Microbial Fuel Cells: Types and Applications

Ravinder Kumar, Lakhveer Singh, and A.W. Zularisam

Abstract Microbial fuel cells (MFCs) are bioelectrochemical devices that convert the chemical energy present in organic or inorganic compounds into electric current by using microorganisms as the catalysts. MFCs are of different types; however, the basic designs used in the laboratories for its applications include double-chamber MFC, single-chamber MFC, upflow MFC and stacked MFC. Moreover, some other designs have also been used for the studies. The type of electrode materials and proton exchange membrane (PEM) used in MFCs has most significant role for its outcomes for different applications such as bioelectricity generation, wastewater treatment, bioremediation of toxic compounds, biohydrogen production and biosensors. Furthermore, MFCs are operated at the optimized parameters such as thermophilic temperatures, neutral pH, etc. to obtain more significant results for respective application. This chapter explores the various types of MFCs, the operational parameters to improve its performance and the most studied applications of the MFCs.

Keywords Microbial fuel cells • Catalysts • Wastewater treatment • Bioelectricity generation • Biosensors • Proton exchange membrane

1 Introduction

The microbial fuel cell (MFC) technology is one of the most attractive technologies at present for renewable energy production and simultaneous wastewater treatment. MFCs are the bioelectrochemical devices that utilize microorganisms as the biocatalysts to convert the chemical energy present in organic or inorganic compounds into electric current (Aelterman et al. 2006; Bermek et al. 2014; Kumar et al. 2016). A typical double-chamber MFC is made up of two chambers, i.e. the anode and the cathode. Usually a proton exchange membrane (PEM) is placed between these two chambers that allows the protons produced at the anode to pass

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through itself to the cathode. The cathode and the anode are connected by an electrical circuit (e.g. with titanium wires or copper wires) to make it a complete system. The organic substrates are oxidized by the microorganisms at the anode chamber and produce electrons, protons and carbon dioxide. The electrons generated from the microbial metabolic activity are firstly transferred to the anode surface by redox-active proteins or cytochromes and then passed to the cathode through electrical circuit (Borole et al. 2011; Kumar et al. 2015). At the cathode chamber, the reduction of electrons takes place. Generally an electron acceptor is provided at the cathode, e.g. oxygen or ferricyanide. Subsequently, electrons combine with protons and oxygen at the cathode and form water. This reaction can be further facilitated by a catalyst such as platinum. The general working process and the components of an MFC are showed in Fig. 1.

$$\begin{aligned} &\text{Anode reaction}: CH_3COO^- + 2H_2O \quad 2CO_2 + 7H^+ + 8e^- \\ &\text{Cathode reaction}: O_2 + 4e^- + 4H^+ \qquad\qquad 2H_2O \end{aligned}$$

MFC technology is an encouraging technology for electric current generation from diverse materials, such as natural organic matter and complex organic waste, and can be beneficially united with applications in wastewater treatment (Chaudhuri and Lovely 2003; Inoue et al. 2010; Jiang et al. 2014). There are some unique characteristics of MFCs that make this technology more advantageous than other technologies. (1) The MFCs provide comparatively higher conversion proficiency for chemical energy to electric current. (2) The MFCs can produce fruitful results at varying temperature conditions (from 20 to 40 °C) that makes MFC technology unique to other present bioenergy practices. (3) During operation of MFCs, they do not require an external electric for aeration to provide oxygen (as electron acceptor) as the cathode can be passively aerated. MFCs are constructed in different designs using diverse materials. These systems are usually operated at optimized conditions to extract more energy from the system, but they can be also operated at varying conditions such as at low or high temperatures; acidic or basic pH, with different electron acceptors; etc. (Amend and Shock 2001; Logan 2004; Oh et al. 2010; Patil et al. 2011; Tang et al. 2015).

2 Materials for Construction of MFC

Anode. The materials used to make it as anode need to be a conductive material. Also the material should be environment-friendly and chemically inert to the electrolyte (anolyte) in the anode chamber. The electrodes made up of carbon materials are widely used in the MFCs, for examples, graphite plates, graphite rods, graphite felt electrodes, graphite granules, carbon cloth, carbon brush and stainless steel, etc. (Logan and Regan 2006; Liu et al. 2014). Generally, the electrode materials that are cheaper and exhibit higher surface area are of great interest in MFCs (Bergel et al. 2005). The bare electrodes that have low surface area

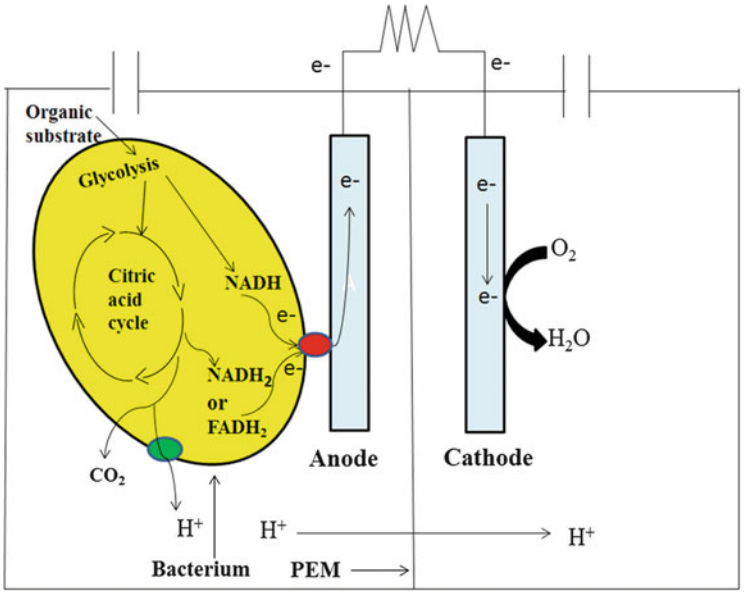

Fig. 1 General principle of a microbial fuel cell (Kumar et al. 2016)

can be easily modified with conductive nanomaterials of higher surface area (e.g. graphene) for improved MFC performance (Tang et al. 2015). There are many techniques to coat the nanomaterial on the bare electrodes. The anodic modifications with the nanoparticles have shown fruitful results so far in the MFCs. Such nanomodifications usually favour the biofilm formation on the anode, decrease the MFC start-up time, facilitate the electron transfer mechanism, also decrease the internal resistance of the system and consequently increase the overall performance of the MFC (Bergel et al. 2005; Jiang et al. 2014; Shen et al. 2014).

Cathode The cathode compartment contains the cathode material, a catalyst to increase the reduction of electrons and an electron acceptor (Wang et al. 2014; Zhang et al. 2012). The electrode materials used as the anode as mentioned above are/can be used as the cathode. Moreover, a catalyst (e.g. platinum) is employed to the cathode electrode to increase the rate of oxygen reduction when oxygen is used as the electron acceptor. Oxygen is one of the best alternatives for the electron acceptor as it is cheapest, abundantly available and has high redox potential (Bond and Lovley 2003; Rhoads et al. 2005; Huang et al. 2012). In contrast, ferricyanide (K_3 [Fe $(CN)_6$]) is a precisely common electron acceptor and has been widely used in MFCs due to its decent enactment. A catalyst is not required at the cathode when ferricyanide is used as the electron acceptor in MFCs. This is particularly because it exhibits a small overpotential with a plain carbon electrode (Huang et al. 2012). But the use of ferricyanide also has some limitations in MFCs, e.g. the inadequate reoxidation by oxygen, which needs the catholyte to be frequently changed.

Moreover, ferricyanide can also be diffused into the anode chamber through the ion exchange membrane; therefore, its use can decrease the performance of MFCs.

Membrane An ion exchange membrane is generally used in an MFC between the anode and the cathode chamber, e.g. proton exchange membrane (PEM) that allows the passage of protons or specific cations from the anode to the cathode compartment (Heilmann and Logan 2006). The best frequently used PEM is Nafion. However, in place of Nafion, Ultrex CMI-7000 is also suitable for MFC applications and is ominously more economical than Nafion. In addition, PEM may be leaky to oxygen, and the anolyte or the bacteria can diffuse to the cathode, while catholyte such as ferricyanide can also move to the anode, which can decrease the performance of an MFC effectively. But, further efficient revisions are indispensable to appraise the influence of the PEM on performance and durable permanence (Min and Logan 2004; Jafary et al. 2013).

3 Types of MFC

3.1 Double-Chamber MFC

Double-chamber MFC (see Fig. 2a) is the simplest design among all MFCs (Niessen et al. 2004; Phung et al. 2004; Kumar et al. 2016). In a typical design, one bottle (can be of different designs) is used as anode while the other one as cathode, separated by PEM. Usually in two-chamber MFC, defined medium (or substrate) in the anode and defined catholyte solution are used to generate energy. In other words, the double-chamber MFC is often operated in batch mode. The double-chamber MFC may be in the shape of bottles or cube. The choice of catholyte in the MFC can define the nomenclature of the design. For example, if the air is used in the cathode to provide the electron acceptor, i.e. oxygen, then the MFC can be called as two-chamber air-cathode MFC (Ringeisen et al. 2006; Shantaram et al. 2005). Such MFCs may prove valuable to generate electricity in remote sensing regions.

3.2 Single-Chamber MFC (SCMFC)

This type of MFC is made up of one chamber only that contains both the anode and the cathode (see Fig. 2b), which was introduced by Doo Hyun Park and J. Gregory Zeikus (2003). The anode is either positioned far or near to the cathode separated by PEM. It has been stated that by decreasing interelectrode spacing, internal ohmic resistance can also be diminished. This can be achieved by evading the use of catholyte as a result of joining two chambers and thus raises the power density. Such MFC is simple and economical and also produces much power in rival to double-chamber MFC (Chaudhuri and Lovley 2003; Ringeisen et al. 2006).

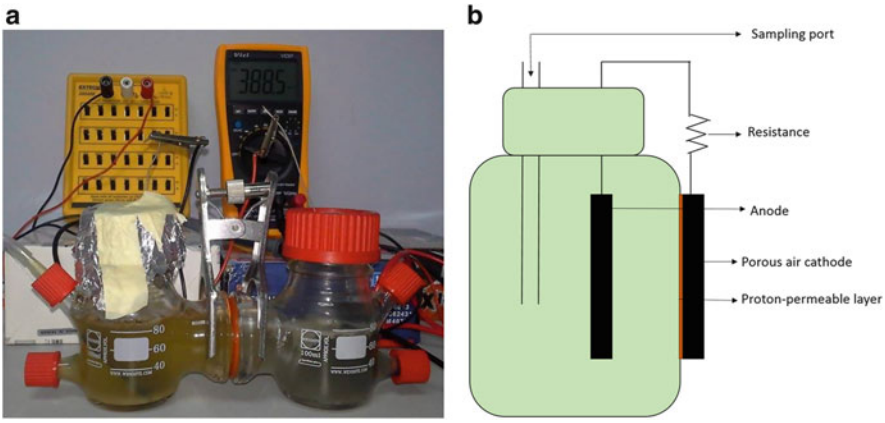

Fig. 2 (**a**) Simple design of double-chamber microbial fuel cell. (**b**) Schematic design of single-chamber microbial fuel cell. (**c**) Schematic design of upflow microbial fuel cell. (**d**) Design of stacked microbial fuel cell

However, in SCMFC the major problems such as microbial adulteration and reverse passage of oxygen from cathode to anode occur normally. SCMFCs propose simpler and economic designs. Such MFCs generally have simply an anodic chamber with no requisite of air in a cathodic chamber (Rabaey et al. 2004; Rabaey et al. 2005).

3.3 Upflow MFC

The new design came into existence with increase in the interest in MFC research. The upflow MFC is cylinder-shaped MFC (He et al. 2006). The MFC is made up of the cathode chamber at the top and the anode at the bottom. Both the chambers are apportioned by glass wool and glass bead layers. The substrate is provided from the bottom of the anode that moves upward to the cathode and leaves at the top (see Fig. 2c). A gradient is formed between the electrodes which also help in the favourable action of the fuel cell (Cheng et al. 2006a). In his design, there are no distinct anolyte and catholyte. Moreover, it does not have any physical parting. Therefore, proton transmission-related difficulties are very less (Zhou et al. 2013; Venkata Mohan et al. 2014).

Upflow mode MFCs are fascinating for wastewater treatment since they can be easily scaled up as compared to other designs of MFCs. However, the major drawback of the fuel cell is the energy costs to pump the substrate that are highly greater than their power outcome (Zhou et al. 2013). So we can conclude that the prime purpose of upflow MFC is wastewater treatment instead of power generation (Brutinel and Gralnick 2012). These kinds of MFCs are commonly employed in basic research, and the studies propose that the power densities are low due to high internal resistance, electrode-based losses and complex design.

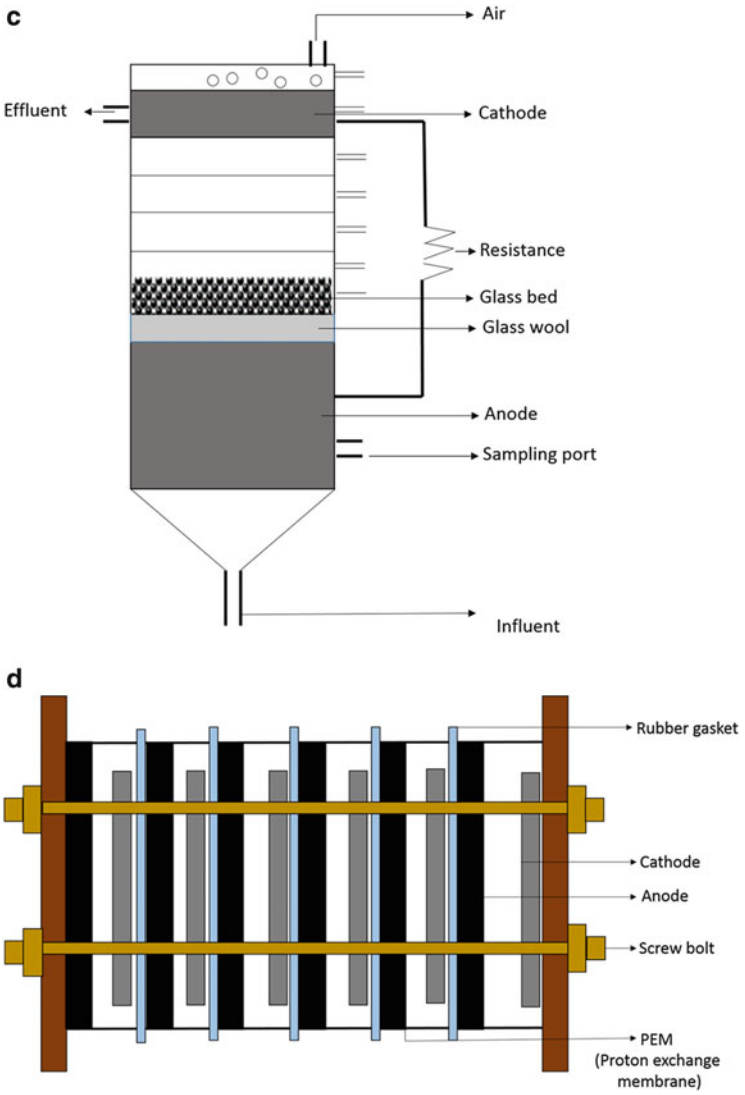

Fig. 2 (continued)

3.4 Stacked MFC

A stacked MFC is generally a combination of some MFCs that are either coupled in series or in parallel to enhance the power output (Logan and Regan 2006; Aelterman et al. 2006; Sun et al. 2012). The output of MFC is increased by connecting some MFCs by multiplying individual power output or current output. Generally a single unit of MFC (with oxygen as an electron acceptor) can generate a

maximum open-circuit voltage (OCV) of 0.8 V (Logan et al. 2005). Therefore, a number of MFC unit cells can be stacked in a series or parallel connection, and their individual power output can be multiplied to get the resultant power output. However, some other operational factors also play an important role in current generation in a stacked MFC, which can either decrease or increase the overall performance of the MFC (Zhou et al. 2013; Venkata Mohan et al. 2014). Moreover, after connecting the individual MFC in a stacked MFC, the final voltage may not be exactly the total of the individual cell voltages because there will be a loss of voltage when every cell is connected either in series or parallel. The parallel-connected stack MFCs have proven to produce more current as in rival when the MFCs are stacked in a series connection. Therefore, we can say that in parallel-connected stack MFCs, higher bioelectrochemical reaction rate is achieved than in series-connected stack MFCs. Moreover, a parallel connection is favoured to maximize chemical oxygen demand (COD) removal for enhanced wastewater treatment efficiency, if the MFC units are not autonomously functioned. In a successful study, six MFCs were connected in series or in parallel with copper wires. The MFC was fed with acetate as substrate in the anode and ferricyanide as the catholyte, and graphite rods were used as the anode and the cathode. The results of the study demonstrated that the stacked MFC in a series connection produced a volumetric power density of 59 W/m^3 and when connected in parallel generated 51 W/m^3 of power density (Aelterman et al. 2006).

The coulombic efficiency (CE) in MFCs can give the estimation of the electrons transferred (from the total electrons generated theoretically from substrate oxidation) from the anode that help to generate the current (Kumar et al. 2015). In stacked MFCs, the different rates of CE can be achieved while linking the cells in different connections. The former study exhibited that the stacked MFC achieved higher rate of CE when operated in parallel, i.e. 78 %, than in series that produced the CE of only 12 %. The major obstacle in stack MFC to achieve higher voltage outputs is the voltage reversal. The voltage reversal may be due to the depletion of the substrate in the cell, pointing to the diminished ability of the bacteria to produce higher voltage (Logan and Regan 2006; Aelterman et al. 2006).

3.5 Other Designs

The basic designs of MFCs are overwhelmingly used for the studies, and less intention is paid to develop new designs to overcome the drawbacks of the existing designs. In order to diminish one obstacle, a flat-plate MFC (FPMFC) in 2004 was designed by Min and Logan to reduce the ohmic resistance that is caused due to more interelectrode spacing (Min and Logan 2004). This kind of design is generally used in chemical fuel cells, also generating more power than the former designs. In FPMFC, the anode and the cathode were made up of flat plates (each plate with a projected surface area of 225 cm^2). A Nafion membrane was placed between the two plates. This reactor generated the power density of 56 mW/m^2 with domestic

wastewater as a substrate, and 58 % COD was achieved in the study (Min and Logan 2004). The reactor was also used to produce power with other substrates like acetate, glucose, starch, etc. but produced less power output than the other designs, i.e. cube reactor. It may be due to the too closely joined electrodes, and oxygen may pass through the membrane to the bacteria in the anode chamber, therefore affecting the growth of the microbial community (Phung et al. 2004; Patil et al. 2011).

4 Factors Affecting the Performance of MFCs

4.1 Electrode Material

In the MFCs , the anode and the cathode are made up of the electrode material that should be conductive in nature, non-corrosive, non-fouling to the bacteria (in case of anode) and cost-effective. The electrode material with high surface area also increases the performance of the MFC (Zhang et al. 2012; Alatraktchi et al. 2014). The development of the electrodes for the MFC has reached to the higher level. Moreover, many electrodes with modification of nanoparticles have produced electricity manifold than the plain electrodes. In the anode, the electrode modification with the nanomaterial or catalyst that can support the biofilm formation and increase the electron transfer rates is highly beneficial for increased power output. For example, magnetite nanoparticles increased the current production in the MFC using *G. sulfurreducens* as an inoculum (Alatraktchi et al. 2014). The study found that the nanoparticles increased the electrical conductivity of biofilm-electrode interface, thus boosted the electron transfer mechanism (Kumar et al. 2016). In the cathode, Pt or Pt-coated cathodes produced higher electric current as compared to plain cathodes containing no catalyst. Pt has been regarded the best catalyst for oxygen (when used as electron acceptor) reduction in MFCs (Bond and Lovely 2003), but its higher cost is also one of the obstacles for the technology to get launched at large-scale applications.

4.2 Proton Exchange System

The proton exchange system of an MFC consists of proton exchange membrane (PEM) between the anode chamber and the cathode chamber. The membrane contains the pores with charged side walls that help the movement of protons from anode to cathode. Hence this membrane has a pivotal function in the MFCs that can affect the power output of the MFCs (Gil et al. 2003; Cheng et al. 2006b). During the operation of the MFC, there might be a diffusion of the anolyte through the membrane to the catholyte. This can cause fouling of the membrane, subsequently can block the passage of protons to the cathode and consequently will

decrease the power output of the MFC. Alternatively, the passage of catholyte to the anode chamber will affect the performance of the bacteria. For example, if the electron acceptor is oxygen, its diffusion to the anode can affect the biofilm growth of the anaerobic bacteria, consequently affecting the whole performance of the MFC (Reguera et al. 2005; Shen et al. 2014). Moreover, the membrane increases the internal resistance of the MFC, and the diffusion of ions or the electrolytes through it causes concentration polarization loss of the system, which has a direct effect on the current generation of the fuel cell. Nafion membrane is the most commonly used PEM in the MFC technology. This is because the membrane is selectively permeable to the protons (Gil et al. 2003). Though, some other cations also transported through Nafion during the MFC operation. But, the use of membrane is highly beneficial to maintain the balance of the charge between the anolyte and the catholyte (Raghavulu et al. 2013). Moreover, it is also found that the ratio of membrane surface area to volume of MFC is vital for electrical output of the system. The results of a study suggested that MFCs with PEM of large surface area generate less internal resistance and hence the higher power output. Some studies have also shown that the MFCs without a PEM produce more power output up to a specific period than membrane-less MFC (Gil et al. 2003). The higher cost of the PEM is also one of its disadvantages. Therefore, we can imagine membrane-less MFCs in the future at large-scale applications.

4.3 Operational Condition

This section includes only the basic parameters for the MFC operation, such as pH, temperature, organic loading, feed rate and shear stress. It is found that performances of MFCs at the small scale such as in the laboratory are still very low than the ideal performances. Therefore, it is highly beneficial to optimize the operating conditions to improve the overall performance of the MFCs.

4.3.1 Effect of pH

In the anodic chamber of the MFCs, the microorganisms oxidize the substrates and produce protons that move to the cathode through the PEM where they combine with electrons and an electron acceptor (if oxygen) to form water. After a long period of the MFC operation, the concentration of protons increases in the anolyte due to the slow or restricted flow of the protons via the PEM. This accumulation of the protons makes the anode chamber more acidic and much unfavourable for the bacterial growth though bacteria are more active at nearly neutral pH (Venkata Mohan et al. 2014). On the second hand, the cathode chamber becomes more alkaline due to the deficiency of replacement of protons from the oxidation reaction and constant diminution of protons by the reduction reaction (He et al. 2006). This

pH concentration gradient across the two chambers leads to an electrochemical/thermodynamic drawback on MFC performance.

The high pH in the cathode chamber can substantially reduce the current generation. The potential of the oxygen reduction increases with a decrease in pH value (according to the Nernst equation). Therefore, the low operational pH is advantageous for the oxygen reduction and subsequently to achieve higher electric current from MFCs (Niessen et al. 2004; Phung et al. 2004; Kumar et al. 2016). Usually, bacteria need a neutral pH for their optimum growth, and bacteria counter to the variations in internal and external pH by regulating their activities. The bacterial growth requirements can change the pH in the anode chamber which can further cause some variations in primary physiological parameters, such as membrane potential, concentration of ions, biofilm formation and proton-motive force (Kumar et al. 2016).

The pH maintenance in the anodic compartment is one of the significant factors, which affects microbial metabolic activity and subsequently disturbs the electron and proton generation mechanism (Kumar et al. 2015). The lower pH in the anolyte decreases the bacterial activity and therefore affects the biofilm formation and current output of the MFC. A study revealed that MFCs worked at low anodic pH exhibited higher proton transfer rates; therefore, higher amount of protons accumulated at the cathode side that further diminished the current density (Bermek et al. 2014). However, an alternative study validated that the pH ranging from 6 to 9 is appropriate for microbial growth and achieving comparatively higher power outputs.

It is more convenient to sustain two different pH conditions in a dual-chamber MFC to optimize the anodic and cathodic reactions as compared to a single-chamber MFC (Huang et al. 2012). On the other hand, it is more difficult to maintain the pH in air-cathode MFC, because of the presence of one electrolyte only that is present in the anode chamber, referred to as anolyte. The electrolyte present in the cathode is referred to as catholyte (in two-chamber MFC). The air-cathode MFCs (the cathode electrode is exposed to the air) exhibit simpler configuration and have proven to generate more power outputs than the conventional MFCs (Bermek et al. 2014). A study demonstrated that the air-cathode MFC can be operated with an anolyte of pH range between 8 and 10. The results exhibited that the anodic bacterial activity was optimum at a neutral pH, while the oxygen reduction reaction was amended at a higher pH.

4.3.2 Effect of Temperature

In MFCs, the temperature is one of the most important factors that affect the kinetics of the whole system (Amend and Shock 2001). Any large deviation in the temperature during the operation of MFC may affect its performance to a great extent. It mainly affects the microbial metabolism, mass transfer and thermodynamics (electrode potentials and Gibbs free energy). The temperature has been included a vital parameter for the MFC's performance toward electricity generation

and wastewater treatment efficiency (Amend and Shock 2001; Logan 2004; Oh et al. 2010; Patil et al. 2011; Tang et al. 2015). Usually, the MFCs are operated at the room temperature nearly in the range between 25 and 30 °C. However, MFCs have shown good results (with respect to both, i.e. power density and COD removal) at higher temperatures as well (Jafary et al. 2013). The increase in power density may be due to the augmentation of the bacterial metabolism and membrane permeability. Moreover, the high temperature can increase the conductivity of the anolyte as well as the catholyte thus decreasing the ohmic resistance of the MFC and hence rising the power density (Phung et al. 2004). It has been observed that the slight increase in the temperature does not the membrane permeability. The studies have shown that the effect of temperature on bacterial activity follows an exponential trend. Therefore, the enhanced power output due to increase in temperature can be directly attributed to the increased bacterial activity. The bacterial activity can be determined in terms of biofilm growth at the anode which has an impact on the current production (Wang et al. 2014; Yang et al. 2015). The studies have shown that the temperature plays a vital role in the start-up of the MFC and hence in the initial biofilm formation. It has been observed that the higher temperatures decrease the start-up time of the MFC operation and lead to the stable biofilm formation (Phung et al. 2004).

A study found that the temperature ranges between 30 and 45 °C are more beneficial for the operation of MFCs to obtain higher power outputs because the bacterial biofilms showed maximum catalytic activity between the mentioned temperature ranges (Yong et al. 2014). However, some particular bacterial species can work effectively in a particular temperature range; it is useful to adjust the temperature range during the MFC operation to achieve the maximum outputs from the system (Kumar et al. 2015). Moreover, the variation in the temperature can result in the different microbial communities in the anodic chamber of the MFC (Phung et al. 2004). After the establishment of a stable biofilm, the bacteria can adjust their metabolism according to the small variations in the temperature.

4.3.3 Feed Rate and Shear Stress

The MFCs can be operated in two modes, the first is batch mode and the second is continuous mode. In the batch mode, the substrate is provided in the initiation of the cycle; on the other hand, in the continuous mode, the substrate is provided after short intervals in the cycle. The operation of MFCs in the continuous mode exhibits hydrodynamic problems that further affect the whole performance of the system. Therefore, the flow rate and the subsequent hydraulic retention time (HRT) and the shear stress are important parameters that should be optimized for MFC operation to obtain the maximum output from the fuel cell (Zhou et al. 2013; Venkata Mohan et al. 2014). It has been found that flow rate affects the performance of MFCs for both power density and COD removal. The studies suggest that higher flow rates decrease the power output as well as COD removal efficiency and coulombic efficiency (Logan et al. 2005; Sun et al. 2012). In practice, the higher flow rates

decrease the HRT. It means the bacteria get less time to oxidize the substrate, therefore waning the COD removal efficiency of the MFC. Moreover, another vital parameter in MFCs is the hydrodynamic strength. It affects the bacterial adhesion and biofilm formation on the anode. The studies have demonstrated that low shear rates lead the formation of thicker biofilms (Logan et al. 2005). The formation of denser biofilms may be attributed to stable bacterial attachment on the electrode (anode). The operation of MFC at different shear rates can also result in different bacterial communities at the anode. It has been seen that higher shear rates in the MFCs decline the microbial diversity, resulting mostly in the homogeneous biofilm formation (Ringeisen et al. 2006; Raghavulu et al. 2013).

5 Applications

In laboratory MFCs have been already experimented for many applications such as electricity generation, wastewater treatment, biosensing and hydrogen production. Each application is discussed in detail further in the chapter.

5.1 Electricity Generation

It is quite evident that most of the studies of MFCs are performed for the electricity generation, and it is the prime application of the technology (Orellana et al. 2013). Some examples of MFC performance for electricity generation are given in Table 1. In the anode chamber of the MFC, the microorganisms oxidize the substrate into protons and electrons that are passed through PEM and electrical connection, respectively, to the cathode (Aelterman et al. 2006; Bermek et al. 2014; Kumar et al. 2015). The two chambers of the MFC can be electrically connected to a multimeter and with an external resistor box, to measure the voltage, and

Table 1 Performance of MFCs for bioelectricity generation

Type of MFC	Substrate	Power density	References
Single-chamber MFC	Glucose	68 mW/m^2	Logan (2004)
	Acetic acid	835 mW/m^2	Oh et al. (2010)
	Ethanol	820 mW/m^2	Logan and Regan (2006)
	Domestic wastewater	114 mW/m^2	Jiang et al. (2014)
Double-chamber MFC	Glucose	855 mW/m^2	Chaudhuri and Lovely (2003)
	Acetate	1926 mW/m^2	Inoue et al. (2010)
	Acetate	1.9 mW/m^2	Tang et al. (2015)
	Acetate	1200 mW/m^2	Patil et al. (2011)
	Cellulose	188 mW/m^2	Liu et al. (2014)
	Wastewater	2485 mW/m^2	Amend and Shock (2001)

subsequently the power can be calculated using Ohm's law. The substrates that can be completely oxidized into electrons are of great importance in MFCs to achieve higher coulombic efficiency and subsequently the power output of the MFCs. A study has shown that *Geobacter sulfurreducens* can reduce the acetate completely into electrons and protons (Reguera et al. 2005). The electrical output of the MFC depends on many factors mainly including the design of MFC, electrode materials, inoculum (pure culture or mixed culture), proton exchange membrane and the operational conditions (Sun et al. 2012). Many approaches are already employed to increase the electrical output in the MFCs. The amendments in MFCs are basically focused on new MFC designs to reduce the internal resistance of the system, cost-effective electrode materials with high surface area, cheaper cation exchange membranes, modifications of the electrode material with nanomaterials (e.g. gold nanoparticles, nickel nanoparticles) and other physical (e.g. heat treatment of stainless steel electrode) or chemical (nitrogen-doped electrodes) treatment methods (Zhou et al. 2013; Venkata Mohan et al. 2014; Kumar et al. 2016).

5.2 Wastewater Treatment

The MFCs have shown the potential to treat different industrial, urban or domestic wastewaters (Rhoads et al. 2005; Oh et al. 2010; Zhou et al. 2013). Some examples of MFC performance for wastewater treatment are given in Table 2. Though, the highly toxic wastewaters cannot be completely treated in MFCs, however MFCs are able to reduce the COD of wastewaters much enough to meet discharge regulations before it is released into the environment. The MFCs have proved up to 98 % COD removal from the wastewater (Oh et al. 2010). Alternatively, the wastewaters rich in organic materials (carbohydrates, proteins, lipids, minerals, fatty acids, etc.)

Table 2 Performance of MFCs for wastewater treatment/bioremediation

Type of MFC	Wastewater/heavy metals	% COD removal	References
Single-chamber MFC	Olive mill wastewaters	65	He et al. (2006)
	Biodiesel wastes	90	Brutinel and Gralnick (2012)
	Brewery wastewater	98	
	Azo dye Congo red	98	Rhoads et al. (2005)
	Cadmium	90	Orellana et al. (2013)
	Chromium (VI)	99	Yong et al. (2014)
Double-chamber MFC	Domestic wastewater	88	Cheng et al. (2006a)
	Chemical wastewater	63	Zhou et al. 2013
	Real urban wastewater	70	Logan et al. (2005)
	Food waste leachate	85	Liu et al. (2004)
	Cyanide	88	Min and Logan (2004)

provide the substrate for microbial metabolism to produce electrons and protons. Moreover, wastewaters are also the source of inoculum. The basic wastewater treatment assays (COD, BOD, total solids, nitrogen removal) can be employed to measure the treatment efficiency of the MFCs before and after the MFC operation (Zhou et al. 2013). The COD removal in MFCs can be further improved by operating the MFCs at optimized conditions such as mesophilic temperatures which have shown to increase the COD removal. Moreover, the MFC operation in fed-batch mode is advantageous to obtain high COD removal rate. Usually, the MFC studies operated for wastewater treatment are coupled with power generation; however the coulombic efficiency obtained in such cases is quite low varying from 10 % to 30 % only (Liu et al. 2004).

5.3 Biosensor

The application of MFC technology besides electricity generation and wastewater treatment is its use as a biosensor for pollutant detection in water (Shantaram et al. 2005; Zhou et al. 2013). The linear relationship between the coulombic yield of MFC and wastewater strength appoints MFC as a BOD sensor. MFC-based biosensor has advantages over conventional biosensors. Such biosensors are comparatively cheaper because they don't need transducer which is generally used in conventional biosensors. Moreover, they can be operated for very long period such as 5 years without any maintenance. Therefore, MFC-based biosensors have more stability and reliability. Several studies have shown that on the basis of linear correlation, wide BOD ranges (low/high) can be measured in the MFC-based biosensors.

5.4 Biohydrogen

The typical double-chamber MFC can be amended to microbial electrolysis cell (MEC) for hydrogen production (Rhoads et al. 2005; Zhou et al. 2013; Kumar et al. 2015). The basic principle of an MEC remains quietly similar; instead electric current is provided at the cathodic chamber. An MEC is also made up of two chambers, i.e. the anode and the cathode. Like MFC, an ion exchange membrane separates both chambers of MEC (Zhou et al. 2013). In the anode chamber, the exoelectrogens metabolize the substrate and produce electrons and protons. The protons are moved to the cathode similarly in MFCs. However, the reaction between protons and electrons to produce hydrogen at the cathode is thermodynamically not possible. To accomplish this reaction, electric current is provided at the cathode. Usually, >0.3 V is enough to fulfil the electrical requirement. Such low voltages can be easily obtained in the MFCs. Therefore, the MFCs employed to generate electricity can be coupled with MEC to fulfil the electrical requirement.

The hydrogen produced from the MEC can be easily stored and subsequently can be used to produce electricity.

6 Future Directions

The MFC technology is still not commercialized despite of 10 years of intensive research on the MFC studies. There is yet to solve many problems in the technology to launch the MFCs in the real-world applications. The main drawback of the MFCs is the insufficient power output. The other limitations are related to the high cost of the electrode materials, membranes and the cathode catalyst. The power output in MFCs can be improved in the future by providing electrode materials of high surface area, while the absence of PEM in futuristic MFC (at large scale) can make the MFC more economical. The MFCs used for wastewater treatment still need effective amendment to completely purify the water. A less work has been done for biosensor application. Because the MFCs are biofilm-based biosensors, the response time is longer in MFC-based biosensor.

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References

Aelterman P, Rabaey K, Pham TH, Boon N, Verstraete W (2006) Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. Environ Sci Technol 40:3388–3394. doi:10.1021/es0525511

Alatraktchi FA, Zhang Y, Angelidaki I (2014) Nanomodification of the electrodes in microbial fuel cell: Impact of nanoparticle density on electricity production and microbial community. Appl Energy 116:216–222. doi:10.1016/j.apenergy.2013.11.058

Amend JP, Shock EL (2001) Energetics of overall metabolic reactions of thermophilic and hyperthermophilic Archaea and Bacteria. FEMS Microbiol Rev 25:175–243. doi:10.1111/j.1574-6976.2001.tb00576.x

Bergel A, Feron D, Mollica A (2005) Catalysis of oxygen reduction in PEM fuel cell by seawater biofilm. Electrochem Commun 7:900–904. doi:10.1016/j.elecom.2005.06.006

Bermek H, Catal T, Akan SS, Ulutas MS, Kumru M, Ozguven M, Liu H, Ozcelik H, Akarsubasi AT (2014) Olive mill wastewater treatment in single-chamber air-cathode microbial fuel cells. World J Microbiol Biotechnol 30:1177–1185. doi:10.1007/s11274-013-1541-8

Bond DR, Lovley DR (2003) Electricity production by *Geobacter sulfurreducens* attached to electrodes. Appl Environ Microbiol 69:1548–1555. doi:10.1128/AEM.69.3.1548-1555.2003

Borole AP, Reguera G, Ringeisen B, Wang ZW, Feng Y, Kim BH (2011) Electroactive biofilms: current status and future research needs. Energy Environ Sci 4:4813–4834. doi:10.1039/C1EE02511B

Brutinel E, Gralnick J (2012) Shuttling happens: soluble flavin mediators of extracellular electron transfer in *Shewanella*. Appl Microbiol Biotechnol 93:41–48. doi:10.1007/s00253-011-3653-0

Chaudhuri SK, Lovley DR (2003) Electricity generation by direct oxidation of glucose in mediator less microbial fuel cells. Nat Biotechnol 21:1229–1232. doi:10.1038/nbt867

Cheng S, Liu H, Logan BE (2006a) Increased performance of single chamber microbial fuel cells using an improved cathode structure. Electrochem Commun 8:489–494. doi:10.1016/j.elecom.2006.01.010

Cheng S, Liu H, Logan BE (2006b) Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing. Environ Sci Technol 40:2426–2432. doi:10.1021/es051652w

Gil GC, Chang IS, Kim BH, Kim M, Jang JK, Park HS, Kim HJ (2003) Operational parameters affecting the performance of a mediator-less microbial fuel cell. Biosen Bioelect 18:327–334. doi:10.1016/S0956-5663(02)00110-0

He Z, Wagner N, Minteer SD, Angenent LT (2006) The upflow microbial fuel cell with an interior cathode: assessment of the internal resistance by impedance spectroscopy. Environ Sci Technol 40:5212–5217. doi:10.1021/es060394f

Heilmann J, Logan BE (2006) Production of electricity from proteins using a single chamber microbial fuel cell. Water Environ Res 78:531–537. doi:10.2175/106143005X73046

Huang L, Chai X, Quan X, Logan BE, Chen G (2012) Reductive dechlorination and mineralization of pentachlorophenol in biocathode microbial fuel cells. Bioresour Technol 111:167–174. doi:10.1016/j.biortech.2012.01.171

Inoue K, Leang C, Franks AE, Woodard TL, Nevin KP, Lovley DR (2010) Specific localization of the c-type cytochrome OmcZ at the anode surface in current-producing biofilms of *Geobacter sulfurreducens*. Environ Microbiol Rep 3:211–217. doi:10.1111/j.1758-2229.2010.00210.x

Jafary T, Ghoreyshi AA, Najafpour G, Fatemi S, Rahimnejad M (2013) Investigation on performance of microbial fuel cells based on carbon sources and kinetic models. Int J Energy Res 37:1539–1549. doi:10.1002/er.2994

Jiang X, Hu J, Lieber AM, Jackan CS, Biffinger JC, Fitzgerald LA, Ringeisen BR, Lieber CM (2014) Nanoparticle facilitated extracellular electron transfer in microbial fuel cells. Nano Lett 14:6737–6742. doi:10.1021/nl503668q

Kumar R, Singh L, Wahid ZA (2016) Exoelectrogens: recent advances in molecular drivers involved in extracellular electron transfer and strategies used to improve it for microbial fuel cell applications. Renew Sustain Energy Rev 56:1322–1336. doi:10.1016/j.rser.2015.12.029

Kumar R, Singh L, Wahid ZA, Fadhil M (2015) Exoelectrogens in microbial fuel cells towards bioelectricity generation: a review. Int Journal Energy Res 39:1048–1067. doi:10.1002/er.3305

Liu H, Ramnarayanan R, Logan BE (2004) Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environ Sci Technol 38:2281–2285. doi:10.1021/es034923g

Liu X, Huang Y, Sun X, Sheng G, Zhao F, Wang S, Yu H (2014) Conductive carbon nanotube hydrogel as a bioanode for enhanced microbial electrocatalysis. Appl Mater Interf 6:8158–8164. doi:10.1021/am500624k

Logan BE (2004) Extracting hydrogen and electricity from renewable resources. Environ Sci Technol 38:160–167. doi:10.1021/es040468s

Logan BE, Murano C, Scott K, Gray ND, Head IM (2005) Electricity generation from cysteine in a microbial fuel cell. Water Res 39:942–952. doi:10.1016/j.watres.2004.11.019

Logan BE, Regan JM (2006) Microbial fuel cells—challenges and applications. Environ Sci Technol 40:5172–5180. doi:10.1021/es0627592

Min B, Logan BE (2004) Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell. Environ Sci Technol 38:5809–5814. doi:10.1021/es0491026

Niessen J, SchroÈder U, Scholz F (2004) Exploiting complex carbohydrates for microbial electricity generation-a bacterial fuel cell operating on starch. Electrochem Commun 6:955–958. doi:10.1016/j.elecom.2004.07.010

Oh S, Kim J, Premier G, Lee T, Changwon K, Sloan W (2010) Sustainable wastewater treatment: how might microbial fuel cells contribute. Biotechnol Adv 28:871–881. doi:10.1016/j.biotechadv.2010.07.008

Orellana R, Leavitt JJ, Comolli LR, Csencsits R, Janot N, Flanagan KA, Gray AS, Leang C, Izallalen M, Mester T (2013) U (VI) reduction by a diversity of outer surface c-type cytochromes of *Geobacter sulfurreducens*. Appl Environ Microbiol 79:6369–6374. doi:10.1128/AEM.02551-13

Park DH, Zeikus JG (2003) Improved fuel cell and electrode designs for producing electricity from microbial degradation. Biotechnol Bioeng 81:348–355. doi:10.1002/bit.10501

Patil SA, Harnisch F, Koch C, Hubschmann T, Fetzer I, Carmona-Martinez AA, Muller S, Schroder U (2011) Electroactive mixed culture derived biofilms in microbial bioelectrochemical systems: the role of pH on biofilm formation, performance and composition. Bioresour Technol 102:9683–9690. doi:10.1016/j.biortech.2011.07.087

Phung NT, Lee J, Kang KH, Chang IS, Gadd GM, Kim BH (2004) Analysis of microbial diversity in oligotrophic microbial fuel cells using 16S rDNA sequences. FEMS Microbiol Lett 233:77–82. doi:10.1016/j.femsle.2004.01.041

Rabaey K, Boon N, Hofte M, Verstraete W (2005) Microbial phenazine production enhances electron transfer in biofuel cells. Environ Sci Technol 39:3401–3408. doi:10.1021/es048563o

Rabaey K, Boon N, Siciliano SD, Verhaege M, Verstraete W (2004) Biofuel cells select for microbial consortia that self-mediate electron transfer. Appl Environ Microbiol 70:5373–5382. doi:10.1128/AEM.70.9.5373-5382.2004

Raghavulu SV, Annie Modestra J, Amulya K, Reddy CN, Venkata Mohan S (2013) Relative effect of bioaugmentation with electrochemically active and nonactive bacteria on bioelectrogenesis in microbial fuel cell. Bioresour Technol 146:696–703. doi:10.1016/j.biortech.2013.07.097

Reguera G, McCarthy KD, Mehta T, Nicoll JS, Tuominen MT, Lovley DR (2005) Extracellular electron transfer via microbial nanowires. Nature 435:1098–1101. doi:10.1038/nature03661

Rhoads A, Beyenal H, Lewandowski Z (2005) Microbial fuel cell using anaerobic respiration as an anodic reaction and biomineralized manganese as a cathodic reactant. Environ Sci Technol 39:4666–4671. doi:10.1021/es048386r

Ringeisen BR, Henderson E, Wu PK, Pietron J, Ray R, Little B, Biffinger JC, Jones-Meehan JM (2006) High power density from a miniature microbial fuel cell using *Shewanella oneidensis* DSP10. Environ Sci Technol 40:2629–2634. doi:10.1021/es052254w

Shantaram A, Beyenal H, Raajan R, Veluchamy A, Lewandowski Z (2005) Wireless sensors powered by microbial fuel cells. Environ Sci Technol 39:5037–5042. doi:10.1021/es0480668

Shen HB, Yong XY, Chen YL, Liao ZH, Si RW, Zhou J, Zheng T (2014) Enhanced bioelectricity generation by improving pyocyanin production and membrane permeability through sophorolipid addition in *Pseudomonas aeruginosa*-inoculated microbial fuel cells. Bioresour Technol 167:490–494. doi:10.1016/j.biortech.2014.05.093

Sun M, Reible DD, Lowry GV, Gregory KB (2012) Effect of applied voltage, initial concentration, and natural organic matter on sequential reduction/oxidation of nitrobenzene by graphite electrodes. Environ Sci Technol 46:6174–6181. doi:10.1021/es300048y

Tang J, Chen S, Yuan Y, Cai X, Zhou S (2015) In situ formation of graphene layers on graphite surfaces for efficient anodes of microbial fuel cells. Biosens Bioelectron 71:387–395. doi:10.1016/j.bios.2015.04.074

Venkata Mohan S, Velvizhi G, Modestra JA, Srikanth S (2014) Microbial fuel cell: critical factors regulating bio-catalyzed electrochemical process and recent advancements. Renew Sustain Energy Rev 40:779–797. doi:10.1016/j.rser.2014.07.109

Wang Y, Wang A, Zhou A, Liu W, Huang L, Xu M, Tao H (2014) Electrode as sole electrons donor for enhancing decolorization of azo dye by an isolated WYZ-2. Bioresour Technol 152:530–533. doi:10.1016/j.biortech.2013.11.001

Yang Y, Ding Y, Hu Y, Cao B, Rice SA, Kjelleberg S, Song H (2015) Enhancing bidirectional electron transfer of *Shewanella oneidensis* by a synthetic flavin pathway. ACS Synth Biol 7:815–823. doi:10.1021/sb500331x

Yong XY, Feng J, Chen YL, Shi DY, Xu XY, Zhou J, Wang SY, Xu S, Yong YC, Sun YM, Shi CL, OuYang PK, Zheng T (2014) Enhancement of bioelectricity generation by cofactor

manipulation in microbial fuel cell. Biosens Bioelect 56:19–25. doi:10.1016/j.bios.2013.12.058

Zhang Y, Sun J, Hu Y, Li S, Xu Q (2012) Bio-cathode materials evaluation in microbial fuel cells: a comparison of graphite felt, carbon paper and stainless steel mesh materials. Int J Hydrogen Energy 37:16935–16942. doi:10.1016/j.ijhydene.2012.08.064

Zhou M, Wang H, Hassett JD, Gu T (2013) Recent advances in microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) for wastewater treatment, bioenergy and bioproducts. J ChemTechnol Biotechnol 88:508–518. doi:10.1002/jctb.4004