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# Enhancing Catalyst Efficiency of Activated Carbon for Oxygen Reduction Reaction in Air Cathode Microbial Fuel Cell Application

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## Abstract

Microbial fuel cell (MFC) air cathode present a great potential among other configurations due to its simple design, low cost and direct use oxygen from air as terminal electron acceptor which could help to save tremendous energy used for aeration in conventional wastewater treatment. However, at the cathode oxygen reduction reaction which is vital to generate high power density is naturally slow, therefore a catalyst is needed to overcome its reaction over-potential. Platinum (Pt) is the standard used catalyst in large number of oxidation reduction reactions whether in basic or acidic electrolytes. But, due to its high cost and limited resources it doesn't make it a sustainable candidate for scaling up of this juvenile technology. Activated carbon was found to be a low cost and environmental friendly Oxygen reduction reaction (ORR) catalyst in microbial fuel cell, but still exhibit lower catalytic behavior in its bare form which results in low power output. In this review we aims at making an overview of different promising technologies currently used to boost Activated carbon catalytic performance toward ORR in MFC air cathode and compare their outcomes in terms of catalytic behavior and MFC power output to the standard Pt and bare activated carbon catalysts. Advantages, disadvantages and bottlenecks of these techniques also will be discussed.

**Keywords:** Microbial fuel cell; Air cathode; Oxygen reduction reaction; Activated carbon; Heteroatoms; Transition metals

## Introduction

Microbial fuel cell (MFC) is a potential environmental friendly bio-electrochemical system as it combines treatment of organic wastes and electric energy generation [1-4]. In MFCs, the electrochemically active microorganisms' biofilm colonizes the anodic surface thus oxidizing organic pollutants producing electrons and protons. Electrons are transferred through an external circuit to the cathode where are received by the terminal electron acceptor while protons migrate through the membrane or solution to the cathode to keep electrical neutrality which creates potential difference [1,5]. Several applications of this technology such as hydrogen gas production [6], hydrogen peroxide generation [7], desalination [8-10], remote sensors and monitoring devices [11,12] metal recovery at cathode [13] and robots [12,14] to mention but few, have been studied and left researchers with more innovation ideas in the field. Having electrochemical processes catalyzed by biological processes in addition to some other design parameters such as engineering of microbial biofilm structure, decrypting electron transfer mechanisms, cell/reactor configuration, electrode materials and geometries, substrate concentration, retention time, and optimizing cathode catalysts [15,16] makes this system more sensitive to internal losses and gives it a certain level of complexity [17,18]. This and other challenges that are still unanswered are the bottlenecks for MFC application in real environment [15,19]. Therefore, current researches focus on limiting factors and ways to curb their effects thus increasing the performance [2,20,21]. Among others, is trying different MFC design configurations where MFC air-cathode proved to more advantageous over double chamber for scaling up because of its simple structure, low cost and direct use oxygen in air, which could removes aeration from conventional wastewater treatment process [5,22]. Due to its high reduction potential and inexhaustible source, Oxygen is the most fairly used terminal electron acceptor and is considered to be competent for MFC air-cathode application and scale up as it plays a critical role in both organic oxidation and energy recovery at the cathode [23].

Following the torpid inherent character of the Oxygen Reduction Reaction (ORR), the design of the air-cathode is the single greatest challenge for making an MFC a useful and scalable technology, therefore a chemical catalyst should be used to increase the rate of the reaction [24]. Besides, this reaction is difficult to engineer as the electrons, protons and oxygen must all meet at a catalyst in a tri-phase reaction (solid catalyst, air, and water). Besides being exposed to both air and water, the catalyst must be also on a conductive surface, in order to make electrons and protons reach the same point in these different phases [1].

Platinum (Pt) is a commonly used catalyst however high-cost [24], low availability and poor stability [25] of this noble metal makes it difficult for massive production of cathodes, thus hinder MFCs scale up for practical application [26]. Alternatives to Pt includes inexpensive non-noble metal materials and their oxides such as transition metal Co [21,27], $Fe_3O_4$ [28] and $MnO_2$ [29]. However, these metal ions found to cause secondary pollution as they exhibited potential leaching into solution. Beside, to have the same performance as platinum high loading is needed which ends up increasing the overall cost [5].

With the advantage of easy access at low-price, good catalytic performance, high conductivity, durability and regeneration [20], recently using activated carbon (AC) powder as catalyst in air-cathodes

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achieved very good results with the production of power densities in MFCs (Table 1) slightly higher than or similar to those obtained using platinum catalyst [30,31]. For instance, a MFC well fitted with an AC cathode bonded with a polytetrafluoroethylene (PTFE) and the current collected by nickel brought about 1220 $mWm^{-2}$ greater to 1060 $mWm^{-2}$ achieved using a Pt catalyst cathode (0.5 mg-Pt $cm^{-2}$ ) and a Nafion binder [32-48]. Another example is a MFC with the same AC cathode configuration but with a diffusion layer made of polydimethylsiloxane (PDMS) coated cloth which produced 1255–1310 $mWm^{-2}$ comparable to 1295 $mWm^{-2}$ obtained with a benchmarking Pt/C cathode (0.5 mg-Ptcm$^{-2}$) [49]. A catalyst layer made of AC/PTFE supported on stainless steel mesh which collects the current as well was made using a rolling process method. This cathode produced 1086 $mWm^{-2}$ in an MFC with a high surface area (1701 $m^2\ g^{-1}$) AC and 1355 $mWm^{-2}$ with a lower surface area (576 $m^2\ g^{-1}$) AC powder [50].

Despite its good ORR catalytic activity, but the power output of MFCs with bare AC catalyst is still low which led researchers to find different ways to enhance it. Various approach of modification of AC like mixing with carbon black [51], heating [52] and using dopants [53] has been attempted to take the performance to the level of practical application. Results showed promising catalytic activity, improved power output, low cost, environmental friendliness, and durability [20].

Herein we are going to take brief look at commonly used methods used to enhance the oxygen reduction reaction's catalytic activity of Activated Carbon for better performance of MFC air cathode application.

## Oxygen Reduction Reaction Kinetics on MFC Cathode

Let's first explore a bit more about oxygen reduction reaction; in aqueous solution at the cathode, oxygen reduction reaction (ORR) is mainly completed by either a direct 4-electron reduction pathway from $O_2$ to $H_2O$ or an indirect 2-electron reduction pathway from $O_2$ to hydrogen peroxide ($H_2O_2$) [54]. However, many intermediate species may be involved depending on the catalyst used, physical chemical characteristics of electrode materials and electrolyte. These makes the mechanism of this electrochemical oxygen reduction reaction a bit complicated as shown in equations below with their respective thermodynamic electrode potential at standard conditions [55]:

Acidic aqueous solution:

$$\mathbf{O}_2 + 4\boldsymbol{H}^+ + 4\boldsymbol{e}^- \rightarrow \boldsymbol{H}_2\boldsymbol{O} \qquad 1.229\boldsymbol{V} \qquad (1)$$

$$\mathbf{O}_2 + 2\boldsymbol{H}^+ + 2\boldsymbol{e}^- \rightarrow \boldsymbol{H}_2\boldsymbol{O}_2 \qquad 0.70\boldsymbol{V} \qquad (2)$$

$$\mathbf{H}_2\boldsymbol{O}_2 + 2\boldsymbol{H}^+ + 2\boldsymbol{e}^- \rightarrow 2\boldsymbol{H}_2\boldsymbol{O} \qquad 1.76\boldsymbol{V} \qquad (3)$$

Alkaline aqueous solution:

$$\mathbf{O}_2 + 2\boldsymbol{H}_2\boldsymbol{O} + 4\boldsymbol{e}^- \rightarrow 4\boldsymbol{OH}^- \qquad 0.401\boldsymbol{V} \qquad (4)$$

$$\mathbf{O}_2 + 2\boldsymbol{H}_2\boldsymbol{O} + 2\boldsymbol{e}^- \rightarrow \boldsymbol{HO}_2^- + \boldsymbol{OH}^- \qquad -0.065\boldsymbol{V} \qquad (5)$$

$$\mathbf{HO}_2^- + \boldsymbol{H}_2\boldsymbol{O} + 2\boldsymbol{e}^- \rightarrow 3\boldsymbol{OH}^- \qquad 0.867\boldsymbol{V} \qquad (6)$$

The fact that with the utilization of half of the reactant (oxygen) amount double amount of electrons is transferred, a 4-electrons transfer pathway is targeted in all researches [56].

Prior to MFC assembly and operation, the Rotating Disk Electrode (RDE) test method is the most efficient tool to evaluate reaction kinetics of ORR. It has advantage of reducing mass transfer limitation to catalyst which allows computing of the limiting current [51]. As shown on figure 1, performance indicators such as onset potential ($E_{onset}$) the more positive the better [57], half-wave potential ($E_{1/2}$), overpotential under a specific current density ($\eta_j$), and diffusion-limiting current density ($j_L$) (better when it's large) are indicated on an ORR-RDE typical polarization curve.

For both ORR and fuel cells performance, the lower the

| Dopants | Method | Power Density | Improvement % | Reference |
|---|---|---|---|---|
| **Heteroatoms** | | | | |
| P | Treatment with $H_3PO_4$ (1 M) at 400°C | 1096 ± 33 mW/m² | 55 | [32] |
| N | Ammonia gas treatment | 2450 ± 40 $mWm^{-2}$ | 28 | [33] |
| N-P | Pyrolysis of cellulose using $(NH4)_3PO_4$ | 2293 ± 50 $mWm^{-2}$ | 36 | [34] |
| P-S | Pyrolysis of petroleum coke | 1029.77 ± 99.53$mWm^{-2}$ | 23.52 | [35] |
| **Transition Metals/Oxides** | | | | |
| Ag | Electrodeposition | 1080 ± 60 mW $m^{-2}$ | 69 | [36] |
| $NiCo_2O_4$ | $Co(NO_3)_2.6H_2O$ , $Ni(NO_3)_2.6H_2O$ and $(NH_2)_2CO$ autoclaved then carbonized | 1730 ± 14mW $m^{-2}$ | 56 | [37] |
| $Fe_3O_4$ | Adding $NSFe_3O_4$ with ethanol in ultrasonic device | 1430mW/m² | 83.3 | [38] |
| $Co_3O_4$ | Cobalt salt $(Co(CH_3COO)_2.4H_2O)$ autoclaved then carbonized | 1500 ± 14 $mWm^{-2}$ | 41.36 | [39] |
| $Cu_{0.92}Co_{2.08}O_4$ | Rolling 20% of the $Cu_{0.92}Co_{2.0}8O_4$ and AC | 1895 mW $m^{-2}$ | 113 | [40] |
| $Cu_2O$ | Electrodeposition | 1390 ± 76 $mWm^{-2}$ | 59 | [41] |
| $MnO_2$ | Electrodeposition | 1554 mW $m^{-2}$ | 50 | [29] |
| **Heteroatom-Transition Metals** | | | | |
| Fe–N | $Fe(III)Cl_3$, EDA and AC mix in ethanol and pyrolyzed at 800°C | 2437 ± 55 $mWm^{-2}$ | 114 | [42] |
| Co-Fe-N | Hydrothermal-assisted annealing | 1770.8 ± 15.0 $mWm^{-2}$ | 72 | [43] |
| Co-N | Aniline + $Co(NO_3)_2.6H_2O$ in 0.5 M $H_2SO_4$ then pyrolysis at 900°C | 11.02 W/m³ | 13.3 | [44] |
| N-$MoS_2$ | Ammonium molybdate + thiourea + Pluronic F127 + melamine followed by calcination at 900°C | 0.815$Wm^{-2}$ | 60 | [45] |
| **Acid and Alkaline Treatment** | | | | |
| $H_3PO_4$ | Disperse AC into 1M 20 ml of acid and stir for 24 h | 1546 ± 43 mW $m^{-2}$ | 115 | [46] |
| $HNO_3$ | | 768 ± 15 mW $m^{-2}$ | 57 | |

| | | | | |
|---|---|---|---|---|
| HCl | | 1260 ± 22 mW $m^{-2}$ | 93.7 | |
| $H_2SO_4$ | | 965 ± 32 mW $m^{-2}$ | 71.7 | |
| $HNO_3$ | Soaking AC into 5.6 M $HNO_3$ and heating 85°C for 6 h | 537 ± 36 $mWm^{-2}$ | -67 | [47] |
| KOH | Soaking AC into 3 M KOH and heating 85°C for 6 h | 957 ± 31 $mWm^{-2}$ | 16 | |

**Table 1**: Power output of some MFCs catalyzed by activated carbon modified by different dopants.

overpotential the higher the current density which gives the maximum power density [55].

To analyze ORR catalytic behavior of a given catalyst, the RDE's electrochemical and hydrodynamic properties are correlated with the Koutecký–Levich (K–L) equation 7 below:

$$\frac{1}{i}=\frac{1}{i_k}-\frac{1}{0.62nFAD_{O_2}^{2/3}v^{-\frac{1}{6}}C_{O_2}\omega^{1/2}} \quad (7)$$

Where i is the measured current, ik is the kinetic (current the higher the better), n represent average number of electrons transferred in the reaction, F is Faraday's constant, A as the projected surface area of the disk electrode, $DO_2$ the diffusion coefficient of oxygen, υ is the kinematic viscosity, $CO_2$ is the concentration of oxygen in solution, and ω is the rotation rate of the electrode [57]. As it can be seen from Table 2, different doping technics improved the catalytic activities of activated carbon where both onset potentials and current densities were seen to be higher than the control i.e., Pt/C or bare AC catalysts. Also the number of electron transferred (n) is close to four, which is the desired oxygen reduction reaction pathway. This is the result of the remarkable reduction in both ohmic and charge transfer resistances.

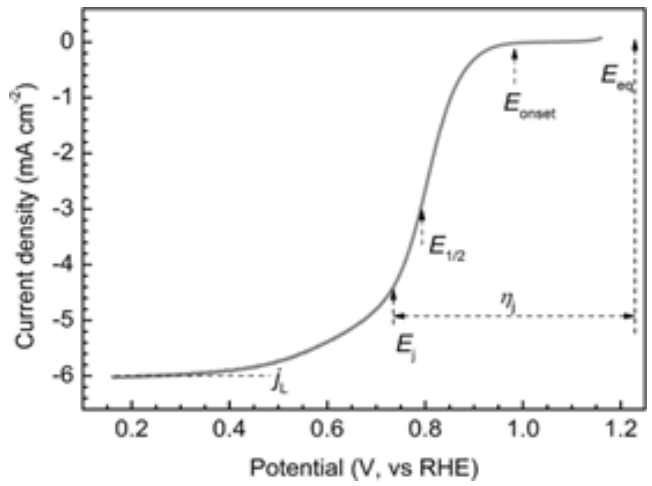


**Figure 1:** Typical ORR polarization curve of Pt/C collected from RDE system with rotating rate of 2000 rpm [58].

| Dopants | $E_{onset}$/V | Current Density | n | Reference |
|---|---|---|---|---|
| P | 0.28 | 2.8 A/$m^2$ | 3.5 | [32] |
| N | 0.12 | 0.83 mA/$cm^2$ | 3.9 | [33] |
| N-P | 0.11 | 0.54 mA/$cm^2$ | 3.8 | [34] |
| P-S | 0.2 | 0.936 mA/$m^2$ | 3.6 | [35] |
| Ag | 0.32 | 2.85 mA/$cm^2$ | 4 | [36] |
| $NiCo_2O_4$ | 0.236 | 25.49 A/$cm^2$ | 3.72 | [37] |
| $Fe_3O_4$ | 0.27 | 8.71 × $10^{-4}$ A/$cm^2$ | 4 | [38] |
| $Co_3O_4$ | 0.28 | 18.865 × $10^{-4}$ A/$cm^2$ | 3.99 | [39] |
| $Cu_{0.92}Co_{2.08}O_4$ | - | 7.85 mA/$cm^2$ | 3.71 | [40] |
| $Cu_2O$ | - | 1.03×$10^{-3}$ A/$cm^2$ | - | [41] |
| $MnO_2$ | 0.31 | 0.81 mA/$cm^2$ | - | [29] |
| Fe–N | 0.1 | 0.81 mA/$cm^2$ | 4 | [42] |
| Co-Fe-N | - | 14.2 A $m^{-2}$ | 3.77 | [43] |
| Co-N | - | 3.81 mA/$cm^2$ | 3.96 | [44] |
| N-$MoS_2$ | 0.24 | 0.61 × $10^{-4}$ A $cm^{-2}$ | 3.84 | [45] |
| $H_3PO_4$ | - | 15.275 × $10^{-4}$ A $cm^{-2}$ | 3.67 | [46] |
| HCl | - | 12.878 × $10^{-4}$ A $cm^{-2}$ | - | [46] |
| $H_2SO_4$ | - | 9.080 × $10^{-4}$ A $cm^{-2}$ | - | [46] |
| $HNO_3$ | - | 7.519 × $10^{-4}$ A $cm^{-2}$ | - | [46] |
| KOH | - | 4.2 A $m^{-2}$ | 4 | [47] |

**Table 2:** Doped activated carbon catalysts performances for ORR.

## Methods for Modification of Activated Carbon Catalyst

### Heteroatom doping

One of the key for real applications of MFC technology is using low cost and sustainable materials especially the cathode. Due to its availability and relatively low cost, Activated Carbon has been one of the best alternative catalysts to replace costly Pt as ORR catalyst in MFC [59-62]. However, the power output and catalytic performance of plain AC cathodes was found in need to be improved for the sake of sustainability. All heteroatoms have a greater or lesser attraction for electrons than carbon does. Thus, each bond between a carbon and a heteroatom is polar, therefore, integrating heteroatoms, such as Nitrogen [63,64], Phosphorus [32,65], Sulfur [66], and Boron [67] into the carbon framework has been demonstrated to largely enhance properties like: surface polarity, semi-conducting, field-emission, mechanical, and electrical behaviors of carbon materials [68]. Heteroatoms breaks electro-neutrality of adjacent carbon atoms, creating complementary charged sites on which oxygen can be absorbed and reduced; thus demonstrating high-efficiency ORR catalytic activities [69]. Methods used to get AC doped with heteroatom include post-treatment of AC with heteroatoms dopants like ammonia [33] or using precursors containing heteroatoms [70] or activating agents for hydrothermal treatment or pyrolysis. Electron-donor properties of activated carbon can be improved by Phosphorus doping leading to an increased ORR catalytic activity as it can be witnessed in a research where MFC was inoculated by domestic wastewater and acetate used as substrate, they used AC treated with $H_3PO_4$ (1 M) at 400°C as ORR catalyst and attained maximum power density of 1096 ± 33 mW/$m^2$ which was 55% higher than the benchmark. This improvement was said to be the result of decreased Ohmic and charge transfer resistance due to the P atom inserted into AC surface [32]. The same increment was observed by Qin Liu et al. [71] when a P-doped carbon obtained from cellulose phosphate and prepared at 1000°C was used in air cathode producing 1312 ± 82 $mWm^{-2}$ maximum power density which was claimed to be three times as that with P-free carbon catalyst and higher than the air-cathode with Pt/C catalyst. Boron-doped carbon also shows great potential as ORR catalysts following the fact that it has a lower electronegativity than carbon, and the positively polarized boron atoms attract the negatively charged oxygen atoms leading to chemisorption. Besides boron sites can also act as electron donors for the reduction reaction, as the electron density of the graphitic π-electron system can be transferred to the free pz orbital of the boron

[69]. Among other heteroatoms, Nitrogen doping drew more attentions because of its strong electron donor behavior and enhanced π-bonding which improve the ORR activity and durability [64]. Findings show that during nitrogen doping process four types of structures (Figure 2) are formed through which nitrogen increase ORR catalytic activity of AC [72]. Pyridinic-N and Pyrrolic-N reduces the thermodynamic barriers of ORR, also Graphitic-N (quaternary) enhances the kinetic performance. Through side-on absorption of oxygen molecules, the O-O bond is weakened by pyridinic-N with the lone pair, while electron transfer from the carbon electronic bonds to oxygen antibonding orbitals is enhanced by graphitic-N [73].

One example showed that treatment of commercial activated carbons with ammonia increased nitrogen to 1.8 atomic % but left oxygen reduced by 29-58% due to decreased amount of acidic oxygen surface functional groups which significantly improved catalytic performance in neutral media as a result of increment of both number of electrons transferred and onset potentials [33]. Zhang et al. [72] made N-doped AC using cyanamide as nitrogen source after 98% $H_2SO_4$ and 3 M KOH pretreatment and resulted in a nitrogen content of 8.65% (atom %) (in which 5.56% is pyridinic-N) on its surface. This N-doped AC exhibited prominent catalytic activity compared to the untreated AC and the commercial Pt/C (10% Pt) catalysts which was due to pyridinic-N indicating that pyridinic-N is the most active site for ORR in the nitrogen-doped AC.

Incorporating two or more heteroatoms into AC surface creates a mutual advantageous conjunction to optimize ORR catalytic behaviors [34,74,75]. Following highly porous surface area and increased active sites, an air-cathode MFC with AC based catalyst prepared from petro-coke naturally containing N and S reached a power density higher than bare AC [35]. The same results was obtained by Guang et al. [76] and Madhumita et al. [74] which are accredited to the a combined actions of highly efficient active sites coming from a larger number of pyridinic N and thiophene S together with the complementary mass-transport properties turning out from the hierarchical porous structure and the high specific surface area. Heteroatoms are a good option, however their incorporation into carbon matrix present another level of complexity to the process, therefore using biomasses natural containing heteroatoms could be a sustainable solution.

## Transition metal/oxides doping

It is relevant to the use of transition metals as electrocatalysts due to their particular properties of forming more than one cationic oxidation state. Besides, these metals can easily change from one oxidation state to another therefore it gives them the ability to tolerate the unchanging reduction and oxidation reactions which take place inside an electrolytic cell, thus improving stability [26,77]. Due to their natural activities, adequate stability in oxidative electrochemical environments, their structural multiplicity, as well as their ability to be mixed, doped, and to be fused with other materials such as carbon and graphene; transition

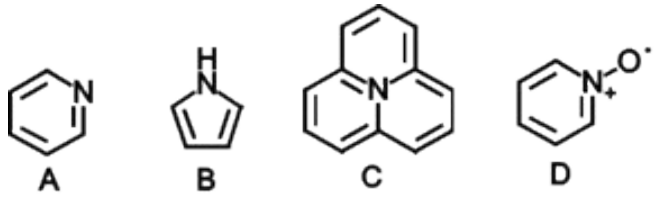


**Figure 2:** Types of nitrogen bonding in N-doped AC: (a) Pyridinic-N, (b) Pyrrolic-N, (c) Graphitic-N and (d) oxidized nitrogen functional groups.

metals and their oxides are regarded as promising way of enhancing AC catalytic activity [26,78]. Various transition metals like cobalt [27,79], manganese [29,77], nickel [80] and iron, have been mostly used as AC dopant for catalysis of oxygen reduction reaction (ORR) among a wide range of these metals.

Doping AC with various transition metals affected its structures and performances differently came up with a structure that look like graphene when they used Fe and Mn as dopant while doping with Co, Ni, and Cu led to a disordered or nanosheet structure where graphene-like structure showed better performance than disordered resulting in the following performance order of their ORR catalytic activity of Fe > Co > Cu > Mn > Ni. The same array of ORR catalytic activity performance for these metals was observed which is consistent with the order of their active sites contents, fortunately Fe is the most abundant metal on earth which makes it a good candidate for this application. However, Fe when used in acidic media suffer from a lower catalytic activity, and from stability issues [26].

Silver was electrodeposited on the activated carbon (AC) air cathode and efficient performance improvement of MFCs was achieved with maximum power density of 1080 ± 60 $mWm^{-2}$, 69% greater than the plain AC. This made ORR at the cathode to take place via four-electron pathway and the electrodes' total resistance were largely reduced due to the fact that silver has the highest conductivity than any metal [36]. The same method of electrodeposition was used to integrate $MnO_2$ into AC which left Carnation-like $MnO_2$ crystals bound to the surface of AC air cathode increasing mesopores thus boosting cathode performance with maximum power density of 1554 $mWm^{-2}$ [29]. Following the same procedure $Cu_2O$ was added into AC surface which increased mesopore, surface area, charge transfer resistance and total resistance decreased significantly and faster electro-transfer kinetics. High conductivity of Cu and increased active sites contributed to high ORR catalytic behavior of AC which led to the utmost MFCs' power density using this original air cathode to 1390 ± 76 $mWm^{-2}$, about 59% greater than the bare AC air cathode [41].

AC doped with non-stoichiometric nano-$Fe_3O_4$ in air cathode achieved utmost power density improvement by 83% from 780 mW/$m^2$ to 1430 mW/$m^2$ compared with bald air cathode. This was a result of boosted charge transfer that led to the oxygen reduction mechanism through 4-electron pathway [38]. The same trend has been observed when ortho-hexagon spinel nano-$Co_3O_4$ was inserted into AC at 10% ration. Significant reduction of the total resistance was observed and a large number of active sites were brought in by higher micropore surface area leading to higher activity for ORR. As a result, the ultimate power density of 1500 ± 14 $mWm^{-2}$ was produced which was said to be 97.36% and 41.24% greater than the air cathode with the plain AC and commercial $Co_3O_4$ respectively [39].

Following a mutually advantageous conjunction for the improvement of activity towards the oxygen reduction reaction and due to the lowering of charger transfer, activation barrier, and higher exchange current density; researchers took into consideration of adding more than one different metal into AC lattice [81]. The air cathode with activated carbon (AC) catalyst doped with $Cu_{0.92}Co_2.0_8O_4$ and calcinated at 600°C achieved utmost power density of 1895 mW $m^{-2}$ which was 113% greater than the benchmark cathode following remarkable decrease of total and charge transfer resistances [40]. This positively correlates with results obtained when air cathode made of AC modified with nano urchin-like $NiCo_2O_4$ using hydrothermal method attaining power density of 1730 ± 14 $mWm^{-2}$ comparable to Pt/C cathode [82].

### Heteroatom-transition metals co-doping

Both heteroatom doped AC and Transition metals doped AC have shown increased ORR catalytic activity which makes them a promising alternative for Pt based cathode in MFC. Nevertheless, following results from various researches, combined heteroatom and transition metals [81,82] onto AC surface exhibited much better performance as a result of advantageous combined action the of both dopants which create massive available active sites [42]. This brings in voluminous surface area, improved mass transport, leading to less total resistance and fast electron transport thus facilitate ORR activity of the electrocatalysts [45]. Co and Fe coupled with N into AC enhanced ORR catalytic activity which was ascribed by the author to fast electron transport due to the reduced total resistance and an extended surface area which resulted in an increased performance of MFC [43]. Among other combinations, Iron-Nitrogen [28,42,83] AC doping has been mostly studied and showed better catalytic advantageous combined effect toward ORR reaction directly correlated to the good coordination of both atoms on the surface of AC. Maximum power density of 2437 ± 55 $mWm^{-2}$ was obtained in MFC with Fe–N–C air-cathode prepared with commercial AC which was 114% higher than the bare AC. This is a result of increased conductivity due to Fe atom and mainly to the increase Fe-N bonding particulary Fe-N4 which enlarge numbers of specific reactive sites. Catalyst performance correlate with surface composition as the increase in amount of nitrogen and especially, N coordinated to metal and pyridinic and pyrrolic types results in increased power density while graphitic nitrogen resulted in worse performance [42]. Similar outcomes were obtained in another study with the synergism of Cu and N dopants in AC catalyst making it to possess excellent ORR catalytic activity. Showing better half-wave potential and both the limited current density and onset potential nearly similar to Pt/C catalyst is the outcome of the hierarchical structure and large number of pyridinic N content in addition to high conductivity induced by Cu. Pyridinic-N plays an important role as $O_2$ molecules can easily adsorb on the carbon atoms next to them, because these carbon atoms serve as the active sites for ORR.

### Acid and alkaline treatment

Acid and Alkaline treatment has been considered as a simple and effective way to enhance ORR catalyst activity of AC resulting in better MFC performance. Despite low numbers of published results, this approach found interest and some studies have been done revealing that different nature and concentrations of acids and bases pose different effects on chemical and physical properties of activated carbon. As it can be seen in a study conducted by Zhong Wang et al. [46], they treated AC using four common acids; i.e., $H_3PO_4$, HCl, $H_2SO_4$ and $HNO_3$ and found out that AC treated with 1M acids had increased ORR catalytic activity followed an order as AC-$H_3PO_4$> AC-HCl> AC-$H_2SO_4$> AC-$HNO_3$> AC where $H_3PO_4$ showed an increase in performance of 115% with the maximum power density of 1546 ± 43 $mWm^{-2}$. The author stated that it was due to a decrease in resistance, enlarged total surface area and degree of graphitization of AC, however too much strong acidic functional group was found to be deleterious to MFC performance. The same adverse effect of high acid concentration treatment of AC was obtained when Wang et al. [47] treated AC with 5.6 M $HNO_3$ which resulted in decrease of power density from 804 ± 70 $mWm^{-2}$ to 537 ± 36 $mWm^{-2}$, however alkaline (3M KOH) pretreatments increased power production by 16%.

## Conclusion

Activated carbon (AC) has been regarded as a potential substitute of costly Platinum as oxygen reduction reaction catalyst in Air cathode Microbial fuel Cell. However, MFCs catalyzed by bare AC showed limited power output which is a critical factor for scaling up and sustainability of this environmental friendly technology. This study shows that, doping with heteroatom, transition metals or their co-doping was found is a good option to enhance the ORR catalytic activity of AC. Among other heteroatoms, Nitrogen doped AC showed better performance than other Heteroatoms because of its strong electron donor behavior and it does so through Pyridinic-N, Pyrrolic-N and Graphitic-N which weaken O-O bond and facilitate electron transfer. Throughout a wide range of transition metal Iron (Fe) doped AC is most favorable as it is abundant and due to its high conductivity, but when used in acidic media suffer from a lower catalytic activity and stability issues as the cathode can easily corrode. Both acidic and alkaline treatment of AC has been used by some researchers and they found out that strong acid are detrimental to AC catalytic activity but moderate acid treatment would increase the total surface area and the degree of graphitization of treated AC, resulting in a better electrocatalytic activity; however due to limited literature alkaline treatment effects are not well known. Heteroatoms and transition metals co-doping wins over other technics as a result of synergic effect brought in by two or more dopants which creates abundant accessible active sites for oxygen reduction, large surface area, improved mass transport leading to less total resistance and fast electron transport thus enhance ORR activity of activated carbon. Though these systems seem promising, however their not only bring another level of complexity and cost to the MFC construction and operation but also the reaction mechanisms are not fully understood which hampers the scale up of the technology. Therefore, more attention should be paid to the use of biomasses naturally containing heteroatoms and transition metals to prepare Activated carbon. Also there should be an increased effort in deciphering mechanisms of oxygen reduction reaction in different settings.

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