Graphene Derived Electrode Materials for Microbial Fuel Cell

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1 Introduction

Microbial Fuel Cell (MFC) is a significant technology that aides in the mitigation of climate change by generation of bioenergy. Fossil fuel depletion, as well as environmental concerns for-example acid rain, greenhouse gas emissions, and global warming, have prompted the growth of substitute energy sources like MFC. MFC's, in particular, are being investigated as an alternate option due to their remarkable ability to produce energy while also removing contaminants. Wastewater treatment, removal of toxic compounds, heavy metal remediation from soil and water, and biogas production are the most typical applications of MFC [1]. The beginning of MFC can be dated back to 1911, when Potter obtained 0.3–0.5 V when working with a platinum electrode put into a liquid solution of yeast and Escherichia coli using a glucose medium. MFC first came to prominence in the 1950s, when researchers

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were looking for a new way to convert human waste to electricity in a timely manner during space missions. Redox-active mediators were commonly utilized in MFC's until the 1980s, and they considerably increased the power density output of MFC's. The practicality of MFC's as modest power supply increased at this point, and more scientists got keen on the innovation work of MFC in relation to alternate renewable energy systems [2].

A conventional MFC system has anode part and cathode part divided by membrane as shown in Fig. 1. The MFC works on the basis that it is a device that converts substrates directly into electricity through substrate oxidation, with exoelectrogenic microbes acting as a biocatalyst. When bacteria oxidize organic and inorganic materials, they produce electrons and protons, which generate electricity. Electrons created by microorganisms on these substrates go through the conductive material to the anode and cathode, leading in power production. The H^+ ions produced by bacteria in the anode flow through the semi permeable membrane to the cathode as a result of electrochemical gradient. Pure water is formed when electrons combine with H^+ ions and oxygen in cathode part. Figure 1. illustrates the schematic representation of MFC, which is made up of anode and cathode part separated by membrane.

The overall process involves the decomposition of the substrate into carbon dioxide and water, as well as the creation of energy as a byproduct. The MFC can produce electron from the anode with substrate oxidation by microorganisms and passed to the cathode part through electrical device connected in externally using the electrode reaction pair described above. The nature of the microbes and operational variables such as conductivity, surface area of electrodes, temperature, membrane, and pH are having significant collision on MFC performance.

A big electrode surface area, good electrical conductivity, excellent stability, and cheap are all important qualities of electrode materials in MFC performance. MFC

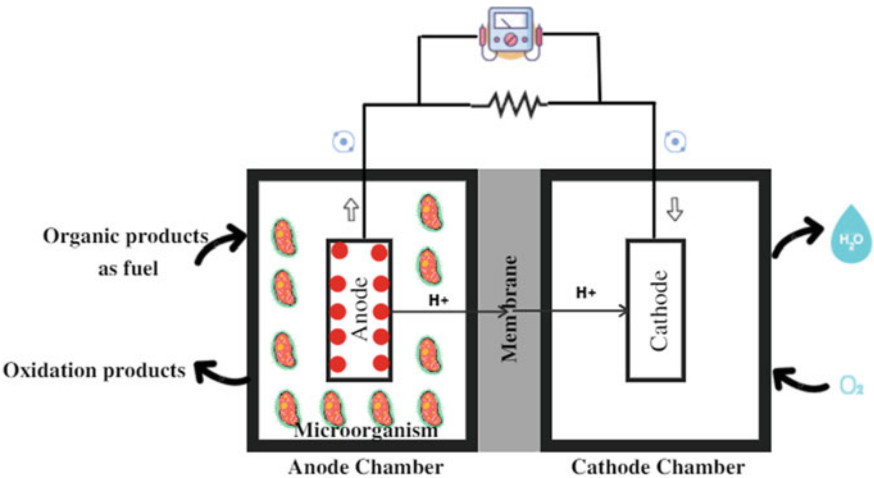


Fig. 1 Schematic representation of double chambered MFC

uses a wide range of anode and cathode materials. Stainless Steel (SS), titanium plate, SS scrubber, SS mesh, brass, silver, nickel, copper, and gold sheets are the most often used metal electrodes. Metal electrodes offer a high electrical conductivity; however, they tend to raise the MFC's cost [3]. The use of expensive, poisonous, and dangerous chemical agents as electrode material is a fundamental flaw in present laboratory scale MFC research [4]. Researchers recently discovered that employing graphene modified materials used as electrodes, which are extra conductive and structurally steady with a greater surface area and greater electrocatalytic activity than standard electrode materials, improved the MFC's performance. The MFC power density was also found to have noticeably improved due to increased catalyst dispersion on the graphene surface [5]. As a result, graphene-derived electrode materials appear to be a superior alternative to standard electrode materials, increasing overall MFC efficiency.

2 An Overview of Conventional Electrode Materials Used in MFC

In MFC, several electrode materials have been used for power production shown in Table 1. The electrode materials have a big collision on the MFC's performance and cost. The anode material in MFC's not only serves as a conductor, as it does in typical fuel cells, but it also provides assist for biofilms formation. So it might be compatible with bacteria exist [6]. There exist not many contrasts in the terminal material choice of anode and cathode, in any case both electrodes have properties like surface area, conductivity, stability and durability, porosity, and cost and accessibility. The most generally utilized customary MFC electrode materials are as follows.

Table 1 Various MFC electrode materials and their related energy output

Anode material	Cathode material	Energy output	Reference
Carbon cloth	Carbon felt	468 mW m^{-2}	Hou et al. [8]
Carbon paper	Carbon paper	142 mW m^{-2}	Zhao et al. [9]
Platinum loaded carbon cloth	Carbon paper	38 mW m^{-2}	Min et al. [10]
Carbon felt	Activated carbon, carbon black and poly binder	680–820 mW m^{-2}	Kim et al. [11]
Graphite felt	Graphite felt	0.57 mA m^2	Chaudhuri and Lovely [12]
Titanium oxide composite coated on to carbon paper	Carbon paper	1060 mW m^{-2}	Zhao et al. [13]

2.1 Carbon Cloth

Carbon cloth is an anode material that is extensively utilized in BES due to its unique qualities, which include huge surface area, high porosity, strong conductivity, and the capacity to build 3D structures with good flexibility and high mechanical strength. Carbon fabric is made from the thermal decomposition of acrylic and consists of long individual carbon fibers with diameters ranging from 5 to 7 μm. These individual strands are bundled together and then woven together to create the carbon cloth [7]. The main drawback is the possible high cost of carbon cloth, which, when compared to other carbon-based electrode materials, is quite cheap.

2.2 Carbon Brush

Carbon brush is a fascinating material made of twisted carbon fibers around a titanium core. Its most commonly used surface area is relatively large, and the area to volume ratio is ideal. The central titanium metal ensures the excellent electrical conductivity while also increasing the material cost. The limitation of carbon brush includes their high cost, and continuous research is aimed at lowering overall cost.

2.3 Carbon Paper

Carbon paper is a planar carbonaceous substance that is moderately permeable yet also expensive and weak, with most demonstrations taking place in a lab setting in batches.

2.4 Carbon Veil

The single layer of carbon veil is very delicate, because the material is adaptable; it very well may be collapsed to shape a robust and porous 3-D terminal. It is a cost effective substance with a good porosity and relatively greater conductivity. The latter is critical for bacteria to be able to approach and conquer all accessible material sites.

2.5 Carbon Mesh

Carbon mesh is another material that is monetarily accessible, cheap and has a poor conductivity. The principle issue is less mechanical strength, which could prompt less sturdiness under high stream environment. Carbon mesh can likewise be folded to make a three-dimensional electrode, yet its porosity is poor.

2.6 Granular Activated Carbon (GAC)

GAC is popular anode material mainly used for its biocompatibility and low cost. Because of its porous form, it has a limited electrical conductivity. GAC is employed as a packing material rather than a freestanding anode because of this disadvantage. Because of the nanoscale pore size of GAC, its great surface area availability cannot be efficiently utilized by bacteria.

2.7 Granular Graphite

Granular graphite has a high electrical conductivity and is more commonly employed as a packing material than as a stand-alone anode. Graphite has excellent electrochemical properties, and its biocompatibility has been established by Scanning Electron Microscopy (SEM), as evidenced by the plenty of a biofilm adhered to surface area of graphite electrode.

3 Non-carbon-Based Electrodes

In spite of the way that carbon-based anodes are the favored electrode in MFC setups because of their underlying flexibility, non-carbon-based terminals have likewise been utilized in MFC's. Anode and cathode electrodes made of non-carbon-based materials include stainless steel, platinum coated titanium metal, and uncoated titanium. According to findings, stainless steel gives greater current density (674 $\mu A\ cm^{-2}$) and nickel (384 $\mu A\ cm^{-2}$) respectively. Due to the production of metal oxides, which act as a barrier for charge transfer between the biofilm and the metal, non-noble metals like cobalt and titanium produced minimal current density.

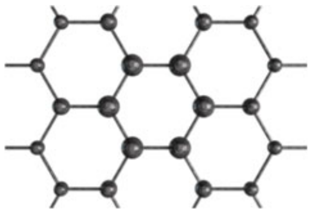
3.1 Graphene Derived Electrode Materials Used in MFC

Graphene, the world's thinnest material, was discovered by Geim and Novoselov in 2004 [14]. Graphene's remarkable qualities, like its good electrical conductivity, ultrahigh specific surface area, exceptional mechanical resilience and flexibility, chemical inertness, and superior biocompatibility, open up new possibilities for MFC's [15]. During MFC operations, graphene has non-toxic impacts on bacterial growth. As a result, the toxicity of other materials, like copper, platinum, etc., can be greatly lowered by altering or combining it with other materials, like metal. The exceptional performance qualities of graphene-based electrodes outperform traditional carbon electrodes [16]. Because of its close physical proximity and advantageous electrical, mechanical, and physicochemical capabilities, graphene is becoming popular in the vitality domains. Its qualities are extremely encouraging and consistent, making it ideal for wide range of application like fuel cells, batteries, super capacitors, photo catalysts, and solar cells [17].

3.2 Graphene Structure

Graphene is a carbon allotrope that takes the shape of a 2D, atomic-scale hexagonal lattice with one atom forming each vertex due to sp^2 hybridization. Figure 2 shows the structure of single graphene sheet. The carbon atoms are organized in a honeycomb lattice. Each lattice has three bonds with strong connections, providing a sturdy hexagonal structure. Carbon atoms connect with adjacent carbon atoms in single layer graphene using sp^2 hybridization to form a benzene ring in which each atom provides an unpaired electron. Because of its closely packed carbon atoms and sp^2 orbital hybridization, a mixture of orbitals s, p_x, and p_y that make up the σ bond of graphene is extremely stable. The π-bond is formed by the final p_z electron. The π-band and π*-bands are formed when the π-bonds combine. The distance between carbon–carbon bond is 0.142 nm. The bond between carbon atoms is strong enough to withstand external strain from a twisting lattice plane, preventing atom reconfiguration [18].

Fig. 2 Structure of single graphene sheet



3.3 Properties of Graphene

Graphene has several excellent qualities in terms of visual clarity, mechanical strength, thermal conductivity, and electric conductivity. Graphene has thickness range of 1/200,000th the dia of a human hair while on the other hand, has a very stable structure. It is made up of only one atomic layer of carbon atoms, which adds to its super thin and lightweight properties. Graphene with several layers would produce different colors and contrasts based on light refraction and interference, which might be used to discern the layers of graphene. Graphene has a good mechanical strength and high thermal conductivity. The fact that graphene is a zero-overlap semi-metal with very good conductivity is one of its most useful characteristics. Table 2 lists the most important graphene properties of graphene [18].

3.4 Graphene-Based Electrodes Synthesize

The fabrication of graphene-modified electrodes has received an interest due to graphene's attractive characteristics and exceptional shapes shown in Fig. 3. In numerous investigations, GO is always used as a forerunner to create graphene and its compounds. Electrochemical reduction, layer-by-layer (LBL) self-assembly, Bio-reduction, Chemical Vapour Deposition (CVD), Direct deposition, and chemical doping are all common methods for fabricating Gr-based electrodes. This section briefly discusses the various categories of synthesis procedures for graphene-altered electrodes in MFC's.

Table 2 Properties of graphene

Properties	Value
Thickness	0.35 nm
Planar density	0.77 mg/m^2
Area of a graphene unit structure	0.052 nm^2
Transparency	97.7%
Conductivity	10^6 S/m
Sheet resistance	31 Ω/sq
Mobility	$2 * 10^5 cm^2/Vs$
Tensile strength	125 Gpa
Elastic modulus	1.1 Tpa
Strength	42 N/m
Thermal conductivity	5×10^3 W/mK
Specific surface area	2630 m^2
Mechanical strength	1060 Gpa
Young's modulus	TPa

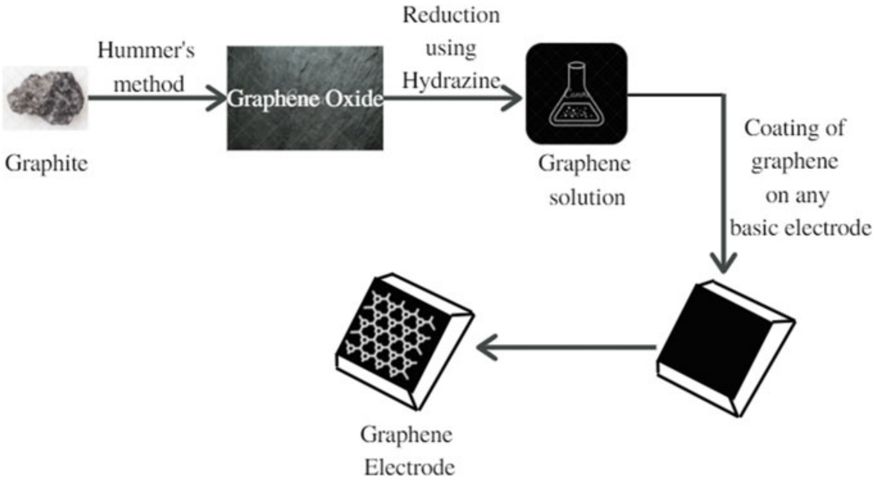


Fig. 3 Synthesize of graphene altered electrode for application in MFC

3.4.1 Direct Deposition

The direct deposition method of fabricating graphene-derived electrodes entails three steps. The first step employs hummer's method to chemically exfoliate graphite and obtain Graphene Oxide (GO). The next step is to use a reducing agent, such as hydrazine, to convert GO to graphene (Gr). The final steps involve coating the arranged graphene on any fundamental electrode such as SS mesh, fiber, and so on using a simple immersion method [19].

3.4.2 Electrochemical Reduction

Another strategy for manufacture is the electrochemical reduction of GO to Gr, which can be done directly from GO nano-sheets organized on the surface of electrode from a solution of dispersed GO nano-sheets. Accordingly, the thickness of the resulting layer can be controlled, replicated, and homogenous without the use of harmful chemicals. Carbon materials, conductive polymers, or their monomers, such as multi-walled carbon nanotubes (CNT's), Poly (3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), or polypyrrole (PPy), could then be placed over the Gr coated electrode using chronoamperometry [19]. Figure 4 depicts the electro-polymerization with graphene.

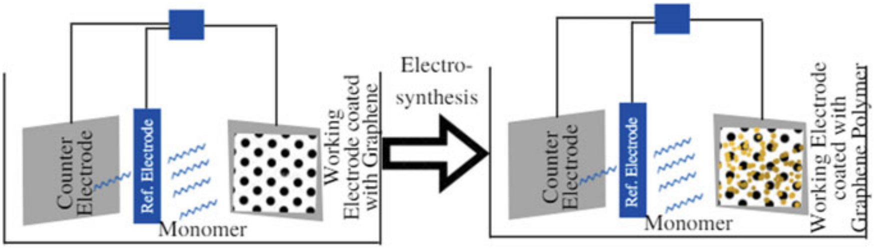


Fig. 4 Electro-polymerization with graphene

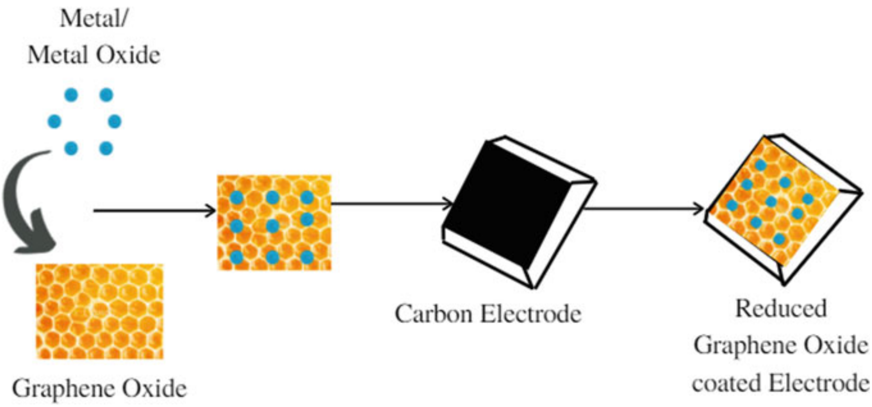


Fig. 5 Graphene oxide hybrid electrode materials using LBL self-assembly technique

3.4.3 Self-Assembly Methods

This is one of the technique in which essential components in a solution, such as molecules, nanomaterials, and big size objects, impulsively form an efficient and constant structure. The gelation procedure is one of the most prevalent methods for producing 3D graphene (3DG) from GO sheets in homogenous liquids. Many approaches, such as altering the pH value of the GO solution, adding cross linking agents, or employing chemical reduction processes, can cause the suspension of GO sheets to gel. There are a variety of ways to make graphene sheets from GO sheets suspended in electrostatic contact utilizing various self-assembly mechanisms. The major self-assembly strategy for synthesizing homogeneous nanostructure films is layer-by-layer (LBL) assembly as shown in Fig. 5.

3.4.4 Bio-reduction

Bacteria can self-assemble utilizing water soluble GO in the Bio-reduction method, which causes in-situ bio-reduction of non-conductive GO to conductive rGO,

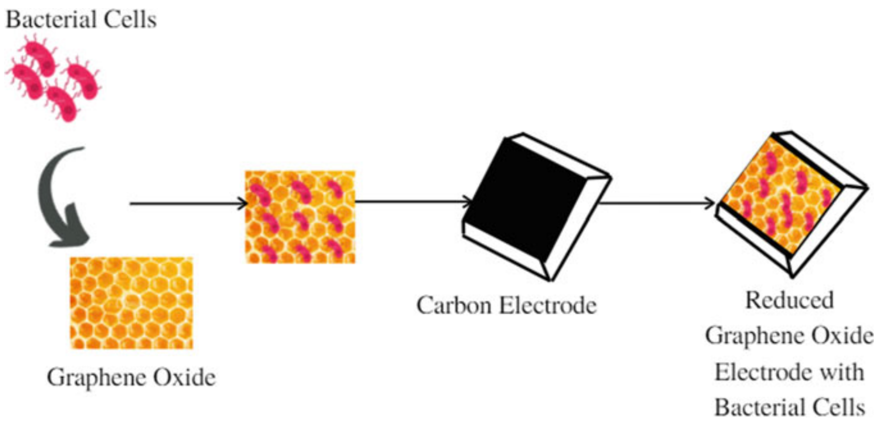


Fig. 6 Bio-reduction of bacterial cells on graphene derived electrode

resulting in a three-dimensional (3D) self-assembled biofilm. When GO solution was given to the anode compartment of a dual chamber MFC, the anolyte turned black with the formation of aggregates, meaning that the water dispersible brown GO was converted to the water precipitated black rGO. Figure 6 shows the bio-reduction of bacterial cells on graphene derived electrode.

3.4.5 Chemical Vapour Deposition (CVD)

CVD is a commonly used process for creating semiconductor films in which a carbon source undergoes a chemical reaction at a high temperature with a high gas flow rate, and the resultant film is deposited on the surface of a heated solid substrate. Figure 7 shows the CVD method of fabricating graphene derived electrodes. Transition metal compounds, such as Cu and Ni, are the most common graphene substrates. The graphene films that have been created can be transferred to different surfaces while

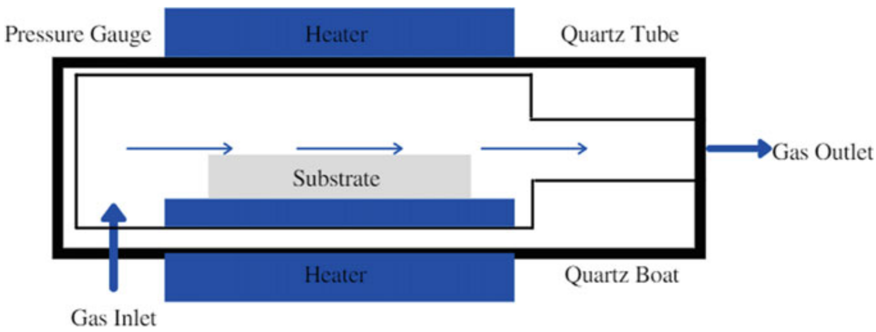


Fig. 7 Chemical vapour deposition method of fabricating graphene derived electrodes

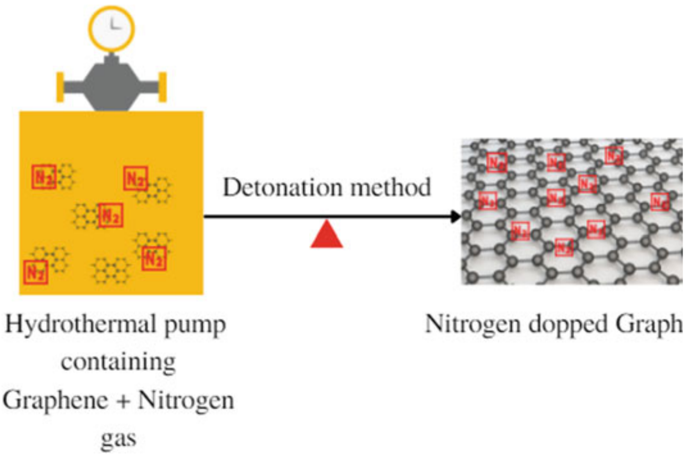


Fig. 8 Schematic of nitrogen doped graphene

retaining their high conductivity and transmittance. This technique can produce large-area, high-quality graphene, but its high cost and complexity prevents it from being used in big-scale applications. Substrate is one of the influenced factors to produce the quality of graphene.

3.4.6 Chemical Doping

Heteroatoms can be chemically doped into graphene. This method is efficient adequate to optimize graphene's physical and chemical properties. Doping Gr with nitrogen (N) atoms was recently investigated as a viable method for increasing its conductivity, resulting in novel nano-materials. The observed increase in electro-catalytic activity of N-doped Gr in basic solution has extraordinary potential as a metal-free catalyst in fuel cells, in which N molecules activate charge delocalization on the carbon design and increase the openness of the edge plane to sustain catalytic activity extraordinarily [20]. Figure 8 illustrates the N doped graphene structure.

In addition to the methods outlined above, spraying, explosion, electrostatic interaction, electrophoresis, the explosion method and other processes can be employed to produce graphene-modified electrodes.

4 Graphene-Based Anode Materials

The anode material, which is aligned with bacterial adhesion and electron transfer from microbes to the electrode via various mechanisms, has a strong influence on the power density of MFC. A bio-anode should be biocompatible and also have a

Table 3 Summary of graphene derived anode electrode materials used in MFC

Anode electrode	Modified anode electrode	Cathode electrode	Power density (mW m^{-2})
3D GF	PANI	Carbon cloth	768
Graphite felt	PPy/GO	Carbon Felt	1326
Graphite block	Graphene	Carbon paper	102
Glassy carbon	Microbially reduced graphene	Carbon cloth/Pt	1905
Carbon cloth	Graphene	Carbon cloth	52.5
Nickel foams	Graphene/TiO_2	Carbon paper	1060
Carbon paper	Graphene/Au	Carbon paper	508
Carbon cloth	PANI-rGO	Carbon felts	1390
Carbon cloth	TiO_2/rGO	Carbon fibre brush	3169
Carbon cloth	Graphene	Carbon cloth	2850

large specific surface area to support a large number of microbes. Graphene-based materials are gaining significance for extremely efficient MFC anodes in this regard [21]. Zhang and colleagues reported that a dual-chamber MFC with a graphene altered stainless-steel mesh (GMS) anode electrode performed better electrochemically. Thereafter, a 3D macro porous anode with graphene coating on stainless steel fiber felts (SSFF's) were proven to induce a maximum power density of 2,142 mW m^{-2} in MFC, substantially outperforming the unmodified SSFF-MFC. Graphene-modified carbon cloth (CC) electrodes have a maximum power density than bare CC, activated carbon, or bare graphite altered electrodes, according to certain research shown in Table 3. Three-dimensional (3D) anodes made from graphene sponge (GS) provided a huge area for microbial colonization in a 3D open space. Microorganisms covered the GS surface, which were connected by microbial nanowires, giving a likely direct conduit for extracellular electron transfer. This highly porous graphene sponge ensures its prospective use in MFC's as a flexible anode material. The greatest power density obtained from the 3D graphene/PANI MFC (768 mW m^{-2}) was almost four times greater than that obtained from the carbon cloth MFCs (158 mW m^{-2}), according to a macro porous and monolithic MFC anode based on PANI hybridized 3D-graphene. A novel 3D chitosan/vacuum-stripped graphene (VSG) scaffold with hierarchically porous structure offered an open space in the anode interior for bacteria colonization and improved the affinitive contact between multilayered bacteria and biocompatible VSG, resulting in a remarkable 78-fold increase in powder density. The BET surface area of a nanocrystal TiO_2/rGO hybrid (324.7 m^2 g^{-1}) was large. It was discovered that a nanocrystal TiO_2/rGO hybrid with numerous mesopores had a greater specific surface area, which was useful to achieving superior electrocatalytic performance.

5 Graphene Derived Cathode Materials

The maximum power output of MFC influenced by the oxygen reduction reaction (ORR) in the cathode chamber. Because of its modest over potential, platinum (Pt) is forever utilized as a catalyst in the cathode process, but it is expensive and limited its use in industrial scale applications. The reduction pathways are strengthened by graphene altered materials, which give a high number of potential active sites [22]. Polymers, metal-based materials are embedded on the surface of graphene, were found to improve ORR activity by means of ever-increasing the active sites of the graphene nanosheets, according to studies. Except in MFC's that use aerobic microorganisms as electron acceptors, no microbes adhered to the electrode surface in comparison to the anode electrode. As a result, improving the surface modification of the electrodes is the recommended way for increasing electrical conductivity. Furthermore, the cost of producing graphene sheets in large quantities is far cheaper than that of CNT's. As a result, much work has gone into developing graphene as a catalyst support for fuel cell applications. The addition of nitrogen atoms (NG) to graphene results in a high electrocatalytic activity for ORR in an alkaline solution, suggesting that it could be used as a cathode catalyst in fuel cells. The greatest power density attained when NG was used as the cathode catalyst in MFC's was comparable to that of typical Pt/C catalysts. More notably, NG-based MFC's produced more stable power than Pt-based MFC's. Figure 4 depicts the graphene modified cathode electrode materials used in MFC (Table 4).

Table 4 Summary of graphene derived cathode electrode materials used in MFC

Cathode electrode	Modified cathode electrode	Anode electrode	Power density mW m^{-2}
Carbon paper	NG	Carbon cloth	764–788
Glassy carbon	Fe- and N-functionalized graphene	Carbon felt	885
Carbon paper	MnO_2-NTs/graphene	Carbon cloth	4.68 Wm^{-3}
Carbon cloth	Pt–Co/G	Carbon cloth	1378
Carbon cloth	Graphene/biofilm	Carbon cloth	302.2–344.2
Carbon cloth	NG	Carbon felt brush	1335–1365
Stainless steel net	NG	Carbon brush	1159.34
Carbon paper	Fe-NG	Carbon felt	1149.8
Carbon cloth	α-MnO_2/GO	Carbon cloth	3359
Stainless steel mesh	Cobalt sulfides/GO	Graphite fibre	1138–1744

6 Pros and Cons of Graphene Derived Electrodes

The huge demand for storage devices has led to increased research in exploring materials of unique properties which can exhibit high performance. Graphene has been identified as one of such materials exhibiting promising results. Graphene is one of largest among aromatic molecules, belonging to the category of polycyclic aromatic hydrocarbons. Many carbon allotropes use its basic structure for formation of graphite, carbon nano tubes, and charcoal. The research works on graphene indicate that it is a promising conducting substance for the upcoming storage equipment. Graphene has several inherent properties that make it an appropriate substance for different real field applications in different sectors of industry. This strongest material possesses high mechanical resistance, larger surface area, superior electrical, and heat conductivity, which makes it the most suitable material for fuel cells and capacitors. When used as electrodes, graphene can be used as a composite and support material. Improved electrode efficiency is generally observed when graphene is used as a support material because it maintains metal ions in regular order.

When graphene is used as a composite material in electrodes, it facilitates the charge, and its performance is ensured by its well—ordered structure and higher conductivity. In general carbon materials possess low density of pores and also low storage density of carbon content electrode resulting in low volume energy density. Since, graphene is a carbon material, it also faces the similar problem, and hence it has been proposed to develop a controlled combination of graphene with other materials for electrode structure design resulting in graphene-based electrodes with high density. Conductive agents or binder are not contained in most of the graphene-based electrodes further improving volume energy density. Promising results were obtained when analyzing graphene-based materials, and there are huge opportunities and challenges in synthesizing and using graphene-based electrode materials. It is one of potential electrode materials for electrochemical energy storage. Because of its appreciable conductivity stable physical structure and large surface area, graphene is the most appropriate material for the majority of the electrochemical energy storage equipment's.

In certain applications, the 2D layered structure is constructed into 3D structures, with adjustments in pore structure. Owing to its unique properties, graphene is used in combination with other materials in applications like lithium-ion batteries, lithium oxygen batteries, and lithium sulphur batteries, higher performance was observed in these applications.

In lithium-ion batteries, graphene is added to electrode formulations to improve the performance. This organic-based electrode overcomes the limitations in surface area, capacitance, and conductivity of inorganic-based electrodes. Graphene is one of the best materials owing to its versatility, which enables it to overcome conventional battery limitations when used in cathode electrode formulations. In electrodes constituted of graphene and metal oxide hybrids, the primary cathode material used is the graphite, which has the ability to store the lithium ions by the process of surface adsorption and also there occurs bonding due to its large surface area.

The downsides of conventional metal oxides used in batteries such as low conductivity, energy density, and loss of contact points are eliminated when used with graphene. The hybrid structure improves greater interaction between the hybrid matrix and the interstitial ions which increases the conductivity of the structure. In the synthesis of graphene—MO structure, graphene with its regular repeating structure acts as a template and produces a uniformly distributed matrix. MO nanoparticle aggregation is largely limited resulting in larger surface area for charge and discharge cycles. As a whole there is a large improvement in the cyclic performance and specific capacity when compared to traditional pure MO electrodes. In first 10 cycles, these hybrid electrodes can exhibit up to 1100 $mAhg^{-1}$. Apart from hybrid electrodes, electrodes made of graphene and carbon nanotubes or fullerenes have also been synthesized and used currently. Dispersing the graphene sheets with either fullerenes or carbon nanotubes increases the inter-graphene spacing, thus increasing the home for more lithium ions resulting increased specific capacity to around 40%. Graphene enhances the performance of Graphene Lithium Sulphur Batteries. Here the sulphur ions are supported by graphene, because of which major problems like less utilization of sulphur cathode and inorganic salt deposition on the cathode are eliminated. High energy sodium-sulphur batteries used at room temperature are also found to use graphene-sulphur composites as electrodes. Graphene-based composites are used as electrocatalyst in zinc-air batteries making it highly efficient. In wholesome, graphene has several other advantages when used in the synthesis of electrodes, which are listed below.

- Thinnest material with pliable and transparent single layer of carbon atoms.
- Incredibly flexible material stronger than steel.
- Higher potential to transfer electrons at a very faster rate compare at the speed of 1000 km /s.
- Superior conduction of heat and electricity.
- Provides faster technological changes for its usage in the production of high speed electronic devices.
- Highly efficient sensors in detecting explosives.
- Storing hydrogen for fuel cell powered cars.

Despite its remarkable advantages and applications, graphene also possess various disadvantages.

- It does not possess band gap; research works have been undertaken in this regard.
- It is susceptible to oxidative environments
- It is synthesized using toxic chemicals in high temperatures; hence, it exhibits toxic qualities which is one of the major limitations in certain applications.
- The practical application of it is not completely recognized; hence, more research is required.
- High quality grapheme materials are expensive, and also the process of synthesis is expensive.
- It is a non-renewable resource and also harder to synthesize.

- It has lesser actual strength than the intrinsic strength.
- There is no control over the size of the graphene sheet produced.
- It is not stable below the size of 20 nm.

7 Applications of Graphene Derived Electrodes

Graphene is extensively utilized electrode material in batteries, light-emitting diodes, transistors, solar cells, and other flexible devices. Some of the applications of graphene are discussed below. Mohammad et al. [22] examined usage of graphene for ultra-lightweight photovoltaics. So as to improve the electrical properties, they employed a roll-to-roll (R2R) transfer technique. It was done on flexible substrates with parylene as an interfacial layer. By the process of chemical vapor deposition a layer of parylene is deposited on graphene-copper foils and then laminated onto ethylene vinyl acetate. Later the samples are then delaminated from the copper using an electrochemical transfer process which resulted in flexible conductive substrates. The results of characterization techniques indicated that the parylene C and D doped graphene had higher carrier density due to the embedded chlorine atoms in the structure. Calculations of density functional theory indicated that the binding energy between graphene and parylene is stronger than the binding energy of EVA and graphene. It resulted in less tear in the graphene during R2R transfer. It is then followed by the fabrication of organic solar cells on ultrathin flexible parylene/graphene substrates. The power conversion efficiency achieved was of 5.86% [22]. Hanrui Su and Yun Hang Hu summarized the applications of graphene-based materials used in fuel cells. When compared with the commercial Pt/C catalyst, heteroatom-doped graphene indicated high electroactivity. Many anchoring sites were provided by doped graphene and rGO for the active metal particles which made the dispersion uniform. Various electrochemical reactions such as ORR, EOR, MOR, and FAOR are supported by the high surface area and electrical conductivity of the graphene-supported catalysts. Long term stability was ensured by the strong metal-graphene interaction. In order to enhance active sites, three dimensional graphene electrodes were also developed, in order to enhance and reduce the diffusion resistance. Graphene and graphene oxide are also found to exhibit high proton conductivity and less permeation of fuel. This enabled them to act as alternative electrolyte material. Graphene which is highly conductive and chemically stable also found to protect metallic plates from corrosion [23]. Syama and Mohanan inferred that graphene is ideal for photo thermal therapy due to its high near-IR absorbance. Hence the multifunctional graphene was found to be a reliable material for the diagnosis and treatment. By interacting with the cell membrane, it also exhibits the antibacterial property. Graphene also has potential application in tissue regeneration because of its nature of attachment and proliferation of the stem cells and neuronal cells. 3D Structure is created with the help of 3D printing is also possible from 2D structures, and this has prominent applications in engineering field. Despite the advantages of graphene in various applications, it also raises concerns on toxicity. Many reports provide evidence for the potential toxicity of graphene and also for various graphene derivatives [24]. Rajni et al. investigated the nature of graphene and identified that it is an appropriate material for both transparent and non-transparent electrodes and can be suitable for double electrode designs for the super capacitors. It was observed from experiments that the in the applications such as flat panel displays, solar cells and in tough screens, graphene can be used for transparent electrodes [25]. In case of super capacitors, energy storage capacity is more important than the transparency. It was found that graphene has excellent potential in the above said application. The review article narrated the trending knowledge graphene and the patent base for its manufacturing. The investigation also included thorough study of US Patent Base to review the existing patents on transparent electrodes made of graphene for super capacitors and flat panel display devices. It was inferred that a large number of patents were on the application and fabrication of graphene super capacitors and flat panel display devices. More than 40 patents were covered in the article from 2015 to 2017 [26]. Rowley observed that as 2D material, graphene has paved way for significant interest due to its higher stability, excellent conductivity, and larger carrier mobility. In order to improve the energy storage performance the integration of graphene with the heterogeneous electrodes was found to be a highly effective method. In the study undertaken, the graphene-based heterogeneous electrodes were completely reviewed for its energy storage capacity. The study also illustrated the ball-milling, electro spinning, hydrothermal, and microwave-assisted approaches [27]. Brahim et al. investigated the innovative breakthroughs in graphene applications. It was observed that the fundamental research and vast industrial applications resulted in the larger and low-cost production of graphene for real world applications [28]. They insisted that graphene being a one-atom thick carbon crystal consist a set of unique physico-chemical properties. It was found to have extreme mechanical behavior, exceptional electrical, and also thermal conductivities. These attributed to the replacement of conventional materials with graphene for various applications. They discussed the probability of successful integration of graphene into a device for various applications in electrorheology, photovoltaic, shape memory, thermoelectricity, self-healing, and space missions [29]. Zhang et al. observed that graphene, an emerging carbon material, would be more of practical applications. The article highlighted research progress in graphene-based materials. Working principle of supercapacitors and research progress in synthesis and of graphene—based materials was studied. The graphene-based materials included for the study are carbon nanotubes, fullerenes, and graphene oxide. The study also included the applications of graphene-based materials for the design of advanced supercapacitors [30].

8 Challenges, Opportunities, and Future Perspectives

Graphene is the sheet of carbon of one atom thick, and the thinnest of all materials is considered as the prominent material of the 21st century materials science. It has greater number of practical applications in the manufacturing of sensors, terahertz imaging, transistors, composites, membranes, batteries, energy storage devices, and thin coatings for LCD displays and solar cells. Above all graphene forms the basis of new breeds of computer chips, which are smaller and faster than those made of silicon. Researchers are now working to meet the challenges in graphene processing.

- One important aspect is to create large enough graphene sheets to pattern with conventional lithography.
- There are very few commercial suppliers of the thin layer of graphene, and it also requires manpower for the synthesis of the thin sheets.
- One cheaper method of production is depositing carbon atoms from a vapor onto an inert support. But in the process, the carbon atoms curl up around impurities, rather than forming as thin sheets.
- The chemistry part of graphene story has only just begun, and it has long way to move forward. However, chemists are working on to modify the structure to functionalize it effectively for various applications.
- Chemically modified graphene is still under research and not reached a level of sophistication yet.

Large scale application of graphene is still a challenging task. In case, flexible electronics require large graphene sheets with lesser defects. Current methods still face this challenge. Presently large-scale synthesis of graphene is dependent on graphene nano platelets produced by the modified hammers method. The process results in large graphene production, but the graphene produced is by non-friendly procedure owing to the nature of chemicals used. Standardization is associated with graphene production. For every run, the graphene produced finds variation in doping, quality, thickness, or even defects. Cost of production remains an empirical exercise and remains unsolved. The variation in graphene quality may occur even in the same lab. The variations in graphene properties may be observed with different vendors also. Hence there is a need for standardizing the production methods of various vendors and also the methods followed by different researchers. Graphene derivatives like graphene oxides, reduced graphene oxides, etc. have also exhibited values much lesser than what has been predicted for graphene material. From the above discussions, it can be inferred that making graphene industry-friendly, more efforts are required for synthesis, storage, and reduction in cost of production [31].

9 Conclusion

Graphene electrodes exhibit superior properties when used in microbial fuel cells. The unique properties of graphene such as transparency enhanced electrochemical property, high electrical, and thermal conductivity makes it the most appropriate material in various fields of application. Due to the superior chemical and physical properties of graphene, they have obtained significant attention in the design of microbial fuel cells for generation of electricity. The working mechanism of the MFC and production techniques were discussed in detail along with detailed study on its applications. The merits and demerits of graphene-based electrodes and application of the same were also discussed. Reviewing the abundant works on graphene derived electrode materials, the chapter concludes with a perspective on the strategies and critical challenges in graphene derived electrode fabrication for further enhancement of MFC performance.

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