Advance in Improving the Electrical Performance of Microbial Fuel Cell

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Abstract. As a bioelectrochemical hybrid system, microbial fuel cell converts chemical energy into electrical energy through microbial metabolism, which has great advantages of energy conservation and environmental protection, high energy conversion efficiency, and reduced sludge volume. Therefore, how to improve the power generation performance and output power of MFC has been a hot topic in recent years. Based on this, on the basis of reviewing many literatures, this review analyzes the main factors influencing the electrical performance of MFC by combining the principle of MFC and its electronic transfer mechanism, including battery reactor structure, exchange membrane, anode microorganisms, electrode materials and parameters, etc. At the same time, the application prospect of MFC is discussed, including CW-MFC coupling technology, biosensor and sewage treatment technology. Finally, the present challenges of MFC are put forward, and a better application research direction is proposed for the future of MFC.

1. Introduction

At a time when the world is running out of fossil fuels, the increasing demand for energy could lead to a global energy crisis, with significant impacts on the environment and human health. In recent years, there has been a growing interest in finding alternative sources of renewable energy. Studies have shown that the chemical energy in organic pollutants in wastewater is 9.3 times of the energy consumed in wastewater treatment. Therefore, effective utilization of chemical energy in wastewater has important environmental and energy significance [1]. The first research on MFC was made by Professor Potter in Britain in 1910 with platinum as an electrode [2]. It can degrade a variety of complex organic pollutants through the metabolic activities of microorganisms themselves, generate electrons and transfer them to the electrode for energy output, and realize the conversion and utilization of biomass energy at the same time. Meanwhile, MFC has the advantages of mild reaction conditions, low sludge production, no secondary pollution and high biocompatibility [3]. MFC is therefore considered to be the most suitable alternative technology for renewable energy today.

In recent years, researchers around the world have done a lot of research experiments on MFC, making its electrical performance show exponential growth [4]. However, due to less research on the expansion of MFC’s low cost and high output, it cannot be put into practical use. Therefore, by combining the principle of MFC and its electronic transfer mechanism, this paper analyzes the main factors affecting MFC’s electrical performance, and then studies how to improve MFC’s electrical performance and reduce the investment cost, thus laying a solid foundation for the practical application of MFC in the future.
2. MFC Principles
MFC usually consists of an anode chamber, a cathode chamber, a separator and an external circuit. Common MFC’s use organics in the anode solution as fuel, and electricity-producing microorganisms oxidize organic pollutants and release electrons and protons, organic pollutants as electron donors, electrons are then transferred to the cathode through an external circuit and energy is released to supply the electron acceptor, while hydrogen protons generated in the anode chamber are moved to the cathode through the polymer electrolyte membrane [5]. Finally, the cathode electrons and protons of the MFC combine with oxygen, and the reduction reaction produces water molecules to form a circuit, which completes the whole bioelectrochemical process and generates an electric current [6]. The greater the potential difference between the electron donor and the electron acceptor, the more energy the microorganism can obtain, and the greater the output power of MFC [7]. The reaction principle is shown in figure 1.

![Figure 1. Schematic diagram of a microbial fuel cell.](image)

2.1. MFC Electron Transfer Mechanism
The power generation efficiency of MFC is related to many factors, among which electron transfer rate is the most critical factor. It is of great significance to find out how electrons are generated and transferred in MFC, so as to put forward methods to improve electron transfer rate. Electrogens are microorganisms that can completely oxidize organic matter and transfer electrons to extracellular electrodes using complete electron transfer chains [8]. Electron transfer of anodic bacterium is divided into intracellular electron transfer and extracellular electron transfer. Among them, the electron transfer between microorganisms and electrodes in extracellular electron transfer is mainly divided into the following four types: (1) direct electron transfer mediated by outer membrane proteins of microbial cells, (2) direct electron transfer mediated by microbial generated nanowires, (3) indirect electron transfer mediated by electron shuttles, (4) Electrokinesis [9]. (as shown in figure 2.) However, considering that some microorganisms have no electric-generating activity, electron transfer can occur between different microorganisms as well as between microorganisms and electrodes. Ha et al. demonstrated the existence of direct inter-species electron transfer between Geobacter sulfurreducens and Prosthecochloris aestuarii bacteria under light conditions [10]. However, no research has been conducted on whether the electron transfer process between microorganisms can improve the electrical performance of MFC, which needs further research in the future.
3. Main Factors Affecting MFC Power Generation

In recent years, MFC has received a lot of attention from researchers around the world because it can generate sustainable electricity by treating wastewater. However, there are few literatures on how to balance the interests between investment cost and capacity, and how to develop low-cost and efficient MFC. In this paper, the main factors influencing MFC electrical performance are analysed, including battery reactor structure, separator material, electrode material, anode microorganism and so on.

3.1. MFC Reactor Structure

Currently, MFC configurations widely used in practical studies are divided into single-chamber MFC (as shown in figure 3), dual-chamber MFC (as shown in figure 4), stacked MFC and double-tubular MFC. The cathode and anode of the single-chamber MFC are in the same reaction chamber. The cathode is directly exposed to the air without external aeration, with small impedance, fast electron transmission rate and no secondary pollution. Literature has pointed out that the output power of single-compartment MFC is much higher than that of batteries with other configurations, but the coulomb efficiency is low [11]. The dual-chamber MFC is easy to assemble and operate, which is convenient to change the experimental conditions. However, due to the distance between the cathode and the anode, the mass transfer resistance is large, the resistance is high, and the power generation density is relatively low. The double-tubular MFC is composed of two concentric cylinders, the inner cylinder is the anode chamber, the polymer electrolyte membrane is wrapped around the outer surface of the inner cylinder, the cathode is covered around the outer surface of the polymer electrolyte membrane, and the inner wall of the outer cylinder constitutes the cathode chamber [12]. Liu found that the area of cation exchange membrane (CEM) in double-tubular MFC was large, and the spacing between electrodes was small, so the battery impedance was small [13]. There was more active biomass attached to the anode electrode, and the electrochemical activity of the biofilm was high, leading to the high battery power, which was 1.33 times that of the rectangular MFC. Li found that if more batteries are connected inside the battery, the maximum output power of the series battery and the parallel battery will increase [14]. Zhang studied the electrical performance of stacked MFC with series connection, parallel connection, and series and parallel connection respectively, and found that the maximum power of MFC is the highest when series connection is made, with 12.1% and 29.1% higher than the maximum power of parallel and mixed connection respectively [15]. However, the impedance effect of stacked MFC is not yet clear, which needs further study in the future.
3.2. Types of Separation Materials
The presence or absence of a separation material is the main basis for distinguishing between a dual-chamber and a single-chamber MFC. The hydrogen protons generated by peroxidation in the anode chamber are transferred to the cathode chamber through the separation material, so the separation material has a great influence on the transfer rate and the electrical performance of the battery. The spacer material should not block proton migration, and can meet the different requirements of cathode and anode for substrate composition, dissolved oxygen concentration, microbial type, etc. [16].

3.2.1. Membrane Materials. There are many kinds of membrane materials in MFC, including proton exchange membrane (PEM), cation exchange membrane (CEM) and anion exchange membrane (AEM). Different membrane materials have great differences in physical and chemical properties, and also have different selective transmittance. The literature pointed out that the membrane bioreactor technology can play a role in retaining biomass while efficiently degrading pollutants [17]. At the same time, microalgae are thought to have great potential as raw materials for biofuel production [18]. Yang established the algal biofilm microbial fuel cell (ABMFC), which can deal with complex and changeable waste water in a continuous flow manner. The removal rates of TN, TP and COD in the waste water reached 96.0%, 91.5% and 80.2% respectively, and the maximum power density of ABMFC (62.93 mW·m⁻²) was higher than that of MFC (52.33 mW·m⁻²) [19]. The study not only found a way to treat wastewater and recycle energy simultaneously, but also gained a deeper understanding of the growth and metabolism mechanism of algal bacteria.

3.2.2. Salt Bridge. In the study of MFC, salt Bridges can also be used as separation materials instead of membrane materials [20]. Salt Bridges are convenient for processing and can block the diffusion of substrates and microorganisms, so as to avoid the direct contact reaction between oxidizer and reducing agent in MFC, which is easy to generate relatively stable current [21]. Xu optimized the battery device by improving the tube diameter of the salt bridge in the dual-chamber MFC. When the tube diameter of the salt bridge was 12 mm, the removal rate of CODcr and NH₃-N was the highest, 95.2% and 71.8%, respectively [22].

3.3. Anodic Microorganism

3.3.1. Types of Electricity-producing Microorganisms. Microorganisms on the surface of the MFC anode can degrade organic matter and generate electricity at the same time. Therefore, the species and activity of bacteria on the surface of MFC are very important to improve the electrical performance of MFC. There are a wide range of electric-producing microorganisms, including Proteobacteria, Escherichia coli [23], Geobacter, Helicobacter [24], Firmicutes, Acidobacteria and Actinomycetes,
which have been found in the anode. Shewanella and Geobacter are currently the most used microorganisms in MFCs research [10]. Studies in recent years have found that high-efficiency electricity-producing microorganisms mainly exist in solid metal oxide reducing bacteria. They are Proteobacteria, Gram-negative, the main reason is that the environment in which MFC operates is similar to the living conditions of bacteria and has a similar electron transfer mechanism. Sun found that under different substrates, the types of bacteria on the surface of the electric-producing anode would change greatly, but several types of bacteria appeared in them, such as gram-positive bacteria with low G+C, β-Proteobacteria and δ-Pro- tecobacteria might be related auxiliary bacteria that produce electricity [25].

3.3.2. Mixed Bacteria MFC. Compared with pure bacteria, mixed bacteria MFC has a strong ability to resist changes in the external environment, so it is convenient to change the experimental conditions to conduct in-depth study on a single factor, and at the same time to play a synergistic effect among the bacteria to improve the electrical performance and stability of MFC. This has great advantages for MFC to be put into actual production in the future. Studies have shown that mixed microbial flora MFC can enrich the dominant flora on the anode surface, making its power generation about 6 times that of pure MFC [26]. However, some literatures also pointed out that there was a competitive relationship between electric-producing bacteria and non-electric-producing bacteria in the degradation process of organic matter, so that the electric-producing performance of mixed bacteria MFC was lower than that of pure bacteria MFC [27]. It should be emphasized that not all of the microorganisms occupying the dominant position in the anode chamber are the electricity-generating bacteria we need. These microorganisms can initially degrade organic matter in water and provide suitable living conditions for true electricity-generating bacteria.

3.4. Electrode Materials and Their Parameters
The choice of electrode material will also affect the battery’s electrical performance, mainly reflected in two aspects: First, the roughness of the electrode surface. Whether the electrode surface is smooth or not affects the adhesion ability of microorganisms on the electrode surface. Studies have shown that, electrode surface roughness and the closer the microbial cell size, microbial adhesion ability stronger, the greater the biomass, the higher the production performance of battery [28]. Second, the modification of electrode materials. Modification of electrode surface by different materials will affect electron transfer efficiency. Zhang used a metal mesh current collector + polydimethylsiloxane composite as the cathode can greatly improve the power generation performance of MFC, and the coulomb efficiency can reach more than 80% [29]. Experiments show that, MFC with poly-neutral red modified cathode (CPNR-MFC) has a maximum nitrate nitrogen removal rate of 0.040 kg·m⁻³·d⁻¹, which is 14.29% higher than that of the control group [30]. Liu used polyaniline (PANI) and graphene oxide (GO) to modify the cathode electrode, which can enhance the reduction rate of the cathode and reduce the potential loss [31]. Table 1 shows some of the anode modification materials and their modified properties. In general, graphene and carbon nanotube materials are regarded as a major direction for future research due to their strong electrical conductivity and catalytic activity.

| Modified material                        | Electrode material | \( P_{\text{max}} \) (m-Wm⁻²) |
|------------------------------------------|--------------------|-------------------------------|
| Nitrogen doped carbon nanoparticles     | Carbon cloth       | 298                           |
| ERGNO-PANI                               | Carbon paper       | 884                           |
| Multi-walled carbon nanotubes            | Carbon cloth       | 560                           |
| N-CNTs / rGO                             | Carbon cloth       | 1137                          |
| CPHs / CNTs                              | Carbon felt        | 1898                          |
| L-cysteine graphene aerogel              | Carbon cloth       | 679                           |
4. Current Status and Future of MFC
Microbial fuel cells are one of the most promising alternative renewable energy technologies. After continuous innovation and improvement, MFC has been put into many practical applications. At present, the main applications of MFC are in three aspects. The first aspect is the application of wastewater treatment. A. Callegari connected two identical dual-chamber MFC in series and continued to treat the dairy wastewater. The organic matter removal rate was 82% when running 65d, and the highest coulomb efficiency was 24% when the organic load rate was 3.7kgCOD /m³·d [38]. Dong designed a 90 L stackable MFC, which was proved to be able to treat brewery wastewater and generate electricity at the same time, with a COD removal rate of 87.6%, and could operate in an energy self-sufficient way for more than 6 months [39]. The second is the application of MFC biosensors. Study has pointed out that bacteria can automatically identify the target substance, and respond when the MFC outputs electrical energy, reflecting the concentration of the analytes through changes in battery voltage and current [40]. Therefore, it is possible to get rid of signal converters and external power constraints and accelerate the development of sensors. At present, it is mainly used for the analysis and research of BOD, toxic substances, microbial quantity and activity, volatile short-chain fatty acids and other substances [41]. The third aspect is coupling technology. The most influential is the constructed wetland - microbial fuel cell (CW-MFC). This is an innovative ecological restoration technology that can simultaneously treat wastewater and produce bioelectricity. MFC generates electricity by microbial degradation of organic matter in sewage, while CW purifies sewage by microbial degradation of organic matter in sewage [42].

Above is the present situation of the MFC application progress. By reviewing the different factors that affect MFC's electrical performance, this paper finds that MFC still faces many limitations when generating electricity and treating wastewater. For example, expensive electrode materials lead to high investment costs and relatively low power generation performance. Some scholars estimated that the electricity generated by MFC was only 0.08 dollar/m³ per day in 2016. The disposal of fresh dirt from the separator is also a new challenge. Therefore, the most urgent solution for the future of MFC is to balance the relationship between cost and power generation efficiency, as well as large-scale practical application. Specific measures to improve MFC power generation performance in the future can be improved from the following points: (1) Optimizing the structure of MFC reactor by using microbial immobilization technology and heavy metal loading technology to improve its reaction efficiency. (2) We should select membrane materials that are conducive to proton transfer, which have a long life cycle and the ability to resist microbial migration, then improve the physical and chemical properties of membrane materials and the domestication mode of biofilms, finally reduce the processing cost. (3) Screening the new electric-producing microorganisms in the anode chamber, and combine the principles of bioengineering to realize the stable operation of the battery under different conditions. (4) In the future experiments, we should choose the appropriate external resistance to promote the electron transfer of the anode microorganisms, so as to improve the battery's electrical performance. (5) We need to further study the mechanism of electron generation, improving the mechanism of extracellular electron transfer and the adhesion of electricity-producing bacteria. (6) Conducting innovative research on materials modifying electrodes, meanwhile, discuss the effects of electrode spacing and electrode area on electricity generation. (7) Adjusting the fluid velocity and shear force in the anode chamber can increase the richness of the bacterial population in order to improve the electron transfer rate and improve the performance of the battery. (8) Combining DNA technology and immune technology to further expand the application range of microbial fuel cell sensors.

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