II. ENVIRONMENTAL BIOTECHNOLOGY

CARBON-BASED CATHODE CATALYSTS USED IN MICROBIAL FUEL CELLS FOR WASTEWATER TREATMENT AND ENERGY RECOVERY

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Abstract. In the past 20 years Microbial fuel cells (MFCs) have been extensively studied regarding the possibility of transforming organic waste directly into electricity. There are significant differences between MFCs and conventional low temperature Fuel Cells (FCs), which make MFCs attractive: biotic catalyst at the anode; the anodic fuel is complex organic waste; MFCs operate under mild reaction conditions (neutral pH, temperature and pressure), close to ambient levels as optimum.

Like chemical fuel cells, MFCs are composed of anode and cathode. Oxygen is an ideal electron acceptor for MFCs because of its high redox potential, availability, and sustainability. However, the Oxygen Reduction Reaction (ORR) is kinetically sluggish, resulting in a large proportion of potential loss. Also, working conditions are quite different because of the type of complex media in which MFCs operate. In order to overcome these limitations, catalysts are often used to lower the overpotentials and accelerate the kinetics of the oxygen reduction reaction. One of the main challenges is the development of efficient and stable cathode catalysts for MFCs. By far, Pt and Pt-based catalysts (PGMs) have been extensively used, due to their catalytic efficiency in gas-diffusion electrodes. But the high cost and low durability have significantly lowered their utilization in MFCs.

A variety of non-precious metal catalysts have been developed for MFC applications including carbon-based catalysts, carbon supported composite catalysts, Me-based catalysts and biocatalysts. It is supposed that the ORR catalyst used for wastewater treatment in MFCs is simple to synthesize, cost-effective, durable after long-term operation in wastewater, tolerant to poisoning and able to restore catalytic activity after cleaning. In this regard carbon-based catalyst may be the most promising candidate for practical applications. This study reviews different carbon-based ORR catalysts for MFC applications for wastewater treatment and energy recovery.

Key words: Carbon-based ORR catalysts, Microbial fuel cells, wastewater treatment.

INTRODUCTION

In the past 20 years Microbial fuel cells have been extensively studied with regard to the possibility of transforming organic waste directly into electricity [1, 2, 3, 4, 5, 6]. There are significant differences between MFCs and conventional low temperature Fuel Cells, which make MFCs attractive. Electroactive bacteria or proteins are used as a catalyst at the anode of MFCs, i.e., the catalyst is biotic [2]. The anodic fuel can range from simple organic molecules to complex organic waste, like waste waters and urine. MFCs operate under mild reaction conditions (neutral pH, temperature and pressure), close to ambient levels as optimum.

Like chemical fuel cells, MFCs are composed of anode and cathode. The electrochemically active microorganisms that grow in the anode are fed by the organic matter in wastewater and respire extracellularly by transferring electrons to the anode [7]. When an appropriate electron acceptor (e.g., oxygen) is present in the cathode, the electrons flow spontaneously through the external circuit to the cathode for reduction reactions. As such, electrical energy is produced and wastewater is treated. Unfortunately, the performance of MFCs is limited by several factors which hinder

their large-scale application. The oxygen reduction reaction is one of the factors that could limit the power output of microbial fuel cells. Oxygen is an ideal electron acceptor for MFCs because of its high redox potential, availability, and sustainability. However, the oxygen reduction reaction is kinetically sluggish, resulting in a large proportion of potential loss. The poor cathode kinetics operating in neutral media is due to the low concentration of H^+ and OH^- which causes high overpotentials and low kinetics. This is one of the major limitations impeding large-scale applications of MFCs. Also, working conditions are quite different because of the type of complex media in which MFCs operate [8].

In order to overcome these limitations, catalysts are often used to lower the overpotentials and accelerate the kinetics of the oxygen reduction reaction. The development of efficient and stable cathode catalysts for the ORR present a major challenge for the practical application of MFCs. The ideal ORR catalyst used for wastewater treatment in MFCs is expected to have high catalytic activity, to be simple to synthesize, cost-effective and durable after long-term operation in wastewater. It should be tolerant to poisoning and able to restore catalytic

activity after cleaning. These properties have to be given priority when developing ORR catalysts for MFC applications.

A number of materials have been studied as ORR catalysts for MFCs. The cathode catalysts are categorized into Biotic (Enzymatic and Microbial catalysts) and Abiotic (Platinum-Group Metal (PGM) and Platinum-Group Metal-free (PGM-free)). PGM-free catalysts can also be subdivided into two categories including carbon-based materials and metals-based materials.

Several enzymes (Laccase, Bilirubin oxidase) [9] have been exploited as catalysts for ORR in neutral media with superb performance. Unfortunately, enzymes are very sensitive to inhibition. They often require sophisticated chemical operations for immobilisation on electrode surfaces and their lifetimes are shortened in the presence of pollutants. [10]. The application of biocatalysts requires advances in engineering to maintain a stable environment for the organisms and enzymes. So, both the high cost and low durability make those materials unsuitable for MFCs applications.

The use of whole microbial cells in MFC for the bioelectrochemical oxidation of fuels is advantageous since it eliminates the need for enzyme isolation. It also allows multiple enzymatic reactions to take place in conditions close to their natural environment. The advantages are environmental benignity, self-sustainable catalyst regeneration, and low operational cost. It has been found that the use of different carbon materials (graphite, activated carbon and others) as supports for biocathodes considerably facilitates electron transfer. Modifying carbon materials with conductive polymers introduce functional groups that encourage biofilm attachment, which could improve the cathode performance [11, 12]. Nano-structured carbon materials (CNTs and graphene) with a high surface area and high conductivity have also been shown to facilitate the electron transfer of biocathodes [13]. MFCs with microbial catalysts can be envisaged suitable for large-scale applications for wastewater treatment [14, 15].

Pt and Pt-based catalysts (named as Platinum Group Metals (PGMs)) have been extensively used catalysts in the initial stages of developing cathode materials for MFCs, due to their catalytic efficiency in gas-diffusion electrodes used in acidic and alkaline Fuel cells. But the high cost and low durability have significantly lowered their utilization in MFCs. It has been established that anions from complex media in which MFCs operate, bind with the catalysts deactivating Pt within few days of operation [16]. To

avoid these limitations, platinum group metal free (PGM-free) catalysts have been developed for cathodic materials in the MFC that are resistant to poisoning in wastewater, activated sludge and other organics / pollutants [17, 18]. At the same time, they are much cheaper [19].

Metals-based materials have been successfully used as cathode catalyst in fuel cells for many decades. However, most of them, for example manganese dioxide catalysts achieve Maximum Power Density (MPD) only half of that with Pt/C. A change in the oxidation state, structure modifications or doping of other transition metals of manganese oxides may affect the catalytic activity [20]. Many other metal oxides, such as lead dioxide, perovskite oxides, vanadium oxides, cobalt oxide and zirconium oxide, have been studied as cathode catalysts in MFCs. Some of them are cheap and produce high normalized MPD (perovskite oxides - cost \$0.041 g⁻¹, MPD of 116 mW \$⁻¹) [21]. The possible leaching of the metals to the treated wastewater, the toxic effects and environmental impacts are reasons that make the metal-based catalysts not competitive to carbon materials. But the hybridization of metal and carbon can combine the advantages of the individual components and thus greatly enhance catalytic performance.

Activated carbons (ACs), Carbon nanotubes (CNTs), graphite and graphene have been used to replace Carbon black (CB) as support material for metal catalysts. Different electrochemical methods, chemical synthesis, pyrolyzing, sonication or simple mixing methods have been used for obtaining hybrids [22]. As a result of modifications functional groups that might serve as the additional active sites in the M-carbon hybrids could be introduced. By varying surface area and pore size distribution, a change in the surface roughness and the pore structure has been achieved [22]. Maintaining the high BET surface area, a high Maximum Power Density is achieved comparable to that with Pt/C [23].

Metal macrocycle and M–N–C complexes present new groups of catalysts with excellent catalytic activity for ORR in alkaline conditions, but they are unstable in acid medium. Many efforts have been made to construct M–N–C catalysts from polymers, simple organic compounds and metal–organic frameworks (MOFs). Pyrolysis of metal macrocycles is used for the interaction between the carbon matrix and the carbon support [24]. Thus, it can significantly improve both stability and activity and makes them feasible for MFC applications. For example, several modifications on cobalt macrocycles and FePc were implemented to further promote the catalytic performance [8, 25]. The

pyrolysis temperature is considered the major factor that affects the structure and the consequent catalytic activity [26, 27]. It can lead to highly defined 3D-structured materials composed of metal centers and organic ligands with high BET surface area [28]. The cost effectiveness of M–N–C complexes largely depends on the precursor. Unfortunately, metal macrocycles do not seem to be economically feasible for wastewater treatment and still not competitive to carbon-based catalysts.

It is assumed that the ORR catalyst used for wastewater treatment in MFC should be easily synthesized (with the possibility of large-scale synthesis), be cost-effective, resistant to poisoning and able to restore catalytic activity after treatment. In this regard carbon-based catalyst may be the most promising candidate for practical applications. This study reviews different carbon-based ORR catalysts for MFC applications for wastewater treatment and energy recovery.

CARBON-BASED ORR CATALYSTS CARBON BLACK

Carbon black-based materials are often used as support for the catalyst in cathode materials for fuel cells due to their high surface area, high conductivity and low-cost. They are also widely used in metal-air systems for the preparation of the gas-diffusion layer for air electrodes. In our previous work [29] we have investigated the influence of different carbon blacks on the properties of air gas-diffusion electrodes with respect to their application as cathode materials in metal-air systems. It was found that the large volume porosity ($\approx 0.9 \text{ cm}^3 \text{ g}^{-1}$) provides a good supply of oxygen from the air, and the small radius of the pores ($r \approx 30 \text{ nm}$) provides gas transport by Knudsen diffusion. Also, the type of carbon material influences the long-term performance of the air electrode.

In addition to the described qualities carbon black also have high stability and durability in "harsh" and polluted environments. These make them attractive materials for use not only as a support but also as catalysts in MFC. It has been found that the introduction of functional groups and/or chemical modification can create active centers in Carbon black, which can turn them into metal-free catalysts. Duteanu at al. [30] treated CB with nitric acid, increasing 3 times the Maximum Power Density compared to pristine CB. Meng at al. [31] pyrolyzed a mixture of CB and polytetrafluoroethylene (PTFE) in an ammonium flow. As a result, nitrogen and fluorine centers were formed in the CB. This led to an increase in the electron transfer number from 2.7 to

3.8 for the co-doped CB. The maximum power density of the MFC with the treated CB reached 672 mW m^{-2} , which was higher than that with commercial Pt/C (572 mA cm^{-2}).

ACTIVATED CARBON (AC)

Activated carbon produced from different precursors will possess different chemical functional groups, BET specific surface areas and active sites, which may synergistically affect ORR catalysis. In a study of Liu at al. [32] carbon samples with different micropore and mesopore and mesoporous structures have been investigated for preparation of air-cathode catalyst layer. They have explored the role of pore structure on oxygen reduction reaction. It was found that micropores provide active centers to facilitate catalytic activity, and mesopores transport oxygen and thus promote ORR.

A number of modifications of AC have been carried out to overcome the limitations caused by the precursors. For instance, chemical treatment with alkali (KOH) or acid (HNO_3 , H_3PO_4) has been reported to increase its surface area and the MPD, as well as to enhance ORR performance via the formation of possible chemical bonds [33]. The pre-treatment of AC with phosphoric acid at 80 and 400 °C showed 35% and 55% increase in the MPD, respectively [34, 35].

The nitrogen doping has been demonstrated to be an effective strategy to enhance catalytic activity [36]. Treatment using nitrogen-containing chemicals is one of the most effective methods for improving the ORR catalysis of AC. Iwazaki at al. [37] have established that activated carbon free of metal elements, prepared from silk fibroin by heat-treatment at up to 1200 °C contained only about 1% of nitrogen atoms, and they are responsible for a high catalytic activity for the oxygen-reduction reaction.

Watson at al. [34] have shown that treating AC in ammonia gas at 700 °C not only decreases oxygen content by 29-58%, but also increases nitrogen content, leading to a MPD of up to 2450 mW m^{-2} . The results show that reduced oxygen abundance and increased nitrogen functionalities on the AC surface can increase catalytic performance for oxygen reduction in neutral media.

Zhang at al. [39] have reported an N-doped AC catalyst with a remarkably high nitrogen content (8.65% total N and 5.56% pyridinic-N) by both acidic and alkaline solutions pre-treatment and using a solid-state nitrogen precursor. The modified AC has achieved an electron transfer number of 3.99 and a MPD (650 mW m^{-2}) 44 % higher than Pt/C. The simple preparation procedure, easily obtained raw

materials makes N-doped AC promising for scale up MFCs.

AC has attracted much attention due to its high-cost effectiveness and excellent electrochemical durability. Yuan et al. [7] in their review have compared commercial Pt/C, whose price is \$28 g⁻¹ (10% Pt on Vulcan XC 72, Premetek Co., Wilmington, DE, USA) and the normalized MPD is only 1 mW \$⁻¹ (with a typical loading rate of 5 mg cm⁻²) with AC costs, which is less than \$0.002 g⁻¹. It has also been estimated that a complete AC cathode (the AC catalyst, the PTFE binder and the metal support) costs \$30–60 m⁻², which resulted in a normalized MPD of 22–41 mW \$⁻¹ depending on the MFC performance. The normalized MPD could be further improved to 94–98 mW \$⁻¹ by pressing AC–PTFE on a stainless steel mesh, demonstrating its potential for practical applications.

While the current density of a Pt/C cathode dropped by 73 % after 7h, a nitrogen-doped AC cathode showed only 30% decrease [7]. Activated carbon is effective and low-cost catalyst for oxygen reduction in air cathodes, but its performance must be maintained over time. Zhang et al. modified AC by different methods of thermal treatment and found that the performance of the AC cathodes can be restored to >85 % of the initial maximum power densities by cleaning with a weak acid solution.

It is well known that cathode is a critical factor that limits the practical application of microbial fuel cells. To develop a cost-effective cathode, Cheng et al. [40] have prepared a cathode using activated carbon as a catalyst, PTFE as a binder and nickel foam as a current collector. Their results indicated that a nickel foam cathode could be used in scaling up the MFC system, because the cost of the cathode described is 1/30 of that of carbon cloth Pt cathode.

Wei et al. [41] reported for a method to construct air cathodes for MFCs enable to optimize and extend the lifetime of cathodes in MFCs. The air cathodes used only inexpensive AC with variable amounts (43–171 mg cm⁻²) and PTFE as inexpensive binder and produced power densities similar to those of Pt/C cathodes with Nafion binder.

A serious disadvantage of the membrane-less system however is the biofouling on the AC cathode. The formation of a biofilm on the electrode surface is the reason for the increase of internal resistance. Li et al. [42] provided a new and promising method to improve both the performance and the sustainability of activated carbon air-cathode by modification with bifunctional quaternary ammonium compound (QAC). The growth of cathodic biofilm was significantly inhibited after modification with disinfectants and

the power density was increased by 33 %. This improves the stability of performance for the future application in wastewater treatments.

GRAPHITE/GRAPHENE

Graphite consists of carbon layers (with covalent and metallic bonding within each layer) linked by weak van der Waals interaction [43]. Due to the in-plane metallic bonding Graphite is a good electrical and thermal conductor within the layers. The electrical conductivity enables graphite to be used as a fuel cell electrode.

Pristine graphite is not considered catalytic toward the ORR because of the lack of active sites. However, Freguia et al. [44] in their study showed that research on microbial fuel cell cathodes should not only focus on catalysts, but also on high surface area materials. They used a non-catalyzed cathode made of granular graphite with high surface. The presence of nanoscale pores on granular graphite provides a high surface area for oxygen reduction. Power outputs up to 21 W m⁻³ (cathode total volume) or 50 W m⁻³ (cathode liquid volume) were attained in a continuous MFC fed with acetate. Furthermore, the Chemical Oxygen Demand (COD) removal (1.46 kg m³ d⁻¹) was higher than that of conventional aerobic processes, which was of practical significance for waste water treatment.

Activation of graphite with HNO₃ or H₃PO₄ could enhance the MPD, which could be attributed to the high BET surface area of the modified graphite and the introduction of nitrogen and oxygen functional groups.

Erable et al. [45] studied that the Nitric acid and thermal treatment activated graphite granules increased the electrocatalytic performance of oxygen reduction in a dual-chamber MFC at neutral pH. The use of modified graphite granules led to a high open circuit voltage of 1050 mV, the stable performance of this cathode material (current density of 96 A m⁻³ at +200 mV/Ag–AgCl) over a period of 10 days. The improvement of ORR performance was correlated to the increase of BET surface of the activated material and the emergence of nitrogen superficial groups.

The carbon layers in graphite are known as graphene layers [43]. Graphene modification has been demonstrated to be effective to carry out ORR via four-electron transfer, abundant active sites and high conductivity [44, 46–52]. These studies suggest that graphene can affect ORR pathway either by the modification of its own structure or by the enhancement of catalytic ability with other doped/coated materials.

Feng et al. [46] implanted mesoporous graphitic carbon nitride (C_3N_4) into NG nanosheet to increase the proportion of nitrogen active sites. As a result, when tested in MFCs, the modified NG yielded 20 % higher power density and noticeably higher stability compared to Pt/C. The remarkable ORR catalysis of the implanted NG is a result of high content of pyridinic and pyrrolic nitrogen in NG because they might facilitate a more efficient four-electron transfer in ORR.

The co-doping of nitrogen and sulfur in mesoporous graphene could provide dual active sites for ORR catalysis. The excellent catalytic activity of N-S-G results from both the large number and the synergistic effect of the dopant heteroatoms [47]. In another work, Yuan et al. [48] developed a simple synthesis for preparation of N and S co-doped porous carbon nanosheets with high surface area ($1004 \text{ m}^2 \text{ g}^{-1}$). This catalyst had a defect structure and active sites, that arose primarily from porous nanosheet morphology. The electron-transfer number of the N/S-CNS was calculated to be ~ 3.5 . It is supposed that ORR on the catalyst proceeds predominantly through the favorable four-electron pathway.

Liu et al. [53] proposed that the presence of oxygen species introduced during the synthesis of N-doped graphene could protect catalytic C – N groups from being attacked by protons. Oxygen-modified materials have also been reported in [54, 55]. The efficiency of the catalyst is explained by the high content of Oxygen (reached of 9.13 %), as well as by the large specific surface area of $1398 \text{ m}^2 \text{ g}^{-1}$. Thus, it has been shown that in addition to the amount of nitrogen sites, sufficient exposure of active sites to reactants using a large specific surface area could effectively promote ORR.

Although in theory graphene possesses high conductivity, potential impurity and topological lattice defects result in increased internal resistance of the cathode electrode, and thus hinders ORR. Therefore, it is of crucial importance to maximize the conductivity of graphene cathodes for practical applications. To reduce resistance, graphene is doped with nitrogen, a versatile polymer PANI or with para-toluene sulfonic acid [51, 46, 56, 57].

Unfortunately, the costs of producing graphene are not comparable to those of activated carbon. Typically, graphene is prepared by a complex synthesis of graphene oxide, which is reduced to graphene and then modified. There are other methods of preparation, but they are expensive and often involve harmful substances in their synthesis [58, 59]. The normalized MPD is estimated to be approximately $12 \text{ mW } \$^{-1}$

for granular graphite, [44] and $10 \text{ mW } \$^{-1}$ for N/S co-doped carbon nanosheets. [48]. Therefore, efforts are focused on creating cheaper and more efficient catalysts that can find real application in ORR.

CARBON NANOFIBERS (CNFs)/NANOTUBES (CNT)

Carbon nanotubes (CNTs) are one or multiple layers of graphene sheets wrapped in a concentric manner [60, 61], so as to form a well-defined cylindrical hollow structure. Carbon nanotubes (CNTs) have adsorption properties and are characterized by a large surface area that can be easily modified.

Carbon nanofibers (CNFs) are composed of stacked corn-shaped graphene sheets and show high electrical conductivity and high BET specific surface area [62, 63].

Different strategies are used to improve the catalytic activity of CNTs and CNFs for ORR: alkaline or acid activation [64, 65]; nitrogen doping [66-69] doping heteroatom doping [70, 71]; combination of chemical activation and nitrogen doping [72]; mixing carbon nanotubes with conductive polymers [73, 74].

Daems et al. [70] have reviewed different carbon materials with nitrogen or, less commonly, with other elements; the synthesis methods employed for the doping as well as the characterization techniques used to investigate their physicochemical properties (dopant content, dopant configuration and surface area). The possible mechanisms for the ORR on N-doped carbon materials are critically discussed and compared to the mechanisms of commercial Pt/C electrocatalysts, with regard to making them particularly suitable for application in fuel cells.

In his study Feng et al. [66] investigated the use of nitrogen-doped carbon nanotubes (NCNTs) as cathodic catalyst for oxygen reduction in MFCs to produce electricity efficiently and durably. Various analyses suggested that NCNTs possessed a higher electrocatalytic activity for the oxygen reduction reaction *via* a four-electron pathway in neutral pH phosphate buffer solution. The obtained maximum power density was 1600 mW m^{-2} , which was higher than the commonly used platinum catalyst (1393 mW m^{-2}) and after continuous work could generate electricity more durably than Pt/C catalyst.

Using a chemical vapor deposition method [67] prepared a novel cathode material by growing vertically-aligned nitrogen-doped carbon nanotubes (N-CNTs) on carbon cloth (CC). The electrochemical experimental results showed higher catalytic activity for oxygen reduction and a smaller resistance of the N-CNT-CC electrode, compared to those of the

Pt/C-CC, which are responsible for their better MFC performance.

In his study Chen [68] proposes a promising low-cost binder-free cathode prepared by growth of nitrogen-doped carbon nanofibers (NCNFs) on stainless steel mesh (SSM).

Heteroatom-doped porous CNFs [71] have been fabricated via a simple pyrolysis method using natural spider silk (SS) as a precursor. The prepared CNFs possess nanofibrillar and porous structure included abundance of electronegative N and S atoms within the carbon lattice, and a high surface area. Zhou et al. think that the excellent ORR catalytic activity in neutral solution (pH 7.0) (half-wave potential of 0.85 V and the on-set potential of 0.98 V vs. RHE and the maximum power density of 1800 mW m⁻², 1.56 times higher than that with a Pt/C cathode) are due to these characteristics.

Ghasemi et al. [64] carried out a chemical and physical activation by KOH reagents and CO₂ gas to increase the electrode surface area and the catalytic activity of carbon nanofibers. As a result, it was found that the MFC with the chemically activated carbon nanofibers (ACNFs) exhibited 78% more power generation than that of the physically activated ACNFs and up to 3.17 times more power than that of the carbon paper. The chemically activated carbon nanofibers were found to be one of the promising candidates for the ORR. Another approach for chemical activation of carbon nanofibers (CNF) with HNO₃ was used by Santoro et al. [65] to increase the surface area. In their investigations CNFs were chemically activated using HNO₃ and then hot pressed on a carbon cloth support. The experiments were carried out in single chamber microbial fuel cells (SCMFCs) over 3-month operational period and compared with clean Pt-based cathode. MFCs were fed with two solutions: synthetic wastewater and real wastewater. A degradation and Pt detachment were noticed on Pt cathodes over time. In contrast, CNF/ACNF cathodes exhibited less deterioration throughout the operational period, which demonstrated a great potential as cost-effective cathodes for long-term operation.

The combination of nitrogen doping and chemical activation with yielded a CNF material with three-dimensional carbon-fiber framework with large specific surface area and pore size distribution spanning the micro-, meso- and macro range [72]. Compared to inactivated nitrogen-doped carbon nanofibers, this material exhibited a high catalytic activity (electron transfer number 3.6) and high-power output of 1377 mW m⁻², similar to that of the Pt/C-based MFC.

In addition to another pre-treatment and doping procedures, mixing CNTs with a conductive polymer, such as polyaniline (PANI) or polypyrrole (PPy), presents a simple method to enhance the cathode performance [73, 74].

Biofilm formation, salt precipitations on the cathode, and the presence of hydrogen sulfide decreased the activity of cathodes. Both CNFs and CNTs as cathode catalysts are more durable than Pt/C [72, 65, 71]. With respect to long-term stability, the activated CNF cathode showed only a slight decrease in the MPD in comparison with the Pt/C cathode due to sulfide poisoning and biofilm growth [65]. The CNF synthesized using spider silk was not affected by the effects of various chemicals and constantly produced high MPD within 3 months of continuous operation [71].

CNFs and CNTs have drawn considerable attention as alternative catalysts for the oxygen reduction reaction. However, their facile and cheap synthesis is still a great challenge. The CNFs obtained from spider silk used free natural materials and might provide insight into the cost-effective fabrication of sustainable cathode catalysts [71]. The cost of CNFs prepared by electrospinning of polyacrylonitrile was estimated to be \$7.5 g⁻¹, and increased slightly to \$9.6 g⁻¹ after KOH treatment [64]. The power per cost of ACNFs with 8 M KOH is 2.65 times greater than that of the traditionally used platinum cathode [64]. The normalized MPD of the polyaniline/multi-walled CNT composite reached 31 mW \$⁻¹ thanks to the low cost of commercial multiwalled CNTs [73]. However, the cost effectiveness of graphite/graphene and CNFs/CNTs is still not competitive to AC.

CONCLUSIONS

AC has attracted much attention due to its high cost effectiveness and appears to be the best choice for long-term performance of MFCs.

The durability of the ORR catalysts in MFCs is the major challenge. In real life conditions the cathode is constantly exposed to wastewater containing organic matter, contaminants and microorganisms and may be poisoned by the intermediate products. Furthermore, regardless of the catalyst materials biofouling on the cathode surface is almost inevitable. The formed biofilm blocks the O₂ transport and degenerate catalytic performance. Most of the ORR catalysts discussed above, reduce oxygen by 2e⁻ pathway and produce a considerable amount of H₂O₂ under MFC operation. This high H₂O₂ production may provide a resolution to the fouling issue and

improve system stability by contributing to fouling mitigation or its removal.

Our experience with the use of two different porous carbon-based catalysts (Activated carbon and Activated carbon promoted with CoTMPP) confirms that unmodified AC is the preferred catalyst for oxygen reduction in a single-chamber MFC during utilization of livestock manure. Also, in addition to its higher price the AC/CoTMPP catalyst has high activity for the electrochemical oxidation of hydrogen peroxide. Therefore, carbon-based catalysts are the most promising candidates for practical applications.

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