Electrochemical performance analysis of microbial fuel cells based on nanomaterials

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Abstract. The use of traditional fossil fuel energy has caused serious environmental pollution problems. It is becoming increasingly urgent to find a green and clean new energy source. Microbial fuel cells (MFCs) have attracted much attention due to their renewable capabilities and green characteristics. MFCs still has certain limitations in its application process, such as its internal complexity, high cost of electrode separators and unstable power generation. Introducing different types of nanomaterials to build MFCs can solve these existing problems. However, how the introduced nanomaterials improve the electrochemical properties of MFCs remains to be further analyzed. To this end, this research will discuss the mechanism by which different regulatory strategies based on nanomaterials alter the electrochemical behavior of MFCs. Specifically, this research will focus on the impact of nanomaterials-based modification on the electrochemical performance of MFCs, including structural changes, material composite and new material preparations. The results show that the introduction of nanomaterials significantly improves the power density, current density and stability of MFCs, while enhancing catalytic activity, microbial adhesion and electron transfer efficiency. In this research, the analysis of changes in the electrochemical properties of MFCs by nanomaterials is conducive to the synthesis of novel electrochemically active nanomaterials and the development of high-performance MFCs.

Keywords: MFCs, Electrochemical performance, Nanomaterials, Modification, Composites.

1. Introduction

With the gradual reduction of fossil fuel reserves and the awareness of environmental pollution caused by its use, the production, storage and consumption of green and renewable energy have gradually become hot topics in modern research. Among them, microbial fuel cells (MFCs) have attracted widespread attention as a potential new energy conversion technology due to their wide range of fuel sources, mild operating conditions, high energy utilization, and energy recovery and protection functions [1, 2].

Due to the complex structure of the MFCs cell and the conditions required for the related microbial chemical reactions, MFCs are relatively expensive and the manufacturing process is complex. In addition, the power generation of various types of MFCs developed today is unstable and generally low, which makes it difficult for MFCs to be applied in industrial production environments with large electricity consumption. The development and selection of the best electrode materials and diaphragms has become the primary issue of current research [3].

Traditional carbon materials generally have large porosity, which will cause microorganisms to remain in the pores and produce side reactions and corresponding by-products, thereby reducing microbial activity and the required reaction efficiency. Due to their unique small size and excellent electrochemical properties, nanomaterials have been experimentally proven to effectively improve the current problems of low power generation efficiency and harsh application environment of MFCs. Graphene-based nanostructures are promising new anode materials because they have excellent electrochemical properties [4]. At the same time, these new nanomaterials are low-cost and have large production, which effectively solves the problem of high cost of MFCs components.

Although the performance of the corresponding MFCs can be effectively improved by changing the material morphology and structure or introducing new materials, the mechanism and impact behind the change in MFCs performance still need further analysis. Therefore, this research will conduct an in-depth analysis on this issue and summarize the advantages and disadvantages of these

representative materials and the impact of material modification, compounding and innovation on MFCs electrode components. In addition, this research also guides strategies and key developments in the direction of electrode materials.

2. Analysis of the application performance of nanomaterials in MFCs

2.1. Effect of nanomaterials modification on MFCs performance

Valipour et al. conducted in-depth research on the performance of MnO_2 with different structures as cathode catalysts and conducted a series of related experiments [5]. The treated carbon cloth was used as the anode and slurred the prepared catalyst and coated it on the carbon cloth to form a catalytic layer as the cathode. They conducted multiple control experiments and constructed the corresponding MFCs.

As shown in Figure 1, at the same mass loading (0.5 mg/cm^2), the maximum power density of MFCs prepared with MnO_2 catalyst (M500) annealed at 500°C was 5-52% higher than that of other unannealed and annealed MnO_2-based cathode MFCs. The maximum power density of MFCs was even higher, which was due to its synergistic α-phases and δ-phases, specific morphology (nanorods), high specific surface area and high catalytic activity, which made it easier for protons to insert into the lattice, providing more reaction active sites, thereby improving the ORR catalytic activity.

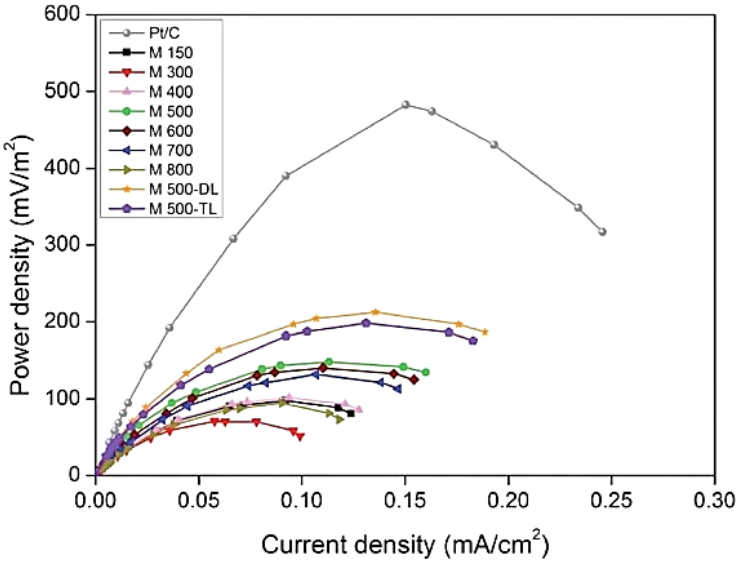

Figure 1. Power density curves of MFCs using different anode catalysts [5].

The OCP of M500-DL (double-loaded) and -TL (triple-loaded) cathode MFCs is similar and 13–50% higher than that of other MnO_2-based cathode MFCs, which is related to their higher electrochemical reaction rates.

Although different morphologies of MnO_2 catalysts and loading amounts lead to different maximum power densities, the CEs are all about 12-13%. This may be due to the fact that the CE is mainly affected by the anode performance (the ability of bacteria to oxidize substrates), or under the current experimental conditions, the difference in cathode materials has no significant impact on the amount of biofilm and oxygen diffusion on the cathode.

The M500 catalyst (especially the dual-loaded M500-DL) has a lower MFCs internal resistance because of its large specific surface area. The α- and δ-phase structures of MnO_2 are conducive to proton insertion. The nanorod morphology and high surface OH groups and Mn^{3+} ion concentration contributes to the four-electron transfer pathway of Oxygen Reduction Reaction (ORR), thereby reducing the internal resistance. The M300 catalyst has a low electron transfer efficiency and a high internal resistance due to its large and dense flower-like structure [5]. When facing MFCs in different environments, the effects of MnO_2 with different morphologies are also different. Farahani et al. introduced three types of MnO_2-based catalysts with different morphologies under different carriers

(α-MnO_2/C, unsupported α-MnO_2 and nitrogen-doped MnO_2/C) in their article. Experimental observations show that in terms of morphological characteristics, α-MnO_2 is a nanowire structure and β-MnO_2 is a nanorod structure [6].

Through a series of electrochemical characterizations and MFCs performance tests, in comparison, in terms of activity, β-MnO_2 nanorods show higher ORR activity, its starting potential is closer to a positive value, and its half-wave potential and limiting current density are similar to those of α-MnO_2/C (Figure 2). In terms of charge transfer resistance, the electrochemical impedance spectrum shows that the charge transfer resistance of β-MnO_2/C(N) is lower than that of α-MnO_2/C, indicating that it has faster charge transfer during the ORR process. In terms of performance comparison, in MFCs, the maximum power density generated by the MFCs with β-MnO_2/C(N) as the cathode is higher than that of the MFCs with α-MnO_2/C and α-MnO_2 as the cathode, and has better cycle stability [6].

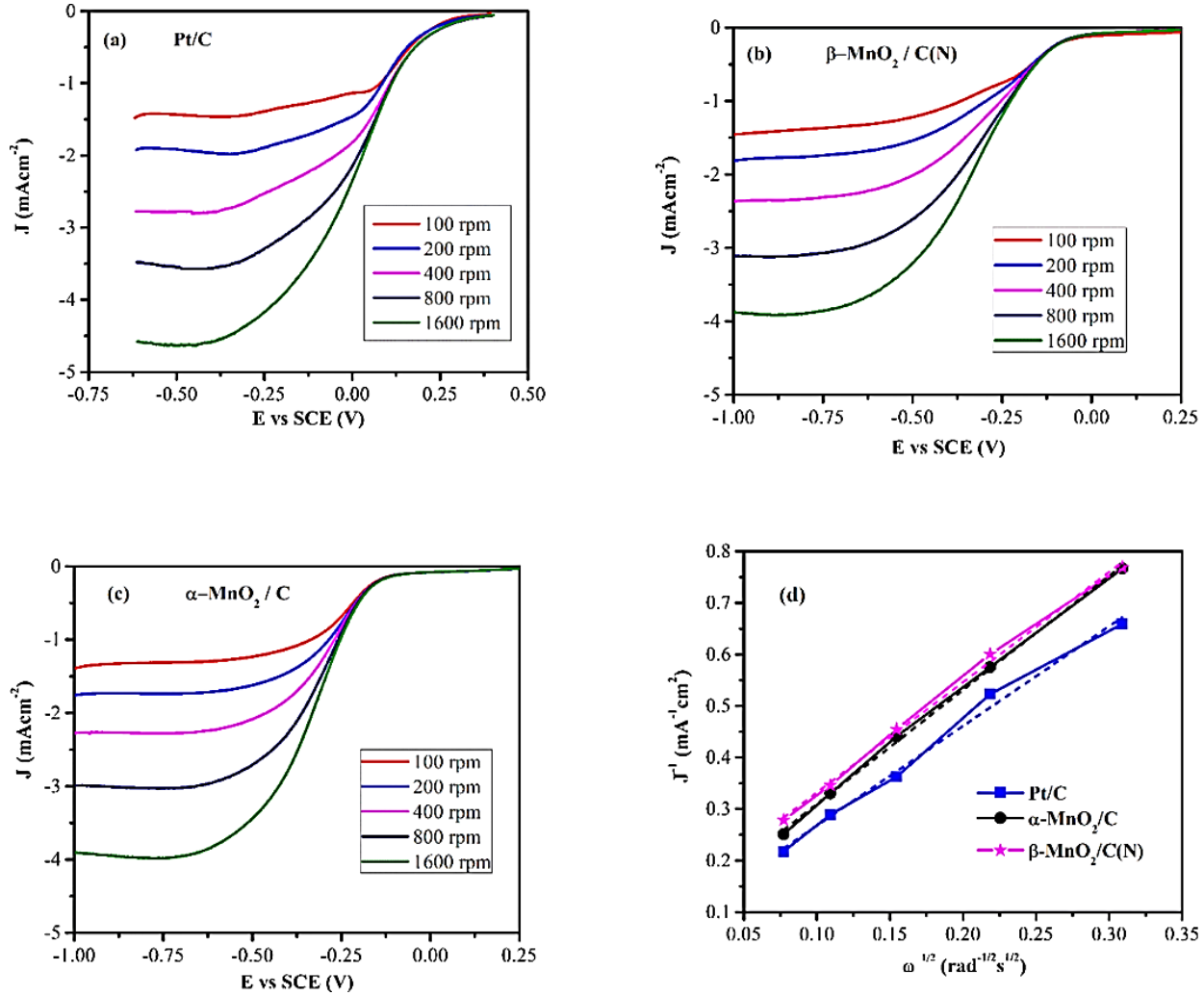

Figure 2. LSV curves of different anode catalysts at different electrode rotation rates: (a) Pt/C, (b) β-MnO_2/C(N), (c) α-MnO_2/C, (d) KL plots of Pt/C, α-MnO_2/C and β-MnO_2 at 0.6 V [6].

Anode modification is a common and simple method to change the morphology and structure of carbon nanomaterials. Modification with other nanomaterials can often make the electrochemical properties of the new electrode better. Liang et al. studied microbial fuel cells (SMFCs) based on graphene (GR), graphene oxide (GO) and multi-walled carbon nanotubes (CNTs) modified with graphite felt (GF) as the negative electrode material [7]. The nanomaterials used have special structures and unique crystal arrangement characteristics. GR and GO have unique honeycomb crystal arrangements, which are composed of two-dimensional sp^2- The three carbon nanomaterials all have a high surface area to volume ratio, which can increase the electrochemically active surface area of the anode and facilitate extracellular electron transfer. In addition, the material structure is uniform.

GR, GO and CNTs are successfully deposited on the anode surface with low intensity and evenly distributed on the GF surface, covering the GF fiber surface in sheets (GR and GO) and curled shapes (CNTs), respectively.

The protein content on the modified anode is higher than that of the unmodified graphite felt anode, indicating that the modification promotes the enrichment of electroactive bacteria on the anode. The analysis of the microbial community structure shows that the microbial diversity on the GR, GO and CNT anodes is higher than that on the GF anode. During the 110 days of operation, GR-SMFCs and GO-S MFCs generated higher electrical energy, followed by CNT-SMFCs, while GF-SMFCs generated the lowest electrical energy. During the stable period, GO-SMFCs output the highest voltage. For sediments close to the anode, the removal rates of loss on ignition, phenanthrene (PHE) and pyrene (PYR) by GR-SMFCs, GO-SMFCs and CNT-SMFCs were higher than those by GF-SMFCs, among which CNT-SMFCs had the best removal effect on PHE, and the removal effect of GO-SMFCs on PYR was similar to and better than that of GR-SMFCs and CNT-SMFCs [7].

More modification methods and more targeted materials have emerged to cope with the use of MFCs in different environments. Lin et al. made a breakthrough in using binder-free Fe nano-oxide to modify the anode [8]. They used a solvothermal method to in situ modify Fe nano-oxide on carbon cloth (CC) and nickel foam (NF) electrodes to prepare CC-Fe and NF-Fe electrodes. A series of physical and chemical characterizations confirmed that the Fe nano-oxide was successfully modified on the electrode surface, and its chemical composition was mainly a mixture of Fe_2O_3 and FeO.

They conducted corresponding electrochemical experiments and performance tests on the MFCs with CC, CC-Fe, NF and NF-Fe as anodes. M-CC/Fe had the highest maximum power density, reaching 471.6 mW/m^2, which are 3.13, 3.61 and 28.5 times higher than M-CC, M-NF/Fe and M-NF respectively. After Fe nanooxide modification, the electrochemical catalytic activity, extracellular electron transfer rate, COD removal efficiency and Coulombic efficiency of MFCs were all improved. At the same time, the charge transfer resistance of the electrode was significantly reduced, and the conductivity and electrochemical activity were improved. After the MFCs stably generates electricity, the CV curve of M-CC/Fe appears with two pairs of characteristic redox peaks, indicating its high catalytic activity. The article also analyzed anode biofilm morphology and microbial community analysis. The experimental results showed that in terms of biofilm, Fe nanooxide significantly improved the biocompatibility of metal-based electrodes, reduced corrosion, and promoted the formation of biofilm, and on the M-CC/Fe and M-NF/Fe anodes, Fe nanooxide particles are converted into nanocubes, which is beneficial to the hydrophilicity, stability and bioaffinity of the electrode. In the treatment of microorganisms, it was found that Fe nanooxide significantly enriched electroactive bacteria, while microbial diversity decreased. The proportion of electroactive bacteria on M-CC/Fe and M-NF/Fe anodes was higher, the biomass was larger, and it is beneficial to improve the power generation performance and COD removal efficiency of MFCs [8].

2.2. Effects of composite nanomaterials on MFCs performance

Polyaniline (PANI) is very common in electrochemistry due to its excellent conductivity and chemical stability. Kumar et al. pioneered the attempt to combine precious metals such as gold and platinum with PANI to prepare new PANI materials with different structures and explore their properties [9].

It was found that the Au@PANI modified electrode showed lower charge transfer resistance and higher conductivity, which promoted the extracellular electron transfer between cells and electrodes. In addition, the modification of Au@PANI core-shell composite material increased the MFCs power by about 1.4 times compared with the use of traditional PANI materials, The specific results are shown in Figure 3 [9].

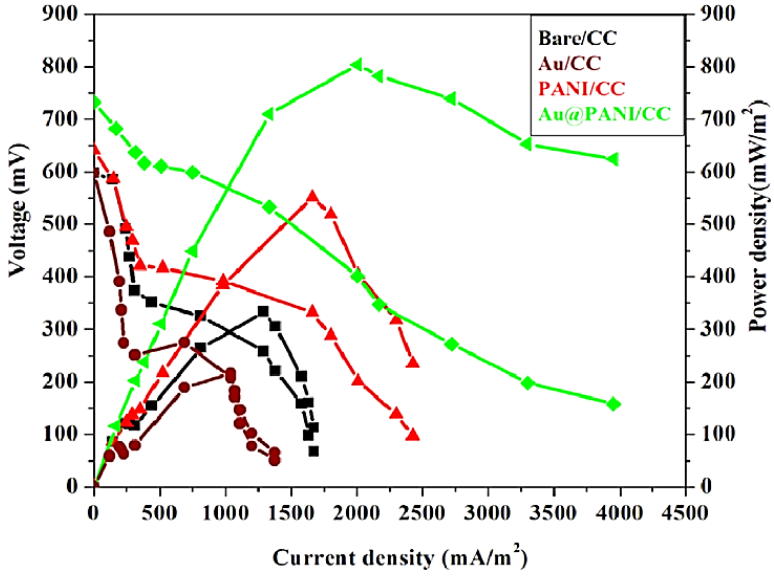

Figure 3. MFCs power density and polarization curves using different anode materials [9].

Similarly, synthesizing new catalysts and combining them with existing cathode materials is also a common cathode material composite method today. Combining catalysts with cathode materials through various mixing methods can effectively improve the efficiency and rate of the reaction and effectively avoid useless side reactions. Qin et al. successfully synthesized a new hybrid porous electrocatalyst: graphene-carbon-coated CoCu alloy nanoparticles were vertically arranged on carbon nanofibers (CoCu@N-CNFs) [10].

For high ORR catalytic activity, its ORR half-wave potential and limiting current density are better than 20% Pt/C, and the exchange current density is also high, indicating that the material has higher intrinsic ORR catalytic kinetics, which can accelerate the reduction rate of oxygen molecules and improve the activity of the catalyst.

For improved maximum power density, the MFCs equipped with CoCu@N-CNFs-1:1 catalyst has a slightly higher maximum power density than the Pt/C cathode, thanks to the material's inherent continuous electron transport pathway and excellent electrolyte ion transport behavior.

For equivalent coulombic efficiency, the coulombic efficiency of the MFCs is comparable to that of Pt/C, indicating that the low charge transfer internal resistance is conducive to the efficient circulation of electrons from the anode to the cathode, and promotes the efficient conversion of sodium acetate into electrical energy.

For improved chemical oxygen demand removal rate, its chemical oxygen demand (COD) removal rate (88.02%) is higher than that of other comparison groups, proving that its cathode kinetics is faster, the anode substrate is more fully utilized, and the system energy output is higher [10].

2.3. Analysis of electrochemical performance of MFCs based on new nanomaterials

Nitrogen-doped carbon nanofibers (NeCFNs) can not only be used in conjunction with other nanomaterials, but their superior electrochemical properties also play a key role in MFCs components even when used alone. Massaglia et al. conducted an in-depth study on the performance of NeCNFs as anode coating materials for single-chamber microbial fuel cells (SCMFCs).

After corresponding electrochemical experiments and performance tests, CV tests showed that NeCNF@600 had a clear current peak, showing a better electrochemical response, and its electroactive surface area was larger than that of NeCNF@900. Besides, electrochemical impedance spectroscopy (EIS) analysis confirmed that NeCNF@600 had a better electroactive surface, its charge transfer resistance (R_{ct}) was smaller than that of commercial carbon felt (CF), and the electron transfer rate was faster. SCMFCs with NeCNF@600 as anode coating had a maximum power density that was an order of magnitude higher than that of SCMFCs with CF-based anodes, and higher than the performance of NeCNF@900. The current density of the SCMFCs was also higher, and the

electroactive biofilm formed within 4 weeks enabled the battery to achieve a high-power density. At the same time, it had a lower internal resistance, which was conducive to electron transfer [11].

The innovative research and development of MFCs electrode materials has gradually become another hot topic after the improvement of electrode materials. Among them, the innovation and practice of new nanomaterials occupy a mainstream position. Sun et al. recently developed a new nanoelectrode material PVDF@Ag nanofiber membrane [12].

They then used the new material as an MFCs component for corresponding experiments and performance tests. It has electrocatalytic activity for oxygen reduction reaction. PVDF@Ag-1 h has the highest current response, low charge transfer resistance, and high exchange current density. As an MFCs cathode, the power density can reach 72% of commercial Pt/C, the chemical oxygen demand removal rate and Coulomb efficiency are good, and it has good stability and antibacterial properties [12].

3. Discussion and outlook

The introduction of nanomaterials has significantly improved the performance of MFCs. Some nanomaterials such as carbon nanotubes and MXene are low-cost and large-yield, which effectively reduces the cost of electrode materials. Different nanomaterial electrodes can handle a variety of substrates. It has strong adaptability to complex wastewater treatment and energy recovery, which undoubtedly broadens the application field of MFCs. After the introduction of nanomaterials as electrodes, MFCs will become the mainstream energy source in more fields due to its superior voltage stability, environmental adaptability and endurance. For example, in terms of power supply for low-power electronic equipment, MFCs can power sensors and small monitoring equipment in remote areas.

However, the construction of MFCs based on nanomaterials still has some limitations. The preparation process of currently developed nanomaterials is complicated. The preparation and modification of some nanomaterials require special equipment, harsh conditions and multi-step operations, which limits their ability to be mass-produced. The stability needs to be improved. In long-term operation, nanomaterials are affected by microbial metabolism, electrolyte corrosion and fluctuations in operating conditions. The quality of their structure and performance stability will affect the life and reliability of MFCs. There are potential environmental risks in misuse. Nanoparticles may be released during the preparation, use and disposal of nanomaterials, causing potential risks to the ecosystem and human health. This requires in-depth assessment and control.

In future scientific research, people can target the shortcomings of nanomaterials in MFCs, deepen the research on the interaction mechanism between nanomaterials and microorganisms, accurately design high-performance electrode materials for different environments, and try to develop more stable, efficient, environmentally friendly and easy-to-prepare nanomaterials and composite systems.

4. Conclusion

The use of different nanomaterials in MFCs can improve the ORR catalytic activity and proton insertion ability by changing the crystal phase, morphology or modifying the electrode, increase the electrochemically active surface area, promote the enrichment of electroactive bacteria and electron transfer, effectively reduce the internal resistance, and improve the maximum power density and stability of MFCs. In addition, it can reduce charge transfer resistance and improve conductivity, enhance catalytic activity, microbial adhesion, Coulomb efficiency and COD removal rate, and comprehensively improve the overall performance and energy conversion efficiency of MFCs. For new nanomaterials, their unique structures and properties effectively improve the electrochemical performance of MFCs. It increases the electroactive surface area and stability. The new material exhibits good chemical oxygen demand removal capabilities and antibacterial properties, providing a new path for the development of MFCs electrode materials.

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