

Improving the Performance of Microbial Fuel Cell Electrode Materials to Enhance Electricity Production

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Abstract This study hopes to investigate novel materials and configurations that can increase bacterial adhesion, improve electron transfer, and ultimately boost power output. The study identified several key findings. Polypyrrole (PPy)-coated electrodes significantly increased initial power production from 20 mW/m² to 160 mW/m² within the first four days, although no significant difference was observed between different coating thicknesses. Granular activated carbon (GAC) electrodes demonstrated high bacterial adhesion and power output, generating 5 W/m³ and maintaining peak power for six days. Additionally, the use of N-doped carbon nanotubes (NCNTs) on carbon felt (CF) as a support for hierarchical Co₈FeS₈-FeCo₂O₄/NCNTs core-shell nanostructures resulted in a power density of 3.04 W/m², a 47.6% improvement compared to bare CF. The study also highlighted the importance of optimizing the microbial community and biofilm formation to enhance electron transfer and power generation. The findings suggest that the use of advanced electrode materials such as PPy-coated electrodes, GAC, and hierarchical nanostructures can significantly enhance the performance of MFCs. These improvements in electrode materials and configurations can lead to higher power densities and more efficient electricity production from organic waste. Future research should focus on further optimizing these materials and exploring their long-term stability and scalability for practical applications.

Keywords Microbial fuel cells; Electrode materials; Electricity production; Polypyrrole; Granular activated carbon; N-doped carbon nanotubes; Biofilm formation; Electron transfer

1 Introduction

Microbial fuel cells (MFCs) have emerged as a promising technology for sustainable energy production by converting organic waste into electricity through the metabolic activities of microorganisms. This innovative approach leverages the ability of electroactive bacteria to transfer electrons to an electrode during the degradation of organic substrates, thus generating an electric current (Pant et al., 2010; Santoro et al., 2017; Rahimnejad et al., 2019). MFCs have been explored for various applications, including wastewater treatment, bioenergy production, and environmental monitoring, due to their potential to utilize a wide range of organic materials and operate under ambient conditions (Mohan et al., 2009; Moqsud et al., 2013; Kusmayadi et al., 2020).

The performance of MFCs is significantly influenced by the properties of the electrode materials used. The anode and cathode materials play a crucial role in the efficiency of electron transfer, biofilm formation, and overall power output of the system. Carbon-based materials, such as graphite and carbon fiber, are commonly used for their high conductivity and biocompatibility, which facilitate effective microbial colonization and electron transfer (Moqsud et al., 2013; Santoro et al., 2017; Saratale et al., 2017; Rahimnejad et al., 2019). Additionally, the development of novel electrode materials and configurations, such as bamboo charcoal and advanced carbon composites, has shown potential in enhancing the electrochemical performance and durability of MFCs (Moqsud et al., 2013; Zhou et al., 2013; Wang et al., 2018).

This study aims to investigate and improve the performance of electrode materials in microbial fuel cells to enhance electricity production. The study will focus on evaluating different electrode materials, their configurations, and the impact of various operational parameters on the efficiency of MFCs. By optimizing the electrode materials and understanding their interactions with microbial communities, this studyh seeks to

contribute to the development of more efficient and sustainable MFC systems for practical applications in energy generation and environmental remediation.

2 Fundamentals of Microbial Fuel Cells

2.1 Working principle of MFCs

Microbial Fuel Cells (MFCs) are bio-electrochemical systems that convert chemical energy stored in organic substrates directly into electrical energy through the metabolic activities of microorganisms. The fundamental working principle involves the oxidation of organic matter by microorganisms in the anode chamber, which releases electrons and protons. The electrons are transferred to the anode and flow through an external circuit to the cathode, generating electricity. Meanwhile, the protons migrate through a proton exchange membrane to the cathode, where they combine with electrons and an electron acceptor, typically oxygen, to form water (Li et al., 2018; Massaglia et al., 2020; Chen et al., 2021a).

2.2 Types of microorganisms used in MFCs

The microorganisms used in MFCs, known as electricigens or exoelectrogens, play a crucial role in the electron transfer process. These microorganisms can be categorized into pure cultures and mixed communities. Pure cultures, such as *Geobacter* and *Shewanella* species, are often used to study specific electron transfer mechanisms due to their well-characterized metabolic pathways. However, mixed microbial communities are generally more robust and efficient in electricity generation and can adapt better to complex environments. Mixed communities can include a variety of bacteria that work synergistically to enhance the overall performance of the MFC (Li et al., 2018; Cao et al., 2019; Chen et al., 2021a).

2.3 Role of electrodes in MFCs

Electrodes are critical components in MFCs, serving as the sites for microbial attachment and electron transfer. The anode, in particular, is where the primary conversion of organic matter into electrons occurs. The material and design of the anode significantly influence the efficiency of electron transfer and the overall performance of the MFC. Advanced materials such as carbon-based nanomaterials, metal oxides, and composite materials have been developed to enhance the electrical conductivity, biocompatibility, and surface area of the anode, thereby improving microbial attachment and electron transfer rates (Cai et al., 2020; Yang et al., 2020; Yaqoob et al., 2020a; Banerjee et al., 2022; Wang et al., 2022). The cathode also plays a vital role by facilitating the reduction reactions and completing the electrical circuit. Innovations in electrode materials and configurations continue to be a major focus of research to optimize MFC performance (Slate et al., 2019; Cai et al., 2020; Wang et al., 2022).

3 Current Electrode Materials in MFCs

3.1 Carbon-based materials (graphite, carbon cloth, carbon paper)

Carbon-based materials are widely used in microbial fuel cells (MFCs) due to their favorable properties such as low cost, high conductivity, and chemical stability. Graphite, carbon cloth, and carbon paper are commonly employed as anode materials. These materials support bacterial attachment and facilitate extracellular electron transfer (EET), which is crucial for electricity generation in MFCs. For instance, carbon cloth modified with polydopamine and reduced graphene oxide (CC-PDA-rGO) has shown significant improvements in power density and electron transfer efficiency (Li et al., 2020). Additionally, carbon felt modified with nickel ferrite and MXene composites has demonstrated enhanced electrochemical performance and higher power densities (Tahir et al., 2020).

3.2 Metal-based materials (stainless steel, titanium)

Metal-based materials such as stainless steel and titanium are also used in MFCs due to their excellent electrical conductivity and mechanical strength. These materials can serve as both anode and cathode components. For example, stainless steel and titanium electrodes have been utilized to improve the overall performance and durability of MFCs. However, their high cost and susceptibility to corrosion in certain environments can limit their widespread application (Slate et al., 2019) (Figure 1).

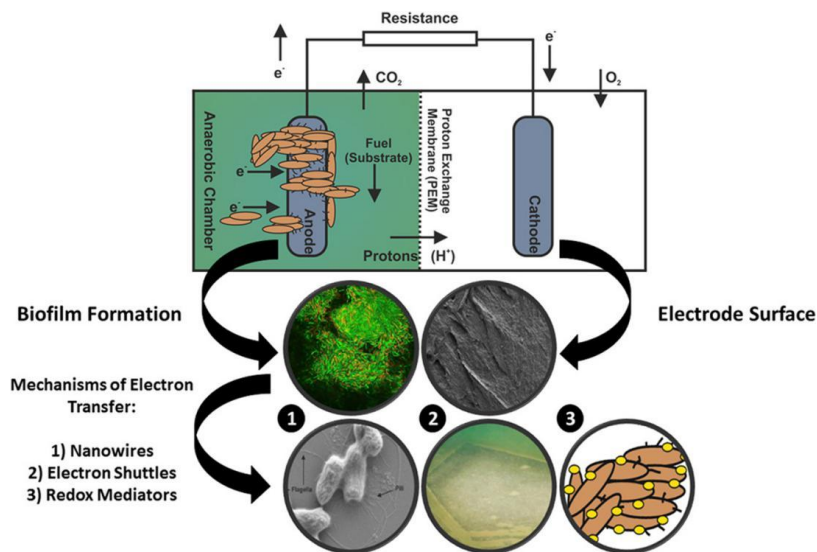


Figure 1 Electron transfer mechanism and application of advanced electrode materials in microbial fuel cells (Adapted from Slate et al., 2019)

3.3 Composite materials

Composite materials, which combine the properties of different materials, have been developed to enhance the performance of MFC electrodes. These materials often incorporate carbon-based substrates with metal oxides or other conductive materials to improve conductivity, surface area, and biocompatibility. For instance, $NiFe_2O_4$ -MXene composites on carbon felt have shown superior bioelectrochemical activity and higher power densities compared to conventional carbon felt electrodes (Tahir et al., 2020). Similarly, hierarchical Co_8FeS_8 - $FeCo_2O_4$ /N-CNTs@CF composites have demonstrated improved microorganism attachment and faster EET rates, leading to higher power densities and better pollutant removal (Wang et al., 2022).

3.4 Limitations of current electrode materials

Despite the advancements in electrode materials, several limitations remain. Carbon-based materials, while cost-effective and stable, may not always provide the highest conductivity or surface area required for optimal performance. Metal-based materials, although highly conductive, can be expensive and prone to corrosion. Composite materials, while offering improved performance, can be complex and costly to produce. Additionally, the scalability of these advanced materials for industrial applications remains a challenge. Further research is needed to develop cost-effective, durable, and high-performance electrode materials to make MFCs economically viable for large-scale applications (Li et al., 2018; Slate et al., 2019; Yaqoob et al., 2021a).

4 Advanced Electrode Materials for Enhanced Performance

4.1 Graphene and its derivatives

Graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO), have shown significant promise in enhancing the performance of microbial fuel cells (MFCs). These materials increase the electrochemically active surface area and improve the electron transfer rate, which are crucial for efficient electricity generation. For instance, a study demonstrated that a polydopamine-reduced graphene oxide (PDA-rGO) modified anode achieved a power density of $2\ 047\ mW \cdot m^2$, significantly higher than unmodified carbon cloth anodes (Li et al., 2020). Another research highlighted the use of a graphene-polyaniline (GO-PANI) composite anode, which showed a fourfold increase in performance compared to unmodified anodes (Yaqoob et al., 2020b). These modifications not only enhance power output but also improve the bioremediation efficiency of toxic metals.

4.2 Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are another advanced material that has been extensively studied for MFC applications. CNTs provide excellent conductivity and a high surface area, which facilitate efficient electron transfer and

biofilm formation. For example, a study reported that nitrogen-doped CNTs (NCNTs) on carbon felt (CF) significantly improved the power density and chemical oxygen demand (COD) removal in MFCs (Wang et al., 2022). Additionally, the combination of CNTs with other materials, such as polypyrrole, has shown to further enhance the performance. A vertical CNT/polypyrrole composite anode achieved a maximum power density of 1 876.62 $\text{mW}\cdot\text{m}^{-2}$, which was approximately 2.63 times higher than unmodified carbon fiber brush anodes (Zhao et al., 2019).

4.3 Conductive polymers (polyaniline, polypyrrole)

Conductive polymers like polyaniline (PANI) and polypyrrole (PPy) have been used to modify electrode materials to improve their conductivity and biocompatibility. These polymers provide a conducive environment for microbial growth and electron transfer. For instance, a cellulose-derived graphene/polyaniline (GO-PANI) nanocomposite anode demonstrated a significant improvement in electron transfer rate and current density in benthic MFCs (Yaqoob et al., 2020b). Similarly, a polypyrrole-carboxymethyl cellulose-titanium nitride/carbon brush (PPy-CMC-TiN/CB) hydrogel anode showed a maximum power density of 14.11 $\text{W}\cdot\text{m}^{-3}$, which was 4.72 times larger than that of a blank carbon brush anode (Wang et al., 2020).

4.4 Metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs) are a class of materials that have shown potential in enhancing the performance of MFC electrodes due to their high surface area and tunable porosity. A study demonstrated that a Ni-catecholate-based MOF grown on NiCoAl-layered double hydroxide/multi-wall carbon nanotubes (Ni-CAT/NiCoAl-LDH/MWCNTs) significantly improved the power generation efficiency and cycle stability of the electrode (Chen et al., 2021b). Another research highlighted the use of zeolitic imidazolate framework-67 (ZIF-67) combined with electrospinning polyacrylonitrile to create a carbon nanofiber composite cathode, which achieved a maximum power density of 1.191 $\text{W}\cdot\text{m}^{-2}$ (Jiang et al., 2021).

4.5 Nanostructured materials

Nanostructured materials, including hierarchical nanostructures and composites, have been explored to enhance the performance of MFC electrodes. These materials offer a high surface area and improved electron transfer properties. For example, a hierarchically porous nitrogen-doped CNTs/reduced graphene oxide (N-CNTs/rGO) composite anode achieved a maximum power density of 1 137 $\text{mW}\cdot\text{m}^{-2}$, which was significantly higher than that of non-doped composites (Wu et al., 2018). Additionally, a 3D hierarchical $\text{Co}_8\text{FeS}_8\text{-FeCo}_2\text{O}_4\text{/N-CNTs@CF}$ anode showed a power density of 3.04 $\text{W}\cdot\text{m}^{-2}$, demonstrating the effectiveness of hierarchical nanostructures in improving MFC performance (Wang et al., 2022).

By leveraging these advanced electrode materials, significant improvements in the efficiency and stability of microbial fuel cells can be achieved, paving the way for their practical applications in energy generation and environmental remediation.

5 Strategies for Improving Electrode Performance

5.1 Surface modification techniques

5.1.1 Physical modifications (nano-patterning, 3D structures)

Physical modifications such as nano-patterning and the creation of 3D structures can significantly enhance the performance of microbial fuel cell (MFC) electrodes. For instance, the development of hierarchical nanostructures like $\text{Co}_8\text{FeS}_8\text{-FeCo}_2\text{O}_4\text{/N-CNTs}$ on carbon felt has been shown to improve wettability, specific areal capacitance, and diffusion coefficient, while reducing charge transfer resistance. This results in a substantial increase in power density and COD removal efficiency (Wang et al., 2022). Similarly, the use of stainless steel cloth modified with carbon nanoparticles has demonstrated a 2.3-fold increase in maximum power density, attributed to the increased electrochemically-active surface area and enhanced electron transfer (Wu et al., 2020).

5.1.2 Chemical modifications (functionalization, doping)

Chemical modifications, including functionalization and doping, are effective strategies for improving electrode performance. For example, the incorporation of covalent organic frameworks (COFs) on carbon felt has led to

significant improvements in bioelectrochemical activity, electrode stability, and power density (Tahir et al., 2022). Additionally, modifying Ti_3C_2MXene with ammonium ions to enhance surface properties has resulted in higher specific surface area, hydrophilicity, and electropositivity, thereby increasing current density and reducing charge transfer resistance (Yang et al., 2021).

5.2 Enhancing biocompatibility

5.2.1 Incorporation of bioactive compounds

Incorporating bioactive compounds into electrode materials can enhance biocompatibility and promote microbial adhesion. For instance, the use of bioactive nanomaterials such as carbon and metal-based nanoparticles can facilitate the growth of thick microbial biofilms, improving electron transfer between the electrodes and the biofilm (Mashkour et al., 2021). This approach not only enhances power generation but also supports the sustainable production of electricity from wastewater (Nosek et al., 2020).

5.2.2 Use of biocompatible coatings

Applying biocompatible coatings to electrodes is another strategy to improve microbial adhesion and activity. For example, the use of polypyrrole (PPy) coatings embedded with carbon nanoparticles has been shown to significantly improve biocompatibility and functional group contents, which are beneficial for bacterial adhesion on electrodes (Wu et al., 2020). This modification leads to enhanced electron transfer and overall MFC performance.

5.3 Increasing electrical conductivity

5.3.1 Integration of conductive nanomaterials

Integrating conductive nanomaterials into electrode structures can greatly enhance electrical conductivity. The use of N-doped carbon nanotubes (NCNTs) on carbon felt, for instance, has been shown to improve specific areal capacitance and reduce charge transfer resistance, resulting in higher power density and COD removal efficiency (Wang et al., 2022). Similarly, the incorporation of conductive polymers like polyaniline (PANI) with metal-organic frameworks (MOFs) has demonstrated significant improvements in power density and current density (Kaur et al., 2021).

5.3.2 Optimization of material composition

Optimizing the composition of electrode materials is crucial for maximizing electrical conductivity. For example, modifying carbon-based electrodes with various metallic nanomaterials and polymers has been shown to provide more electrochemically active sites and improve microbial adhesion, leading to enhanced power output (Nosek et al., 2020). Additionally, the use of hybrid materials such as $FeCo/NCNTs@CF$ has been shown to facilitate the enrichment growth of exoelectrogens and promote extracellular electron transfer (EET) (Wang et al., 2022).

By employing these strategies, the performance of MFC electrodes can be significantly improved, leading to higher power generation and more efficient wastewater treatment.

6 Case Study: Enhanced MFC Performance Using Modified Electrode Materials

6.1 Description of the experimental setup

The experimental setup for this study involved the use of microbial fuel cells (MFCs) equipped with various modified electrode materials to evaluate their performance in electricity production and wastewater treatment. The MFCs typically consisted of two chambers separated by a cation exchange membrane, with the anode and cathode placed in the respective chambers. The anode materials were modified using different nanomaterials and composites to enhance microbial attachment and extracellular electron transfer (EET) rates.

6.2 Materials and methods used

Several innovative materials and methods were employed to modify the electrodes in the MFCs. For instance, N-doped carbon nanotubes (NCNTs) were grown on carbon felt (CF) to create a hierarchical $Co_8FeS_8-FeCo_2O_4/NCNTs$ core-shell nanostructure ($FeCo/NCNTs@CF$) (Wang et al., 2022). Another study utilized covalent organic frameworks (COFs) to modify the carbon felt surface, resulting in the $TpPa-1@CF$

anode (Tahir et al., 2022). Additionally, graphene oxide (GO) and GO-polymer-metal oxide (GO-PANI-Ag) composites were prepared from biomass and used as anode materials (Yaqoob et al., 2022). These modifications aimed to improve the surface area, conductivity, and biocompatibility of the electrodes, thereby enhancing microbial growth and electron transfer.

6.3 Results and discussion

The modified electrode materials demonstrated significant improvements in MFC performance compared to conventional materials. The FeCo/NCNTs@CF anode exhibited a power density of 3.04 W/m² and a chemical oxygen demand (COD) removal rate of 221.0 mg/L/d, representing improvements of 47.6% and 290.1%, respectively, over bare CF (Wang et al., 2022). Similarly, the TpPa-1@CF anode showed a 4.3-fold increase in power density (1 069 mW/m²) and a 12.7-fold increase in current density (1 954 mA/m²) compared to uncoated electrodes (Tahir et al., 2022). The GO-PANI-Ag composite anode achieved an energy efficiency of 2.09 mW/m² and demonstrated high heavy metal removal rates, with 78.10% removal of Pb(II) and 80.25% removal of Cd(II) (Yaqoob et al., 2022) (Figure 2).

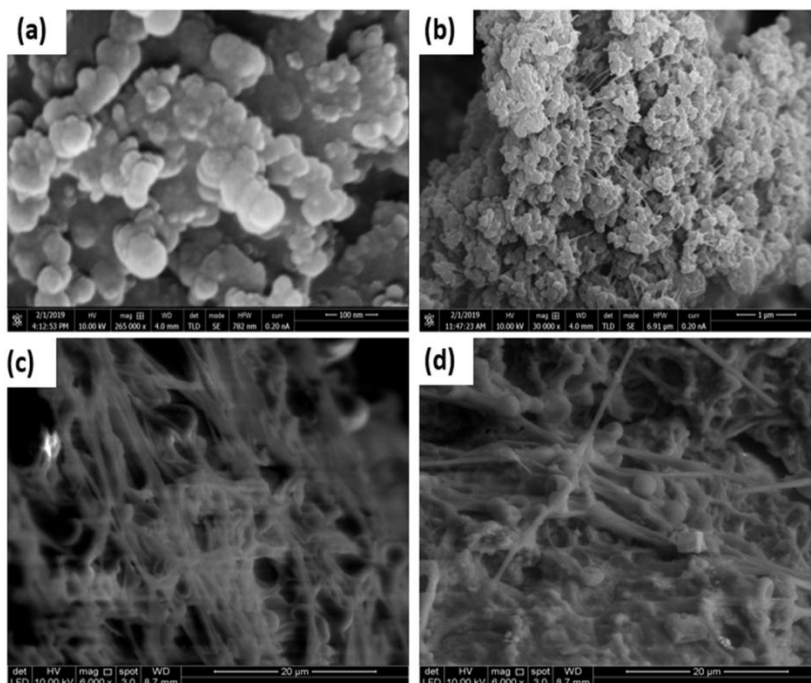


Figure 2 SEM images before and after the operation of MFCs: (a) GO anode before operation, (b) GO-PANI-Ag anode before operation, (c) GO anode after operation, and (d) GO-PANI-Ag anode after operation (Adopted from Yaqoob et al., 2022)

6.4 Comparison with conventional electrode materials

Conventional electrode materials such as carbon, graphite, stainless steel, and ceramics have been widely used in MFCs but often suffer from limitations in electron transfer efficiency and microbial attachment (Abd-Elrahman et al., 2022; Starowicz et al., 2023). The modified electrodes in this study, including those incorporating nanomaterials and advanced composites, showed superior performance by enhancing the surface area, reducing charge transfer resistance, and promoting biofilm formation. For example, the hierarchical nanostructures and COF-modified surfaces provided more active sites for microbial adhesion and facilitated faster EET, leading to higher power outputs and better wastewater treatment efficiency (Liang et al., 2022; Tahir et al., 2022; Wang et al., 2022).

6.5 Implications for future MFC designs

The findings from this study have significant implications for the future design and development of MFCs. The use of advanced nanomaterials and composite structures for electrode modification can substantially improve the performance and efficiency of MFCs. Future research should focus on optimizing these materials for large-scale

applications and exploring new combinations of nanomaterials to further enhance microbial interactions and electron transfer processes. Additionally, the integration of these advanced materials into practical MFC systems could pave the way for more efficient and sustainable bioenergy production and wastewater treatment technologies (Abd-Elrahman et al., 2022; Tahir et al., 2022; Wang et al., 2022; Yaqoob et al., 2022).

7 Challenges and Future Perspectives

7.1 Technical challenges in material synthesis and modification

The synthesis and modification of electrode materials for microbial fuel cells (MFCs) present several technical challenges. One significant issue is achieving a balance between enhancing conductivity and maintaining biocompatibility. For instance, while nanomaterials such as graphene oxide (GO) and metal oxides (e.g., TiO₂) have shown promise in improving electron transfer rates and biocompatibility, their synthesis can be complex and costly (Mashkour et al., 2021; Yaqoob et al., 2021c). Additionally, the integration of these materials into existing MFC systems without compromising their structural integrity and long-term performance remains a challenge (Li et al., 2020; Yaqoob et al., 2021b). Advanced materials like NiFe₂O₄-MXene composites have demonstrated improved electrochemical performance, but their fabrication processes are still in the experimental stages and require further optimization for practical applications (Tahir et al., 2020).

7.2 Scalability and cost-effectiveness

Scalability and cost-effectiveness are critical factors for the widespread adoption of MFC technology. The high cost of advanced electrode materials, such as carbon-based nanomaterials and metal-based catalysts, poses a significant barrier (Slate et al., 2019; Cai et al., 2020). Moreover, the production processes for these materials often involve expensive and complex techniques, making large-scale manufacturing challenging (Mashkour et al., 2021). Efforts to develop low-cost alternatives, such as biomass-derived graphene oxide and acrylic-based graphite paints, have shown potential, but further research is needed to ensure these materials can deliver comparable performance to their more expensive counterparts (Masoudi et al., 2020; Yaqoob et al., 2021c).

7.3 Long-term stability and durability

The long-term stability and durability of electrode materials are crucial for the sustained operation of MFCs. Materials must withstand harsh environmental conditions, including varying pH levels and the presence of contaminants, without significant degradation (Gajda et al., 2020). For example, surface modifications with polydopamine and reduced graphene oxide have been shown to enhance the stability and electron transfer capabilities of carbon cloth anodes, but their long-term performance under real-world conditions needs further validation (Li et al., 2020). Additionally, maintaining the structural integrity of biofilms on the electrode surface over extended periods is essential for consistent power generation (Mier et al., 2021; Yaqoob et al., 2021b).

7.4 Potential environmental impacts

The environmental impacts of using advanced materials in MFCs must be carefully considered. While nanomaterials and metal-based catalysts can significantly enhance performance, their potential toxicity and environmental persistence pose risks (Mashkour et al., 2021). The disposal and recycling of these materials at the end of their lifecycle also present challenges. Research into environmentally friendly and biodegradable materials, such as biomass-derived electrodes, is ongoing and offers a promising direction for reducing the ecological footprint of MFC technology (Yaqoob et al., 2021c).

7.5 Future research directions

Future research should focus on several key areas to address the challenges outlined above. First, developing cost-effective and scalable synthesis methods for advanced electrode materials is essential (Slate et al., 2019; Cai et al., 2020). Second, enhancing the long-term stability and durability of these materials through innovative surface modifications and composite structures should be prioritized (Li et al., 2020; Tahir et al., 2020). Third, investigating the environmental impacts of new materials and developing sustainable alternatives will be crucial for the responsible advancement of MFC technology (Mashkour et al., 2021; Yaqoob et al., 2021c). Finally, interdisciplinary research combining electrochemistry, materials science, and microbiology will be vital for optimizing the performance and scalability of MFCs (Mier et al., 2021; Yaqoob et al., 2021b).

8 Concluding Remarks

This study has explored the potential of advanced electrode materials to significantly enhance the performance of microbial fuel cells (MFCs). Key findings indicate that the use of novel materials such as 2D nanomaterials, carbon-based compounds, and metal-organic frameworks can dramatically improve the power output and efficiency of MFCs. These materials enhance the electrochemical properties of the electrodes, facilitate better electron transfer, and improve the adhesion and activity of electrogenic bacteria. Additionally, modifications to the anode, such as the incorporation of carbon nanotubes and cobalt phosphate, have shown promising results in increasing power densities and overall MFC performance.

Advanced electrode materials play a crucial role in the development and optimization of MFC technology. These materials address several of the key limitations currently hindering the practical application of MFCs, such as low power output, high operational costs, and scalability issues. By improving the electrical conductivity, surface area, and biocompatibility of the electrodes, advanced materials enhance the efficiency of electron transfer processes and support the growth and activity of electroactive bacteria. This not only boosts the power generation capabilities of MFCs but also extends their operational lifespan and reduces maintenance costs, making them more viable for large-scale applications.

The advancements in electrode materials for MFCs have significant implications for sustainable energy production. By harnessing the metabolic processes of microorganisms to generate electricity, MFCs offer a renewable and eco-friendly alternative to fossil fuel-based energy sources. The improved performance of MFCs through advanced electrode materials can lead to more efficient and cost-effective energy production, contributing to the reduction of greenhouse gas emissions and the mitigation of climate change. Furthermore, the ability of MFCs to treat wastewater while generating electricity adds an additional layer of environmental benefit, making them a versatile technology for sustainable development. Continued research and development in this field are essential to fully realize the potential of MFCs as a cornerstone of future renewable energy systems.

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Conflict of Interest Disclosure

The authors affirm that this research was conducted without any commercial or financial relationships that could be construed as a potential conflict of interest.

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