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Metal-based cathode catalysts for electrocatalytic ORR in microbial fuel cells: A review

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ABSTRACT

Microbial fuel cells (MFCs) have a simple structure and excellent pollutant treatment and power generation performance. However, the slow kinetics of the oxygen reduction reaction (ORR) at the MFC cathode limit power generation. The electrochemical performance of MFCs can be improved through electrocatalysis. Thus far, metal-based catalysts have shown astonishing results in the field of electrocatalysis, enabling MFC devices to demonstrate power generation capabilities comparable to those of Pt, thus showing enormous potential. This article reviews the research progress of metal-based MFC cathode ORR catalysts, including the ORR reaction mechanism of MFC, different types of catalysts, and preparation strategies. The catalytic effects of different catalysts in MFC are compared and summarized. Before discussing the practical application and expanded manufacturing of catalysts, we summarize the key challenges that must be addressed when using metal-based catalysts in MFC, with the aim of providing a scientific direction for the future development of advanced materials.

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1. Introduction

With the rapid industrialization of human society, the extraction and consumption of fossil fuels have reached an unprecedented and alarming rate [1–3]. The extreme depletion of fossil fuels and the emission of waste (waste liquids, waste gases, and solid wastes) from human industrial activities have caused various environmental problems, such as global warming [4,5], destruction of the ozone layer [6,7], disintegration of glaciers at Earth's poles [8,9], and changes in the communities of various biota in Earth's ecosystem [10,11]. Environmental problems have also significantly affected human health, and the global incidence of cancer has skyrocketed in response to the increase in hazardous substances in the environment. Over the past two decades, many countries around the world have enacted various laws and regulations to reduce waste discharge and promote the protection of the natural environment to address growing environmental problems. For example, China announced that it will strive to achieve its carbon dioxide emissions peak by 2030 and carbon neutrality by 2060. In addition to reducing and treating environmental pollutants, the development of new renewable energy sources has become an urgent requirement [12–18].

Microbial fuel cells (MFCs) are an alternative to traditional coal-based energy sources. They use electrochemically active bacteria (EAB) to oxidize organic or inorganic substrates to generate an electric current [19–23]. An MFC works on the principle that bacteria produce electrons during substrate metabolism and conduct them to the anode, where they flow to the cathode through an external circuit under the effect of a potential difference and undergo a reduction reaction with an electron acceptor [24,25]. As an emerging alternative to fossil fuels, MFCs have significant advantages, such as (i) direct conversion to energy using bioelectric catalysts; (ii) the ability to operate efficiently under ambient conditions without the need for low or high operating temperatures; (iii) the ability to operate at different pH values and biomass; and (iv) low energy input. Owing to the dual functions of power generation and waste disposal, MFC technology can not only realize sewage treatment while generating power but also has many advantages, such as a wide source of raw materials, low cost, good safety performance, and environmental cleanliness and protection [26–28]. Therefore, it has broad application prospects in the fields of wastewater treatment and new energy development and has great significance in the treatment of pollutants and the provision of new energy.

The two most common types of MFCs are single- and dual-chamber MFCs, as shown in Fig. 1. The structure of a dual-chamber MFC typically consists of an anaerobic anode chamber, an anode where bacteria can attach and grow, cathode and anode cham-

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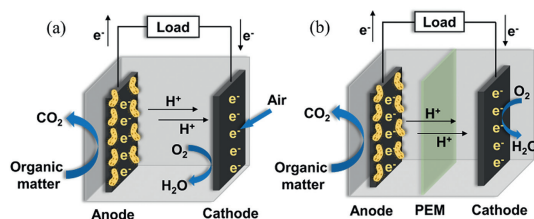


Fig. 1. Schematics of (a) single-chamber MFCs and (b) two-chamber MFCs.

bers where an oxygen reduction reaction (ORR) occurs, and a diaphragm separating the cathode and anode chambers. A diaphragm separates the two chambers to maintain an anaerobic environment in the anode chamber. Additionally, the diaphragm allows H^+ or OH^- to flow between the two chambers to maintain a relative pH balance. The membrane can be a proton exchange membrane (PEM), cation exchange membrane (CEM), anion exchange membrane (AEM), or a salt bridge connecting the two chambers. At the cathode, an ORR occurs by accepting electrons and reducing O_2 to water. The extracellular electron transfer rate of the anode microorganisms and the reaction kinetics of the cathode ORR are the main limitations of MFC cell efficiency [29,30]. Single-chamber air-cathode MFCs have an obvious advantage over dual-chamber MFCs because the cathode is directly exposed to air, thus avoiding the limitation of the ORR reaction due to low oxygen solubility in solution. Despite improvements from dual-chamber to single-chamber air-cathode MFCs, the slow kinetic process of the ORR on the cathode is still the main factor limiting performance [31,32].

At the MFC cathode, electrons are received by their final acceptor, and a reduction reaction occurs to obtain the reduced product. For an MFC with oxygen as the electron acceptor, the development of cathode catalysts and optimization of cathode mass transfer structures have become popular topics of research [33]. When no catalyst is used, the cathodic oxygen reduction reaction exhibits severe polarization and a slow reaction rate [34–36]. Moreover, the oxygen reduction reaction of the cathode occurs between the gas and liquid in the solid phase, commonly known as a three-phase interface reaction [37,38]. Adjusting the cathode structure to achieve a perfect balance among the diffusion of oxygen, wetting of the electrolyte on the electrode surface, and discharge of the generated water is another urgent problem that must be solved in the amplification process of MFC [39]. The research and development of MFC cathode catalysts are currently mainly focused on platinum group metals and their alloys, such as Pt [40], metal oxides [41], organic compounds [42], and nitrogen- and carbon-doped materials [43,44]. Pt, which exhibits excellent electrocatalytic activity, has become the most widely used ORR cathode catalyst. However, the high price of platinum accounts for 50% or more of the total cost of MFC. Consequently, the development of high-performance substitutes for the cathode catalysts is critical.

Therefore, this article reviews the research progress on metal-based catalysts for MFC cathode ORR catalysis, with a focus on their selection and preparation strategies (Fig. 2) [45–50]. The key challenges that must still be addressed when using metal-based catalysts in MFC are also summarized.

2. ORR Mechanisms

In abiotic cathodic MFCs, oxygen is the most commonly applied cathodic electron acceptor because of its widespread availability, high redox potential (+0.81 V), and environmental friendliness. The most common oxygen reduction reaction (ORR) process in solutions of different pH values is shown in Fig. 3a. The

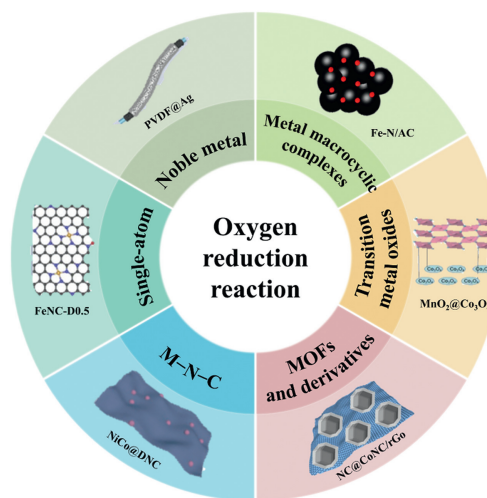
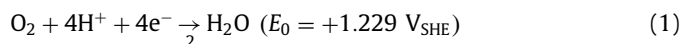


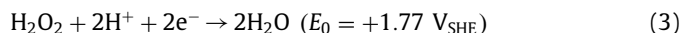
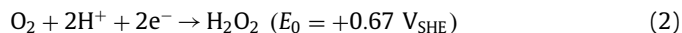
Fig. 2. Schematic of Metal-Based Cathode Catalysts for Electrocatalytic ORR in Microbial Fuel Cells. Reproduced with permission [45]. Copyright 2022, Elsevier. Reproduced with permission [46]. Copyright 2018, Elsevier. Reproduced with permission [47]. Copyright 2021, Elsevier. Reproduced with permission [48]. Copyright 2020, ACS Publications. Reproduced with permission [49]. Copyright 2021, Wiley-VCH. Reproduced with permission [50]. Copyright 2020, Wiley-VCH.

4-electron and 2-electron transfer pathways are different in acidic and alkaline solutions [51,52]. The ORR in acidic solutions is generally believed to occur as follows (Eqs. 1–6):

4-electron pathway

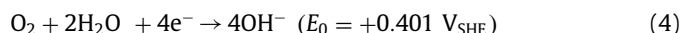


2-electron pathway

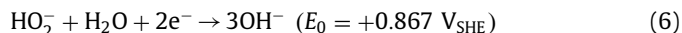
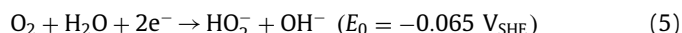


Whereas in alkaline solutions the following reaction occurs:

4-electron pathway

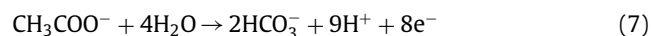


2-electron pathway



The reaction process varies depending on the electron acceptor of the MFC cathode. Under the condition of pH=7, the reaction of MFC with sodium acetate as the organic substrate and oxygen as the cathode electron acceptor on the anode can be divided into two pathways: one is the 4-electron pathway, which directly reduces O_2 to water; the other is the 2-electron pathway, which first generates an intermediate H_2O_2 and then further reduces to H_2O . The equations for the ORR under both of these paths are as follows (Eqs. 7–11):

(1) Reaction of the anode



(2) Reaction of the cathode

4-electron pathway:



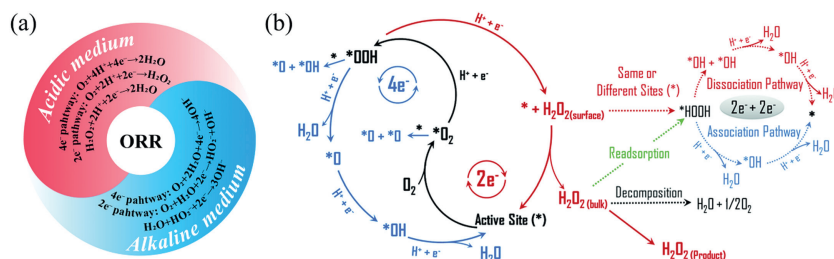
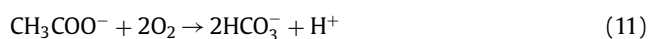


Fig. 3. (a) ORR pathways in acidic and alkaline media. (b) Electrocatalytic ORR pathways. Reproduced with permission [53]. Copyright 2019, Wiley-VCH.

2-electron pathway:



(3) The reaction of the MFC



Comparing the two pathways, the 4-electron pathway shows lower energy loss [53]. In addition, this pathway enables the direct reduction of oxygen, generates larger currents, and achieves more efficient energy conversion. Hence, this path is advantageous for MFC applications and is the most desirable ORR reaction path. Fig. 3b shows the electrocatalytic ORR pathway. The solid blue line on the left represents the classical 4-electron ORR (4e-ORR). In this part, O_2 is adsorbed at the active site ($*O_2$) and eventually turned into H_2O through four consecutive proton-coupled electron transfer (PCET) steps involving the adsorption of three $*OOH$, $*O$, and $*OH$ intermediates at the active site. This is accompanied by the cleavage of $*O_2$ ($*O_2 + * \rightarrow *O + *O$) and $*OOH$ ($*OOH + * \rightarrow *O + *OH$) at the active site. The 4e-ORR typically limits the efficiency of fuel cells, whereas the 2e-ORR provides an electrochemical pathway for hydrogen peroxide production. As shown in the red part of the right half of Fig. 3b, through a continuous reaction pathway, the intermediate product H_2O_2 is first generated by a 2-electron reaction. It may then continue to undergo a 2-electron reduction reaction to generate H_2O , or it may be directly precipitated from the solution to further generate H_2O_2 . This can provide a technical method and theoretical basis for the electrocatalytic bulk preparation of H_2O_2 . Moreover, the intermediate products of the process are unstable and may decompose into O_2 , which may participate in the reduction reaction. Therefore, the 4-electron reaction of O_2 is facilitated by weakening the O–O bond and making it easier to break.

3. Metal based MFC cathode oxygen reduction catalyst

Due to the significant impact of MFC cathodic reaction kinetics on overall MFC performance, the development and study of MFC cathodic reaction catalysts to lower the energy barrier of intermediates in the MFC cathodic reaction process, weaken the O–O bond, and more easily evolve the reaction toward a 4e-ORR pathway is crucial [51,54,55]. Common ORR catalysts include carbon and doped carbon materials, noble metals, transition metal materials, and biomass materials. Because of their ability to adsorb oxygen molecules through strong interactions, metal-based catalysts (noble metals, transition metals, and their derivatives) are excellent candidates for promoting the cleavage of O–O bonds. In general, oxygen can be adsorbed onto a metal surface in three ways (Fig. 4): One end-on type (Pauling) and two side-on types (Griffith and Yeager) [56]. In Yeager-type and Griffiths-type adsorption,

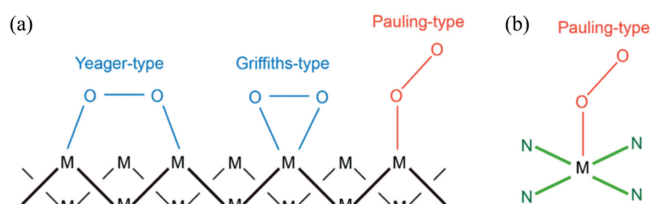


Fig. 4. Types of molecular oxygen adsorption on metallic surface. Molecular oxygen adsorption on the surface of (a) metal particles and (b) single atom catalyst. Reproduced with permission [56]. Copyright 2020, Elsevier.

both O atoms are adsorbed on the metal surface, making O–O bond cleavage difficult. In contrast, in Pauling-type adsorption, only one oxygen atom of O_2 is adsorbed onto the metal surface, and thus O–O bond cleavage is more likely to occur, promoting the 4e-ORR. Metal-based catalysts have become a popular research topic. These mainly include precious metal catalysts, metal macrocycle-based catalysts, metal oxide catalysts, carbon- and nitrogen-doped metals, and other emerging metal-based catalysts such as metal-organic frameworks and metal single-atom catalysts.

The oxygen reduction performance of the cathode catalytic material is one of the key factors affecting MFC performance. Previously, we mentioned that the ORR process can be accelerated by weakening the O–O band, making it easier to break. Common ORR catalysts include carbon and doped carbon materials, noble metals, transition metal materials, and biomass materials. Metal-based catalysts (including, for example, noble metal materials and transition metal materials and their derivatives) can be excellent ORR catalysts because the d orbitals of the central atomic vacancies of metals have strong interactions with oxygen molecules that can facilitate the breaking of the O–O bond [54]. In the following section, the ORR performance of metal-based catalysts is described.

3.1. Noble metal catalysts

Noble metals with numerous empty orbitals and trapped electrons exhibit higher electron mobility and conductivity and are often excellent electrocatalysts. The noble metals commonly used for cathodic catalysis in MFCs are platinum (Pt), palladium (Pd), gold (Au), and so on. Research on the use of noble metals for the catalytic ORR mainly involves the following two aspects: the first is the adjustment of the size, shape, or crystal shape to increase the number of active sites on the catalyst surface, and the second is the design of multi-metal alloys to change the atomic and electronic structures of materials [55,57,58]. Pt, a catalytically active and stable substance, is the most effective and widely used cathodic catalyst in fuel cells. Even newly developed catalysts cannot compete with Pt [59,60]. However, the main reason for researchers to reduce the use of Pt and develop new materials is its high cost and limited resources, which limit the large-scale application of MFCs [61–63].

Table 1
Performance comparison of different noble metals as MFC cathode catalysts.

Catalyst	Type of MFC	Synthesis strategy	Power density (mW/m ²)	Compared cathode	Power density (mW/m ²)	Ref.
PVDF@Ag NM	Dual chamber	Formation of a polydopamine layer on electrospun PVDF nanofibers. Silver mirror reaction.	180	Pt/C	250	[45]
N ₃ /Fe/C-Pt	Single chamber	Mixed solution containing 2-aminopyridine and ferric nitrate was gelled to form the gel, immersed in H ₂ PtCl ₆ solution. Pyrolysis at 900 °C	504	Pt/C	608	[64]
Ag ₃ Pt alloy	Single chamber	AgNO ₃ and H ₂ PtCl ₆ metal precursors supported on carbon black. Reduction with NaBH ₄	999 ± 31	C-Pt No catalyst	903 ± 61 106 ± 5	[65]
Pd-CeO _{2-NR} /G _{D1}	Dual chamber	CeO _{2-NR} and PdCl ₆ (NH ₄) were added to graphene supports (solvothermal treatment using hydrazine as source of nitrogen). Reduction with NaBH ₄	12.47	Pt/C	5.43	[66]
Pt-Co/C	Single chamber	Carbon support (80 mg) was dispersed with known amounts of Pt and Co precursor in EG with ultrasonic. Reduction with NaBH ₄	1730	Pt/C	1424	[67]
Pt ₃ -Fe/C	Dual chamber	Carbon, H ₂ PtCl ₆ ·6H ₂ O, and FeCl ₃ were mixed with carbon powder in deionized water. pH was adjusted. Reduction with NaBH ₄	1680 ± 15	Pt/C	1422 ± 18	[68]
PtSnP/C	Single chamber	H ₂ PtCl ₆ ·6H ₂ O and SnCl ₂ ·2H ₂ O were mixed with carbon powder in deionized water. pH was adjusted. Reduction with NaBH ₄	361 ± 7.5	Pt/C	307 ± 11.5	[69]

Therefore, reducing the use of Pt and improving the efficiency of power generation by preparing Pt complexes with other materials is a more feasible and economical approach. Some cathode ORR catalysts using noble metals and their derivatives as MFC materials are summarized in Table 1 [45,64–69]. Wang *et al.* [64] obtained a Pt-containing gel matrix with a three-dimensional structure, large specific surface area, and high dispersion via one-step synthesis, impregnation, and annealing. Using the coordination effect of transition metal Fe ions and electrostatic interactions, Pt ions were fixed in a conductive gel, and the ORR was catalyzed by the synergistic effect of Fe-N-C, pyridine N, and graphite N. During this process, the size and loading content of the Pt nanoparticles could be controlled. By using a supporting substrate to disperse Pt nanoparticles as a means for improving their accessibility, the catalytic centers can be more fully utilized, which has broad practical application prospects.

The preparation of precious metals to form alloys with other metals is a common strategy. Noori *et al.* [65] prepared an Ag-Pt bimetal alloy on carbon black by adding silver to Pt and used it as an MFC cathode catalyst (Figs. 5a and b). The bimetallic component of Ag₃Pt reduces the d-band center of Pt, thus weakening the chemisorbed oxygen, oxide, or anion. Meanwhile, the upward shift of the d-band center of the Ag component in the bimetal system enhances the chemisorption intensity of reactive oxygen during the ORR, realizing the synergistic effect of the Pt and Ag components to enhance the ORR. The power density of MFC loaded with Ag₃Pt can reach 999 ± 31 mW/m², which is higher than that of the Pt-C control. The compounding of precious metals with other metal oxides is another common strategy. Carrillo-Rodriguez *et al.* [66] synthesized a novel cathodic electrocatalyst, CeO_{2-NR}/G_{D1}, based on Pd and cerium oxide nanorods on homemade graphene. The MFC with Pd-CeO_{2-NR}/G_{D1} as cathodic catalyst had an open circuit voltage of 0.308 V and a maximum power density of 12.47 mW/m² (Fig. 5c). Cathodic electrocatalysts are used to improve the oxygen supply through cerium oxide and are potentially valuable cathode catalysts for MFC. Sun *et al.* [45] used electrospun nanofibers as flexible supports and prepared a silver layer catalyst on the nanofibers, PVDF@Ag nanofiber membrane (NM), by a simple chemical silver-plating method and used it for the cathodic catalysis of a dual-chamber MFC. By using a 3D mesh nanofiber structure with a large specific surface area and high porosity as a support for noble metal

Ag nanoparticles, the nanoparticles could be better dispersed, and a silver-encapsulated network structure was constructed, increasing the accessibility of the catalytic center as well as the power density of the MFC to approximately 72% of commercial Pt/C catalysts (Fig. 5d). As a precious metal, silver's electron distribution allows it to better adsorb oxygen molecules during the ORR process, which leads to the breaking of chemical bonds on the metal surface, promoting the production of intermediate ORR reactions such as *O, *OOH, and *OH. This catalyzes and promotes the development of ORR toward four electrons in MFC, thereby improving the overall performance of MFC. Although the cost of noble metal catalysts is relatively high, their catalytic performance is advantageous owing to their electronic structures. Therefore, methods to reduce costs without forgoing the catalytic effect of noble metal catalysts are being keenly explored.

3.2. Metal macrocyclic complexes

The use of metal macrocyclic complexes (mainly phthalocyanines and porphyrins) for catalytic MFC cathodic reactions was first reported in a study by Jasinski on metal phthalocyanine compounds [70]. The catalytic activity of the metal macrocyclic compound cobalt naphthalocyanine (CoNpc) can be improved by controlling the particle size, surface morphology, and dispersion during thermal treatment. In such metal macrocycles, the ligand acts as a bridge for electron transfer from the central metal to the catalyst carrier while protecting the central metal ion [71]. Phthalocyanine compounds have a unique structure in which four nitrogen atoms (N₄) form a symmetry surrounding the metal center (Fe, Co, Ni), thus creating synergy between the d-band electron-sharing and electron-leaving domains of the N₄ matrix to improve the catalytic activity for the ORR [65]. Yu *et al.* [72] used doped iron porphyrin (Fe(por)) as the cathode in a microbial fuel cell (MFC). They found that the electron transfer number of Fe(por)-0.05 was 3.97, indicative of a direct four-electron transfer pathway in the ORR, proving the advantages of Fe(por) as an ORR catalyst for the MFC cathode and its strong potential as a substitute for the Pt/C catalyst (Fig. 6a). Yu *et al.* [73] used zinc phthalocyanine (ZnPc) as a cathode catalyst to assemble an MFC device with a higher current density and lower charge-transfer resistance than the control group. The maximum power density of

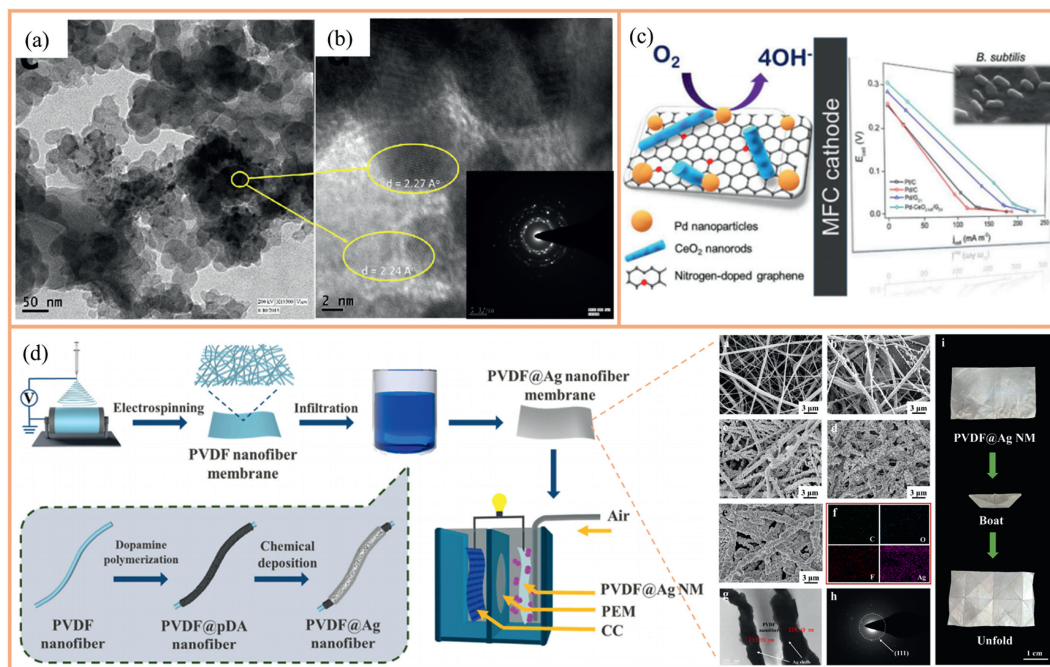


Fig. 5. TEM micrographs of (a) C-Ag₃Pt and (b) corresponding lattice image (SAED micrograph in inset). Reproduced with permission [65]. Copyright 2018, Elsevier. (c) Schematic of the ORR mechanism using Pd-CeO₂-NR. Reproduced with permission [66]. Copyright 2018, Elsevier. (d) Schematic of the preparation of PVDF@Ag NM. Reproduced with permission [45]. Copyright 2022, Elsevier.

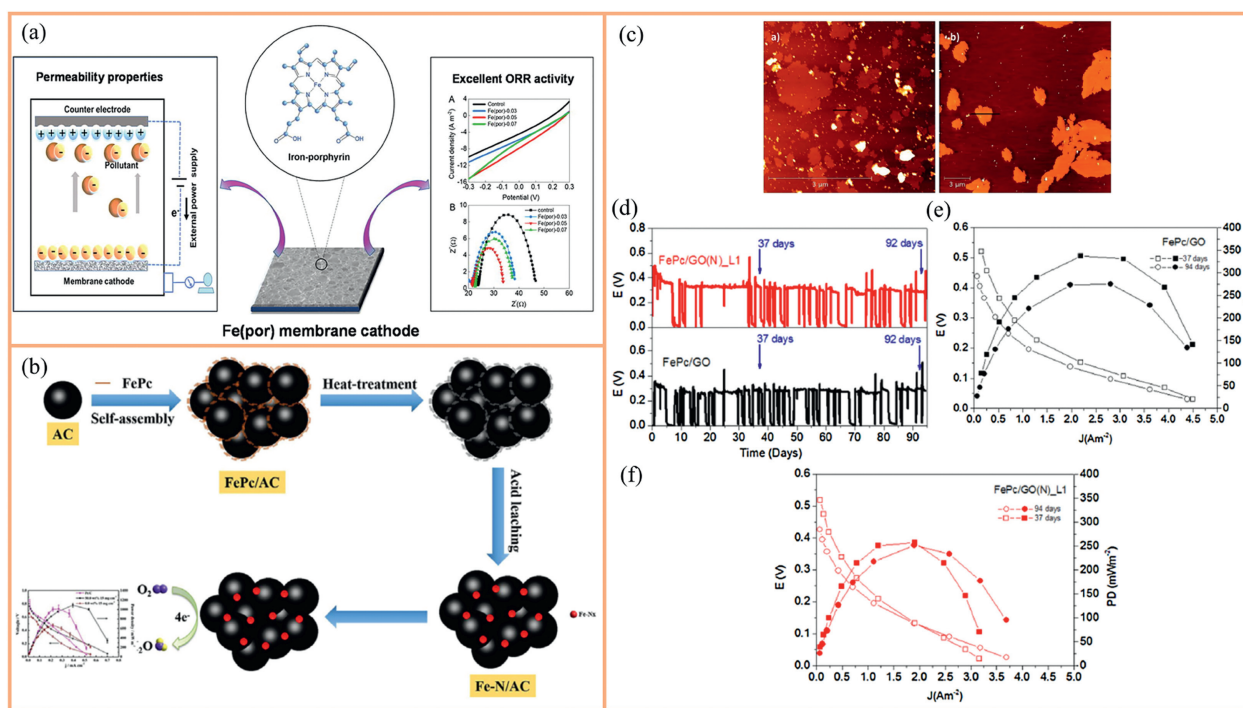


Fig. 6. (a) Schematic of Fe(por) membrane cathode. Reproduced with permission [72]. Copyright 2020, Elsevier. (b) Schematic of Fe-N/AC. Reproduced with permission [46]. Copyright 2018, Elsevier. (c) AFM images of GO(N)₁L1 and GO(N)₂L2. (d) voltage generation cycles and (e, f) polarization and power density (right) curves of MFC assembled with FePc/GO(N)₁L1 and FePc/GO as cathodes taken after 37 and 94 days from acclimation. Reproduced with permission [74]. Copyright 2018, Elsevier.

the MFC was $1820 \pm 22 \text{ mW/m}^2$. This is because ZnPc has excellent conductivity and a large electrochemically active surface, and the improvement in the cathode catalytic performance enhances the overall power generation capacity of the MFC. Liu *et al.* [46] prepared iron-nitrogen/activated carbon (Fe-N/AC), an excellent electrocatalyst for the oxygen reduction reaction (ORR), by pyrolyzing iron(II) phthalocyanine (FePc)-coated activated carbon

(AC), which was formed *via* an evaporation-induced self-assembly method, to improve the power production of MFC (Fig. 6b). The Fe-N/AC synthesized with a 50.0 wt% FePc loading exhibited enhanced ORR electrocatalytic activity considering the high content of nitrogen and iron elements, crystalline structure, high surface area, and proper composition of micro- and mesopores. Fe-N/AC can catalyze ORR in neutral media *via* an indirect four-electron pathway

Table 2

Performance comparison of different transition-metal-oxide catalysts as MFC cathode catalysts.

Catalyst	Type of MFC	Power density (mW/m ²)	Compared cathode	Power density (mW/m ²)	Ref.
MnO ₂ @Co ₃ O ₄	Single chamber	476	MnO ₂	180	[47]
OV-MnO ₂ NRs	Dual chamber	1639	Pt/C	1238	[82]
Mn-Co ₂ oxide	Single chamber	113	Pt/C	148	[83]
β -MnO ₂	Single chamber	172 $\pm$ 7	Pt/C	268 $\pm$ 7	[84]
Flower-like Co ₃ O ₄	Dual chamber	248 $\pm$ 16	Bare cathode	39 $\pm$ 9.7	[85]
Cu-MnO ₂	Single chamber	198	Pt/C	115	[86]
CoO/MgO@NC	Single chamber	2258	NC	1426 $\pm$ 52	[87]
NiMn ₂ O ₄	Single chamber	439 mW/m ³	Pt/C	549 mW/m ³	[88]
V ₂ O ₅ supported by rGO	Single chamber	533 $\pm$ 37	Pt/C	512 $\pm$ 51	[89]

with an onset potential of 0.883 V relative to a reversible hydrogen electrode, and the electron transfer number was 3.91. The charge transfer resistance and exchange current density of Fe-N/AC were reduced by 62% and increased by a factor of three, respectively, compared with those of AC.

As Figs. 6c-f illustrates, Mecheri *et al.* [74] reported a simple method for the preparation of Fe-based catalysts supported on graphene oxide (GO), which was obtained by the electrochemical exfoliation of graphite in an aqueous ammonium sulfate solution. Two different strategies were used to incorporate nitrogen functionality into the GO matrix. Iron(II) phthalocyanine (FePc) was used as an iron source and was deposited on GO using a non-pyrolytic impregnation method. By tuning the parameters of the material preparation, GO nanosheets with unique morphologies and surface properties could be produced to enhance the interaction with FePc. The MFC equipped with FePc/GO (N)_{L1} and FePc/GO showed high stable voltage output within 90 days (average voltage of 0.32 V and 0.28 V, respectively), and the power density of the device can reach up to 280 mW/m² and 260 mW/m², respectively. Macrocyclic-based compounds with active sites of metal and pyridine N can improve the stability of catalysts prepared by pyrolysis; however, FePc molecules are prone to agglomeration when thermally compounded with other substances, leading to uneven distribution on the carbon material and thus inhibiting the catalytic activity of Fe-N for the ORR. On the other hand, metals can be easily precipitated under acidic conditions, and the H₂O₂ generated during the operation of an MFC can also destroy the structure of macrocyclic groups and deactivate them. Therefore, it is important to adopt a reasonable preparation method to reduce aggregation during FePc doping, avoid the reduction of Fe-N active sites, and expand the application of metal macrocyclic groups. Many metal macrocyclic compounds with different ligands have been used to promote ORR under basic and neutral conditions. However, their stability in acidic media is poor because of the demetallization of the macrocycles. In the simple pyrolysis of metal macrocycles, large carbon particles are easily formed owing to the aggregation of metal atoms at high temperatures and the decomposition of metal macrocycles. The disadvantages of using large carbon particles as ORR electrocatalysts are their low specific surface area, low volumetric active site density, and poor mass transfer. Therefore, it is important to increase the dispersion of the metal macrocycles and avoid sintering.

3.3. Transition metal oxides

Metal oxides not only have excellent catalytic activity and good stability but are also widely available, inexpensive, environmentally friendly, and have good prospects for application as cathode catalysts, which have been extensively studied by domestic and international researchers [75–81]. The performances of various transition metal oxide catalysts are listed in Table 2 [47,82–89]. Xin *et al.* [90] compared the output voltage, coulombic effi-

ciency, and microbial community of a single-chamber MFC with Cu₂O/rGO cathode catalysts with those of commercial Pt/C (Fig. 7a). The results showed that the MFC with the Cu₂O/rGO cathode catalyst produced a higher output voltage (0.223 V) and coulombic efficiency (92.5%) than the commercial Pt/C (0.206 V, 90.3%). In addition, the Cu₂O/rGO cathode exhibits good ORR catalytic activity and promotes O₂ diffusion to the cathode surface. Interestingly, the highest relative abundance of the known electrolytic microorganism *Geobacter* was found in the MFC anode biofilm using the Cu₂O/rGO cathode catalyst (49.28%), which was higher than that using commercial Pt/C (32.33%). The abundance and diversity of microorganisms in the MFC cathode biofilm using Cu₂O/rGO catalysts were significantly lower than those of commercial Pt/C because of the antibacterial properties of Cu₂O/rGO, which could expose more catalytically active sites in the cathode and further improve the power-generation performance of the MFC. These results provide insights into the potential application of Cu₂O/rGO as a highly catalytically active antimicrobial cathode to replace commercial Pt/C for power generation.

Chen *et al.* [47] successfully prepared MnO₂@Co₃O₄ composites by the *in situ* growth of nanoparticulate Co₃O₄ on nanorods of manganese dioxide, compounded with various metal elements, which provided abundant electrochemical properties; the maximum voltage of MnO₂@Co₃O₄-MFC is 425 mV, and the maximum stabilization time is 4 d (Fig. 7b). The maximum output power is 475 mW/m², which is 2.24 times that of the Co₃O₄-MFC (212 mW/m²) and 2.63 times that of the MnO₂-MFC (180 mW/m²). The rod-like structure of MnO₂ can effectively improve the ion flow efficiency and reduce the transport resistance, whereas the dot-like structure of Co₃O₄ can increase the specific surface area of the complex and provide more active sites. Although transition metal oxides have better electrocatalytic activity and lower cost than platinum noble metals, their conductivity is low because of the nature of the oxides; therefore, improving their conductivity and reducing the resistance of the materials is necessary. Fig. 7c showed Qiu *et al.* [82] prepared manganese dioxide nanorods on flexible CC substrates by electrodeposition and hydrogenation and named them OV-MnO₂ NRs. Using OV-MnO₂ NRs as the cathode catalytic layer of MFC, the maximum power density of MFC devices is 1639 mW/m². This is because of the advantages of rich metal active sites on the OV-MnO₂ NRs, faster charge transfer at the three-phase interface, and fast reaction kinetics.

3.4. Metal organic framework materials

In the past few years, metal-organic framework (MOF) materials and their derivatives have gradually become a research hotspot as emerging materials because of their unique properties. MOFs are two-dimensional or three-dimensional topological framework materials composed of metal ions, ion clusters, and organic ligands [91–94]. MOFs have significant properties, such as high surface area, high porosity, diverse ligand structures, flexibility in functionalization of functional groups, and high stability (chemical and

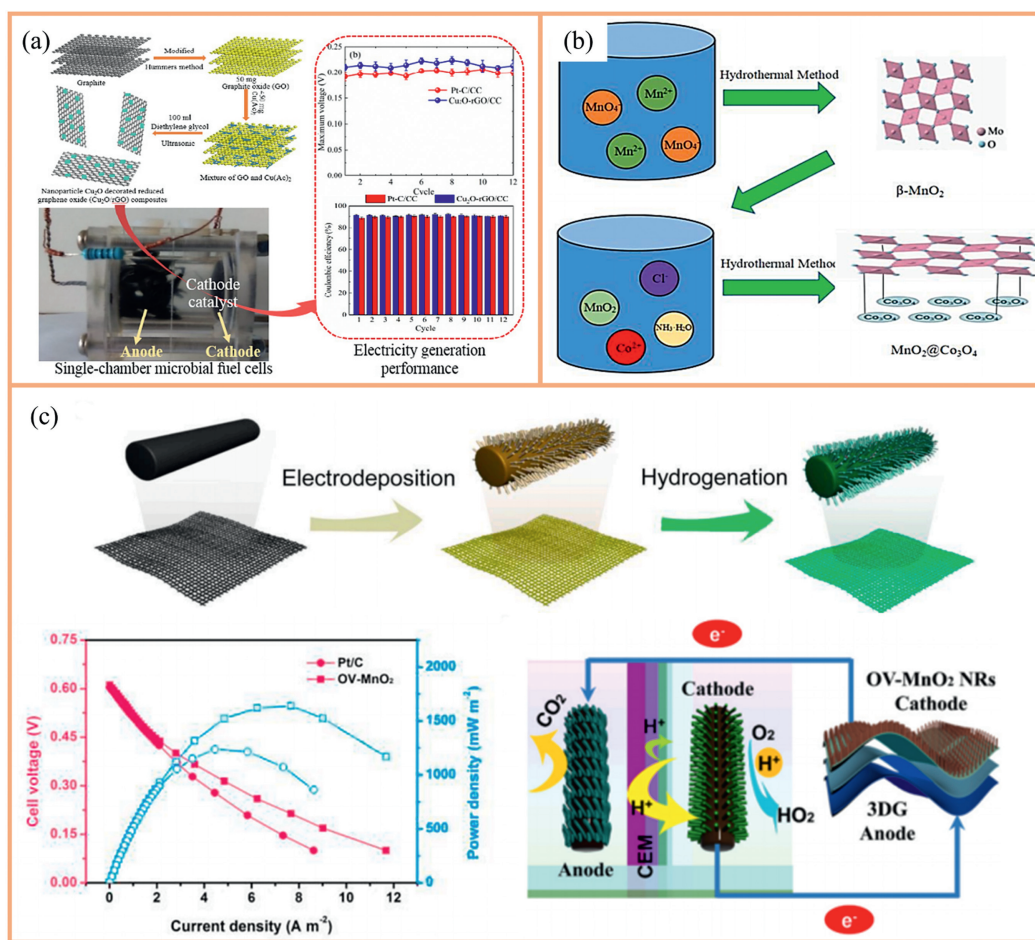


Fig. 7. (a) The Cu_2O nanoparticle decorated reduced graphene oxide ($\text{Cu}_2\text{O}/\text{rGO}$) as cathode catalyst of simple-chamber microbial fuel cells. Reproduced with permission [90]. Copyright 2020, Elsevier. (b) The preparation flow chart of $\text{MnO}_2@\text{Co}_3\text{O}_4$. Reproduced with permission [47]. Copyright 2021, Elsevier. (c) Schematic of the OV-MnO₂ NRs and MFCs-ASCs; the output and polarization curves of MFCs-ASCs device. Reproduced with permission [82]. Copyright 2021, Elsevier.

Table 3

Performance comparison of different metal organic framework catalysts as MFC cathode catalysts.

Catalyst	MOFs precursor	Type of MFC	Power density (mW/m^2)	Compared cathode	Power density (mW/m^2)	Ref.
$\text{NC}/\text{CoNC}/\text{rGO}$	$\text{ZIF-8}/\text{ZIF-67}$	Dual chamber	2350	Pt/C	2002	[48]
$\text{Co}/\text{CoP}/\text{Co}_2\text{P}/\text{N-CNF}$	ZIF-67	Dual chamber	375.16	Pt/C	333.70	[96]
$\text{Co}/\text{CoS}_2/\text{N-CNF}$	ZIF-67	Dual chamber	400.06	Pt/C	333.70	[96]
$\text{CoNi-LDH}/\text{CNFs}$	ZIF-67	Single chamber	1390.37	Pt/C	843.67	[98]
$\text{NH}_2\text{-UiO-66}(\text{Zr}/\text{Ni})$	$\text{NH}_2\text{-UiO-66}$	Dual chamber	822	Pt/C	730	[110]
$\text{UiO-66}(\text{Zr-MOF})$	UiO-66	Single chamber	131	Pt/C	128	[111]
Ni-CoNC	ZIF-67	Single chamber	4335	Pt/C	2520	[112]
$\text{NiCo-CAT}/\text{MWCNTs}$	NiCo-CAT	Dual chamber	530 ± 9	Pt/C	407 ± 9	[113]
Ni-MOF-74	MOF-74	Single chamber	446	Pt/C	1152	[114]
CuCo/NCNT	HKUST-1	Single chamber	2757	Pt/C	2313	[115]
$\text{Cu}_3(\text{BTC})_2$	$\text{Cu}_3(\text{BTC})_2$	Single chamber	1772	bare AC	624	[116]

thermal), and have rapidly developed and attracted great interest [95–97]. At present, more than 20 thousand different MOFs have been synthesized using various methods, demonstrating enormous application potential in fields such as catalysis [98–100], gas storage [101,102], separation [103–105], drug delivery [106,107], and electronic/photovoltaic devices and sensors [95,108,109]. Because MOFs have unsaturated metal ion active sites, they exhibit electrochemical catalytic performance, which means that MOFs and their derivatives have potential applications in electrocatalysis. Performance comparison of different MOFs derivatives catalysts as MFC cathode catalysts was shown in Table 3 [48,96,98,110–116]. Zhao *et al.* [48] manufactured ZIF-8 and subsequently grew ZIF-67 on its surface to create a core-shell structure. Through pyro-

lysis and modification, the ZIF-8@ZIF-67 core/shell structure was transformed into a porous carbon composite graphene oxide material named NC@CoNC/rGO (Fig. 8a). NC@CoNC/rGO has abundant Co metal active centers and N doping, and its large surface area and pore volume are conducive to the mass transfer of oxygen molecules and protons at the three-phase interface in a liquid environment. In addition, the conductive graphene skeleton improves charge-transfer efficiency. NC@CoNC/rGO has a maximum power density of $2350 \text{ mW}/\text{m}^2$, which is higher than the $2002 \text{ mW}/\text{m}^2$ of commercial Pt/C. The synergistic effect of graphene with Co and N doping in NC@CoNC/rGO carbon matrix resulted in enhanced MFC performance. The conductive framework of graphene increases its conductivity, while the abundant active Co and N sites are benefi-

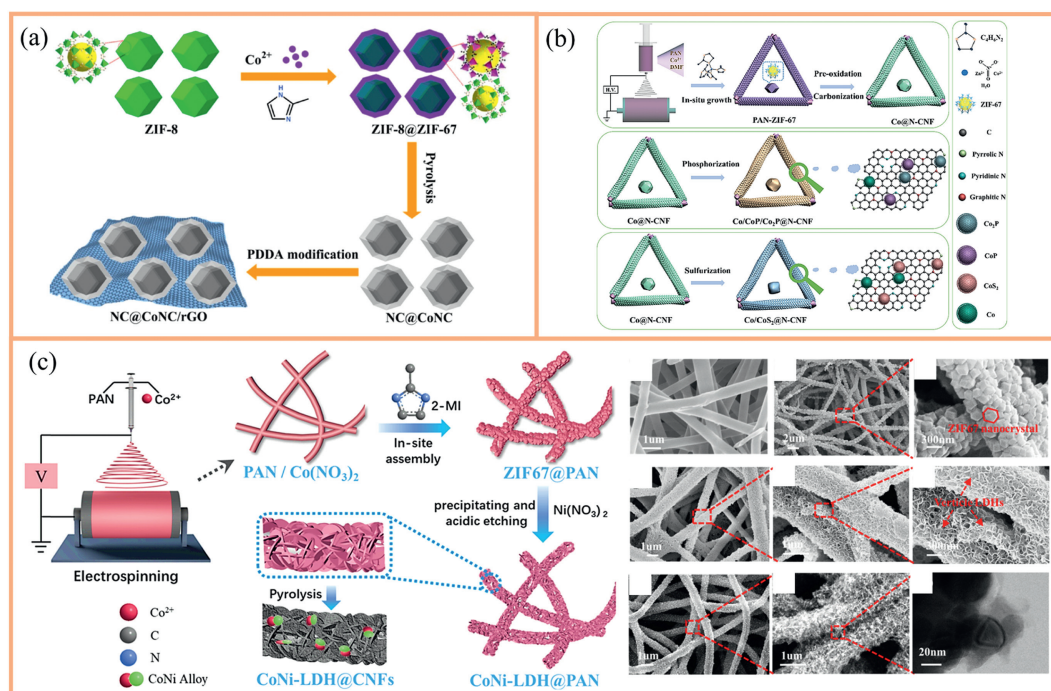


Fig. 8. (a) Schematic of preparation procedure of NC@CoNC/rGO composites. Reproduced with permission [48]. Copyright 2020, ACS Publications. (b) Schematic of the synthesis of the Co@N-CNF, Co/CoP/Co₂P@N-CNF, and Co/CoS₂@N-CNF composites. Reproduced with permission [96]. Copyright 2023, Elsevier. (c) Schematic of the synthesis of CoNi-LDH@CNFs. Reproduced with permission [98]. Copyright 2022, Elsevier.

cial for the cleavage of O–O bonds during the ORR process, thereby enhancing ORR.

MOFs self-assemble through metal-active centers and organic ligands. During this process, MOFs can be easily functionalized, such as by modifying the organic ligands with functional groups or adding other metal salts to compete with the existing metal ions, by partially replacing the existing metal active centers, or by preparing MOFs with bimetallic or even polymetallic active centers [117–119]. Due to the d-orbital regulation effect of the bimetallic active centers, the catalytic performance of the metal active centers can be further improved. Noori *et al.* [110] synthesized monometallic (Zr) and bimetallic (Zr, Ni) MOFs with novel amino functionalities, namely, NH₂-UiO-66 (Zr) and NH₂-UiO-66 (Zr/Ni). The MFC using NH₂-UiO-66 (Zr/Ni) as the catalytic cathode can achieve high power density (0.8 W/m²) and excellent Coulombic efficiency (75%), surpassing the performance of traditional 10% Pt/C-based cathodes. MOF materials have a high specific surface area and porosity but poor conductivity. Therefore, a commonly used technology is to pyrolyze MOFs at high temperatures to enhance their electron-transfer capability.

MOFs have the potential to replace precious metals as emerging electrocatalytic catalysts. However, because of their powder properties, they are prone to agglomeration, which affects the performance of the active metal centers. In addition, the low conductivity of MOFs significantly limits their large-scale applications. To address this low conductivity issue, improvements have been made by developing conductive MOFs, nano-MOFs, and two-dimensional MOFs to adjust the particle size and morphology [92,93,120,121]. To solve the problem of agglomeration of the former, MOFs can be combined with a base material to fully disperse them through the base, such as by using aerogels and electrospun nanofibers. Guo *et al.* [96] achieved the goal of fully dispersing MOF particles by growing ZIF-67 on three-dimensional polyacrylonitrile (PAN) electrospinning nanofibers. Co/CoP/Co₂P@N-CNF and Co/CoS₂@N-CNF were prepared by pyrolysis and modification with P or S (Fig. 8b). The power densities of the corresponding MFC can reach

375.16 and 400.06 mW/m², respectively, which are superior to those of the platinum carbon control group. Here, PAN electrospun nanofibers with high porosity uniformly dispersed the ZIF-67 particles, carbon control group. Here, PAN electrospun nanofibers with high porosity uniformly dispersed the ZIF-67 particles, whereas the derived cross-carbon fibers greatly increased the electrochemically active area and synergistically improved the catalytic ORR.

As shown in Fig. 8c, Li *et al.* [98] conducted a "reverse" operation by depositing LDH onto ZIF-67 grown along PAN nanofibers and then using pyrolysis to capture Co in the ZIF-67 structure, ultimately forming a derivative catalyst containing CoNi alloys. By utilizing the 2D porous dispersion structure of the LDH, uniformly dispersed CoNi alloys were obtained to a great extent, providing a new approach for preparing metal catalysts. The derived three-dimensional ordered network structure is conducive to lowering the activation energy barrier of ORR and accelerating the smooth construction of cathodic reactions with the help of nanofibers and MOFs. Although MOFs have excellent catalytic capabilities, their inherent powder properties make them prone to agglomeration during use, resulting in insufficient utilization of the active metal centers and limiting their application. Therefore, further developments and improvements are required.

3.5. Metal nitrogen doped carbon materials (M–N–C)

Compared to metal oxides, the conductivity of metal-nitrogen-doped carbon materials is significantly enhanced. Owing to its low cost and excellent ORR catalytic activity, this material has been widely used. Heteroatoms generally include B, N, S, and P [122]. The coordination of metal and nitrogen in the matrix effectively regulates the local electronic structure, improves the distribution of local charge density, produces more active sites, and thus enhances catalytic activity. Heteroatom-doped carbon materials exhibit high conductivity, adjustable structure, high catalytic efficiency, and high corrosion resistance [123,124]. Huang *et al.* [49] successfully prepared N-doped catalysts containing nickel-cobalt alloys through

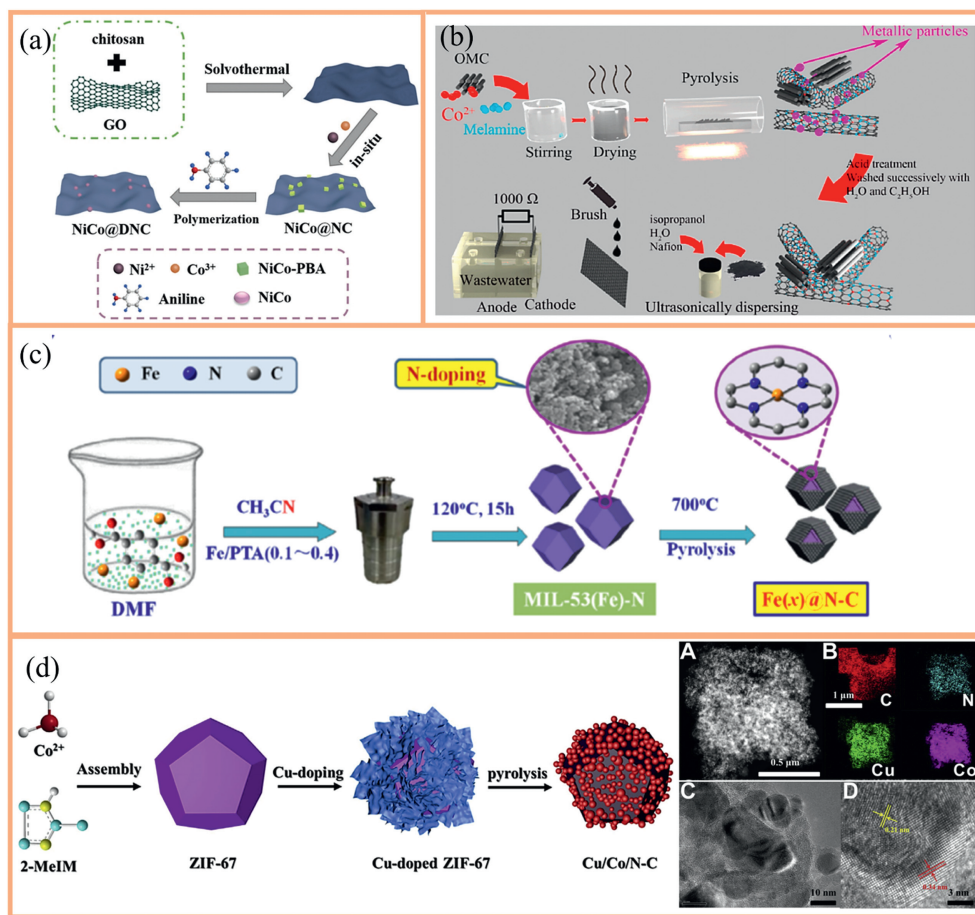


Fig. 9. (a) Synthesis of NiCo@NC and NiCo@DNC. Reproduced with permission [49]. Copyright 2021, Wiley-VCH. (b) Synthesis protocol for $\text{Co}_x\text{-N-OMC}$ catalysts and their installation into the single chamber microbial fuel cell. Reproduced with permission [125]. Copyright 2020, Elsevier. (c) Schematic for the synthetic method of $\text{Fe}_{(x)}\text{-N-C}$. Reproduced with permission [128]. Copyright 2022, Wiley-VCH. (d) Schematic and TEM and SEM images of the highly efficient ORR catalyst, Cu/Co/N-C. Reproduced with permission [44]. Copyright 2020, Elsevier.

simple hydrothermal, growth, solution polymerization, and pyrolysis methods using NiCo@DNC- x (where x represents the pyrolysis temperature, Fig. 9a). Using NiCo@DNC-800, the maximum *in situ* power density of the cathode catalyst is $2325.60 \pm 41.96 \text{ mW/m}^2$, which is approximately 2.6 times that of the platinum carbon control group. It exhibits good long-term durability and stability for approximately 30 days after operation. By heat treating a mixture of cobalt nitrate, melamine, and ordered mesoporous carbon (OMC), Zhuang *et al.* prepared cobalt and nitrogen co-doped ordered mesoporous carbon ($\text{Co}_x\text{-N-OMC}$) (Fig. 9b) [125]. The catalyst exhibited excellent ORR catalytic performance in neutral media with an initial potential of 0.79 V and a half-wave potential of 0.59 V, which is equivalent to the platinum-carbon catalyst. Recently, the utilization of the framework structure of MOFs to dope heteroatoms has become a popular strategy [126,127]. Owing to their high porosity, abundant carbon-skeleton precursors, and functional groups, MOFs have unique advantages in terms of heteroatom doping. Cui *et al.* [128] used inexpensive acetonitrile as a raw material and obtained $\text{Fe}_{(x)}\text{-N-C}$ (where x represents the molar ratio of Fe/terephthalic acid) by co-doping MIL-53(Fe) with N (Fig. 9c). Through the synergistic effect between the transition metal Fe nanoparticles and a small number of Fe_3C and Fe-N_x sites, the ORR was co-catalyzed. In this process, the high specific surface area of MIL-53(Fe) can fully disperse the metal active site and make full use of the metal active centers, which increased the power density of an MFC with $\text{Fe}_{(0.3)}\text{-N-C}$ (604.6 mW/m^2), such that the MFC output voltage was comparable to that of a cell with Pt/C catalyst.

A large amount of graphite N in the material is conducive to electron transfer and reduces the internal resistance of the material, thereby synergistically improving the catalytic effect. As shown in Fig. 9d, Wang *et al.* [44] obtained Cu/Co/N-C catalysts by preparing bimetallic and nitrogen-fixing doped hollow carbon structures using Cu-doped ZIF-67 as the precursor. These catalysts have various ORR catalytic active sites: $\text{Cu-N}_x\text{-C}$, $\text{Co-N}_x\text{-C}$, pyridinic-N, graphitic-N, $\text{Cu}_{0.5}\text{Co}_{2.84}\text{O}_4$, etc. In conclusion, doping with heteroatoms can improve the conductivity of materials, facilitate electron transfer, improve the distribution of local charge density, and synergistically catalyze the ORR with active metal centers, further improving their catalytic effect.

3.6. Single-atom catalysts

Numerous studies have shown that reducing the size of metal nanoparticles can improve their catalytic performance. Since the concept of single-atom catalysts (SACs) was proposed in 2011, monatomic catalysts have been widely studied because they use nearly 100% of the metal active sites and their coordination structures are accurate and controllable. The advantage of single-atom catalytic ORR is that the Pauling-type adsorption for oxygen is more prone to O-O bond breakage, thereby accelerating the ORR process [129]. The preparation of classic SACs is completed through high-temperature pyrolysis assisted by carbon and nitrogen sources, resulting in transition metal monoatomization as well as the doping of heteroatoms and material graphitization.

Table 4

Performance comparison of different single-atom catalysts as MFC cathode catalysts.

Catalyst	Type of MFC	Power density (mW/m ²)	Compared cathode	Power density (mW/m ²)	Ref.
FeNC-D0.5	Single chamber	1041.3	Pt/C	704.6	[50]
Pt SAs-BCN ^a	Single chamber	936.31	BCN	799.07	[129]
			Pt/C	1407.76	
SA-Fe-AC	Single chamber	2264 ± 46	Pt/C	1207 ± 38	[132]
CB@Co-N-C	Dual chamber	727.2	Pt/C	704.3	[133]
Ni-SA/CN3	Single chamber	430	Ni-SA/CN1	—	[134]
			Ni-SA/CN2		
			Ni-SA/CN4		
			Ni-SA/CN5		
Cu/NC-700	Single chamber	489.2	Cu/NC-600	164.8	[135]
			Cu/NC-800	172.1	
FeN ₃ -Pd@NC NBs	Single chamber	831.2	Pt/C	656.8	[136]

^a BCN is the abbreviation for boron-nitride-carbon.

Commonly used organic compounds are nitrogen-containing polymers, such as polyaniline. In recent years, the repetitive three-dimensional structure and organic ligands in metal-organic frameworks have made them promising precursors. However, the load capacity of SACs has always been a major factor that significantly limits their application. The free energy on the surfaces of metal particles increases significantly as they become smaller, making the migration of metal atoms and their aggregation during the preparation of SACs easy [130,131]. To ensure the dispersibility of single metal atoms, their loading is usually low, which means that the overall number of catalytically active centers decreases, thereby limiting catalytic activity. As mentioned above, the classic preparation method for single transition metal atoms is high-temperature pyrolysis assisted by carbon and nitrogen sources, in which the metal components are monatomized at high temperatures.

In recent years, the study of monodisperse Fe sites has demonstrated the high catalytic activity of monoatomic Fe-N₄. Simultaneously, methods for preparing Fe monoatoms have also emerged. This type of material has been widely studied to improve the activity and stability of catalysts and identify catalytically active sites. Performance comparison of different single-atom catalysts as MFC cathode catalyst was shown in Table 4 [50,129,132–136]. Shao *et al.* [50] constructed porous carbon nanosheets using the spatial constraints of Si and the coordination of diethylenetriaminementaactic acid (DTPA), providing a large reaction interface area and sufficient exposure of the metal positions. Owing to the strong coordination of DTPA and the confinement effect of silica, the encapsulated iron atoms are effectively fixed during annealing, forming a single Fe atom structure (Fig. 10a). The MFC battery loaded with this catalyst shows a power density of 1041.3 mW/m², whereas the platinum carbon control group has a power density of 704.6 mW/m². Liang *et al.* [132] used a single iron atom on activated carbon as the active center (SA-Fe-AC), resulting in a maximum power density of 2264 mW/m² in MFCs, which is equivalent to that of Pt/C catalysts. By comparing SA-Fe-AC prepared with phthalocyanine (Pc) and NP-Fe-AC prepared without Pc, NP-Fe-AC without Pc was found to agglomerate iron atoms to form Fe nanoparticles (in the presence of Fe⁰ in the XPS results) during the annealing process, whereas SA-Fe-AC containing Pc formed metal single-atom centers with greater ORR catalytic activity. Compared to the control group material, SA-Fe-AC follows an efficient 4-electron ORR pathway with a larger specific surface area and microporous mesoporous structure, which can promote oxygen mass transfer and synergistically improve the cathode ORR of MFC with single iron atoms. As shown in Fig. 10b, Du *et al.* [133] prepared CB@Co-N-C, which are Co single-atom catalysts on activated carbon black, using a simple adsorption pyrolysis method. Under alkaline and neutral pH environmental conditions, the cathode 4-

electron ORR pathway of the corresponding MFC can be catalyzed, resulting in a power density of 727.2 mW/m², which is higher than that of the Co-free single-atom CB@N-C (620.8 mW/m²) and can be comparable to that of the Pt/C control group, indicating that CB@Co-N-C has the potential to serve as an effective cathode catalyst for MFCs. In addition, using the structure of MOFs to disperse single metal atoms is a common strategy. Shao *et al.* [137] assembled ZIF-8 with a microporous structure into porous nanosheets, greatly dispersed the Fe monoatoms, and fully exposed the active sites of the Fe monoatoms, thereby increasing the availability of the catalytic active sites (Fig. 10c).

Although the performance of monatomic catalysts is high, owing to their stability and other reasons, the application of monatomic catalysis in the cathode half-reaction of catalytic microbial fuel cells is still low and remains in the laboratory stage. Greater efforts are needed to develop monatomic catalysts with large monoatomic loading, good hydrothermal stability, and acid-base stability to cope with the complex environment of the MFC cathode.

4. Conclusion

As a new clean energy source, the electrical efficiency of a microbial fuel cell depends on the reaction kinetics at the anode and cathode. Using catalysts that can improve the ORR at the cathode is an effective means of improving the electrical efficiency of MFCs. Metals have the great advantages of adsorbing oxygen molecules and promoting O-O bond cleavage and are thus widely studied as the main types of applicable catalysts. This article summarizes the recent research progress in metal-based MFC cathode ORR catalysts, including platinum-group precious metals, metal macrocyclic compounds, metal oxides, metal organic framework structures, and metal single-atom catalysts. The catalytic performance of precious metal catalysts is superior, but their cost is relatively high, and large-scale use will greatly increase costs. Metal macrocyclic compounds can obtain active sites of metal and pyridine N through pyrolysis, but metal detachment is prone to occur under acidic conditions. Metal oxides have a wide range of sources, low prices, and good stability and catalytic performance, but their conductivity is slightly insufficient. The metal-organic framework has a large specific surface area and porosity, which exposes metal catalytic sites to a greater extent, but is prone to aggregation, leading to a decrease in catalytic performance. Single atom metal catalysts can fully utilize the catalytic power of metal atoms, but low metal loading can also limit their catalytic performance. Irrespective of the preparation strategy used, the goal is to fully utilize the catalytic effect of the active metal centers and the four-electron ORR process. Several issues must be addressed to develop metal-based catalysts. (1) The metal center is the key active center for catalytic performance. Metal macrocyclic compounds, metal oxides, metal

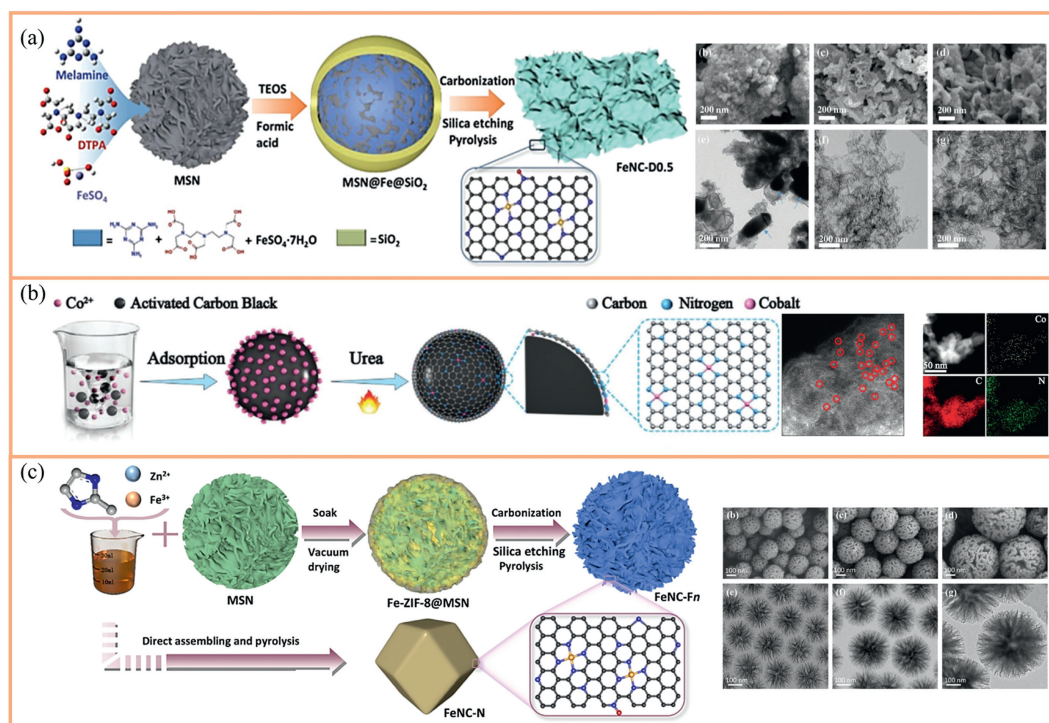


Fig. 10. (a) Schematic for the preparation of FeNC-D0.5 catalyst. Reproduced with permission [50]. Copyright 2020, Wiley-VCH. (b) Preparation procedure of CB@Co–N–C. Reproduced with permission [133]. Copyright 2023, Wiley-VCH. (c) Illustration of the fabrication of FeNC-Fn catalysts. Reproduced with permission [137]. Copyright 2021, Elsevier.

frame materials with larger porosity and specific surface area, or metal single-atom catalysts are all designed to fully disperse the metal active center and use it fully. However, in this process, the loading amount of metal shows a negative correlation with metal dispersion; that is, the total number of metal active centers decreases, thereby affecting the final catalytic effect. The design of catalysts with better dispersion and higher metal loading is a challenge that researchers must overcome. (2) The vast majority of the metal-based catalysts mentioned above exhibit solid powder-like properties, which require coating and other means to combine them with the cathode material of the MFC during use. The most commonly used method involves the use of binders. During this process, the internal resistance of the electrode increases and greatly affects the dispersion and porosity of the catalyst, leading to the wastage of metal active centers and reduction in the catalytic effect. (3) During the ORR, metal catalysts achieve their catalytic function by changing the valence of the metals. During this process, a portion of the metals inevitably dissolves in the MFC, which may affect the environmental safety of water bodies in practical applications. (4) Owing to the complexity of the microbial living environment in MFC devices, their design must take into account that biomass membranes can significantly affect electron transport during MFC operation, thereby affecting the effectiveness of MFC. Therefore, the design of catalyst materials should focus on improving the antibacterial performance of the materials to ensure optimal the operating time of the MFC as much as possible. Fortunately, multiple metals can cause damage to bacteria, which can improve the antibacterial performance of the catalyst.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccllet.2023.109418.

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