Advances in Electrode Materials for Bio-electrochemical Systems:A Comprehensive Review

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Abstract. This article reviews the latest research progress on electrode materials in bio-electrochemical systems (BES), with a focus on the performance, advantages, disadvantages, and optimization strategies of anode and cathode materials in microbial fuel cells (MFC) and microbial electrolysis cells (MEC). As the core component of BES, electrode materials directly affect the system's energy conversion efficiency, operational stability, and cost-effectiveness. Currently, commonly used electrode materials include carbon-based materials (such as carbon cloth and graphene), metal materials (such as stainless steel and titanium), and composite materials (such as carbon nanotube-modified materials and metal oxide-coated electrodes). Although these materials have made some progress in terms of conductivity, specific surface area, and biocompatibility, they still face challenges such as limited catalytic activity, high costs, and susceptibility to corrosion. Additionally, this article summarizes optimization strategies for different electrode materials, such as surface modification techniques and nanostructure design, to enhance the catalytic activity, conductivity, and biocompatibility of electrodes. Future research directions include the development of biomimetic catalytic electrodes, intelligent materials, and the realization of large-scale production of electrode materials, thereby advancing bio-electrochemical systems from laboratory to industrial applications. By summarizing existing research achievements and proposing future research directions, this article aims to provide a reference for further innovation and application of BES electrode materials.

Keywords: Microbial fuel cells, Microbial electrolysis cells, Electrode materials.

1. Introduction

Bio-electrochemical systems (BES) are devices that use microorganisms or enzymes as biocatalysts to convert chemical energy into electrical energy or achieve other electrochemical processes. These systems combine the advantages of electrochemistry and biotechnology, showing great potential in energy, environmental, and sensing fields [1]. Depending on their functions and application scenarios, bio-electrochemical systems are mainly divided into the following categories: microbial fuel cells (MFC), which convert chemical energy from organic matter into electrical energy; and microbial electrolysis cells (MEC), which are used for hydrogen production or the synthesis of high-value-added chemicals. The core of these systems lies in the use of electron transfer between microorganisms and electrodes to achieve energy conversion or target reactions [2].

Electrode materials are key components of bio-electrochemical systems, and their performance directly affects the system's energy conversion efficiency and operational stability. Currently, commonly used electrode materials include carbon-based materials (such as carbon cloth, carbon felt, and graphene), metal materials (such as stainless steel and titanium), and composite materials (such as carbon nanotube-modified materials and metal oxide-coated electrodes) [3]. Although these materials have made some progress in terms of conductivity, specific surface area, and biocompatibility, they still face many challenges. For example, carbon-based materials have limited catalytic activity, metal materials are costly and prone to corrosion, and composite materials have complex preparation processes and are difficult to scale up. Therefore, the development of efficient, low-cost, and environmentally friendly electrode materials remains a focus of current research [2].

Based on current research progress and remaining knowledge gaps, it is assumed that a comprehensive summary of the latest advances in electrode materials for bio-electrochemical systems, clarifying the development and future research directions of these materials, will help promote material innovation, reduce costs, and improve system performance. Therefore, the objectives of this article are: 1) to summarize the advantages and disadvantages of different types of electrode materials in BES; 2) to summarize optimization strategies for different electrode materials; and 3) to propose future research directions for BES electrode materials.

2. Electrode Materials for Microbial Electrolysis Cells

Electrode materials are the core components of MEC, and their performance directly affects the system's hydrogen production efficiency, energy input, and operational stability. Traditional MEC materials are mostly carbon-based materials, while new MEC materials such as nickel foam have low electrochemical activity and need to use suitable catalyst coatings to optimize the overall performance, but it has the advantages of high porosity and surface area, which cannot be compared with traditional materials.

2.1. Anode Materials for MEC

The anode is the core site for microbial attachment and electron transfer. Anode materials must meet the following requirements: high conductivity, high specific surface area, biocompatibility, and chemical stability. Table 1 describes the advantages and disadvantages of carbon-based materials, metal materials, and composite materials. For example, the preparation process of composite materials is complex and cannot be applied in a large area, and the cost of graphene materials is high and it is difficult to be applied in production and life.

Table 1. MEC Anode Materials and Their Advantages and Disadvantages.

Material Type	Material Name	Advantages	Disadvantages	Reference
Carbon-based materials	Carbon cloth/carbon felt	Low cost, good conductivity	Limited catalytic activity	[4]
	Graphene/carbon nanotubes	High specific surface area and conductivity	High cost	[5]
	Biochar	Made from agricultural waste pyrolysis, low cost and sustainable	Requires activation or doping to improve performance	[6]
Metal materials	Titanium mesh/stainless steel	High mechanical strength	Prone to corrosion and poor biocompatibility	[7]
	Nickel foam	Porous structure suitable for microbial attachment	Poor long-term stability	[3]
Composite materials	Carbon-based-metal oxide composites (e.g., carbon felt/Fe_3O_4)	Strong electron transfer efficiency and anti-pollution ability	The preparation process is relatively complex.	[3]
	Conductive polymer-modified materials (e.g., polyaniline/carbon cloth)	Strong electrode conductivity and biocompatibility		[3]

2.2. Cathode Materials for MEC

Whether it is an anode material or a cathode material, high conductivity is a basic requirement. Compared to anode materials, the main function of cathode materials is to accept electrons to produce hydrogen or to carry out other reduction reactions. Cathode materials must meet the following requirements: high catalytic activity, corrosion resistance, etc. Table 2 evaluates from three aspects: precious metal catalysts, non-precious metal catalysts, and biological cathodes. Special emphasis is placed on the fact that non-precious metal materials can be comparable to precious metal materials after treatment.

Table 2. MFC Cathode Materials and Their Advantages and Disadvantages.

Material Type	Material Name	Advantages	Disadvantages	Reference
Noble metal catalysts	Platinum (Pt)	Highest hydrogen production catalytic activity	Extremely high cost and prone to poisoning	[8]
	Palladium (Pd)	Catalytic activity second to Pt	Still high cost	[9]
Non-noble metal catalysts	Transition metal alloys (e.g., Ni-Mo, Ni-Fe)	Low cost and catalytic activity close to platinum	Not applicable	[9]
	Transition metal sulfides/phosphides (e.g., MoS_2, Ni_2P)	Platinum-like catalytic activity	Not applicable	[8,10]
	Carbon-based catalysts (e.g., nitrogen-doped carbon nanotubes)	High catalytic performance through heteroatom doping		[10]
Biocathode	Microbial catalytic cathode	Diverse products (e.g., methane production)	Low efficiency	[9]

3. Electrode Materials for Microbial Fuel Cells

Both the electrode materials of MFC and MEC need to possess high conductivity, good biocompatibility, and stability to ensure the long-term operation and efficient performance of the system. Compared to MEC electrode materials, MFC converts organic matter into electrical energy through the action of microorganisms, with its electrode materials focusing on electron transfer and current generation. To date, the vast majority of MFC systems have been developed for wastewater treatment by biodegrading organic-rich waste to recycle energy. Under this premise, the requirements for MFC materials will be more stringent, it must have good corrosion resistance and stability to work in harsh working environments, and the cost should not be too high to achieve the purpose of waste water utilization.

3.1. Anode Materials for MFC

The anode is the key site for microbial attachment and electron transfer. Anode materials must meet the following requirements: high conductivity, high specific surface area, biocompatibility, and chemical stability. Table 3 introduces the advantages and disadvantages of carbon-based materials, metal materials, and composite materials. Taking carbon-based metal oxide composites as an example, the catalytic activity and electron transport efficiency of the electrode are high, but the preparation process is complex and difficult to apply.

Table 3. MEC Anode Materials and Their Advantages and Disadvantages.

Material Type	Material Name	Advantages	Disadvantages	Reference
Carbon-based materials	Carbon cloth/carbon felt	Low cost, good conductivity	Limited catalytic activity	[1]
	Graphene	Extremely high specific surface area and conductivity	High cost, complex preparation process	[1]
	Carbon nanotubes	Excellent conductivity and mechanical strength	High cost	[1]
	Carbon brush	Made of carbon fibers, high specific surface area and good microbial attachment	Difficult to popularize	[2]
	Biochar	Made from biomass pyrolysis, low cost and environmentally friendly	Poor conductivity and stability	[2]
Metal materials	Stainless steel	High mechanical strength and conductivity	Prone to corrosion and poor biocompatibility	[11]
	Titanium	Strong corrosion resistance	High cost	[11]
Composite materials	Carbon-based-metal oxide composites (e.g., carbon cloth modified with MnO_2, Fe_3O_4)	High catalytic activity and electron transfer efficiency	The preparation process is complex.	[12]
	Carbon-based-conductive polymer composites (e.g., polyaniline (PANI), polypyrrole (PPy) modified carbon materials)	High electrode conductivity and biocompatibility	Not applicable	[12]

3.2. Cathode Materials for MFC

The cathode is the site where the oxygen reduction reaction (ORR) occurs, and its materials need to possess high catalytic activity, high electrical conductivity, and good chemical stability. Although there are similarities between cathode and anode materials in terms of basic materials and functional requirements, the need to consider the compatibility of cathode materials with catalysts and the adhesion of catalysts means that cathode materials require additional processing before they can be used. Table 4 introduces some representative advantages and disadvantages of MFC cathode materials from the perspectives of carbon-based and platinum-based materials. In particular, perovskite materials have high ORR catalytic activity, but they are difficult to produce and put into production.

Table 4. MEC Cathode Materials and Their Advantages and Disadvantages.

Material Type	Material Name	Advantages	Disadvantages	Reference
Carbon-based materials	Carbon paper/carbon cloth	Low cost, good conductivity	Low catalytic activity	[1,13]
	Activated carbon	High specific surface area	Poor conductivity	[1,13]
	Graphene/carbon nanotubes	High conductivity and catalytic activity	High cost	[1,13]
Platinum-based materials	Platinum (Pt)	Extremely high ORR catalytic activity	High cost and prone to poisoning	[1]
	Platinum alloys	Reduced platinum usage and improved catalytic performance	Not applicable	[1]
Non-noble metal materials	Transition metal oxides	Low cost and high catalytic activity	Stability is relatively poor.	[11]
	Transition metal-nitrogen-carbon materials (M-N-C)	Catalytic activity close to platinum and good stability	High cost	[11]
	Perovskite materials	High ORR catalytic activity and corrosion resistance	Difficult to produce.	[11]
Biocathode materials	Biofilm cathode	Low cost and environmentally friendly	Low catalytic efficiency	[13]

4. Optimization Strategies for Electrode Materials

4.1. Surface Modification Techniques

Using chemical, physical, or biological methods to modify the electrode surface to enhance its catalytic activity, conductivity, and biocompatibility. Surface modification techniques, such as nitrogen doping and oxygen plasma treatment, enhance electrode catalytic activity, conductivity, and biocompatibility. For example, nitrogen-doped graphene can improve electron mobility and enhance ORR catalytic activity [14]; oxygen plasma treatment of carbon felt can increase surface roughness and expand the specific surface area [15].

4.2. Nanostructure Design

Using nanotechnology to control the microstructure of electrodes, optimizing electron transfer paths and reaction sites. For example, designing three-dimensional porous carbon foam with a porosity >90% and a specific surface area of 2000 m^2/g can significantly increase microbial loading [16]; Nanostructure design, such as three-dimensional porous carbon foam and hierarchical porous Ti_3C_2Tx MXene electrodes, optimizes electron transfer paths and reaction sites, significantly improving system performance. [17].

5. Conclusion and Outlook

In this paper, the advantages and disadvantages of different types of electrode materials in different BES systems are introduced, and the commonalities and anisotropic characteristics of electrode materials in different BES systems are proposed. Then, the optimization strategies of different electrode materials are summarized and discussed, and the two most mainstream optimization strategies of electrode materials are briefly introduced by taking surface modification technology and nanostructure design technology as examples, hoping to help the future research and development progress of electrode materials.

In future research, the optimization of BES electrode materials may not be limited to microscopic modifications and macroscopic structural design. By simulating natural electron transfer chains, biomimetic catalytic electrodes can be developed, and intelligent materials and large-scale production should not be overlooked. This will enable bio-electrochemical systems to move from the laboratory to industrial applications.

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