



Review

A review on the effect of proton exchange membranes in microbial fuel cells

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HIGHLIGHTS

- MFC is a novel knowledge that can be used to obtain bioenergy in the form bioelectricity.
- Transfer of produced electrons to anode is one of the main parts in MFCs.
- Some MFCs needs artificial electron shuttle in their anaerobic anode compartment.
- The important goal of MFCs is to reach a suitable power for application in small electrical devices.

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ABSTRACT

Microorganisms in microbial fuel cells (MFC) liberate electrons while the electron donors are consumed. In the anaerobic anode compartment, substrates such as carbohydrates are utilized and as a result bioelectricity is produced in the MFC. MFCs may be utilized as electricity generators in small devices such as biosensors. MFCs still face practical barriers such as low generated power and current density. Recently, a great deal of attention has been given to MFCs due to their ability to operate at mild conditions and using different biodegradable substrates as fuel. The MFC consists of anode and cathode compartments. Active microorganisms are actively catabolized to carbon sources, therefore generating bioelectricity. The produced electron is transmitted to the anode surface but the generated protons must pass through the proton exchange membrane (PEM) in order to reach the cathode compartment. PEM as a key factor affecting electricity generation in MFCs has been investigated here and its importance fully discussed.

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1. Introduction

In a near future, fossil fuels will be depleted. Furthermore, traditional sources of energy have many a lot of disadvantages such as greenhouse gas production. In fact the emissions produced from these energy sources through human activities has proven to be the main cause of global warming and climate change (Barat et al., 2008; Najafpour et al., 2011). Several countries in the world, however have responded to the threats of energy security and global warming by diversifying their fuel sources to include renewable and alternative energy and developing clean energy technologies to replace the conventional ones (Daud et al., 2011).

Generating energy from renewable sources, such as biomass, is not only reliable and sustainable but also helps reduce global carbon dioxide emissions (Jung and Regan, 2007; Greenman et al., 2009; Kim and Chang, 2009; Oh et al., 2009).

A key method for generating renewable and alternative energy is through use of fuel cell technology. However, most fuel cell technologies require hydrogen, which is derived from fossil fuels (Jafary et al., 2013). The use of fossil fuels may lead to global warming, environmental pollution and climate change (Gunkel, 2009). Therefore, generating hydrogen from fossil fuels may not be a suitable alternative for replacing an energy resource (Stoica et al.,

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2009). Microbial fuel cells (MFC) are one type of fuel cells, which are reliable for limited power production (Oh and Logan, 2005).

MFC is a novel knowledge that can be used to obtain bioenergy in the form of hydrogen and/or electricity, directly from different organic and inorganic compounds, while simultaneously treating biodegradable contaminants in wastewaters (Oh and Logan, 2005; Rahimnejad et al., 2012a). In MFCs, the electrons are provided from chemical bonds with the aid of active microorganisms such as enzymes or bacteria. Then, the generated electrons are transported to the anode electrode and the produced protons are moved through a proton exchange membrane toward the cathode compartment (Wen et al., 2009). The electron flows through an electrical external circuit while the anode is connected to the cathode (Fatemi et al., 2012; Rahimnejad et al., 2011b; Rahimnejad et al., 2012b). The flow of electron creates a current (I) and a power (P). The reduction of organic substances in the anode was catalyzed by living organism in the anode chamber (Chen et al., 2008; Rahimnejad et al., 2009).

2. Effective parameter on MFCs

The performance of MFC may be enhanced through several important process parameters which are critical to its operation such as: (i) cell metabolism, (ii) microbial electron transfer, (iii) proton exchange membrane transfer, (iv) external and internal resistances and (v) cathode oxidation. These process parameters have great influence on the transfer of the electron and power generation (Rabaey et al., 2003; Jafary et al., 2012).

The basic part in MFCs technology is the active biocatalyst. Active electrogenic bacterial strains can transfer the produced electrons via metabolism across the cell membrane to an external electrode directly without adding any artificial components (Tardast et al., 2014). This mechanism plays an important role in harvesting bioelectricity in the MFC bioreactor. Even though the mechanism of extracellular electron transfer has not yet been fully understood, some possible pathways have been suggested, including direct outer membrane c-type cytochrome/anode coupling, through either redox electron shuttles or electrically conductive pili (see Fig. 1). Fig. 1 shows the principles of two-chambers of an MFC (Qian and Morse, 2011). Generally, oxygen is used as the final electron acceptor in the cathode. Eventually the combination of electrons and protons with oxygen forms water and ends this transfer cycle. Oxidized mediators can further accelerate the water formation process in the cathode chamber (Heitner-Wirguin, 1996).

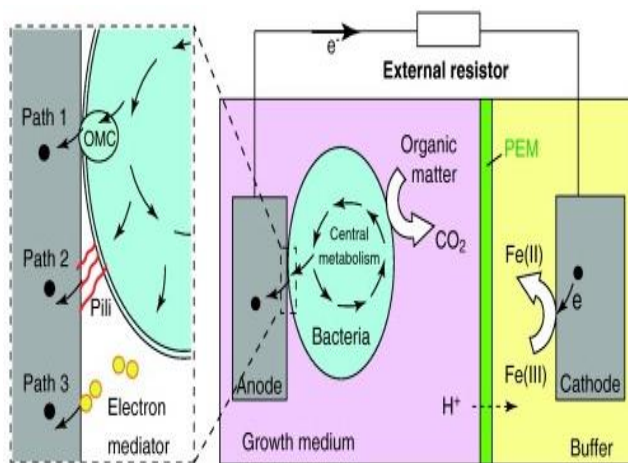


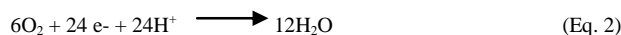
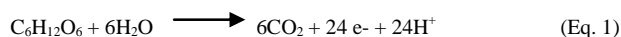
Fig.1. Principles of a two-chamber MFC.

Traditional MFCs consist of a cathode and anode compartment that is separated by a salt bridge or proton exchange membrane (PEM) (Fatemi et al., 2010). The active microorganisms are inoculated in the anaerobic anode

chamber, where this biocatalyst used substrate and generate bioelectricity via their central metabolism (Jafary et al., 2013; Rahimnejad et al., 2011b; Mokhtarian et al., 2012a). Some of the produced electrons can transfer to the anode surface and then form an external circuit, move to the cathode and react with oxidants in the cathode electrode surface (Rahimnejad et al., 2010). To preserve the neutrality of the electrochemicals, the generated protons in the anode compartment are passed through the PEM to the cathode compartment. The important factors that need to be taken into account when investigating the MFCs performance include Coulombic efficiency, power and current density, biological oxygen demand removal efficiency and sustainability (Oh et al., 2009; Qian and Morse, 2011).

2.1. Electron Transfer in MFCs

In an anaerobic anode compartment, electrogenic active microorganisms catalyze the oxidation of organic matter and generate electrons (represented by black circles in Fig. 1) in their central metabolism. Some of these produced electrons are extracellularly transferred to an anode electrode via distinct pathways, path 1: including through direct outer membrane protein/anode coupling, path 2: conductive pili, and/or path 3: via self-secreted electron shuttles (Qian and Morse, 2011). Microorganisms as biocatalyst in the MFC consumed different substrates (such as glucose) as their source of carbon in the anode chamber and the produced electrons and protons. In the case of glucose being used as fuel for the MFC, the anodic and cathodic reactions have been presented in equations 1 and 2.



The performance of the MFCs can be improved through the addition of artificial electron mediators (Rahimnejad et al., 2009b; Mokhtarian et al., 2012b; Rahimnejad et al., 2012b). Electron mediators are used to shuttle electrons from the broth to the anode electrode surface. Mediators are artificial compounds or produced by the microorganism itself. Some active microorganisms produce nanowires to transfer the produced electrons directly without using any mediator but other organisms need to add artificial electron shuttles into the anode chamber (Rahimnejad et al., 2011). Park and Zeikus (2000) investigated the interactions between bacterial cultures and electron mediators. The effect of thionine and neutral red as mediators for the oxidation and reduction of energy carriers such as nicotinamide adenine dinucleotide (NAD^+) was investigated. The biomolecules, NAD^+ and NADH are in the oxidized and reduced forms, respectively. Several types of mediators were used in MFCs to enhance the electron transfer (Bennetto et al., 1985).

The soluble redox mediators have been added to the anode chamber to improve electron transfer. Several researchers have developed advanced anode materials by impregnating the anode with chemical catalysts (Park and Zeikus, 2000; Choi et al., 2004).

Thionine is one of the potential mediators for transferring the produced electron to the anode surface in MFCs. Thionine as mediator is not involved in any biochemical reaction. It has been reported that thionine may not be necessary for short incubation time while for long durations, thionine enhances electron transfer (Choi et al., 2007; Rahimnejad et al., 2012b). Table 1 shows some of the MFCs that were examined with mediators and different components as substrate.

Recently, MFCs as a new renewable source of energy have been extensively reviewed by different researchers. Their investigation includes studies on the different substrates used in MFCs (Pant et al., 2010), the different Nano-composite materials used as electrode material for MFCs (Ghasemi et al., 2013d; Ghasemi et al., 2013e). The development of MFCs and their applications (Franks and Nevin, 2010), decreasing the size of MFCs

Table 1

Maximum generated power and current of MFC with different types of mediators and microorganisms

Reference	Current density	Power density	Microorganism	Substrate	Mediator
(Najafpour et al. 2011)	1600 mA m ⁻²	190 mW m ⁻²	<i>Saccharomyces cerevisiae</i>	Glucose	Neutral Red
(Ringeisen et al. 2006)	44.4 mA m ⁻²	22.2 mW m ⁻²	<i>Shewanellaoneidensis</i>	Lactate	Anthraquinone-2,6-disulfonate (AQDS)
(Thygesen et al. 2009)	85 mA m ⁻²	28 mW m ⁻²	Domestic waste water	Glucose	Humic acid
(Vega , Fernández 1987)		–	<i>Streptococcus lactis</i>	Glucose	Ferric chelate complex
(Thygesen et al. 2009)	589 mA m ⁻²	123 mW m ⁻²	Domestic waste water	Acetate	Humic acid
(Rabaey, Korneel et al. 2005)	–	479m W m ⁻³	Mixed consortium	Glucose, Sucrose	Mediator-less
(Thygesen et al. 2009)	145 mA m ⁻²	32 mW m ⁻²	Domestic waste water	Xylose	Humic acid

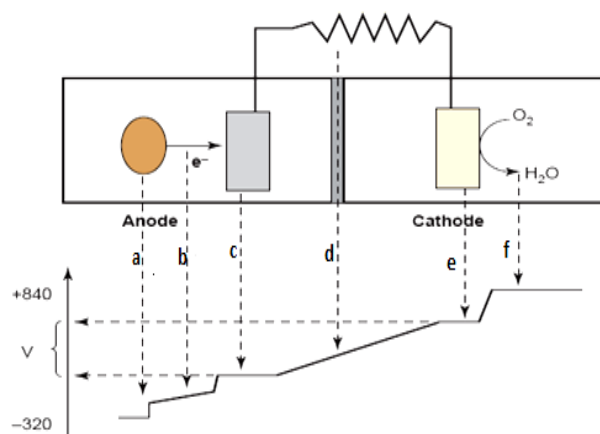
(Wang et al., 2011a), the introduction of several terminologies and in MFCs (Logan et al., 2006), the mechanisms used for current generation (Logan, 2009), state of the art information on MFCs and recent progresses in MFC technologies (Du et al. 2007) comparison of MFCs with conventional anaerobic digestion (Pham et al. 2006), cathodic limitations in MFCs (Rismani-Yazdi et al., 2008) and electrode material in MFC (Zhou et al., 2011). But, a comprehensive review on the effect of proton exchange membrane (PEM) is still lacking. PEM is important for any MFCs as it acts to transfer the produced protons from the anode to the cathode compartment. The efficiency and economic viability of MFCs depend strongly on the performance of PEM. The aim of this paper is to highlight the PEMs materials that have been used in MFCs, their improvement and also their effect on the performance of MFCs. (Tardast et al., 2012; Tardast et al., 2014).

2.2. Resistances in MFCs

Several parameters affect the performance of MFCs and the generated bioelectricity, namely microbial inoculums, chemical substrates, mass transfer areas, absence or existence of proton exchange materials, mechanism of electron transfer to the anode surface, the internal and external resistance of cells, solution ionic strength, electrode materials and the electrode spacing (Park and Zeikus, 2000; Gil et al., 2003; Liu and Logan, 2004; Li et al., 2011).

Mass transfer is also one key parameter in MFCs. Fig. 2 shows all different resistances in MFCs and also biological fuels. There are three kinds of over potentials such as over potentials for activation, ohmic losses and concentration polarization. For MFCs, the activation over potential appears to be the major limiting factor. Furthermore, membrane resistance has an important role on MFC performances because the produced protons must be transferred from the anaerobic anode to the cathode compartment (Rabaey et al., 2005b). In addition to this, there is another important parameter related to PEM. The cathode of MFCs works in aerobic conditions while the anode would be working in anaerobic conditions. This means the oxygen that exists in this chamber should diffuse from the cathode to the anode chamber through PEM that reduces the performance of MFCs. These two parameters affect the power generated by MFCs and must be taken into consideration. If the oxygen diffuses through PEM and makes the anode aerobic, the MFC cannot produce power and can only be applied for COD removal and wastewater treatment (Ghasemi et al., 2012).

Quantitative investigation of the electrochemical dynamics and resistances at different parts of MFCs can be conducted by a potentiostat or electrochemical station. Exploration of different MFC configurations, materials for the anode and cathode electrodes, bacterial strains, substrates and kinds of PEMs are the major focus of current MFC researches.

**Fig.2.** Potential losses during electron transfer in a MFC.

a: loss owing to bacterial electron transfer, **b:** losses owing to electrolyte resistance, **c:** losses at the anode, **d:** losses at the MFC resistance (useful potential difference) and membrane resistance losses, **e:** losses at the cathode, **f:** losses owing to electron acceptor reduction (Rabaey and Verstraete, 2005).

2.3. Proton Exchange Membranes

Most of the MFCs consist of two separate parts. In a two-chamber design, the anode and the cathode compartments are separated by an ion-selective membrane, allowing proton transfer from the anode to the cathode and preventing oxygen diffusion in the anode chamber from the cathode compartment. The membrane in the MFCs plays an important role on MFC performance. The membrane must have good capability for exchanging protons (Watanabe, 2008). Generally, there are two types for PEM; porous proton exchange membranes and nonporous membranes called dense membranes (Mayahi et al., 2013). In fuel cells, the main duty of dense

membranes is to separate the anode and the cathode and to prevent the migration of the anode electrolyte to the cathode compartment as well as preventing the air from moving, which was purged in the cathode compartment, to the anode compartment (Leong et al., 2013). Fig. 3 shows the micrograph for the cross section of a porous membrane. It should be noted that porous or nonporous membranes are distinguished by their cross section. The micrograph for the cross section of a nonporous membrane is shown in Fig. 4.

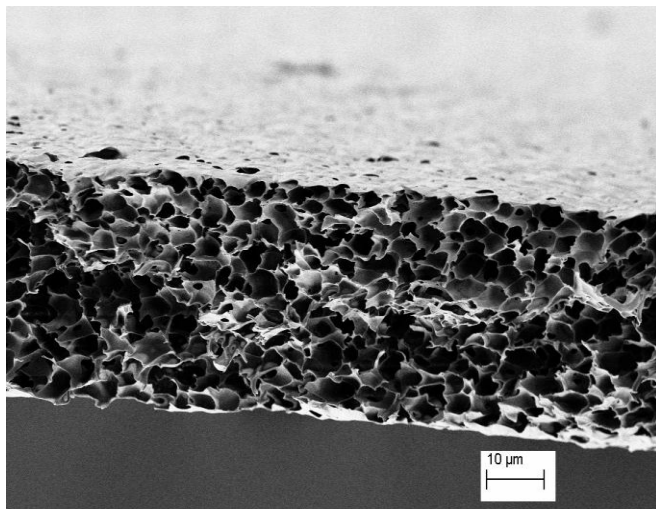


Fig. 3. Cross section SEM image of porous membrane.

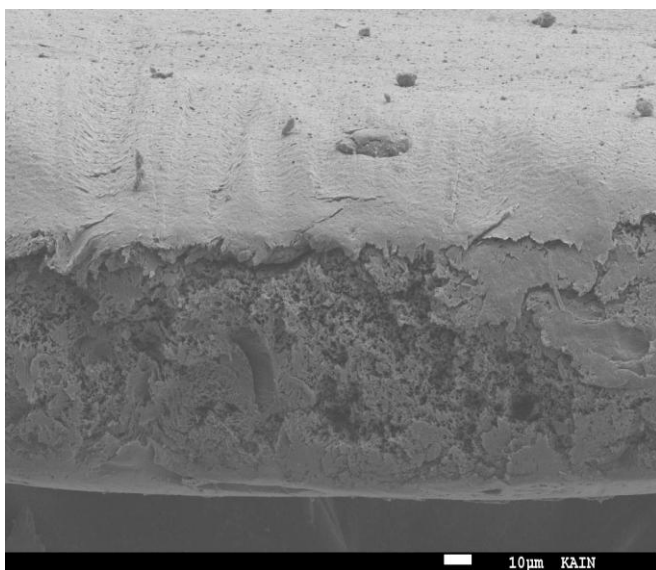
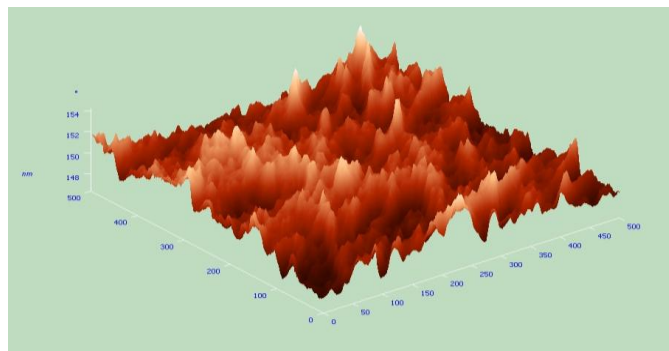


Fig. 4. Cross section SEM image of nonporous membrane.

From the SEM images, it is obvious that the porous membrane has a lot of pores along its cross section while there is no pore for the dense membrane. The AFM images of a dense membrane have been shown in Fig. 5 (a-b) revealing a dense layer on top of the membrane without any pores.

(a)



(b)

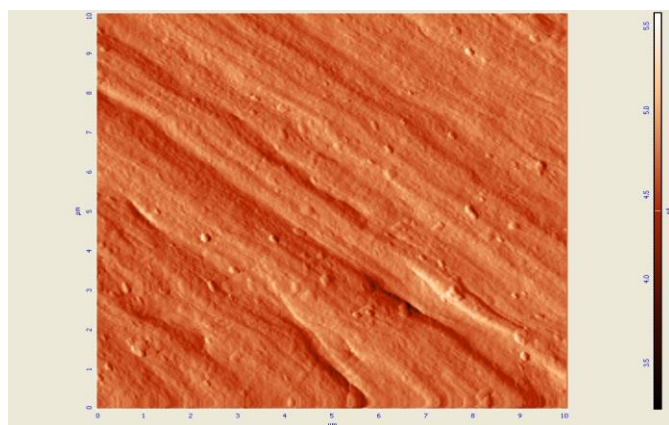


Fig. 5. a) 3D AFM image of a dense membrane, b) 2D AFM image of a dense membrane.

2.3.1. Nafion as traditional PEM

In the MFC, the Nafion membrane equilibrates with the cation species present in the anolyte and catholyte (Rahimnejad et al., 2010). This equilibration quickly changes the membrane from its proton form to a form in which mainly other cation species occupy the negatively charged sulfonate groups. More than 99.999% of the sulfonate groups are occupied by non-proton cations, because the sulfonate groups of Nafion have a higher affinity for most other cation species (Okada et al., 1997; Okada et al., 1998; Kelly et al., 2005). Subsequently, these cations combined with the sulfonate groups of Nafion stop the movement of protons that are produced at the time of substrate degradation.

In addition, other cation species have a higher concentration in the anolyte than protons which make proton transport slightly minor compared to the transport of other cations, causing a decrease in MFC performance. The diffusion coefficient of protons in the Nafion is relatively higher than other cations.

Chae et al. (2007) also, considered cation transport in an uninoculated MFC and reported an increase in the concentration of the cation species in the catholyte. The cation transport rates were slower than the reported ones in previous studies using an inoculated MFC (Rozendal et al., 2006).

Currently, the most available PEM for MFCs is Nafion from Dupont but this cannot operate efficiently at temperatures higher than 90 °C due to thermal instability (Rowe and Li, 2001; Ghassemi et al., 2006). The fuel cell electrochemical processes research group at the Fuel Cell Institute however,

have successfully developed a new high temperature composite called Nafion-silicon oxide (SiO_2)- acid (PWA) a composite membrane with lower resistance, higher proton conductivity, higher current density and better thermal stability at 90 °C than the Nafion membrane from Dupont (Daud et al., 2004; Mahreni et al., 2009) and the Aciplex membrane from Asahi (Wang et al., 2011a). Rozendal et al. (2006) examined the effects of cation transport through Nafion 117 membrane on the cathode PH and MFC performance. In a two-compartment MFC, the number of cations other than the protons (K^+ , Na^+ , Mg^{2+} , Ca^{2+}) transported from the anode compartment to the cathode compartment were found to be the same as the number of electrons transferred through the circuit. An analysis of the membrane of the MFC showed that K^+ and Na^+ occupied about 74% of the sulfonate residues of the membrane. The cation transport was not driven by the concentration gradient, but was an electro dialysis process. This means that virtually no proton was transported in the MFC and that electroneutrality was sustained mainly through the transport of cations and not through proton transport. This phenomenon causes a number of electrochemical and microbiological problems for the efficient operation of MFCs. The anode compartment is acidified, raising the anode potential and producing adverse conditions for the microorganisms catalyzing the anode reaction, while the cathode compartment is alkalized, which lowers the cathode potential (Gil et al., 2003; Liu and Logan, 2004). This preferential transport of cations rather than protons may be avoided by either removing the membrane (Jang et al., 2004; Liu and Logan, 2004) or by using an electrolyte containing a low cation concentration.

Ghasemi et al. (2012) has developed a new Nano-composite membrane and compared it with Nafion 117. Their creation operates by activating the carbon Nano fiber/Nafion PEM and applying it in the MFC. Their data shows that this Nano-composite membrane can produce about 1.5 times more power than the Nafion 117. Also the CNF without activation and Nafion produced 27% more power than Nafion 117. They concluded that CNF and ACNF increase the conductivity of the membrane as well as the porosity, so the capability of membranes for proton exchange increases.

Furthermore, in another research, this group evaluated the effect of pretreatment on membrane performance. Nafion 117 was the PEM that was evaluated before and after the treatment. The effect of biofouling on membrane performance was also investigated. The results show that the minimum amount of power generation belongs to the biofouled Nafion 117 which is 20.9 mW m^{-2} . This means biofouling has a negative effect on membrane performance. The untreated membrane produced about 52.8 mW m^{-2} of power whereas the treated membrane produced about 2 times more power equivalent to 103 mW m^{-2} . Results showed that pretreatment is highly effective in membrane performance and biofouling can have a very unfavorable effect on the membrane (Ghasemi et al., 2013f).

MFC is a device for simultaneous wastewater treatment and energy production but one of the obstacles for the commercialization of MFC is the high price of PEM. Ghasemi et al. (2013e) compared the economic investigation of MFCs that are working with Nafion 117 and sulfonated poly ether ether ketone (SPEEK). They found that the MFC working with Nafion 117 can produce 106.7 mW m^{-2} of power that is much more than the power produced by SPEEK (77.3 mW m^{-2}). But the COD removal of the system working with SPEEK was 88% which is higher than the system working with Nafion 117 (76%). They compared the economic issues of both systems and found that the power per cost of the MFC with SPEEK as PEM is 2 times higher than the MFC with Nafion 117. This means that the system with SPEEK is two times more economical than the system with Nafion 117.

Due to the high price of Nafion 117, scientists have always been interested in replacing Nafion 117 with a less expensive PEM. Mokhtarian et al. (2013) used Nafion 112 and four different Nafion 112 /Pani in the MFC as a separator. They prepared these separators by pretreating the Nafion 112. Then, they immersed the Nafion 112 in an aniline solution that was dissolved

in HCl for 1, 2, 3 and 4 hours and called the end product Nafion/Pani1, Nafion/Pani2, Nafion/Pani3 and Nafion/Pani4. These four membranes and Nafion 112 were then applied to the MFC to see whether or not they could be used as PEMs. Results showed that among the membranes, Nafion/Pani3 produced the highest power density of (124 mW m^{-2}) which is 93% of the power produced by Nafion 117. Results The results also showed that Nafion 112 could be modified for application in the MFC.

2.4. Effect of mass transfer area on MFC performances

Nafion mass transfer area affects the production of power in MFCs as was shown in Fig. 6. Three different mass transfer areas (3.14 cm^2 , 9 cm^2 and 16 cm^2) were tested and the results were presented in Fig. 6(a,b). The MFC memberane allows the generated hydrogen ions in the anode chamber to be transferred to the cathode chamber (Rabaey et al., 2005a; Cheng et al., 2006; Venkata et al., 2007; Aelterman et al., 2008). The results show that the maximum current and power occur when the area of Nafion is 16 cm^2 . The maximum power and current generated were 152 mW m^{-2} and 772 mA m^{-2} , respectively.

Table 2

Effect of mass transfer area on performance of MFC.

PEM surface area (cm^2)	maximum voltage (mV)	maximum power density (mW m^{-2})	maximum current density (mA m^{-2})
3.14	848	105.8	595
9	851	126	710
16	850	152	772

Furthermore, the thickness of PEM has an important role in MFCs' performances. In one study, *Saccharomyces cerevisia* was used as a biocatalyst for power generation in a dual chamber MFC. Nafion 112 and 117 were selected as membranes to transport the produced proton from the anode to the cathode compartment at ambient temperatures and pressures. Initial glucose concentrations were 30 g/l. The maximum obtained voltage and the, current and power density for Nafion 117 were 668 mV, 60.28 mA m^{-2} and 9.95 mW m^{-2} respectively. For Nafion 112 these figures were 670 mV, 150.6 mA m^{-2} and 31.32 mW m^{-2} respectively (Rahimnejad et al., 2010).

3. Problems associated with commercial PEM in MFCs

While Nafion is the common PEM used these days, there are several problems associated with Nafion membranes. These problems include oxygen leakage from the cathode to the anode chamber, high costs, substrate losses, cation transport and accumulation rather than that of protons and biofouling (Chae et al., 2008). Because of these disadvantages, researchers are working to fabricate a new kind of PEM which does not have these negative features and performs better than the Nafion membrane (Liu and Logan, 2004). Nowadays, due to the many existing and potential applications of polymer/inorganic nanoparticle membranes in energy, environment and biomedical materials, more attention is being paid to membrane science and technology. Nanoparticles improve separation performance by generating preferential permeation paths while they prevent the permeation of undesired species as well as increasing thermal and mechanical properties (Taurozzi et al., 2008; Jadav, 2009; Pan et al., 2010). This means the distribution of nanoparticles through the polymer matrix modifies chemical and physical properties of polymeric membranes (Mahreni et al., 2009). Recently, due to the unique and promising properties of Fe_3O_4 nanoparticles (magnetic, conductive, easy synthesis, eco-friendly and catalytic characteristic), intensive attention has been paid to them (Iida et al., 2007; Chen et al., 2009).

However until now, there have been different problems in making MFCs economical. MFC performance like other fuel cells is dependent on power, current density and the rate of fuel oxidation. Several important factors can influence the rate of fuel oxidation including the catalytic activity of the anode, fuel diffusion and the diffusion and consumption of electrons and protons.

One of the important challenges is the cost of the catalyst (such as platinum) that is used for accelerating the rate of oxygen-reduction reactions which account for more than half of the cost associated with MFCs (Lefebvre et al. 2009). Many researches have been done to replace or decrease the consumption of platinum or use less expensive and stable non-noble metals as cathodic catalyst to make it more practical (Kerzenmacher et al., 2008). Nowadays, nanostructured carbon-based materials specially carbon nanotubes are becoming popular catalysts or are used as a support for the catalyst due to their high surface area (Baughman et al., 2002), high mechanical strength (Meincke et al., 2004), high electrical conductivity (Berber et al., 2000) and catalytic activity (Gong et al., 2009). The higher catalytic activity of CNT-based materials may be due to the high surface area that cause better dispersion of materials as well as creating more space for functionalization and bonds (Ghasemi et al., 2011). Wang et al. (Wang et al., 2011c) used carbon nanotubes for modification of the air cathode's single chamber MFC. They concluded that the power produced by CNT was more than double that of traditional carbon cloth cathodes.

In addition, Ghasemi et al. (2013e) compared the effect of carbon nanotubes on increasing the power generation of MFCs. They compared an MFC that is working with Pt as cathode catalyst and another one which is working by CNT/Pt composite cathode catalyst and concluded that the power generation of the MFC which is working by CNT/Pt is 1.3 times higher than neat Pt. Furthermore, they tested Pani/Vanadium as an alternative cathode catalyst in the MFC. Due to the nature of Nano-composite conducting polymers, Pani/V₂O₅ has high catalytic activity. Compared to the MFC with Pt used as its cathode catalyst, the nanostructure Pani/V₂O₅ generated 79.3 mW m⁻² of power, 10% more than the Pt which generated 72.1 mW m⁻² power.

Ghasemi et al. (2013d) also studied the effect of using macrocyclic compounds as an alternative to Pt as cathode catalyst for the MFC. They applied phthalocyanine (Pc), copper phthalocyanine (CuPc) and nickel nanoparticles as macrocyclic in the cathode catalyst of the MFC and compared their performance with that of the Pt as the most common cathode catalyst used in MFCs. Their results showed that CuPc produced 118 mW m⁻² power which is very close to that produced by the Pt (120.8 mW m⁻²). Nickel nanoparticles also produced 94.4 mW m⁻² power which shows they can be used as cathode catalyst in MFCs. Although the produced bioelectricity from MFCs has improved considerably and researchers are also working on obtaining better results, the generated power is related to small lab-scale systems and the MFCs' scale-up is still a big challenge. Moreover, the high cost of PEM, the potential for biofouling and related high internal resistance restrains bioelectricity production and limits the practical application of MFCs (Hu, 2008).

There are some practical ways for overcoming the existing limitations in regards to MFCs. It is agreed that most MFCs generate too little power for any envisioned applications. Besides, the high cost of metal catalysts such as platinum which is usually needed on a cathode is also a big hindrance for the scale-up of these systems. The open air biocathodes proposed by Clauwaert et al. (2007) might be a possible solution in the future.

The cathode is the most challenging aspect of the MFC design due to its need for a three-phase interface: air (oxygen), water (protons), and solid (electricity). So far, the cathode is more likely to limit power generation than the anode. Most of the MFCs use Pt as a catalyst in the cathode electrode but this is too expensive and one of the challenges facing MFCs. The replacement of platinized cathodes with non-platinized ones with a similar efficiency is a

major improvement in this area. The use of manganese dioxide as an alternative cathode catalyst in MFCs and stainless steel and nickel alloys in MECs has also been suggested (Pant et al., 2010).

4. Important applications of MFCs

Our petroleum resources will be depleted in about 200 years and after that, vehicles will no longer be equipped with petrol tanks. Researchers in the world are working to find an alternative for this. One very good alternative which is less wasteful and cleaner, is producing bioelectricity for vehicles directly from different substrates such as carbohydrate sources using MFCs. Complete oxidation of a monosaccharide such as glucose or disaccharide like sucrose to water and carbon dioxide can generate 16×10⁶ J/Kg energy. This amounts to about 5 kWh of generated electrical energy. The most important goal of MFCs is to reach a suitable power generation level for application in small electrical devices. Rahimnejad et al. used MFC stacks as a power source and succeeded in turning on one digital clock and ten LED lamps. These small consumer devices managed to operate successfully for the duration of 2 days (Rahimnejad et al., 2012a). Another application of MFCs for waste water treatment (Izadi and Rahimnejad, 2013). Active microorganisms present in the anode compartment can discharge the dual duty of degrading effluent and bioelectricity production. An active biocatalyst can oxidize organic compounds presented in waste materials and produce electricity. But the produced power in these systems is still too little. If the generated power level increases in future, MFCs can decrease operating costs in waste water treatment plants (Najafpour et al., 2010; Rahimnejad et al., 2013). Different kinds of MFC reactor designs based on chemical engineering principles such as packed bed reactors, fluidized bed reactors, dual chamber reactors, single chamber reactors etc. are under investigation to reach this important aim. 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 (Gotvajn et al., 2009; Mehmood et al., 2009). Rabaey et al. demonstrated that MFCs by using specific microbes can remove sulfides from wastewater (Rabaey et al., 2006). Up to 90% of the COD can be removed in some cases (Puig et al., 2011; Wang et al., 2012) and a columbic efficiency as high as 80% has been reported (Kim et al., 2005).

The application of MFCs as biosensors for pollutant analysis and process monitoring are another application of this technology (Chang et al., 2005). Batteries have restricted lifetime and must be changed or recharged, thus MFCs are suitable for powering electrochemical sensors and are small telemetry systems that can transmit obtained signals to remote receivers (Ieropoulos et al., 2005; Greenman et al., 2009).

5. Conclusion

The idea of generating electricity in biological fuel cells theoretically exists, but as a practical method for energy production, it is quite new. MFC is a new technology for bioelectricity production from sustainable materials. This new source of energy can produce bioelectricity by using microorganisms or enzymes as an active biocatalyst. The present study has revealed that MFCs have a good ability for production of low voltage electricity and PEM has an important role on two chamber MFCs performances. MFCs produce current through the action of bacteria that can pass electrons to an anode, the negative electrode of a fuel cell. The electrons flow from the anode through a wire to a cathode. Some MFCs don't need any artificial mediators to pass the produced electrons but some others need mediators in the anode compartment. In MFCs, however, operating with wastewater at neutral pH conditions, the concentrations of other cation species (e.g. Na⁺, K⁺, Ca²⁺ and Mg²⁺) are typically 105 times higher than that for protons. Though Nafion is known as a PEM, but parallel to all other commercial cation exchange membranes other cations can pass through it.

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