



Bio Energy Production Using Carbon Based Electrodes in Double and Single Chamber Microbial Fuel Cells: A Review



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Abstract

Microbial fuel cells (MFCs) are novel electrochemical devices, which can directly convert microbial metabolic power into electricity using biodegradable organic materials. One of the fundamental challenges to commercialize MFCs is the development of efficient, stable, and cost-effective catalysts for oxygen reduction reaction. A different kind of approaches has been done to enhance the efficiency of MFCs including architecture, electrodes, caution exchange membrane and biocatalyst. In this review, author has focused on single and double chamber MFC which are using carbon based electrodes.

MFC

The world's climate is being gradually altered by the burning of fossil fuels; which increases carbon dioxide in the atmosphere enormously. In addition, the high consumption of fossil fuels may cause fossil fuel energy deficiencies. Thus, the world's population needs to explore clean sources of energy as an alternative to fossil fuels. Extensive research has been carried out on different types of fuel cells, including direct alcohol fuel cells, proton exchange membrane fuel cells, solid oxide fuel cells, hydrogen fuel cells, alkaline fuel cells, and phosphoric acid fuel cells for increased power generation [1,2]. Although these fuel cells have a high operating efficiency, this benefit is somewhat offset by (i) the limited viability and expense of catalysts, (ii) corrosive electrolytes, and (ii) high operating temperatures. To overcome these problems, bio-electrochemical fuel cells are a better option for renewable energy production. Major efforts are thus being directed towards the development of technologies based on renewable sources that can transform biomass into various forms and produce electricity [3,4]. In this category, MFCs are promising electro-biotechnology tools that directly convert microbial metabolic power into electricity by catalyzing organic and inorganic matter using bio-electrochemical reactions in an anaerobic medium [5]. Electricity production by MFCs has many benefits including cleanliness, effectiveness, and recyclability with no harmful toxic product production [1-3,6]. Typically, MFCs consist of a two-electrode assembly that contains an anode and cathode. At the anode, the redox reaction occurs in the presence of organic matter and biocatalysts such as bacteria,

which generate protons and electrons. At the cathode, reduction of atmospheric oxygen occurs in the presence of catalysts and generates electricity along with water production [3,7-9]. Currently, MFCs show a potential use in the recovery of metals and nutrients from industrial effluents along with municipal or domestic wastewater treatment [10,11]. Two types of MFCs are commonly available: (i) double chamber and (ii) single chamber (SMFC) [9,12].

Double chamber microbial fuel cells

In general, double chamber MFCs consist of two chambers separated by a proton exchange membrane (PEM). Microorganisms oxidize organic material under anaerobic conditions and generate electrons and protons at the anode chamber. The electrons move to the counter electrode through an external circuit, while protons diffuse to the cathode through the PEM. These electrons and protons react with oxygen in the presence of a catalyst and produce water [13,14]. Presently, the comparatively lower power generation and expensive fabrication cost of double chamber MFCs are the major obstructions to their commercialization.

There are several factors that influence the efficiency and stability of MFCs, including the types of cathode and anode materials, the compositions of the anolyte and catholyte, PEM, electron transfer, pH, and the types of biocatalyst used [15-18]. The anode and cathode separately perform important roles in electricity generation in MFCs because the anode is directly responsible for electron transfer, while the surface of the cathode is accountable for oxygen reduction [14,19].

Two types of mechanisms are recognized for electron transfer from bacteria to anode. The first mechanism is the direct transfer of electrons from bacteria to the anode surface through self-mediation of the extracellular electron transfer via redox compounds such as c-type cytochromes or bacterial nanowires/pilli. *E. coli* is a very common example of the former mechanism [20,21]. Therefore, the biocompatibility and the electronic/ionic conductivity of the anode material are essential for bacteria to transfer electrons. In the second type of mechanism, direct oxidation of bacteria metabolites occurs on the anode surface, and hydrogen and other organic compounds including lactate, ethanol and for mate are key bacteria metabolites [22,23]. The appropriate electro-catalytic activity of the anode is required for the oxidation of metabolites in the latter type of mechanism which contributes to MFC current generation [24]. Therefore, the above-mentioned characteristics are required for a superior quality of anode. There are several artificial supplied mediators, such as methyl blue, neutral red and thionine, which are used to facilitate electron transfer from bacteria to the anode surface. However, these mediators are not desirable in MFCs because they are expensive and toxic to the microbes and must be replaced in a short time [25,26]. Therefore, several electrochemically active microorganisms, such as *Shewanella putrefaciens*, *Rhodospirillum rubrum*, and *Geobacteraceae sulfurreducens*, have been used in MFCs and do not require a mediator [26].

Due to its high oxidation potential and free availability, atmospheric oxygen (air) is frequently used as the electron acceptor in the cathode chamber of the MFCs. Thus, the cathode is also a restrictive feature of the MFCs and extensively affects their efficacy [14]. The use of cathode is restricting because of slow reduction rate and large over potential of oxygen. To reduce this foremost problem, nano-catalyst materials are used in MFCs, which provides more active sites for oxygen reduction [14]. So far, platinum (Pt) is the dominant nano-catalyst used for oxidation of metabolites and reduction of oxygen. Unfortunately, the high cost of Pt limits its commercialization for MFCs applications.

In consideration of the aforementioned properties, researchers have widely studied carbon materials such as carbon felt, carbon cloth, activated carbon fibre/ carbon nano fibre (ACF/CNF), ACs, carbon soot and other carbon nano composites as electrodes in MFCs. There are several advantages of carbon including good stability, high conductivity, large surface area, low fabrication cost and easy availability which favor fabrication of carbon electrodes for MFCs [2,4,15,27]. During the past decades, carbon-based porous electrodes with some nano modifications have been used to enhance the efficiency of MFCs. Different studies have been performed using carbon cloth as an anode where as the cathode was platinized titanium mesh or Pt doped carbon cloth including plain carbon cloth. In these studies, it was concluded that these carbon electrodes were highly electro-chemically active and able to reduce atmospheric oxygen, resulting in high performance of the prepared MFCs [28-30].

There are several studies where different types of electrodes were used for high power generation in double chamber MFCs.

These electrodes were iron- and nitrogen-functionalized graphene for good oxygen reduction reaction (ORR) [31,32], Au-NPs sputtered carbon-paper [17], ruthenium/tin/Pt loaded carbon nanotubes/ nitrogen doped carbon nanotubes [33,34], melamine sponges coated with reduced graphene oxide/carbon nanotubes [35], reticulated carbon foam [36], Ti/Pt based and graphitic felt [15,37] and graphitic carbon brush electrodes [19,38]. In most of the studies, it was concluded that doping of NPs and enhancing the graphitic content were responsible for enhancing the conductivity of electrodes and facilitating electron transfer, which were responsible for the high performance of the prepared MFCs. Transitional metals and heteroatom doping on ACF/CNF are considered to be favourable for enhancing the efficacy of bio energy via microbial fuel cell [4,9,12].

Single chamber microbial fuel cells

Recently, research has shifted towards development of SMFCs rather than double chamber MFCs. In double chamber MFCs, poor diffusion of protons through the PEM enhances the acidity of the anolyte while basicity increases in the catholyte over time. This directly affects the performance of double chamber MFCs due to destruction of the anodic bio-film under low pH conditions and lowers the cathode potential. Hence, significant consideration has been given to the removal of PEM and enhancement of proton transfer [7,8,39,40].

There are many advantages of SMFCs over double chamber MFCs including reduced cell volume, greater economy, low internal resistance and sustainability of the free electron acceptor at the air cathode [41,42]. The basic principles of both MFCs are the same. There are only two main differences: (i) PEMs are removed in SMFCs and (ii) the anolyte (waste water) is directly in contact with both the anode and the cathode, i.e. bio-films develop on both anode and cathode. The advantage of removing the PEM in SMFCs is the lowering of internal resistances compared to those found in the double chamber MFCs. This significantly enhances power generation. The major drawbacks of SMFCs are: (i) the cathode is directly exposed to the anolyte which facilitates bio-film formation on the cathode surface, which then reduces proton diffusion resulting in lower power generation [43], (ii) oxygen diffusion to the anode occurs through the cathode which lowers the efficiency of SMFCs [44,45]. To sort out this problem in membrane-less SMFCs, newly developed cathodic bio-films are used as a barrier for oxygen diffusion through the porous cathode and maintain the anaerobic atmosphere by consuming oxygen [46].

There are several factors which make the cathode an essential part of SMFCs including slow oxygen reduction kinetics, mass transport limitations due to diffusion of oxygen through porous cathodes, cathode material, low solubility, spacing between anode and cathode, ionic strength of solution, diffusivity of oxygen in water and accumulation of inert gas in the pores [47-49].

Researchers have been used efficient and inexpensive catalysts such as iron phthalocyanine, cobalt naphthalocyanine, Fe-phenanthroline, cobalt porphyrin, manganese oxide, lead dioxide,

activated carbon, mesoporous nitrogen-rich carbon, carbon nanotubes, electrospun polyacrylonitrile based CNFs and nickel foam for ORR other than platinum (Pt) [50-55]. It was concluded that these materials had a good electro-catalytic property for ORR and could be an alternative to Pt. Atmospheric oxygen is a frequently used electron acceptor in SMFC because of its relatively high redox potential, availability, and sustainability. It is also mentioned that the presence of an oxidized metal at the cathode enhances the electron acceptor property [45,56].

Several materials have been used as separators to avoid short circuiting between the anode and cathode including J-cloth nylon, cellulose, glass fiber, PEM and polycarbonate filters which increased power generation in SMFCs [57,58]. However, there are several drawbacks to these materials such as fast degradability, reduced proton diffusion capability, and enhanced internal resistances. To avoid such problems, membrane-less SMFCs have been developed where air cathodes are prepared by the doping/brushing of a Pt catalyst with a Nafion, poly (dimethylsiloxane) (PDMS), and polytetrafluoroethylene (PTFE) binder on wet proof carbon cloth/mesh on the water-facing side of the electrode, and brushing 2-4 layers of hydrophobic PTFE/PDMS/ polyvinylidene fluoride/ poly methyl vinyl ether-alt-maleic anhydride (PMVEMA) as diffusion layers on the air-side of the cathodes because both are highly permeable to oxygen and stop water losses [7,8,59,60]. Ideally, the separator used on a cathode in solution must be inexpensive, have good film-forming properties, possess excellent mechanical strength, be chemically inert, have superior hydrophilicity for high cation transport, and possess low internal resistance [61,62]. In this category, poly methyl vinyl ether-alt-maleic anhydride (PMVEMA) is another inexpensive copolymer which has a proton exchange property and may be used as an alternative to Nafion. Specifically, PMVEMA is a water soluble copolymer which contains two main functional groups: (1) maleic anhydride units with two carboxylic groups, acts as proton-donors and form hydrogen bonds with hydroxyl and ether groups, and (2) methyl vinyl ether which is a proton-acceptor with respect to the hydroxyl groups [63,64].

Conclusion

MFCs are one among all kinds of bio-electrochemical systems. From the above review, it could be concluded that electrodes are still one of the challenging parameters for commercializing the MFCs. Nonetheless, many approaches have been adopted by researchers to improve the electrode materials for the efficient power generation of MFCs in last five years. However, MFCs are considered as a green approach owing to simultaneous bio electricity generation and wastewater treatment. As per author belief, this review will explain the fundamental and existing challenges to the new researches.

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