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Microbial Fuel Cell (MFC): Recent Advancement and Its Application

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ABSTRACT

Microbial fuel cells have received increased attention as a means to produce "green" electricity from natural substances such as carbohydrates, agricultural wastes or dairy waste. A microbial fuel cell is a biological system in which bacteria do not directly transfer their produced electrons to their electron acceptor, rather transported over an anode, conducting wire and a cathode. It is divided into two halves: aerobic and anaerobic. The aerobic half has a positively charged electrode and is bubbled with oxygen. The anaerobic half does not have oxygen, allowing a negatively charged electrode to act as the electron receptor for the algal processes. The cathode chamber was sterilized and then refilled with basal medium with Chlorella vulgaris as inoculom to provide electron that transferred from cathode to anode for electricity production. The electricity producing bacteria are known as electrogens. Proton conductive materials in an MFC should ideally be able to inhibit the transfer of other materials such as the fuel (substrate) or the electron acceptor (oxygen) while conducting protons to the cathode at high efficiency. Thus bacterial energy is directly converted into electrical energy. The potential between the respiratory system and electron acceptor generates the current and voltage needed to make electricity. The electrons and protons react with oxygen molecules in the cathode chamber to form water. In nutshell, the novel reactor design and idea of using photosynthetic algae for oxygen supply to cathodic reaction green are also helpful in CO_2 sequestration.

Key words: *Exoelectrogen, MFC, Microorganisms, Power, Proton exchange*

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INTRODUCTION

The purpose of this literature review is to organize relevant information and apply the principles of a feasibility study to Microbial fuel cell (MFC) technology. This article contains an overview of the biological mechanism of a MFC, current design structures, and its development, parameter estimation etc. Microbial fuel cells are not yet commercialized but they show great promise as a method of waste water treatment and as power sources for bioelectricity. The power produced by these systems is currently limited, primarily by high internal (ohmic) resistance[1]. However, improvements in the system architecture will soon result in power generation that is dependent on the capabilities of the microorganisms. The bacterial communities that develop in these systems show great diversity, ranging from primarily δ-Proteobacteria that predominate in sediment MFCs to communities composed of α-, β-, γ- or δ-Proteobacteria, firmicutes and uncharacterized clones in other types of MFCs. Much remains to be discovered about the physiology of these bacteria capable of exocellular electron transfer, collectively defined as a community of 'exoelectrogens' as discovered by Pham *et al*[2]. Here, we review the microbial communities found in MFCs and the prospects for this emerging bioenergy technology. Microbial fuel cell (MFC) technologies represent the newest approach for generating electricity. It refers to the bioelectricity generation from biomass using bacteria. It has been known for many years that it is possible to generate electricity directly by using bacteria to break down organic substrates[1]. 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[3]. MFCs can also be used in water treatment facilities to breakdown organic matters. Thereby, it is helpful in prevention of water as well as land pollution and simultaneously responsible for bioelectric production to meet the increasing need of electricity that is in demand by growing human population.

1. History of microbial fuel cell (MFC) development

Theoretically, most microbes can potentially be used as a biocatalyst in Microbial fuel cell (MFC). The earliest MFC concept was demonstrated by Potter[4]. Electrical energy was produced from living cultures of *Escherichia coli* and *Saccharomyces* by using platinum electrodes[4]. This did not 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. In the early 1990s, researcher started to give more interest on fuel cells and work on MFCs began to increase[5]. A microbial fuel cell is a biological system in which bacteria do not directly transfer their produced electrons to their electron acceptor, rather transported over an anode, conducting wire and a cathode. It is divided into two halves: aerobic and anaerobic. The aerobic half has a positively charged electrode and is bubbled with oxygen. The anaerobic half does not have oxygen, allowing a negatively charged electrode to act as the electron receptor for the algal processes. The cathode chamber was sterilized and then refilled with basal medium with *Chlorella vulgaris* as inoculom to provide electron that transferred from cathode to anode for electricity production. These organisms are referred as exoelectrogens[6].

2. Exoelectrogens

An exoelectrogen normally refers to a bacterium or prokaryote that has the ability to transfer electrons extracellularly. This normally occurs *via* an external electron acceptor such as strong oxidizing agent in aqueous solution or a solid conductor/electron acceptor[6]. The electrons are thought to be transferred along pili (external cell structures used in conjugation and adhesion). Cells are able to do this strictly in the absence of oxygen as during aerobic respiration a cell converts an energy source into ATP, carbon dioxide and

water via glycolysis, the Krebs cycle and oxidative phosphorylation whereas in the absence of oxygen, water is not created and in its place electrons and hydrogen ions are formed[7]. These bacteria are called exoelectrogens, "for exocellular and "electrogen" based on the ability to directly transfer electrons to a chemical or material that is not the immediate electron acceptor. Many anaerobes can only transfer electrons to soluble compounds such as nitrate or sulfate (not cell synthesized) that can diffuse across the cell membrane and into the cell[7]. Exoelectrogenic bacteria are distinguished from these anaerobes by their ability to directly transport electrons outside of the cell which permits them to function in an MFC[5]. The diversity of bacteria capable of exoelectrogenic activity is just beginning to be discovered. Marine sediment, soil, wastewater, freshwater sediment and activated sludge are all rich sources for these microorganisms. A tremendous amount of information has recently been obtained studying exoelectrogens from two dissimilatory metal reducing genera (*Shewanella sp.* and *Geobacter sp.*). The electron transfer mechanism in MFC is a key issue in understanding the theory of how MFCs work.

3. Mechanisms of electron transfer

In normal microbial catabolism, a substrate such as a carbohydrate is initially oxidized anaerobically when its electrons are released by enzymatic reactions[8]. The electrons are stored as intermediates (e.g., NADH, quinones) which become reduced and are then used to provide the living cell with energy. The ending location for the electrons is molecular oxygen or dioxygen at the end of the respiratory chain. A MFC uses bacteria to catalyze the conversion of organic matter into electricity by transferring electrons to a developed circuit[8]. Microorganisms can transfer electrons to the anode electrode in two ways: exogenous mediators (ones external to the cell) such as potassium ferricyanide, thionine, or neutral red; using mediators produced by the bacteria; or by direct transfer of electrons from the respiratory enzymes (i.e., cytochromes) to the electrode[8]. These mediators can divert electrons from the respiratory chain by entering the outer cell membrane, becoming reduced, and then leaving in a reduced state to shuttle the electron to the electrode[9]. *Shewanella putrefaciens, Geobacter sulfurreducens, Geobacter metallireducens* and *Rhodoferax ferrireducens* have been shown to generate electricity in a mediator less MFC. Bacteria present in mediator less MFCs have electrochemically active redox enzymes on their outer membranes that transfer the electrons to external materials and therefore, do not require exogenous chemicals to accomplish electron transfer to the electrode[9]. When these bacteria oxidize the organic matter present in the wastewater, the electron is shuttled to the electrode and the protons produced diffuse through the water to cathode giving this particular electrode a positive characteristic. Oxygen, the hydrogen protons, and the electron that is connected by a circuit from the anode to the cathode, are then catalytically combined with a platinum catalyst to form water at the cathode[8,10]. 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. Bacteria are so far known to transfer electrons to a surface via two mechanisms: electron shuttling via self-produced mediators such as pycocyanin and related compound produced by *Pseudomonas aeruginosa*[11] and nanowires produced by both *Geobacter and Shewanella* species[12]. Research shows that ferric iron reduction by *Shewanella* involves membrane bound electron carriers[12]. However, such information on electron transfer mechanisms is insufficient to describe how bacteria colonize and maintain viable cells at a surface; competition among bacteria for the surface has not yet been examined.

3.1. Nanowires

Gorby and Beveridge[12] and co-workers reported the occurrence of conductive appendages for both Geobacter and Shewanella species which were termed as bacteria "nanowires". The conductivity of the appendages was examined using conductive scanning tunneling microscopy (STM). Microscopic observations concluded that the appendages were conductive in the x-y plane (i.e., between the cell and a surface), and thus could function as nanowires carrying electrons from the cell to a surface[12]. The structure of nanowires produced by *G. sulfurreducens* appears to be quite different than those made by *S.* oneidensis[9,11,12]. The appendages produced by *G. sulfurreducens* look to be relatively thin single strands, while those produced by *S. Oneidensis* have the appearance of thick "cables" that might possibly consist of several conductive wires bundled together[9]. The production of conductive nanowires has been shown by microorganisms other than iron reducing bacteria. The capability to produce conductive appendages has also been demonstrates in phototropic, oxygenic cyanobacteria (*Synechocystis sp.)*[12]. Subsequent examination of these cultures in MFCs demonstrates that when these cells are grown under CO_2 limited conditions, that they can produce electricity in an MFC in the light, but not in the dark[7].

3.2. Cell-surface electron transfer

The close examination of micrograph shows that there are surface blebs, i.e., protrusions on the surface that do not exist as nanowires but certainly could be conductive points of contact. Still, the small proteins responsible for electron transfer from the cell surface might not even be visible in such micrographs[13]. Anaerobically grown *Shewanella oneidensis* adhered to an iron surface with two to five times greater force than aerobically grown cells, and so the observation that this strain was more adhesive under anaerobic might allow closer contact required for electron transfer from cell bound cytochromes even in the absence of nanowires[14].

3.3. Mediators

The outer layers of the majority of microbial species are composed of non-conductive lipid membrane, peptidoglycans and lipopolysaccharides that hinder the direct electron transfer to the anode. Mediators accelerate the transfer of electrons from microbes to anode[13]. Mediators in an oxidized state can easily be reduced by capturing the electrons, 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 as mentioned by Ieropoulos *et al*[15] that it should be able to cross the cell membrane easily and able to grab electrons from the electron chain, it should possess a high electrode reaction rate and should have a good solubility in the anolyte, it must be a non-biodegradable in nature and non-toxic to microbes and it should be cheaper.

Typical synthetic exogenous mediators include dye and metallorganics such as neutral red, methylene blue, thionine 2-hydroxy-1, 4-napthoquinone and Fe(III)EDTA. Unfortunately, the toxicity resulted into instability of synthetic mediator that leads to production of exoelectrogens. Several mediator producing isolates were obtained by plating from an MFC producing a high power density of 4310 nW/m^2 as evaluated by Rabaey *et al*[11] . Electrochemical activity of several isolates was shown to be due to excreted redox mediators, primarily pyocyanin produced by *Pseudomonas aeruginosa*. While most *Geobacter spp*. Are not known to produce mediators, there is evidence for mediator production by *Geothrix fermentans*[9]. When the medium was replaced in an MFC that had stable power generation with this isolate, power dropped by 50% and required 10 days to resume the original level reported by Chaudhuri and Lovley[16]. This observation was in contrast to experiments with *Geobacter sulfurreducens* which immediately produced

comparable power levels with fresh medium[9]. Filtrate from the anode chamber suspension with *G. sulfurreducens* better than the addition of 25μM anthraquinone-2-6, disulfonate (AQDS) suggested by Jang *et al*[9].

3.4. Biofilm

A real breakthrough was made when some microbes were found to transfer electrons directly to the anode[16,17]. These microbes are operationally stable and yield a high coulombic efficiency[16]. *Shewanella Putrefaciens*[17], *Geobacter metallireducens*[18], *Geobacter sulferreducens*[8] and *Rhodoferax ferrireducens*[18] are all bio-electrochemically active and can form a biofilm on the anode surface and transfer electrons directly by conductance through the membrane. When they were used, the anode acts as the final electron acceptor that produced by the respiratory chain of the microbes in the biofilm[16,17,18]. Biofilm forming on the cathode surface may also play an important role in electron transfer between the microbes and the electrodes. Cathode can serve as electron donors for *Thiobacillus ferrooxidans* suspended in a catholyte for an MFC system that contained microbes in both anodic and cathodic chambers[19].

4. Performance of microbial fuel cells

The idea 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[20]. However, its idea cell voltage is uncertain because the electrons are transferred to the anode from the organic substrate through a complex respiratory chain that varies from the microbe to microbe and even for the same microbe when growth condition differs[20]. The key anodic reaction that determines the voltage is between the redox potential of the mediator (if one is employed) or the final cytochrome in the respiratory chain system and the anode[17]. In mediator-less MFC utilizing anodophiles such as *G. Sulfurreducens* form a bio-film on the anode surface and use the anode as their end terminal electron accepted in their anaerobic respiration as confirmed by Bond and Lovley[8]. The anode potential can be evaluated by the ratio of the final cytochrome of the chain in reduced to that of the oxidized states. The idea potential of MFCs can be calculated by the Nernst equation and they range from several hundred mV to over 1000 mV discovered by Bond and Lovley[8].

5. Actual MFC performance

The actual cell potential is always lower than its equilibrium potential because of irreversible losses. Ohmic losses 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 electrode obey Ohm's law, it can be expressed as IR_i, where I is current flowing through the MFC and R_i is the total cell internal resistance of the MFC was established by Cheng *et al*[21].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[21]. PEM produce a transmembrane potential difference that also constitutes a major resistance. The possible measures to minimize the overall potential drop include selection of microbes and modification to MFC configurations such as improvement in electrode structure, better electrocatalysts, more conductive and short spacing between electrodes[22].

6. Effects of operating conditions

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, pH, temperature and reactor configuration[1]. With a given MFC system, the following operating parameters can be regulated to enhance the performance of an MFC.

6.1. Effect of electrode materials:

Using better performing electrode materials can improve the performance of an MFC. Pt and Pt black electrodes are superior to graphite, graphite felt and carbon-cloth electrodes that should be preferred for construction of both anode and cathode but they are too costly[22]. Chaudhuri and Lovley16 reported that a current of 2-4 mA could be achieved with platinumized carbon-cloth anode in an agitated anaerobic culture of E. coil using a standard glucose medium at 0.55 mmol/L, while no microbial 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 density than those with graphite felt cathodes[9,22,23]. One drawback of using Pt or Pt black electrode is that their activities are reduced by the formation of a PtO layer at the electrode surface at positive potentials[23].

6.2. ph buffer and electrolyte:

Theoretically there is 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[24]. However, the pH difference increases the driving force of the proton diffusion from the anode to the cathode chamber and finally a dynamic equilibrium acheived[24]. 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[11]. 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[3,24]. It was possible that the buffer compensated the slow proton transfer rate and improved the proton availability for the cathodic reaction. 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, possibly due to the fact that NaCl enhanced the conductivity of both the anode and cathode[3,9,24].

6.3. Proton exchange system

Proton exchange system can affect an MFC system's internal resistance and in turn influence the power output of the MFC. Nafion is most popular because of its highly selective permeability of protons. The ratio of PEM surface area to system volume is important for the power output[22]. 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[25]. Membrane is prone to fouling if the fuel is something like municipal wastewater. Membrane becomes a problem in such applications.

6.4. 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[22]. Many systems have shown that electricity generation is dependent on fuel concentration both in batch and continuous flow mode of MFCs. Usually a higher fuel concentration yields a higher power output in a wide concentration range. Gil *et al*[24] investigated the effects of fuel concentration on the performance of an MFC and came to the conclusion that the power density would increase with the increase in the fuel concentration. Moon *et al*[22] found that the current increased with a wastewater concentration up to 50 mg/L in their MFC.

6.5. Operation 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. Dissolved oxygen (DO) was a major limiting factor when it remained below the air saturated level[2,23,24]. Surprisingly, a catholytic sparged with pure oxygen that gave 38mg/L DO did not further increase the power output compared to that of the air-saturated water (at 7.9 mg/L DO) illustrated by Pham *et al*[2], Min and Logan[7] and Oh *et al*[23]. Rate of oxygen diffusion toward the anode chamber goes up with the DO concentration. Thus, a part of the substrate is consumed directly by the oxygen instead of transferring the electrons through the electrode and the circuit[26]. Power output is much greater using ferricyanide as the electron acceptor in the cathodic chamber. This is likely due to the greater mass transfer rate and lower activation energy for the cathodic reaction offered by ferricyanide[23]. Using hydrogen peroxide solution as the final electron acceptor in the cathodic chamber increased power output and current density[27]. As a consequence, aeration is no longer needed for single-compartment MFCs with a cathode that is directly exposed to air.

7. Applications of MFCs

7.1. Electricity generation

MFCs are capable of converting the chemical energy stored in the chemical compound in a biomass to electrical energy with the aid of micro-organisms. Because chemical energy from the oxidization of fuel molecules is converted directly into electricity instead of heat, a much higher conversion efficiency can be achieved (>70%) just like conventional chemical fuel cells. Chaudhuri and Lovley[16] reported that *Rhodoferax ferrireducens* could generate electricity with an electron yield as high as 80%. Higher electron recovery as electricity of up to 89% was also established by Rabaey *et al*.[28]. An extremely high columbic efficiency of 97% was reported during the oxidation of formate with the catalysis of Pt black[29]. However, MFC power generation is still very low because the rate of electron abstraction is very low[30,31]. 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 system and wireless sensors that have only low power requirements to transmit signals such as temperature to receivers in remote locations[32,33]. MFCs are viewed by some researchers as a perfect energy supply candidate for Gastro-robots by self-feeding the biomass collected by themselves[28]. 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 behaviour including motion, sensing, computing and communication[34,35]. Application of MFC in a spaceship is 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 as predicted by Chai[36].

7.2. Waste water treatment

In early 1991, the MFCs were considered to be used for treating wastewater[37]. Municipal wastewater contains magnitude of organic compound that can fuel MFCs. MFCs yield 50-90% less solids to be disposed off to reduce the pollution[38]. Furthermore, organic molecules such as acetate, propionate, and 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 sulphides as required in wastewater treatment[39,40]. MFCs can enhance the growth of bioelectrochemically active microbes during wastewater treatment, thereby, the entire system operate in a smooth and stable manner. Continuous flow of MFCs either in single-compartment MFCs or in membrane-less MFCs are favoured for wastewater treatment due to concerns in scale-up[9,22]. Sanitary

wastes, food processing wastewater, swing wastewater and corn stover are all great biomass source for MFCs because they are rich in organic matter[10,41,42].

7.3 Electricity generation in a rice paddy field

Recently, electricity generation has been achieved in a rice paddy field due to plant-microbe interaction. Soil is rich in organics, particularly those that support growth of plants. These organics are possible sources of sustainable energy, and a microbial fuel cell (MFC) system can potentially be used for this purpose[43,44]. A paddy field is a flooded parcel of arable land used for growing rice and other semi-aquatic crops. In Japan, rice paddy field cover 2.5 million hector and occupy more than 50% of the total arable land areas in the country (Ministry of Agriculture, Forestry and Fisheries 2006). When a paddy field is flooded, the soil immediately below the surface becomes anaerobic that would be responsible for rising up of a community of anaerobic microbes (comprised mainly of sulphate-reducing bacteria, iron-reducing bacteria, fermenting bacteria and methanogenic archaea) was determined by Takai[45], Grosskopf *et al*[46] and Chin *et al*[47]. Since a potential gradient is known to be formed between the soil and the flooded water, it was anticipated that an MFC system could operate in a paddy field. The graphite felt electrodes were used as anode and cathode[43]. An anode was set in the rice rhizosphere, and a cathode was in the flooded water above the rhizosphere. It was observed that electricity generation (as high as 6 mW/m^2) was sunlight dependent. Artificial shading of rice plants in the daytime inhibited the electricity generation was discovered by Chin *et al*[47]. In rhizosphere, rice roots penetrated, rice roots penetrated the anode graphite felt where specific bacterial populations occurred[44]. Supplementation to the anode region with acetate (one of the major root-exhausted organic compounds) enhanced the electricity generation in the dark illustrated by Holzman[38]. These suggest that the paddy-field electricity generation system was an ecological solar cell in which the plant photosynthesis was coupled to the microbial conversion of organics to electricity[40].

7.4. 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 produces by the metabolism of microbes in an MFC is thermodynamically unfavourable. Liu *et al*[1] applied an external potential to increase the cathode potential in an MFC circuit and thus overcome the thermodynamic barrier. In this mode, protons and electrons produced by the anodic reaction and combined at the cathode to form hydrogen. The required external potential for an MFC is theoretically 110mV. MFCs can potentially produce about 8-9 mile H_2/mol glucose compare to the typical 4 mol H_2/mol glucose achieved in conventional fermentation[3]. In bio-hydrogen 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 source that can contribute to the overall hydrogen demand in a hydrogen economy[38].

7.5 Biosensor

MFC technology is also used as a sensor for pollutant analysis and *in situ* process monitoring and control[48,49]. The proportional correlation between the columbic yield of MFCs and the strength of the wastewater make MFCs possible biological oxygen demand (BOD) sensor[50]. An accurate method to measure the BOD value of a liquid stream is to calculate its Columbic yield. However, a high BOD concentration requires a long response time because the Columbic yield can be calculated only after the BOD has been depleted unless a dilution mechanism is in place[50]. A low BOD sensor can also show the BOD value based on the maximum current

since the current values increases with the BOD value linearly in an oligotrophic-type MFC[48,50]. During this stage, the anodic reaction is limited by substrate concentration. This monitoring mode can be applied to real time BOD determination for either surface water, secondary effluents or diluted high BOD waste water samples[50,51]. MFC type of BOD sensors is advantageous over other type of BOD sensors because they have excellent operational stability and good reproducibility and accuracy. An MFC type BOD sensor with the microbes enriched in it was constructed that can be kept operational for over 5 years without extra maintenance[50].

7.6 Bioethanol

The MFC technology has to compete with the mature methanogenic anaerobic digestion technology that has seen wide commercial applications because they can use the same biomass in many cases for energy production[38,52]. MFCs are capable of converting biomass at temperatures below 20^0C and with low substrate concentrations, both of which are problematic for methanogenic digestors[26]. It is likely that the MFC technology will co-exist with the methanogenic anaerobic digestion technology in the future. Mutagenesis and even recombinant DNA technology can be used in the future to obtain some "super bugs" for MFCs[26,38]. Compared to biogas, bio-ethanol has the main advantage that it is a liquid fuel with high performance in internal combustion engines. Despite its decreasing production cost over recent years due to the development of more efficient pre-treatment methods and enzymes, bio-ethanol production even from refined materials (e.g., sugar cane or pure starch) is still not cost competitive with gasoline production discovered by Lusk[52]. The main cost involved in the process is the need for high enzyme loadings during the simultaneous saccharification and fermentation process. The distillations costs have already decreased considerably and will probably further decrease in the future because of increased heat recovery[53]. The overall conversion efficiency from organic waste to electricity via ethanol is low (10-25%) and involves the use of an energy consuming distillation step. As a result, bio-ethanol is expected to primordially play a role in the powering of combustion engines by blending with gasoline[52].

8. Microorganisms

8.1. *Axenic* bacterial cultures

Some bacterial species that used in MFCs, particularly metal-reducing bacterial have recently been reported to directly transfer electrons to the anode. Metal-reducing bacteria are commonly found in sediments, where they use insoluble electron acceptors such as Fe (III) and Mn (IV). Specific cytochromes at the outside of the cell membrane make *Shewanella putrefaciens* electrochemically active in case it is grown under anaerobic conditions[54]. The same holds true for bacteria of the family *Geobacteraceae*, which have been reported to form a biofilm on the anode surface in MFCs and to transfer the electrons from acetate with high efficiency. *Rhodoferax* species isolated from anoxic sediment were able to efficiently transfer electrons to a graphite anode using glucose as a sole carbon source[16]. Remarkably, this bacterium is the first reported strain that can completely mineralize glucose to CO_2 while concomitantly generating electricity at 90% efficiency[16]. In terms of performance, current densities in the order of 0.2-0.6 mA and a total power density of 1-17 mW/m^2 graphite surface have been reported for *Shewanella putrefaciens*, *Geobacter sulfurreducens* and *Rhodoferax ferrireducens* at conventional (woven) graphite electrodes[8,16,54]. However, in case woven graphite in the *Rhodoferax* study was replaced by highly porous graphite electrodes, the current and power output was increased up to 74 mA/m^2 and 33 mW/m^2, respectively. Although these bacteria generally show high electron transfer efficiency, they have a slow growth rate, a high substrate specificity (mostly acetate or lactate) and relatively low energy transfer efficiency compared to mixed cultures[28]. Furthermore, the use of a pure

culture implies a continuous risk of contamination of the MFCs with undesired bacteria.

8.2. Mixed bacterial cultures

MFCs that make use of mixed bacterial cultures have some important advantages over MFCs driven by axenic cultures: higher resistance against process disturbances, higher substrate consumption rates, smaller substrate specificity and higher power output[11]. Mostly, the electrochemically active mixed cultures are enriched either both of the sediment from marine or lake sediment[8,30] or activated sludge from wastewater treatment plants[8,11,55]. By means of molecular analysis, electrochemically active species of Microbial fuel cells *Geobacteraceae*, *Desulfuromonas*, *Alcaligenes faecalis*, *Enterococcus faecium*, *Pseudomonas aeruginosa*, *Proteobacteria*, *Clostridia*, *Bacteroides* and *Aeromonas* species were detected in the before-mentioned studies. Most remarkably, the study of Kim *et al*[54] also showed the presence of nitrogen fixing bacteria (e.g., *Azoarcus* and *Azospirillum*) amongst the electrochemically active bacterial populations. While Rabaey *et al*[11] studied that by starting with methanogenic sludge and by continuously harvesting the anodic populations over a 5-month period using glucose as carbon source, an electrochemically active consortium can be obtained that mainly consists of facultative anaerobic bacteria (e.g. *Alcaligenes*, *Enterococcus* and *Pseudomonas* species). In this particular study, very high glucose-to-power efficiencies could be reached in the order of 80%. So far, only the study of Liu and Logan[10], Tender *et al*[30] and Kim *et al*[54] confirmed that the use of complex substrates, respectively sediments on the sea floor and organics present in wastewater (latter two) to generate electricity in MFCs. It should be remarked that in order to maximize the power output, experiments with varying external resistance should be performed. To estimate the power per unit surface to putative power output per unit reactor volume, one can take into account that at present some 100-500 m^2 of anode surface can be installed per m^3 anodic reactor volume. Hence, the state of the art power supply ranges from approximately 1 to 1800 W per m^3 anode reactor volume installed. To render the anode more susceptible for receiving electrons from the bacteria, electrochemically active compounds can be incorporated in the electrode material. This approach has already been investigated by Park and Zeikus[55], who incorporated that dyes like neutral red and metals like Mn^{+4}, Fe^{+3} or graphite contained anode rods were responsible for attracting more electron from bacteria. Moreover, bacteria could able to form a biofilm on the modified anode surface.

CONCLUSION

The algae assisted cathode can be successfully implemented in microbial fuel cell. The reactor design of a microbial fuel cell was quite successful for using photosynthesis ability of algae for oxygen supply to cathode. Dissolved oxygen concentration of around 3.6 to 5.5 mg/l of oxygen can be maintained at cathodic chamber for bioelectric production. The above mentioned concentration is sufficient enough to run a microbial fuel cell for wastewater treatment and bioelectricity production. Furthermore, other species of algae may also try out for taking benefit like oil-algae can be grown in cathode chamber which can be use for oil recovery and greenhouse gas (like CO_2) sequestering. As far as COD removal is concerned, COD removal efficiency of the MFC having 3% dairy wastewater was found to be more efficient to that of 6% dairy wastewater. Power density and current density of the MFC having 3% dairy wastewater and 6% dairy wastewater was sufficient enough to produce electric current efficiently. Decrease in power can be explained on the basis of consumption of carbon source with time. Usually the carbon source gets exhausted with time due to continue consumption by microbial communities present in anode chamber. Performance of this reactor may further be enhanced by continues feeding and optimising other design and operational parameters like distance between electrode, arrangement of

strict anaerobic condition at anode chamber by use of chemical oxygen scavengers like L-cystine. In nutshell, the novel reactor design and idea of using photosynthetic algae for oxygen supply to cathodic reaction. The green algae's are also helpful in CO_2 sequestration. So, the design and operational parameters should be optimized for performance enhancement of this reactor. Furthermore, use of beneficial species of algae can enhance the benefits (like bio diesel production) of Microbial fuel cell and can make it more beneficial.

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