

Microbial fuel cells: recent developments in design and materials

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Abstract:

Microbial Fuel Cells (MFCs) are the promising devices which can produce electricity by anaerobic fermentation of organic/ inorganic matter from easily metabolized biomass to complex wastewater using microbes as biocatalysts. MFC technology has been found as a potential technology for electricity generation and concomitant wastewater treatment. However, the high cost of the components and low efficiency are barricading the commercialization of MFC when compared with other energy generating systems. The performance of an MFC is largely relying on the reactor design and electrode materials. On the way to improve the efficiency of an MFC, tremendous exercises have been carried out to explore new electrode materials and reactor designs in recent decades. The current review is excogitated to amass the progress in design and electrode materials, which could bolster further investigations on MFCs to improve their performance, mitigate the cost and successful implementation of technology in field applications as well.

1. Introduction:

In the recent times, prodigious energy consumption has been reported in conjunction with the fleet growth of population. Energy sources available have been classified into fossil fuels, nuclear and renewable energy sources based on their mode of origin and reliability. Fossil and nuclear energy sources are considered as non-renewable, which includes major portion of energy being used. Unearthing and combusting fossil fuels add CO₂ that had been trapped underneath the layers of earth some years ago to the atmosphere, thereby, contributing majorly to the global warming and environmental pollution [1]. To overcome the energy crisis and threats associated with fossil fuels, countries from all around the world are with keen eye to find alternate renewable energy sources. One of the outcomes of such efforts is Fuel cell technology, generates electricity with the use of precious metal catalysts. Fuel cell technology has plenty of advantageous over the other energy generating methods such as devoid of harmful inorganic oxides generation (CO₂, SO_x, NO_x and CO), higher efficiency and so on. However, high material and operational costs are the major disadvantages drawing back the fuel cell technology to commercialize [2].

On the other side, providing adequate potable water to the rapidly growing world's population is becoming an unmanageable task day by day. The problem of water pollution is being increased in pace with the urban population growth rate. It will lead to hazardous health issues of the public, if unchecked. However, low economic countries should spend a major fraction of its capital in order to provide clean



water and sanitation. Even though the economically forward countries can offer the clean water, but disbursing a significant number on the wastewater treatment [3]. For example, United States is expending 3-4% of its electrical energy for wastewater treatment, which is equal to the annual consumption by 9.6 million homes. United Kingdom is spending approximately 1% of the England and Wales's average electricity consumption per day on the waste water treatment [4]. On analyzing the statistics of energy associated with wastewater and energy required for wastewater treatment, it is revealed that based on the quality and process adopted, wastewater requires approximately 0.5-2kWh/m³ of electrical energy. At the same time, wastewater contains energy 3-10 times to that required for its treatment [5]. The energy associated with wastewater is majorly available in three forms such as degradable organic matter, heat energy and nutritional elemental energy (N₂, P etc). Approximately 26% of the chemical energy is attributed by carbon, measured as COD and other nutrients [4]. Even though extracting heat energy from wastewater is tedious and economically hardly tenable process, by harvesting the chemical energy trapped in the wastewater, treatment of wastewater can become a net positive energy (energy generating) process instead of energy consuming one and also an optable method that is devoid of environmental pollution [6].

In major parts of the world, currently practicing wastewater treatment methods are designed in relation with conventional activated sludge process. Albeit activated sludge process is well established, quick processing method resulting in excellent outputs in wastewater treatment, still it is an energy intensive process. On the other side, activated sludge process involves the addition of chemical compounds, which accounts for major capital as well as resulting in added contaminants to the water. According to a report by US Environmental Protection Agency in 2008, more or less 75% of the total energy cost of a wastewater treatment plant is being spent on the aeration process alone during activated sludge process. Moreover, United States is incurring about \$300 and \$25 billion on public plants and domestic water treatment works respectively per year [4]. It has also been estimated that a typical domestic wastewater treatment plant requires 0.6kWh of energy/m³ of water treated, of which around 50% is dropped in the form of electrical energy to supply air to aerobic and anaerobic systems [4,7].

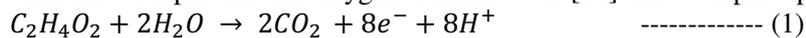
Generally, energy from wastewater is recovered through anaerobic digestion of organic matter in the form of sludges obtained from primary and secondary treatments. In anaerobic digestion, the organic carbon is transformed into energy rich methane gas. It involves a series of complex reactions where fats are primarily hydrolyzed into sugars, amino acids and fatty acids, which are further digested into short chain, volatile fatty acids and hydrogen through acetogenesis and acidogenesis processes. Terminally, the resultant intermediates are converted in to methane (methanogenesis) and CO₂ [8]. By means of conventional treatment methods for organic pollutant degradation, large quantity of CO₂ is added to the environment. Approximately, for every 1,000 tons of wastewater treated, 15,000 tons of CO₂ is being released in to the atmosphere [5]. To overcome the constraints associated with existing wastewater treatment methods, research and development is to be focused towards the development of potential, economically viable and environmentally amicable treatment methods.

2. Microbial Fuel Cells (MFCs):

Bio electrochemical systems (BESs) are the biological systems that could convert chemical energy of organic matter ranging from complex lignocellulosic biomass to low strength wastewater into electrical energy, hydrogen or other valuable products. Comparatively, BESs can efficiently work under mild conditions and are capable of utilizing a wide range of substrates without the use of precious metal catalysts unlike its peers such as conventional fuel cells. Based on the type of biocatalyst used, BESs are classified majorly into two classes, i) Microbial fuel cells (MFCs) and ii) Enzymatic Fuel Cells (EFCs). Depending on the application, BESs can be further classified into, i) Microbial fuel cells (MFCs), ii) Microbial Electrochemical Cells (MECs), iii) Microbial Desalination Cells (MDCs) and iv) Microbial

Solar Cells (MSCs) [9]. M.C.Potter in 1991 discovered through his experiments that a certain bacteria can release electrons extracellularly (exoelectrogens) on degrading organic matter. Later, it has been inferred that breaking down of organic matter by the microorganisms accompanies generation of electrical energy. Development of such electron releasing microorganisms' biofilm facilitates renewable bioelectricity generation as well as removal of organic carbon simultaneously from waste water through a defined BES, called Microbial Fuel Cell technology [9].

MFC is a compact reactor which can generate electricity spontaneously from the biomass through metabolic activity (anaerobic oxidation) of microorganisms. MFCs are found to be the potential devices to harvest bioenergy from the wastewater and concomitantly clean the wastewater, thereby, reducing the operational costs expending on the treatment of wastewater by conventional methods [10]. A simple MFC set up consists of an anode in anodic chamber, a cathode in cathodic chamber, separated by a proton exchange membrane (PEM). MFC operates on a principle that biocatalysts oxidize organic substrates in the anodic chamber and releases protons and electrons in the process along with the generation of CO₂. Anode garners the electrons and passes them to the cathode through external circuit with simultaneous movement of protons from anode chamber to cathode chamber via PEM. At the cathode, the electrons combine with protons and oxygen to form water [11]. The complete process can be represented as [1],



Electricity generated from wastewater through MFCs is pristine and can be used directly. It doesn't require further purification, separation or other conversion processes unlike hydrogen and methane produced from anaerobic digestion process which cannot be used directly. MFC technology is environmentally benign as they can operate at ambient conditions and produces pollution free energy [4]. Even though CO₂ is produced as one of the end products of microbial oxidation, it is considered as carbon neutral process as the substrates consumes CO₂ during their life cycle by photosynthesis [1]. MFC can produce 1.43kWh/m³ to 1.8kWh/m³ of energy depending on the strength of the effluent. However, consumes only 0.024kW, which is roughly one order of magnitude less than what is consumed through anaerobic digestion process (~0.3kW). It can be inferred from the numerals that MFC requires approximately 10% of the energy for their operation compared to activated sludge process, exhibiting greater potentiality towards economical wastewater treatment and renewable energy generation [4]. Despite the fact that MFC technology can efficiently treat wastewater with concomitant energy generation, it is still facing the challenges to move out of the boundaries of lab for field applications or commercialization. A number of factors such cost of the electrode materials, requirement of precious metal catalysts, low performance, low power densities and costly PEMs are limiting MFC technology in direct field applications. Even though these issues can be addressed at lab scale, ultimately pilot scale studies are necessary for analyzing the performance and longevity of materials at large scale especially when dealing with wastewater which doesn't possess constant conditions (composition, temperature etc) with time [12]. A sundry of studies have been reported in recent decades focusing majorly on the reduction of cost of the electrode materials and the configuration of MFCs to maximize current densities. The present review is an attempt to address the recent advancements MFCs design and electrode materials.

3. Developments in design of MFCs:

The performance of an MFC largely depends on the materials by which it is made rather than biocatalysts activity alone. As discussed before, electricity production in an MFC is a multistep process involving, a) microbial catabolism of organic matter, b) electron capture by the anode, c) electron acceptors reduction at cathode and d) simultaneous proton movement from anode to cathode via PEM. All

these processes govern the performance and efficiency of an MFC, a number of studies have been reported addressing the issues associated with these processes. Besides these, overall performance of MFC is also influenced by reactor configuration [13].

Initially, two chamber MFC was designed as a basic model. A typical two chamber MFC consists of an anode chamber, a cathode chamber separated by a PEM as shown in Figure 1 [14].

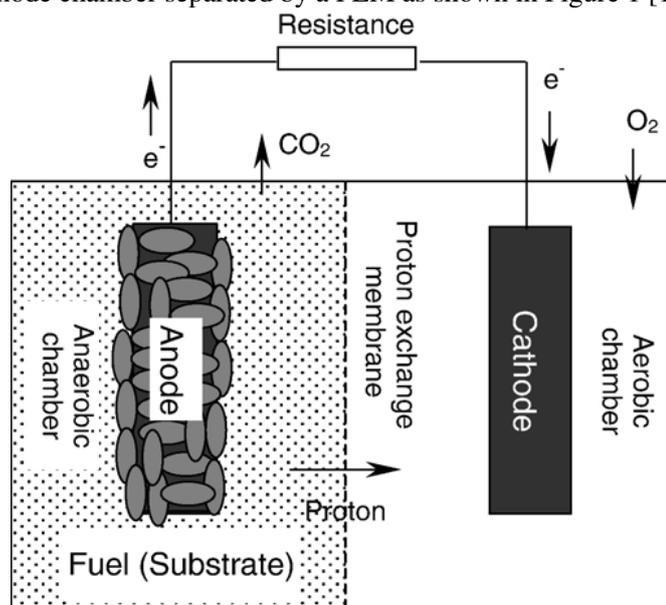


Figure 1. Diagrammatic representation of a typical two chamber MFC [14].

Anaerobic oxidation of organic matter occurs in the anodic chamber using microbes and oxygen reduction (most common) takes place in the cathode chamber. Two chamber MFCs are basic reactors generally being used to study the electrode materials, microbial activity and optimization of parameters. This basic design cannot reduce the energy costs of wastewater treatment as it requires continuous sparging of air to the cathode chamber, which is an energy consuming process [3]. In MFCs, on increasing the reactor volume, the ratio of surface area to volume decreases, thereby influencing the reactions at electrode surface. Hence, implication of bench scale designs at field applications (large scale) will inevitably result in reduced power densities and performance. It is widely acknowledged that the reduced power densities are due to over potentials and energy losses with increased size. Therefore, developments in reactor designs could bolster the practical applications of MFCs in waste water treatment [3]. Later, a single chamber MFC was configured based on the studies on hydrogen fuel cells by Lui, suggesting that direct bonding of cathode to PEM will allow direct interaction of oxygen from air with the cathode. Single chamber MFC consists of an anode chamber, a gas diffusion layer, which separates cathode from anode chamber and also allows passive transportation of oxygen to the cathode. This design eliminates energy consuming aeration step unlike two chambered MFC [15].

Later, a single chambered tubular MFC was developed with granular graphite as anode material and ferricyanide as catholyte for continuous flow operations as shown in Figure 2 [16]. Maximal power outputs of $90W/m^3$ and $60W/m^3$ (net anodic compartment) were obtained with acetate and glucose respectively. The reactor could generate $48W/m^3$ (net anodic compartment) of power density with domestic wastewater and was capable of showing around 96% of Coulombic efficiency with wastewater. It was inferred from the results that the reported design can be used for the treatment of waste streams which contain significant concentrations of volatile acids such as back waters from anaerobic digesters.

However, on considering the power outputs, the setup costs roughly \$900/1W installation capacity, which is 1000 orders of magnitude higher than that of other electricity generating systems (wind mills) [16].

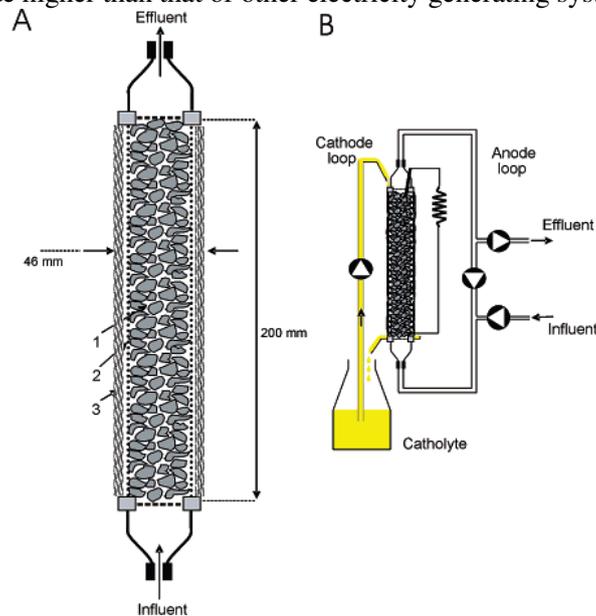


Figure 2. Tubular MFC showing anode, cathode, membrane (A) and overall setup (B) [16].

A pilot scale study was carried out to analyze the performance of an MFC with multi anode/cathode configuration towards solids removal, removal of nutrients, COD, BOD and cathode fouling using domestic wastewater as anodic fuel. The reactor with 12 anodes/cathodes was capable of generating 380mW/m^2 (at the loading rate of $0.19\text{-}0.66\text{kg/m}^3/\text{day}$) of power density and removed 80% of contaminants (at 8h hydraulic retention time). In spite of cathodic fouling due to the deposition of Ca and Na, appreciable performance was observed with metal doped MnO_2 (Co-MnO_2 , Cu-MnO_2) cathodes than Platinum based cathodes [17]. In an attempt to design the MFC more compactly, Yang Q, et al [18] have used spacers to reduce the size of the MFC reactor without sacrificing the performance. With the use of 1.5mm plastic expanded spacer, the firm could produce $973\pm 26\text{mW/m}^2$, which was similar to the results obtained without the use of spacers. It was also reported that reducing the thickness of the spacer to 1.3mm resulted in reduced power densities due to the leakage of oxygen into the reactor. The firm has concluded that the use of spacers can maintain pressure driven airflow, thereby reducing the reactor volume as well as cost. In approaching the ways to develop scalable MFCs, Ahn Y and Logan B E [19] have developed a single chamber MFC with graphite fiber brush multi anodes and an air cathode. To minimize the electrode spacing to a greater extent, the bioanode and air cathode were associated to a separator on either side, termed as Separator Electrode Assembly (SEA). The group was successful in achieving $0.20\pm 0.04\text{V}$ within 8h of hydraulic retention time and highest Coulombic efficiency of 85% with the designed reactor under continuous flow condition. It was also demonstrated that this multi electrode design can facilitate constant current and power generations under continuous mode of operation. In later years, a hybrid MFC was fabricated by combining with membrane bioreactor (MFC-MBR) for concomitant wastewater treatment and ultrafiltration, which results in directly utilizable clean water. The MFC-MBR system is shown in Figure 3 [20].

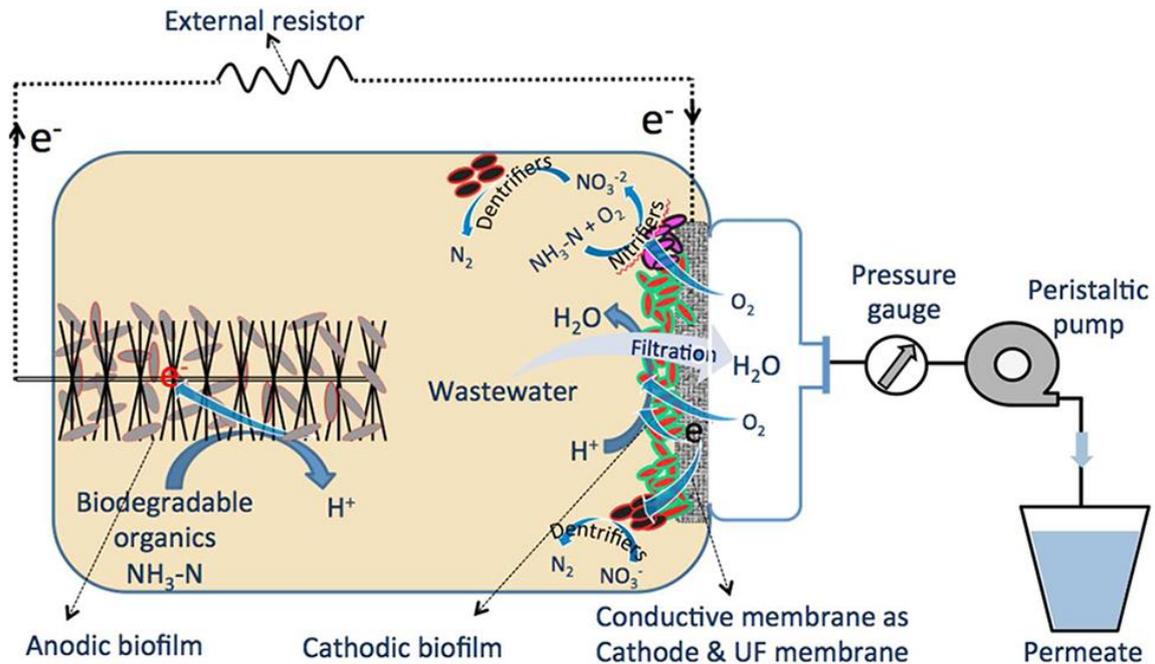


Figure 3. Schematic representation of MFC-MBR [20]

Conductive ultrafiltration membrane used in the design has performed both the functions of cathode and membrane. The reactor could successfully remove 97% of COD, 91% of total bacteria and 97% of Ammonia and nitrogen when 0.1mm domestic wastewater (prefiltered) was used. It has been concluded from the results that wastewater treatment can be achieved at the expense of low energy through MFC-MBR reactor [20]. In another study by Ren L, et al [21], a two stage MFC adjoined anaerobic fluidized bed membrane reactor (MFC-AFMBR) of lab scale capacity was developed to address the issue of quality water from domestic wastewater at minimal energy inputs. The reactor system was run continuously for 50 days using domestic wastewater (total COD $210 \pm 11 \text{ mg/L}$) at ambient temperature without any back washings of the membrane and total suspended solids were almost completely removed at a hydraulic retention time of 9h. From the outcomes of the study, the group has concluded that the MFC-AFMBR combined system can produce high quality water from the domestic primary effluents even at mild atmospheric conditions, thereby, reduces the cost of the water treatment process. A multi chamber MFC with four anode chambers and a cathode chamber separated by a membrane was constructed to overcome the longer times required for the treatment of large quantities of wastewater and at the same time sustained power generation even when any one of the cells failed to work. The MFC was fabricated in such a way that the four anodes and cathode chamber behave as individual cells connected in parallel as shown in Figure 4 [22]. A peak power density of 135.4 mW/m^2 was achieved with graphite electrode and potassium ferricyanide catholyte (100mM) using wastewater of concentration 8720 mgCOD/L . From the results, it was concluded that the design may be used for scale up to produce high power within a limited space [22].



Figure 4. Photograph of a multi chamber MFC fabricated by Samsudeen N et al [22]

In the process of anaerobic oxidation of organic matter by the biocatalysts, protons are released into the anolyte. Higher concentrations of protons in the anode chamber show negative effect on operational stability of a two chamber MFC. To transcend this problem, a hybrid MFC was developed by stacking a single chambered MFC with double chamber MFC as a self sustaining, P^H regulating stack of MFCs. On comparing with individual cells, the hybrid stack exhibited higher power outputs and higher conversion efficiencies with acetate [23].

4. Electrode materials:

In general, in an MFC, generation of electrons occur at anode through anaerobic oxidation of fuel by microbes and are transported through the external circuit to cathode, where reduction of oxidizing agent takes place. The co-occurrence of oxidation and reduction processes causes continuous flow of electrons, thereby generating electricity. Several factors such as configuration of electrode, electrode materials, membranes, mediators and the biocatalysts are believed to influence the performance of an MFC. Among all the factors listed out, electrode materials affect the performance to a greater extent as the fluctuations in electron transportation between microbes and electrodes would result in limited power productions [24]. The selection of materials for electrodes (base materials) is a crucial step where utmost care is to be taken to prevent the corrosion. For instance, copper seems to provide higher power densities when used as electrodes due to galvanic corrosion. On the other side, copper ions are found to possess antibacterial property. In the similar way, use of stainless steel electrodes depends on the percentage of chromium in the alloy [25]. Most widely used base materials for all type of electrodes are presented in Figure 5 [26].

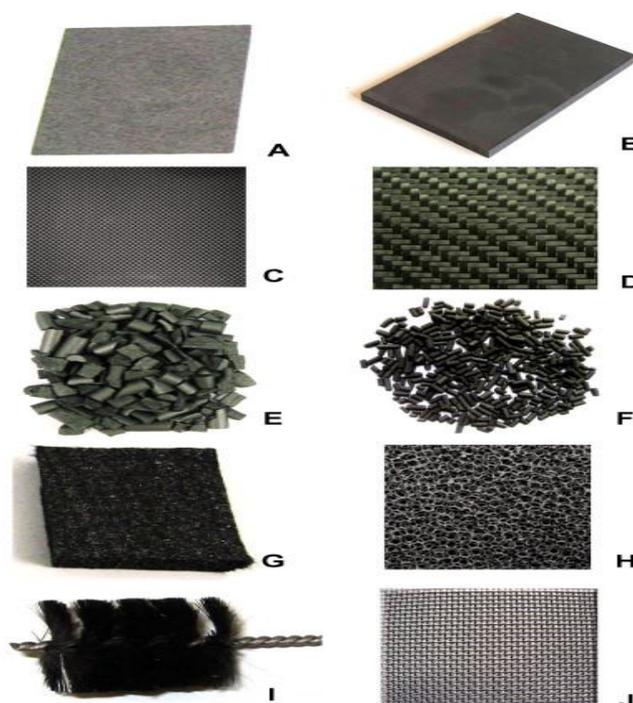


Figure 5. Photographs of base electrode materials, A) carbon paper, B) graphite plate, C) carbon cloth, D) carbon mesh, E) granular graphite, F) granular activated carbon, G) carbon felt, H), reticulated vitrified carbon, I) carbon brush, J) stainless steel mesh [26].

Performance of an MFC is also governed by various electrode parameters such as biocompatibility, active surface area, high conductivity, nature of electrode surface etc. Albeit an extensive research has been carried out on finding the materials for MFC, the urge for cheaper electrode materials is limiting the MFC technology from out of the lab implementation. In recent years, the focus of research has been spotted on to the electron collectors rather than electrodes that can accommodate maximum number of bacteria. In current scenario, metals capable of transferring electrons over longer distances are preferable. Though precious metal catalysts like platinum can improve the power generations, their application in large scales would result in unbearable material costs [27]. This review focuses on the progress in the development of cost effective electrode materials (anode/cathode) for MFCs.

4.1 Anode materials:

Efficiency of an MFC is predominantly decided by anode performance as it is a centre for crucial bioelectrochemical reactions as well as mediator of electron transport from exoelectrogens to electrode. Therefore, it is essential to concentrate on the anode materials and design. There are several anodic parameters such as surface area, chemical resistivity, longevity and electrical conductivity show significant impact on MFC performance [28].

Plenty of studies were carried out to improve the performance of MFCs within the limited expenditure through treating low cost basic electrode materials under different conditions. In an attempt to improve the performance of MFC, carbon cloth anodes were treated with phosphate buffer and ammonia gas. The treatment resulted in significant improvement in the performance by enhanced solution conductivity and surface charge of electrode. The cumulative effect of these two treatments caused raise in power

production by 48% when compared to MFC with an electrode devoid of the treatment. This novel approach achieved an increased power density of 1970mW/m^2 [29]. Further, a low cost carbon mesh was examined as anode material. Individually heat treated and high temperature ammonia gas treated carbon mesh anodes produced 922mW/m^2 and 1015mW/m^2 power densities respectively, which are greater than that obtained with untreated mesh (893mW/m^2) as well as ammonia gas treated expensive carbon cloth (988mW/m^2). The improvements in the power densities were found to be attributed to the increased N/C atomic ratio on the surface of the mesh electrodes. It has been deduced from the reports that the ammonia gas treated carbon mesh can be a potential competitor to the costly carbon cloth and paper electrodes [30]. Carbon fiber brushes were subjected to three different conditions: soaking in acid, heating and a combined process of both acid soaking and heating. Combined acid and heat treated carbon mesh anode has shown increased power production by 34%, which is greater than 25% and 7% to that of acid soaking and heat treated ones respectively. This novel method of combined acid soaking and heat treatment of anodes showed better performance than heat and ammonia gas treated carbon cloth anodes. Contrastingly, it has been concluded that the proposed approach would not be an adoptable method to develop cost effective MFC for practical applications as it involves energy intensive heat treatment and ammonia gas usage [31].

Surface modification of the anode materials also contribute to the boosted up performance of the MFCs. A carbon cloth was modified by coating with biologically reduced Palladium nanoparticles to develop a bifunctional anode. With this surface modified carbon cloth, MFC has shown improved power density and coulombic efficiencies by 14% and 31% respectively. The better performance could be due to the reduced charge transfer resistance by the biogenic palladium [32]. Mink J E, et al [33] have developed an anode of vertically grown multiwalled carbon nanotubes with nickel silicide. This fabricated electrode produced current density of 197mA/m^2 and power density of 392mW/m^3 in a micro-sized MFC of $1.25\mu\text{L}$ capacity. The results were comparatively higher than that achieved with a plain carbon cloth. It was claimed that the enhanced performance was attributed to increased surface to volume ratio for microbial adhesion, electron transfer and low resistance by the nickel silicide contacting material. It has been concluded that since the process does not involve any expensive materials to fabricate MFC, it can substantially reduce the associated costs. Carbon paper modified with multiwalled carbon nanotubes and polyethyleneimine through layer by layer assembled technique was used as anode in an MFC. The modification has brought about reduction in interfacial charge transfer through providing three dimensional network structure for bacterial adhesion. This modified anode was capable of producing 20% higher power densities than unmodified carbon cloth electrode [34]. Stainless steel meshes coated with heat treated and untreated goethites obtained from mining mud were used as anode materials in MFC applications. Higher powers and coulombic efficiencies were recorded with goethite catalyst based electrode than conventional stainless steel mesh electrode. The improved performance was due to reduced mass transfer losses and accelerated electron transfer between biocatalysts and electrode. Goethite being cheaper can provide the economically feasible electrode materials with acceptable power generations in MFC [35]. The use of carbon cloth or graphite granules as anodes in lab scale MFC even though showed better performances, still combating the challenges of scale up. Carbon cloth being expensive cannot be used in large scale systems. In the same way, well established lab scale configurations of carbon cloth would be difficult to use in large scales [36]. Similarly, graphite granules are vulnerable to clogging due to low porosities. Materials to be used in biofilm based bioreactors (MFCs) for wastewater treatment must have high structural strength and should be free from clogging since, they are to be in constant contact with the electron transfer. In addition, the material supports should be intact with the biofilm under any operational condition from open-flow to saturated flow systems. Hence, the use of such support materials is impractical. To overcome the clogging issues, Logan B E, et al [36] have configured a new anode with

high surface area graphite fiber brush bounded to a central core collecting material. The design has led to the development of a successful high conducting and high specific surface area anode which can be used for scale up MFC applications.

4.2 Cathode materials:

In MFC, cathode chamber is considered as a sink of electrons, in which oxygen is reduced to water. In cathode chamber, reduction of oxygen occurs at air, liquid and solid three phase interface. A typical MFC cathode is composed of an electrode support, catalyst and air diffusion layer. Electrode materials used for anode can also be used for cathode but a potential cathode should have the properties of high electric conductivity, high mechanical strength and effective catalytic nature. Most commonly, MFCs are being operated under neutral P^H and mild temperatures. At these conditions, the rate of oxygen reduction is very low, leading to increased over potentials and thereby limiting the performance of an MFC. For robust cathodic reactions in MFCs, the cathodic carbon based support materials must be amended with additional catalysts [37]. Platinum is most commonly used cathode catalyst due to its high efficiency towards oxygen reduction. The use of expensive metal catalysts as cathode materials in MFCs is constraining the practical applications of MFC technology. In addition to high cost, Platinum catalysts are more liable to fouling when used with low quality water [38]. Plenty of research efforts have been placed to reduce the cost of cathodic catalysts by finding cheaper alternatives to Platinum without sacrificing the performance. This review discusses about the cost effective cathode materials and their influence on MFC performance.

In one study, the carbon cloth was coated on one side with mixture of carbon powder and polytetrafluoroethylene base layer followed by several coatings of polytetrafluoroethylene as diffusion layer. The water facing side of the carbon cloth was coated with platinum catalyst. Thus fabricated carbon cloth was used as cathode in a single chamber MFC. The MFC has shown enhanced power densities (42%) and coulombic efficiencies (200%) when compared to carbon cloth with base layer alone. It has been reported that four coatings of polytetrafluoroethylene produced maximum power density as it can reduce the water losses through cathode [39]. Cathode catalysts made of metal porphyrines and pthalocyanines supported on Ketjenblack carbon were studied for their catalytic activity towards oxygen reduction in MFCs. Iron pthalocyanin based cathode has shown greater oxygen reduction rates at neutral P^H than Platinum catalyst in neutral P^H . On comparing the effect of carbon substrate, Ketjenblack carbon has reported better activity than Vulcan XC carbon due to higher surface area of Ketjenblack carbon. Maximum power density of 634mW/m^2 was achieved with Iron pthalocyanin - Ketjenblack carbon at neutral P^H , which is higher than that of expensive Platinum catalyst (593mW/m^2) at similar conditions. It has been deduced from the studies that the transition metal based macrocyclic catalysts are cheaper and can be successfully used in large scale MFCs for commercialization of the technology [40].

In an approach to develop cost effective alternate to Platinum catalyst, Zhang F, et al [41] have developed activated carbon air cathode. The cathode was fabricated by cold pressing activated carbon with polytetrafluoroethylene around a nickel mesh current collector. The firm has reported the maximum power density of 1220mW/m^2 with thus fabricated cathode, which is comparatively much higher than that obtained with platinum catalyst (1060mW/m^2). From the results, it was concluded by the group that activated carbon-metal mesh collector derived cathodes can be used as efficient and economically feasible air cathodes in MFCs. Another firm has reported that activated carbon-polytetrafluoroethylene air cathodes have shown improvements in power densities with the increase in activated carbon loading. This could be due to the reductions in Warburg impedance, contact resistance and charge transfer resistance with the activated carbon load. Despite of cathodes degradation over 1.5-5 months of usage, still these cathodes exhibited power densities comparable to Platinum based cathodes [42]. In a different study,

commercial activated carbons from different source materials were ammonia gas treated to improve the performance as oxygen reducing catalysts in MFCs at neutral P^H . Ammonia gas treated activated carbon catalysts have resulted better performances than untreated activated carbon because of the reduction in oxygen content and enhancement in nitrogen groups on the surface of the catalyst material [43]. To enhance the cathode catalytic activity of activated carbon, Xia X, et al [44] have developed an activated carbon – Iron ethylenediaminetetraacetic acid cathode with stainless steel mesh current collector. Thus developed cathode has exhibited significantly improved power density ($1580 \pm 80 \text{mW/m}^2$), which is ten percent greater than plain activated carbon cathode and also the power density is comparable to platinum catalyst based cathode. It was reported that the electrode is more durable than platinum cathodes. The enhanced performance of the carbon – Iron ethylenediaminetetraacetic acid cathode was found to be due to the active pyridine, quaternary nitrogen and iron groups. The study has reported that the catalytic activity of economically viable activated carbon cathodes will be improved by pyrolyzing activated carbon with Iron ethylenediaminetetraacetic acid. Later, Zhang X, et al [45] have blended activated carbon with carbon black to boost up the performance and longevity of activated carbon cathodes. It was reported that the maximum power density was reduced by 7% for the carbon black based cathode whereas, 61% reduction was reported with platinum catalyst after five months of continuous operation. Zuo Y and Logan B E [46] have examined the power densities of carbon cloth by changing the configurations (tube/flat). Initially use of a single carbon cloth tube resulted lower power density than flat carbon cloth electrode. It was noticed that with the increase in number of concentric tubes, the power density increased due to increase in the cathode surface area. The firm has obtained a power density of 83mW/m^3 with two carbon cloth tubes as cathode. It was also reported that on wrapping the cathode around anode like a tubular MFC, power density increased to 128mW/m^3 . Finally, from the analysis of the results, it has been concluded that geometry of cathode either tube or flat will not affect the power density. The power density is a dependent factor of cathode surface area rather than geometry.

Generally, major costs of MFC cathodes are ascribed by catalysts and catalyst binders. Packed bed air cathodes were developed with four carbon based materials (granular activated carbon, granular semi coke, carbon felt cubes and granular graphite) and the fabrication was devoid of expensive binders and catalysts. Granular activated carbon based packed bed air cathode has shown highest power density of $676 \pm 93 \text{mW/m}^2$ and lowest was reported with carbon felt based cathode ($60 \pm 43 \text{mW/m}^2$). It was observed that on increasing the amount of granular activated carbon and semi coke with an intention to increase the surface area, power generation was significantly dropped. Thicker layers of carbon materials limited the diffusion of oxygen, thereby reducing the oxygen reduction rate. From the reports it was deduced that packed bed air cathodes of granular activated carbon and granular semi coke can be used as potential cost effective alternates to platinum air cathodes [47]. Mesoporous nitrogen rich carbon developed at different temperatures was used as cathode material to address the issue associated with expensive platinum catalyst. Mesoporous nitrogen rich carbon cathode reported 14% less power production than platinum cathode but showed only 7% reduction after one month operation when it was 11% for platinum cathode [48]. Zhang X et al, [49] have experimented with nitrogen doped ionothermal carbon aerogel as air cathode to improve the rate of oxygen reduction. This aerogel based electrode resulted 1.7 times higher power density than usual platinum electrode as well as most of the oxygen reducing catalyst air cathodes due to highly porous nature, high surface area and large pore volume. The firm has reported that the proposed aerogel electrode could be an efficient cost effective air cathode catalyst for MFC applications.

In recent years, tremendous studies have been carried out towards the development of design and electrode materials to boost up the performance of MFCs. However, still the technology is facing the challenges for commercialization. In sum up, stringent research is needed to further develop the hard ware

and economically tenable materials for MFCs that could find a permanent solution for the scale up issues as well as maximal power generations.

5. Conclusion:

This review summarizes different reactor configurations and both anode and cathode materials that have been developed to improve the performance as well as cost reduction of MFCs. It is deduced that reactor design has significant effect on the performance of MFCs. Carbon based electrode materials are capable of competing with expensive catalysts in power generation and durability. Concerning the cost perspective, further exploration of new materials or evolution of existing electrode materials will widen the applications of MFCs. Also, MFC conjugated bioreactor systems can produce prominent results in wastewater treatment at economically achievable numerals.

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