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REVIEW

Microbial fuel cell as new technology for bioelectricity generation: A review



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Abstract Recently, great attentions have been paid to microbial fuel cells (MFCs) due to their mild operating conditions and using variety of biodegradable substrates as fuel. The traditional MFC consisted of anode and cathode compartments but there are single chamber MFCs. Microorganisms actively catabolize substrate, and bioelectricities are generated. MFCs could be utilized as power generator in small devices such as biosensor. Besides the advantages of this technology, it still faces practical barriers such as low power and current density. In the present article different parts of MFC such as anode, cathode and membrane have been reviewed and to overcome the practical challenges in this field some practical options have been suggested. Also, this research review demonstrates the improvement of MFCs with summarization of their advantageous and possible applications in future application. Also, Different key factors affecting bioelectricity generation on MFCs were investigated and these key parameters are fully discussed.

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1. Introduction

In the recent decades, consumption of energy within the world has had a prosperous trend [1]. Energy sources are classified into three batches: fossil fuels, renewable sources and nuclear sources [2], in which non-renewable sources of energy, which include an enormous portion of energy consumption, could be categorized into two major classifications: nuclear and fossil energy [3]. Fossil fuels negatively influence the nature owing to the emission of carbon dioxide. It follows logically from what has been said that the consumption of fossil fuels has severely imperiled human life through its drastic aftermaths, such as global warming and atmospheric pollution [4].

However, miscellaneous countries around the world have made remarkable efforts to find a piece of cogent solution for energy crisis by turning the eyes into renewable energy sources such as solar energy, energy produced from wind and water. As an upshot of these efforts, one of the latterly proposed alternative energy sources is fuel cell (FC) which generates energy using high value metal catalysts (in the traditional version). In actual fact, FC is of plethora advantages over other kinds of energy generators, e.g. no emissions of environmental polluting gases (such as SO_x, NO_x, CO₂ and CO), higher efficiency, no existence of mobile parts, as a result, lack of sonic pollution, and so forth [5]. In contrast, high cost and high mass generation are the only disadvantages of these new energy sources [5,4].

One type of FCs is microbial fuel cell (MFC) that uses an active microorganism as a biocatalyst in an anaerobic anode compartment for production of bioelectricity [6,7]. Although electrical current produced by bacteria was observed by Potter in 1911 [8], limited feasible results were acquired in this area by the next 50 years [9]. However, in the early 1990s, FCs became far more appealing devices; consequently, MFCs were considered as promising technology [10]. Furthermore, research domain of MFCs turned much vaster in 1999 once it was discovered that mediator was not a compulsory component within MFCs [11–13].

Approximately all MFCs, as it is shown in Fig. 1, consist of anode and cathode chambers, physically separated by a proton exchange membrane (PEM) [14]. Active biocatalyst in the anode oxidizes the organic substrates and produces electrons and protons [15]. The protons are conducted to the cathode chamber through the PEM, and the electrons are conveyed through the external circuit [16]. Protons and electrons are

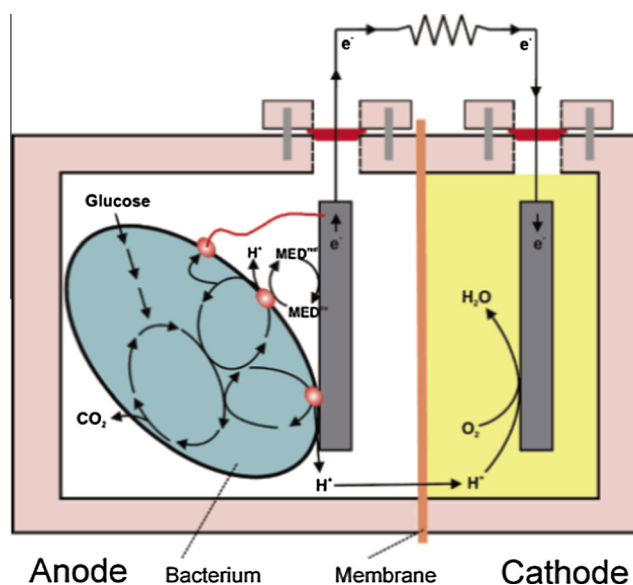
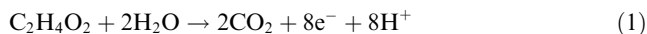


Figure 1 The MFC system is consisted of anode and cathode compartments [22].

reacted in the cathode chamber along with parallel reduction of oxygen to water [17]. It is worth mentioning that active biocatalyst in the anode compartment oxidizes the carbon sources or substrates, and generates electrons and protons. As a further illuminating illustration, anodic reaction of acetic acid is presented in Eq. (1). Oxygen in the anode chamber will inhibit the production of electricity; thus, a pragmatic system must be designed to keep the bacteria separated from oxygen (anaerobic chamber for anodic reaction) [18].

Biocatalyst is able to be divided from oxygen by posing a membrane between two separate chambers that allow charge to be transferred between the electrodes, the anode chamber, where the bacteria grow, and the cathode chamber, where the electrons react the oxygen [19].



Based on transfer of produced electron by active microorganisms from media to anode electrode, MFCs could be of two different categories: MFCs with mediator and mediator-less MFCs [20].

Despite the fact that diverse electrochemical parameters such as power density, cell voltage, and biological parameters, for instance substrate loading rate in continuous systems, are able to describe MFCs [6], performance of MFCs is mainly influenced by several factors such as ensuing: (1) supply and consumption of oxygen in cathode chamber, (2) oxidation of substrates in anode chamber, (3) electron shuttle from anode compartment to anode surface, and (4) permeability of proton exchange membrane [17].

MFC technology has been improved significantly in the recent decades. However, it has encountered several challenges in scale-up and practical application, such as turbulence in each compartment, membrane resistance in the proton transportation process. [21]. Coupled with those, MFCs have confronted two bottleneck problems in power generation. (1) The power production in MFCs and substrate concentrations has direct relationships, although in a significant scope in each system. More than a specific value of substrate concentration, the power generation, will be prevented [17] (2). MFCs output is restricted while high internal resistance utilizes considerable amount of power production in MFCs [17]. It should be added here that the proton exchange membrane (PEM), which separates anode and cathode chambers, has been found the main source of high internal resistance (R_{in}) in two chambers of MFCs. To overcome the requirement for catalysis by oxygen oxidation on the cathode, biocathodes have been explored" by "Biocathode can improve oxygen oxidation in MFCs [21]. Likewise, novel designs of MFCs have been proposed to amplify the power generation, by reducing internal resistance by removing PEM, as follows: single-chamber MFC (SCMFC), stacked MFC and up flow MFC [17].

Soil and sediments are derived from plant and animal detritus, settlement of dead bacteria and plankton, fecal matter and anthropogenic organic materials [10]. Sediments organic carbon content is generally from 0.4% to 2.2% by weight [11]. Thus, sediments organic carbon content is a sufficient power generation source in some locations. These materials can be consumed by exoelectrogens and directly transport electrons outside of the cell. So, Sediment-type microbial fuel cell (SMFC) consists of an anode electrode embedded in the anaerobic sediment and connected through an electrical circuit and a cathode electrode suspended in overlying water [12,13]

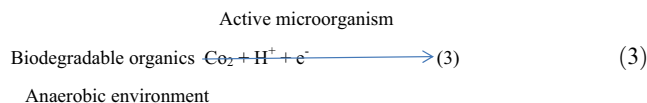
In the current article several portions of an MFC including anode, cathode and separator, which play important roles in MFC design, are investigated.

2. Effect of anode in MFCs

Microorganisms play important roles in anode chamber and generated electrons. These generated electrons are utilized to reduce electron acceptors in cathode once they passed through external circuit. Likewise, so as to complete the circuit produced protons must bore into proton exchange membrane (PEM) from anode to the cathode. It follows logically from what has been mentioned that this process leads to electrical power and organic waste removal contemporarily [23].

As mentioned above Anaerobic anode compartment is one of the main parts of MFCs. All the essential conditions to degrade the biomass are provided in the anode chamber. This compartment is filled with substrate, mediator (it is optional), microorganism and the anode electrode as electron

acceptor. General reaction in the anode chamber is summarized in Eq. (3).



It is necessary to point out that activation energy required for anodic reactions must be lowered by means of commensurate catalysts. Available bacteria in the anode chamber usually function as catalysts [24–27].

As it is a generally acknowledged fact, there are various agents affecting the performance of MFCs for instance, electrode material, equipment configuration and so forth [22,28]. In this regard, for enhancing the performance of an MFC, optimizing these agents would be so effective [29]. One of the most effective factors which influences the performance of an MFC is anodic microbial electron transfer, thus thereby amplifying microbial electron transfer rate, through miscellaneous applied manners such as adding electron mediators, and optimizing cell design and electrode [30–32]. In this connection it should be added here that electrodes are critical parts of an MFC which are essential in enhancing the MFC efficacy [33]. Hence, various materials have been studied at different studies. Furthermore, ideal electrode materials should be of ensuing features: (i) good electrical conductivity and low resistance; (ii) strong biocompatibility; (iii) chemical stability and anti-corrosion; (iv) large surface area; and (v) appropriate mechanical strength and toughness [22].

The most frequently used materials in anode are made of carbon materials containing: graphite fiber brush, carbon cloth, graphite rod, carbon paper, reticulated vitreous carbon (RVC) and carbon felt, for their stability in microbial cultures, high electric conductivity and vast surface area [22]. In addition graphite granules (GGs) or granular activated carbon (GAC) have a high degree of micro-porosity and catalytic activities. Also GGs are less expensive with higher conductivity [34].

Modification of anode electrode could be useful in promoting the performance of MFCs. In this regard, recently, several researchers have started to modify anode using different nano-engineering techniques that are able to make easier the electron transfer [35]. Moreover, for enhancing the power density and enlarging the capability of electron accepting heterogeneous fabrication methods and modification manners involving nanomaterials have been tried [36]. Qiao et al. illustrated that carbon nanotubes (CNTs) could amplify the electron transfer feasibility and electrode surface area with utilizing carbon nanotube/polyaniline nanostructure composite as anode materials [37].

One feasible manner to improve MFC output power is using modified carbon and metal-based anodes with conductive polymers [38]. To use such organic polymers with microorganism of substrate, attention must be paid to certify modified electrode stability. Between different types of conductive polymers, polyaniline (PANI) has been utilized mostly to modify the anode electrode [39]. It has been illustrated that utilizing the modified PANI polymers (fluorinated PANI [38], and PANI/titanium dioxide composite [37]) has generated enhanced current densities [39]. CNTs/polyaniline composite can be used in an MFC as the anode material [36]. Moreover, the composition of composite anode could enhance

Table 1 Effect of different anodes on MFC performances.

Substrate	Anode	Bacteria	System configuration	Maximum power density (mW/m ²)	Refs.
Glucose	Carbon paper	<i>GeobacterSPP</i> (Firmicutes)	Two-chamber	40.3 ± 3.9	[50,41]
Glucose	Graphite	<i>Saccharomyces cerevisiae</i>	Two-chamber	16	[19]
Acetate	Carbon paper	<i>G. sulfurreducens</i>	Two-chamber	48.4 ± 0.3	[50,41]
Lactate	Carbon paper	<i>Geobacter SPP</i>	Two-chamber	52 ± 4.7	[50,41]
Ethanol	–	<i>Betaproteo bacterium</i>	Two-chamber	40 ± 2	[36,42]
Cyctenin	Carbon paper	<i>Gammaproteo</i> and <i>shewanellaaffinis</i> (KMM3586)	Two-chamber	36	[51,43]
Marine sediment reached in acetate	Graphite	<i>Deltaproteo bacterium</i>	Two-chamber	14	[52,44]
Marine sediment	Noncorroding graphite	<i>Desulfurmonas SPP</i> and ...	Two-chamber	25.4_26.6	[53,45]
Sewage sludge	Graphite with Mn ⁴⁺	<i>Escherichia coli</i>	Single chamber	91	[54,46]
Sewage sludge	Graphite with neutral red (NR)	<i>Escherichia coli</i>	Single chamber	152	[54,46]
Sewage sludge	Platinum and polyanilineco-modified	<i>Escherichia coli</i>	Single chamber	6000	[55,47]
Glucose	Composite electrode (graphite/PTFE)	<i>Escherichia coli</i>	Single chamber	760	[26,40]
Glucose	Teflon treated carbon fiber paper	Electrochemically active bacteria	Two chamber (H-type MFC)	15.2	[16]
Lactose	“	“	“	17.2	[15]
Cellulose	Non-wet-prof carbon paper	Cellulose derading bacteria	“	188	[56,48]
Glucose	Graphite plates	Mixed culture	2-chamber air-cathode MFC	283	[8][6]
Glucose	Carbon paper with PPY-CNTs	<i>Escherichia coli</i>	DCMFC	228	[8,49]

the MFC performance [40]. Due to chemical stability and hydrophobic nature, polytetrafluoroethylene (PTFE) was utilized in MFCs as electrode. Also, Zhang et al. reported that the graphite/PTFE composite with optimized 30%(w/w) content of PTFE could be excellent anode for bioelectricity production and the produced power density was 760 mW/m² when *Escherichia coli* was selected as active biocatalyst [40].

The performance of different systems with their individual anode was investigated in the past decades which is listed in Table 1.

3. Effect of cathode in MFCs

Protons produced in the anode chamber migrate into the cathode through the proton exchange membrane which complete the electrical circuit. The electrons (generated at the anode site pursuant to Eq. (4)) travel to cathode chamber and transmit onto oxygen. This radical oxygen and produced positive ions in the anode participate in the following reaction to form water which spreads by the way of the ion permeable membrane on the cathode along with the assistance of catalysts [50] as follows:



A steady current is generated by this process with the wire connecting the anode and cathode [50]. The concentration and species of the oxidant (electron acceptor), proton availability, catalyst performance, and electrode structure and its catalytic ability affect the reaction yield of the cathode. Catalysis is

needed in anodic and cathodic reactions. Moreover, for the fact that an appropriate catalyst can lower the activation energy and enhance the reaction rate, the presence of a commensurate catalyst is of paramount importance [51,52]. Oxygen has usually been a final electron acceptor in the cathode due to its accessibility, intense oxidation potential, and not being a chemical waste product (water is formed as the only end product) [22], being free and producing no poisonous end products [39].

Needless to say, the slow reduction kinetic on plain graphite of oxygen normally needs the usage of a commensurate catalyst, albeit resulting in high potential; therefore, it is one of the restricting agents in MFCs [53]. In this regard, to alleviate this challenge, Potassium Ferricyanide (K₃[Fe(CN)₆]) has been proposed [22,54]. In contrast, for the fact that oxygen does not adequately oxidize K₃[Fe(CN)₆], its regeneration could be a problem; thus it must be refilled periodically [55]. Likewise, anaerobic conditions of anodic chamber are affected by K₃[Fe(CN)₆], which is penetrated into anodic chamber via the PEM [56], on the other hand, so far, Ferricyanide has been advantageous for its low over potential on plain carbon electrodes.

Another frequently used abiotic catalyst is Platinum owing to the cathodic reaction. It should be added here that due to its poisoning sensitivity toward some substances in the substrate solution, platinum is not an appropriate catalyst in MFCs [46].

To amplify MFC performance, many researchers normally have added alternative oxidants, i.e. artificial electron redox mediators, into cathode compartment, such as potassium permanganate [28,57]. Najafpour and et al. showed that low concentration of potassium permanganate as the oxidizing agent

had a very good ability to increase the current, power, and voltage in MFC [18].

The cathode is subject to being dissolved in the compartment on one side and exterior air on the opposite side [50]. Although the presence of Co as a catalyst on the air-side of cathode is able to improve MFC performance (similar to Pt cathode), wet-proofing may limit proton access to the catalyst layer [58]. If oxygen diffusion of membrane to the anode could be controlled, power output of MFC would be enhanced by raising the air pressure of cathode [59].

To overcome the requirement for catalysis by oxygen oxidation on the cathode, biocathodes have been explored [52,60]. A biocathode, in which cathodic reactions are catalyzed using microorganisms [39,61], has been used to improve electricity production in a MFC, as a result, it can be adopted into MFC to enhance the cathode performance instead of artificial mediators or catalysts using nitrate, sulfate, tetrachloroethene, fumarate, perchlorate, and trichloroethene, Co_2 , H^+ , Fe(III) , Cr(VI) , U(VI) and Mn(IV) as electron acceptor and without the help of exogenous [7,18,21,60].

Biocathodes are more beneficial in contrast to abiotic cathodes, as configuration and expenses could be decreased by utilizing them; hence, expensive catalysts (e.g. pt) and mediators are not needed [39]. Another advantage of biocathodes is generating practical products or removing by-products using microbial metabolism [62]. In addition, obviating challenges such as the requirement for electron mediators in the cathodic and sulfur poisoning of Pt chamber could enhance the MFC sustainability [62].

Table 2 Several reactions and attributed E^0 at constant pH[62].

Reaction	pH	E^0 (V)
$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	7.2	0.6
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	7	0.36
$\text{CO}_2 + \text{H}_2\text{O} \xrightarrow{h\nu} (\text{CH}_2\text{O})_x + \text{O}_2$	-0.28	7
$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$	7	0.43
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	7	-0.24
$\text{Fumarate} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Succinate}$	7	0.03

Based on adopted terminal electron acceptors (e.g. nitrate and sulfate) in cathode, biocathodes can be classified into two major categories: aerobic and anaerobic. In aerobic categories oxygen could be reduced by an aerobic biocathode. Coupled with that, the oxidation of transition metal compounds is able to be catalyzed by virtue of the biofilm which is on the surface of cathode, for instance Fe(II) and Mn(II) . Beyond that, MFCs utilizing aerobic biocathodes could generate greater power density compared to MFCs using anaerobic biocathodes [63]. Likewise, an MFC composed of a biocathode is potentiated to treat surplus wastewater stream in the cathodic chamber [63]. Moreover, microbial activities within the cathode chamber could be prevented by the accumulation of microbial metabolites. Furthermore, the performance of an MFC can cast doubt upon metabolites that serve as electron donors for bacteria [64]. Besides, it was demonstrated that, in the work of Zhou et al., after subtracting miscellaneous over potentials the voltage result for the oxidation of an organic carbon and the combined redox reaction might be of minute value for MFC [65].

In addition, Experimental results show that the charge transfer (part of internal resistance) of cathode decreases using biocathode [66] (several reactions and attributed E^0 of biocathode are illustrated in Table 2).

The performance of cathode is considered the main limitation [21,67]. To make an MFC scalable, the design of cathode is the immense challenge [68]. However, the surface area of cathode has insignificant effect on power output [50] and cathode efficiency can be improved using high surface area materials or granular materials (e.g. graphite) [69]. In contrast, one of the important challenges in MFC configuration is identifying materials that maximizes power generation and columbic efficiency and simultaneously minimizes expenses. Some of used materials in cathode are: carbon paper, carbon felt, carbon brush, carbon fiber, graphite of various type, Pt (Pt is commonly used as cathode catalyst, while alternative polymer binders have also been assayed, such as perfluorosulfonic acid (Nafion) [69]), Cu, Cu-Au, tungsten carbide, granular graphite (reported as excellent material), reticulated vitreous carbon (RVC). [21,70,71]. The requirement for catalysts is the main difference when these materials are used for cathode [68]. Different outputs attained using heterogeneous materials as cathode are manifested in Table 3.

Table 3 Some of used electrodes in MFCs with maximum generated power, current and voltage.

Cathode	Max power density	Max current density	Max Voltage	Reference
Activated carbon fiber felt (ACFF)	315 mW/m^2 (0.7 W/m^3)	$1.67 * 10^{-3} \text{ mA/m}^2$	679 mV	[69]
Air-cathode with graphite	283 mW/m^2	1210 mA m^{-2}	440 mV	[1]
Carbon felt	77 mW/m^2 (0.2 W/m^3)	$6 * 10^{-3} \text{ mA/m}^2$	575 mV	[69]
Plain carbon	67 mW/m^2 (0.1 W/m^3)	1.5 mA/m^2	598 mV	[69]
Pt-coated carbon paper	0.3 W/m^3	4.69 mA/m^2	644 mV	[69]
Tubular ACFF	784 mW/m^2	3.17 A/m^2	716 mV	[69]
ACFF granules (1 cm)	667 W/m^3	3.34 A/m^2	658 mV	[69]
Biocathode	19.53 W/m^3	41.78 A/m^3	432 mV	[21]
Graphite felt	539 mW/m^2	3145 mA/m^2	742.3 mV	[72]
Parallel sheets of carbon paper secured by carbon fiber coated with pt	7.29 W/m^3	13.16 A/m^3	553 mV	[59]
Air-cathode with Carbon cloth	50 W/m^3	363 A/m^3	710 mV	[73]

4. Transfer of produced protons from anode to cathode chamber

A bio-potential developed between the bacterial metabolic activity [reduction reaction generating electrons (e^-) and protons (H^+)] and electron acceptor conditions (separated by a membrane) leads to generate a bioelectricity in MFCs [74]. As it could be conjured up from what has been mentioned, separator is one of the significant parts in MFCs which physically separates the cathodic and anodic biological reactions (cathode for a single-chamber MFC) [75,76]. However, besides the advantages of using separators, utilizing separators can bring some not favorable aftermaths. First of all, protons produced in the anode chamber are transferred via separator, but the permeation of substrate and oxygen is prevented by the separator [37]. Ergo, removing separator the penetration of substrate and oxygen will be improved; consequently, in MFC, columbic efficiency and the activity of microorganism will be lowered [77]. In addition, increasing pH in the cathode chamber and reducing in anode chamber, i.e. pH splitting, are the main challenges. It is worth mentioning that pH splitting will decrease the performance and system stability [39,90]. These issues are raised once proton (which is not of sufficient rate) transfers from anode chamber to cathode. Amplifying overall internal resistance and also the overall cost of MFCs is the other challenge of utilizing separator [76]. To overcome these problems, various separators were developed continuously in the past decade [78]. In this connection it should be added here that the materials of diverse separators can be classified into three categories in terms of their traits of filtration as ensuing: salt bridge, size-selective separators and ion exchange membranes (IEMs) [78]. Needless to say, Typical ion exchange membranes based on the sort of ionic groups fastened to the membrane matrix could be in two major categories as anion exchange membranes and cation exchange membranes [5]. These separators generally contain ultrafiltration membrane (UFM) [75], salt bridge [79], bipolar membrane (BP2M) [72], cation exchange membrane (CEM) [80,81], anion exchange membrane (AEM) [75], glass fibers [82,83], microfiltration membrane (MFM) [84,85], porous fabrics [86,87] and other course pore filter materials [83].

4.1. CEM

The role of CEMs is one of the most noteworthy factors influencing MFCs performance. Otherwise stated, they must function instrumentally to transport produced protons to cathode chamber in MFCs. Moreover, CEMs must be able to prevent the transfer of other materials such as substrate or oxygen from anode and cathode compartments [88,69,89–91].

CEM is a widespread ion-penetrable separator and positive charges have to be transferred through it. Connotatively speaking, groups with negative charges are inclusive cation exchange membranes (e.g. $-PO_3^-$, $-COO^-$, $-C_6H_4O^-$) attached to the backbone of membrane which subsequently permit the cations to pass through them, but, in contrast negative ions are refused [92]. Hence, they are often referred to as proton exchange membranes (PEMs) which have been extensively utilized as separators in MFCs [78]. Thanks to low internal resistance and high conductivity of cations, PEM is one of the well-known applicable separators [75,83].

Different kinds of materials were used as CEM in MFCs such as ultrex, Nafion, bipolar membranes, dialyzed membrane, polystyrene and divinylbenzene with sulfuric acid group, glass wool, nano-porous filters and microfiltration membranes [85,93–95]. As it is generally accepted, among the assigned membranes, Nafion is one of the most common CEMs in MFCs [96] which was first developed by Dupont in 1970 and, consequently, fuel system utilized this membrane as well as the industry of chlor-alkali production [97]. It is worth reiterating that Nafion is one of the most popular CEMs utilized most frequently, a perfluorosulfonic acid membrane consisting of hydrophobic fluorocarbon backbone ($-CF_2-CF_2-$) to which hydrophilic sulfonate groups (SO_3^-) are attached [98], and due to the existence of these negatively charged sulfonate groups, Nafion demonstrates high conductivity to different kinds of cations [99]. As advantages, not only Nafions are of more specific conductivity for protons and more lifetime [5], but they also have an appropriate level of hydration and thickness, both of which affect the cell performance [100]. Besides the encountered advantages, Nafion is not suitable for neutral pH and in the presence of cation species such as Na^+ , K^+ , and NH_4^+ (that 10^5 times higher than H^+ concentrations). These species have more potential to transfer through the membrane rather than protons; thus, this process causes pH increase in the cathode chamber. It needs to be added here that, the ability of interception of pH that is increased in cathode compartment is a major criterion for membrane performance [93]. Furthermore, the high cost of Nafion (owing to the complexity of fluorine chemical structure [101]) that includes 38% of MFCs along with the physical instability at the temperatures higher than $100^\circ C$ [102] is the other challenge in using Nafion as membrane material. For the mentioned facts, researches have decided to test another type of practical membrane [103,104]. In comparison with Nafion, Ultrex with great mechanical stability and more affordability is a common alternative for CEMs [93,105]. As a further instance, Ultrex CMI 7000 is another commonly utilized CEM [75,81,105]. CMI 7000 is a strong acid polymer membrane with gel polystyrene and divinylbenzene cross-link structure which includes numerous sulfonic acid groups. It illustrates comparable mechanical durability, albeit a high ohmic resistance, and comparable cation conductivity in comparison with Nafion [105].

Zirfon [106] and Hyflon (Solvay-Solexis, Italy) [107] are another alternative cut-rate CEMs. Zirfon, which consists of 85 wt.% of a hydrophilic ZrO_2 powder and 15 wt.% polysulfone, is a macro porous organ mineral material [108]. In comparison with Nafion, Zirfon is of higher oxygen permeability (penetrability) which is detrimental to anodic reactions, but its specific resistance is much lower [106]. In addition to Zirfon, Arico et al. reported that in conductivity and chemical stability, Hyflon is better than Nafion [109]; in contrast, it demonstrated larger internal resistance in comparison with Nafion. Needless to say, recent efforts have focused on nanoparticle, and nonofibers membrane because of cost-effective materials [110,111]. In this connection it should be added here that Rahimnejad et al. prepared Fe_3O_4/PES nanocomposite with a variety of Fe_3O_4 content with applied *Saccharomyces cerevisia* as biocatalyst and the result demonstrated that for low roughness and high conductivity, the MFC performance was affected to a considerable degree with optimized content

(e.g. PES-15% Fe₃O₄) rather than Nafion and all other fabricated membrane [112].

Biofilm enrichment during long-time operation occasions membrane fouling which decreases the following factors: conductivity, capacity of ion transfer and diffusion coefficient [113]. These factors affect MFC performance negatively, reduce electricity generation and finally enlarge operation costs due to PEM replacement [113].

In the final analysis, it should be mentioned here that High cost of CEM and oxygen permeability are the constraints that have restricted the MFC performance [114]. High internal resistance and pH splitting could be other presented barriers [76]. One of the greatest restrictions that has limited internal resistance and conductivity in CEM is low proton transfer capability [115].

4.2. AEM

Due to the limitations of CEMs encountered above, researchers have suggested AEM which utilizes carbonate and phosphate as pH buffer [94] to improve proton transfer [116]. To utilize buffer anion in AEM separator, the substrate permeability is commonly higher than CEM. Kim et al. demonstrated higher power density of nearly 0.61 W/m² using AEM in comparison with using CEM when 0.48 W/m² of power density has been obtained [75]. AEM includes ions with positive charges (e.g. -PR₃⁺, -SR₂⁺, -NH₃⁺, COO⁻) that join the membrane and transmit anions through it [5]. Another investigation illustrated that AEM-based membrane cathode assembly achieved much higher power of 13.1 W/m³ in comparison with 8.3 W/m³ when CEM was used for membrane cathode assembly [94].

4.3. Bipolar membrane (BPM)

BPM that consists of two monopolar membranes (CEM and AEM) is another alternative separator that has been implemented in MFCs in which Protons and hydroxide ions were conducted. As a more application, it has been used for treating high salinity water [116].

Generally, in bipolar membrane studies, the principal anxiety improves the electrical conductivity and reduces weight especially cost. Ergo, metallic materials such as graphite and stainless steel have been vastly exploited for bipolar plate membrane. Graphite is a well-known plate for bipolar membrane thanks to easy fabrication, good conductivity and low density. Coupled with graphite, electrical conductivity and chemical stability are the reasons for utilizing stainless steel as another bipolar plate [117].

As the final point, in the stack version of MFC, five typical functions are considered for every bipolar plate that supports two adjacent cells: (i) to detach single cells in the stack, (ii) to facilitate water management inside the cell, (iii) to transport current away from the cell, (iv) to distribute fuel and oxidants of fuel inside the cell, and (v) to facilitate heat management [118].

5. Application

The main applications of MFCs developed in recent decades are classified in the following forms:

5.1. Generation of bioelectricity

MFC is a fantastic technology that can use a wide variety of substrates, materials, and system architectures with bacteria to achieve bioenergy production despite the fact that power levels in all these systems were relatively low [68].

It is particularly preferred for sustainable long-term power applications, with potential health and safety issues [103]. Clytonbetin (2006) demonstrated if an MFC could convey 25mW of power, it would be suitable for cardiac stimulation; however, the amount of surface area needed is quite large [50]. The main objective of MFCs is to achieve a suitable current and power for the application in small electrical devices. Rahimnejad and et al. turn on ten LED lamps and one digital clock with fabricated stacked MFC as power source and both devices were successfully operated for the duration of 2 days [4].

5.2. Biohydrogen production

MFCs can be readily adjusted to the harvest of biohydrogen, instead of producing electricity. Hydrogen can be accumulated for later application [103]. MFCs supply a renewable hydrogen source that can be donated to the overall hydrogen demand in a hydrogen economy [119]. To generate hydrogen gas in typical MFC, anodic potential must be increased with an additional voltage of about 0.23 V or more, and also the oxygen at the cathode chamber should be vanished [68].

5.3. Wastewater treatment

As energy source, large potential is kept in wastewaters including diverse types of organic substrate [17,120,121]. Different kinds of Wastewaters such as sanitary wastes, food processing wastewater, swine wastewater and corn stover contain energy in the form of biodegradable organic matters [103]. MFC technology that was considered to be used for wastewater treatment early in 1991 [122] is favorable as a completely different method because of capturing energy in the form of electricity or hydrogen gas [68].

For an efficient treating system, high operational sustainability and low material costs are worthwhile characteristics [123].

Scientists have reported that to remove nitrogen and organic matters from leachate, biological treatment is prevalently used as a credible and highly cost-effective Method [124,125].

Simultaneous methane and electricity generation from waste materials are anaerobic digestion processes with long detention time that are suitable for high-strength wastewaters [68]. In 2006, Rabaey et al. demonstrated that MFCs using specific microbes were excellent techniques to remove sulfides from wastewater [126].

Up to 90% of the COD can be removed in some cases [123,127] and a coulombic efficiency as high as 80% has been reported [128].

The capability of MFC technology for simultaneous electricity generation and the removal of salinity from Se-containing wastewater were observed and it was concluded that at higher serenity concentration, both power output and CE are lower [129].

Also MFC could be an efficient method of electricity generation and odor removal, and Kim et al. demonstrated MFC-based technology accelerates the rate of removing odor when the electricity generation reaches a maximum of 228 mW/m^2 [130].

Puig et al. demonstrated that biofuel cells used landfill leachate as a method of treating biodegradable organic matter and electricity production even with high content of nitrogen and salinity. The amount of removal organic matter was $8.5 \text{ kgCODm}^{-3} \text{ d}^{-1}$ when the power density was 344 mWm^{-3} [127].

A novel MFC-membrane bioreactor (MBR) for the treatment of wastewater has recently been reported to achieve a maximum power density of 6.0 W/m^3 with the average current of $1.9 \pm 0.4 \text{ mA}$ and good pollutant removal performance attributed to the high biomass retention and solid rejection [123].

5.4. Application of MFCs in biosensor

Using MFC technology as sensor for pollutant analysis and process monitoring is another application of biofuel cells [57]. Batteries have restricted lifetime and must be changed or recharged; thus, MFCs are suitable for powering electrochemical sensors and are small telemetry systems to transmit obtained signals to remote receivers [131,132]. To design this type of system, having appropriate cathodic and anodic reactions is the first step [132]. It is possible to use MFCs as biological oxygen demand (BOD) sensor [53], and it is exhibited that this type of BOD sensor has excellent operational sustainability and reproducibility and can be kept operating for 5 years [103].

Different types of enzymatic glucose sensors have been developed [50]. The first type measures the amount of produced hydrogen peroxide and the lack of oxygen with the advantages of being easily fabricated and assembling small sized systems [133,134]. The another one uses chemical mediators such as ferrocene to convey electron to electrode [50]. MFCs may have many other applications besides wastewater treatment and renewable energy. The first and practical application of MFC is using this system for energy recovery to sustainable water infrastructure [68].

Also a potential of remediating toxicants, such as phenols and petroleum compounds is another application of MFC [135,136].

Biological electricity from wastes produced onboard on a spaceship is also a possible applicability [103].

6. Limitations

Power generated by the cell may not be enough to run a sensor or a transmitter continuously. This is the principal problem with using microbial cells. It can be solved by increasing the surface area of the electrodes. Also the other solution is to use a suitable power management program: the data are transferred only when enough energy is stored and this occurs by using ultra capacitor [132,137]. Finally, the other limitation of MFCs is that they cannot operate at extremely low temperatures due to the fact that microbial reactions are slow at low temperatures [132].

7. Conclusion

As petroleum source is depleted, energy crisis encouraged researchers in the world to consider for alternative sources of energy. Moreover, using of fossil fuels may cause environmental pollution. Clean fuels, significantly fuel cells and biofuels, as new sources of energy without any pollution are suitable replacements of traditional fossil fuels. MFCs are individual kinds of FCs which use active biocatalysts such as microorganisms or enzymes to generate energy. MFCs are one of the newest technologies to produce energy from different sources of substrates. Because of the promise of sustainable energy generation from different substrates such as organic wastes, research has been intensified in this field in the last few years. MFCs have different applications based on generated power. The generated power in MFC is still too low and researchers are working to improve it for commercial application.

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