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Examining the Structure and Efficiency of the Microbiological Fuel Cell

Abstract

Microbiological fuel cells (MFC) are considered one of the significant future potentials in providing clean and renewable energy. Besides providing electrical energy, the most widely used and flexible one among the other types of energy, MFCs not only does not cause the slightest pollution to the environment but also purify and eliminate environmental pollution and have a significant effect on municipal sewage and the leachate from municipal solid waste. MFC technology has not yet reached commercial and mass production because of low efficiency. With the commercialization of this industry, municipal sewage will be raised not only as a problem but also as a source of clean energy supply as municipal sewage is a rich source of microorganisms used in microbiological fuel cells. MFCs could convert the chemical energy stored in the chemical compounds of biomass into electrical energy with the help of microorganisms. MFCs are especially proper for supplying the power of remote measurement systems (Telemetry) and wireless sensors that need low power to transmit signals like temperature to final receivers in distant locations.

Keywords: *MFC, fuel cell efficiency, microorganisms, energy supply*

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Introduction

MFC refers to a reactor that converts the chemical energy stored in the chemical bonds of organic compounds into electrical energy by the catalytic reactions of microorganisms and under anaerobic conditions. For many years, scientists have figured out that one can directly decompose organic materials and generate electricity using bacteria. In wastewater treatment, MFCs could be used to decompose organic substances. Furthermore, some papers have tried to use MFCs as biological sensors like BOD display sensors. Output power and Coulombic efficiency (CE) in MFCs are affected by factors like the type of microbes in the anode cell, MFC configuration, and operating conditions. Currently, the practical applications of MFCs are limited as their low output power is in the range of several thousand milliwatts per square meter (mW/m^2). Scientists try to enhance the performance of MFCs and reduce their manufacturing and operating costs. The paper tried to present an overview of the recent progress in the study and explain the advances in MFCs and the configuration and efficiency of MFCs.

The ever-increasing use of fossil fuels has faced an energy crisis. Biological renewable energy is suitable for compensating for human society's energy needs. Many studies have recently been conducted to develop various methods of energy production. Here, electricity generation from renewable sources that do not emit carbon dioxide into the environment is more important than any other method (Lovley, 2006; Davis and Hingson, 2007). Recently, the technology of microbial fuel cells, MFCs that convert the energy stored in the bonds of organic compounds into electrical energy through catalytic reactions by microorganisms, has received great attention (Allen and Bennetto, 1993; Gil et al., 2003; Moon et al., 2006; Choi et al., 2003).

The bacteria used in MFCs can generate electricity while simultaneously decomposing wastewater and organic matter in biological methods (Park and Zeikus, 2000; Oh, and Logan, 2005). The microbes in the anode cell oxidize the organic materials inside the anode cell. Electrons and protons are produced during this process. Carbon dioxide is produced as a product of oxidation. However, no carbon dioxide is released in this process. This is because the carbon dioxide present in the biological mass was originally imported from the ambient air during photosynthesis. Unlike the direct combustion process, electrons are absorbed by the anode and transferred to the cathode through an external circuit. Protons are absorbed by the anode and transferred to the cathode through an external circuit. Protons enter the cathode cell and react with the oxygen in the cathode cell to produce water by passing through a proton exchange membrane, PEM, or a salt bridge. Microbes in the anode cell extract electrons and protons from the organic materials inside the anode cell by oxidizing organic materials and through separate and dissimilar processes (Rabaey and Verstraete, 2005). Electricity generation is only possible when the microbes are kept separate from oxygen or any other electron-accepting substance other than what is in the anode cell that creates anaerobic conditions for the anode chamber.

Over the recent years, quick and great development has been made in MFC studies, and the number of papers and journals associated with MFC technology has increased drastically in the last three years, and more scholars have joined the group of

MFC researchers. There are many papers on MFCs, each of which has focused on various parts of MFCs. Logan et al. (2006) examined the design of MFCs, characteristics, and performance of MFCs. Rabaey and Verstraete (2005) examined metabolism in MFCs. Lovley (2006) mainly examined Benthic Unattended Generator (BUG) systems to power remote-sensing equipment or display instruments from the perspective of microbial physiology. Pham et al. (2006) reviewed the advantages and disadvantages of MFCs compared to collected anaerobic digestion technology for biogas production as renewable energy. Chang et al. (2006) discussed the electrochemically active bacteria used in non-intermediate MFCs and the rate-limiting factors of electron transfer. Bullen et al. (2005) summarized many recent experimental results on MFCs. Based on the points stated, the purpose of the study is to examine the structure and efficiency of the MFCs.

Theoretical foundations

1. Configuration of MFCs

MFC components

For instance, an MFC has an anode chamber and a cathode chamber separated by a PEM. In a single-component MFC, the cathode chamber is removed as the cathode is directly associated with air (Logan et al., 2006; Rabaey and Verstraete, 2005; Bullen et al., 2006; Lovley, 2006). Figure (1) is the schematic view of an MFC used to generate electricity.

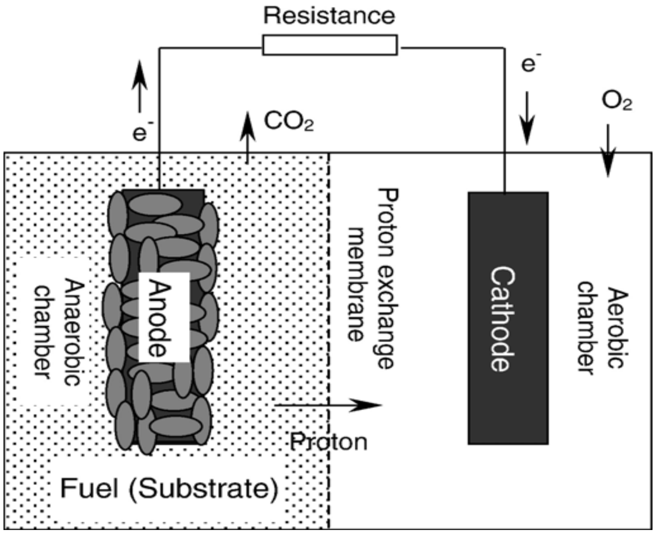

Figure 1. Schematic view of an MFC

As the figure shows, an MFC has anode and cathode cells separated by a proton exchange membrane (PEM) (Wilkinson, 2000; Gil et al., 2003).

Two-component MFC systems

Generally, two-component MFCs operate in Batch mode, for which a medium like glucose solution or acetate solution is defined, using which energy is generated. MFCs are currently created and used at the laboratory level. A two-component MFC has a cathode chamber connected to the anode chamber by a PEM and sometimes a salt bridge. Passing protons, PEM, or salt bridges transfers them from the anode to the cathode and deters oxygen penetration into the anode compartment. In practice, each of these components can have various forms.

Min and Logan (2004) developed a flat-plate microbial fuel cell (FPMFC) with a chamber and a PEM. Its compact configuration looked just like a chemical fuel cell. A carbon-cloth cathode attached to a Nafion-type PEM is connected to a carbon sheet that acts as the anode. This type of MFC configuration is completed by attaching two polycarbonate plates on both sides of FPMFC, which are non-conductive. The cathode and anode chambers are connected by a PEM, as shown in Figure b. Wastewater or biomass could be used as feed for the anode chamber. Dry air can be blown into the cathode compartment. Both chambers could have a continuous operation (Min and Logan, 2004).

Single-component MFC systems

Given the complex configuration of two-component MFCs, one cannot scale them up easily. Even though these MFCs could work in both batch and continuous mode, single-component MFCs have a simpler configuration and lower cost. They generally have only the anode chamber, and the cathode and aeration chamber is omitted, as shown in Figure (2) a. Park et al. (DATE) designed a single-component MFC with a rectangular anode chamber and a porous cathode exposed to air. Protons were transferred from the analyte solution to the porous cathode in the vicinity of air (Park and Zeikus, 2003). Logan and Lin (2004) designed an MFC in which the anode was placed in a plastic cylinder and the cathode outside the cylinder (Figure 2a).

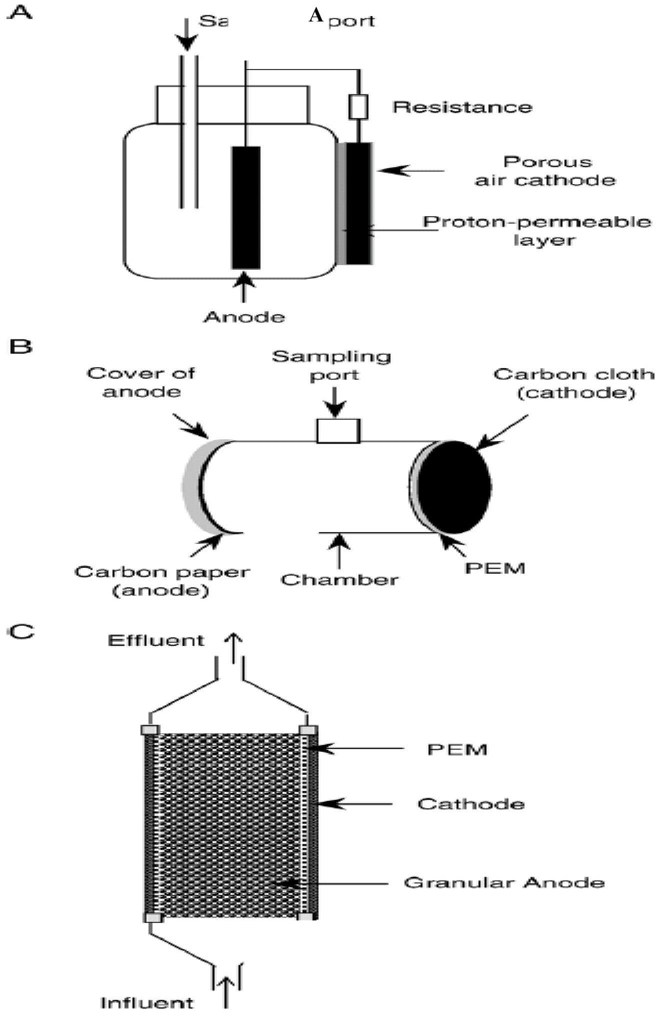

Figure 2. Schematic of other MFC examples

Figure (2) is a schematic of an MFC-type biological reactor at the standard laboratory level. The anode is made of a carbon sheet. The cathode could be either a flexible carbon-coated electrode attached to a PEM or a solid carbon sheet without a PEM (Liu and Logan, 2004; Liu et al., 2005; Cheng et al., 2006).

A tubular MFC system has an outer cathode and an inner anode where carbon granules are used. This system is given in Figure (2) c (Rabaey et al., b2005). Without a cathode chamber, the catalyst is sprinkled drop by drop on the graphite surface to prevent it from drying out. Rabaey et al. (b2005) stated that the continuous use of a cathode in the vicinity of air is essential in the practical use of such MFCs. Another type of single-component reactor called SCMFC was reported by Liu et al. (2004). Their SCMFC housed the anode and cathode in the same chamber.

Up-flow type MFC systems

Jang et al. (2004) designed another type of MFC (Figure (3) a) that operated in continuous mode. A Plexiglas cylinder was divided into two parts using glass wool or glass beads. As Figure (3) shows, these two parts have the role of cathode and anode housing. The anode and cathode are made of compressed graphite and placed in the shape of a disk at the bottom and top of the reactor. Figure (3) b shows another MFC design inspired by the general idea shown in Figure (3), except that it is rectangular, and the bone is physically separated with glass wool or glass beads (Tartakovsky and Guiot, 2006).

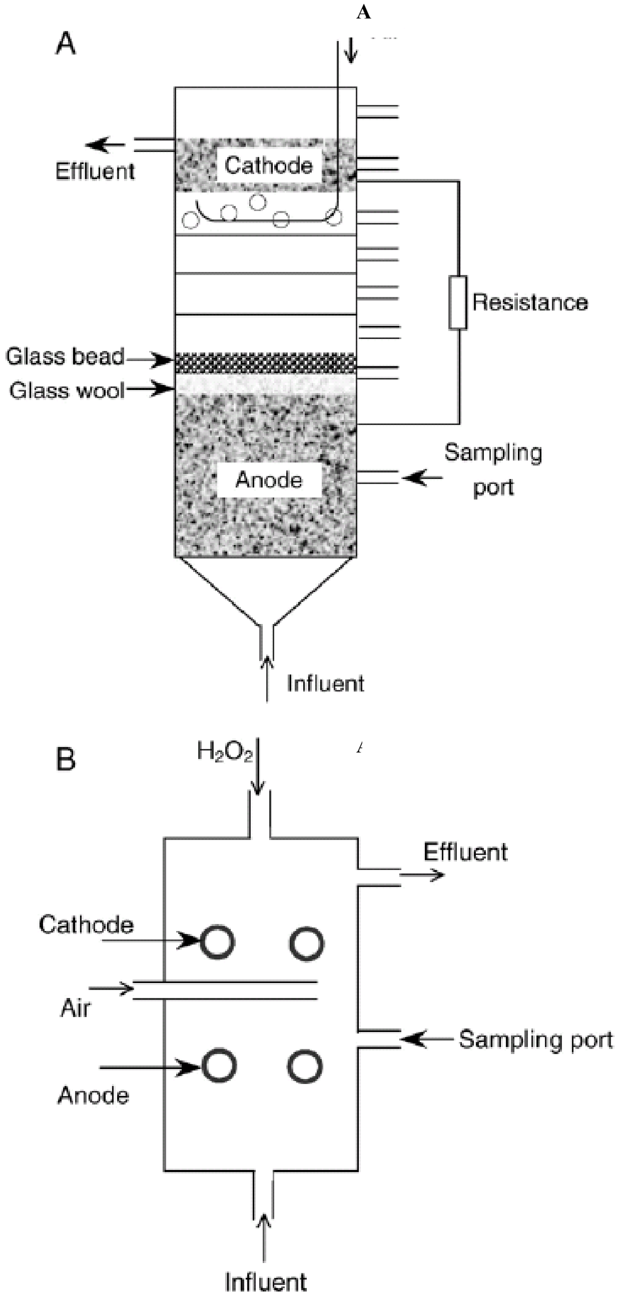

Figure 3. The schematic of two examples of Upflow type MFCs

The influent enters the anode from the bottom, and the effluent exits continuously through the cathode chamber at the top (Jang et al., 2004; Moon et al., 2005). In this type of MFCs, the analyte or catalyst is not separate, and the obstacles between the anode and the cathode create a DO gradient inside the MFC that enhances its performance.

Stacked MFC

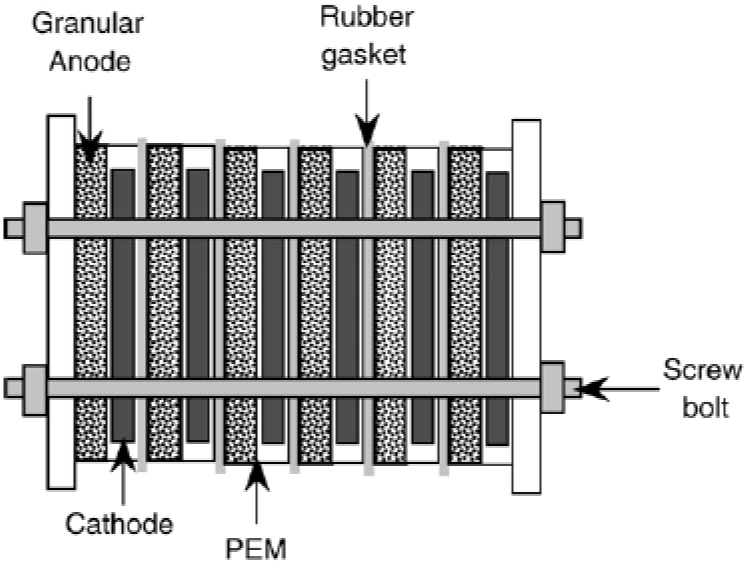

Figure 4. Schematic of a stacked MFC sample

As Figure 4 shows, the stacked MFC was used for research on various MFCs connected in parallel (Aelterman et al., 2006).

By connecting several MFCs in series or parallel, one can obtain a large output voltage or current. The opposite effect was not seen on the maximum output power of individual MFCs. CE (which is not, in fact, the real CE and is the Coulomb conversion percentage. The CE describes the value of electrons that can be extracted from the electron-rich substrate using electrodes and is not changed by the speed of electron transfer. In contrast, the researchers described how the substrate used to generate electricity before a current discharge out of the MFC assembly or stacked MFC) differed significantly in these two arrangements. The efficiency of the parallel mode was six times higher than the series mode with the same discharge rate.

A parallel-connected stack is nothing but a short-circuit current to a series-connected stack. This does not mean that the maximum bioelectrochemical reaction speed is obtained by connecting MFCs in parallel. Hence, except for the independent operation of MFC units, the parallel connection mode is preferable to maximize the removal of COD (Aelterman et al., 2006).

2. MFCs performance

The actual efficiency of MFC

The real potential of the cell is always lower than its equilibrium state potential because of the irreversible losses. Equation (1) (Appleby and Foulkes, 1989) shows different losses in a real MFC:

$$V_{cell} = E_{cathode} - \eta_{act,c} + h_{conc,c} - E_{anode} - \eta_{act,a} + \eta_{conc,a} - iR \quad (1)$$

Here, $\eta_{act,c}$, and $\eta_{act,\ a}$ are, respectively, activation polarization losses on the cathode and anode. Furthermore, $\eta_{conc,c}$, and $\eta_{conc,\ a}$ are concentration polarizations in the cathode and anode chambers. Ohmic losses, η_{ohm}, are because of the resistance to the flow of ions in the electrolyte and the resistance to the flow of electrons in the electrode. As the resistances in the electrolyte and the electrodes both obey Ohm's law, one can express it by the expression *iRi*, where *i* is the current flowing in the MFC and *Ri* is the total internal resistance of the cell in the MFC.

Activation polarization refers to the activation energy that the reactants must overcome. When the speed of an electrochemical reaction on the surface of the electrodes is controlled by slow reaction kinetics, this step is considered a limiting step. In processes where the surface adsorption of reactants, transfer of electrons across the cell bilayer membrane, elimination of products, and physical nature are involved, all these polarization factors increase the activation of the reaction in it. Activation polarization is an obstacle that can be overcome by adding intermediates for the microbes that cannot easily release electrons to the anode surface. In MFCs without an interface, activation polarization is reduced because of the conductive pili. Cathodic reaction faces activation polarization too. For instance, platinum (Pt) is preferred to graphite cathode as it has a lower energy barrier in the cathode reaction, resulting in water production. Activation polarization is usually more effective at low current intensity. The electronic barriers at the cathode and anode must be overcome before current and ions can flow (Appleby and Foulkes, 1989).

The resistance against the ions flows in the electrolyte, and the flow of electrons between the electrodes causes ohmic losses. Ohmic losses in the electrolyte are more important and can be reduced by reducing the distance between the electrodes and increasing the electrical conductivity of the ions in the electrolyte (Cheng et al., 2006). PEM creates a potential difference across the membrane that increases the total resistance too.

Concentration polarization is the loss of potential because of the inability to maintain the initial concentration of the substrate in the fluid with the stain. Low mass transfer rates for reactants and products raise another problem. The high cathode potential obtained from the lack of DO for the cathodic reaction limits the output power of some MFCs, too (Oh et al., 2004). A good MFC bioreactor should minimize concentration polarization by increasing the mass transfer rate. Mixing can be very effective in reducing the concentration gradient in an MFC.

Nonetheless, the mixing operation calls for a pump, and its energy consumption is usually higher than the output power of the MFC. Hence, one should consider balancing output power and energy consumption in MFC operation. A polarization curve analysis (Rhoads et al., 2005) of an MFC could reveal to what extent the losses listed in Equation 4 can affect the total potential drop. This can refer to the minimum criteria used to reduce this information to reach the ideal potential. These criteria could involve selecting the type of microbes and modifying the MFC configuration, including improvements in the electrode structure, better electrocatalyst, better conductive electrolyte, and short distance between electrodes. For a known MFC system, one can enhance the efficiency of the cells by adjusting the operating conditions (Gil et al., 2003).

The effect of operating conditions

The efficiency of laboratory MFCs has not yet reached the ideal level, which could be due to different reasons. Power generation in an MFC is affected by different factors such as the type of microbe, biological mass and its concentration, ionic strength, pH, temperature, and reactor configuration (Liu et al., 2005 b). The effect of the reactor structure and the type of microbes used in MFC were explained in sections 2 and 3. In a known MFC system, one can increase MFC efficiency by changing the parameters described below to reduce polarization.

The effect of electrode type

One of the obstacles to using Pt or black platinum in electrodes is the formation of a PtO layer on the surface of the electrode which leads to a positive potential. Schroder et al. (2003) examined the role of polyaniline when added to the surface of the platinum black anode. The produced current intensity reached 1.45 $mA^{-1}cm^{-2}$ with a black platinum anode coated with polyaniline from 0.84 with the black platinum anode. Fluorinated polyanilines such as poly2-fluoroaniline and poly 2, 3, 5, and 6-tetrafluoroaniline performed better than polyaniline (Niessen et al., 2004, 2006). These conducting polymers act as soluble mediators because of their high similarity to reduction mediators (Schroder et al., 2003). The cathode reaction has a Monod-type kinetic relationship with dissolved oxygen concentration (Oh et al., 2004; Pham et al., 2004). Oxygen cathodes with iron II phthalocyanine (FePc) and cobalt tetra methoxyphenyl porphyrin (CoTMPP) bases are not expensive and are a suitable alternative for use in MFCs given their efficiency similarity to platinum oxygen electrodes (Zhao et al., 2005, 2006).

pH buffer and electrolyte

there will be a pH difference in the cathode and anode chambers if no buffer is used in the solution. Nevertheless, protons and sufficient oxygen in the cathode are the rates of production of protons in the anode, the pH will not change if the rate of reaction of electrons. PEM creates an obstacle against the transfer of protons through penetration through the membrane, and in the early stages of MFC operation, electron transfer through the membrane is slower than the speed of its production in the anode chamber and the speed of its consumption in the cathode chamber, which is the result creating a pH difference in the two compartments (Gil et al., 2003). However, the pH difference increases the driving force of proton penetration from the anode compartment to the cathode compartment, which ends in "dynamic balance." Some of the protons produced from the biological decomposition of the organic substrate transferred to the cathode chamber could react with dissolved oxygen, whereas some protons not transferred to the cathode chamber at a sufficient speed through the PEM or salt bridge accumulate in the anode chamber. Gil et al. (2003) reported a pH difference of 4.1 (9.5 in the cathode and 5.4 in the anode) after 5 hours of operation with an initial pH of 7 without buffer. By adding phosphate buffer (pH = 0.7), the pH of both the cathode and anode compartments reaches less than 0.5, and the output current is 1 and increases up to 2-fold. The buffer probably compensates for the slow proton transfer and enhances the value of protons available to the cathode. Jang et al. (2004) added HCl solution to the cathode chamber and found that the output current increased by almost 1. This report clarifies that proton availability to the cathode is a limiting factor in electricity generation. Increasing the ionic strength by adding NaCl to MFCs enhanced the power output (Jang et al., 2004; Liu et al., b2005), which probably bettered the analyte conductivity.

3. Applications

Electricity generation

MFCs could convert the chemical energy stored in the chemical compounds of biological mass (biomass) into electrical energy with the help of microorganisms. The chemical energy from the oxidation of fuel molecules is directly converted into electricity instead of heat and the Carnot cycle is obtained with a much higher conversion efficiency (>70%) (just like chemical fuel cells). Chaudhury and Lovley (2003) reported that R. ferrireducens could produce electrons with an efficiency of more than 80%, with an electron recovery as high as 89%. Rabaey et al. (2003) stated a very high efficiency of CE, 97 %, during the oxidation of formate with platinum black catalyst (Rosenbaum et al., 2006). However, the level of power generation in MFC is still very low (Tender et al., 2002; Delong and Chandler, 2002), which means that the intensity of electron extraction is still very low. An easy way to solve this problem is to store the electricity in rechargeable devices and then distribute it to the end consumer (Ieropoulos et al., 2003). Capacitors were used in robots called EcoBot-I to store the energy produced by MFCs. The performance of MFCs in these robots was pulsating

Biohydrogen

MFCs could be easily modified to produce hydrogen instead of electricity. Under normal operating conditions, the protons released by the anodic reaction migrate to the cathode to combine with oxygen to form water. Hydrogen production from protons and electrons from microbial metabolism in an MFC is not thermodynamically favorable. Liu et al. (2005) used an external potential to overcome thermodynamic barriers by increasing the cathode potential in an MFC circuit. In this case, the protons and electrons produced from the anode reaction combine at the cathode to produce hydrogen. The external potential needed for an MFC is theoretically 110 mV, much lower than 1210 mV, which is the value needed for direct electrolysis of water at normal pH because some energy is obtained from the oxidation process of biological mass (biomass) in the anode chamber. MFCs can produce approximately 8 to 9 molH2/mol glucose, comparable to 4 molH2/mol glucose from conventional fermentation processes (Liu et al., c2005).

Wastewater treatment

In early 1991, MFCs were considered for wastewater treatment. Municipal sewage has a variety of organic compounds that can be considered fuel for MFC. The energy produced by MFCs in wastewater treatment could potentially cut the need for conventional treatment processes that consume much electrical energy to aerate the sludge. MFCs leave 50% to 90% less solid waste. Furthermore, an MFC can completely break down organic molecules like acetate, propionate, and butyrate into CO_2 and H_2O. Electrophilic and endophilic bonding is especially useful for wastewater treatment in MFC as more organic materials can be decomposed by using a variety of organic materials. MFCs that use specific microbes have a special ability to remove sulfates, which is important in wastewater treatment (Rabaey et al., 2006).

Biological sensors (Biosensors)

Apart from the applications already stated, another application of MFC technology is using it as a sensor for pollutant analysis and on-site process display and control (Chang et al., 2004, 2005). The interaction between MFCs and wastewater concentration allows MFCs to be referred to as BOD sensors (Kim et al., 2003). A precise method to calculate the BOD value of a liquid stream is to calculate its CE. Several studies (Chang et al., 2004; Kim et al., 2003) have revealed a good linear relationship between CE and wastewater concentration over a wide range of BOD. Nevertheless, high BOD concentrations call for long response times as the CE can only be calculated after all the BOD has been consumed unless a dilution mechanism is used instead. Much has been done to enhance the dynamic responses in MFCs used as sensors (Moon et al., 2004).

Conclusion

MFCs technology must compete with the methanogenic anaerobic digestion technology that has reached its full growth and has wide industrial applications. MFC technology can use the same biological mass to produce energy for various applications. MFCs could convert biological mass into electricity at temperatures lower than 20°C and even with low substrate concentrations, both problematic for methanogenic digesters. The main problem of MFCs depends on biofilm for unmediated electron transfer, whereas anaerobic digesters like up-flow anaerobic sludge blanket reactors meet this requirement using microbial complex effectively without the need for stabilization in the cell. MFC technology and methanogenic anaerobic digestion technology will be complementary in the future.

The need for endophilic microbes that could accelerate the intensity of electron transfer from the biofilm covering the anode to the anode itself is strongly felt to enhance the production capacity. Lovley claimed that if Geobacter transferred electrons to the anode at the same rate as its natural electron acceptor of the iron ion, the current intensity of the MFC could be increased by 4 times. It is possible to use DNA technology with new hereditary traits and Mutagenesis technology to produce superbugs for MFCs. Microbes can be used in pure form or as a mixture of microbes that form a group of microbes that act in conjunction with each other to enhance the efficiency of MFC. One kind of bacteria in the microbial community could provide electron transport interfaces used by another type of bacteria to better transfer electrons to the anode (Rabaey and Verstraete, 2005). One could also obtain a set of optimized microbes in the future by which the intensity of mass and electron transfer became very high, and there was no need for biofilm or external interfaces.

MFCs could have different applications. When they are used for wastewater treatment, the large surface area of the anode is necessary for biofilm formation. An important discovery is required to make cheap electrodes that work well and do not fail fast. It is unrealistic to expect the output power from an MFC to equate to the output power from a chemical fuel cell like a hydrogen fuel cell. The fuel used in an MFC is usually a relatively “dilute” biological mass (such as sewage) in the anode chamber that contains limited energy (indicated by BOD). Another restriction is the slow catalytic speed inherent in microbes. Even though in some cases, CE of more than 90% is attained, it has little effect on the basic problem of slow reaction intensity of microbes. Although little information is gained in MFC studies, there are still many points to be examined on MFCs scale-up for large-scale applications that require examination.

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Conflict of interest

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Ethics statement

None.

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