Review

Non-Pt catalyst as oxygen reduction reaction in microbial fuel cells: A review

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ABSTRACT

Oxygen Reduction Reactions (ORR) are one of the main factors of major potential loss in low temperature fuel cells, such as microbial fuel cells and proton exchange membrane fuel cells. Various studies in the past decade have focused on determining a method to reduce the over potential of ORR and to replace the conventional costly Pt catalyst in both types of fuel cells. This review outlines important classes of abiotic catalysts and biocatalysts as electrochemical oxygen reduction reaction catalysts in microbial fuel cells. It was shown that manganese oxide and metal macrocycle compounds are good candidates for Pt catalyst replacements due to their high catalytic activity. Moreover, nitrogen doped nanocarbon material and electroconductive polymers are proven to have electrocatalytic activity, but further optimization is required if they are to replace Pt catalysts. A more interesting alternative is the use of bacteria as a biocatalyst in biocathodes, where the ORR is facilitated by bacterial metabolism within the biofilm formed on the cathode. More fundamental work is needed to understand the factors affecting the performance of the biocathode in order to improve the performance of the microbial fuel cells.

1. Introduction

The global energy crisis and human-induced climate change have become the main controversies over the past decade. The rate of anthropogenic carbon dioxide emission has increased rapidly due to the development of industrial activities [1]. With an increasing dependence on fossil fuels, it is predicted that fossil fuels such as oil and gas will be depleted by 2042, and coal will be depleted by 2112 [2]. Therefore, there is a dire need to look for alternative energy sources to reduce the dependency on fossil fuels for energy and transportation purposes, as well as reducing CO2 emissions. There are two types of biomass: energy crops for the production of bioethanol, and waste materials for the production of biogas (methane) and hydrogen by anaerobic digestion, of which the
latter is preferable [3]. However, the utilization of biomass for energy needs to take into account a few factors, such as the global population and diet, the efficiency of food production, the yield of energy crops in surplus agriculture areas, and future competing products [4]. Currently, Microbial Fuel Cells (MFC), an emerging renewable energy technology, have attracted the attention of many researchers because of the wide range of applications, including electricity generation, biohydrogen production, wastewater treatment, and biosensing [5]. MFC is a bioreactor that directly converts chemical energy from organic materials into electrical energy by using the catabolic metabolism of electrochemically active bacteria [3]. It is a very promising device in treating various domestic and industrial wastewater if further advances are made to improve current MFC technologies [6,7].

Despite MFC having many advantages over energy generation from biomass, such as high energy conversion efficiency, low operating temperature, no requirement for gas treatment, and no energy input [8], commercialization of MFC still remains impracticable. This is due to the low power density output of MFC [5], the high cost of the conventional cathode catalyst of Pt, which constitutes almost half of the MFC capital cost [9], and the high cost of commercial membrane separators (Nafion® perfluorinated membrane) [10]. Although Pt has been proven to have high catalytic activity towards oxygen reduction in microbial fuel cell cathodes, there are still several disadvantages, such as CO intolerance [11] and limited availability [12]. Other precious metals, such as gold (Au) nanoparticles, have shown a high potential as catalysts for oxygen reduction; because of their preferential low ORR overpotential [13,14]. Apart from the sluggish kinetics that impose a large overpotential to the overall MFC system, the performance of the MFC cathode is further limited by a series of voltage losses, such as ohmic loss, which is caused by the internal resistance of the fuel cell cathode, as well as mass transport loss, due to the limited oxygen concentration within the cathode. The integrated work of optimising the catholyte, the membrane, the operational conditions, and the MFC’s configuration, is crucial in improving cathode performance [15].

However, this paper only discusses the recent development of non-Pt and other no-precious metal catalysts that have been used in microbial fuel cells over the past decade, as well as the kinetics and mechanisms of oxygen reduction reactions that occur in fuel cell cathodes. Recent developments for alternative catalysts in oxygen reduction are: (1) metal oxide based, (2) metal macrocycle based, (3) carbon related materials, (4) electroconductive polymer, and (5) biocathode.

2. Kinetics and mechanisms of oxygen reduction reactions

In microbial fuel cell aqueous cathodes, many oxidants are candidates for electron acceptors in MFCs. Although cathodic mediators, such as ferricyanide [16,17], permanganate [18], dichromate [19], and persulfate [20] have been proposed as electron acceptors in MFCs in previous studies, oxygen still remains the most suitable electron acceptor in MFC cathodes, because it is easily available, has a low cost, is non-toxic, and is more sustainable than the alternatives [21]. The addition of mediators also renders MFC unsustainable, because replenishment of new catholyte is necessary over a period of operation, due to the loss of these mediator ions [22]. From this point, this section focuses only on oxygen as an electron acceptor in a cathode electrode. The main reaction occurring in an MFC cathode is an oxygen reduction reaction, where oxygen molecules are reduced by accepting electrons from the electrode.

ORR involves a series of electron transfer processes that depend on the type of catalyst used at the cathode. Generally, the electroreduction of oxygen occurs through two different pathways, namely 2-electron and 4-electron pathways. 4-electron pathways are more favourable, because the 2-electron pathways involve hydrogen peroxide production, which can lead to high overpotential.

4-electron electroreduction of oxygen pathway:

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2\text{O} \]  

2-electron electroreduction of oxygen pathway:

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \]
The rate determining step of ORR is the initial oxygen adsorption on the surface of the electrode catalyst before the oxygen is further reduced to hydrogen peroxide and H₂O [23]. Fig. 1 shows a simplified diagram of the proposed mechanism of electroreduction of oxygen in an acid media [24]. Ab initio quantum chemistry modelling and simulations have also suggested an adsorption mechanism of oxygen reduction with a metal catalyst [25]. The ORR of good, new, non-Pt catalysts should follow the 4-electron pathway as closely as possible. In non-Pt catalyst electrochemical ORR, the reduction of oxygen on carbon materials generally follows two different mechanisms; depending on the type of carbon [26]. Possible oxygen reduction mechanism on glassy carbon electrode has been suggested (as shown in Equations (3)–(8)). A two-step ORR mechanism on a pyrolytic graphite electrode has also proposed to reduce oxygen molecules to the final product of hydroperoxyl ion (as shown in Equations (9) and (10)) [27]. Both oxygen reduction pathways indicate that glassy carbon and pyrolytic graphite only facilitate 2-electron reduction to H₂O₂.

**ORR Mechanism on glassy carbon electrode**

\[ \text{O}_2 \rightarrow \text{O}_2^{(ads)} \]  
\[ \text{O}_2^{(ads)} + e^- \rightarrow [\text{O}_2^{(ads)}]^– \]  
\[ [\text{O}_2^{(ads)}]^– \rightarrow \text{O}^{–}\text{O}_2^{(ads)} \]  
\[ \text{O}^{–}\text{O}_2^{(ads)} + \text{H}_2\text{O} \rightarrow \text{HO}_2^{(ads)} + \text{OH}^- \]  
\[ \text{HO}_2^{(ads)} + e^- \rightarrow \text{HO}_2^{–}\text{O}_2^{(ads)} \]  
\[ \text{HO}_2^{–}\text{O}_2^{(ads)} \rightarrow \text{HO}_2^\cdot \]  

**ORR Mechanism on pyrolytic graphite**

<table>
<thead>
<tr>
<th>Cathode materials</th>
<th>Catalysts</th>
<th>Preparation methods</th>
<th>Cathode types</th>
<th>Maximum power density</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon cloth</td>
<td>MnO/C</td>
<td>Chemical oxidation of MnSO₄ by permanganate</td>
<td>Aqueous-air cathode</td>
<td>1600 W m⁻²</td>
<td>[32]</td>
</tr>
<tr>
<td>Carbon cloth</td>
<td>α – MnO₂</td>
<td>Chemical oxidation</td>
<td>Air-cathode</td>
<td>221 W m⁻²</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>β – MnO₂</td>
<td>Hydrothermal synthesis</td>
<td></td>
<td>978 W m⁻²</td>
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<tr>
<td></td>
<td>γ – MnO₂</td>
<td>Hydrothermal synthesis</td>
<td></td>
<td>826 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>Carbon cloth</td>
<td>Co doped octahedral molecular sieve MnO₂</td>
<td>Hydrothermal synthesis</td>
<td>Air-cathode</td>
<td>1800 W m⁻²</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>Cu doped octahedral molecular sieve MnO₂</td>
<td>Hydrothermal synthesis</td>
<td></td>
<td>1980 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>Carbon cloth</td>
<td>α – MnO₂</td>
<td>Chemical oxidation</td>
<td>Air-cathode</td>
<td>3380 W m⁻²</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>β – MnO₂</td>
<td>Hydrothermal synthesis</td>
<td></td>
<td>4660 W m⁻²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>γ – MnO₂</td>
<td>Hydrothermal synthesis</td>
<td></td>
<td>2390 W m⁻²</td>
<td></td>
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<tr>
<td>Glass carbon electrode</td>
<td>Manganese–Polypyrrole–CNT</td>
<td>In-situ chemical polymerization and in-situ Mn deposition</td>
<td>Air-cathode</td>
<td>213 mW m⁻²</td>
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</tr>
<tr>
<td>Carbon paper</td>
<td>MnO₂–graphene nanosheet</td>
<td>Modified Hummers method</td>
<td>Air-cathode</td>
<td>2083 mW m⁻²</td>
<td>[37]</td>
</tr>
</tbody>
</table>
The ORR pathway occurring at electrodes having different catalysts is determined by first running a Rotating Disc Electrode (RDE) analysis [28] and calculating the number of electrons transferred, \( n \) from the slope of the Koutecky–Levich plot where \( 1/I vs 1/u^{1/2} \) is plotted according to Equation (1) as shown in Fig. 2 [29].

\[
\text{1} \quad I = \frac{1}{I_k} + \frac{1}{I_L} + \frac{1}{I_0} + \frac{1}{0.62nFAD^{1/3}Cv^{1/6}}
\]

where \( I_k \) is the kinetic current for the ORR, \( I_L \) is the mass transport limiting current, \( n \) is the number of electrons involved in the ORR per oxygen molecule, \( F \) is the Faraday constant, \( A \) is the area of electrode, \( C \) is the saturation concentration for oxygen in water, \( D \) is the aqueous binary diffusion coefficient of oxygen, \( n \) is the kinematic viscosity of the solution, \( \omega \) is the rotation rate and \( 1/0.62nFAD^{1/3}Cv^{1/6} \) is the Koutecky–Levich slope. For example, Koutecky–Levich plots obtained from the RDE results for a thin-film, polycrystalline CoPd3 show that the catalyst catalyses a 4-electron oxygen reduction reaction [24].

Alternatively, the number of electrons involved can also be determined by a Rotating Ring Disc Electrode (RRDE) analysis where the number of electrons transferred, \( n \), is calculated from RRDE data using Equation (2) [26],

\[
n = \frac{4i_R}{i_D + i_R/N}
\]

where \( i_D \) is the reduction current density at the disc, \( i_R \) is the oxidation current density at the ring, and \( N \) is the collection efficiency of the RRDE. For example, RRDE analysis of the Pt/C electrode shows the ORR mechanism is a 4-electron transfer pathway [26].

Fig. 4 – TEM image of (A) pure CNT, (B) pure MnO2, (C) mechanically mixed MnO2/CNT and (D) chemically coated MnO2/CNT (adapted from Ref. [35]).

Fig. 5 – Cyclic voltammograms of (A). The electrodes with different catalysts at a scan rate of 10 mV s\(^{-1}\), and (B). The electrode with a MnO2/GNS catalyst at scan rates (from inner to outer) of 10, 15, and 20 mV s\(^{-1}\) in 50 mmol L\(^{-1}\) phosphate buffered solution (pH 7.0) (adapted from Ref. [37]).

Fig. 6 – Schematic diagram of molecular structure of metal phthalocyanine (MePc) (adapted from Ref. [40]).
Once the number of electrons transferred is determined by either RDE or RRDE analysis, or both, the transfer coefficient, $\alpha$, can be determined from the Tafel slope of the linearized polarization curve or Tafel plots, according to Equation (3) below,

$$\eta = -\frac{RT}{2.303nF} \log \frac{i}{i_0} - \frac{RT}{2.303nF} \log \frac{\eta}{i^0}$$

where $i$ is the ORR current density, $i_0$ is the exchange current density, $\alpha$ is the transfer coefficient, $R$ is the gas constant, $T$ is the temperature, $\eta$ is the over potential of ORR, and $RT/2.303nF$ is the Tafel slope. A smaller value Tafel slope implies the over potential of ORR increases at a slower rate when the current density is increased. Fig. 3 shows the Tafel plots of different nitrogen doped carbon nanotubes (NCNT) and their Tafel slopes [30]. Tafel slopes for a Pt catalyst are 60 mV dec$^{-1}$ and 120 mV dec$^{-1}$ at low current and at high current densities, respectively [26].

3. Metal oxide based catalyst

The application of cheaper transition metal oxides as ORR catalysts in MFCs, instead of using Pt, is drawing much attention; especially in the use of manganese (IV) dioxide ($\text{MnO}_2$), which has been studied extensively by researchers worldwide. Table 1 shows manganese dioxide and its composite catalysts, which have been used in microbial fuel cell applications over the past decade. $\text{Mn}^{III}$ ions serve as the intermediate ions that reduce oxygen and the electrocatalytic activity of MnO$_2$, which is strongly dependent on the surface concentration of $\text{Mn}^{III}$ ions [31]. The proposed mechanism of oxygen reduction by this catalyst is given as follows [31]:

$$\text{Mn}^{IV} \text{O}_2 + \text{H}_2 \text{O} + e^- \rightarrow \text{Mn}^{III} \text{OOH} + \text{OH}^- \quad (14)$$

$$2\text{Mn}^{III} \text{OOH} + \text{O}_2 \rightarrow \text{Mn}^{IV} \text{OOH} \cdot \text{O}^- \quad (15)$$

$$\text{Mn}^{IV} \text{OOH} \cdot \text{O}^- + e^- \rightarrow \text{Mn}^{IV} \text{O}_2 + \text{OH}^- \quad (16)$$

Manganese dioxide is synthesized by the oxidation of manganese sulphate by potassium permanganate according to the following chemical reaction [32]:

$$2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2 \text{O} \rightarrow 5\text{MnO}_2 + 2\text{H}_2 \text{SO}_4 + \text{K}_2 \text{SO}_4$$

The unique morphology of MnO$_2$ is claimed a significant factor on oxygen reduction activity. The oxygen reduction activity of $\beta$-MnO$_2$ exhibits higher catalytic activity than $\alpha$-MnO$_2$, $\beta$-MnO$_2$, and $\gamma$-MnO$_2$ because of its larger BET surface area [33]. However, the high oxygen reduction activity of $\beta$-MnO$_2$ could also be caused by the interaction between $\beta$-MnO$_2$ crystallographic structure and CNT support that results in delocalized electrons in CNT and Mn [34]. In addition, the ORR activity of MnO$_2$ is also influenced by the method of deposition of MnO$_2$ on CNT, where there is better distribution of
MnO₂ on chemically coated MnO₂/CNT, as shown in Fig. 4. It has been shown to have enhanced catalytic activity to that of physically mixed MnO₂/CNT [35]. Furthermore, nanostructured MnO₂ on carbon paper made by cyclic voltammetrical deposition at different scan rates shows good ORR activity and a high maximum power density in MFC application [36].

The reduction peak of MnO₂/Graphene nanosheet (GNS) nanocomposite of −0.43 V, as shown in Fig. 5, is higher than that of MnO₂ at −0.71 V, but is approximately the same level as that of a Pt/C catalyst at −0.44 V. This indicates that the MnO₂/GNS catalysis of ORR is higher than that of MnO₂ but is at a similar level to that of a Pt/C catalyst [37]. The ORR activity of another oxide of Mn, Mn₂O₃, is higher than that of Fe₂O₃ since the power density of the former in MFC, 31.7 W m⁻², is twice that of the latter’s, 15.4 W m⁻². The former’s Coulombic efficiency of 42.6% is also approximately 50% higher than that of the latter’s, at 31.4% [38]. The power density of MFC using another transition metal oxide, PbO₂/Ti, is higher than that of Fe₂O₃ since the power density of the former in MFC, 31.7 W m⁻², is twice that of the latter’s, 15.4 W m⁻². The former’s Coulombic efficiency of 42.6% is also approximately 50% higher than that of the latter’s, at 31.4% [38]. The power density of MFC using another transition metal oxide, lead oxide (PbO₂) brushed on a titanium sheet using either Nafion, PbO₂/Ti (Nafion as binder), PbO₂/Ti (butanol as binders), are similar, at 78 mW m⁻² and 77 mW m⁻² respectively [39]. However, the cost of PbO₂/Ti is 1.7 times lower than the cost of a Pt catalyst, and 8 times lower if butanol is used as a binder instead of Nafion [39]. These results show that cheap transition metal oxides are cheaper and viable alternative ORR catalysts, but still need further optimization and improvements.

4. Metal macrocycles-based catalysts

A cheaper class of oxygen reduction catalysts for microbial fuel cells are metal macrocyclic compounds, such as metal phthalocyanines and tetramethoxyphenylporphyrins. In a schematic diagram of metal phthalocyanine structure, shown in Fig. 6, the centre metal ion, M is bonded with 4 nitrogen atoms [40]. Research on metal phthalocyanines as oxygen reduction catalysts, which began as early as 1964 [41], has produced metal macrocycles compounds with many different ligands that can facilitate ORR in acid [29], alkaline, and...
neutral conditions [40]. However, metal macrocycles only have short-term stability in acidic media where the pH is lower than 3 because of the demetallation of the macrocycles rings [40]. For example, the central Fe ion of iron phthalocyanine (FePc) in an acid media is replaced easily by two hydrogen atoms (H2Pc) which cannot catalyse ORR [42].

The ORR activity of macrocyclic compounds is influenced by the centre metallic ion and type of ligand [43]. The highest ORR catalytic activity is obtained if iron (Fe) or cobalt (Co) is used as the centre metallic ion in either phthalocyanines [43,44] or tetramethoxyphenylporphyrin Refs. [44–46]. Even though both Co-naphthalocyanine modified carbon (CoNPc/C) and naphthalocyanine modified carbon (NPC/C) catalyse ORR without the production of hydrogen peroxide, CoNPc/C has a more positive onset potential and peak potential in CV reduction (as shown in Fig. 7a). As shown in Fig. 7c, the presence of the centre Co metal in the former caused the catalyst to reduce oxygen through 4-electron pathways, within a wide potential range of –0.6 V to 1.0 V in a neutral condition. Furthermore, an MFC working with CoNPc/C catalyst, showed a power density closer to Pt than NPC/C [47]. Both iron phthalocyanine (FePc) [45] and cobalt tetramethoxyphenylporphyrin (CoTMPP) [45,46] were found effective ORR catalysts for MFC because of the presence of the centre metals. However, the stability of both centre metals in both complexes needs to be improved [40,46].

The performance of the macrocyclic compound can be improved further by modifying its structure through pyrolysis or by replacing the carbon with more active carbon materials, such as graphenes. The ORR activity of pyrolyzed iron ethylenediamininetetraacetic acid (PFeEDTA) is better than FeEDTA, because the former reduction peak potential of 0.32 V has shifted more positively than the latter’s and it is similar to the reduction peak of the Pt catalyst but with a lower peak current (as shown in Fig. 8). The study also showed that quaternary nitrogen, modified by iron, is the active site responsible for the ORR catalysis of the PFeEDTA catalyst [48]. However, a novel iron tetrasulfophthalocyanine functionalized graphene (FeTsPc-graphene) has a comparable catalytic activity to Pt/C. Although FeTsPc-graphene has a peak potential similar to Pt/C, but Pt/C still possesses a more positive onset potential and a higher peak current than other catalysts tested based on the analysis of CV and LSV (as shown in Fig. 9) [49].

5. Carbon related materials

Since the discovery of nanotechnology, research on carbon nanostructured materials has become a dominant research theme all over the world [50]. The unique electrical and mechanical properties of carbon nanostructure, such as carbon nanotube and carbon nanofiber, have made it become a promising material for catalysts and catalyst supports [51,52], supercapacitors [53], sensors [54] and hydrogen storage materials [55].
Activated carbon nanofiber (ACNF) synthesized by the electrospinning and pyrolysis of a polyacrylonitrile precursor, followed by the chemical activation of 8 M KOH, has the highest ORR activity in MFCs, compared to others chemically activated at lower KOH molarities and with CO$_2$ [52]. In addition, a CNT-graphene composite has a high onset potential of 0.89 V and a Tafel slope that indicates the ORR occurs by a direct 4-electron pathway, similar to a Pt catalyst [56].

Recent great interest on nitrogen doped carbon nanotubes (N-CNT) as alternative catalysts for ORR has generated many papers that examine the various factors affecting their properties. N-CNT (as shown in Fig. 10) shows great catalytic activity in an alkaline solution. From the plot shown in Fig. 11, N-CNT displayed a much more positive onset potential than the Ag/C catalyst, which was similar to the Pt/C catalyst in the polarization curve. Besides, the electron transferred number in Koutecky–Levich plot for N-CNT was 3.27, which implies that the ORR in the N-CNT mainly follows a 4-electron reduction mechanism; similar to the ORR catalysed by Pt/C [57].

The numbers of electrons transferred by three N-CNT with different nitrogen contents of 3.28%, 2.84%, and 2.51%, produced by the Chemical Vapour Deposition (CVD) of pyridine, ethanol, and ferrocene, were 3.63, 3.20, and 2.76, respectively [30]. The RRDE voltammogram shown in Fig. 12 indicates a slight enhancement of the onset potential and the half wave potential, when the nitrogen content in CNT increased [30]. Meanwhile, H$_2$O selectivity increased significantly from 38.16% to 81.82%, which meant that oxygen was more likely to be reduced in 4-electron pathway to water [30]. Also, ORR at N-CNT tended to follow a 4-electron pathway in an alkaline media. Nitrogen doped carbon nanofibers (NCNF) grown on heated stainless steel from nitrogen and pyridine have high ORR activity in a neutral media because of the high content of the pyridine type nitrogen in the NCNF [58].

![Fig. 12 - RRDE voltammogram of N-CNT-a, N-CNT-b and N-CNT-c samples for oxygen reduction in 0.1 M of potassium hydroxide saturated with O$_2$. (a) Disk current and (b) ring currents. Scan rate 10 mV s$^{-1}$ and rotation rate 2500 rpm (adapted from Ref. [30]).](image)

![Fig. 13 - Power density curves (A) and electrode potential's curve (B) for MFCs with different cathode catalysts (adapted from Ref. [61]).](image)

![Fig. 14 - Bridge model of oxygen adsorption on PANI (adapted from Ref. [64]).](image)
Enhancement of ORR activity in N-CNTs is dependent on the type of nitrogen inclusion in the N-CNTs, whose growth depends on the synthesis method and presence of Fe\[59\]. For example, the ORR of nitrogen doped graphene synthesized by CVD of methane in ammonia atmosphere, which is more stable and tolerant towards methanol and CO than Pt, follows a 4-electron oxygen reduction pathway\[60\]. Metal and nitrogen doped graphene has also been reported as an effective catalyst material for ORR. Fig. 13 shows that the maximum power density of MFCs using iron functionalized nitrogen graphene (Fe\textsubscript{e}N-G) as ORR catalysts (1149.8 mW m\textsuperscript{2}) is twice that of MFCs using conventional Pt/C catalysts (561.1 mW m\textsuperscript{2}). The power density of the MFC depends solely on cathode potential, since anode potentials are similar for all MFCs\[61\].

6. **Electroconductive polymer-based catalyst**

Another type of molecular-based catalyst capable of oxygen reduction catalysis are electroconductive polymers (ECPs), such as polyaniline (PANI), polypyrrole (PPy), and polythiophen (PTh). Their high conductivity and environmental stability make them very suitable for applications in electrocatalysis and as capacitors\[62,63\].

An early extensive study on ORR activity of PANI, PPy, PTh, poly(3-methyl)thiophene (PMeT) and, poly(3,4-ethylenedioxythiophene) (PEDOT) produced via oxidative polycondensation shows that PANI and PPy have higher electrocatalytic activity in ORR than the other ECPs \[64\]. However, the reduction of PANI emeraldine to leucoemeraldine during ORR renders PANI non-conductive in the presence of oxygen\[64\]. The catalysis of the ORR on ECPs is due to weakening of molecular O\textsubscript{e}O bonds during the chemisorption of oxygen on the ECPs’ surface\[64\]. Fig. 14 shows the bridge model of adsorption of oxygen molecule on PANI\[64\].

The application of bare electroconductive polymers as ORR catalysts in MFCs is rarely reported. However, ECPs in MFC applications are usually combined with other active electrocatalytic materials to enhance performance. For example, with respect to carbon black/PPy composite, the peak potential (−0.34 V) has a more positive value than carbon black (−0.60 V), as shown in the cyclic voltammetry curves in Fig. 15\[65\]. However, the power drops dramatically when PPy catalyst loading is more than 0.2 mg cm\textsuperscript{2} because of low oxygen diffusion in the highly packed surface of the electrode. In addition, MFC electrodes containing Prussian blue dye (PB), PB/PANI/spectrographic pure graphite (SPG) composites, have been shown to have higher catalytic activity in acidic media than bare PANI/SPG without Prussian blue dye, as shown in Fig. 16\[66\].

Macrocyclic compounds, such as phthalocyanines and anthraquinones, could also be added to electroconductive polymers to improve its ORR performance in MFC application. ORR activity of phthalocyanine polyaniline/carbon black composite supported iron (PANI/C/FePc) is higher compared to...
C/FePc, where the reduction potential is slightly more positive and its reduction peak current is double than those of the latter [67]. Furthermore, the addition of PANI into C/FePc is believed to facilitate an ORR that is similar to Pt/C. For example, the PANI/C/FePc catalyst has a more positive peak potential and higher peak current than the C/FePc (as shown in the linear sweep voltammogram shown in Fig. 17(B)) [67]. Although air-cathodes using polypyrrole/anthraquinone-2-sulfonate (PPy/AQS) coated stainless steel mesh in membraneless MFC have achieved a maximum power density of 575 mW m$^{-2}$, its ORR activity was not investigated [68].

![Fig. 17 – (A) CV and (B) LSV of various electrodes for oxygen reduction at a scan rate of 100 mV s$^{-1}$ and (C) 1 mV s$^{-1}$ (adapted from Ref. [67]).](image)

### 7. Biocatalysts

Since abiotic cathode catalysts have many disadvantages, such as high cost, complexity of fabrication, and are non-environmental friendly, numerous initiatives have attempted to develop biocathode, which are cathodes covered by biofilms full of bacteria acting as biocatalysts, as oxygen reduction agents in MFC. Generally, biocathodes are categorized into two main groups: aerobic and anaerobic biocathodes [69]. In aerobic biocathodes, oxygen is the ultimate terminal electron acceptor and both manganese and iron act as electron mediators. On the other hand, anaerobic biocathodes utilize nitrates and sulphates as major terminal electron acceptors [69]. Recently, it was observed that a small amount of exoelectrogens in the cathode biofilm attachment can facilitate ORR, as well as non-exoelectrogens, which might be advantageous in enhancing the performance of a biocathode [70].

The species of electrochemically active bacteria present in the biofilm attached to the biocathode affects electrocatalytic activity and performance of the biocathode significantly [71,72]. For example, the maximum power density of MFCs whose biocathodes use isolates of Sphingobacterium sp. as the biocatalyst (49 mW m$^{-2}$) is twice of biocathode using isolates of Acinetobacter sp. as the biocatalyst (24 mW m$^{-2}$) and more than thrice of abiotic cathodes (15 mW m$^{-2}$) where no biofilm exists; the current density at maximum power of the former (690 mA m$^{-2}$) is one and a half times of the latter (486 mA m$^{-2}$) and more than twice of abiotic cathodes (316 mA m$^{-2}$) [71]. On the other hand, MFCs whose biocathodes use mixed cultures have six times the maximum power density (303 mW m$^{-2}$) and one and a half time the current density at the maximum power of MFCs (996 mA m$^{-2}$) whose biocathodes use isolates of Sphingobacterium sp. as the biocatalyst [71].

The power density of MFCs with a carbon fiber brush embedded in graphite granules bed as a cathode using mixed cultures with dairy manure as a substrate also increases from 7.85 W m$^{-3}$ to 8.15 W m$^{-3}$ when increasing the total solids of dairy manure from 2 to 6% [72]. However, increasing the total solids beyond 6% reduces the power density to 5.63 mW m$^{-3}$ at 10% total solids, most likely because the pH drops as a result of dairy manure hydrolysis [72]. Increasing the loading rate of COD from 0.5 to 1.5 kg m$^{-3}$ day$^{-1}$ increases the power density of continuous MFC using graphite brush cathodes from 8 to 65 W m$^{-3}$ [73].

The kind of electrode materials used as a biocathode in MFCs also affects the performance and electrocatalytic activity of the biocathodes, especially carbon materials [73–76]. The maximum current density of a MFC with a Graphite Felt
(GF) biocathode (350 mA m\(^{-2}\)) is more than one and a half times that of a MFC with a Carbon Paper (CP) biocathode (210 mA m\(^{-2}\)), and nearly 20 times that of a MFC with Stainless Steel Mesh (SSM) biocathode (18 mA m\(^{-2}\)); the maximum power density of a MFC with a GF biocathode (109.5 mW m\(^{-2}\)) is more than 3 times that of a MFC with a CP biocathode (32.7 mW m\(^{-2}\)) and nearly 30 times that of a MFC with a SSM biocathode (3.1 mW m\(^{-2}\)) [74]. Based on the cyclic voltammogram in Fig. 18, the ORR activity of these cathode materials with biofilm can be ranked in the order of GF > CP > SSM [74].

The power densities of cheaper biocathode materials with a higher surface area, granular semicoke (GS) (20.1 W m\(^{-3}\)), and Granular Activated Carbon (GAC) (24.3 W m\(^{-3}\)) are higher than those of granular graphite (14.1 W m\(^{-3}\)) and carbon felt cubes (17.1 W m\(^{-3}\)) [75]. A combination of differently structured carbon materials, such as a Graphite Fiber Brush (GFB) and Granular Graphites (GG) increases the maximum power density to 99.83 W m\(^{-3}\) and the current density to 240.62 A m\(^{-2}\) compared to that of GG (72.84 W m\(^{-3}\) and 175.74 A m\(^{-2}\)) and GFB (72.35 W m\(^{-3}\) and 181.80 A m\(^{-2}\)) cathodes alone [73].

The electrocatalytic activity of carbon cloth biocathodes impregnated with microbially-reduced graphene (CC/Graphene), where the graphene/biofilm composite is formed, is enhanced because the graphene quickly conducts electrons away [77]. The power density of CC/Graphene biocathodes (320 mW m\(^{-2}\)) is twice that of CC biocathodes (105 mW m\(^{-2}\)) and the former's current density (0.16 mA m\(^{-2}\)) is about one and half that of the latter (0.115 mA m\(^{-2}\)) [77]. Catalytic activity of biofilm is also boosted by the addition of CNT on stainless steel mesh (SSM) as a cathode electrode. The CV curves, as shown in Fig. 19, show that the peak current of biofilm attached-CNT-SSM is much higher than biofilm attached-SSM; thus indicating that ORR occurred much faster with the CNT-SSM electrode [78]. Consequently, utilization of biocatalyst for ORR in MFC is sustainable and practicable, because it does not require replacement of the catalyst and reduces the operational cost of MFC.

8. Conclusion

In this work, abiotic non-Pt cathode catalysts and biocatalysts for oxygen reduction reaction in MFCs with the potential to reduce the cost of MFCs are reviewed extensively. Although many previous works have focused on advanced nano-materials, including transition metal oxide nanoparticles, transition metal macrocyclic compounds, nitrogen doped carbon nanotube, and graphene, as abiotic catalysts for MFC’s cathodes because of their high ORR activity, they are still costly when applied in MFCs whose power and current...
densities are relatively low compared to conventional fuel cells. Instead of abiotic catalysts in air cathodes, an attractive alternative is a biocathode where bacteria are used as biocatalysts on cheap carbon cathodes. Hence, more fundamental research is needed on the various factors affecting the performance of biocathodes in order to understand its limitations and hence maximize the power output of MFCs in the near future.

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