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Review

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Utilization of Nanomaterials as Anode Modifiers for Improving Microbial Fuel Cells Performance

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Abstract: Microbial fuel cells (MFCs) are an attractive innovation at the nexus of energy and water security for the future. MFC utilizes electrochemically active microorganisms to oxidize biodegradable substrates and generate bioelectricity in a single step. The material of the anode plays a vital role in increasing the MFC's power output. The anode in MFC can be upgraded using nanomaterials providing benefits of exceptional physicochemical properties. The nanomaterials in anode gives a high surface area, improved electron transfer promotes electro-active biofilm. Enhanced power output in terms of Direct current (DC) can be obtained as the consequence of improved microbe-electrode interaction. However, several limitations like complex synthesis and degeneration of property do exist in the development of nanomaterial-based anode. The present review discusses different renewable nanomaterial applied in the anode to recover bioelectricity in MFC. Carbon nanomaterials have emerged in the past decade as promising materials for anode construction. Composite materials have also demonstrated the capacity to become potential anode materials of choice. Application of a few transition metal oxides have been explored for efficient extracellular electron transport (EET) from microbes to the anode.

Keywords: Microbial fuel cell (MFC); anodic modifications; capacitance; carbon nanotubes; graphene; porous carbons; metallic nanomaterials; power density; coulombic efficiency

1 Introduction

With the advancement in life and needs, the level of energy consumption has tremendously increased over the decade. The energy sources can be divided into renewable and non-renewable type. The enormous portion of the total is a non-renewable source that majorly includes fossil fuels and nuclear power [1]. However, the use of fossil fuels is believed to impose negative effects on nature due to the emission of carbon dioxide and other harmful gases. Thus, consumption of fossil fuel as an energy source has added to air pollution and the greenhouse effect [2–4]. The environmental concern hence made the researchers develop new methods of energy production that were both pocket and environment friendly. This should be a sustainable renewable source of energy [5–7].

The MFCs comprise of an anode chamber and a cathode chamber which are separated by an ion exchange membrane. The anode chamber comprises of an electrode and microorganisms which act as biocatalysts. These organisms degrade the organic matter from the wastewater and the electrons that are released are transported to the anode. This transport is either facilitated by the direct cytochrome proteins or by indirect mode using mediators like thionine, which is further discussed in this review. A channel connecting both the electrodes, which has an external resistance of its own, helps the electrons flow from anode to cathode [8]. The protons released diffuse through the ion exchange membrane and get reduced by the arriving electrons leading to completion of the circuit [9]. Electricity is thus produced on electron travel through the external resistance. Proton reduction in the presence of oxygen results in production of water as a by-product. MFCs are efficient bioelectrochemical systems which have shown efficiency up to 80% in terms of conversion of waste matter to energy [8].

The reactions in both the chambers are as follows:

$$\text{At anode}: \quad CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^- + 8e^-$$

$$\text{At cathode}: O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

The by-products of these reactions are free electrons with flow via the circuit to give energy in the form of electrical energy [10].

A basic set up of MFC requires an anode, a cathode, an ion exchange membrane, and organic matter as fuel for growth of the microorganisms. The anode chamber has anaerobic conditions while cathodic chamber has presence of oxygen. Usually the material used is looked for properties like good conductivity, surface that allows biofilm formation and is non-corrosive [11]. Hence graphite rods, carbon cloth, stainless steel mesh, etc. are used. In case of cathodes, materials like Platinum rods or sheets, MnO_2, etc., are used since they are catalytic in nature [12]. In a double chambered MFC, often separators like anion exchange membranes like Ultrex and cation exchange membranes like Nafion are used [13]. MFCs use microbes as catalysts over other noble metals to produce bioenergy from organic as well as inorganic substrate as shown in Tab. 1. The microorganisms in MFCs that perform biochemical catalysis are called exoelectrogens [14]. The anodic surface plays a crucial role in the advancement and operation of bio-catalytic activity. Surfaces may be improved for providing optimal environments to biofilms capable of enhancing electron transfer from bacteria to the surface of the anode. Generally, the attainment of further bacterial cell attachment facilitates more electricity to be generated with minimal loss [15]. Studies have reported that surface alteration not only enhances the overall performance of the MFC system but also reduces the start-up time required by the system [16]. Furthermore, several studies have established and investigated widely the usage of graphene-based anodes, composite anodes, and modified anodes on surfaces [17]. Pocaznoi et al. [18] reported that stainless steel is the most suitable substrate for MFC anodes in most metals. However, there is still a great deal of room for improvement, for the usage of stainless steel as MFC anodes and other modern low-cost effective materials. Excellent conductivity, large surface area for attachment and development of bacteria and surface alteration for improved biofilm formation and extracellular electron-transfer capacity are main criteria for the high-performance anode content. Recently, it has been approved that the use of advanced nanomaterials (such as polymers, metallic or metal oxide nanomaterials and their composite materials) as an anode material is amongst the most efficient strategies of accelerating extracellular electron transfer performance and thus improving the power output of MFCs. Achieving large-scale production and economic feasibility of MFC systems includes the availability of cost-effective anodes capable of achieving better efficiency for long-term service while often requiring simple maintenance or being fully maintenance-free where necessary [19].

MFC is a type of green-energy conversion technology that produces electricity and has many other advantageous applications such as toxic compounds removal, biosensor etc. (Fig. 1) [6,20]. The advantages of MFC include high efficiency of energy conversion, source supplies in abundance along with mild condition requirement for operation [21–23]. In regards with the biodegradable nature of catalysts, fuel and the product, the energy production from MFCs have an advantage to the environment [24–26].

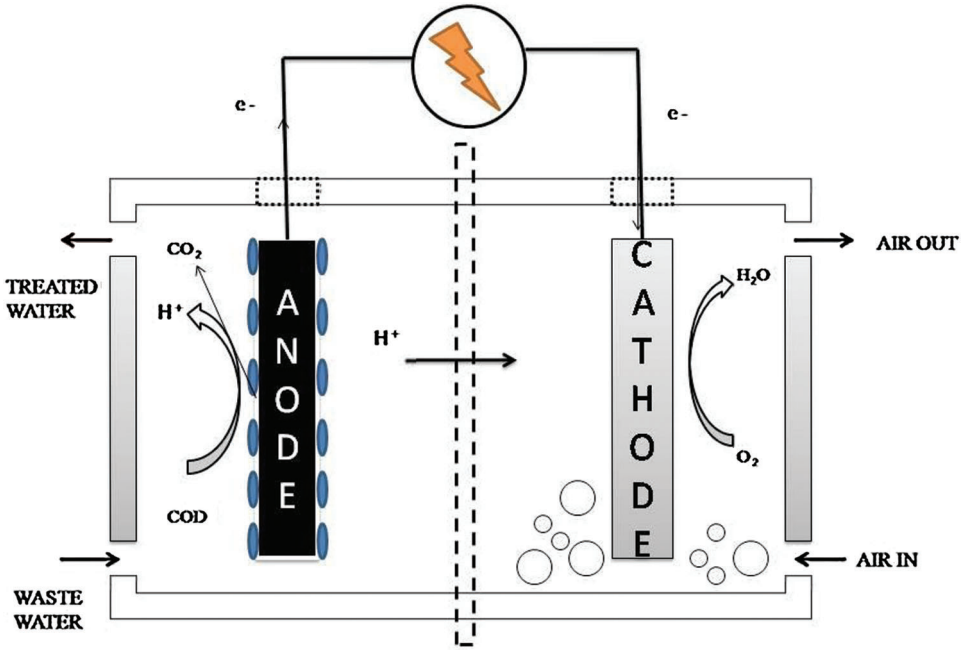

Figure 1: Schematic representation of a microbial fuel cell (MFC)

Table 1: Performance of MFC in respect to variation in substrate

Substrate	Power Density	Current Density	Reference
Acetate	–	2 mA/m^2	[27]
	1.79 mW/m^2	–	[28]
	27.4 mW/m^2	98.6 mA/m^2	[29]
	900 mW/m^2	1500 mA/m^2	[30]
	1487 mW/m^2	500 $\mu A/cm^2$	[31]
Lactate	0.358 $\mu W/cm^2$	–	[32]
	4.75 mW/m^3	16 A^{-3}	[33]
	1303 mW/m^3	2.74 A^{-2}	[34]
Glucose	2.4 W/m^2	5042 mA/m^2	[35]
	187 mW/m^2	–	[36]
	290 mW/m^2	568 mA/m^2	[37]
	1641 mW/m^2	7 A^{-2}	[38]
	2066 mW/m^2	8 A^{-2}	[38]
	2686 mW/m^2	0.30 mA/cm^2	[39]
Wastewater	4.22 W/m^3	4.62 mA/cm^2	[40]
	97.8 mW/m^2	–	[41]
	–	1600 mA/m^2	[39]
	393.8 mW/m^2	–	[42]
	1098 mW/m^2	7.2 A^{-2}	[43]

2 Electron Transport Mechanisms

2.1 Indirect Mechanism

In an indirect microbial fuel cell, a mediator is required for the transfer of electrons. The system works in anaerobic conditions where the fermentative bacteria use substrate catabolism to release electrons and hence reduce the intermediate products such as protons and acids to form end products. In an indirect microbial fuel cell system, an external mediator is supplemented that can shuffle between the anode and the cell membrane of the fermentative bacteria. Some examples of artificial external mediators used for this process include Benzylviologen, 2,6-dichlorophenolindophenol, thionine, and 2-hydroxy-1,4-naphthoquinone [44].

2.2 Direct Mechanism

In a mediator free MFC, the electrons are transferred via electroactive bacteria. They capture electrons released by the oxidised organic matter and transport it directly to the anode. This form of direct electron transfer is further divided into three pathways: Cytochrome mediated, Nanowire, Electron shuttle or soluble mediators.

2.2.1 Cytochrome Mediated Direct Electron Transfer

This mechanism involves the formation of biofilms on the electrode which enable direct transfer via pilli, nanowires or cytochrome C. Cytochrome C (CTC) plays a very important role in electron transfer. It is a heme-containing protein present in archaebacteria as well as eubacteria. Cytochrome C aids the harvesting of electricity. An important example of CTC is CymA, whose N-terminal is attached to the inner membrane while the C-terminal exposed to the periplasm. CymA is an important electron channel as it connects the inner membrane to the periplasmic area. It plays a major role in anaerobic respiration and can interact with many terminal reductases such as nitrate or fumarate reductase. It has been observed that on inactivation or deletion of CymA there is a drastic reduction in the current generation by approximately 80%. Redox proteins such as CymA and MtrA can show pairwise interactions due to the presence of a two-hybrid system in the bacteria. When CymA reacts with the other redox proteins in the periplasmic space it leads to the formation of a transient protein complex. This study was favored by an experiment in which an electrode was used as an electron donor for the reduction of fumarate utilizing *Shewanella oneidensis* MR-1. The study proved that almost 85% of electrons were transported to fumarate using CymA and about 15% of them were transferred using MtrA which signified the presence of a transient protein complex i.e., CymA-FR-MtrA. An alternative electron transfer conduit can be made by replacement of IS-insertion activated SirCD expression partially by CymA. The Mtr ABC channel can be comprehended as an extended branch of the periplasmic complex. It is a tunnel-like complex which connects the intracellular electron flux to the anode. Mtr ABC is a complex that contains three proteins which physically and functionally associated with each other. For example, MtrA is a periplasmic protein that delivers electrons from CymA to MtrC. More than 90% reduction of power production was observed on the deletion of the MtrC component in MFC. According to a comparative study, six *Geobacter* species displayed an average of 79 putative CTCs in each of their genomes. Out of which only 14% of them were found to be conserved in all genomes [45]. The MacA transported electrons from the inner membrane to PpcA in the periplasm, and PpcA further transfers electrons to the OMCs.

2.2.2 Microbial Nanowire

One of the latest techniques used for the transport of electrons is by using microbial nanowires. These nanowires are the pilus present on the bacteria, they are electrically conductive, and this was discovered by reducing iron oxide using *Geobacter sulfurreducens* bacteria. Such an electrically conductive pilus was also found in other bacteria signifying the presence of bacterial appendages in the environment. The *S. oneidensis* MR-1 has a bunch of pili-like outgrowths called nanowires with a radius of 1.5–2.5 nm in the electron acceptor limiting regime and or diffusion limiting or low agitating regime. It has recently been observed

that *S. oneidensis* MR-1 nanowires are outer membrane and periplasmic extensions [46]. *G. sulfurreducens* nanowires are expressed when it uses metal oxides as electron mediators or when fumarate is reduced at low temperatures. Two Pil A isoforms with unique characteristics have been observed in *G. sulfurreducens* nanowires. The electronic conductivity of *G. sulfurreducens* nanowires are 6 mS/cm and is comparatively large compared to its threshold value 10^{-3} mS/cm. The large electro-conductivity is the reason for the high volumetric generation of power. *G. sulfurreducens* nanowires are very similar to synthetic metallic nanostructures. OMC-dependent conductivity of *Shewanella* nanowires, *Geobacter* nanowires possess typical metallic electronic property [47].

2.2.3 Electron Shuttles or Mediators

The electron shuttles or electron mediators are secretions of Gram-negative bacteria; they aid power production in MFC's [25]. Ideally, these mediators should be dissolvable, stable, reusable, and environment-friendly and should have a redox potential ranging between the bacterial membrane protein and anodic material. One well-known electron shuttle in MFC's are endogenously produced flavins by Shewanella species. They mainly comprise of riboflavin (RF) and flavin mono nucleotide (FMN) [48]. Both these flavins consist of different characteristics and features. FMN is capable of percolating through the outer membrane, further, on penetrating the extracellular space these are transformed into RF. The transformed flavin cannot re-percolate into the periplasm. When a mediator is absent, the transfer rate of electrons extremely low. Another example of electron shuttle produced within MFC is Phenazines. These ate intrinsic electron shuttles produced by diverse bacterial species such as *Pseudomonas* [49]. The ability to generate power from a non-electroactive Gram-positive bacteria such as *Brevibacillus* sp. is generally optimized by phenazines. This signifies that in the presence of soluble mediators there is a collaborative effect for non-EAB's to produce electricity. Other than the bio-generated organic compounds, Hydrogen is gradually developed during fermentation or other chemical responses and can also function as electron shuttles or donors for *Shewanella* and *Geobacter* sp. in MFC [50].

3 MFC Performance

There are several factors that can affect the performance of MFC like the electrode materials, the membranes, the mediators, electrode configuration and the microbial strain used [21,51,52] as shown in Fig. 2. Since the rate of flow of electrons occurring between microbes and anode/cathode directly limits the performance of a microbial fuel cell, the material of which electrodes are made is a major factor [53]. The organic substances are oxidized in the anode chamber, by the metabolism of exo-electrogens i.e.; the microbes, and these generated electrons are then transferred to the external circuits via multiple extracellular electron-transfer pathways. These electrons when further transferred to the cathode get consumed by the reactions occurring on cathode, enabling a closed electrical circuit. This makes the harvesting of electrical energy possible. The low performance of anode is the major limitation in the application of MFCs. Hence to overcome these limitations, improvement in the electron transfer efficiency and anode performance have been made which includes optimization of operation conditions, using electro-active microbial committees in the anode chamber, genetically engineered exoelectrogens, and modified anode material for increasing the efficiency of extracellular electron transfer [54]. There were several approaches made out of which the modification of anode material showed required upgradation in the performance of MFCs, for the scale-up and commercialization. The characteristics of an ideal anode material are excellent conductivity, high surface area for better attachment of bacteria and its growth, enhanced biofilm formation through surface modification along with good extracellular electron transfer efficiency. Due to the possibility of using wastewater as a substrate for MFCs, it not only functions as a source of energy but a potential method of water treatment. Thus, MFCs are not only typical for industries but also in research [55,56].

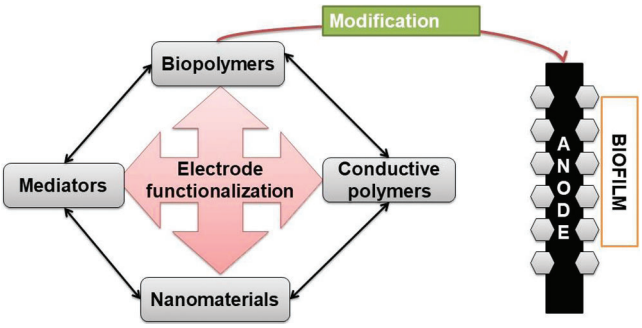

Figure 2: Concept map of electrode functionalization

There have been recent studies that approve the application of advanced nanomaterials as anode substrate can effectively accelerate the efficiency of electron transfer occurring extracellular. This thus improves the MFC's power output. Over the course of development, there are still some limitations to MFCs like unstable system performance, high cost and the low electron-recovery rates. These nanomaterials can be polymers, oxides, metallic nanomaterials, and their composite materials. The recent advancements on design and application of anode nanomaterial like carbon nano-tube (CNT), graphene, graphite granules, carbon cloth, porous carbon, and other nanomaterials of metallic origin for construction of enhanced performance exhibiting MFCs are discussed further.

4 Traditional Carbon-Based Anodes for MFCs

In the current MFCs, carbon is the most abundantly used material for anodes. This is because they offer low resistance to charge transfer and are cost-effective. They provide a large surface area for microbial attachment and growth, have anti-corrosive properties, and are well stable in the mixture of microbial inoculum.

The hydrogen fuel cells frequently used carbon cloth and carbon paper which was later adopted by the MFCs [57]. These materials however had some limitations like lack of durability and a higher cost, relatively. Carbon felt with 95.5% of carbon content has the properties of a good anode but offers large resistance [58]. Due to its good electrical conductivity, along with chemical stability and cheap price, graphite rods have widely been used in MFCs. However, an increased surface area is still difficult to be achieved with graphite rods. Hence, anodes with graphite fiber brush were designed that showed enhanced MFC power production [59]. Graphite fiber brushes were developed and introduced which had conductive corrosion resistant titanium wire. This added higher specific surface areas in MFCs [57]. Thus, these designs showed that high porosity in structures with larger surface area which essentially produced high power densities. There were MFC researches where carbon mesh, another carbon-like material was utilized which was cheaper than carbon cloth [57].

5 Requirement of Anodic Modification

MFC often generates a low operating voltage (V_{op}) in comparison to the electromotive force (E_{thermo}) of the cell, often termed as thermodynamically predicted potentials that are irreversible in nature. Energy loss may occur because of several different ways such as activation loss, bacterial metabolism loss, mass transfer loss, and ohmic losses caused because of various reasons but the most common reason is excess biofilm and the organic compounds produced by the inoculum may cause biofouling of the anode thereby reducing the electron transfer from the organism to the anodic material. Various strategies have been utilized for reducing this activation over-potential which could be reduced by increasing electrode catalysis, adding mediators to facilitate efficient electron transport from microbial cell membrane to anode surface, by increasing the electrode surface area, and enriching electrogenic

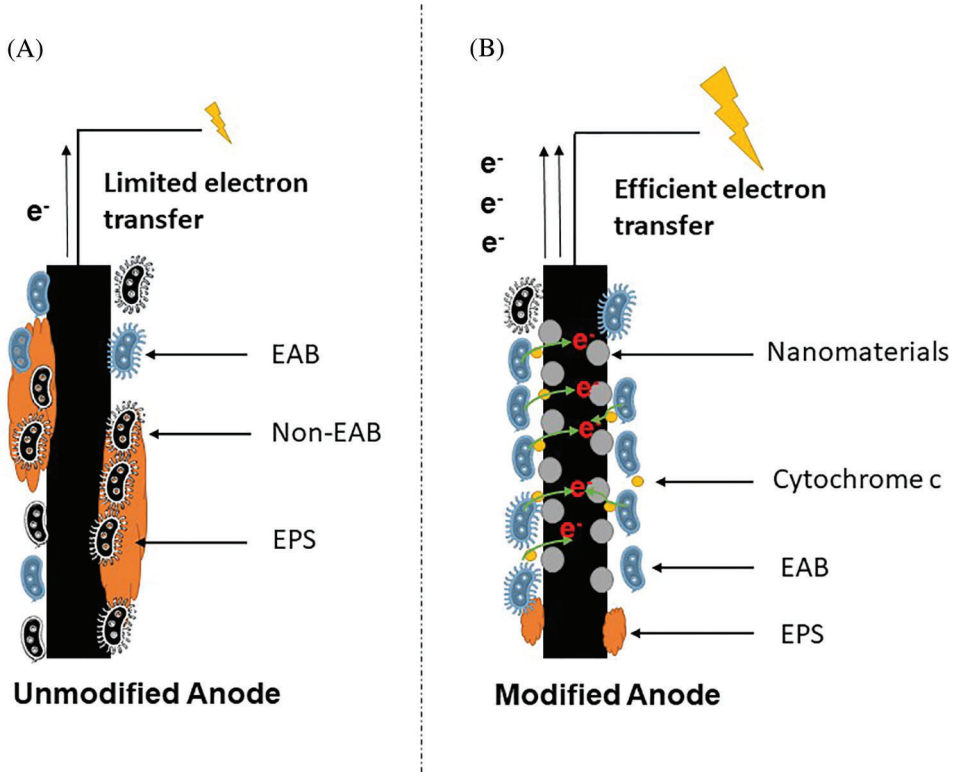

Figure 3: (A) Anode without nanomaterial modification; (B) Anode with nanomaterial modification

biofilm on anode and operational conditions inside anode and cathode compartments. However, one such a strategy is the utilization of nanomaterials in anodic modification. The nanomaterials facilitate the formation of electroactive bacteria and thereby promote electron transfer which can be illustrated in Fig. 3 [60].

6 Anodic Surface Modification Using Nanoparticles

Several different types of nano metals or metal oxides like manganese oxide, iron oxide, titanium oxide are being utilized for anode surface modification as shown in Tab. 2 in an attempt, enhancing the adhering capacity of inoculum (as illustrated in Fig. 2) and increasing its electrochemical activity for accelerating the electron transport rate thereby increasing the electricity output which is shown in Tab. 3.

6.1 Iron Oxide

Iron oxide can promote EET through two mechanisms; inside biofilm in the form of an electrical conduit or interface by accumulation on the cell surface [62]. In a study, it was reported that these inside-biofilm particles could promote the expression of c-type cytochromes responsible in electricity generation. On the basis of inside biofilm mechanism, according to Kato et al. [66] iron oxide (Fe_2O_3) in nano-colloid form could be utilized for self-assembly of *Shewanella* in form of interconnected network resulting in 50-fold more power generation in comparison to the control. On the basis of interface mechanism; iron oxides can be served as redox couple between Fe (II) and Fe (III) at the interface of the anodic surface accelerating the EET process. According to a study, conductive iron oxide can be utilized in substrate degradation by promoting EET [67]. Most of the metal oxides are electrically non-conductive but enhance biofilm formation by promoting cell adhesion. Thus, there is a requirement of a carbon conductive material or filler e.g., CNT, Graphene, etc. which can enhance the electrical conductivity for increasing the extracellular electron transfer from the organism to the anode [17].

Table 2: Depicting several types of mechanisms of nanoparticles for improving EET

Sr. no.	Type of modification	Description	Example	Reference
1.	Inside-Membrane	The metal nanoparticles can intercalate in cell envelope thereby accelerating the EET process as shown in Fig. 4A	Pb, oligomer	[61]
2.	Inside-Biofilm	In most cases, biofilm formation may cause a limiting factor in EET process but, insertion of nanoparticles inside the biofilm may exhibit the process by a connecting the biofilm to the anode facilitating electron transfer as shown in Fig. 4B	Iron oxide	[62]
3.	Inter species	Nanoparticles acting as electrical conduit for transmitting electrons from one organism to another which is quite essential for various possibilities of reactions as shown in Fig. 4C	Iron oxide	[63]
4.	Interface	Nanoparticles form structures porous to the anodic surface area which exhibit inoculum adherence along with improvement in EET process by establishing redox-active centers on the interface as shown in Fig. 4D	Polymers, CNT, graphene, etc	[64,65]

6.2 Carbon Black (CB)

Carbon blacks is a well suited biological interfaces as it is they are extensively used for enzyme fabrication which is useful for anode and cathode i.e., they have high porosity and large surface area with high conductivity [68]. Determining the oxidation & heme iron contraction for immobilization of hemoglobin on standard carbon black powder with the help of cyclic voltammetry (CV) [69]. Redox protein, cuprous oxidase with Ketjen black results in bio electrocatalyst which sometimes use as oxygen as terminal electron acceptor & gives cathodic current [57]. The current density of biocathode allowed by the addition of ketjen black to increase 3–4 mA/cm^2 of cuprous oxide on pyrolytic graphite electrodes. Emulsion of Teflon & CBN is created for composites by readily modified CBN. For the suitable equity of hydrophobic-hydrophilic properties by a merging of CBN and teflon polymer which gives mixed element by which electrolyte-carbon-air yields which necessary for gas diffusion electrodes (GDE) [70].

6.3 Carbon Nanotube (CNT)

In MFCs, CNT & CNT hybrid material are highly beneficial as bioelectrode modifiers as CNTs promote scaffold porosity for biofilm formation, along with enhancing electrocatalysis [33]. CNT's used to development of a surface area of anode increases the potential of porous scaffolds for biofilm production and improves electrocatalysis.

With the help of physio-adsorption process, redox protein may come in contact with the hydrophobic-hydrophilic CNT surface, through van der Waals force the protein adhering to hydrophobic-hydrophilic CNT surface. Non-covalent interactions have been utilized for establishing direct electron transfer (DET) with various enzymes [71].

Chemical oxidation is the most commonly recognized process for functionalizing CNT's through which the carboxylic acid group has been added at the CNT surface. By carbodiimide chemistry, carboxyl groups can be mobilized which resulting in the formation of unstable ester which reacts with available amino

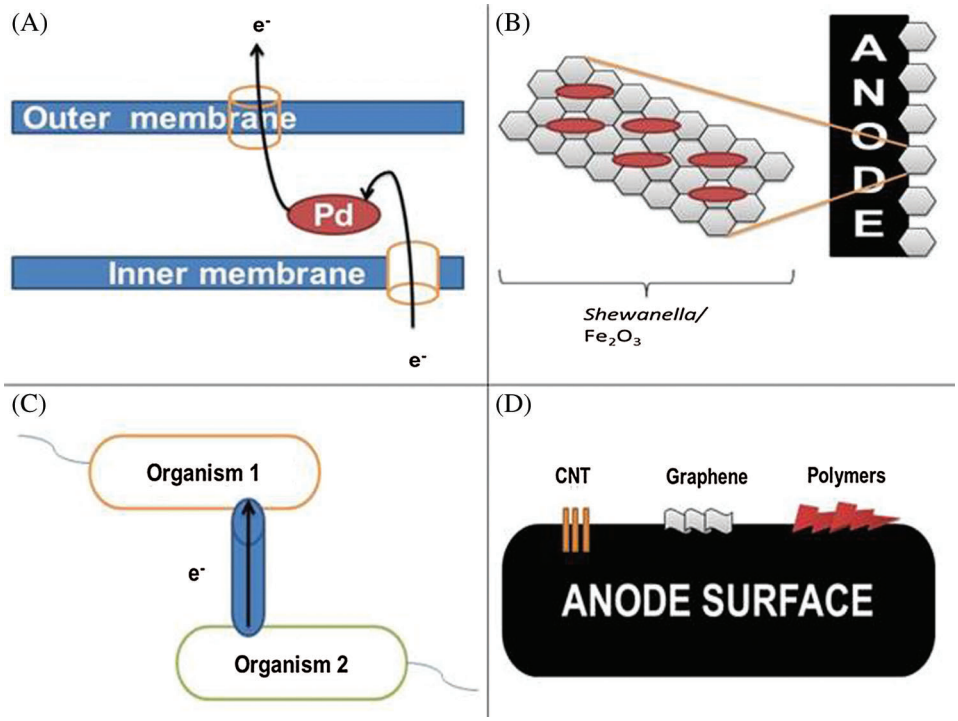

Figure 4: Depicting various mechanisms of nanoparticles for improving the EET process. (A) Inside-membrane mechanism; (B) Inside-biofilm mechanism; (C) Inter-species mechanism; (D) Interface mechanism

groups on the protein surface thereby producing covalent amide bonds. A distance between protein and CNT surface stabilizes the interactions and minimizes by covalent link, by which it promotes electronic conductivity and DET. The conductivity of material decreases because of oxidation which creates a defect in CNT's. Catalytic activity reduction by shortening covalent links can result in steric pressure on protein structure [72]. For improving electrolysis, materials CNT's are modified with metal nanoparticles and metal collides which take advantage of its properties. For the MFC anode preparation from metals like stainless steel, titanium and platinum several efforts were made. However, the properties of carbon like its economic value, surface area for attachment and such as mentioned made it more popular. A CNT coated sponge was prepared and investigated for its performance by Xie et al. [42] offering lower resistance along with greater stability. Moreover, it had a three-dimensional scaffold with a uniform microporous structure promoting microbial colonization. This helped in achieving the maximum current density about 48% higher in comparison to the CNT-textile, when operated under the same condition. The extracellular electron transfer through microbes gets boosted up under the application of three dimensional nanostructured electrodes. Similar study was conducted by Jourdin et al., by constructing a nano Web-RVC which resulted in effective mass transfer and ~3 folds higher current density in comparison to the control electrode [74].

Apart from improving biosensor's performance [75], the nitrogen doped CNTs also find an application in MFC for power output enhancement. Nitrogen doped CNT was prepared similar to a bamboo with the catalytic pyrolysis of ethylenediamine [54]. Which enhances the MFC performance through several mechanisms like enhanced electrochemical performance, biocompatibility as well as increased active sites for electrochemical reactions [76]. CNTs can also enhance biofilm formation due to the presence of micropores (~5–10 μm) and mesopores (~100 μm) on structures on the anode.

According to Inoue et al. [77], investigations utilizing molecular docking for predicting several interactions of different forms of CNT like chiral, armchair and zigzag with proteins like PilA and OmcZ,

It was reported that the binding affinities for all the three forms of CNTs with PilA and OmcZ were –7.6, –7.7, –8.6 kcal/mol and –8.9, –7.9, –9.2 kcal/mol respectively. These investigations indicated that CNTs show promise in electrode functionalizing for various other properties like bacterial adherence, formation of biofilm along with improving EET process [78].

6.4 Graphene Based Anodes

Conventionally, carbon-based anodes are being used for the MFC activity. However, new studies point towards the utilization of graphene as a substitute material for anodic development. Using this, the surface area has been increased for the electrochemical activity of the fuel cell [79]. Graphene although promises high energy output as it provides higher surface area, but the orientation of its fabricated electrode matters the most. Graphene has a plate shaped electrode and crumpled one. Researches show the utilization of crumpled graphene can double the generation of electricity as shown in Fig. 5. i.e., from 1.7 to 3.6 mW/m^2 [80].

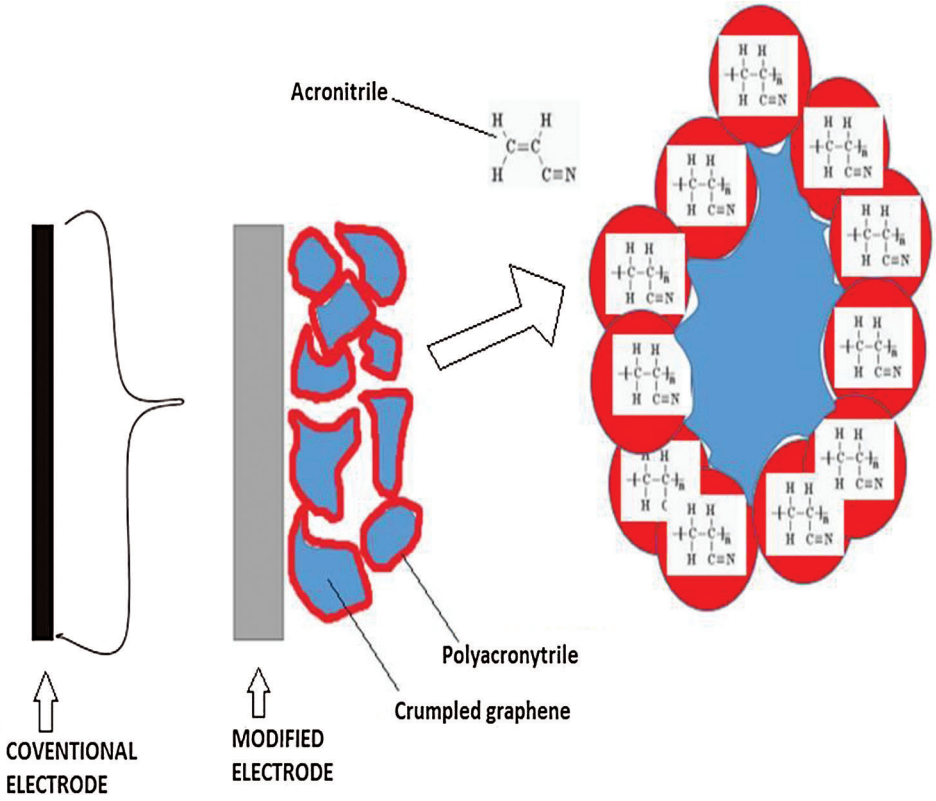

Figure 5: Graphene based anodic modification

Apart from the physical aspects, chemical modification in the graphene electrode proved to be the better option. In recent studies, electrode from graphene oxide is used in its reduced form coated with tin oxide. The material stated is produced in two step procedure [81–83]. Graphene oxide is reduced using hydrothermal methods were used and coated it with tin oxide using a microwave method. Thus, utilizing RGO/SnO_2 (Reduced graphene oxide/Tin oxide) in MFC produces 1624 mW/m^2 of power density. As graphene usage is ubiquitous for MFC and for oxygen reduction reaction (ORR), strategies focusing on graphene utilization has been developed [84]. In MFC, the generation of electricity is done by flow of electron from cathode

and the acceptor of cathodic electron is oxygen. Thus, is order to improve the MFC performance, oxygen reduction reaction is studied. There are various ORR catalysts which work on the specified mechanisms, each having different step [84] MFC for ORR have electrodes of graphene doped with iron and nitrogen as catalysts [85] having power density of 1149.8 mW/m^2. Reduced graphene is also coated with Polyaniline (PANI) in carbon cloth and is prepared in suitable solvent of phosphate buffer [86] producing power density of 1390 mW/m^2. Generation of power is not only the game of higher energy sometime chip uses very minute amount of power, thus MFC having graphene electrode with nickel coating can be used in the laboratories for generation of microvolts [87]. Graphene electrodes with all such advantages are the best electrodes used so far and can efficiently generate the maximum power output [88].

Table 3: Nanomaterials with their catalyst and their application in MFC

Category	Catalyst	Substrate	Method of synthesis	Comment/ Application	Reference
Carbon black	Polypyrrole/Carbon black composite	Activated sludge + Glucose	Polymerization by electrochemical process	ORR process, Anodic modifier	[96]
Activated carbon	Activated carbon/ Carbon black mixture	Wastewater	Carbonization by electrochemical process	ORR catalyst, Inhibit biofilm growth	[97]
Graphene	N/S co-doped carbon nanosheets	Sodium acetate + Sodium sulphate + Sodium carbonate + magnesium chloride + calcium chloride	In-situ electro-polymerization	ORR, High electron transfer capacity	[98]
Carbon nanotubes	Polyaniline/ multi-walled CNTs composite	Glucose	Chemical vapour deposition of hydrocarbons	ORR catalyses, More durable	[99]
Polyaniline	Polyaniline/ Graphene oxide	Lactate	Electro polymerization	Improves electricity generation	[100]

According to Inoue et al. [77], investigations utilizing molecular docking for predicting several interactions of different dimensions of graphene like 1.1 × 1.1 nm, 1.4 × 1.4 nm and 1.9 × 1.9 nm with proteins like PilA and OmcZ. It was reported that the binding affinities for all the three dimensions of graphene with PilA and OmcZ were –8.8, –9.2, –10.1 kcal/mol and –7.5, –7.9, –10.2 kcal/mol respectively. These investigations indicated that these different dimensions of graphene show promise in electrode functionalizing for various other properties like formation of biofilm along with improving EET process [78].

6.5 Conductive Polymers

Several types of conductive polymers are being used for anodic modification to enhance the EET rate. One of such study was reported, where conductive porous polyaniline (PANI) was utilized in MFC resulting in improved power output in comparison to the control [89–91]. Another such study was conducted utilizing nanostructures of polypyrrole (PPy) which resulted in ~2–5 folds better power generation along with long term MFC stability and enhanced cell viability [34,92,93]. According to Li et al. [94] utilizing poly (aniline-co-aminophenol) (PAOA) in combination with carbon felt at the anodic surface could result in 118% better performance in comparison to the unmodified control. A similar type of study was reported where poly (3, 4-ethylene dioxythiophene) was utilized for modifying the anodic surface through

electrochemical polymerization, resulted in 43% better power output in comparison to the control [95]. This electrochemical polymerization is a quite tuned technology along with the increased stability of polymers can favor the performance of long term MFCs.

6.6 Composite Material

CNT-polyaniline composite helps cell adhesion and enhance electrocatalytic property because polyaniline increases surface area of the electrode thereby increasing the power output which was explained by Sharma et al. [35] Carbon paper-CNT electrodes enhance the power density by ~6 folds in comparison to graphite electrode. Some literature surveys stated that to increase bacteria adhesion activated carbon should be treated with concentrated nitric acid and ethylenediamine, then the nitrogen carbon ratio increases which is favorable for microbial adhesion [101,102]. Polypyrrole-CNT showed high electron transfer [103].

The performance of MFC will be increased by using functional Trimethylene oxide (TMO) & conducting polymer materials. By using functional TMO & conducting polymer the optimization of the anode is possible through the insertion of nano catalytic mediators in either of electrodes or the feeding solution [104], e.g., Transition metal oxides such as Mn & can be used as anode material. They take part in ORR & increases power density as compared to the activated carbon [105]. However, there is activation loss of MnO_2 due to the high overpotential, thus considered a major drawback of manganese oxide [106]. Sarma et al. manufactured magnetic nanoparticle containing Fe_3SO_4 encapsulated with aniline and pyrrole composite polymer which facilitates biofilm formation and extracellular electron transfer [107].

Magnetic nanoparticle composite with biofilm was highly efficient to degrade the azo dye & associated power generation in MFC [107]. Pu et al. [108] used stainless with in situ electrochemical decomposing Polypyrrole (PPy) over stainless steel (SS) followed by the formation of PPy/SS anode. Stainless steel has low, along with the maximum power density outputs hence it is considered as a better material for anodic modification. On the other side, its poor biocompatibility & low ability towards corrosion limits the application. This modification results in maximum power density. Some recent reports stated that the decrease in contact angle would facilitate the attachment of bacteria & reduces the e^- transfer resistance. This is proved by the Chen et al. [109]. Chen et al. [109] constructed that MnO_2/PPy composite a modified anode via in situ chemical polymerization method. Using wettability test contact angle was reduced and thereby improving microbial adhesion. Yuan et al. [110] demonstrated that carbon cloth is combined with MWCNT high-performance MnO_2/PPy/MnO_2 nanocomposites, results in maximum power density was increased. Electrochemical spectroscopic studies indicate that the modified anode leads to high charge transfer rate & facilitates unique sites for more efficient electrocatalysis [110].

The hydrothermal method was used with a facile two-step for preparation of composite [111]. Polymerization of PANI, Carbon Felt (CF) embedded with NiO was doped on the bare CF electrode, producing 1078.8 mWm^{-2} of maximum power density output.

The maximum power density of 670 mWm^{-2} & 722 mV of open-circuit voltage was obtained, when combination of CNT based NiO nanocomposite was utilized. 100 mV open-circuit voltage could not achieve when MFC with pure NiO [112].

Durable electrocatalytic activity for ORR has been prepared using Ni-NiO/PPy-rGO composites which has synergistic effects on the components of supporting matrix which resulting in Ni^+ & Ni^{2+} ions homogenously dispersed over PPy-rGO sheet. ORR enhancement, superior stability, conventional Pt/C catalyst & electrocatalytic activities of Ni-NiO/PPy-rGO have been studied using CV. 2D graphene for functional rGO coming from synergistic action of metal oxide nanocomposite structure have a good contribution towards a high activity as bioelectrochemical material [113]. Under experimental conditions, power density improved by 70%, when SS wool was coated with PANI-Co-

PPy. As a sole carbon source, the inoculum was composed of synergistic wastewater containing sodium acetate (25 mM) & landfill leachate (4%) [114]. Utilization of various other composite materials in MFC are shown in Tab. 4.

Table 4: Composite material as anode used in MFC with biocatalyst and their power density

Sr. no	Electrode Material	Biocatalyst	Power Density	Substrate	Reference
1	CNT/Polyaniline composites	*E. coli*	42 mW/m^2	Glucose	[115]
2	Nitrogen-doped/CNT/rGO	*E. coli & Shewanella putrefacient*	1137 mW/m^2	–	[116]
3	3D CNT/Chitosan microchannel nanocomposites	*Geobacter sulfurreducens*	2.87 mW/m^2	Acetate	[117]
4	Nano-molybdenum carbide (Mo_2 C)/CNT	*E. coli*	170 mW/m^2	Glucose	[118]
5	Graphene oxide/Nanofibers modified carbon paper	*Shewanella* MR-1	34.2 mW/m^2	Lactate	[119]
6	Polypyrrole/Graphite oxide	*Shewanella oneidensis*	1326 mW/m^2	–	[120]
7	Graphene modified stainless steel mesh	*E. coli*	2668 mW/m^2	Lactate	[119]

7 Other Methods of Anode Modification

Titanium oxide (TiO_2) nanoparticles, due to their features like stability, abundance and low cost are used to dope carbon nanotubes which resulted in double electricity generation [121]. Au-NPs, the multi-layered gold nanoparticles, are the electron receivers providing better fast biofilm formation and enhanced current output. Guo et al. [122] constructed carbon-paper anodes modified with gold colloids. This had high electroactive surface area with reduced electron transfer resistance.

There are several other nanomaterial oxides used for the anode modification in the MFC. The copper doped ferrous oxide nanomaterials are used as the modifier of anode. Nanomaterial oxide coated anode was improved in the porosity i.e., the hydrophilic property of the anode was improved [123].

The modified anode doped with graphene oxide increases its efficiency based upon the concentration of doped graphene oxide. The hydrophilicity in any compound is defined by the amount of surface coming in contact with water. In terms of water contact angle (θ), the less the angle of contact, more is the hydrophilicity [124].

Thus, using graphene oxide doped graphene composite as an anode modifier we can achieve the maximum hydrophilicity has been shown in Tab. 5.

Table 5: Depicting the relation between the water angle and the amount of graphene oxide in respect to power and current density

Concentration of graphene oxide doped	Substrate	Current density (mA cm^2)	Power density (mW cm^2)	Water angle
0.15 mg·L^{-1}	Anaerobic sludge + Sodium acetate + Phosphate buffer saline	0.23 (max)	940 (max)	74.2 ± 0.52°
0.2 mg·L^{-1}		0.35 (max)	1100 (max)	64.6 ± 2.75°
0.25 mg·L^{-1}		0.17 (max)	7000 (max)	41.7 ± 3.69°

Reference [125].

7.1 Fabrication Mechanism for Anode

Electrodes and its fabrication in MFC are not just limited to a single process, it covers a vast and distinct processes. Each process somehow influences the cost or the power generation in a positive way. A simple methodology for the development of PANI in the carbon cloth electrode was developed and demonstrated the positive flow of electricity. The aniline monomer was evenly spread over the carbon cloth which is polymerized in-situ [111]. Also, in other methods 16.7% of molybdenum was used as the composite in CNT's can fulfil the need of (20%) platinum catalyst. It is also used so that it can synthesize hydrogen and biofilm which is used by *E. coli* in order to generate electricity [118,126]. In web-based nickel-CNTs electrodes, the electrons produced by bacteria is transferred through the electrode [127]. MFC as stated has its application in the production of electrical energy, thus there are some models in which the electricity is produced in microvolts, where electrodes are sandwiched in the stack of paper filters, this induces the easy transmission of electron and generation of voltage in paper chips [128]. Sometimes, ferric oxide rod of nano size was used in MFC, which is layered in the matrix of polymer. This approach of fabrication is a self-assembled technique [129].

7.2 Chemical Modification of Anodes

Surface treatments for the anode modification have been practiced prior to the nano-material techniques. Ammonia treatment on carbon-cloth [101] or graphite fibers [59] increased the positive charge on anode which enhanced microbial adhesion hence increasing the power density. For scale up MFCs, this method was not cost-effective, and hence heat treatment, an economical alternative was adopted. Pre-acid treatment of anodes with nitric acid is another strategy of making anode extra positively charged [130].

The conductive polypyrrole matrix containing polymeric mediators such as Osmium (Os) is used to immobilize the exoelectrogens over the electrode surface. Thus, an efficient electron transfer to anodes could occur enhancing MFC's performance [131].

Grafting of a range of functional groups with different physical and chemical properties is another method of electrode modification. Graphite is covalently modified by electrochemical reduction of aryl diazonium salts. Results showed that negatively charged groups on anode surface decreased MFC power output, but a positive group can double the power output.

7.3 Electrochemical Modification of Anodes

Plasma-based N^+ ions were employed to modify carbon anodes for enhanced electricity generation capacity by implantation [132]. This removed surface roughness and hydrophobicity which enhanced cell adhesion, biofilm formation along with that it decreases the charge transfer resistance. This technique was also applicable to other electrode materials like metal and polymer in MFCs. Carbon fiber materials are prepared by electrospinning [133]. This adjustable technique produces nanofibers that are easy to handle and have a high specific surface areas. These have 3D interface for immobilization and support for the growth of MFC's exoelectrogens. Results showed decrease in start-up time and a ten-fold increase in current generation as compared to conventional graphite electrode.

The various methods described above are used in the recent scenarios to develop anode in MFC, whereas the method of developing the anode is specific in each category. In the anode of polypyrrole in CNT, there are various other chemical species involved in the fabricating mechanism. The method used in the development of the polypyrrole as a composite over the CNT is in situ hybridization using ammonium persulfate [134].

Apart from ppy(polypyrrole) in the anode, PANI is also used as the anode modifier in the MFC. Polyacrylonitrile (PAN) is polymerized over the graphite surface having a porosity of around 75 micrometer [135]. After this, the process of electrochemical deposition of CNT over the PANI modified mesoporous surface of graphite is done [116]. Apart from the materials we use in the anode, we can also

modify the intensity and porosity of the anode material along with the electrode spacing, which is proved to increase the power intensity by 50%. A less porous anode is used with a decreased gap of 1–2 cm between electrodes can generate more power. Larger pore size sometimes hinders the transfer of charges due to the clogging of the substrate. Glucose as the substrate is the best option for MFC [56].

Table 6: Advantages and disadvantages of various nanomaterials used for anodic modification

Sr. No.	Nanomaterial	Advantage	Disadvantage	References
1	Transition metal oxides —Iron oxide	High specific capacity (60–1000 mA g^{-1}) Better stability	Low coulombic efficiencies Larger potential hysteresis Low conductivity	[136,137]
2	Carbon black	High electric conductivity Low cost	Low specific capacity Low rate capacity	[137]
3	CNT	High electrical conductivity (10^6 m^{-1}–10^5 m^{-1}) Flux regeneration properties High permeability	Formation of bubbles may cause the blockage of pores, decrease in mass transfer, and increase in back pressure Agglomeration tendencies	[138]
4	Graphene based	High specific capacity High electrical conductivity Mechanical flexibility	Graphene containing impurities is difficult to handle Cost of purity	[137]
5	Conductive polymers	High electrical conductivity (160 S cm^{-1}–210 S cm^{-1}) High thermal stability Better cell adhesion	High cost	[94]

8 Techniques for Evaluating MFC Performance

8.1 Cyclic Voltammetry (CV)

This is an electrochemical technique in which a variable potential is applied to a functional electrode in a system to measure the resultant current. Microbial electrochemical system (MES) cyclic voltammetry is used to estimate the biocatalytic activities taking place at the anode biofilm at different operating conditions and to observe and characterize these changes in electrochemical behavior after transferring it into Microbial Electrochemical Systems (MESs). Electrons generated during voltammetry analysis are pushed in and pulled out of the cells due to changing electrode potentials within a specific range, hence inducing a reduction and oxidation event by each redox center accessible to the electrodes [139].

8.2 Electrochemical Impedance Spectroscopy (EIS)

This method is precise and is commonly used for diagnosis of the internal resistance of the system. The impendence spectrum provides important data to understand the electrochemical reactions at the electrodes. EIS is used mainly to characterize the properties of the electrodes material and scrutinize the biofilm formed along with understanding the kinetics of the reaction. EIS is preferred over methods such as slope method and current interruption as certain characteristics such as the ohmic resistance, charge transfer resistance, diffusion transfer resistance can be measured separately only using this technique. This technique exploits the features of a potentiostat to measure over a range of frequencies (100 kHz to 1 MHz). Furthermore, the variations in the cell potential and current are recorded using a frequency response analyzer [140]. Measurements through this technique are represented by Nyquist or Bode plot. The Nyquist plot marks negative values of imaginary impedance (Z00) against the original impedance (Z0). Each point in the plot represents impedance at a certain frequency. The major disadvantage of Nyquist plots is that it does not provide information about the original frequency used to record a particular point. The Bode plot marks the impedance against the

logarithm of frequency on the X-axis and both the phase angle as well as absolute values of impedance plotted on Y-axis. The resultant resistance is obtained at the highest frequency point. The analysis of low or high-frequency data is easily obtained using the Bode plot, and the difference between them represents Polarization resistance (Rp). A Warburg element is utilized to form an equivalent circuit by linking in parallel with Solution resistance (Rs) or Rp to represent the diffusion mechanism [141].

8.3 Tafel Plot Analysis

Tafel plot can be obtained by plotting current density against overpotential. Tafel plot is an important analytical tool that aids one to examine the electrolytic activity of the electrodes in an MFC system. It provides a brief understanding of the reaction mechanism of the kinetic reaction. One of the most important characteristics of a Tafel plot includes its ability to investigate the half-cell of the MFC independently. They can understand the charge transfer mechanism taking place at the anodic chamber without considering the charge transfer process taking place at the cathodic terminal. The exchange current density (i_0), Tafel slope, and charge transfer resistance (R_{ct}), charge transfer coefficient (β), are an important kinetic feature used to examine the electrochemical activities taking place at the electrodes. The exchange of current density exposes the intrinsic rates at which electrons are transferred between an electrode and electrolyte. It is an essential feature in the rate of electro-oxidation or electro-reduction of a chemical species at an electrode at equilibrium. Large i_0 indicates reaction in MFC is faster whereas a smaller i_0 indicates that the reaction is taking place at a slow pace. Tafel slope is an intensive feature, which suggests that it does not depend on the surface area of the electrode. This signifies that an increase in the rate of overpotential concerning an increase in current density was observed. A higher Tafel slope signifies higher electrocatalytic activity alongside better electron transfer efficiencies with a slow increase in the overpotential hence there is a decrease in the energy loss. Charge transfer coefficient defines a fraction of the interfacial potential of an electrolyte-electrode interface. Low charge transfer coefficient values signify that less activation energy is required for the electron acceptor to exchange electrons with an electrode; therefore lower energy loss will generate higher output [142].

8.3.1 Determination of Exchange Current Density of Electrode Using Tafel Plot

Voltage drop due to activation losses in MFCs can be expressed by a semi-empirical Tafel equation (Eq. (1)), where ΔV is the overvoltage, A is Tafel constant, i current density and i_o is the exchange current density (cell current normalized to cathode surface area).

$$\Delta V = A \ln\left(\frac{i}{i_o}\right) \tag{1}$$

8.3.2 Determination of the Columbic Efficiency and Energy Efficiency

Columbic efficiency (CE) can be calculated as per Eq. (2) by dividing total coulombs obtained from the cell and theoretical amount of coulombs that can be produced from anolyte.

$$\mathrm{CE} = \frac{\mathrm{M}\int_0^t \mathrm{Idt}}{\mathrm{Fbv}\Delta\mathrm{COD}} \tag{2}$$

where v is the volume of the anode chamber of MFC, *M*is 32 i.e., molecular weight of oxygen, Faraday's constant (F) is 96485 C/mol; b is 4 i.e., the number of electrons exchanged per mole of oxygen; Δ*COD* is the difference in the initial substrate or anolyte concentration in terms of COD_{ini} (g/L) and final substrate or anolyte concentration or COD_f.

8.3.3 Determination of Capacitance of Electrode

Capacitive behavior of an electrode can be evaluated by employing charge discharge technique. Specific capacitance of electrode was measured by following equation using charge discharge experiment—as per Eq. (3).

$$C = \frac{I_{charge-discharge} \times t}{U_{charge-discharge} \times A} \tag{3}$$

where $I_{charge\text{-}discharge}$ is the charge-discharge current; t is the discharge time; $U_{charge\text{-}discharge}$ is the potential window; and 'A' is the projected anode surface area.

Cyclic voltammetry (CV) was extensively used to study the catalytic and capacitive behavior of different electrodes (modified and unmodified). The specific capacitance of various anodes was measured by the Eq. (4).

$$C = \frac{\int_{V1}^{V2} IdV}{A\Delta V(dV/dt)} \tag{4}$$

where 'C', 'A', 'ΔV' and '(dV/dt)' indicated specific capacitance per unit area (F/cm^2), surface area of anode (cm^2), potential window (V) and scan rate (V/s) respectively [48].

9 Conclusion

The development of various advanced nanomaterials-based anode like CNTs, graphene, porous carbon and the metallic nanomaterials have been used for designing and construction of evolved MFCs. The electro catalysis occurring at anode in case of MFCs is quite complicated as it involves bio catalytic process carried out by microbes. Hence, the electro catalysis enhancement in MFCs can strategically be carried out by modifying electrode material and microbial cells. There is a systematic relation between bio-electrochemical cell configuration and the anode potential. This anode potential affects the microbial attachment, growth, diversity and the response from biofilm. The principle of MFC electrode can be understood as bacteria turned into super-capacitor electrodes [131]. The nanomaterials having high conductivity, excellent biocompatibility with microbial inoculum mixture, and good stability find application in MFC designing and fabrication. Intimate bacterial adhesion for growth and efficient electron transfer make their ways in research approach and realization.

These nano-engineered anode materials improve the power output for a cleaner and more sustainable energy production through MFCs. Different carbon-based electrode materials ranging from classic graphene to add functional polymers can be fabricated by the process of electro spinning. But the power generation and the electrode costs are not quite suitable currently to be commercialized. There is a need of further research on easy, economic, and high-efficiency electrode preparation. The electron-transfer mechanisms responsible for bio-catalytic processes occurring must be guided for the preparation of novel MFC's electrode materials.

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