The Development of Electrode Materials for Microbial Fuel Cells

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ABSTRACT: Microbial fuel cell (MFC) is a new device which can purify the wastewater and convert the chemical energy to electricity using electricigen as catalyst. The MFC device has attracted extensive attentions due to its ability of simultaneous treating waste water and recovering electrical energy. It has many advantages such as mild reaction, nonhazardous product compared to traditional energy sources. In this paper, the development and situation of the anode/cathode materials for MFC were reviewed. However, low columbic efficiency and costly electrode materials are still the bottlenecks restricting its large-scale application. So the common modification methods were shown as well, such as the combination of nanotube and polymer, heating and acid-soaking treatment, which could overcome the disadvantages. Finally, the existing problems which limit the practical application of MFC were presented. It’s believed that the application of MFC will have a great prospect if these problems are solved.

Keywords: MFC; anode; cathode; materials

1 INTRODUCTION

With the consumption of unsustainable resources such as natural gas and the misusage of energy, which have caused severe environment pollution, the existence of human has been threatened seriously. It is urgent that exploring some sustainable ways to alleviate the huge pressure of energy and environment. Microbial fuel cell (MFC) is a new prospective technology, which can purify the wastewater and generate electrical energy simultaneously, using microorganisms as catalyst. In the reactor, substrate such as glucose is oxidized by microorganisms, and electrons as well as protons are both generated at the anode chamber. Electrons transfer through the external circuit to the cathode and the protons also transfer to the cathode, but through the solution. Finally, in the cathode chamber, electrons combine the protons and oxygen to form water.

The reaction equations in the anode:

\[ C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \]

in the cathode: \[ 6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O \].

A typical reaction principle[1] can be seen in Figure 1. Figure 2 shows a common double chamber MFC reactor, of which cathode is carbon cloth.

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The low production and high cost both are main limitations to the large-scale application of MFC. There are many factors that affect the output performance of MFC, including microbial species, electrode materials and types of substrate etc\(^2\). In all these factors, electrode is a key component. The favorable electrode materials should be electrochemically and biologically stable with excellent conductivity, high specific surface area and roughness. It also should be non-corrosive and cost-efficient as well. The traditional electrode materials, such as carbon paper, carbon cloth, carbon fiber brush, etc. usually have a lower price and good biocompatibility, but their columbic efficiency is low. Fortunately, a lot of novel materials and modification methods have been developed in recent years, which have largely improved the performance of MFC.

In this paper, some recent developments of electrode materials were explored, and the advantages and disadvantages of these materials were also compared in terms of their characteristics, performance and cost.

2 ANODE MATERIALS

In the MFC, the electrigen is the catalyst of energy transformation and the anode of MFC provide a habitat for these microorganisms. It is known that the biomass of electrigen on anode can significantly affect the power density of MFC. Therefore favorable anode materials are supposed to have good biocompatibility and high specific surface area.

2.1 Traditional carbonaceous materials

Because of their good biocompatibility and chemical stability, carbonaceous materials such as carbon paper and carbon cloth are widely used as the MFC anode.

2.1.1 Carbon paper

Carbon paper is very thin and relatively stiff but has high specific surface area. Zhong et al\(^3\) structured some double-chamber MFCs and compared the effect of superposition of one, three and five layers of carbon paper as the anode materials on the performance of MFC. The results demonstrated that the highest power density increased with the number of carbon paper layer and the highest power density of 674.65 mW/m\(^2\) was achieved by the five-layer MFC. She also found the internal resistance of MFCs decreased with the superposition of carbon paper. Her study demonstrated that carbon paper could provide extensive habitat for microorganisms and low internal resistance with the increase of layer number.

2.1.2 Carbon cloth

Carbon cloth is more flexible and porous than carbon paper. Zhou \(^4\) modified the carbon cloth by the mixture-soaking of nitric acid and sulfuric acid, then used it as the anode of a single chamber MFC and achieved the maximal power density of 908 mW/m\(^2\). Nimje et al\(^5\) used glycerol as substrate in a single chamber MFC equipped with carbon cloth anode and got the highest power density of 600 mW/m\(^2\). However, the carbon paper and carbon cloth are both low-efficiency, which can limit the scalable application of MFC.

2.1.3 Carbon fiber brush

Compared to the carbon paper and carbon cloth, carbon fiber brush has a good toughness, which can provide higher specific surface area for microorganisms and produce higher power density in MFC. Feng et al\(^6\) modified the carbon fiber brush with the combination of heating and acid-soaking and increased the highest power density to 1370 mW/m\(^2\). Pan et al\(^7\) investigated the effect of anode structure and surface on the maximal power output of MFC by changing length and number of the carbon fiber. The maximal power density of 2.92 W/m\(^2\) was achieved using an anode with 4 pieces of 2cm-length carbon fiber, which was 2.78 times larger than that generated with a single 8cm-length carbon fiber. He also observed the biofilm on the carbon fibers surface by optical microscopy and found the biofilm was thicker at the place near current leading-out terminal than it at other parts of carbon fiber. However, the size of carbon fiber brush would constrain the minimal electrode spacing, which could bring lower ohmic resistance than the larger spacing at electrodes.

2.1.4 Carbon mesh

Carbon mesh has a more open structure than carbon cloth due to a more open wave, which could help with the reduction of biofouling. Zhou et al\(^8\) modified the carbon mesh anodes by soaking them in three different kinds of electrolyte, namely, nitric acid, ammonia nitrate and ammonia persulfate respectively. He compared the performance of MFCs equipped with the anodes before and after modification and confirmed that all these material modifications had positive effect on the performance of MFCs. The maximal power density of 792 mW/m\(^2\) was obtained from the nitric acid modified anode, which was 43% larger than that of the unmodified one (552 mW/m\(^2\)). Wang et al\(^9\) treated the carbon mesh by the ammonia gas process and promoted the highest power density to 1015 mW/m\(^2\). The reason of enhancement in power density after ammonia gas treatment was the increase of N/C ratio, which might produce nitrogen related functional groups that facilitated electrons transfer. These results showed the modification methods which could increase the N/C ratio would improve the performance of MFC.

To sum up, some modifications on traditional anode materials can improve the performance of MFC anode to some extent. However, the electricity generation of MFC still could not be significantly enhanced. Therefore, more and more new efficient materials had been studied recently.
2.2 Novel materials

2.2.1 Carbon nanotube
Carbon nanotube, due to its high specific surface area and unique nanoscale, is an ideal electrode material. Yan et al. [10] used the composite of 20wt% carbon nanotube (CNT) and polyaniline (PANI) as the anode of MFC. The highest density of 42mW/m² was acquired, which was larger than that of another MFC with 1wt% CNT/PANI composite anode. The result illustrated that the CNT anode was excellent to enhance the electricity production of MFC. Liang et al. [11] used CNT as the anode of MFC, which reached the highest power density of 402mW/m². He also found the CNT anode could reduce the internal resistance. Xie et al. [12] used carbon nanotube-textile (CNT-textile) composite as the anode of MFC. CNT-textile is a novel material with intertwined structure, which could provide an open 3D space for efficient substrate transportation. His study demonstrated that the CNT could enhance the transfer of electrons from electricogens to the anode, and MFC equipped with the CNT-textile anode achieved better performance than the one equipped with a traditional carbon cloth anode of which maximal power density was 68% higher.

2.2.2 Graphite materials
Some new graphite materials such as graphite felt and graphene usually have better conductivity and higher strength than carbon paper. Bruce et al. [13] used graphite brush as anode, which was a composite of lots of graphite fiber wound around a noncorrosive conductor. At 9600 m²/m³ reaction volume, his reactor achieved a maximum power density of 2400 mW/m², which was the highest value yet achieved by an air-cathode MFC system. Du [14] modified plain graphite felts by ammonium peroxydisulfate soaking and electrochemical method respectively. The result showed that the MFCs using soaking-modified and electrochemically modified graphite felts as anode achieved 510mW/m² and 609mW/m² respectively, which was much higher than unmodified one (283mW/m²). XPS analysis data indicated that the different treatments had changed the N/C ratio which was consistent with the power density of MFC. Although graphite materials had a compact structure and relatively smooth surface, both of which could facilitate the quantitative measurement of biomass per unit of surface area, the low specific surface area and high cost were still the restriction factors for the application in practice.

Zhang [15] structured a double chamber MFC using novel graphite paper as anode and got the highest power density of 2249mW/m². He used the scanning electron microscopy to observe the anode surface and found that the high power density was due to the good biocompatibility of the new material. In her another experiment, the MFC equipped with anode made of stainless-steel mesh modified by graphene and binder polytetrafluoroethylene and achieved the highest power density of 2668mW/m². Moreover, the graphene was considered to be the most efficient ingredient, the reason was that the corresponding power density was 18 times larger than that obtained from the MFC with plain stainless-steel mesh anode and was 17 times larger than that obtained from the MFC with polytetrafluoroethylene modified stainless-steel mesh anode.

2.2.3 Conductive polymer
Conductive polymers such as polyaniline and polypyrrole were also widely used as the electrode materials in MFC. Bin et al. [16] modified carbon cloth anode with polymerization of aniline in 5% H₂SO₄ solution and used the modified material as anode in a double chamber MFC. The maximal power density achieved was 1275mW/m², which was 2.66 times higher than the corresponding value of the MFC with unmodified anode. Zheng [17] electrochemically modified the graphite anode of MFC with polyaniline, and the experiment result illustrated that the modified anode got better performance than the non-modified one. These results indicated that the polyaniline modification was an efficient approach for improving the performance of MFC.

3 CATHODE MATERIALS
The cathode of MFC is another barrier to its large-scale application in practice. Generally, the anode materials also can be used as cathode materials, such as carbon cloth, carbon paper and graphite felt etc. The cathode can be classified to traditional cathode and bio cathode, according to the existence of microorganisms. Traditional MFC usually use oxygen as cathode electron acceptor. Therefore traditional cathode materials such as carbon paper loading platinum (Pt) usually have good conductivity and high catalytic efficiency. With the development of bio-cathode MFC, the bio-cathode material becomes a most component of cathode material.

3.1 Traditional cathode
Traditional MFC usually uses oxygen as cathode electron acceptor, so traditional cathode materials such as platinum/carbon paper (Pt/C) have good conductivity and high catalytic efficiency. However, with the development of bio-cathode MFC, the bio-cathode material has become a most component of cathode material.

Cheng et al. [18] used carbon cloth loading Pt as the cathode of a MFC and increased power density approximately 4 times after modification. It was also found that the dosage of Pt from 0.1 to 2 mg/cm² could not obviously influence the performance of MFC, which provide the evidence of reducing the use of Pt. However, Pt was still too expensive to be popu-
larized in practice. Fortunately, some other cheaper catalysts have been researched to replace Pt. Roche et al \[19\] used carbon loading manganese oxide nanoparticles as cathode in a double chamber MFC and got the peak power density of 161mW/m², which was comparable with that using Pt/C as catalyst (193mW/m²). In addition, it was found that the replaced catalyst had a good stability in the pH varying from 7.0 to 10.0. More importantly, it was cheaper than the Pt/C. Lu et al \[20\] synthesized a new type electrocatalyst, manganese–polypyrrole–carbon nanotube composite, and the MFC got the maximum power density of 213mW/m² when the loading dosage was 2 mg/cm². Mean time, he noticed that the catalyst had displayed good long-term stability. His experiment successfully demonstrated that cheap manganese–polypyrrole–carbon nanotube composite catalyst could displace the Pt/C electrode to improve the possibility of MFC’s large-scale practical application.

Yong et al \[21\] employed polypyrrole/carbon black (PPy/C) composite as electro-catalyst in the air-cathode of MFC. He obtained the highest power density of 401.8mW/m², which was higher than the most value of 90.9mW/m² using plain carbon black cathode. Although the power density of the MFC with PPy/C cathode was lower than that with a commercial Pt/C cathode, the power/cost of a PPy/C cathode was 15 times cheaper than that of the Pt/C cathode. His research illustrated that the PPy/C could be a good alternative to the Pt/C in MFC due to its economic advantage.

Ding et al \[22\] synthesized nickel oxide (NiO) via hydrothermal method and applied it as cathode catalyst in a single chamber air-cathode microbial fuel cell. He acquired the maximal power density of 21.7 mW/m², which was 78.9% of that in a MFC equipped with Pt/C cathode (27.5mW/m²). He also used the electrochemical impedance spectroscopy to analyze the internal resistance and found that the charge transfer resistance of NiO and Pt./C was 14.6Ω and 11.1Ω respectively. The results indicated that the NiO probably could displace the expensive Pt./C in MFC.

Zeng et al \[23\] loaded Mo2C on the carbon felt and used it as the cathode of MFC. The experimental results showed that the Mo2C had significant catalysis on the oxidation-reduction reaction, and the catalytic effect could be enhanced with the increase of the loading. The Mo2C loading was 2 mg/cm² and substrate was 2 g/L glucose, her MFC reactor got power density of 1.95 W/m², as 81.5% much as the power density of MFC using Pt. catalyst cathode.

3.2 Bio cathode

Traditional cathode of MFC uses catalyst such as metal compound, polymer etc. However, the bio cathode MFC which use microorganism as catalyst is rising. The bio-cathode MFC has many advantages comparing to the traditional cathode MFC, including the low cost of construction and operation, avoidance of the chemical catalyst efficiency loss and long-term stability due to the microorganisms’ self-duplication.

According to the terminal electrons acceptor, the bio cathode can be classified into aerobic bio-cathode and anaerobic bio-cathode. Anaerobic bio-cathode directly reduces terminal electrons acceptor such as nitrate and sulfate, other than aerobic bio cathode used oxygen as the terminal electrons acceptor \[24\].

Bergel et al \[25\] had reported that the highest power density descended from 270mW/m² to 2.8mW/m² after the cleaning of biofilm in the cathode chamber. Chung et al \[26\] found that with the elimination of cathode biofilm, the maximal power density of MFC reduced to 200mW/m² from 570mW/m². Ter et al \[27\] studied the factors which limiting bio-cathode performance, and found that transfer of oxygen posed a serious limitation for the use of dissolved oxygen as an electrons acceptor in MFC by mass transfer calculations.

4 CONCLUSIONS

This paper summarized progresses of some traditional and novel materials, compared the advantages and disadvantages of these materials in terms of their characteristics. Although the price of electrode materials has been largely cut, the electrode materials and catalyst are still expensive, and the performance is not essentially improved. There are still some problems limiting its practical application:

1) Most of the traditional anode materials have good biocompatibility, but low coulomb efficiency. Novel anode materials, which have high specific surface area and good electrical conductivity, can largely accelerate the electrons transfer efficiency, but their cost is too high to be largely applied.

2) The common cathode material (Pt./C) is expensive. However, the existing cheap cathode materials have low catalytic efficiency.

Even if there are still some problems in the preliminary stage, the MFC has presented a promising technology for renewable energy production and still have some potential application, such as strengthening waste water treatment \[28\], monitoring water quality \[29\], and producing hydrogen \[30\] et al. In the coming decades, MFC will involve more and more scientists and engineers who major in waste water treatment and energy production.

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