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An Outlook of Microbial Fuel Cell Recoginsed as Reneweable and Clean Energy Source

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ABSTRACT

With the increasing time, energy is becoming most prominent parameter as air, water and shelter. Non-renewable sources of energy are foremost polluting agent of environment. Like R's principle, now there is need of E's principle for Energy security, Energy growth, Environmental protection and opt for environmentally friendly source of energy. The residual of coal, coal tars, oil shales and methane hydrates greatly affect climatic condition and thus accelerate global warming. Most recent approach of such type of energy is Microbial Fuel Cell (MFC) which involves treatment of waste water to harvest energy from it along with serving the purpose of purification of wastewater. This review paper discusses the component of MFC, working principle of MFC, describes about the materials used as anode, cathode, Proton Exchange Membrane (PEM) with its properties. It emphasis on the different proton exchange membranes.

Key words : *Component Parts of MFC, Energy, Proton Exchange Membrane, Renewable.*

Introduction

Energy demand is growing day by day. Energy can be generated from renewable and non-renewable source. The non-renewable sources create lot of pollution while generating energy for utilization and are limited and eventually may run out over the time frame. The deterioration of environment is being rapidly increased to meet rising demand for energy, accumulative population, rapid urbanization and industrialization. One of the more focused and under research area of energy source is Microbial Fuel Cell (MFC) technology. The MFC approach has acknowledged considerable interest in the present because of its uniqueness to accomplish energy and waste water treatment (Logan and Rabaey, 2012).

The microorganisms or enzymes would be recycled as a catalyst in electrochemical reactions opens up several potential applications for this technology. The MFCs could have applications in the areas such as energy recovery and wastewater treatment and (Erable *et al.*, 2010; Liu *et al.*, 2004) energy generation from biomass (Rittmann, 2008; Strik *et al.*, 2008; Venkata *et al.*, 2008) onsite power generation in distant regions and power supply for sensors utilizing local biodegradable fuels (Fan *et al.*, 2007) biosensors for the discovery of numerous oxidizable compounds (Karube, 1985) bacterial food contamination rapid estimation (Patchett *et al.*, 1988) in finding of microbial cell population in contaminated water streams (Maoyu and Zhang, 1989); bio-hydrogen production (Chae *et al.*, 2008) and petroleum contaminants bioremediation in the groundwater (Morris and Jin, 2008).

This review paper is about the component parts of MFC, working principle of MFC, PEM and the properties of the same and application of the MFC. It mainly highlights on the different proton exchange membranes.

Working Principle of MFC

The proto type illustration of dual chamber MFC is represented in Fig.1. Microbial fuel cell has two chambers as aerobic and anaerobic. An electrode in the aerobic chamber is positively charged, with oxygen supply where reduction occurs. The anaerobic chamber comprises of anode electrode, substrate (organic material) and the bacteria. The anaerobic chamber is lacking of oxygen, permitting a negatively charged electrode performing as the electron receptor in bacterial processes A membrane separates the aerobic and anaerobic chambers such that oxygen cannot enter the anaerobic chamber but hydrogen ions (H^+) may. The organic matter is decomposed by bacteria on anode to free H^+ ions and electrons. From the anode, electrons go along a wire and then onto the cathode. The semipermeable membrane allows the H+ ions to go to the cathode. The electrons flowing towards the cathode associate with dissolved oxygen and the H^+ ions to formulate pure H_2O. Anaerobic chamber is supplied with solution or waste water holding food for the bacteria. This food rich source of acetate, glucose or compounds ordinarily found in food waste and sewage. Food supplied to bacteria would be metabolized by first fragmenting apart the molecules of food into hydrogen ions, carbon dioxide and electrons. The following is an example of an oxidation process that occurs in the anodic compartment and is carried out by electrochemically active bacteria utilizing acetate as a fuel source: (Logan *et al.,* 2006).

Anodic reaction

$$CH_3COO - + 4H_2O \rightarrow 2HCO_3 - + 9H + + 8e^- \quad .. (1)$$

After the proton has diffused through the PEM to the cathode, it may interact with any oxygen there to produce water through the subsequent oxygen reduction process (ORR), which is best described as (Oh and Logan, 2006)

$$O_2 + 4H + + 4e - \rightarrow 2H_2O \quad .. (2)$$

MFCs depend on the actions of microbes that can use cytochromes to transmit electrons straight to an anode. A device must be able to have its fuel source, which is oxidized at the substrate-anode interface (e.g., wastewater), refilled either periodically or constantly in order to be classified as an MFC; otherwise, the system is known as a biobattery (Logan *et al.*, 2006). MFCs are typically run as closed-system devices, with the anodic compartment maintained in an anaerobic environment. The development of essential anaerobic bacteria capable of electron transfer such as Geobacter. Sulfur reducens require an anaerobic environment (Pant *et al.,* 2012).

The performance of MFC can be outlined by the power density, electric current generated and the electric efficiency which are dependent on many parameters. MFC is complex system of multidisciplinary subjects and would require many experts from various fields to optimize its full potential.Microorganisms, substrates that can be used as sources of electron donors, required to operate conditions in terms of pH, temperature, electrode surface area, and material and construction of the anode, cathode, and membrane could all have a significant influence on the electricity generation when it comes to MFC performance and energy production in wastewater treatment (Aghababaie *et al.*, 2015).

About Components of MFC

The basic design of most of dual chamber MFC is as presented in Fig. 1. which consists of anode and cathode compartments. The assembly of microbial fuel cell comprises of component parts as electrodes-anode and cathode, substrate, air sparger, electrical circuitand proton exchange membrane.

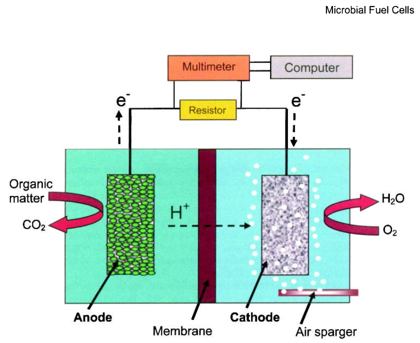

Fig. 1. Basic Microbial Fuel Cell Components in a Diagram (Logan and Rabaey, 2012)

Electrode

The transport of electrons over an exterior circuit is facilitated via electrodes, resulting in electricity. The electrode materials required to be studied commencing the energy production perspective and to optimize the removal efficiency of pollutants. Any non-corrosive substance may be used to create it. e.g. carbon, graphite, platinum, steel etc. Electrode material should have properties such aselectrical conductivity, bio-compatible, chemically stability, highly suitable of its mechanical strength and smallcharge for being viable. The best electrode material for MFC performance in terms of bacterial adhesion, electron transfer rate, and electrochemical efficiency. In order to use MFC technology in real-world applications, materials costs must be brought down and power densities must also be increased. The cathode material need to exhibit oxygen reduction catalytic characteristics (Mustakeem, 2015).

Fig. 2 presents the base materials that are most often used for all types of electrodes.

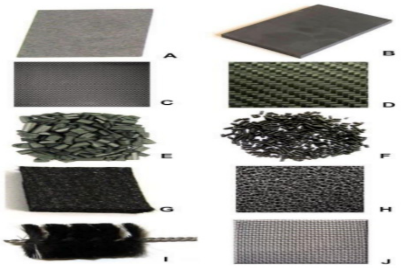

Fig. 2. Base electrode materials A) carbon paper, B) graphite plate, C) carbon cloth, D) carbon mesh, E) granular graphite, F) granular activated carbon, G) carbon felt, H) reticulated vitrified carbon, I) carbon brush, J) stainless steel mesh (Wei *et al.* 2011).

Substrate

Matter that has to be oxidized is called a substrate and is housed in the anode chamber. Any type of organic material can serve as a substrate. It is essential for establishing the generation of electricity since it is an electron donor. In addition to providing the bacterial cells in MFCs with energy to develop, the substrate also affects the MFCs' general performance, including their power density and coulombic efficiency. The microbial community and power generation are also impacted by the composition, concentration, and type of the substrate, as indicated in Table 2. Various other substrates used are cellulose particles, corn stover biomass, ethanol, lactate, landfill leachate, phenol, starch, sucrose. Brewery wastewater, paper recycling wastewater, swine wastewater, chocolate industry wastewater, dairy industry wastewater was used as substrate.

Air Sparger

Air is required to be supplied in aerobic chamber

Table 2. Dissimilar categories of substrates and their current densities (Pant *et al*., 2010)

Substrate	Concentration	Current Density (mA/cm^2)
Acetate	1.1 g/l	0.9
Lactate	19 mM	0.0061
Glucose	6.8 mM	0.8
Sucrose	276 mg/l	0.20
Phenol	500 mg/l	0.12
Starch	11 g/l	1.45
Cellulose particles	5 g/l	0.09
Xylose	7.6 mM	0.78
Domestic wastewater	800 mg/l	0.09
Brewery wastewater	2250 mg/l	0.3

Table 1. Basic components of microbial fuel cell

Item	Materials	Remark
Anode	Graphite, graphite felt, carbon paper, carbon cloth, carbon brush, Pt, Pt black, reticulated vitreous carbon (RVC)	Essential
Cathode	Graphite, graphite felt, carbon paper, carbon cloth, Pt, Pt black, RVC	Essential
Anodic chamber	Glass, polycarbonate, Plexiglass	Essential
Cathodic chamber	Glass, polycarbonate, Plexiglass	Non-compulsory
Proton exchange system	Nafion, Uitrex, poly(styrene -co-divinylbenzene), salt bridge, porcelain septum or solely electrolyte, polyvinyl alcohol (PVA), PVA-Nafion, Ceramic separators, Activated carbon coconut shell (ACCS) clay membrane, selemion	Essential
Electron catalyst	Pt, Pt black, MnO_2, Fe^{3+}, polyaniline, electron mediator immobilized on anode	Optional

continuously to maintain aerobic condition. Air supply means such as air sparger or aerator which are used in fish tank can serves the purpose.

Electrical Circuit

The electrons are liberated as hydrogen from the anode electrode changes into hydrogen ions. The electrical current is created as these electrons go through the circuit and toward the cathode. Electrons leave the anode and go across the circuit. These electrons contribute to the load's power.

Proton Exchange Membrane

The proton exchange membrane is the main element of the MFC. PEM is used in MFC systems to separate the anode and cathode compartments. PEM should be inexpensive, have a high proton conductivity, a low electrical conductivity, a low internal resistance, strong mechanical stability, chemical and thermal stability, and the capacity to withstand prolonged inactivity without harming MFC. All of these qualities cannot exist in a single substance. Nafion is the PEM that is most frequently used, however it is not economical. Ultrex CMI-7000, an alternative to Nafion that works well for MFC applications and is significantly less expensive.

Apart from these commercial membranes, research is focused on synthesized membrane which can be a substitute for commercial costly membrane. Commercialization of MFC technology would be possible only then onwards. Pilot projects are going on for the same. PEM is discussed in detail in subsequent section.

MFC Configurations

Depending on the objectives of the investigation, we may envision a wide range of appropriate structures for laboratory studies. For MFCs to be used in practical applications, the design must not only provide high power and coulombic efficiency but also be inexpensive to mass produce due to the availability of inexpensive materials and a workable production technique. MFCs come in a variety of structural forms, including single-, two-chamber designs, stacked MFC, up flow MFC and with or without the use of PEM. The design of MFC is continually being developed and improved upon in order to make it a viable technology. The proper design of MFCs is a fundamental need.MFCs are built according to a range of architectural requirements and various kinds of MFCs are usually appraised by power output, coulombic efficiency, stability and longevity (Prakash, 2016).

Proton Exchange Membrane (PEM)

Anodic and cathodic chambers are physically separated using a separator called a PEM or Cation Exchange Membrane (CEM). It is possible for the anode's generated protons to go through the solution and across the PEM. This is a crucial component of MFC systems since it affects internal resistance and concentration polarisation loss, both of which have an impact on the MFC's production of power. The Grotthus mechanism and the vehicular mechanism are the two major proton hopping processes. According to the Grotthus mechanism, excess protons are transported via hydrogen bonds by neutral H_2O molecules, whereas the surplus protons are transported by vehicles (like H_2O) as complex ions (H_3O^+) in the vehicular process.A totally porous membrane cannot be used in a fuel cell since a higher mass transfer rate would interfere with the system's ability to operate as a whole. Nonporous membranes are therefore advised in fuel cell operations to limit substrate loss from the anode to cathode compartment and to reduce oxygen diffusivity from cathode to anode compartment (Kumar *et al.*, 2018). Due to its extremely selective protons' permeability, Nafion (a product of DuPont, USA) is the PEM that is most frequently utilized. Today, there is increased emphasis on the synthesis of PEM that is both economical and energy-efficient. Numerous researchers have created synthetic versions of the materials Hyflon, Zirfon, Selemion, SPEEK (Sulfonated Polyether Ether Ketone), GO-SPEEK (Graphene Oxide/SPEEK), Nafion-PVA-borosilicate, PVA-Nafion Sulfonated Polyethersulfone (SPES), ceramic separators, Activated Carbon Coconut Shell (ACCS) clay membrane (GA). Nafion is still the best option even if researchers are working for a less priced and more robust membrane material alternative. The Nafion membrane is not appropriate for large-scale BES because of its high cost. Ultrex CMI 7000 is another another popular CEM (Membranes Inc., USA). Strong acid polymer membrane CMI 7000 has cross-links made of gel polystyrene and divinyl benzene, as well as a significant number of sulphonic acid groups. Ultrex CMI-7000, a cost-effective CEM that contains the sulphonic acid (SO_3H) group, has the potential to be a good substitute for nafion PEM. It has a high ohmic resistance yet displays comparable cation conductivity and mechanical toughness to Nafion. A short-side-chain perfluoropolymer membrane called Hyflon has a greater conductivity and better chemical stability than Nafion. Compared to Nafion, it had a greater internal resistance. Zirfon has substantially lower specific resistance than Nafion, but anodic reactions suffer from its increased oxygen permeability. The insufficient proton transfer capacity is the main restriction. Under neutral circumstances, they transport other cations (such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH^{+4}) rather than proton because their concentrations are larger. Other cation transport often results in pH splitting in MFCs (an increase in cathodic chamber pH and a drop in anodic chamber pH), which has a variety of knock-on effects. Japanese company Asahi Glass Co. has designed and produced a PEM of the hydrocarbon kind called Selemion. As Selemion offers lower internal resistance, lower oxygen permeability, and a cheaper price than Nafion 117, it has been shown to be an appropriate substitute.

To increase proton conductivity, the polyether ether ketone (PEEK) membrane is sulphonated, and SPEEK is the end result. Their research demonstrated improved power output and decreased substrate loss during MFC operation, as well as an order of magnitude lower oxygen permeability of SPEEK than Nafion 117. A self-fabricated sulfonated polyether ether ketone (SPEEK) is used to construct a composite proton exchange membrane using graphene oxide/SPEEK (GO-SPEEK).

The MFC with GO-SPEEK membrane produces a high efficiency and comparable maximum power density, indicating that GO-SPEEK membrane is a viable replacement membrane for the pricey Nafion® 117 as a separator in the MFC. The potential use of Nafion-PVA-borosilicate and PVA-Nafion borosilicate membranes as a low-cost, practical separator in MFCs was investigated through their fabrication, characterization, and testing in MFCs. When Nafion solution is added to PVA, oxygen diffusion is decreased. The performance was increased because it facilitated proton transport over the borosilicate membrane. When compared to MFC utilizing Nafion 117, the power density produced using PVA-Nafion borosilicate was found to be somewhat lower (4.41%). In the case of the PVA-Nafion borosilicate membrane, hydrogen bonding and electrostatic forces should be regarded as the major interactions between the constituents. The PVA-Nafion borosilicate membrane's performance in the MFC shown that it can be an effective, low-cost, and simple-to-synthesize substitute for Nafion 117 membrane.

In this work, four high-performance blended polyethersulfone and sulfonated polyethersulfone proton exchange membranes were created using the wet phase inversion approach and their efficacy was compared to Nafion 117 in a dual chamber MFC. The SPES membrane has the potential to increase the productivity of MFCs, as evidenced by a few attributes such as minimal biofouling, low oxygen permeability, high power production, high COD elimination, and coulombic efficiency.

By employing the solution casting process and the somewhat less expensive material polyvinyl chloride with various quantities of silica (SiO_2), citric acid, and phosphotungstic acid (PWA), a new proton exchange membrane was created. Investigations are conducted into a number of membrane features, including surface shape, water absorption capability, ion exchange capacity (IEC), tensile strength, leaching test, and prospective uses in MFCs. The research leads to the creation of membranes with readily available, inexpensive materials, which lowers costs.

In order to make microbial fuel cell (MFC) technology more widely available, high-performing, affordable, and environmentally friendly separators are being created. One of the possible substitute materials for this is ceramic. To find out how the performance of ceramic separators was affected by the characteristics of the ceramic material, three different varieties of clay were utilised to create separators with the same thickness of 3 mm. In place of the Nafion 117 membrane separator, a low-cost proton exchange membrane separator made with activated carbon from coconut shells and clay for use in MFC has been developed. It is hypothesized that the enhanced proton transfer for this cast membrane is due to the presence of effective hygroscopic oxides like SiO_2, TiO_2, Al_2O_3, $Al_2(SO_4)^3$, and Al 2SiO5 in the clay and the highly porous and superior specific surface area of AC that helped in retaining bound water for proton hopping. In comparison to Nafion 117 membrane, the cast ACCS/clay membrane displayed attributes such as a two-fold increase in ion exchange capacity, a decrease in charge transfer resistance, a reduction in oxygen diffusion coefficient, and a modest increase in proton diffusion coefficient.

A Nafion alternative membrane is made from

Table 5. Different synthesized and commercially available PEMs used in MFC

Material used for PEM	MFC configuration	Max. power density	Reference
Sulfonated polystyrene –ethylene-butylene-polystyrene (SPSEBS)	Single chamber MFC	590mWm^{-2}	(Ayyaru *et al*., 2012)
Custom made ceramic separator –white ceramic based with brown spot membrane white ceramic based with red spot membrane Red ceramic separator	Single material ceramic cylinder	71.8 W.m^{-3} 71.5W.m^{-3} 67.1W.m^{-3}	(You *et al*., 2019)
Porcelain septum made from kaolin	Single chamber air cathode MFC	788 mWm^{-2}	(Park and Zeikus, 2003)
Terracotta pot	Single chamber air cathode MFC	33.13 mWm^{-2}	(Ajayi and Weigele, 2012)
Pyrophylite	Single chamber air cathode MFC	6.93 W.m^{-3}	(Pasternak, 2016)
Polyethersulfone (PES) / SPES (sulfonated polyethersulfone) blend proton exchange membrane Nafion	Dual chamber MFC	58.726 mWm^{-2} 45.512 mWm^{-2}	(Zinadinia, 2017)
PVA –borosilicate (MP) PVA – Nafion–borosilicate (MPN) Nafion	Dual chamber MFC	2.7 W.m^{-3} 6.8W.m^{-3} 7.1 W.m^{-3}	(Tiwari *et al*., 2016)
Graphene oxide/SPEEK (GO/SPEEK) Self-fabricated sulfonated polyether ether ketone (SPEEK) Nafion	Dual chamber MFC	902 mWm^{-2} 812 mWm^{-2} 1013 mWm^{-2}	(Leong *et al*., 2015)
Polyvinyl chloride (PVC)	Dual chamber MFC	43.91 mWm^{-2}	(Kumar *et al*., 2019)
Poly (vinyl alcohol) glutaraldehyde (PVA-GA)	Dual chamber MFC	158.28 mWm^{-2}	(Das *et al*., 2021)
Clay and activated carbon derivative from coconut shell	Dual chamber MFC	3.7 Wm^{3}	(Neethua *et al*., 2019)
Earthen pot	Dual chamber MFC	48.64 mWm^{-2}	(Behera *et al*., 2010)
Red soil with montmorillonite	Dual chamber MFC	7.55Wm^{-3}	(Ghadge and Ghangrekar, 2015)
Mfensi clay	Dual chamber MFC	78 mWm^{-2}	(Tamakloe, 2015)
Natural Clay and geothite	Dual chamber MFC		(Das *et al*., 2020)
Polyvinyl alcohol (PVA) polymer membrane crosslinked with sulfosuccinic acid (SSA)	Cubic-shape, air cathode reactors with cylindrical chamber	759 ± 4 mWm^{-2}	(Hou *et al*., 2014)
Polyvinyl alcohol (PVA) chitosan (CS) composite PVA : CS	H type MFC	5.7 mWm^{-2} 11.5 mWm^{-2} 20.8 mWm^{-2}	(Gonzalez-Pabon *et al*., 2019)

poly (vinyl alcohol) (PVA) that has been crosslinked with glutaraldehyde (GA). In order to make MFC technology more affordable and effective, low-cost membrane that is made from unrefined raw materials including clays, zeolite, apatite, waste products like fly ash, rice husk ash, and cement is now more frequently produced.

Challenges

It is necessary to go over a number of obstacles in order to acquire the long-term steady performance from MFC, such as lowering the cost of electrodes, PEM, and catalysts without sacrificing operating efficiency. For the modification of the MFC design, low-cost ceramic material from a nearby source is used. machine learning-based strategies for composition and processing optimization. To get beyond the obstacles presented by the expansion of MFC technology.

Conclusion

World is facing problems like global warming and climate change. The use of carbon-based fuel sources has to be reduced and there is necessity to think of renewable sources of energy generation. To tackle the energy problem in future, there is need of sustainable and clean development of energy. Microbial Fuel Cell technology can serve this purpose if developed economically for harvesting more energy. MFC not only generates electricity but the source for energy generation is waste, which makes it more special compared to the traditional energy sources. Proton exchange membranes and electrodes used in MFCs increases the capital cost of MFC's and hence are required to be replaced with low-cost materials which would be easily available. Efforts are required for commercialization of MFC for large scale use. In attempt to use MFC technology in real-world applications, materials costs must be brought down and power densities must be increased.

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