartmentalized fuel cell with less resistance and an electrode having a high oxygen reducing activity with efficient mediator less bacteria should be developed for efficient Microbial Fuel cell. Apart from electricity generation it can be effectively used as BOD sensor as the concentration of substrate affects the electricity generation.

Key Words: *Anode, Microbial Fuel Cell, Extracellular Electron Transfer, Conductive Bio Film, Cathode.*

INTRODUCTION

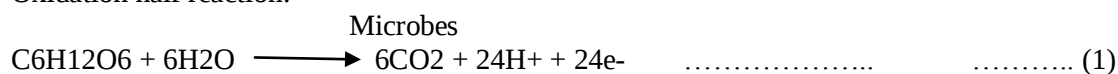
Three E's are the national Energy policy drivers of any country of the world. Energy security, energy growth, environmental protection. Energy has become an indispensable part of everybody human life which is compromising the environmental protection. The global warming situation is worsened by the fact that power generation is continuously increasing through the world using fossil fuel. Low reserves of fossil fuels and the environmental impact of their use to produce energy are leading to a search for novel renewable energy technologies. The idea of using microbial cells in an attempt to produce electricity was first conceived in the early twentieth century. M. Potter a professor of botany at the University of Durham managed to generate electricity from *E.coli* in 1911 (Potter, 1911). Electrical effects accompanying the decomposition of organic compounds. Royal Society (Formerly Proceedings of the Royal Society) B, 84, p260-276), but the work was not to receive any major coverage. In 1931, however, Barnet Cohen drew more attention to the area when he created a number of microbial half fuel cells that, when connected in series, were capable of producing over 35 volts, though only with a current of 2 milliamps (Cohen, B. (1931). The Bacterial Culture as an Electrical Half-Cell, Journal of Bacteriology, 21, pp18-19). Electricity generation and waste water treatment using Microbial Fuel Cells are among such technologies (Ashley E. Franks *et al.*, 2010). Microbial fuel cells (MFCs) provide a method of adding wastewater to the list of renewable energy sources (Ashutosh Patra *et al.*, 2008). MFCs are attractive for wastewater treatment, because they could allow for harvesting energy from wastewater for producing electricity. The anaerobic microbes required for MFCs are commonly found in wastewater (Lui *et al.*, 2004; Min and Logan, 2004), so influent wastewater could act as both a substrate and a source of microorganisms. Logan (2005) estimates that electricity accounts for roughly 25% of the total operating costs of a wastewater treatment plant. The wastewater from 100,000 people amounts to 1.64×10^7 Liters/year from which MFCs could, at a maximum, produce 2.3 MW/year (Logan, 2005) The discovery that bacteria can be used to produce electricity from waste and renewable biomass (Bond *et al.*, 2002) has gained much attention. Recently the increased interest in microbial fuel cell (MFC) technology was highlighted by the naming of *Geobacter sulfurreducens* KN400, a bacterial strain capable of high current production, as one of the top

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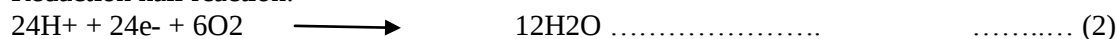
50 most important inventions for 2009 by Time Magazine. The discovery that microbial metabolism could provide energy in the form of an electrical current (Potter *et al.*, 1910) has lead to an increasing interest and a dramatic raise in the number of publications in the field of MFC research. These systems are very adaptable and hold much promise to provide energy in a sustainable fashion.

A typical microbial fuel cell consists of anode and cathode compartments. In the anode compartment, fuel is oxidized by microorganisms, generating electrons and protons. Electrons are transferred to the cathode compartment through an external electric circuit, and the protons are transferred to the cathode compartment through a separator. Electrons and protons are consumed in the cathode compartment, combining with oxygen to form water. (Ashutosh Patra *et al.*, 2008) As a result of these two half reactions, a potential difference develops between the anode and the cathode and current flows in the external circuit. The following equations illustrate the two half reactions and the equation (3) explains overall oxidation/reduction reaction using a monosaccharide (e.g. glucose) as the organic matter.

Oxidation half reaction:



Reduction half reaction:



Overall oxidation/reduction reaction:



MFCs rely on the activities of microorganisms that can directly transfer electrons to an anode using cytochromes. Examples of microorganisms with this capability include *Shewanella putrefaciens*, *Geobacter sulfurreducens*, *Geobacter metallireducens*, and *Rhodospirillum rubrum* (Bond *et al.*, 2002).

MATERIALS AND METHODS

Microorganisms in a Microbial Fuel Cell

In its most basic form, a MFC is a device that uses microorganisms to generate an electrical current through the oxidation of organic material (Figure 1). Microorganisms in the MFC metabolize organic substrates and extracellularly transfer electrons to an electrode surface. The oxidation of the organic material liberates both electrons and protons from the oxidized substrate. Electrons are transferred to the anode and then to the cathode through an electrical network. The protons migrate to the cathode and combine with the electron and a catholyte, a chemical such as oxygen, which is reduced at the cathode surface. As such, an electrical current is generated in a fashion similar to a chemical fuel cell, but with microbes acting as a catalyst on the anode surface as shown in Figure 1. Catalysts generally increase the rate of a reaction without being changed by or receiving energy from the reaction they catalyze. The microbes in a MFC are not true catalysts since they obtain energy from the oxidation of the substrate to support their own growth and create an energy loss. Microbes in a MFC may gain all the energy and carbon required for cellular growth from the oxidation of the complex organic material and as such MFC technology has been considered self-sustaining (Lovley *et al.*, 2006). As long as conditions remain favorable for current production by the anode-associated microbes, a MFC has the potential to produce electricity indefinitely.

A diverse range of microorganisms are found in association with substrates as shown in Table 1 in MFC systems, especially when an environmental inoculum is used to seed the MFC. A general term for bacteria associated with a surface is a biofilm.

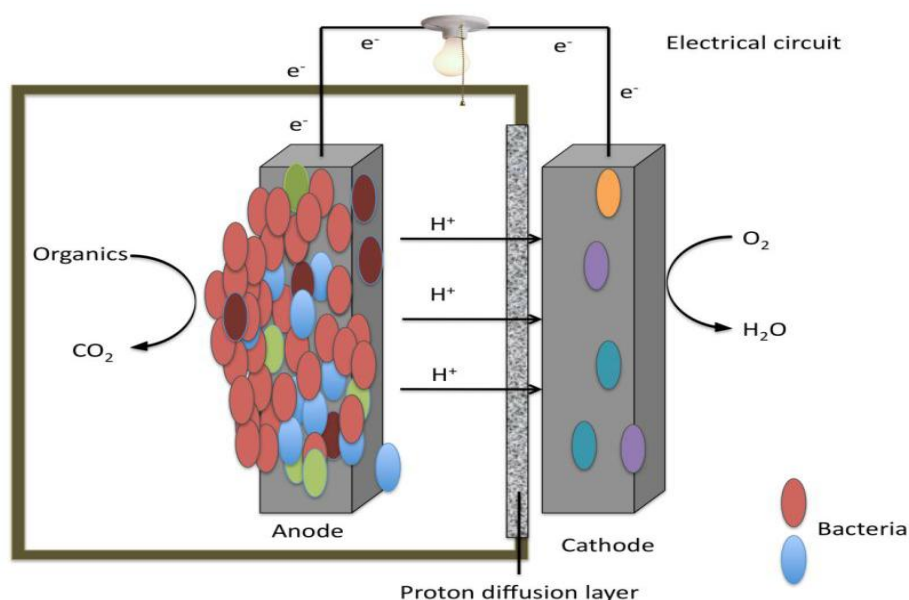


Figure 1: A diagram of a MFC containing a graphite anode acting as an electron acceptor for anaerobic microbial oxidation of organic compounds separated by a proton diffusion layer from an aerobic graphite cathode (Lovley *et al.*, 2006).

It is likely that not all of the organisms associated anode biofilm interact directly with the anode but may interact indirectly through other members of the electrode community.

Table 1: Various Microbes and their applications which can be used in MFC with different substrates.

Microbe	Substrate	Applications	Reference
Actinobacillus succinogenes	Glucose	Neutral red or Thionin as electron mediator	Park <i>et al.</i> , (1999)
Aeromonas hydrophila	Acetate	Mediator-less MFC	Pham <i>et al.</i> , (2003)
Clostridium beijerinckii	Starch, glucose, lactate, molasses	Fermentative bacterium	Niessen <i>et al.</i> , (2004)
Clostridium butyricum	Starch, glucose, lactate, molasses	Fermentative bacterium	Park <i>et al.</i> , (2001)
Erwinia dissolven	Glucose	Ferric chelate complex as mediators	Vega and Femandez (1987)
Escherichia coli	Glucose, sucrose	Mediators such as methylene blue needed	Schroder <i>et al.</i> , (2003)
Geobacter metallireducens	Acetate	Mediator-less MFC	Min <i>et al.</i> , (2005)
Geobacter sulfurreducens	Acetate	Mediator-less MFC	Bond and Lovely (2003)
Klebsiella pneumonia	Glucose	HNQ as mediator biomineralized manganese as electron acceptor	Rhoads <i>et al.</i> , (2005)

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Lactobacillus plantarum	Glucose	Ferric chelate complex as mediators	Vega and Fernandez (1987)
Proteus mirabilis	Glucose	Thionin as mediator	Choi <i>et al.</i> , (2003)
Pseudomonas aeruginosa	Glucose	Pyocyanin and phenazine-1-carboxamide as mediator	Rabaey <i>et al.</i> , (2004)
Rhodospirillum rubrum	Glucose, xylose, sucrose, maltose	Mediator-less MFC	Chaudhuri and lovely (2003)
Shewanella oneidensis	Lactate	Anthraquinone 2,6 disulfonate as mediator	Ringeisen <i>et al.</i> , (2006)
Shewanella putrefaciens	Lactate, pyruvate, acetate, glucose	Mediator-less MFC	Park and Zeikus (2002)
Streptococcus lactis	Glucose	Ferric chelate complex as mediators	Vega and Fernandez (1987)

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 bio cathodes 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 over potential (Logan and Regan, 2006). Bio cathodes increase the power by decreasing the over potential (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 bio electro catalytic activity of the microbes (Logan, 2010; Wen *et al.*, 2010).

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 which are shown in Table 2 (Cheng and Logan, 2011; Pant, 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, 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

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columbic efficiency and power output have been reviewed by many authors (Lee *et al.*, 2008; Niessen *et al.*, 2004; Pant, 2010; Zuo *et al.*, 2006). However, the economics of substrate is not known.

Table 2: Different types of substrates and their current densities (Pant, 2010).

Substrate	Concentration	Current Density (mA/cm ²)
Acetate	1g/l	0.8
Lactate	18mM	0.005
Glucose	6.7mM	0.7
Sucrose	267mg/l	0.19
Phenol	400mg/l	0.1
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

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.

In Figure 2 and in Figure 3, it is clearly shown that how the operating conditions like pH, time and resistance influence the current density. It is observed that at pH 7, current is maximum and as time increases till sometime current increases and it will get reduces as per the m.

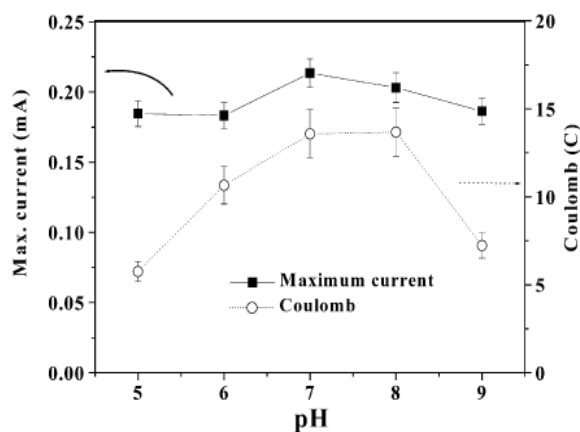


Figure 2: Variation of current density with pH (Zhang *et al.*, 2009)

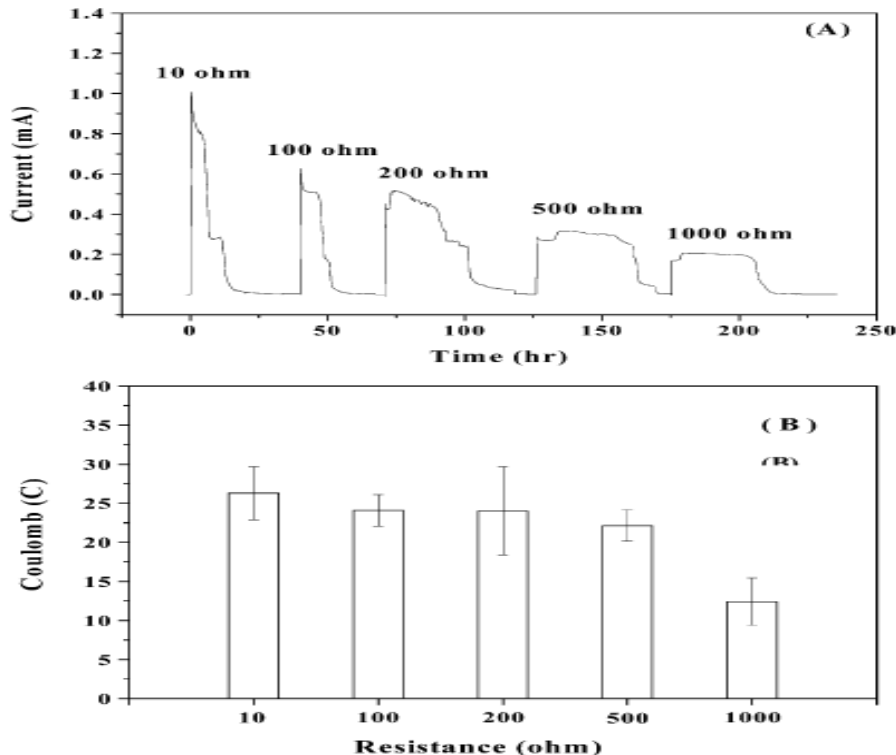


Figure 3: Effect of resistance on current and coulombic efficiency (Zhang *et al.*, 2009).

Challenges

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 *et 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 Iting *et al.*, (2006) reported that befoiling 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 befoiling, 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

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(Balat, 2009). Min *et al.*, (2005) described that diffusion of oxygen into the anode chamber lowers the coulombic 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 CO₂ (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, and micro bial 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 reversal⁵ 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).⁵Voltage reversal: When the voltage in the cells is not matched or when one cell suffers the loss of fuel or shows higher resistance than other cells.

Other Factors:

One of the limited 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 its 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 biochemical pathway used by the exo-electricigens for higher metabolic rate and transfer of electrons to acceptors outside the cell need further investigation.

Potential Applications for Microbial Fuel Cells

One of the most active areas of MFC research is the production of power from wastewaters combined with the oxidation of organic or inorganic compounds. Studies are demonstrating that any compound degradable by bacteria can be converted into electricity (Pant *et al.*, 2010). The ability of the MFC microbial communities to degrade a wide range of environmental pollutants may be more valuable than production of electricity itself in certain settings, especially when the MFC technology can be used for environmental cleanup *in situ*. *Geobacter* species have been shown to be important in the anaerobic degradation of petroleum components and landfill leach ate contaminants in ground water. The use of an electrode as an electron acceptor in the soil is attractive, as the microbes responsible for degradation will co-localize with the contaminant at the graphite anode. Once in position the electrode can provide a continuous long-term electron sink for the degradation of the harmful environmental contaminants. In this setting the electrons produced by the microbes in the form of current is irrelevant when compared to the increased rates of bioremediation. Likewise experiments have shown that MFCs may potential be able to remove fermentation inhibitors which accumulate in process water after the pretreatment of cellulosic

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biomass. The removal of the inhibitors allows for increased fermentation product yields while providing small amounts of energy. An unusual application for MFC technology is to power implanted medical devices using glucose and oxygen from blood. An implanted MFC could provide power indefinitely and negate the need for surgery to replace batteries. Abiotic fuel cells based on noble metal catalysts and activated carbon have been demonstrated to produce energy from blood glucose *in vitro* and *in vivo*. Fuel cells based on enzymatic catalysts have also been shown to operate under physiological conditions but still require much improvement to become viable. Interest has also been expressed in using human white blood cells as a source of electrons for an anode (Calabrese Barton S *et al.*, 2004). Experiments using white blood cells in phosphate-buffered saline solution with a ferric-cyanide cathode produced a low current level of 1-3 $\mu\text{A cm}^{-2}$ but it could not determine if electron transport to the anode was through a direct or indirect process.

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; MFC Tech) proving that this technology could have greater impact in development of clean energy with waste water treatment 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 Int Act'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 groups at Penn state universities 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 is a non-comprehensive list of players and their research.

CONCLUSION

MFCs are a promising technology for the production of electricity from organic material and wastes. Currently limited applications are possible because of low MFC power output. An understanding of the microbiology of the current producing process is required before further advances in power output are possible. The proton accumulation within the bio film and over potential at the cathode is the two major problems which have to be addressed. MFCs where current production is not the major advantage, but wastewater treatment or bioremediation using a cathode or anode maybe much more promising then the electrical production of the MFC itself.

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